

APPENDIX III
MATES V
FINAL REPORT

Monitoring and Laboratory Analysis Protocol

DISCLAIMER

Any or all reference made in this Appendix to a specific product or brand name does not constitute an endorsement of that product or brand by the South Coast Air Quality Management District.

Appendix III

Monitoring and Laboratory Analysis Protocol

III.1. INTRODUCTION

III.1.1 Background

In 1986, the South Coast Air Quality Management District (South Coast AQMD) performed a study of ambient air toxics impacts in the South Coast Air Basin. Although this study involved only limited measurements, it was an important beginning of the Multiple Air Toxics Exposure Study (MATES). In 1998, the South Coast AQMD conducted a follow up to that initial study, but included an intensive ambient air toxics monitoring program, which became 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. Sampling for MATES II was performed over a one-year period at ten sites throughout the South Coast Air Basin (Basin). The MATES II Final Report was approved by the South Coast AQMD Board in March 2000.

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, sampling continued for a second year due to concerns of the impact of heavy rains on data collected during the first year. The MATES III Final Report was published in September 2008.

From July 2012 through July 2013, MATES IV monitoring was performed to build upon prior ambient toxics data sets, to evaluate spatial and temporal trends and better understand current risk associated with air toxics in the Basin. Black carbon (BC) and ultrafine particle (UFP) measurements were included in this study. The MATES IV report was released in May 2015¹.

For MATES V, sampling was conducted for a year from May 2018 through April 2019. In addition to continued monitoring efforts for air toxics measured in previous MATES, this study incorporated measurements for biomass burning indicators (sugars) and bromomethane (methyl bromide).

¹ South Coast Air Quality Management District (2015). *MATES IV*. <https://www.aqmd.gov/home/air-quality/air-quality-studies/health-studies/mates-iv>

III.2. MONITORING EQUIPMENT

III.2.1 Introduction

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

Table III-2-1. MATES V Samplers

Sampler Type	Vendor and Model Number
Volatile Organic Compounds (VOCs)	Xontech 910A/ 912
Carbonyls	ATEC 8000
Metals, Hexavalent Chromium (Cr ⁺⁶)	Xontech 924
PM _{2.5} Speciation	Met One Instruments SASS
Black Carbon (BC)	Teledyne API 602 (Aethalometer)
Ultrafine Particles (UFPs)	Teledyne TSI 651 (CPC)
Polycyclic Aromatic Hydrocarbons (PAHs)	TISCH Polyurethane Foam (PUF+)

The siting, acceptance testing, and calibration functions for each type of equipment identified above are defined below.

III.2.2 Equipment Characteristics

III.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 were prepared for all sampling sites and can be found in the South Coast AQMD Annual Network Plan². 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 known 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.

² South Coast Air Quality Management District (Current). *Monitoring Network Plan*.
<http://www.aqmd.gov/home/air-quality/clean-air-plans/monitoring-network-plan>

- 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 is not placed where a building is an obstruction or where equipment is easily vandalized.
- E) The probe extends at least two meters away from the supporting structure. If the probe is located on a building, it is mounted on the prevailing windward side of the building.

III.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 operations manuals.

III.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.

III.2.2.4 Sample Pickup

The sampling media were prepared in the South Coast AQMD laboratory and retrieved by Air Quality Instrument Specialists (operators). Filters and carbonyl cartridges were transported at $<4^{\circ}\text{C}$ in coolers with blue ice and the canisters were capped during transportation. Once the

filters and carbonyl cartridges were used to collect samples, they were refrigerated at <4 °C until returned to the South Coast AQMD Laboratory.

III.2.2.5 Troubleshooting

The routine maintenance and quality control checks were based on U.S. EPA *Quality Assurance Project Plan for the Air Toxics Monitoring Network*³ and U.S. Environmental Protection Agency (EPA) *National Air Toxics Trends Stations Technical Assistance Document (NATTS TAD)*⁴. For the instruments that were not included in the NATTS program, a maintenance guide based on the equipment manufacturers suggested operating procedures was the basis for maintenance activity including frequency and quality control checks for each instrument. If an instrument drifted out of the criteria, or if there was a component failure, the operator immediately contacted the South Coast AQMD STA/AM Support and Repair Section to schedule a repair.

III.2.2.6 Repair

The potential failure of instrument and equipment components such as pumps and flow controllers were addressed by South Coast AQMD maintaining an inventory of staff replaceable spare parts.

III.2.3 SAMPLING EQUIPMENT

III.2.3.1 Xontech 910A and 912

III.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 within NATTS program criteria, making it useful for sampling a wide variety of gases.

