APPENDIX III

MATES III

DRAFT FINAL REPORT

MATES III Monitoring and Laboratory Analysis Protocol

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MATES III

APPENDIX III

MONITORING AND LABORATORY ANALYSIS PROTOCOL

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Chapter 1.0
Introduction

This protocol document provides detailed information about the procedures and processes required to conduct the field measurement element of the Multiple Air Toxics Exposure Study III (MATES III) [1].

1.1 BACKGROUND

In 1998, the South Coast Air Quality Management District (AQMD) conducted an intensive ambient air toxics monitoring program, the Multiple Air Toxics Exposure Study (MATES II). The objective of MATES II was to establish a baseline of existing air toxics ambient emissions, exposure and risk level data and an assessment of model accuracy. The AQMD conducted MATES II over a one-year period at ten sampling sites in the South Coast Air Basin (Basin). The MATES II Final Report was approved by the AQMD Board in March 2000[2].

The microscale monitoring element of MATES II was conducted to determine if communities were experiencing localized hot spots not otherwise identified through the regional modeling. Microscale sampling was conducted over six-week intervals at selected locations throughout the Basin using three mobile sampling platforms. During the year-long monitoring period, the platforms were deployed to collect ambient toxics measurements.

For MATES III, specific compounds will be sampled and analyzed. These compounds are identified in Appendices A and B. Compounds listed in Table 1 (Appendix A) will be measured on a routine basis, while compounds listed in Table 2 (Appendix B) will undergo more limited measurement and sampling due to methodological limitations, high cost of analysis, or other limitations.

Field sampling will begin in April 2004 and continue for a minimum of one year. This document describes the monitoring, laboratory analysis, quality control (QC), and quality assurance (QA) activities necessary to support both the regional and microscale sampling programs.

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[1] MATES I was run in 1987. Copies of the final report are available from the AQMD library.

[2] South Coast Air Quality Management District (2000). *MATES II Final Report*. Diamond Bar, CA

Chapter 2.0
Monitoring Equipment

2.1 INTRODUCTION

For the purposes of this protocol, the descriptions and operational and maintenance procedures of the following equipment used in MATES III sites will be delineated.

Sampler Type	Vendor and Model Number
Volatile Organic Compounds (VOC)	XonTech 910A/ 912
Metals; Carbonyls	XonTech 920 and 924
Carbonyls	ATEC 800 Sequential Sampler
PM2.5 Speciation Air Sampling System	Met One Instruments SASS
Wind, Speed, and Direction (WSD)	Gill Solent 2 Axis Ultrasonic Anemometer (Met-One)
PM_{10}	Graseby-GMW 1200 PM_{10} Sampler

The siting, acceptance testing, and calibration functions for each type of equipment identified above are basically identical. Therefore, these functions are defined below. Non-generic functions will be discussed under each equipment heading.

2.2 EQUIPMENT CHARACTERISTICS

2.2.1 Siting

A) Monitoring site selection criteria will be the same in most regards whether the site will be used for a fixed or mobile site. Site uniformity will be achieved to the greatest degree possible. Descriptions will be prepared for all sampling sites. The description should include, at a minimum, the type of ground surface, the direction, distance, and approximate height to any airflow obstruction, and the direction and distance to any local pollutant sources.

B) The sampler platform will be located in an area with unobstructed airflow, especially in the direction of any recognized sources of the sampled compounds. Turbulence and eddies from obstructions will cause non-representative results. The distance between the obstruction and the sampler should not be closer than two times the height of the obstruction.

C) Locations unduly influenced by nearby sources or activities or where reactive surfaces may cause chemical changes in the air sampled will be avoided. Micro-meteorological influences caused by nearby hills, bodies of water, valley drainage flow patterns, etc. will be taken into consideration.

D) The recommended intake probe height for criteria pollutants is 3 to 15 meters above ground level as near breathing height as possible, but not where a building is an obstruction or the equipment is easily vandalized.

E) The probe should extend at least two meters away from the supporting structure. If the probe is located on a building, it must be mounted on the windward side.

2.2.2 Acceptance Testing

Acceptance testing will be performed on all instrumentation for approximately one month after receipt. After acceptance testing is conducted on the instruments, they will be deployed in the field and ambient sampling will commence. Acceptance testing will be conducted through the following steps:

A) All instruments will be carefully unpacked from their shipping containers and checked for completeness, broken parts, and correct subunits.

B) The units will be assembled according to manufacturer guidelines and prepared for start-up.

C) The flowrate/flow meter portion of the pneumatic system will be checked using the most appropriate calibration-transfer standard to verify the operating flow/flowrate.

D) Timer accuracy will be evaluated by comparing it to an elapsed-timer standard. All timers must hold their accuracy to ±5 minutes over a 24-hour period.

E) Any deficiency will be corrected following the manufacturer’s procedures.

F) Each microscale site will be operated for an intensive six to eight-week sampling period. Following sampling, each microscale monitoring mobile platform will be loaded on the transport vehicle and moved to the next sampling site. The lease agreement for each monitoring site will be executed for a minimum eight-week period. Within this contractual time frame, the temporary power can be hooked up, temporary fencing installed and all samplers at the new site can be calibrated prior to beginning the next intensive eight-week sampling period. Sampling will be conducted at each microscale site on the same one day in three schedule as the MATES III fixed sites.

2.2.3 Calibration

At each sampling site, final dynamic calibration will be performed on each analyzer prior to the start of the intensive six-week sampling period. At the end of this sampling period, an “As Is” dynamic calibration will be performed on each analyzer to ascertain the amount of analyzer drift.

2.2.4 Sample Pickup

The AQMD senior chemist sample custodian will distribute the sampling media to the field technician. Filters and carbonyl cartridges will be transported in coolers with blue ice and the canisters will be kept capped at all times during transportation. Once the filter and carbonyl cartridge has been used to collect a sample, they must be refrigerated until they are returned to the AQMD. The sampling media will be returned to the senior chemist sample custodian as soon as possible following sampling.

2.2.5 Troubleshooting

A maintenance guide based on the equipment manufacturers’ suggested operating procedures will be available for each instrument. If an instrument falls out of the correct operating range, or if there is a component failure, the operator will immediately place a call to the AQMD STA/AM Support and Repair Section to schedule a repair.

2.2.6 Repair

Due to anticipated failure of standard components such as pumps and flow controllers, the AQMD will warehouse standard-component spare parts. Since the sampling time at each location will be relatively brief, repair of microscale monitoring platform samplers will receive priority.

2.3 SAMPLING EQUIPMENT

2.3.1 XonTech 910A and 912

2.3.1.1 XonTech 910A - Description

The XonTech 910A air sampler is designed to take air samples at a constant flow rate for a known sampling period. It is durable, serviceable and accurate making it useful for sampling a wide variety of gases. Its compact, constructed simply, and offers long term reliability.

Specifically, the 910A sampler takes air from the sample inlet and injects it into a canister at a constant flow rate for the preset period of time. Excess air is exhausted through a bypass exhaust. The constant flow rate and elapsed time allow the operator to calculate the integrated air sample volume. The sample will be pumped through a metal bellows pump that develops sufficient pressure to control the flow with a mass flowmeter. The XonTech 910A is operated according to the guidelines set forth in XonTech's *Model 910 Toxic Air Sampler Operations Manual*[3].

2.3.1.2 XonTech 912 - Description

The XonTech 912 adapter may be added to the XonTech 910A to enhance sampling capability over a reduced period of time. It cannot operate independent of the 910A. It is designed to route gas samples to a maximum of 16 canisters. An internal time base can be used to step a rotary valve from canister to canister at a user-selected rate. The 912 will also accept timing signals from the model 910A. The XonTech 912 adapter is operated according to the guidelines set forth in XonTech's *Model 910 Toxic Air Sampler Operations Manual*[4].

2.3.1.3 Pre-Testing

All canister samplers will be test run at the AQMD headquarters to assure proper operation. Most samplers are also field tested during field sampling.

2.3.1.4 Cleanliness Check

To perform a system bias check, ultra-pure air or nitrogen will be injected into the sample manifold to fill one, 3-hour canister. Additionally, the 24-hour sampler can be tested by maximally increasing its sample flow to fill a canister in approximately 6 hours. A field blank will be filled at the site by flowing pure air or nitrogen into an evacuated cylinder. A difference of less than 1 part per billion (ppb) per compound between the field blank and the bias samples indicates that the system is non-biasing (non-contaminated). A value greater than 1 ppb per compound requires corrective action. A system bias check will be repeated until all biases are demonstrated to be eliminated. The AQMD's Ambient Monitoring Support Group will perform system repairs. This group will assemble, leak check, disassemble, and clean the sample manifold and the Auditing Group will calibrate the mass flow controller (MFC) for flow.

2.3.1.5 Sample Pickup

An AQMD Instrument Specialist will pick up clean VOC canisters in the laboratory. Evacuated canisters will be transported by vehicle to the respective air monitoring stations. Each canister has a tag attached (Appendix G). This tag will be completed to contain the following information: sample site, operator initials, sample date, and canister number in sampling sequence. The air monitoring station operator should complete this tag once the canister is set up for sampling. Once the canister is filled

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[3] XonTech, Inc. (1987). *Model 910 Toxic Air Sampler Operations Manual*. Van Nuys, CA: Author.
[4] Ibid.

and disconnected from the 910A or 912 sampler, and prior to returning the sampled canister to the laboratory, the canister number, start vacuum, end pressure (psig), and elapsed time will be recorded on the canister sample log (Appendix F and F-1). The time on the QC chart must also be checked and adjusted. This value must be within ± 10 minutes of actual Local Standard Time. The canister will be delivered to the senior chemist sample custodian as soon as possible.

