

APPENDIX III

MATES IV

FINAL REPORT

MATES IV Monitoring and Laboratory Analysis Protocol

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MATES IV

APPENDIX III

MONITORING AND LABORATORY ANALYSIS PROTOCOL

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**Science and Technology Advancement
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Chapter 1.0 Introduction

This appendix document provides detailed information about the procedures and processes which were used to conduct the field measurement and laboratory analysis elements of the Multiple Air Toxics Exposure Study IV (MATES IV).

1.1 BACKGROUND

In 1998, the South Coast Air Quality Management District (SCAQMD) conducted an intensive ambient air toxics monitoring program, the Multiple Air Toxics Exposure Study II (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 SCAQMD 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 SCAQMD Board in March 2000¹.

As a follow up study to MATES II, MATES III was conducted from April 2004 through March 2006. The initial scope of the study was for one year, however, due to heavy rains in the first year of the study a second study year was added over concern of atypical meteorology. The MATES III Final Report was published in September 2008².

MATES IV was conducted to build upon prior ambient toxics data sets, evaluate spatial and temporal trends and better understand current risk associated with air toxics in the Basin.

For MATES IV, organic and metal compounds were sampled and analyzed. These compounds are identified in Appendix A. Compounds listed in Appendix A were measured on a routine one-in-six day basis.

Field sampling began July 2012 and continued for one year. This document describes the monitoring, laboratory analysis, quality control (QC), and quality assurance (QA) activities necessary to support the MATES IV program.

¹ South Coast Air Quality Management District (2000). *MATES II Final Report*. Diamond Bar, CA

² South Coast Air Quality Management District (2008). *MATES III Final Report*, Diamond Bar, CA

Chapter 2.0 Monitoring Equipment

2.1 INTRODUCTION

For the purposes of this appendix, the descriptions and operational and maintenance procedures of the following equipment are stated.

TABLE 2-0 MATES IV Samplers

<u>Sampler Type</u>	<u>Vendor and Model Number</u>
Volatile Organic Compounds (VOC)	XonTech 910A/ 912
Metals; Carbonyls, Cr ⁺⁶	XonTech 924
PM _{2.5} Speciation Air Sampling System	Met One Instruments SASS
Wind, Speed, and Direction (WSD)	R.M. Young Mechanical Wind Sensor
PM ₁₀	Graseby-GMW 1200 PM ₁₀ Sampler
Aethalometer	Teledyne API 602
UFP (CPC)	Teledyne TSI 651

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

2.2 EQUIPMENT CHARACTERISTICS

2.2.1 Siting

- A) Monitoring site selection criteria was the same for all fixed sites. Site uniformity was achieved to the greatest degree possible. Descriptions have been prepared for all sampling sites and can be found in the annual network plan at www.aqmd.gov/home/library. The description includes, 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 was located in an area with unobstructed airflow, especially in the direction of any recognized sources of the sampled compounds. This is critical since turbulence and eddies from obstructions will cause non-representative results. The distance between an obstruction and the sampler is not to be closer than two times the height of the obstruction.
- C) Locations significantly influenced by nearby pollutant sources, activities potentially impacting air quality or where reactive surfaces may cause chemical changes in the air

sampled were avoided. Micro-meteorological influences caused by nearby hills, bodies of water, valley drainage flow patterns, etc. were considered when selecting a monitoring site.

- D) The recommended intake probe height for criteria pollutants is 3 to 15 meters above ground level as near breathing height as possible with the additional criteria that a site will not be placed where a building is an obstruction or where 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 prevailing windward side.

2.2.2 Acceptance Testing

Acceptance testing was performed on all instrumentation and sampling equipment approximately one month after receipt. After acceptance testing was completed and instruments were found to meet acceptance criteria, they were deployed in the field and ambient sampling commenced. Acceptance testing was conducted according to the following steps:

- A) All instruments were carefully unpacked from their shipping containers and checked for completeness, broken parts, and correct subunits.
- B) The units were assembled according to manufacturer guidelines and prepared for start-up.
- C) The flowrate/flow meter portion of the pneumatic system, if any, was checked using the most appropriate calibration-transfer standard to verify the operating flow/flowrate.
- D) Timer accuracy was 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 was corrected and addressed following the manufacturer's recommendations and procedures as stated in the operations manuals.

2.2.3 Calibration

At each sampling site, final dynamic calibrations were performed on each analyzer and sampler prior to the start of the program. At the end of the sampling period, an “As Is” calibration was performed on each analyzer to ascertain the amount of analyzer drift.

2.2.4 Sample Pickup

The SCAQMD Senior Chemist sample custodian distributed the sampling media to the field technician. Filters and carbonyl cartridges were transported in coolers with blue ice and the canisters were kept capped at all times during transportation. Once the filter and carbonyl cartridge were used to collect a sample, they were refrigerated until returned to the SCAQMD Laboratory. The sampling media was returned to the sample custodian as soon as possible following sampling.

2.2.5 Troubleshooting

For instrument usage overlapping the NATTS program usage, the routine maintenance and quality control checks were based on U.S. EPA *Quality Assurance Project Plan for the Air Toxics Monitoring Network* (EPA-454/R-01-007) and U.S. EPA National Air Toxics Trends Station (NATTS) technical assistance document (NATTS TAD, 2009) and are listed in Appendix P. For the instruments that were not present in the NATTS program, a maintenance guide based on the equipment manufacturers’ suggested operating procedures was made available for each instrument. If an instrument fell out of the correct operating range, or if there was a component failure, the operator immediately placed a call to the SCAQMD STA/AM Support and Repair Section to schedule a repair.

2.2.6 Repair

The potential failure of instrument and equipment components such as pumps and flow controllers was addressed by SCAQMD maintaining an inventory of staff replaceable spare parts.

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 was 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 also accepts timing signals from the model 910A. The XonTech 912 adapter was 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 were field tested prior to and during field sampling.

2.3.1.4 Cleanliness Check

To perform a system bias check, ultra-pure air or nitrogen was injected into the sample manifold to fill one, 3-hour canister. Additionally, the 24-hour sampler was tested by maximally increasing its sample flow to fill a canister in approximately 6 hours. A field blank canister was 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 test samples is the acceptance criteria for this test and indicates that the system is not contaminated (non-biasing). A value greater than 1 ppb per compound required investigation and corrective action. A system bias check was repeated until all biases are demonstrated to be eliminated. The SCAQMD's Ambient Monitoring Support Group performed system repairs. This group assembled, leak checked, disassembled, and cleaned the sample manifold, and the Auditing Group calibrated the mass flow controller (MFC) for flow.

2.3.1.5 Canister Sample Pickup

An SCAQMD Instrument Specialist picked up clean verified clean silica lined stainless steel canisters from the Laboratory. Evacuated canisters were transported by vehicle to the respective air monitoring stations. Each canister has a tag attached (Appendix F). This tag was completed and contained the following information: sample site, operator initials, and sample date. The air monitoring station operator completed this tag once the canister was set up for sampling. Once the canister is filled and disconnected from the 910A or 912 sampler, and prior to returning the sampled canister to the Laboratory, the canister number, start

³ XonTech, Inc. (1987). *Model 910 Toxic Air Sampler Operations Manual*. Van Nuys, CA.

⁴ Ibid.

vacuum, end pressure (psig), and elapsed time was recorded on the MATES IV sample log (Appendix E). The time on the QC chart was also checked and adjusted. This value must be within ± 10 minutes of actual Local Standard Time. The canister was delivered to the sample custodian in the Laboratory as soon as possible.

2.3.2 XonTech 924

2.3.2.1 Description

The 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 were brought to the SCAQMD 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 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 inserted the sample filter cassette or sorbent tube into the sampling head and keyed 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 was removed from the printer and submitted to the Laboratory with the filter for analysis.

The XonTech 924 samples carbonyl compounds for an integrated 24-hour period only. Warm and cold-start options as well as all other operational specifications are discussed in XonTech, Inc. *Model 924 Toxic Air Sampler Operations Manual*⁵ and SCAQMD SOP 00094, *RM Environmental Systems Inc. (RMESI) 924 Toxics Sampler*.

⁵ XonTech, Inc. (1987). *Model 924 Toxic Air Sampler Operations Manual*. Van Nuys, CA.

2.3.3 MET One SASS

2.3.3.1 Description

The MET One Speciation Air Sampling System (SASS) accommodates up to five sampling canisters which may 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 coarse 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 unloading/loading of sampling substrates. Every element of the sampler 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 compounds⁶.

2.3.3.2 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 chosen filter media are suitable for the type of analysis to be conducted. For example, Teflon filters were used for gravimetric mass and trace metal determinations. Quartz fiber filters were used for elemental and organic carbon analysis as well as anions and cations analysis.

2.3.4 R.M. Young Mechanical Wind Sensor

2.3.4.1 Description

The R.M. Young Mechanical Wind Sensor is used to measure wind speed and direction (WSD) data. The performance specifications of this wind system are delineated in Table 2-1. Data is stored in a data logger until it is telemetered to the SCAQMD's information system.

For a complete description of anemometer operations, refer to *R.M. Young AQ Wind Monitor User Manual and Product Specification*⁷.

⁶ MET One Instruments, Inc. (2001), *Model SASS & SuperSASS PM_{2.5} Ambient Chemical Speciation Samplers*, Grants Pass, Oregon.

⁷ R.M. Young Company. *SAQ Wind Monitor User Manual (05305) and Product Specification*
<http://www.youngusa.com/products/7/6.html>

TABLE 2-1 Performance Specifications - R.M. Young Mechanical Wind Sensor

<u>Wind Speed</u>	<u>Wind Direction</u>
1. Starting Threshold 0 mph	0 degrees
2. Range 0-112 mph	0-360 degrees
3. Accuracy $\pm 1\%$	± 3 degrees

2.3.4.2 Siting

WSD measurement, barometric pressure, relative humidity, and temperature monitoring equipment were housed in monitoring stations. The stations meet Environmental Protection Agency (EPA) criteria for National Air Monitoring Stations (NAMS) and State and Local Air Monitoring Stations (SLAMS) as cited in part 40 Code of Federal Register (CFR) Part 58.

When the meteorological equipment was located at a permanent air monitoring station, it was installed on a 10-meter tower in an unobstructed position. When the equipment was installed in a mobile platform, it was mounted on a 6.1-meter mast.

2.3.4.3 Installation

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

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

2.3.4.4 Telemetry Interfacing

At each fixed monitoring site an existing telemetry system was used to transfer WSD data from the station to the SCAQMD central computer.