Specifically, the 910A sampler takes air from the sample inlet and injects it into a canister at a constant flow rate for the preset duration. 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. Airflow to the canister is uniformly maintained by a mass flow controller that fills each canister with a representative sample volume and sufficient pressure for analysis. The Xontech 910A is operated according to the guidelines documented in the South Coast AQMD SOP00080 *Standard Operating Procedure for Xontech 910 Canister Sampler/912 Multi-Channel Controller*.

³ U.S. EPA. (2001). *Quality Assurance Project Plan for the Air Toxics Monitoring Network*.
<https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=200120XJ.PDF>

⁴ U.S. EPA (2016). *Technical Assistant Document For The National Air Toxics Trends Stations Program*.
www3.epa.gov/ttn/amtic/files/ambient/airtox/NATTS%20TAD%20Revision%203_FINAL%20October%202016.pdf

III.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 duration. 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 procedures in the South Coast AQMD SOP00080, *Xontech 910 Canister Sampler/912 Multi-Channel Controller*.

III.2.3.1.3 Cleanliness Check

To ensure data quality objectives are met, sampling units are checked for contamination and bias following the South Coast AQMD Standard Operating Procedure for *Time-Integrated And Instantaneous Canister Sampling*, SOP 00199. To perform a system bias check, zero air was passed through the sample manifold to fill one, 3-hour canister. Additionally, the 24-hour sampler was tested by increasing its sample flow to fill a canister in approximately 6 hours. A field blank canister was filled at the site by flowing zero air 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 were demonstrated to be eliminated. The District'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.

III.2.3.1.4 Canister Sample Pickup

Field operators retrieved verified clean silica lined stainless steel canisters from the South Coast AQMD Laboratory. Evacuated canisters were transported by vehicle to the respective air monitoring stations. Each canister had an informational tag attached (Appendix III-E). This tag contains the following information: sample site, operator initials, and sample date. The air monitoring station operator recorded sampling information on this tag once the canister was set up for sampling. Once the canister was filled and disconnected from the 910A or 912 sampler, and prior to returning the sampled canister to the Laboratory, the canister number, start vacuum, end pressure (psig), and elapsed time was recorded on the MATES V sample log (Appendix III-D). The times on the QC chart was also checked and adjusted. This value was required to be within ± 10 minutes of actual Local Standard Time.

III.2.3.2 ATEC 8000

III.2.3.2.1 Description

The ATEC Model 8000 sampler is designed for the unattended collection of ambient air samples used in the determination of carbonyl compounds (aldehydes and ketones) in ambient air using acidified DNPH cartridges, according to EPA Compendium Method TO-11A. The ATEC 8000 has eight ports; each port can be programmed to collect samples over a specific time period.

Flow rates are regulated using mass flow controllers (MFC). Optional channels can be configured for collocated sampling. A touch screen display provides information on the samples, including sampling date, start time, stop time, average flowrate, minimum flowrate, maximum flowrate, total volume sampled, sampling time duration, and error status.

III.2.3.2.2 Operation

To setup for sampling, the operator attaches the DNPH cartridges to the ATEC sampler and programs the instrument for collection of samples by selecting the channels/ports used and entering sampling parameters (flow rate, start time, stop time) and identification labels. Leak checks are performed prior to sampling to verify cartridge connections are leak free prior to sampling. Detailed operational procedures are available in the South Coast AQMD SOP 00119, *ATEC Model 8000 Automated Sampler*.

III.2.3.3 Xontech 924

III.2.3.3.1 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. Samples collected using this sampler were brought to the South Coast AQMD headquarters for Laboratory analysis. The sampler 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 accommodates 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 that the electronics have been upgraded in the 924 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 capacity for simultaneous operation of three, 30 liters per minute (lpm) and 200 cubic centimeters per minute (ccm) sampling channels.

III.2.3.3.2 Operation

To use the sampler, the operator inserts the sample filter cassette or sorbent tube into the sampling head and keys 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 is removed from the printer and submitted to the Laboratory with the filter for analysis.

Operational specifications are discussed in South Coast AQMD SOP 00094, *RM Environmental Systems Inc. (RMESI) 924 Toxics Sampler*.

III.2.3.4 MET One SASS

III.2.3.4.1 Description

The MET One Speciation Air Sampling System (SASS) accommodates up to five sampling canisters which can 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 are equipped with a diffusion denuder ahead of the filter to remove selected gaseous compounds. Additional sampler description and operation is available in the South Coast AQMD Standard Operating Procedure, SOP00086 for the *Collection of PM_{2.5} Air Samples with the Met One Instruments Speciation Air Sampling Systems (SASS) SOP00086*.