2.3.2 XonTech 920 and XonTech 924

2.3.2.1 Description

The Model 920 and equivalent Model 924 Toxic Air Samplers are designed to collect ambient air particulate samples on a variety of filter materials and sorbent media in unattended field use. These samples will be brought to the AQMD headquarters for laboratory analysis. The sampler precisely controls the sampling time and flowrate through each sampling head using a microprocessor and mass flow controller (MFC). Sampler design is modular to facilitate installation of individual sampling channels. Each sampler may accommodate eight sampling channels for two types of sample collection media: one that accepts 37 or 47 millimeter filters and another that accepts sorbent tubes.

The sampler consists of three modules, each contained in a separate enclosure. The heart of the system is the control module. This module contains the microprocessor, controller, mass-flow controllers, and front panel, displays, printer, and keypad. The difference between the Model 920 and 924 is the electronics have been upgraded to reflect the increase in microprocessor functionality presently available that was not available in the circa 1995 Model 920. The sampling module is equipped with isolation valves that protect the sampling media from passive sampling before or after sampling or sample loss after sampling. The sampling module and the pump module have not changed between the Model 920 and 924. The sampling inlet height is 1.2 meters above ground level. The third element of the sampler is the pump module. It contains the vacuum pump that provides adequate capacity for simultaneous operation of three, 30 liters per minute (lpm) and 200 cubic centimeters per minute (ccm) sampling channels.

2.3.2.2 Operation

To use the sampler, the operator will insert the sample filter cassette or sorbent tube into the sampling head and will key in the filter or sorbent head number. Start and stop times, and flow rates are pre-programmed or can be manually input. Following the sampling period, a report is automatically printed which may be removed from the printer and submitted to the laboratory with the filter for analysis.

When the sampling period concludes, a report is automatically printed. This report is removed from the printer and submitted with the sample to the laboratory. Sampler start up may be achieved by either a cold or warm start. Warm and cold-start options as well as all other operational specifications are discussed in XonTech, Inc. *Model 920 Toxic Air Sampler Operations Manual*[5].

2.3.3 ATEC 800 Sequential Sampler

2.3.3.1 Description

An ATEC Model 800 sequential sampling instrument will be used to perform 6 or 8 hour integrated carbonyl sampling. The ATEC 800 instrument contains multiple channels that can be independently programmed for specific flowrates. Channel 1 is a multi-port channel containing eight ports. Each port can be programmed to sample over a specific time period. Optional Channels 2 and 3 consist of single ports that can be activated for parallel or different time periods than Channel 1. The Xontec 920/924 samples carbonyl compounds for an integrated 24 hour period only

2.3.3.2 Operation

The sampler can be operated in either program or run modes, depending on the position of the program/run switch on the front panel. In program mode, all of the front panel function keys can be used to program operation cycles, display or print data, perform manual operations, set the MFC flowrate, or change the date and time. In the run mode, the sampler is activated according to the cycle programmed. If a sample is being collected, the sampler will display the current data for the active port or channel. For a full explanation of ATEC 800 operational procedures, refer to *Models 800 and 1600 Automated Samplers Operations and Maintenance Manual*[6]. Following sampling, the operator will remove the cartridges from the sampler, place them in a sealed container, and chill them in preparation for transport back to the laboratory for analysis. The operator will record all appropriate data on the sample log. Note; if a power failure should occur during port sampling, the data collected for that port before the power failure will be lost. The sampler will resume operation at whatever port is active at the time power is restored.

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[5] XonTech, Inc. (1987). *Model 920 Toxic Air Sampler Operations Manual*. Van Nuys, CA: Author.

[6] ATEC. (1996). *Models 800 and 1600 Automated Samplers Operations and Maintenance Manual.* Calabasas, CA: Author.

2.3.4 MET One SASS

2.3.4.1 Description

The MET One Speciation Air Sampling System (SASS) accommodates up to five sampling canisters to hold multiple 47 millimeter filters to capture $PM_{2.5}$ particles. The $PM_{2.5}$ separation is produced by a sharp cut cyclone (SCC) that removes both solid and liquid course particles. Particle penetration through the SCC mimics the $PM_{2.5}$ cutoff curve of the WINS impactor as defined by the U.S. Environmental Protection Agency. All routine maintenance can be done in the field. Filter containers are transported to the laboratory for inspection, cleaning and changing of sampling substrates. Every element of the sampler that is contacted by the sampled air stream ahead of the filter, including the inlet can be cleaned with each sample change. The SASS was designed with individual sharp cut cyclone inlets. Particles larger than 2.5 micron aerodynamic diameter are removed by the cyclonic inlet mounted with each Filter container. The filter containers may be equipped with a diffusion denuder ahead of the filter to remove selected gaseous compounds. [7].

2.3.4.2 Module and Media Description

The integrated SASS canister contains the following components: a sharp cut cyclone, a denuder to remove nitric acid or ammonia gases, a 47 mm front filter for particle capture, a 47 mm tandem or backup filter as needed, and a cover to protect the components.

Several types of filter media are needed for assaying the different chemical constituents of ambient particles. The filter media must be suitable for the type of analysis to be done. For example, Teflon filters are used for gravimetric mass and trace metal determinations. Quartz fiber filters are used for elemental and organic carbon analysis as well as anions and cations analysis.

2.3.5 Gill Solent 2 Axis Ultrasonic Anemometer

2.3.5.1 Description

The Gill 2 Axle Ultrasonic Anemometer is used to measure wind speed and direction (WSD) data. The performance specifications of this anemometer are delineated in Table 2-1. Data is stored in a data logger until it is telemetered to the AQMD’s information system.

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[7] MET One Instruments, Inc. (2001), *Model SASS & SuperSASS $PM_{2.5}$ Ambient Chemical Speciation Samplers*, Grants Pass, Oregon: Author.

The wind-observer, ultrasonic anemometer consists of a sensing head with four transducers arranged in two pairs, surmounting a cylindrical electronic base enclosure. The onboard electronics provide all ultrasonic processing and vector computation required to output wind data in digital and analog form. For a complete description of anemometer operations, refer to *Solent 2 Axis Ultrasonic Anemometer (Heated & NonHeated) User Manual and Product Specification*[8].

TABLE 2-1 Performance Specifications - Gill Solent 2 Axis Ultrasonic Anemometer

Wind Speed	Wind Direction
1. Starting Threshold 0 mph	0 degrees
2. Range 0-145 mph	0-360\540 degrees
3. Accuracy ± 5 percent rms	±4 degrees

2.3.5.2 Siting

WSD measurement, barometric pressure, relative humidity, and temperature monitoring equipment is housed in monitoring stations located in buildings or mobile monitoring platforms. The stations meet Environmental Protection Agency (EPA) criteria for National Air Monitoring Stations (NAMS) and State and Local Air Monitoring Stations (SLAMS) as sited in part 40 Code of Federal Register (CFR) Part 58 attached and included herein by reference.

If the meteorological equipment is located in a one-story building, it is installed on a 6.1-meter tower in an unobstructed position. If the equipment is installed in a platform, it is mounted on a 6.1-meter mast. In those cases involving buildings higher than one story, the mast is made sufficiently high to rise above the surrounding geography.

2.3.5.3 Installation

WSD equipment is assembled and oriented according to the manufacturer's instructions. The manufacturer’s manuals are used as the primary installation guide.

The mast base support is hinged to allow quick raising of the tower. The base will be welded to the top of the platform or secured to a cement base when positioned on a building. If the tower is erected close to an existing building, it will be secured to that building by an L-bracket. If the mast is mounted on the housing roof, guy wires will secure it. Tower vertical alignment may be checked during this process using a

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[8] Gill Instruments, Ltd. *Solent 2 Axis Ultrasonic Anemometer (Heated & Non-Heated) User Manual and Product Specification* (Doc No 1172 - 0003 - lss3). Lymington, Hampshire, England: Author.

bubble level. If the tower is out of vertical alignment, shimming and the use of turnbuckles may be necessary. When the tripod is secured, the mast is fully extended with the sensor orientated in the generally correct direction. Additional guy wires further secure the tower.

Once the WSD monitoring equipment has been assembled, mounted on the mast, and raised to its full height in the correct orientation, the direction sensor will be aligned to true north using a true-north-calibrated compass. Although alignment must be performed from a distance, accuracy within five degrees is possible.

2.3.5.4 Telemetry Interfacing

A telemetry system is used at existing AQMD sites where such capabilities now exist. This system transfers WSD data from the station to the AQMD central computer. The telemetry system accepts direct current (DC) voltage signals from 0 to 5 volts. Since sensors other than WSD are not DC compatible, they must be converted to 0 to 5 volts DC. To convert to DC, input the barometric pressure, temperature, and humidity sensor outputs through the *converter box* that changes the sensor output to the proper voltage. The converter box consists basically of ± 15 and ± 5-volt DC power supply and an alternating current (AC) to DC converter. The input to the converter box comes directly from the sensors.

2.3.5.5 Routine Servicing

The air quality instrument specialist responsible for each monitoring site will perform routine servicing and periodic checks of the WSD system, barometric pressure, and temperature. The instrument specialist must note and initial the type of service performed and the results of each periodic check on the strip chart, in the system's daily log, and on the WSD Monthly Quality Control Maintenance Sheet (Appendix D).

Any suspected operational problem must be communicated in detail by the instrument specialist to the appropriate supervisor. The supervisor, when informed of the problem, will contact the station operator to determine if the problem can be corrected in-house. If the problem cannot be corrected in-house (by the station operator), the AQMD supervisor will arrange for a system repair team. Anemometer servicing will be conducted on daily, weekly, and monthly bases as described below.