2.3.4.5 Routine Servicing

The air quality instrument specialist responsible for each monitoring site performed routine servicing and periodic checks of the WSD system, barometric pressure, relative humidity, and temperature. The instrument specialist also noted and initialed the type of service performed and the results of each periodic check in the system's logbook, and on the WSD Monthly Quality Control Maintenance Sheet (Appendix C).

Any suspected operational problem were communicated in detail by the instrument specialist to the appropriate supervisor. The supervisor, when informed of the problem,

contacted the station operator to determine if the problem could be corrected in-house. If the problem could not be corrected in-house, the supervisor arranged for a replacement of the WSD system. Anemometer servicing was conducted as described below.

A) Weekly Checks

The mechanical anemometer, barometric pressure, and temperature were checked for daily trends as an indication of acceptable operation.

B) Monthly Checks

The mechanical anemometer was lowered from the tower and visually checked, relative humidity and temperature aspirators were cleaned as necessary. The mounting of all three sensors was checked to verify they were securely attached.

2.3.4.6 Calibration

The RM Young Model 05305VP/101283-G2 Wind Monitor-AQ type wind speed and wind direction sensors are calibrated at the factory before receipt. Prior to the deployment of the sensor to the field, an initial calibration check was performed. Field calibrations were performed annually and/or immediately after sensor repair (bearing replacement), rewiring or replacement of the sensor per Draft SOP00070, October, 2011.

2.3.4.7 Data Handling

All data generated from the WSD system was stored in a data logger before being transmitted to SCAQMD headquarters. Data was also recorded on an electronic strip chart recorder on site. During site visits any maintenance or repair work was noted on the strip chart. Strip chart data is uploaded to the SCAQMD quarterly.

2.3.5 Graseby-GMW 1200 PM₁₀ Sampler

2.3.5.1 Description

The Graseby-GMW Model 1200 two-stage, size-selective inlet (SSI) head sampler is used to sample particulates with an aerodynamic diameter of 10 microns and less at Pico Rivera, Compton, Huntington Park and the Hudson school site in Long Beach. 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) pass through the nozzle and are deposited onto the flat surface below the nozzles. The air sample is then drawn through vent tubes, the second-stage fractionator, and the filter where particulate matter is collected. The height of the vent-tube inlets above the acceleration nozzle plate prevents re-suspension and transport of particles.

The PM₁₀ sampler draws air into a specially shaped inlet at a flowrate of 40 ±4 cubic feet per minute (cfm). PM₁₀ particulate matter collects on an 8 x 10 inch matted quartz fiber filter. The concentration of PM₁₀ 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 completes a PM₁₀ sampler site report and sends it to the appropriate SCAQMD supervisor for review using the criteria of compliance with SLAMS total suspended particulates (TSP) siting as stated in 40 CFR Part 58, Appendix E. The PM₁₀ sampler may be calibrated according to Appendix A, Section A.5.9 of the SCAQMD's *Quality Assurance Plan for Air Monitoring*⁸.

The matted, quartz-fiber filter is very delicate and can be easily torn or gouged. Because a damaged filter invalidated results, it was important to carefully handle it by the edges. Complete operational details are contained in *Instruction and Operation Manual High Volume PM₁₀ Sampler*⁹.

2.3.6 Black Carbon as Measured Using an Aethalometer

The term soot often refers to impure carbon particles resulting from the incomplete combustion of fossil fuels and various types of biomass burning. Soot is a key component of atmospheric aerosols because of its strong ability to absorb solar radiation, causing a warming effect on global and regional climate. Soot is also of interest because of its potential adverse health effects.

Various analytical methods have been developed to quantify the concentration of atmospheric soot particles. Depending on the measurement method used, the non-Organic Carbon fraction of soot is referred to as Black Carbon (BC) or Elemental Carbon (EC). While BC is an "optical term" that is used to denote strong light-absorbing carbon, EC is a "chemical term" that refers to thermally-refractory carbon with a graphite-like structure. Thus, BC and EC are two methodologically defined species that are typically measured using optical (summarized here and described in greater detail in Appendix VI) and thermal-optical methods (described in section 3.3 of this Appendix), respectively.

BC Measurements

The Aethalometer® (developed by Magee Scientific, Berkeley, CA) is an instrument that uses optical analysis to determine the mass concentration of BC particles collected from an air stream passing through a filter. Aethalometers are the most common instruments used to measure BC in real time. The principal and working of the Aethalometer are described in detail elsewhere [Hansen et al., 1984]. Briefly, the gas stream (frequently ambient air) passes through a filter material which traps the suspended particulates, creating a deposit of increasing density. A light beam projected through the deposit is attenuated by those particles which are absorbing ('black') rather than scattering ('white'). Measurements are made at successive regular time intervals. The increase in attenuation from one measurement to the next is proportional to the increase in the density of optically absorbing material on the filter. This, in turn, is proportional to the concentration of the material in the sampled air stream. The sample is collected as a spot on a roll of filter tape. When the density of the deposit spot reaches a pre-set limit, the tape advances

⁸ Applied Science & Technology. (1996). *Quality Assurance Plan For Air Monitoring*. Diamond Bar, CA: South Coast Air Quality Management District.

⁹ Graseby Anderson. (1988). *Instruction and Operation Manual High Volume PM₁₀ Sampler*. Atlanta, GA.

to a fresh spot and the measurements continue. Measurement of the sample gas flow rate and knowledge of the instrument's optical and mechanical characteristics permit a calculation of the average concentration of absorbing particles in the gas stream during the sampling period. Aethalometers may operate on time-base periods as rapid as 1 second, providing quasi-real-time data. One minute to one hour averages are commonly used in most field applications. Comparison of aethalometer data with other physical and chemical analyses allows the output to be expressed as a concentration of BC. A more detailed description of the Magee Scientific Aethalometer along with monitoring results can be found in Appendix VI.

2.3.7 Ultra Fine Particulate (UFP)

Ultrafine Particles (UFPs) are typically defined as particles with an aerodynamic diameter less than 100 nm. UFPs are emitted from both natural and anthropogenic sources, although in most urban environments vehicular fossil fuel combustion constitutes the major contributing source. The terms UFPs and nanoparticles (NP; diameter < 0.05 μm) are often used interchangeably, and the definitions of each generally vary with the study or application. While fine particulate matter ($\text{PM}_{2.5}$) dominates the mass distribution of atmospheric particles, UFPs account for about 90% of the total particle number. For this reason, their concentration is usually expressed in terms of total particle count (i.e. # per cubic centimeter of sampled air, or $\#/ \text{cm}^3$), even though a small fraction of the particles being counted may be above 100 nm.

Condensation Particle Counters (CPCs) are instruments that provide the total number concentration of particles above a lower size limit (~3-20 nm, depending on make and model) in real-time. By means of CPCs, UFPs are grown through condensation in a controlled supersaturation environment to larger sizes and then measured/counted using a photodetector. Although CPCs are the most widely used instruments in most applications, they do not provide any information on the original size of the particles counted.

UFP Measurements

The CPC used to measure the ambient number concentration of UFPs at the ten fixed MATES IV sites is commercialized by Teledyne Advanced Pollution Instrumentation PI (Teledyne API, San Diego, CA). This particular model (651) was specifically designed for network operation and its performance was thoroughly evaluated by SCAQMD Staff prior to the beginning of MATES IV. The Teledyne 651 CPC utilizes a patented laminar-flow, water-based condensation growth technique. Particles which are too small (nanometer scale) to scatter enough light to be detected by conventional optics are grown to a larger size by condensing water on them. An air sample is continuously drawn through the CPC inlet via an external pump and a portion of the flow is sent to the exhaust as bypass flow. The aerosol sample is pulled through a cool region saturated with water vapor and its temperature is equilibrated. The sample then passes to a growth section where wetted walls are heated to produce an elevated vapor pressure resulting in a thermodynamic "supersaturation" condition. The small cool particles in the flow stream act as nuclei for condensation, and grow into micron sized droplets. The droplets are passed through a laser beam and create a large light pulse. Every particle pulse event is detected and counted. In this technique particle concentration is measured by counting every individual particle in the air stream. The CPC model 651 is able to detect particles as small as 7 nm in diameter and has a

detection range between 0 and 1,000,000 #/cm³. A more detailed discussion of the Teledyne 651 CPC monitoring results can be found in Appendix VI.

2.3.8 Polycyclic Aromatic Hydrocarbons (PAH)

Polycyclic Aromatic Hydrocarbons (PAHs) on polyurethane foam (PUF) sampling media were analyzed by Eastern Research Group (ERG), Morrisville, North Carolina. Sampling was performed by SCAQMD staff of Instrument Technicians and Laboratory Technicians. Chain of Custody was maintained from receipt of sampling materials received from ERG through the return of the samples for analysis. SCAQMD staff was responsible for calibration, calculating and reporting of the total air volume of each sample. This included calibration of the sampling instrument flow rate. A short method description is given in Appendix L.

Chapter 3.0 Laboratory Procedures

3.1 INTRODUCTION

Since 1994, the SCAQMD has implemented the U.S. EPA Photochemical Assessment Monitoring Stations (PAMS) program to gather data on ozone precursors. In 2008 the National Air Toxics Trends Stations (NATTS) was implemented in the South Coast Air Basin. Some of the same sampling instruments currently used in the PAMS and NATTS programs were used in MATES IV. Hence, many of the procedures and protocols for the MATES IV program were based on the SCAQMD *Quality Management Plan for Environmental Measurement Programs*¹⁰ (January 2009), QAPP, Chemical Speciation of PM_{2.5} Filter Samples (2005), and National Air Toxics Trends Stations Technical Assistance Document (NATTS TAD, 2009). However, MATES IV also utilizes several analytical methods not performed under the federal programs and the protocols included herein are based upon manufacturer's measurement and quality control procedures that are intended to ensure that the data quality is suitable for the intended purposes of MATES IV.

The SCAQMD utilized Air Quality Instrument Specialists to collect field samples and deliver them to the Laboratory sample custodian. The Laboratory sample custodian handled logging and distribution within the SCAQMD Laboratory. Procedures for proper sampling and initial chain-of-custody are outlined in the SCAQMD *PAMS Air Monitoring Network Quality Assurance Plan*¹¹, Section 7E Parts 1 and 2.

3.2 SAMPLE HANDLING

All sampling media were handled according to the Laboratory practice for implementation of toxics analysis and particulate matter network programs, as applicable. Field instrument specialists completed the sampling information and chain-of-custody forms¹², and delivered the samples to the Laboratory sample custodian.