III.2.3.4.2 Module and Media Description

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

Several types of filter media are needed for assaying the different chemical constituents of ambient air particles. The chosen filter media are suitable for the type of analysis intended. 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.

III.2.3.5 Black Carbon Measurements 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. 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 thermal-

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 III.2.3 of this Appendix), respectively.

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 operation of the Aethalometer is described in detail in the South Coast AQMD's *Standard Operating Procedure For the Operation, Maintenance, and Calibration of the Aethalometer – Teledyne "Dual Spot" Model 633 (Magee/Aerosol AE33)*, SOP00142. During sampling, the gas stream (frequently ambient air) briefly 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 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.

III.2.3.6 Ultrafine Particle (UFP) Measurements

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 sometimes used interchangeably, and the definitions of each generally vary with the study or application. While fine particulate matter (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 #/cm³), 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.

The CPC used to measure the ambient number concentration of UFPs at the ten fixed MATES V 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 evaluated by South Coast AQMD 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 particle in the air stream. The CPC model 651 is able to detect particles as small as 7 nm in diameter and is operated with an upper size cutoff of approximately 600 nm. The detection range is between 0 and 1,000,000 #/cm³. The instrument is operated according to South Coast AQMD's SOP00143, *Operation, Maintenance, and Calibration of Teledyne's Ultrafine Particle Monitor Model 651*.

III.2.3.7 Polycyclic Aromatic Hydrocarbons (PAH)

Polycyclic Aromatic Hydrocarbons (PAHs) are collected using TISCH Environmental Polyurethane Foam (PUF+) samplers designed to hold a circular 4-inch diameter quartz fiber filter and a 2.5 inch diameter by 5 inch long cylindrical glass cartridge containing a 3 inch PUF sorbent trap and granular solid sorbent material. The South Coast AQMD Laboratory staff prepared sample collection canisters using sampling media supplied by ERG, deconstructed the samples post-sampling, and mailed samples back to ERG for analysis. The South Coast AQMD Instrument Technicians setup the PUF instrument for sample collection, retrieved the canisters after sampling, and returned PUF samples to the South Coast AQMD Laboratory for deconstruction. Chain of Custody was maintained beginning from receipt of sampling media from ERG until the samples were shipped to ERG for analysis. South Coast AQMD staff was responsible for calibrating, calculating and reporting of the total air volume of each sample. This included calibration of the sampling instrument flow rate. The TISCH sampler was operated and maintained according to SOP00114, Standard Operating Procedure for TISCH PUF+ POLY-URETHANE FOAM (PUF) SAMPLER. A short method description is given in Appendix III-K.

III.3. LABORATORY PROCEDURES

III.3.1 Introduction

In 2008 the National Air Toxics Trends Stations (NATTS) program was implemented in the South Coast Air Basin. Some of the existing sampling instruments for NATTS, additional U.S. EPA programs, and South Coast AQMD programs, were utilized in MATES V. Hence, many of the procedures and protocols for the MATES V program were based on the South Coast AQMD

Quality Management Plan for Environmental Measurement Programs (2016), the South Coast AQMD *Quality Assurance Project Plan (QAPP) for PM_{2.5} Speciation Program* (2013), and the EPA NATTS TAD⁵. However, MATES V also utilizes several analytical methods not performed under the federal programs and the procedures 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 V.

The South Coast AQMD utilized Air Quality Instrument Specialists to collect, retrieve, and deliver samples to the Laboratory. The Laboratory sample custodians handled sample logging within the South Coast AQMD Laboratory. Procedures for proper sampling and initial chain-of-custody are outlined in the South Coast AQMD standard operating procedures (SOPs).

III.3.2 SAMPLE HANDLING

All sampling media were handled according to Laboratory standard practices for toxics analysis and particulate matter network programs, as applicable. Operators completed the sampling information and chain-of-custody forms⁶, and delivered samples to the Laboratory for receipt by sample custodians. .

III.3.2.1 Canister Cleaning

The South Coast AQMD Laboratory has a canister cleaning oven system operated according to SOP00091 "*Canister Cleaning System (CCS) Ovens 3 & 4 Toxics.*" These systems use humidified nitrogen to flush and clean canisters in a heated oven to less than 5 ppb total non-methane organic carbon (TNMOC). The canisters are held at 80°C and are flushed a minimum of seven times over a 2 ½ -hour period. Canisters are removed from the canister cleaning oven and batch 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 canister-cleaning oven system is sufficient to provide clean canisters meeting federal PAMS and NATTS cleanliness requirements. Any hydrocarbons and TNMOC above the threshold concentrations in one or more canisters 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.