A) Daily Checks (where chart recorder is used)
Each day a site is visited, the station operator will write the date, station designation, comments, and initials on the strip chart. The operator will also provide a distinct and accurate time check on the chart. If the time is off, the operator must provide time checks both before and after adjusting the strip chart.

B) Weekly Checks

The sonic anemometer, barometric pressure, and temperature will be checked for daily trends as an indication of proper operation.

C) Monthly Checks
The sonic anemometer will be lowered from the tower and the transducers will be cleaned with a dry towel and water when necessary. The mounting of all three sensors will be checked to verify they are securely attached. The WSD sensor will be aligned with true north.

2.3.5.6 Diagnostics

The Gill 2 Axle Ultrasonic Anemometer microprocessor-based system is designed with continuous internal diagnostics. These diagnostics are used to ensure that the unit is operating correctly within calibration and without potential problems. In the unlikely event of a problem with the anemometer, or if anything physically obstructs its ultrasonic pulses, the anemometer will display different status codes. The transducers will not display inaccurate data. Thirteen different status codes may result. These codes are:

Status code 00 - System is okay
Status code 01 - Transducer pair 1 failed
Status code 02 - Transducer pair 2 failed
Status code 04 - Transducer pairs 1 and 2 failed
Status code 08 - Non-volatile checksum error
Status code 09 - Volatile memory checksum error
Status code 10 - System gain at maximum
Status code 50 - Marginal system gain condition
Status code 51 - Measurement average building
Status code 60 - Heating operational
Status code 61 - Heating operational but under power
Status code 62 - Heating tripped
Status code 63 - Temperature sensor fault
Status code 64 - Heating operational but over power

A status code will result when an object partially blocks the transducer pulse or the transducer begins to lose efficiency. WSD transducers normally receive pulses from each other within a specific range of intensity amplified and fed to the receiving and recording electronics. When the intensity is lower than normal, the transducer will display the status code 10 as a percentage output. A status code 10 is normally reported just before transducer failure. The amplifier gain is automatically increased to keep the system stable and maintain transducer accuracy.

Transducers have stainless steel bodies capable of handling a harsh marine environment. They are manufactured to meet National Equipment Manufacturer's Association (NEMA) 4X or IP 65 Standards and are pretested in a wind tunnel.

The unit, consisting of a transducer and electronics, continuously checks itself, the transducers, and the calibration integrity and describes random access memory (RAM) faults. During each measurement cycle, the unit will perform 39 WSD measurements every second. This data is averaged and output one to four times per second.

2.3.5.7 Calibration

The calibration process is completely computer controlled. However, operator intervention is necessary to change the erasable prompt chip (EPROM) found in the anemometer. An anemometer undergoing calibration is initially fitted with special firmware that operates within reciprocal tables and transducer delays stored in RAM rather than EPROM as is customary. The first requirement is to input the two axis path lengths and the wind tunnel temperature requirements. At this point, the wind tunnel is switched off and the air is still. Reciprocal tables are produced for each axis based upon the path lengths entered and transmitted to the anemometer. The wind tunnel is operated up to a speed of 40 knots and the anemometer is rotated through 360 degrees at 5-degree steps. The perceived WSD is recorded for 5 seconds at each step and the results are averaged and stored.

Because the unit has no moving parts, calibration and accuracy will not drift. The unit has been designed to announce calibration corruption. Anemometer calibration can be tested by inputting a zero value for the WSD and checking the outputs or by using a calibrated fan. The unit should only be placed in a chamber that does not reflect ultra-sonic pulses. The only way the unit can lose its calibrations, is if the distance between the traducers (path length) is altered. The path length can only be altered if the stainless steel arm is bent or physically damaged. To verify path length accuracy, the path length is measured and checked against the original calibration.

2.3.5.8 Data Handling

All data generated from the WSD system will be recorded. Specifically, the station name or number, time and date of the data run, and a brief discussion of any maintenance or repair work required will be noted on the strip chart each day the station is visited. The wind charts may not be cut at any time. When the wind chart is removed from the recorder and the data is reduced, the time and date of chart removal, the station location, and the station reporter's signature must be noted on the bottom of the printed side of the strip chart. The expended chart will be returned to the box in which it was received. The station name or number and the dates of the strip chart will be noted on the end flap of the box. Completed Wind Data Summary Sheets and strip charts will be submitted to the principal air quality instrument specialist responsible for the station.

2.3.6 Graseby-GMW 1200 PM_{10} Sampler

2.3.6.1 Description

A cross-sectional drawing of the Graseby-GMW Model 1200 two-stage, size-selective inlet (SSI) head is shown in Figure 2-1. This sampler is used to sample particulate with an aerodynamic diameter of 10 micron and less. The inlet head is symmetrical and therefore insensitive to wind direction and relatively insensitive to wind speed. The air is drawn through the acceleration nozzles at 40 cfm. Particles larger than 10 microns (aerodynamic diameter) cannot follow the air stream and are deflected below the nozzles onto the flat surface. The air sample is then drawn through vent tubes, the second-stage fractionator, and the filter where the particulate matter is collected. The height of the vent-tube inlets above the acceleration nozzle plate prevents re-entrainment of particles.

The PM_{10} sampler draws air into a specially shaped inlet at a flowrate of 40, ±4, cubic feet per minute (cfm). PM_{10} particulate matter collects on an 8 X 10 inch matted quartz fiber filter surface. The concentration of PM_{10} particulate matter (in micrograms per cubic meter) is calculated by weighing the particulates collected on the filter and dividing by the measured air sample volume. The standard sampling frequency is every sixth day.

To initiate sampler start-up, the operator will complete a PM_{10} sampler site report and send it to the appropriate AQMD supervisor for review of compliance with SLAMS total suspended particulates (TSP) siting criteria 40 CFR Part 58, Appendix E included herein by reference. The PM_{10} sampler may be calibrated according to Appendix A, Section A.5.9 of the AQMD’s *Quality Assurance Plan for Air Monitoring*[9].

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[9] Applied Science & Technology. (1996). *Quality Assurance Plan For Air Monitoring.* Diamond Bar, CA: South Coast Air Quality Management District.

The matted, quartz-fiber filter is very delicate and can be easily torn or gouged. Because a damaged filter will be invalid or invalidate results, it is important to carefully handle it by the edges. To avoid electrical shock, the 115V AC power should be disconnected before working on the motor. Complete operational details are contained in *Instruction and Operation Manual High Volume PM_{10} Sampler*[10].

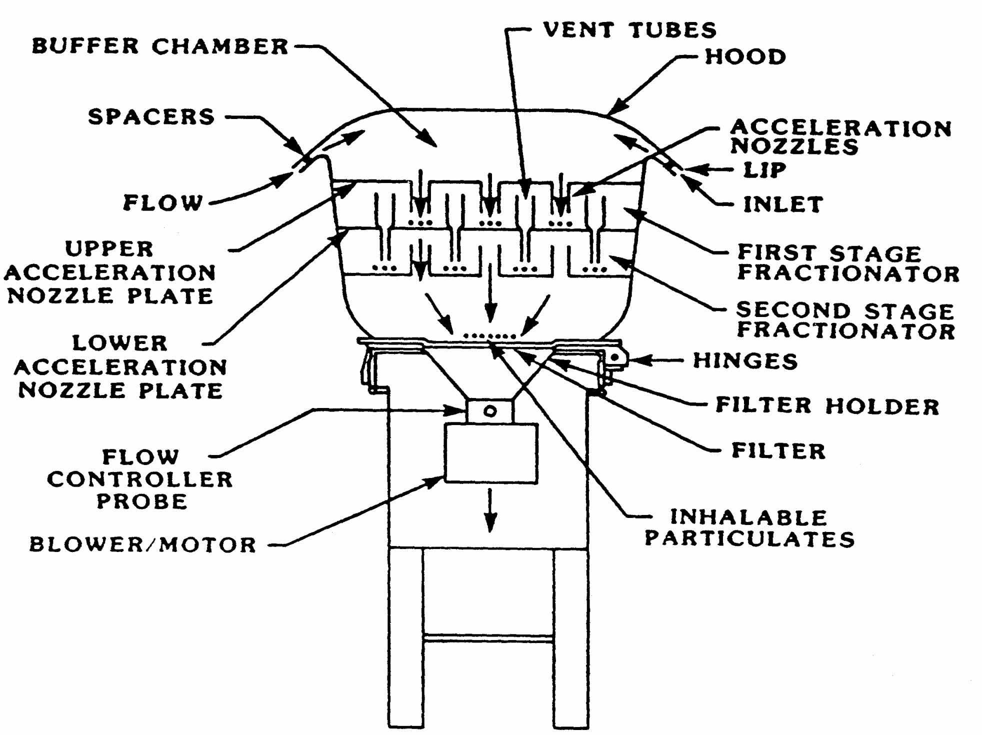

FIGURE 2-1 Graseby-GMW PM_{10} Sampler, Model 1200 with Two-Stage, SSI Head

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[10] Graseby Anderson. (1988). *Instruction and Operation Manual High Volume PM_{10} Sampler.* Atlanta, GA: Author.

Chapter 3.0
Laboratory Procedures

3.1 INTRODUCTION

Since 1994, the AQMD has implemented the U.S. EPA PAMS program to gather data on ozone precursors. Some of the same sampling instruments currently used in the PAMS program may be used in the MATES III and microscale efforts. Hence, many of the procedures and protocols for the MATES III program will be taken from the AQMD *Quality Assurance Plan for Air Monitoring*[11] (updated July 1997). However, MATES III also utilizes several analytical methods not performed in the PAMS program and the protocols include herein will parallel accepted ARB and EPA procedures.

The AQMD will rely upon air quality instrument specialists to take the field samples and deliver them to the laboratory sample custodian. The laboratory sample custodian will handle logging and distribution within the AQMD. Procedures for proper sampling and initial chain-of-custody is outlined in the AQMD *PAMS Air Monitoring Network Quality Assurance Plan*[12], Section 7E parts 1 and 2.