3.2.1 Canister Cleaning

The SCAQMD Laboratory has a canister cleaning oven system. Per SOP00091 entitled "Canister Cleaning System (CCS) Ovens 3 & 4 Toxics," these systems utilize 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 80°C 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. Data collected in performance of SOP00091 demonstrates the cleaning procedures satisfy cleanliness requirements and long-term experience has proven that the

¹⁰ Applied Science & Technology. (2009). *Quality Management Plan for Environmental Measurement Programs*. Diamond Bar, CA: South Coast Air Quality Management District.

¹¹ Applied Science & Technology. (1992). *PAMS Air Monitoring Network Quality Assurance Plan*. Diamond Bar, CA: South Coast Air Quality Management District.

¹² These forms consist of the Size-Selective Inlet PM₁₀ Sampler Envelope (Appendix B), MATES IV Sample Log (Appendix E), and VOC Canister Tag (Appendix F).

canister-cleaning oven system is sufficient to provide clean canisters. Any hydrocarbons (above the threshold concentrations) found in canister trigger investigation and corrective action. All canisters (8) in the batch are re-cleaned and tested again to assure they meet cleanliness requirements. The cleaning date and operator are noted on the canister tag and in an electronic database that serves as the primary chain-of-custody.

3.2.2 Field Canister Use

Canisters were transported by the instrument specialist to the site and installed in accordance with the sampling SOP00080 included in the *PAMS Air Monitoring Network Quality Assurance Plan*. Once the sample was taken and the sample time, canister number, and start and stop vacuum were noted on the MATES IV Sample Log (Appendix E) that accompanied the canister starting with sample collection. All samples were promptly returned to the Laboratory for log-in and distribution to the appropriate Senior AQ Chemist.

3.2.3 Sample Distribution in the Laboratory

The Laboratory sample custodian (Senior Chemist) logs in received samples and distributes them to the appropriate AQ Chemist following established Laboratory procedures. The sample custodian distributed samples to Laboratory personnel starting with the responsible Senior AQ Chemist.

3.3 ANALYSIS METHODS – APPENDIX A COMPOUNDS

Gaseous compounds listed in Appendix A were analyzed using gas chromatography with mass spectrometry and flame ionization detection (FID) after cryo-focusing. This technique provides for instrument sensitivity sufficient for meeting MATES IV measurement criteria. 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)*, as found in SCAQMD SOP0008B. Carbonyl analysis was 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*¹³ and SCAQMD SOP0006. A short method description for sampling and analysis of VOCs by GC/MS can be found in Appendix K.

¹³ 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)

Carbonyl measurements were performed using the NATTS sampling and analysis methodology delineated in the NATTS TAD (2009). The California Air Resources Board (CARB) toxic network design method was followed using the XonTech 924 with a carbonyl channel. A potassium-iodide-coated ozone denuder was also used in all carbonyl samplers. Waters[®] silica gel cartridge impregnated with dinitrophenyl hydrazine was used to sample for carbonyl compounds. A short method description for the carbonyl sampling and analysis can be found in SOP #00094 and in Appendix G.

Metals collected on Teflon filters using XonTech 924 samplers were analyzed by Energy Dispersive X-ray Fluorescence (XRF) following the procedure found in SCAQMD SOP00004 *Standard Operating Procedure for the Analysis of PM_{2.5} Filter Samples by Energy Dispersive X-Ray Fluorescence Spectrometry*. For PM_{2.5} samples, a Teflon filter was also used, and XRF was used for metals analysis. A short method description for sampling and analysis of elements by XRF is attached to this document as Appendix H. Filters were also analyzed by ICP/MS following the procedure found in SCAQMD SOP#00005, *The Determination of Metals in Ambient Particulate Matter by Inductively Coupled Plasma Mass Spectrometry (ICP/MS)*, March 9, 2010.

Hexavalent chromium in ambient air is measured by collecting total suspended particulate matter on 37-mm cellulose filters impregnated with 0.12M sodium bicarbonate solution using the Xontech 924 Toxic Air Sampler. The samples were analyzed by a Dionex[®] ion chromatograph (IC) equipped with a UV-Vis detector. Hexavalent chromium is detected at 530 nm after a post-column derivatization reaction with diphenylcarbazide. The method description for hexavalent chromium sampling and analysis is found in Appendix M.

Particulate filter samples for both PM₁₀ and PM_{2.5} were analyzed for metals, ions, total mass, organic carbon (OC), elemental carbon (EC), and total carbon (TC). The procedure for mass and ion determinations follows the methodology used in support of the SCAQMD (federally recognized) PM₁₀ Network activity. Analysis for EC, OC and TC of the PM₁₀ and PM_{2.5} filter samples was analyzed using the Interagency Monitoring of Protected Visual Environments A (IMPROVE A) method. The method evolves carbon from filters by heating and optically monitors carbon as it is evolved from the filter. After catalysts oxidize then reduce the carbon, it is measured by a flame ionization detector. A more detailed description of the IMPROVE A method can be found in Appendix J.

The compounds listed in Appendix A were sampled on a one-day-in-six sampling schedule synchronized with the national PM₁₀ and PM_{2.5} network schedules. These samples were integrated 24-hour samples. SCAQMD personnel conducted both the sampling and analysis. Contract Instrument Technicians and Chemists assisted SCAQMD employees.

Some of the compounds listed in Appendix A do not have consensus methods of analysis; however, ASTM International or American Industrial Hygiene Laboratory test methods and test methodologies were followed or adapted as needed.

3.4 SAMPLING SCHEDULE

MATES IV sampling was conducted on the same schedule as used by the air-monitoring network. The air monitoring network sampling schedule can be found on the U.S. EPA website at; www.epa.gov/tmn/amtic , and follows a six-day monitoring schedule for TSP, Pb, PM₁₀, PM_{2.5} and VOCs. This sampling schedule has several benefits:

- 1) Data from MATES IV can be correlated with ambient data taken on the same day.
- 2) Additional staff time to service and maintain MATES IV sampling equipment and instrumentation was minimized.
- 3) Sample set-up, retrieval, and delivery time to the Laboratory was minimized.

3.5 COMPARISON OF ICP/MS TO XRF

For MATES IV, in addition to the use of XRF for the analysis of ambient metals collected on filters; Inductively Coupled Plasma Mass Spectrometry (ICP/MS) was also employed. While both the XRF and ICP/MS instruments are designed for metals analysis, the principals of analysis are vastly different. In short, XRF is a whole sample non-destructive technique requiring no sample preparation. ICP/MS, however, requires a vigorous acid extraction process prior to analysis. A more detailed of these methods can be found in Appendix N along with charts for selected metals comparing analytical results.

3.6 NICKEL ANALYSIS BY ICP/MS

Nickel overestimation by ICP/MS was determined to be caused by the ubiquitous and proportionally very high concentration of Calcium and Sodium which form interfering molecular ions in the plasma. The subsequent correction for Ni by changing the isotope of acquisition to 58 Amu from 60 Amu is described in Appendix O.

Chapter 4 Quality Assurance and Quality Control

4.1 INTRODUCTION

To achieve the maximum data quality in the MATES IV program, SCAQMD implemented the following Quality Assurance/Quality Control (QA/QC) plan. This Chapter contains the objectives, procedures, documentation, and data review techniques that were used by the SCAQMD to assure that MATES IV produced data that met or exceeded the accepted criteria for its intended use as described below.

4.2 OBJECTIVES

There were two major objectives for the MATES IV Quality Assurance Project Plan. These objectives were: (1) to provide one year MATES IV monitoring which would meet SCAQMD data requirements for accuracy and precision to serve as inputs to accepted risk assessment model(s) and comparisons to other air toxics measurements and (2); to provide time and spatially resolved comparison of black carbon and ultrafine particle concentrations. Thus MATES IV provides data that meets the measurement objectives (MQOs) displayed in Table 4-1. Where practicable, MATES IV MQOs were designed to meet or exceed U.S. EPA Monitoring Programs MQOs such as NATTS and PM_{2.5} Speciation for comparability to other national air toxics monitoring data, including historical SCAQMD NATTS and PM_{2.5} speciation data. Measurements not present in the Federal programs such as black carbon and ultrafine particles, are not intended to directly calculate risk. They serve as real time indicators of pollution for comparison over time and space and thus have MQOs that are appropriate.

TABLE 4-1 Measurement Quality Objectives

ASSESSMENT	MEASURES	PROCEDURE	CRITERIA/PARAMETER			
			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 SCAQMD is one of the four Primary Quality Assurance Organizations (PQAO) responsible for air monitoring in California, and is committed to achieving the highest possible data quality level in the MATES IV programs. The Quality Management Plan (QMP), which is the foundation document for ensuring high quality and defensible data (approved in 2009) presents SCAQMD quality system and describes the organizational structure, functional responsibilities

of management and staff, lines of authority, and general methodology for assessing all activities conducted in support of air monitoring and analysis, air quality assessment and other environmental measurement activities conducted by the agency.

The quality goals and QA requirements for the particle and gaseous pollutants measured during MATES IV are found in various Quality Assurance Project Plan (QAPP) documents as outlined in the following paragraphs. These QAPPs also describe the responsibilities within the organization for carrying out each program and meeting specific QA/QC objectives. They address the Data Quality Objectives (DQOs) of accuracy, bias, comparability, completeness, detectability and representativeness, list the Method Quality Objectives (MQOs) of precision, bias, completeness, sensitivity and, where applicable, flow rate accuracy for the analytes of interest. They document the Standard Operating Procedures (SOPs) and Operational Assistance Guides (OAGs) which are directions for specific performing measurement activities. Finally, they list the required QA/QC requirement for each activity and provide instructions for data review, QA oversight, and corrective actions.

The quality goals and QA requirements (with the exception of siting) for monitoring ambient levels of volatile organic compounds (VOCs), carbonyls, hexavalent chromium, and polycyclic aromatic hydrocarbons (PAHs) were adopted from the US EPA National Air Toxics Trends Stations (NATTS) program. These requirements can be found in the SCAQMD NATTS QAPP, which was last revised in 2013 and is currently under review by the US EPA Region 9.

The quality goals and QA requirements (with the exception of siting) for monitoring the main components of fine particulate matter (PM_{2.5}) including Organic and Elemental Carbon (OC/EC), Anion and Cations, and trace metals were adopted from the US EPA Chemical Speciation Network (CSN) program. These requirements can be found in the SCAQMD PM_{2.5} Speciation QAPP, which was last revised in 2013 and was approved by the US EPA Region 9 in 2014.