3.2 SAMPLE HANDLING

All sampling media will be handled according to the laboratory practice for implementation of toxics analysis and particulate matter network programs as applicable. Field instrument specialists will complete the sampling information and chain-of-custody forms[13], and deliver the samples to the laboratory sample custodian.

3.2.1 Canister Cleaning

The AQMD laboratory has a canister cleaning oven system. This system utilizes humidified nitrogen to flush and clean canisters in a heated oven to less than 5-ppb carbon of total organic compounds. The canisters are held at a 80°C temperature and are flushed a minimum of seven times over a 2 ½ -hour period. Every canister is removed from the canister cleaning oven and analyzed for residual hydrocarbons. Long-term experience has proven that the canister-cleaning oven system is sufficient to provide clean canisters. Any hydrocarbons (above the threshold concentrations) found in the checked canister are cause for investigation and corrective action. The cleaning date and operator is noted on the canister tag and in an electronic database that serves as the primary chain-of-custody.

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[11] Applied Science & Technology. (1996). *Quality Assurance Plan For Air Monitoring.* Diamond Bar, CA: South Coast Air Quality Management District.

[12] Applied Science & Technology. (1977) *PAMS Air Monitoring Network Quality Assurance Plan.* Diamond Bar, CA: South Coast Air Quality Management District.

[13] These forms consist of the Size-Selective Inlet PM_{10} Sampler Envelope (Appendix C), MATES II Sample Log (Appendix F), and VOC Canister Tag (Appendix G).

3.2.2 Field Canister Use

The canisters are transported by the instrument specialist to the site and installed in accordance with the sampling SOP included in the *PAMS Air Monitoring Network Quality Assurance Plan*[14]. The sample is taken and the sample time, canister number, and start and stop vacuum are noted on the MATES III Sample Log (Appendix F) that follows the canister from the field onward. The sample is promptly returned to the laboratory for log-in and distribution to the appropriate senior chemist.

3.2.3 Sample Distribution in the Laboratory

The laboratory sample custodian (Senior Chemist) will log in the samples received from the courier and distribute them to the appropriate chemist following established laboratory protocol. The sample custodian will distribute samples to the laboratory personnel starting with the responsible Senior Chemist.

3.3 ANALYSIS METHODS

Table 1 gaseous compounds (Appendix A) will be analyzed using gas chromatography with multiple detection for the gaseous compounds. The method generally follows the EPA Method TO-15; *Determination of Volatile Organic Compounds (VOCs) in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS).* Carbonyl analysis will be conducted using EPA Method TO-11, *Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Pressure Liquid Chromatography*. These methods are detailed in the EPA *Compendium of Methods for the Determination of Toxic Organic Compounds*[15].

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[14] Ibid.

[15] Winberry, William, Murphy, Norma & Riggan, R.M. (1988). *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.* Research Triangle Park, NC: Quality Assurance Division, Environmental Monitoring Systems Laboratory, Office of Research and Development, US Environmental Protection Agency. (EPA-600/4-84-041)

3.4 SAMPLING AND ANALYSIS - TABLE 1 COMPOUNDS

The VOCs and halogenated VOCs found in Table 1 (Appendix A) will be analyzed by cryogenic freeze-out to obtain the lowest possible detection limits. These compounds will be detected using a combination of gas chromatography with mass spectrometry and flame ionization detection. A short method description for sampling and analysis of VOCs by GC/MS can be found in this document as Appendix M.

Carbonyl measurement will be conducted utilizing the PAMS sampling and analysis methodology delineated in the *PAMS Air Monitoring Network Quality Assurance Plan*[16]. The Waters ® silica gel cartridge impregnated with dinitrophenyl hydrazine will be used to sample for carbonyl compounds. A potassium-iodide-coated ozone denuder will be used in all carbonyl samplers. The California Air Resources Board (CARB) toxic network design method will be followed using the XonTech 920/924 with a carbonyl channel. A short method description for the carbonyl sampling and analysis can be found in this document as Appendix H. The ATEC Model 800 sampler will be used for sampling at the microscale sites. This model is similar to the AQMD's PAMS sampler.

Inorganic measurements will be taken on Teflon filters using XonTech 920/924 samplers and analyzed by Energy Dispersive X-ray fluorescence (EDXRF). For the $PM_{2.5}$ samples, a Teflon filter will be used, and EDXRF will be used for analysis of elemental constituents. A short method description for sampling and analysis of elements by energy dispersive X-ray fluorescence spectrometry is attached to this document as Appendix J.

Proposed for particulate filter samples both in the coarse (PM_{10}) and fine ($PM_{2.5}$) aerodynamic diameter regions will be analyzed for metals, ions, total mass, OC, EC, and total carbon (TC). The protocol for mass and ions will follow the same methodology as used in the AQMD (federally recognized) PM_{10} Network. Analysis for EC, OC and TC upon the PM_{10} filter samples will be analyzed using the Interagency Monitoring of Protected Visual Environments (IMPROVE) method with some overlapping National Institute of Occupational Safety and Health (NIOSH) Method 5040 analysis. Analysis for EC, OC and TC upon the $PM_{2.5}$ filter samples will be analyzed using the IMPROVE method with some overlapping NIOSH analyses. Both methods similarly evolve carbon from the filters by heating but differ operationally in their temperature and optical monitoring protocols. The results of the overlapping analyses between the NIOSH and IMPROVE methods will be compared. The results from the IMPROVE and NIOSH methods are expected to not be directly comparable, a factor may be realized which will allow for a comparison of the future NIOSH data with AQMD's historical PM database consisting of data measured by the IMPROVE method. Furthermore, seasonal and annual trend analysis will be conducted on data acquired from air monitoring stations used in both MATES II and MATES III.

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[16] Applied Science & Technology. (1977) *PAMS Air Monitoring Network Quality Assurance Plan.* Diamond Bar, CA: South Coast Air Quality Management District.

The preceding discussion covers all Table 1 compounds (Appendix A) that will be sampled on a regular, one day in three sampling schedule synchronized with the national PM_{10} and $PM_{2.5}$ network schedules. The samples will be integrated over a 24-hour period. AQMD personnel will conduct the sampling and analysis. Hired contract instrument technicians and chemists will assist regular AQMD employees.

3.5 SAMPLING AND ANALYSIS - TABLE 2 COMPOUNDS

Although many Table 2 compounds (Appendix B) do not have a widely recognized analytical method, every effort will be made to follow American Society of Test Methods or American Industrial Hygiene Laboratory methodologies. The compounds ethylene dibromide and ethylene dichloride can be seen on chromatograms of the halogenated hydrocarbons analyzed for Table 1 compounds. Since these compounds are rarely used in the Basin, they are on the Table 2 list because they will be evaluated on an infrequent basis.

Compounds found in Table 2 are difficult to measure. Some Table 2 compounds may be sampled by the AQMD and analyzed by external laboratories. Special efforts may be directed to analyzing the ambient air for naphthalene, one of the PAHs.

3.6 SAMPLING SCHEDULE

MATES III sampling will be conducted on the same schedule as utilized by the air-monitoring network. The air monitoring network sampling schedule can be found on the U.S. EPA website at; www.epa.gov/tnn/amtic , and is for the 6-day and 3-day monitoring schedule for TSP, Pb, PM10, PM2.5 and VOC. Using the same sampling schedule results in several benefits:

1) Data from MATES III can be correlated with the ambient data taken on the same day.
2) Additional staff time to service and maintain MATES III sampling equipment and instrumentation is minimized because the existing sampling schedule can be largely utilized.
3) Sample set-up, retrieval, and delivery time to the laboratory is minimized.

Microscale site sampling shall be conducted on a similar schedule to MATES III sampling. The AQMD will operate two to three microscale site sampling platforms. Platforms will be sited for eight weeks at each of a variety of different locations. Sampling will occur on days the MATES III fixed sites are sampling. The schedule for microscale site sampling is depicted in Table 3-1. Sampling at the microscale sites will coincide with the MATES III sampling schedule (that is on a one day in three schedule for approximately six weeks.

Table 3-1 Sample Mobile Platform Sampling Schedule

	Mon	Tues	Wed	Thurs	Fri	Sat	Sun
Week 1	**X**			**X**			**X**
Week 2			**X**			**X**	
Week 3		**X**			**X**		
Week 4	**X**			**X**			**X**
Week 5			**X**			**X**	
Week 6		**X**			**X**		

Chapter 4
Quality Assurance and Quality Control

4.1 INTRODUCTION

To achieve the highest possible data quality level in the MATES III, the AQMD has implemented the following Quality Assurance/Quality Control (QA/QC) plan. This Chapter contains the objectives, procedures, documentation, and data review techniques that will be used by the AQMD to assure that the MATES III will produce accurate data.

4.2 OBJECTIVES

There are three objectives of the QA/QC procedures for the MATES III. These objectives are: 1) to provide accurate and precise data to meet AQMD monitoring requirements, 2) to minimize data loss, and 3) to assess air monitoring data quality and provide data that meets the QA/QC data quality objectives displayed in Table 4-1.

TABLE 4-1 QA/QC Data Quality Objectives

			CRITERIA/PARAMETER			
ASSESSMENT	**MEASURES**	**PROCEDURE**	VOCs	carbonyls	PM_{10}	$PM_{2.5}$
Accuracy	Percent Deviation from True Value	Audits	± 25%	± 25 %	± 10%	± 10%
	95% Probability Limits		< 30%	< 30%	< 15%	< 15%
Precision	Percent Deviation from True Value	Collocation	± 25%	± 25%	< 10%	< 10%
	95% Probability Limits		< 30%	< 30%	< 15 %	< 15 %
Completeness	Percent of Valid Data		85%	75%	90%	90%

4.3 PROCEDURES

4.3.1 Quality Assurance Procedures

The AQMD will perform annual flow audits on all PM_{10} and $PM_{2.5}$ samplers. These flow audits will be conducted according to the procedures outlined in the AQMD's *Quality Assurance Plan for Ambient Monitoring*, Appendix K. In addition the California Air Resources Board (CARB) performs quarterly audits of flows at District air monitoring stations. The CARB also annually audits laboratory systems related to mass measurement in the PM 2.5 and PM 10 networks. The EPA and CARB will annually audit the performance of the AQMD laboratory for VOCs, carbonyls and lead (Pb) using the EPA's National Performance Audit Program and the CARB's toxic VOC performance audit.

Resources permitting, the AQMD will operate a Xontec 920 for collocated measurement of metals, hexchrome and carbonyls at the Rubidoux fixed site. The AQMD will operate collocated Hi-Vol PM10 samplers at Rubidoux for a 24-hour average. The collocated samplers will operate on a one-day-in-six sampling schedule. VOC sampling will be collocated at Pico Rivera on a one-day-in-three sampling schedule.

The AQMD will endeavor to enlist outside laboratories to analyze a small number of split samples for a majority of the compounds measured. The ARB has the capability of performing system audits of the AQMD laboratory, through the probe toxics audits, whole air samples (round robins) and will be the primary outside auditor of the program.

4.3.2 Quality Control Procedures

A) Field Checks

AQMD staff will perform a number of functions when conducting a field check. Specifically, staff will:

1) observe and record all required data for each sampler's monthly maintenance sheet, chain-of-custody form, and sample identification tag
2) check and reset all timers if off by more than ± 5 minutes Local Standard Time
3) check and adjust the flow settings if they are not within ± 5 percent of the calibrated setting

B) Laboratory Daily Checks

AQMD staff will monitor the balance using a NIST traceable check standard; conduct a gas chromatograph standard check using a NIST traceable gas standard; will observe, record, and correct all sample media equilibration conditions if they are out of tolerance.

C) Semi-Annual Checks

AQMD staff will conduct multipoint calibrations of all mass-flow controllers in all samplers; perform instrument leak checks; determine the level of detection (LOD) for each analytical method; and will clean the PM_{10} inlet head.

D) Annual Checks

AQMD staff will clean the sample probe using de-ionized water and a soft cloth; conduct sample probe leak checks and repair if necessary; and will conduct 24-hour tests by operating the sampler with a daytime start-stop time to observe actual run length. Actual start and stop must be observed. The timer will be repaired if the sample period varies from setting by more than ± 20 minutes.

4.4 DOCUMENTATION

A critical element of an effective QA/QC system is proper documentation. To ensure that all samples are properly handled, inspected, collected, analyzed, and reported, a comprehensive set of QA/QC documents will be completed. The information reported in these documents is crucial to determining the validity of reported data. Lack of proper documentation can be grounds for data invalidation. A summary of QA/QC sampling activities is attached as Appendix L.

A) Chain-of-Custody Forms

Chain-of-custody forms (Appendices C, F, F-1 and G) are necessary to identify and control the disposition of the samples through the multiple steps of preparation, sampling, retrieval, analysis, and data reporting. As appropriate, by sample type, chain-of-custody forms will accompany all samples collected in the MATES III and MSS programs. These forms will be originated by the field operators, delivered to the laboratory, and submitted to the assigned laboratory staff. The laboratory will be responsible for storing all chain-of-custody documents.

B) Maintenance Check Sheets

Maintenance check sheets (Appendices D and E) will be completed by field instrument operators for the PM_{10} sampler and ultrasonic wind speed and direction anemometer. These monthly maintenance sheets will be submitted to senior field operators for review, approval, and storage.

C) Calibration Reports

Field and laboratory staff performing semi-annual and post-repair multipoint calibrations will prepare calibration reports. The calibration reports will be reviewed, approved, and retained by field and laboratory staff.

D) Equipment Relocation Notes (ERN)

ERNs are an element of the documentation required in MATES III. Because the microscale monitoring element involves frequent relocation of equipment, it is the responsibility of the field operations supervisor or repair supervisor to note in the station logbooks for each instrument the location and time period the instrument was in service.

E) Station and Equipment Logbooks

Logbooks are provided for each sampling site and piece of sampling equipment. Each and every monitoring station visitor will note the station logbook at each and every visit. The notation should include the date, reason for the visit, and the visitor’s clearly identifiable signature or initials. Instrument logbooks will be noted each time an instrument is repaired, calibrated, or audited.

4.5 DATA REVIEW

Program data validity is directly attributable to the proper implementation of all the operating and QA/QC procedures described in this protocol. To assure that the program's data quality objectives are met, responsibility for data review is distributed between the field operators, calibrators, auditors, and supervisors, laboratory chemists and supervisors, QA supervisors, and the laboratory and air monitoring managers.

A) Field Supervisors

Field supervisors are responsible for locating and setting up the sites, scheduling operators, training field operators, coordinating supply ordering, supply receipt and distribution, and review of monthly QC maintenance sheets. The field supervisors are responsible for notifying the laboratory supervisor of every event that could invalidate the sample.

B) Field Operators

Field operators are responsible for operating all samplers and analyzers according to the operating procedures specified in this protocol. The field operators must observe and annotate all information in the monthly QC maintenance sheets, chain-of-custody forms, sample tags, and logbooks. The field operators are responsible for notifying their supervisors of every out-of-control flow setting, timer setting, expected start or ending pressure, or any other instrument malfunction.

C) Field Calibrators

Field calibrators are responsible for performing semiannual multipoint calibrations on all flow control-devices according to AQMD calibration procedures. Any as-is calibration showing a deviation from design flowrate in excess of ± 15 percent will be reported to the field supervisor. Any samples collected while flow percentage deviation from design flow exceeded ± 15 percent will be invalidated back to the previous flow calibration, audit, or malfunction date.

D) Field Auditors

AQMD field auditors will conduct flow audits on 25 percent of the entire network each calendar quarter. Auditors are responsible for notifying the QA supervisor of any audit indicating a greater than ± 15 percent average percent deviation from design flow.

E) QA Supervisor

The QA supervisor is responsible for reviewing field audit reports, scheduling audits, coordinating with ARB QA staff, and compiling and reporting QA flow accuracy reports.

F) Laboratory Chemists

The laboratory chemists are responsible for receiving field samples, maintaining and storing chain-of-custody documents, performing and documenting QC activities on the QC monthly maintenance sheets, performing laboratory audit analyses, and conducting preliminary data analysis for outliers and out-of-control conditions.

G) Laboratory Supervisor

The laboratory supervisor is responsible for final raw data review, calculation of precision based upon collocated, reviews monthly QA/QC sheets, makes final evaluation of data validity based on satisfactory reports from QA supervisor, field supervisor, and assessment of laboratory precision data.

H) Air Monitoring Manager

The air-monitoring manager is responsible for overseeing field operations and QA auditing operations.

I) Laboratory Manager

The laboratory manager is responsible for overall coordination of MATES III and to ensure that all staff fulfills their responsibilities as detailed in this protocol. Additionally, the laboratory manager is responsible for establishing the final acceptance criteria for sample validity once actual precision and accuracy data become available.

Chapter 5.0
Data Processing and Reporting

5.1 INTRODUCTION

MATES III monitoring for ambient air toxics will develop a large data resource for future analysis. Table 1 compounds, when multiplied by the projected frequency of sampling in MATES III, will result in more than 20,000 individual data points representing a concentration of a toxic compound at a particular time and location. The purpose of this chapter is to outline the data handling of such a large database. This section will only pertain to the laboratory work performed and not to the meteorological, criteria pollutant, or monitor calibration data.

The AQMD Laboratory has had prior experience handling such a large data base as part of MATES II. Reporting templates for the carbon analysis and XRF elemental analysis (inorganics) will follow the outline used in MATES II. Reporting templates for the VOCs, halogenated hydrocarbons, and carbonyls will follow the PAMS format.

The aim of the reporting will be to generate Excel data files for electronic transfer to interested parties. The data will be checked for transcription errors and quality assured to represent the most accurate determinations possible. The laboratory will strive to disseminate the data in a timely fashion to facilitate feedback.

5.2 DATA BASE COMPILATION

The laboratory chemists will generate a data point representing the concentration of a particular compound found over a particular time period at a particular site. The instrument analyzes the sample and determines the volume concentration on a parts-per-billion basis. These concentration numbers will be compiled into a spreadsheet along with the name of the sampling site and the date the sample was taken. The chemist (analyst) is responsible for checking data point accuracy. The technician in charge of copying the data points into the spread sheet is responsible for their accurate transcription. The senior chemist is in charge of double checking the chemists' and technicians' data transcription work.

If resources permit, one chemist will operate the instrument while another chemist reduces the data and transcribes it to the Excel spreadsheet. This method would lead to the quickest turnaround time possible. One chemist may reduce the data from several instruments depending on the workload.

MATES III data will encompass PM_{10} and $PM_{2.5}$ mass, ions for both fractions, VOCs, carbonyls, XRF, ICP/MS and carbon analysis results. The run date will be encoded with the year, month, and day in six numerals. This information will be followed by a two-letter acronym representing the station and concentration. The column header has the name of the compound and the concentration units. Uncertainties were given for each data point. These uncertainties encompass the calculated limits for the sampling and analysis errors introduced into the measurement system.

The MATES III data will be compiled into several spreadsheets. These spreadsheets will conjugate components along the lines of the analysis technique. Each instrument will have a separate spreadsheet for the compounds it analyzes.