The quality goals and QA requirements (with the exception of siting) for monitoring fine and coarse PM (PM_{2.5} and PM₁₀ FRM) were adopted from the US EPA Criteria Pollutant Monitoring Program. These requirements can be found in the SCAQMD Criteria Pollutant Monitoring Program QAPP, which was last revised in 2012 and approved by the US EPA Region 9 in 2013.

The quality goals and QA requirements (with the exception of siting) for monitoring ultrafine particles (UFPs) and black carbon (BC) can be found in the SCAQMD Special Monitoring Program QAPP, which also describes the protocols and procedures followed by SCAQMD for monitoring other "non-criteria" pollutants and performing short-term measurement studies similar to those conducted during MATES IV (see Chapter 5 for details). The current version of this QAPP was last revised in 2013 and is currently awaiting approval by the US EPA Region 9.

The SCAQMD objectives, procedures, documentation, and data review techniques assure the MATES IV program will produce data that are accurate, precise, reliable and legally defensible. The technical procedures for QA/QC include annual system audits on all equipment in the laboratory and at all MATES sampling sites. Quality control procedures also include proper

record keeping, standard checks, routine calibrations of the sampling and analytical equipment, and collecting collocated samples at regular intervals and are described in the next section.

4.3.2 Quality Control Procedures

The SCAQMD performed annual flow audits on all PM₁₀ and PM_{2.5} samplers. These flow audits were conducted according to the procedures outlined in the SCAQMD'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 PM₁₀ networks. The EPA and CARB annually audits the performance of the SCAQMD Laboratory for VOCs, carbonyls and lead (Pb) using the EPA's National Performance Audit Program and the CARB's toxic VOC performance audit.

A) Field Checks

SCAQMD staff performed a number of activities concurrent with conducting field checks. Specifically, staff:

- 1) observed and recorded all required data for each sampler's monthly maintenance sheet, chain-of-custody form, and sample identification tag
- 2) checked and reset all timers if off by more than ± 5 minutes Local Standard Time
- 3) checked and adjusted the flow settings if they are not within $\pm 5\%$ of the calibrated setting

B) Laboratory Daily Checks

SCAQMD staff monitored the PM 2.5 room balance using a NIST traceable check standard; conducted a gas chromatograph standard check using a NIST traceable gas standard; observed, recorded, and corrected all sample media equilibration conditions if they were out of tolerance.

C) Semi-Annual Checks

SCAQMD staff conducted multipoint calibrations of mass-flow controllers in samplers; performed instrument leak checks; and cleaned PM₁₀ inlet heads for all instruments and samplers used in support of MATES IV.

D) Annual Checks

SCAQMD staff cleaned sample probes using de-ionized water and a soft cloth; conducted sample probe leak checks and repaired them as necessary; and conducted 24-hour timer tests by operating the sampler to observe actual run length. Actual start and stop were observed. The timer was repaired if the sample period varied by more than ± 20 minutes from 24 hours.

4.4 DOCUMENTATION

A critical element of an effective QA/QC system is complete and accurate documentation. To ensure that all samples are properly handled, inspected, collected, analyzed, and reported, a comprehensive set of QA/QC documents was prepared and completed. The information reported in these documents was crucial in validating reported data quality. Lack of properly documented data could be grounds for data invalidation. A summary of QA/QC sampling activities is attached as Appendix P.

A) Chain-of-Custody Forms

Sample forms (Appendices B, D, and E) 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, chain-of-custody forms accompanied samples collected under MATES IV. These forms originated with field operators, were delivered to the Laboratory, and submitted to the assigned Laboratory staff. The Laboratory is responsible for storing all chain-of-custody documents.

B) Maintenance Check Sheets

Maintenance sheets (Appendices C and D) were completed by field instrument operators for PM₁₀ samplers and wind speed and direction systems. These monthly maintenance sheets were submitted to senior field operators for review, approval, and storage.

Other types of QA/QC, station and laboratory documentation and their descriptions are listed in Table 4-1 through 4-4 and 4-6.

TABLE 4-2 QA/QC Records

Document Name	Brief Description	Format	Storage Location
Training Files	Records substantiating the training and proficiency of staff relevant to this program	Hard copy	AM Branch: File Cabinet in "Bullpen" in AM Area; LSST Branch: Training Binder at Laboratory Front Desk, PDF copies: e:\astd\quality assurance\laboratory\training\scanned forms
QAPP	Master version of QAPP, including pending revisions	Hard copy or electronic	QA Branch Records or M&A online resources and e:\astd\quality assurance\current_documentation\QAPP_SOPs
SOPs	Current version of all SOPs	Hard copy or electronic	QA Branch Records or M&A online resources and e:\astd\quality assurance\current_documentation\QAPP_SOPs
Performance Evaluations and Audits	Results of internal and external assessments	Hard copy and/or electronic	QA Branch Records; AM Branch: Principal AQIS Operations; LSST Branch: Laboratory Report Binder and e:\astd\quality assurance\quality assurance branch\audits
Corrective Action Reports	Results or identified QA problems and their resolution	Electronic	Program Office, QA Office and e:\astd\quality assurance\quality assurance branch\QA CAR

TABLE 4-3 Laboratory Records

Document Name	Brief Description	Format	Location
Laboratory Notebooks	Includes the following types of notebooks and bound data sheets: - analysts' notebooks - instrument maintenance logs - reagent preparation logs - materials acceptance tests	Hard copy	Instrument benches
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	Instrument benches
Control Charts or Equipment	QC information displayed in sequence to help diagnose problems with analytical instruments. Usually includes acceptance limits that are periodically recomputed.	Hard copy or spreadsheet	Hardcopies: Instrument benches. Electronic: instrument control PCs.
SOPs	Current copies of SOPs relevant to the analyses performed in a particular laboratory	Hard copy	Instrument benches, M&A online resources and e:\astd\quality assurance\current_documentation\QAPP_SOPs
QAPP	A current copy of this QAPP. The Principal Chemist must ensure that each analyst has access to a current copy of the QAPP	Hard copy	QA Branch Records or M&A online resources and e:\astd\quality assurance\current_documentation\QAPP_SOPs
Analytical Results Database	Results for each chemical analysis with identifying information	Spreadsheet or LIMS	Analyst computer/ LIMS Server
Analytical QC Database	Includes all QC information for each weighing session including standard weights, duplicates, field blanks, and laboratory blanks.	Spreadsheet or LIMS	Analyst computer/ LIMS Server

TABLE 4-4 Station Records

Document Name	Brief Description	Format	Location
Station Notebooks	Logs station activity	Hard copy	Station
Instrument User's Manual and/or Manufacturer's Instructions	Information for setting up, using, and troubleshooting the continuous gaseous monitors	Hard copy	Station
Calibration Certificates and Records	Includes certificates for gases and other chemicals used for calibration	Hard copy/ Electronic	Station/ Shared Drive
QC Records	Results of instrument blanks, calibrations, standard recoveries, and replicate precision	Computer files and hard copy	Maintenance Sheets/ Calibration Sheets/ Database
Raw Data Records	Results of instrument analyses (including supporting data that is not uploaded to the database)	spreadsheets; hard copy; and DMS, chessell, custom database	Database/ Server

4.5 DATA REVIEW

MATES IV data validity was based upon the appropriate implementation of operational and QA/QC procedures described in this appendix. To assure that the program's DQOs were met, responsibility for data review was distributed between the field operators, calibrators, auditors, and supervisors, Laboratory Chemists and Supervisors, QA Supervisors, and the Laboratory and Atmospheric Measurement Managers.

TABLE 4-5 Position Responsibilities

Position	Responsibilities	Upward Lines of Communication
Health Effects Officer	Principal Investigator of MATES IV responsible for direction and implementation of the study; coordinate MATES IV TAC	ADEO: Planning, Rules and Area Sources
Laboratory Services and Source Test Engineering Manager	Responsible for preparation of sampling media and analysis of samples submitted to laboratory	ADEO: Science Technology Advancement
Atmospheric Measurements Manager	Responsible for establishment, operation and maintenance of monitoring stations	ADEO: Science Technology Advancement
Quality Assurance Manager	Responsible for reviewing, developing, documenting, and implementing QA/QC practices and procedures	ADEO: Science Technology Advancement
Principal Air Quality Chemist: Aerosol Analysis	Responsible for laboratory operations of the Aerosol Analysis group which conducts analysis of PM _{2.5} and PM ₁₀ Mass and TSP Lead filters.	Manager: Laboratory Services and Source Test Engineering
Senior Air Quality Chemist: Aerosol Analysis	Responsible for supporting Aerosol Analysis group operations and 2 nd level data validation of data analyzed from PM _{2.5} and PM ₁₀ Mass and TSP Lead filters.	Principal AQ Chemist: Aerosol Analysis
Principal Air Quality Chemist: Ambient VOC/ Toxics	Responsible for laboratory operations of the Ambient VOC/ Toxics group which conducts carbonyl and VOC analysis	Manager: Laboratory Services and Source Test Engineering
Senior Air Quality Chemist: Ambient VOC/ Toxics	Responsible for supporting Ambient VOC/ Toxics group operations and 2 nd level data validation on carbonyl and VOC analyses.	Principal AQ Chemist: Aerosol Analysis
Air Quality Chemist and Assistant Air Quality Chemist	Responsible for following SOPs and GLP in the analysis of samples; submittal of data into LIMS	Principal AQ Chemist: Aerosol Analysis
Laboratory Technician	Responsible for following SOPs and GLP for the preparation of samples or sampling media	Principal AQ Chemist: Aerosol Analysis
Principal Air Quality Instrument Specialist	Responsible for station operations and deployment and/or coordinating repair and calibrations	Atmospheric Measurements Manager
Senior Air Quality Instrument Specialist	Responsible for supporting operations and 2 nd level data validation	Principal Air Quality Instrument Specialist
Air Quality Instrument Specialist I and II	Responsible for following SOPs and GLP in the collection of samples from the field sites, maintaining the station site, and/or repair and calibration of instruments	Principal Air Quality Instrument Specialist

A) Field Supervisors

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

B) Field Operators

Field operators were responsible for operating all samplers and analyzers according to the operating procedures specified in this document. Field operators annotated all information in the monthly QC maintenance sheets, chain-of-custody forms, sample tags, and logbooks. Field operators were also 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 were responsible for performing semiannual multipoint calibrations on flow control-devices according to SCAQMD calibration procedures. Any as-is calibration showing a deviation from design flowrate in excess of acceptable criteria was reported to the field supervisor. Any samples collected while flow percentage deviation from design flow exceeds acceptable criteria were invalidated back to the previous flow calibration, audit, or malfunction date.