The laboratory can work with the end data user to supply the electronic version in whatever file length or configuration is desired. The data can also be translated into ASCII flat files.

5.3 PERIODIC REPORTS

The laboratory will strive to meet a two-month turnaround time from the date of sampling to the finished and checked report. The VOCs, carbonyls, XRF, and carbon analyzer will all be sampled individually, yet in very similar formats. Extra effort will be made to analyze duplicate samples and other QC samples and compile into a separate report for monthly reporting. The reports will be available in electronic file and printed spreadsheets.

5.4 FINAL REPORT

Past experience has proven that the final report including the QA report can take from four to six months after the last day of sampling to complete. The data will be compiled on a monthly basis and the final report is slated to be complete within two months of the end of sampling. Resources permitting, laboratory staff will migrate the Excel spreadsheets to the Access database software. The final report will be stored in several files segregated by date and analysis. The AQMD Laboratory has the ability to write the files to CD-ROM. Only limited hard copies of the report will be printed.

Glossary

Quality Assurance (QA)
The practice of establishing procedures external to the day-to-day monitoring operations that indicate whether or not air quality data is accurate, representative, precise and complete enough to satisfy the needs of the data users. QA activities include, but are not limited to, system and performance audits and collocated and parallel sampling. These activities are described in detail in Chapter 4.

Quality Control (QC)
Any procedure incorporated into the internal, day-to-day operations of collection and analysis of air quality samples to satisfy the data user's need for valid data. These activities are described in detail in Chapter 4.

Accuracy
A determination of how closely reported data values are to true values. Annually conducted performance audits will challenge the various samplers and instruments used in this program to assess their accuracy. All program data accepted as valid, will meet the criteria set forth in Table 4-1. Accuracy is expressed as "percent" deviation from true and is calculated as follows:

$$\text{Percent Deviation from True} = \frac{\text{Indicated Value - True Value}}{\text{True Value}} \times 100$$

Precision
The measure of monitoring system repeatability. Precision is determined by amassing a variety of measurements of the same true value over a period of time and assessing the variability of those measurements. Precision objectives for the various monitoring methods used in MATES II and MSS programs are presented in Table 4-1.

Data Completeness (DC)
The percent of valid data points actually collected out of the total number of data points possible. The data completeness objectives for the MATES II and MSS programs are presented in Table 4-1. DC is calculated using the following formula:

$$\text{percent DC} = \frac{\text{Total valid data points}}{\text{Total number of possible data points}} \times 100$$

Representativeness
The goal that samples are representative of both temporal and/or spatial scales at all sites. This is accomplished by conforming to 40CFR58 siting and sampling requirements for PM_{10}.

Performance Audit
A procedure conducted to establish individual analyzer and overall sampling and analysis accuracy. Probe audits are used to measure the integrity of both the sampling and analysis

systems. Flow audits measure the accuracy of the flow metering devices that assure the sample's temporal representativeness. Gas standard audits determine accuracy of laboratory analyzers in measuring known concentrations of toxic compounds.

System Audit
An on-site inspection and review of the entire monitoring program.

Collocated Sampling
The process of running two identical samplers concurrently at the same location. Collocated data measures a method's precision. One of the samplers is designated *A* and is treated as the true value; while the other sampler is designated *B* and is regarded as the indicated value.

Parallel Sampling
The process of two different agencies such as the AQMD and ARB operating two different samplers side-by-side.

ACRONYM LIST

AC	alternating current
AIHL	American Industrial Hygiene Laboratory
AM	Air Monitoring
AQMD	South Coast Air Quality Management District
ARB	Air Resources Board
AST	Applied Science and Technology
ASTM	American Society of Test Methods
Basin	South Coast Air Basin
cc	cubic centimeters
ccm	cubic centimeters per minute
cfm	cubic feet per minute
CFR	Code of Federal Records
DC	direct current
DNPH	2, 4-dinitrophenyl-hydrazine
EDB	ethylene dibromide
EDC	ethylene dichloride
EJ-2	Environmental Justice Initiative Number 2
EPA	Environmental Protection Agency
EPROM	erasable prompt chip
ERN	equipment relocation notice
ETM	elapsed time meter
FPC	filter paper cartridge
HPLC	High Performance Liquid Chromatograph
ICP/MS	Ion coupled Plasma/Mass Spectrometry
LIMS	Laboratory Information Management System
LOD	Level of Detection
lpm	liters per minute
MATES II	Multiple Air Toxics Study II
MATES III	Multiple Air Toxics Study III
MFC	mass flow controller
mph	miles per hour
MSS	Microscale Study
MTBE	methyl tert butyl ether
NAMS	National Air Monitoring Stations
NEMA	National Equipment Manufacturer’s Association
PAH	polycyclic aromatic hydrocarbon
PAMS	Photochemical Assessment Monitoring Station
PM	particulate matter
ppb	parts per billion
ppbC	parts per billion carbon
PSI	pounds per square inch
PST	Pacific Standard Time
PTEP	Particulate Technical Enhancement Program

PUF	polyurethane foam
QA	quality assurance
QC	quality control
RAM	random access memory
rms	root mean standard
SASS	speciation air sampling system
SCAQMD	South Coast Air Quality Management District
SCC	sharp cut cyclone
SCFM	standard cubic feet per minute
SLAMS	State and Local Air Monitoring Stations
SOP	standard operating procedure
SSI	size selective inlet
TAC	toxic air contaminant
TSP	total suspended particulates
V	Volt
VOC	volatile organic compound
WSD	wind speed and direction
XRF	X-ray fluorescence

APPENDIX A Proposed Table 1 Air Contaminants for Inclusion in the Measurement Program

(Compounds in bold are proposed for U.S EPA AIRS database reporting)

CAS No.	Chemical Name	Lab Test Method	Sampling Freq.	Comment
VOCs				
71-43-2	**Benzene**	**GC/MS/FID**	**1 in 3 days**	
106-99-0	**Butadiene [1,3]**	**GC/MS/FID**	**1 in 3 days**	
(o-) 95-50-1	Dichlorobenzene [ortho- & para]	GC/MS/FID	1 in 3 days	
100-41-4	Ethyl Benzene	**GC/MS/FID**	**1 in 3 days**	
100-42-5	Styrene	GC/MS/FID	1 in 3 days	
108-88-3	Toluene	GC/MS/FID	1 in 3 days	
(m-) 108-38-3	Xylene [m+p, o-]	GC/MS/FID	1 in 3 days	
75-01-4	**Vinyl chloride**	**GC/MS/FID**	**1 in 3 days**	
Halo-HCs				
56-23-5	**Carbon tetrachloride**	**GC/MS/FID**	**1 in 3 days**	
67-66-3	**Chloroform**	**GC/MS/FID**	**1 in 3 days**	
75-09-2	**Methylene chloride (Dichloromethane)**	**GC/MS/FID**	**1 in 3 days**	
127-18-4	**Perchloroethylene (tetrachloroethene)**	**GC/MS/FID**	**1 in 3 days**	
78-87-5	**Propylene Dichloride (1,2-dichloropropane)**	**GC/MS/FID**	**1 in 3 days**	**Not in MatesII**
79-01-6	**Trichloroethylene**	**GC/MS/FID**	**1 in 3 days**	
Carbonyls				
75-07-0	**Acetaldehyde**	**HPLC**	**1 in 3 days**	
67-64-1	Acetone	HPLC/ **GC/MS/FID**	1 in 3 days	Not Reported
50-00-0	**Formaldehyde**	**HPLC**	**1 in 3 days**	
78-93-3	Methyl ethyl Ketone (MEK)	HPLC/GC/MS/FID	1 in 3 days	Not Reported
1634-04-4	Methyl tert-Butyl Ether (MTBE)	HPLC/GC/MS/FID	1 in 3 days	Not Reported
Inorganics				
7429-90-5	Aluminum	ICP/MS:XRF	1 in 3 days	
7440-38-2	**Arsenic**	**ICP/MS:XRF**	**1 in 3 days**	
7440-41-7	**Beryllium**	**ICP/MS:XRF**	**1 in 3 days**	
7440-43-9	**Cadmium**	**ICP/MS:XRF**	**1 in 3 days**	
7440-70-2	Calcium	ICP/MS:XRF		
7440-47-3	Chromium (total)	ICP/MS:XRF	1 in 3 days	
	Chromium (hexavalent)	**IC**	**1 in 3 days**	
7440-48-4	Cobalt	ICP/MS:XRF	1 in 3 days	
7440-50-8	Copper	ICP/MS:XRF	1 in 3 days	
7439-89-6	Iron	ICP/MS:XRF	1 in 3 days	
7439-92-1	**Lead**	**ICP/MS:XRF**	**1 in 3 days**	
7439-95-4	Magnesium	ICP/MS:XRF		
7439-96-5	**Manganese**	**ICP/MS:XRF**	**1 in 3 days**	
7440-02-0	**Nickel**	**ICP/MS:XRF**	**1 in 3 days**	
7723-14-0	Phosphorous	ICP/MS:XRF	1 in 3 days	
7440-09-7	Potassium	ICP/MS:XRF	1 in 3 days	
7782-49-2	Selenium	ICP/MS:XRF	1 in 3 days	
CAS No.	**Chemical Name**	**Lab Test Method**	**Sampling Freq.**	**Comment**
7440-21-3	Silicon	ICP/MS:XRF	1 in 3 days	
7440-62-2	Vanadium	ICP/MS:XRF	1 in 3 days	
7440-66-6	Zinc	ICP/MS:XRF	1 in 3 days	
Others				
	Elemental & organic carbon	C analyzer	1 in 3 days	
Criteria Pollutants				
	PM2.5	SASS	1 in 3 days	Speciation
	PM10	SSI-Hivol	1 in 3 days	PM network

APPENDIX B Proposed Table 2 Air Contaminants that Potentially May Be Monitored on A Limited Basis

		Laboratory	
CAS No.	**Chemical Name**	Test Method	Comment
VOCs			
	Acrolein		No ambient method
Halo-HCs			
106934	Ethylene dibromide {EDB}	GC/MS	
107062	Ethylene dichloride {EDC}	GC/MS	
Others			
	PAHs	HPLC	Send out for analysis
	Napthalene	HPLC	Send out for analysis
	Diesel exhaust “Markers”	TBD	Send out for analysis

APPENDIX C Size-Selective Inlet PM_{10} Sampler Envelop

South Coast Air Quality Management District
Applied Science & Technology

Size-Selective Inlet PM_{10} Sampler Envelop

FIELD OPERATOR USE	LABORATORY USE ONLY
STATION #________________________	SAMPLE #___________________________
LOCATION________________________	FLOWRATE, CFM____________________
SAMPLER #_______________________	VOLUME OF AIR, M^3_________________
QUARTZ FILTER #_________________________	FINAL WEIGHT (gm)_________________
DATE_____________________________	TARE WEIGHT (gm)__________________
TIME	SAMPLE WEIGHT (gm)_______________
END_________________________	PM_{10}(ug/M^3)____________________
START_______________________	SAMPLE RECV'D____________________
TOTAL______________________	
REMOVED FROM SAMPLER________	SAMPLE WEIGHED__________________
SENT TO HQ______________________	SAMPLE EXTR.______________________
RECEIVED AMB___________________	SAMPLE ANALYSIS__________________
	REF. ______________________________

DATE SAMPLER CALIBRATION_______________________________

STATION OPERATOR____

Remarks (unusual activities sampling conditions, etc.):

APPENDIX D WSD Monthly Quality Control Maintenance Check Sheet

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

MONTHLY QUALITY CONTROL MAINTENANCE CHECK SHEET

MAKE/MODEL________________________________Wind Speed and Direction System

Location ____________________________________ Month/Year _________________________
Station No.___________________________________ Specialist __________________________
Control No._______________ Reviewed by ________________________ Date _______________

Date	**Zero Speed**		**Zero Direction**		**Visual Wind Transmitter Check**	**Chart Time**	
	As Found	**Final**	**As Found**	**Final**		**As Found**	**Final**

OPERATOR INSTRUCTIONS:

Daily Checks: Chart trace and time.
Weekly Checks: Zero speed and direction inking system
Visual wind transmitter check. The station operator will visually check the wind transmitter to confirm the direction coincides with recorder. Notify supervisor immediately if problem occurs.

Bi-monthly
Maintenance:

DATE	**COMMENTS OR MAINTENANCE PERFORMED**

Calibration Date:__________________ Operator _____________________

APPENDIX E High Volume Monthly Quality Control Maintenance Check Sheet

High Volume
Monthly Quality Control Maintenance Check Sheet

MAKE/MODEL

HIGH VOLUME SAMPLER

Location________________________________
Station No.______________________________
Control No.______________________________
Operating Set Point_______________________
Date SSI Head Cleaned____________________

Month/Year______________________
Specialist________________________
Reviewed by/Date_________________
Cubic Feet per Meter______________
Due Date_________________________

Sample Date	**Initial Flow cfm**	**Final Flow cfm**	**Filter No.**	**Initial Elapsed Time**	**Final Elapsed Time**	**Total Time**
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
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APPENDIX F MATES III Sample Log

South Coast Air Quality Management District

Mates III Sample Log

Location:____________________________

Sample Date:__________________________

Station No.:__________________________

Retrieved By:_________________________

Retrieval Date:________________________

Lab No.:________________________

Date Sample Received:____________

Reference No.:____________________

Analyst:__________________________

Canister Log – XonTech 910

Sample Time	Canister No.	Start Vacuum	End Pressure	Comments
24 hour				
Blank				
Collocated				

DNPH Cartridge Log – XonTech 920

Sample Time	Cartridge No.	Elapsed Time	Flow Rate	Comments
24 hour				
Blank				
Collocated				

Filter Log – XonTech 920

Sample Time	Filter No.	Flow Rate	Comments
Teflon (Metals)			
Cellulose (Chrome VI)			
PM_{10} (Hi-Vol)			

(Staple Printout Here)

APPENDIX F-1 MATES III Sample Log

South Coast Air Quality Management District

Microscale Sample Log

Location:__________________________

Sample Date:_______________________

Station No.:_______________________

Retrieved By:_______________________

Retrieval Date:______________________

Lab No.:________________________

Date Sample Received:____________

Reference No.:___________________

Analyst:__________________________

Canister Log – XonTech 910

Sample Time	Canister No.	Start Vacuum	End Pressure	Comments
24 hour				
0-8 hour				
8-16 hour				
16-24 hour				

DNPH Cartridge Log – XonTech 920

Sample Time	Cartridge No.	Elapsed Time	Flow Rate	Comments
24 hour				
0-8 hour				
8-16 hour				
16-24 hour				

Filter Log – XonTech 920

Sample Time	Filter No.	Flow Rate	Comments
Teflon (Metals)			
Cellulose (Chrome VI)			
PM_{10} (Hi-Vol)			

(Staple Printout Here)

APPENDIX G VOC Canister Tag

VOC CANISTER TAG

SCAQMD PAMS CAN

#___________

	STATION		LAB		
Code	**Date**	**Time**	**Initial**	**Analysis**	**Clean**
Notes					
Notes					
Notes					
Notes					
Notes					
Notes					
Notes					
Notes					
Notes					
Notes					
Notes					

APPENDIX H Method Description for Sampling and Analysis of Carbonyls by HPLC at the AQMD Laboratory

Sampling - Ambient air is drawn through a glass and/or stainless steel probe at the air monitoring site and pulled through DNPH coated silica cartridges mounted in the A-Tech 800 sampler. The sampling cartridges are coated with a minimum of 300 mg of DNPH on Waters Sep-Pak silica cartridges. The sample is pulled through the cartridge at approximately one lpm for 8-hour sampling and at 0.7 lpm for 24-hour sampling. Before and after sampling the cartridges are kept capped and refrigerated in small vials to prevent loss and contamination.

Laboratory Analysis- The laboratory uses a Waters Millennium system high performance liquid chromatograph (HPLC) with autosampler. After elution of the Sep-Pak cartridge with 3 milliliters of acetonitrile, the samples are placed in the autosampler. Samples are run isocratically (55 percent acetonitrile and 45 percent H_20) on a Waters C-18, 5 micron, 4.6 mm by 250-mm column. Flow is one milliliter per minute. Twenty microliters are injected onto the column by the autosampler.

Quantification - A calibration curve is derived from multi-point injections of standards obtained from Radian Corporation. One point control standards are run daily with the sample analysis. PAMS compounds, acetaldehyde, formaldehyde, and acetone, are quantified by comparison to the calibration curve.

QA/QC- The limit of detection is determined for the HPLC response and the system LOD is calculated for a typical air volume sampled. A collocated cartridge is run every 6 days of sampling in the field. Blank cartridges are run at a similar frequency. Replicate samples are run every ten samples.

APPENDIX I Method Description for Sampling and Analysis of Elements by Energy Dispersive X-ray Fluorescence Spectrometry at the AQMD Laboratory

Sampling-Ambient air is drawn through a 47 mm Teflon filter loaded in a TSP or $PM_{2.5}$ sampler. Typically, 24 hour sampling at about 20 lpm provides sufficient sample mass on the filter for a successful analysis. The sampler must collect a homogeneous sample across the surface of the filter. The Kevex XRF instrument examines a very small cross section of the filter near the center.

Laboratory Analysis-A Kevex Energy Dispersive X-ray fluorescence spectrometer is used to analyze 35 elements in the filter sample. There is no need for sample preparation other than bringing the filters to room conditions. Each filter is loaded onto a sample wheel brought to a vacuum and scanned under five different instrumental conditions. Each condition is optimized for certain groups of elements. After spectral acquisition, an identification and deconvolution process extracts the net contributions of counts of each of the 35 elements.

Speciation and Quantification-Each element has a unique spectral pattern. After accounting for overlaps, each of the elements is identified qualitatively. By using previously calibrated standard values the net counts for each element are converted to actual concentrations in ug/filter. Using air volume data gathered during sampling, the ug/filter concentrations of the elements are converted to ug/M^3.

QA/QC-The X-ray analytical instrument is calibrated using 35 single element standards. These calibration standards are checked using an NIST multi-element film standard. Filter blanks are analyzed for subsequent background correction during the spectral analysis of the run. Field blanks are taken at specified times depending on the frequency of sampling. Field blank results are either subtracted or reported in accordance with data reporting and analysis requirements. Finally, collocated runs are utilized to check precision.

APPENDIX J Method Description for Sampling and Analysis of Elements by Energy Dispersive X-ray Fluorescence Spectrometry at the AQMD Laboratory

Sampling-Ambient air is drawn through a 47 mm Teflon filter loaded in a TSP or $PM_{2.5}$ sampler. Typically, 24 hour sampling at about 20 lpm provides sufficient sample mass on the filter for a successful analysis. The sampler must collect a homogeneous sample across the surface of the filter. The Kevex XRF instrument examines a very small cross section of the filter near the center.

Laboratory Analysis-A Kevex Energy Dispersive X-ray fluorescence spectrometer is used to analyze 35 elements in the filter sample. There is no need for sample preparation other than bringing the filters to room conditions. Each filter is loaded onto a sample wheel brought to a vacuum and scanned under five different instrumental conditions. Each condition is optimized for certain groups of elements. After spectral acquisition, an identification and deconvolution process extracts the net contributions of counts of each of the 35 elements.