D) Field Auditors

SCAQMD field auditors conducted flow audits on 25 percent of the entire network each calendar quarter. Auditors were responsible for notifying the QA Manager of any audit indicating a greater than $\pm 15\%$ average percent deviation from design flow for follow up.

F) Laboratory Chemists

Laboratory Chemists were 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 review for outliers and out-of-control conditions.

G) Laboratory Supervisors

Laboratory supervisors were responsible for final raw data review; calculation of precision based upon collocated sampling; reviewing monthly QA/QC sheets; making final evaluation of data validity based on reports from the QA group and field supervisor; and assessment of Laboratory precision data.

H) Atmospheric Measurements Manager

The Atmospheric Measurements Manager was responsible for overseeing MATES IV field operations.

I) Laboratory Services and Source Testing Engineering Manager

The Laboratory Services and Source Test Engineering Manager was responsible for overall coordination of field and analytical activities for MATES IV.

J) Quality Assurance Manager

The Quality Assurance (QA) Manager was responsible for implementing the quality assurance program for the MATES IV program including independent performance and system evaluations, the corrective action process, establishing acceptance criteria for sample validity once with consideration of quality control data and review of quality control procedures.

4.6 ASSESSMENTS AND RESPONSE ACTIONS

SCAQMD participates in field and laboratory assessment or proficiency programs established by U.S. EPA and CARB, and maintained any analyst or laboratory certification required for the program. Examples of assessments applicable to the MATES IV program are listed in Table 4.6. The QA Manager, or his designee, performed or arranged performance of periodic technical systems audits of SCAQMD activities. These audits covered all aspects of SCAQMD's work, including sample receipt, custody, conditioning, weighing, chemical/speciation analysis, shipping, data reduction and reporting. Prior to each audit, a checklist was prepared, based on the MATES IV workplan, SOPs, and applicable guidance documents. After audits, the QA Manager communicated to the Atmospheric Measurement Manager and/or the Laboratory Manager to specify areas in which corrective action were necessary and prepared a corrective action report (CAR) tracked by the QA Branch. If any serious problems were identified that required immediate action, such as a large, systematic analytical bias, the QA Manager informed the respective manager verbally or through electronic mail the day that such problems are

identified as well as issued a Corrective Action Report. The corrective action followed the Corrective Action Process as described in the SCAQMD QMP (2009).

TABLE 4-6 QA Assessments Applicable to the MATES IV Program

Audit Name	Description	Frequency	Agency
SCAQMD Speciation network Performance Evaluation	Flow check, temperature, and pressure evaluation of the samplers (PM10, PM2.5, TSP, and SASS)	Twice a year	SCAQMD, QA Branch and/or an Approved Contractor
EPA Chemical Speciation Monitoring Program and IMPROVE Laboratory Performance Audit Samples.	1. Anions/Cations collected on nylon/quartz filters and analyzed by ion chromatography. 2. Organic and elemental carbon collected on quartz filters and analyzed by TOR/TOT 3. Metals collected on 47mm Teflon filters and analyzed by EDXRF and ICP/MS. 4. PM _{2.5} mass collected on 47mm Teflon filters and analyzed by gravimetry.	Annual	U.S. EPA OAQPS
PM _{2.5} Weighing Room Evaluation	Conditioning Room Audit	Annually	SCAQMD, QA Branch
PM _{2.5} Weighing Room Evaluation	Gravimetric Mass Analysis performance evaluation and Conditioning Room Audit	Annually	CARB
U.S. EPA Systems Audit	All lab and field instrumentation, practices and procedures used to collect data for Federal Programs	Every 3 – 5 Years	U.S. EPA Region 9
CARB Ambient Gaseous Toxic Inter-laboratory Comparison Check.	Intercomparison of TO-15 compounds in ambient air matrix	Annually	CARB
CARB Ambient Gaseous Toxic Performance Evaluation.	Single Blind Challenge PE of TO-15 compounds in a standard VOC mix	Annually	CARB
SCAQMD QA Branch Carbonyl PE	Carbonyls – As specified by the PAMS/NATTS Programs	Annual and as needed	SCAQMD QA Branch

TABLE 4-6 QA Assessments Applicable to the MATES IV Program (Continued)

Audit Name	Description	Frequency	Agency
NATTS Carbonyl PT	Carbonyls: Formaldehyde and Acetaldehyde	Annually	EPA-OAQPS-AQAD
SCAQMD QA Branch VOC PE	TO-15 compounds	As needed or follow up to CAR	SCAQMD QA Branch
NATTS PT	NATTS VOCS on Select TO-15 compounds in a canister & metals by ICP/MS.	Annually	EPA-OAQPS-AQAD
Quarterly Pb Performance Evaluation	Technical evaluation on manual filter samplers (TSP)	Quarterly	SCAQMD, QA Branch
Annual Performance Evaluation	Technical evaluation on manual filter samplers (PM2.5, PM10)	Annually	SCAQMD, QA Branch
Meteorological Evaluation	Technical evaluation on surface meteorology instruments	PAMs stations; Annually	SCAQMD, QA
National Performance Evaluation Program	PM2.5 PM10, and TSP collected on appropriate filters from FRM samplers and analyzed by independent, certified, EPA approved laboratory.	Annual; 20% of the network	U.S EPA OAQPS/ Region 9
National Performance Audit Program – Pb Analysis	Technical evaluation of Pb Analysis from strips; Quarterly audit strip analysis	Quarterly	U.S. EPA Region 9; SCAQMD, QA Branch

4.6.1 Total Systems Audits (TSAs)

During MATES IV, a series of internal systems audits were conducted on the monitoring network and data quality, under the oversight of the QA Manager. Due to the number of methods and the size of the monitoring network for MATES IV, the systems audit was an on-going process. The systems audit included inspections of monitoring sites, a periodic review of the Laboratory by section or types of analyses, and a review of the data validation systems from the initial source of the data through the archiving and reporting of that data. The various aspects of the annual systems audit were conducted by QA staff or under contract with an independent contractor working under the oversight of the QA Manager.

In addition, as part of Federal air monitoring programs, external systems audits are carried out by the U.S. EPA and CARB, at their discretion and using either agency staff or through independent consultants working under the oversight of U.S. EPA or CARB. SCAQMD also contracts with independent consultants to conduct an external audit of selected systems in addition to the regular annual internal audit. These audits include a majority of methods and analyses conducted under MATES IV and review and follow-up of the audit findings, if necessary, is conducted through the QA Branch.

4.6.2 Performance Evaluations (PEs)

Performance evaluations are conducted for determining the accuracy and precision of monitoring and analytical instrumentation and procedures that provide the data for the various monitoring programs, including MATES IV. All performance audits whether performed by SCAQMD QA staff, independent consultants or other entities are required to satisfy requirements under the appropriate QAPPs and SOPs. These audits may be internal and/or external.

Internal performance audits may be conducted by QA staff or through independent consultants under the oversight of the QA Manager. Due to the size and scope of the program, performance evaluations were conducted on an on-going basis. Performance audits were scheduled for each specific instrument and target U.S. EPA measurement criteria (when applicable).

External performance evaluations are carried out by the U.S. EPA and CARB, at their discretion and using either agency staff or through independent consultants working under the oversight of the U.S. EPA or CARB. SCAQMD QA Branch may also conduct a performance evaluation or contract with independent consultants to conduct an external audit of selected systems in addition to the regular annual internal audit.

Chapter 5.0 Data Processing and Reporting

5.1 INTRODUCTION

MATES IV monitoring of ambient air toxics developed a large data base which is available for future analysis. Appendix A compounds, given the frequency of sampling in MATES IV, resulted in more than 25,000 individual data points including data for concentration, time and location of sampling. The purpose of this chapter is to outline the data handling of this large database. This section will only pertain to laboratory work performed and not to the meteorological, criteria pollutant, or monitor calibration data.

The SCAQMD Laboratory has experience handling large data bases including those generated under MATES II and III. Reporting templates for carbon analysis and XRF elemental analysis (inorganics) were based upon those used in MATES II and III and US EPA's PM Speciation Network requirements. Reporting templates for the VOCs, halogenated hydrocarbons, and carbonyls adhered to the PAMS and NATTS formats.

The aim of reporting is to generate Excel data files for electronic transfer to interested parties. The data has been checked for transcription errors, to assure that it meets DQOs and for adherence to other QA criteria such that the data represent the most accurate determinations possible. The Laboratory made every effort to disseminate the data in a timely fashion to facilitate feedback.

5.2 DATA BASE COMPILATION

Laboratory chemists generated data presenting the concentration of a particular compound found over a particular time period at a particular site. Samples were analyzed and results presented as the volume concentration on a parts-per-billion or ng/m³ basis. These concentrations have been compiled into a spreadsheet along with the name of the sampling site and the date the sample was taken. The chemist (analyst) was responsible for checking data accuracy. The technician in charge of copying the data into the spread sheet was responsible for their accurate transcription. The Senior AQ Chemist was responsible for double checking the chemists' and technicians' data entry and transcription work.

As resources permitted, one AQ Chemist operated a particular instrument while another AQ Chemist reduced the data and transcribed it to an Excel spreadsheet. This structure led to the most efficient data handling. Chemists also reduced the data from several instruments depending on their workload.

MATES IV data encompasses PM₁₀ and PM_{2.5} mass and ions, VOCs, carbonyls, metals, PAHs, and carbon results. Run dates are encoded with the year, month, and day in six numerals. This information is 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 encompass the calculated limits for the sampling and analysis errors introduced into the measurement system.

The MATES IV data has been 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 will work with data end users 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's goal was to meet a two-month turnaround time from the date of sample receipt to the finished and checked report. VOCs, carbonyls, metals, and carbon will be sampled individually, but in similar fashion. Duplicate and other QC samples were analyzed with each batch analysis run. The reports are available in electronic file and as printed spreadsheets.

5.4 FINAL REPORT

Experience with MATES II and III report preparation has demonstrated that the final MATES IV report including QA information may take in excess of six months to complete after the last day of sampling. Laboratory staff have migrated Excel spreadsheets to an Access database. The final report has been stored in several files segregated by date and type of analysis.

Glossary

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:

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

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.

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:

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

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.

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.

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.

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 PM₁₀.

System Audit

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

ACRONYM LIST

AC	alternating current
AIHL	American Industrial Hygiene Laboratory
AM	Air Monitoring
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	Inductively 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
MATES IV	Multiple Air Toxics Study IV
MFC	mass flow controller
mph	miles per hour
MTBE	methyl tert butyl ether
NAMS	National Air Monitoring Stations
NATTS	National Air Toxics Trends Stations
NEMA	National Equipment Manufacturer's Association
PAH	polycyclic aromatic hydrocarbon
PAMS	Photochemical Assessment Monitoring Station
PE	performance evaluation
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
TSA	Total System Audit
TSP	total suspended particulates
V	Volt
VOC	volatile organic compound
WSD	wind speed and direction
XRF	X-ray fluorescence

APPENDIX A Air Contaminants Measured in MATES IV Program

CAS No.	Chemical Name	Lab Test Method	Comment
VOCs			
67-63-0	Acrolein (2-propenal)		No Ambient Method
71-43-2	Benzene	GC/MS/FID	
106-99-0	Butadiene [1,3]	GC/MS/FID	
(o-) 95-50-1	Dichlorobenzene [ortho- & para]	GC/MS/FID	
100-41-4	Ethyl Benzene	GC/MS/FID	
100-42-5	Styrene	GC/MS/FID	
108-88-3	Toluene	GC/MS/FID	
(m-) 108-38-3	Xylene [m+p, o-]	GC/MS/FID	
75-01-4	Vinyl chloride	GC/MS/FID	
Halo-HCs			
56-23-5	Carbon tetrachloride	GC/MS/FID	
67-66-3	Chloroform	GC/MS/FID	
107062	Ethylene dichloride {EDC} (1,2 Dichloroethane)	GC/MS	
75-09-2	Methylene chloride (Dichloromethane)	GC/MS/FID	
127-18-4	Perchloroethylene (tetrachloroethene)	GC/MS/FID	
78-87-5	Propylene Dichloride (1,2-dichloropropane)	GC/MS/FID	Not in Mates II
79-01-6	Trichloroethylene	GC/MS/FID	
Carbonyls			
75-07-0	Acetaldehyde	HPLC	
67-64-1	Acetone	HPLC/ GC/MS/FID	Not Reported
50-00-0	Formaldehyde	HPLC	
78-93-3	Methyl ethyl Ketone (MEK)	HPLC/GC/MS/FID	Not Reported
1634-04-4	Methyl tert-Butyl Ether (MTBE)	HPLC/GC/MS/FID	Not Reported
Inorganics			
7429-90-5	Aluminum	ICP/MS:XRF	
7440-38-2	Arsenic	ICP/MS:XRF	
7440-41-7	Beryllium	ICP/MS:XRF	
7440-43-9	Cadmium	ICP/MS:XRF	
7440-70-2	Calcium	ICP/MS:XRF	
7440-47-3	Chromium (total)	ICP/MS:XRF	
	Chromium (hexavalent)	IC	
7440-48-4	Cobalt	ICP/MS:XRF	
7440-50-8	Copper	ICP/MS:XRF	
7439-89-6	Iron	ICP/MS:XRF	
7439-92-1	Lead	ICP/MS:XRF	
7439-95-4	Magnesium	ICP/MS:XRF	
7439-96-5	Manganese	ICP/MS:XRF	
7440-02-0	Nickel	ICP/MS:XRF	
7723-14-0	Phosphorous	ICP/MS:XRF	
7440-09-7	Potassium	ICP/MS:XRF	
7782-49-2	Selenium	ICP/MS:XRF	
7440-21-3	Silicon	ICP/MS:XRF	
7440-62-2	Vanadium	ICP/MS:XRF	
7440-66-6	Zinc	ICP/MS:XRF	
Others			
	Elemental & organic carbon	C analyzer	
Criteria Pollutants			
	PM _{2.5}	SASS	Speciation
	PM ₁₀	SSI-Hivol	PM network

APPENDIX B Size-Selective Inlet PM₁₀ Sampler Envelop

**South Coast Air Quality Management District
Applied Science & Technology**

Size-Selective Inlet PM₁₀ 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 (μg/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 C 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 D 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						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						

APPENDIX E MATES IV Sample Log

South Coast Air Quality Management District
Mates IV 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 924

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

Filter Log - XonTech 924

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

(Staple Printout Here)

APPENDIX F VOC Canister Tag

VOC CANISTER TAG

		CANISTER #					
		1	2	3	4	5	6
Field	Code						
	Date						
	Time						
	Initial Pressure						
	Final Pressure						
	Initials						
	Non-Routine Sample?						
	Comments						
Laboratory	Analyst						
	Cleaner						
	Blank Reference						
	Comments						

APPENDIX G Method Description for Sampling and Analysis of Carbonyls by HPLC at the SCAQMD Laboratory

Sampling - Ambient air is drawn through a dinitrophenylhydrazine (DNPH) coated silica cartridges mounted in the Xontec 924 sampler. The sampler is located on a stand outdoors to EPA siting specifications. The Xontec 924 incorporates a potassium iodide (KI) impregnated filter upstream of the cartridge for ozone destruction. 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 0.7 lpm for 24-hour sampling. Before and after sampling the cartridges are kept capped and refrigerated in small vials to prevent loss or 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 three milliliters of acetonitrile, the samples are placed in the autosampler. Samples are run isocratically (55% acetonitrile and 45 % H₂O) 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 multipoint injections of standards obtained from two separate sources. One point control standards are run every 10 samples with the batch analysis. PAMS/NATTS compounds, acetaldehyde, formaldehyde, and acetone, are quantified by comparison to the calibration curve.

QA/QC - The instrument Minimum Detection Level (MDL) is determined for the HPLC response (EPA Appendix B to Part 136, 40CFR Ch.1) and the system MDL 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. All samples are run in duplicate.

APPENDIX H Method Description for Sampling and Analysis of Elements by Energy Dispersive X-ray Fluorescence (XRF) Spectrometry at the SCAQMD 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 Panalytical Epsilon5 XRF instrument examines a very small cross section of the filter near the center.

Laboratory Analysis - A Panalytical Epsilon5 Energy Dispersive X-ray Fluorescence spectrometer is used to analyze 43 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 an autosampler, brought to a sample chamber kept under vacuum and scanned under ten 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 43 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 $\mu\text{g}/\text{cm}^2$. Using air volume data gathered during sampling, the $\mu\text{g}/\text{filter}$ concentrations of the elements are converted to ng/M^3 .

QA/QC - The X-ray instrument is calibrated using 35 single element standards. These calibration standards are checked using an NIST multi-element film standard. The NIST is run at the beginning and end of each sequence. Filter blanks are analyzed and used to subtract background from subsequent runs using the Epsilon 5 software. 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, all runs are checked in duplicate for precision.

APPENDIX I Method Description for Sampling and Analysis of Elements by
Inductively Coupled Plasma Mass Spectrometry (ICP/MS) at the
SCAQMD Laboratory

Sampling - Ambient air is drawn through a 47 mm Quartz filter loaded in a TSP sampler. Typically, 24 hour sampling at about 12 lpm provides sufficient sample mass on the filter for a successful analysis. The Perkin Elmer ICP/MS instrument examines total metal concentrations on the whole filter.

Laboratory Analysis - A Perkin Elmer ICP/MS is used to analyze 38 elements in the filter sample. Sample preparation procedures include digesting the whole filter in 11% nitric acid in a microwave oven, centrifuging the digested solution and diluting 10 times with 2% nitric acid. The diluted solution is then analyzed by ICP/MS.

Speciation and Quantification - The elements in the samples are ionized with inductively coupled plasma and are separated in the mass spectrometer based on their mass to charge ratio and then their concentrations are determined by the detector based on the intensities of ion counts. Using air volume data gathered during sampling, the $\mu\text{g/L}$ concentrations of the elements are converted to ng/m^3 .

QA/QC - The ICP/MS instrument is calibrated using a calibration standard mixture containing all the interested elements. The standard is diluted to eight concentrations and a 9 point calibration curve is generated and used to determine the concentration of samples. After the initial calibration is completed, a calibration check is required at the beginning and end of each analysis period for one analytical batch and at intervals of ten samples to verify the calibration. A blank filter and a blank filter spike sample is also digested and analyzed in each batch to examine the extraction efficiency and matrix effect.

Nickel Analysis by ICP/MS - Nickel overestimation by ICP/MS was determined to be caused by the ubiquitous and proportionally very high concentration of Calcium and Sodium which form interfering molecular ions in the plasma. The subsequent correction for Ni by changing the isotope of acquisition to 58 Amu from 60 Amu is described in section 3.6 and Appendix O.

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

Sampling - Ambient air is drawn through a 47-mm quartz filter loaded in a PM_{2.5} 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 μg 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 scans 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 $\mu\text{gC}/\text{filter}$ concentrations are converted to $\mu\text{gC}/\text{M}^3$ 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 reported in accordance with the data reporting and analysis requirements. Finally, collocated runs are utilized in checking precision.

APPENDIX K Method Description for Sampling and Analysis of VOCs by GC/MS/FID at the SCAQMD

Sampling - Ambient air is pumped into an evacuated Summa® polished and/or a silonite coated (Entech™) 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 12 PSI, following SOP00080 “XonTech 910 Canister Sampler/Multichannel Controller.” The canister is returned to the laboratory for subsequent analysis by Gas Chromatography with a Mass Spectrometer and Flame Ionization Detector (GC/MS/FID).

Laboratory Analysis - The Laboratory uses an Agilent 6890 Gas Chromatograph with an Agilent 5973 Mass Selective Detector. The sample is concentrated with an Entech 7100A cryo-concentrator for input to the GC/MS/FID. The sample canister is attached to the cryo-concentrator and a 600-milliliter aliquot is chilled in a trap to minus 150 degrees centigrade. For removal of the ambient humidity (water), the trap is heated to 10 degrees centigrade and transferred to a second trap cooled to -45 C for mitigation of the CO₂ 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. The FID quantifies non-toxic hydrocarbons per SOP 0008B “Standard Operating Procedure for TO15 (VOC).”

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. Non-toxic hydrocarbons are quantified by FID by a split from the column to the MS detector.

QA/QC - The Method Detection Limit (MDL) is determined for the GC/MS/FID by multiple injections of the lowest standard amount available (EPA Appendix B to Part 136, 40CFR Ch.1). Collocated samples are run in the field at one station. All canisters from the canister cleaning system are filled with the purified humidified nitrogen and tested for the presence of the compounds of interest. Above 0.2 ppb of any compound of interest or 10 ppb total of all compounds (compared to the benzene response factor) is cause for corrective action.