Speciation and Quantification-Each element has a unique spectral pattern. After accounting for overlaps, each of the elements is identified qualitatively. By using previously calibrated standard values the net counts for each element are converted to actual concentrations in ug/filter. Using air volume data gathered during sampling, the ug/filter concentrations of the elements are converted to ug/M^3.

QA/QC-The X-ray analytical instrument is calibrated using 35 single element standards. These calibration standards are checked using an NIST multi-element film standard. Filter blanks are analyzed for subsequent background correction during the spectral analysis of the run. Field blanks are taken at specified times depending on the frequency of sampling. Field blank results are either subtracted or reported in accordance with data reporting and analysis requirements. Finally, collocated runs are utilized to check precision.

APPENDIX K Method Description for Sampling and Analysis of Organic and Elemental Carbon by Thermal/Optical Carbon Analyzer at the AQMD Laboratory

Sampling-Ambient air is drawn through a 47-mm quartz filter loaded in a PM2.5 sampler or an 8 X 10 inch quartz fiber filter loaded in a SSI-Hi-Vol sampler. Typically, 24 hour sampling provides sufficient sample mass on the filter for a successful analysis. The sampler must collect a homogeneous sample across the surface of the filter. A one-centimeter diameter punch from any quadrant of the filter is used in the instrument.

Laboratory Analysis-A Desert Research Institute (Reno, Nevada) thermal/optical carbon analyzer is used to determine the total carbon content of aerosol deposited on quartz filters. The analyzer is able to distinguish and characterize organic and inorganic carbon by a thermal/optical method with flame ionization detection. There is no need for sample preparation other than bringing the filters to room conditions. A small circular filter area is punched out from the quartz filter and loaded on to the carrier quartz tube. The filter is pushed into an oven whose temperature is raised in steps from ambient to approximately 850 degrees Celsius. An inert gas, such as nitrogen is continuously passed over the filter. At the same time the surface of the filter is monitored with a laser beam to determine the exact point at which all the elemental carbon (soot) is burned off. The combusted carbon forms carbon dioxide that is carried over to a methanizer. The methanizer (active nickel with the addition of hydrogen gas) converts the carbon dioxide to methane. The methane flows to a flame ionization detector. The detector output is integrated and converted to ug of carbon per filter using previously calibrated standards.

Speciation and Quantification-The light organic fraction is driven off the filter at the early stages of heating. The elemental carbon fraction is then oxidized at a higher temperature with an oxygen enriched carrier gas. A laser beam constantly scanning the filter surface indicates the exact point at which the organic and elemental carbon fractions are removed from the filter. The two fractions are summed to give the total carbon concentration of the sample. The analysis results in the elemental, organic, and total carbon content of the sample. Using air volume data gathered during sampling, the ugC/filter concentrations are converted to ugC/M^3 of air.

QA/QC-The optical-thermal carbon analyzer is calibrated using two types of standards. One set consists of carbon containing gases, methane and carbon dioxide in an inert gas mixture. These are passed through the entire system to calibrate the instrument. In addition, filters impregnated with solution containing a known concentration of carbon are run as external standards. Filter blanks are analyzed for subsequent background correction during the run. Field blanks are taken at specified times depending on the frequency of sampling. Field blank results are either subtracted or reported in accordance with the data reporting and analysis requirements. Finally, collocated runs are utilized in checking precision.

APPENDIX L QA/QC Matrix Summary

Process	Interval	Activity	Criteria	Corrective Action
	Before & After Each	QC - Note Activities in Log Book, Canister	Notes For Each Canister	N/A
		QC - Check Chart Time	± 10 Minutes of Actual PST	AQIS Resets
Field Canister	Annually	QC - Clean Manifold	Pass Leak Check	AM Support Repairs
Sampler		QC - Calibrate Flow	± 5 Percent True Flow	AM Operations Calibrates
	1 Day in 3	QA - Collocated Sample	10 Percent Of Network	Run A + B Make-Ups if Possible
	Annually	QA - ARB Through-the-Probe Audit	Within ± 25 Percent of True For all Compounds	Isolate & Repair, Validate Data
		QA - Flow Audit	Indicated Flow Must Be Within ± 10 Percent of True Flow	Notify Operations If Outside Limits, Delete Data
	Before & After Each	QC - Note Activities in Log Book	N/A	N/A
	Sampling Event	QC - Check Start & Stop Times & Volume	Note On Canisters Log Sheet	AQIS Resets Time
Field Carbonyl		QC - Clean Manifold	Pass Leak Check	AQIS Cleans & Tests
Sampler	Annually	QC - Calibrate Flow Controller	± 5 Percent True Flow	AM Operations Calibrates
If Equipment	1 Day in 6	QA - Collocated Sample	10 Percent of Network	Run A + B Make-Ups if Possible
Available	Annually	QA - Through-the-Probe Audit By ARB	Within ± 25 Percent of True For All Compounds	Isolate & Repair, Validate Data
		QA - Flow Audit	Indicated Flow Must be Within ± 10 Percent of True Flow	Notify Operations if Outside Limits, Delete Data
		QC - Chain-of-custody	Log Sheet & Cartridge Numbers Agree	Chemist Corrects Any Errors
		QC - Propane Peak	± 10 Percent Of Previous	Chemist Adjusts Span
	Daily	QC – System Blank	< 10 ppb/C Total NMOC	Chemist Repairs/ Leak Checks
		QC – Replicate Sample	Visual Evaluation of Chromatogram	Chemist Repairs/Leak Checks
Laboratory	Semiannually	QC – Replicate Standard Analysis	± 10 Percent on All Compounds	Chemist Repairs
		QC - Bias Check	2 ppb/C Per Compound	Chemist Repairs/Leak Checks
	Annually	QC - LOD Check	All Loads Must Be Less Than 1 ppb/C	Chemist Repairs/Rechecks
	1 Day In 6	QA – Collocated Samples	± 25 Percent On All Compounds	Chemist Repairs
	Quarterly	QA – Parallel Sampling	All Compounds Must Be Within ± 30 Percent	
	Annually	QA – NPAP Performance Audit	Within ± 30 Percent of True For All Compounds	Chemist Repairs
		QC – Standard Response	± 10 Percent of Previous	Chemist Repairs/Adjusts Span
	Daily	QC – Purge Cycle	System Pressure Between 800 & 1700 PSIG	Chemist Leak Checks
Laboratory	Semiannually	QC – Multipoint Calibration	± 10 Percent Of Previous	Chemist Develops New Calibration Curve
		QC - Bias Check	<3 ppb Per Compound	Chemist Repairs
	Annually	QC - LOD Check	<1 ppb Per Compound	Chemist Repairs/Leak Checks
	Quarterly	QA – Parallel Sampling	All Compounds Must Be Within ± 30 Percent	
	Annually	QA – NPAP Performance Audit	Within ± 30 Percent of True For All Compounds	Chemist Repairs
	Before & After Each Sample	QC - Note the Maintenance Sheet, Log	Notes as Required	N/A
	Semiannually	QC – Change Motor & Multipoint	Create New Calibration Curve	N/A
		QC - Clean Inlet		
Field PM$_{10}$ SSI	Annually	QC - Timer Check	Timer Tested For Start With 20 Minutes of Setting & Elapsed	Repair or Replace
	1-Day-in- 6	QA - Collocate	Run At 10 Percent Of Sites	N/A
	Annually	QA - Flow Audit	Actual Flow Must be Within ± 10 Percent of True Flow	Request Repair; Investigate & Confirm Data Validity
		QC - Balance Checks		
Laboratory	Daily	QC - Inspect Filters	No Light Leaks or Tears	
PM$_{10}$ SSI		QC - Equilibrate Filters		
	1 Day in 6	QA - Collocate Filters	Agreement Within ± 20 Percent, all Compounds	

Appendix M Method Description for Sampling and Analysis of VOCs by GC/MS at the AQMD

Sampling- Ambient air is pumped into an evacuated Summa® polished 6 liter canister by a Xontech 910A air sampler at the sample location through a properly sited probe and manifold. The sample is integrated over 24 hours to fill the canister to approximately 10 PSI. The canister is returned to the laboratory for subsequent analysis by Gas Chromatography with a Mass Spectrometer Detector (GC/MS).

Laboratory Analysis- The laboratory uses a Hewlett-Packard 6890 Gas Chromatograph with an HP 5973 Mass Selective Detector. The sample is concentrated with an Entech 7100 cryo-concentrator for input to the GC/MS. The sample canister is attached to the cryo-concentrator and a 400-milliliter aliquot (600 ml for MSS samples) is chilled in a trap to minus 150 degrees centigrade. For removal of the fixed gases the trap is heated to 20 degrees centigrade and transferred to a second trap cooled to -45 C for mitigation of the CO_2 and H_2O collected. The concentrator loop is then heated and the contents cryo-focused at the head of the GC column for subsequent separation of the VOCs. The mass selective detector records the mass spectrum of each peak (compound) and the analyst uses previously determined standards to compare selected ions for each compound to determine the concentration.

Quantitation- A calibration curve is derived by injection of a gas standard containing the compounds of interest at ppb levels. Every sample run is preceded and ended with a calibration check. Every analysis day is begun with a system blank run. Selected quantitation ions for each compound are compared to the gas standards injected to determine concentration in parts per billion.

QA/QC-The Limit of Detection (LOD) is determined for the GC/MS by multiple injections of the lowest standard amount available (within 10 times the estimated LOD). Collocated samples are run in the field at one station. All canisters from the canister cleaning system are filled with the purified nitrogen and tested for the presence of the compounds of interest. Above 0.2 ppb of any compound of interest or 4 ppb total of all compounds (ppbc) is cause for corrective action.