APPENDIX L Method Description for Sampling and Analysis of PAH Compounds

Sampling - Ambient air is drawn through an Andersen Instruments Poly-Urethane Foam (PUF) sampler. The method uses a high volume (Hi-Vol) air sampler equipped with a quartz fiber filter and PUF/Tenax glass adsorbent module for sampling between 325 and 400 cubic meters of air in a 24 hour sampling period. The laboratory is responsible for receipt of the quartz fiber filter and PUF/Tenax sorbent collection module, pre-cleaned and blanked, from Eastern Research Group (ERG), transported in a cold pack. The received modules are refrigerated until needed and then constructed for sampling by a Laboratory Technician for use by the field Instrument Technician. The Instrument Technician then installs the filter with PUF/Tenax collection module onto the Hi-Vol sampling unit and collects the sample on the appropriate day. The Instrument Technician returns the sample immediately after sampling and places it in the laboratory refrigerator. The Laboratory Technician then deconstructs the sampling module for shipment to ERG in a cooler with blue ice. Turnaround time for the sample to reach ERG from the sampling date is 7 days.

Laboratory Analysis- Analysis of the collected sample (in accordance with the chain of custody) is performed by ERG, Morrisville, North Carolina. The protocol used is EPA Compendium Method TO-13. The results are reported to the SCAQMD Project Manager and US EPA Air Quality System (AQS). Per ERG, “The test results are in compliance with NELAC accreditation requirements for certified parameters. All analyses are performed as described in the US EPA approved QAPP, under the contract for NATTS.”

QA/QC- Quality Assurance/Quality Control is limited to the sampling process. The Thermo Andersen PUF sampler is calibrated using an orifice transfer standard that has been standardized against a primary standard Roots meter. The orifice transfer standard is referenced to 25 degrees centigrade and 760 millimeters of mercury (Hg). In the field leak checks and sampling flow rate checks are performed each run. Field blanks are run at the prescribed frequency as found in the National Air Toxics Trends study work plan. Non-contaminating and cold transfer of all materials is maintained up through the shipment under cold conditions to ERG.

APPENDIX M Method Description for Sampling and Analysis of Hexavalent Chromium by Ion Chromatography at the SCAQMD Laboratory

Sampling - Ambient air is drawn through a 37-mm sodium bicarbonate treated cellulose filter loaded in a Xontech 924 sampler. Ambient air is pulled through the filter at a rate of approximately 12.0 liters per minute for 24 hours with an aggregate total air volume of approximately 17.2 m³. Samples must be refrigerated to minimize the reduction of hexavalent chromium to trivalent chromium.

Laboratory Analysis - A Dionex ICS-3000 ion chromatograph (IC) is utilized to determine the hexavalent chromium concentration in ambient air samples. The entire filter sample is extracted in 10 mL of 20mM sodium bicarbonate solution via sonication for one hour. The extract is then filtered to remove solids/particles and analyzed by the Dionex IC. This system is comprised of an autosampler, guard column, analytical column, post-column derivatization module, a UV-Vis detector, and Chromeleon software. Hexavalent chromium is detected by a visible lamp at a wavelength of 530nm after forming a complex with diphenylcarbazide in a post-column reaction.

Quantification - A five point calibration curve is generated from prepared standards ranging from 50 to 1000 part per trillion (ppt). The hexavalent chromium sample concentrations are quantified by area comparisons to the area obtained for the calibration standards. The Chromeleon® software calculates the concentrations for each sample based on the calibration curve. (The ppt concentrations are then converted to ng/m³ by multiplying the ppt by the extraction volume (in Liters) and dividing by the air volume (m³).

Quality Control - All analyses are performed following the Standard Operating Procedure for The Analysis of Hexavalent Chromium in Ambient Air by Ion Chromatography (SOP 0046). Performance qualifications are conducted annually to determine the LOD for the Dionex IC. Linearity of the calibration curve is also an important aspect of instrument performance. The IC is calibrated weekly to achieve a minimum correlation coefficient of 0.9990. MDLs are obtained annually to determine the analytical method sensitivity. Blank and check standard analyses are performed every 10 samples to verify the precision of the analytical data. Additionally, an external standard is prepared for every batch of samples to verify the accuracy of the calibration standard. Blank and spike QCs are extracted with every sample batch. Spike QCs are spiked with known hexavalent chromium concentrations and are prepared with the samples. The amount of the spike concentration recovered during the analytical procedure will indicate the accuracy of the method. All samples require duplicate injections, which test precision of IC measurements. Field blanks are collected throughout the sampling duration to determine if there are errors and/or contamination in sample acquisition and the analytical process. The field blank results are reported in accordance with data reporting and analysis requirements. Collocated samples are collected at specified sites and times. The collocated data is used to verify sampling and analytical precision.

Method Enhancements - The analytical method has improved since MATES III in several aspects. A newer Dionex ion chromatograph replaced the previous instrument used in the analysis of MATES III samples for hexavalent chromium. The detection limit for the previous

system and the new system were 0.06 ng/m^3 and approximately 0.02 ng/m^3 , respectively. The detection limit was further improved by the implementation of additional filter pre-sampling treatment procedures, such as nitric acid washing followed by deionized (DI) water rinsing, and impregnation with sodium bicarbonate. The incorporation of nitric acid washing of cellulose filters eliminated the hexavalent chromium background concentrations prior to sampling. This resulted in the removal of a positive hexavalent chromium bias and improved the precision and accuracy during the MDL determination for the analytical method. The resulting MDL after the implementation of these protocols was 0.002 ng/m^3 .

There were also additional enhancements to the sample preparation procedure. The efficiency of the sample extraction process was improved by decreasing the sonication time from 3 hours to 1 hour. This minimized the sample preparation time prior to analysis and prevented the possible change in hexavalent chromium concentration during the sonication process. Further improvement to the detection limit was done by decreasing the extraction volume from 15 mL to 10 mL. The older method of higher extraction volume would have diluted the samples and could have decreased the accuracy of the results for samples near the detection limit. Prior to sampling, the sodium bicarbonate treated cellulose filters had little variability in pH. However, during sampling, the pH of the filters could change depending on proximity to sources or different environmental conditions. In order to ensure that the pH of the extracts was consistent among all samples post-sampling, the extraction solution was changed from DI water to 20mM sodium bicarbonate. The addition of dilute sodium bicarbonate stabilizes the pH, reducing the variability in pH in the samples. For consistency, all standard solutions were also prepared in a 20mM sodium bicarbonate solution. Improvements in the hexavalent chromium method follow the procedures outlined in the National Ambient Toxics Trend Stations Technical Assistance Document (NATTS TAD).

APPENDIX N Comparison of ICP/MS to XRF**Background:**

Energy Dispersive XRF has been used to determine metals in the previous two air toxics study; MATES II & MATES III. The two important differences between the two methods are sample pretreatment and sensitivity. ICP/MS requires acid digestion of filter samples, whereas filters can be run as is on the XRF method. However, for all the air toxic metals, the ICP/MS has significantly better detection limit. Further, the XRF method is not as well suited for TSP filters as it is for PM_{2.5}. The presence of coarse particles on TSP filters creates serious absorption effects on many metals, requiring multiple and complicated corrections. Even these corrections may not work well because they require knowledge of the mass density of each individual filter. As TSP filters are never weighed, XRF determinations on TSP samples are not the ideal matrix for the XRF method. The only advantage of XRF over ICP/MS was the ability to measure crustal elements such as Aluminum & Silicon without sample prep which otherwise would have required very strong acid mixture (including HF) for ICP/MS. Since the toxic metals list for MATES did not include these crustal elements, it was decided to analyze all MATES IV TSP filters for selected toxic metals using ICP/MS.

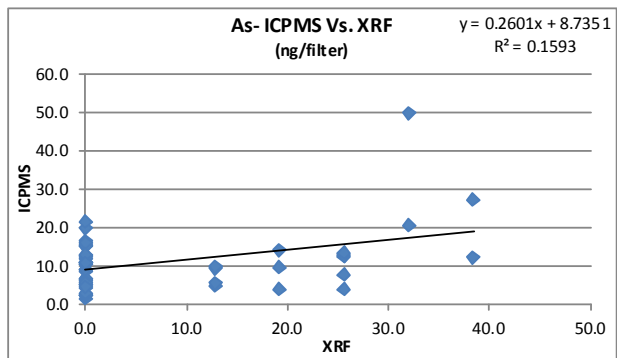
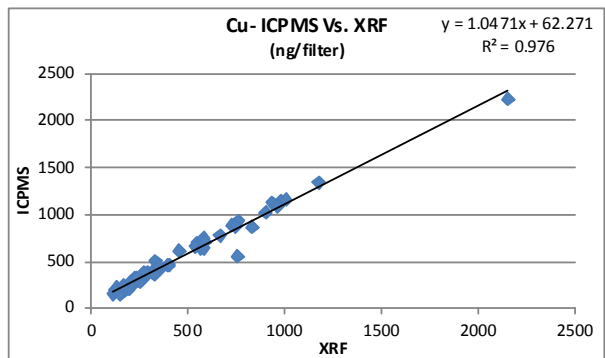
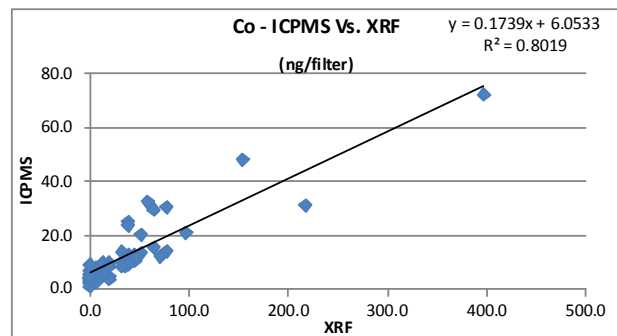
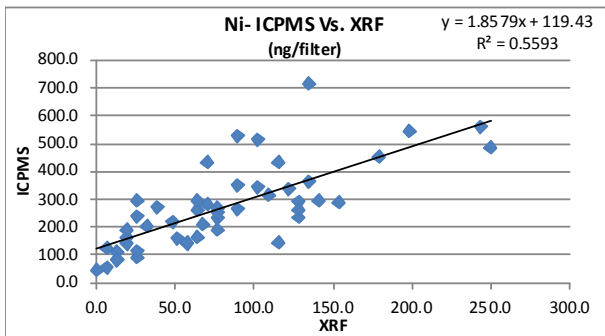
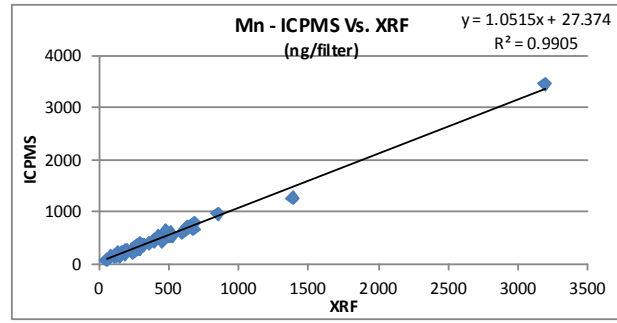
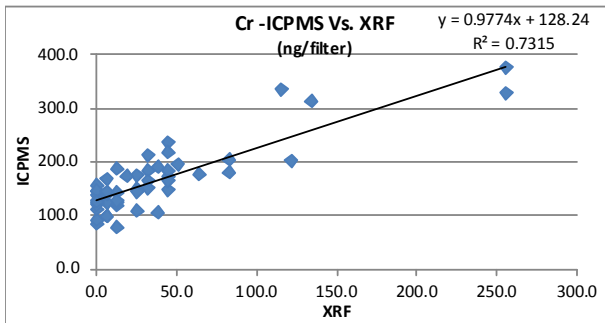
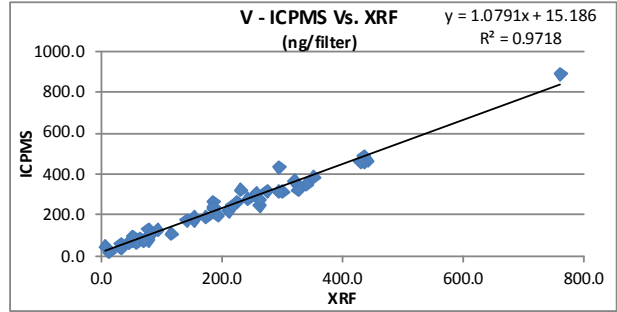
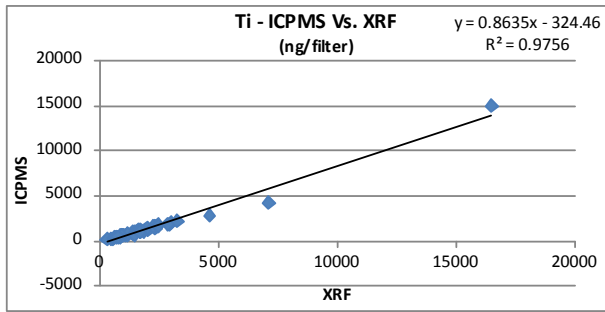
Method:

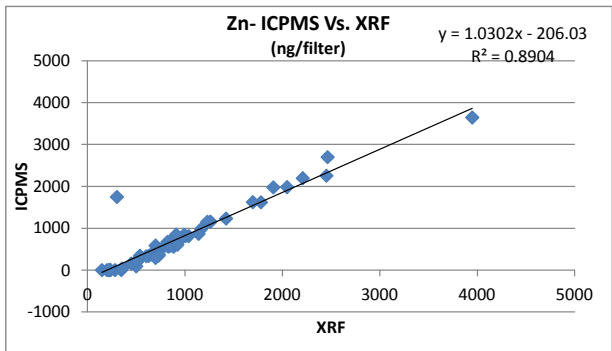
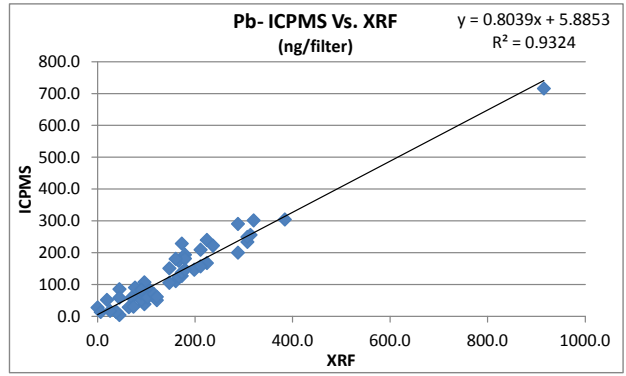
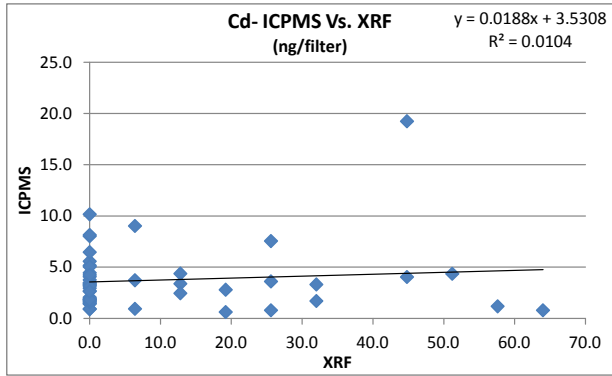
Comparison between the two methods was performed using 50 TSP filters from two sites from a previous project. These filters were run on the PANalytical Epsilon 5 EDXRF analyzer in accordance with SCAQMD S.O.P. #0004. The same filters were then digested in nitric acid and analyzed by ICP/MS in accordance with the SCAQMD S.O.P. #0005. Data from both methods were reported in µg/filter unit and compared to each other. Charts comparing these methods for selected metals are found below.

Results:

- Comparison for most metals was very good with slope in the range of 0.8 to 1.1.
- Metals such as Co, As, and Se did not fare well, primarily because the superior detection limit of ICP/MS over XRF. Almost all non-detect values by XRF were quantitatively reported by the ICP/MS. This was especially serious for Se where most XRF reported values are below the MDL.

Nickel overestimation by ICP/MS was determined to be caused by the ubiquitous and proportionally very high concentration of Calcium and Sodium which form interfering molecular ions in the plasma. The subsequent correction for Ni by changing the isotope of acquisition to 58 Amu from 60 Amu is described in section 3.6 and Appendix O.





APPENDIX O Nickel Analysis by ICP/MS

Background:

Average Nickel Basin-wide concentrations were found to be significantly higher during the first half of MATES IV when compared to same period during MATES III. This apparent increase in Nickel concentration occurred while all other metals either did not change or showed reduction in concentrations during the same period. This observation prompted a re-examination of the data.

Although quality control criteria were met for each of the batches analyzed by the ICP-MS, it became clear that an unknown interference with significant additive properties was responsible for the elevated values of Nickel. The target mass used in the ICP-MS determination of Nickel was 58 atomic mass units (AMU). The primary interferant was determined to be several molecular ions whose combined molecular weight equaled 58, including $^{23}\text{Na}^{35}\text{Cl}^+$, $^{40}\text{Ar}^{18}\text{O}^+$, $^{40}\text{Ca}^{18}\text{O}$, as well as other ions found at lower concentrations with smaller impacts. Once this was determined, the analysis method was changed such that ^{60}Ni isotope was selected as the target for analysis instead of ^{58}Ni .

Method:

The samples that were received after the method change to ^{60}Ni were analyzed and reported as is. All available filter samples and extracts previously analyzed with the ^{58}Ni target ion were re-analyzed using ^{60}Ni as the target isotope. These re-analyzed samples were then reported using the ^{60}Ni values. There were however a limited number of samples for which no filters or extracts were available. The re-analyzed samples generated data that was used to calculate an average ratio of $^{58}\text{Ni}/^{60}\text{Ni}$ concentration at each sampling site which was used to correct previously analyzed data from samples for which no filters or extracts were available to repeat the analysis under the new analytical condition. Instead of using one average ratio for all MATES IV sites, average ratios for each individual site were calculated and used to correct values at each respective site. Each of the initial concentration values was corrected by multiplying that value with appropriate site ratio. These interference corrected Nickel data have been flagged. The table below shows the ratio of ^{58}Ni to ^{60}Ni at each of the MATES IV sites.

Station	Average $^{58}\text{Ni}/^{60}\text{Ni}$
Anaheim	3.315
Burbank	4.233
Compton	2.813
Fontana	4.843
Hudson	3.338
Huntington Park	2.614
Long Beach	2.909
Los Angeles A	3.921
Pico Rivera	3.009
Rubidoux A	5.213

APPENDIX P QA/QC Matrix Summary

Process	Interval	Activity	Criteria	Corrective Action
Field Canister	Before & After Each	QC - Note Activities in Log Book, Canister	Notes For Each Canister	N/A
Sampler		QC - Check Chart Time	± 10 Minutes of Actual PST	AQIS Resets
	Annually	QC - Clean Manifold	Pass Leak Check	AM Support Repairs
		QC - Calibrate Flow	± 5 % True Flow	AM Operations Calibrates
	1 Day in 6	QA - Collocated Sample	10 % Of Network	Run A + B Make-Ups if Possible
	Annually	QA - ARB Through-the-Probe Audit	Within ± 25 % of True For all Compounds	Isolate & Repair, Validate Data
		QA - Flow Audit	Indicated Flow Must Be Within ± 10 % 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 % True Flow	AM Operations Calibrates
If Equipment Available	1 Day in 6	QA - Collocated Sample	10 % of Network	Run A + B Make-Ups if Possible
	Annually	QA - Through-the-Probe Audit By ARB	Within ± 25 % of True For All Compounds	Isolate & Repair, Validate Data
		QA - Flow Audit	Indicated Flow Must be Within ± 10 % 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 % 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 % 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 % On All Compounds	Chemist Repairs
	Quarterly	QA - Parallel Sampling	All Compounds Must Be Within ± 30 %	
	Annually	QA - NPAP Performance Audit	Within ± 30 % of True For All Compounds	Chemist Repairs
		QC - Standard Response	± 10 % 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 % 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 %	
	Annually	QA - NPAP Performance Audit	Within ± 30 % of True For All Compounds	Chemist Repairs
	Before & After Each	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 PM₁₀ 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 % Of Sites	N/A
	Annually	QA - Flow Audit	Actual Flow Must be Within ± 10 % of True Flow	Request Repair; Investigate & Confirm Data Validity
		QC - Balance Checks		
aboratory	Daily	QC - Inspect Filters	No Light Leaks or Tears	
PM₁₀ SSI		QC - Equilibrate Filters		
	1 Day in 6	QA - Collocate Filters	Agreement Within ± 20 %, all Compounds	