III.3.2.2 Field Canister Use

Canisters are transported by Instrument Specialists to the site and are installed in accordance with the South Coast AQMD Standard Operating Procedure for *Xontech 910A Canister Sampler/912 Multi-Channel Controller* (SOP00080).

⁵ U.S. EPA. (2016). *National Air Toxics Trends Stations Technical Assistance Document*. https://www3.epa.gov/ttn/amtic/files/ambient/airtox/NATTS%20TAD%20Revision%203_FINAL%20October%202016.pdf

Once sample collection was completed and the sample time, canister number, and start and stop vacuum were documented in the MATES V Sample Log (Appendix III-D) that accompanied the canister, samples were promptly returned to the Laboratory for receipt, log-in, and distribution to appropriate staff.

III.3.2.3 Sample Distribution within the Laboratory

The Laboratory sample custodians logged received samples and distributed them to the appropriate staff member following established Laboratory procedures.

III.3.3 Analytic Methods – Appendix III-A Compounds

Gaseous compounds listed in Appendix III-A were analyzed using gas chromatography with mass spectrometry (GC/MS) after cryo-focusing. This technique provides for instrument sensitivity sufficient for meeting MATES V measurement criteria. The method generally follows EPA Method TO-15; *Determination of Volatile Organic Compounds (VOCs) in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*. Procedures specific to the South Coast AQMD Laboratory are found in South Coast AQMD SOP0008B. A short method description for sampling and analysis of VOCs by GC/MS can be found in Appendix III-J.

Carbonyl measurements were performed according to EPA Method TO-11, *Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Pressure Liquid Chromatography*, with NATTS sampling and analysis criteria delineated in the NATTS TAD (2016). 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 III-F.

TSP metals samples were collected on cellulose filters using Xontech 924 samplers and were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) following the procedure found in South Coast AQMD SOP00096 *Standard Operating Procedure for the Determination of Metals in Ambient Particulate Matter by Inductively Coupled Plasma Mass Spectrometry*.

For PM_{2.5} samples, a Teflon filter was used, and Energy Dispersive X-ray Fluorescence (ED-XRF) was used for metals analysis following the procedure found in South Coast AQMD SOP00004 *Standard Operating Procedure for the Analysis of PM_{2.5} Filter Samples by Energy Dispersive X-Ray Fluorescence Spectrometry*. A short method description for sampling and analysis of elements by XRF is attached to this document as Appendix III-G.

Hexavalent chromium in ambient air was measured by collecting total suspended particulate matter (TSP) on cellulose filters impregnated with sodium bicarbonate solution using a Xontech 924 Toxic Air Sampler. The samples were analyzed by a Thermo Scientific ICS-5000 ion chromatograph (IC) equipped with a UV-Vis detector following South Coast AQMD SOP00046

The Analysis of Hexavalent Chromium (Cr(VI)) in Ambient Air by Ion Chromatography. The method description for hexavalent chromium sampling and analysis is found in Appendix III-L.

Particulate filter samples for 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 South Coast AQMD (federally recognized) PM_{2.5} Network activity. Analysis for EC, OC and TC of PM_{2.5} filter samples was performed 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 III-I.

Particulate filter samples for PM_{2.5} were analyzed for levoglucosan and other monosaccharide anhydrides. A portion of the quartz fiber filter sample was extracted in acetonitrile, derivatized with a silanizing reagent, and analyzed using a Gas Chromatograph/Mass Spectrometer. A detailed description of the method can be found in Appendix III-M.

The compounds listed in Appendix III-A were sampled on a one-day-in-six sampling schedule synchronized with the national PM_{2.5} network schedule (BC and UFP measurements are real time). These samples were integrated 24-hour samples. South Coast AQMD personnel and contract employees conducted both the sampling and analysis with the exception of polycyclic aromatic hydrocarbons (PAHs), where the analysis was performed by Environmental Research Group, LLC (ERG).

III.3.4 Sampling Schedule

MATES V 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/tnn/amtic, and follows a six-day monitoring schedule for TSP lead, PM_{2.5} and VOCs. This sampling schedule has several benefits:

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

III.3.5 Quality Control/Quality Assurance

Appendix V contains the objectives, procedures, documentation, and data review techniques that were used by the South Coast AQMD to quality assure that MATES V data that met or exceeded the acceptance criteria for its intended use.

III.4. Data Processing and Reporting

III.4.1 Introduction

MATES V monitoring and analysis of ambient air toxics has generated a large database which is available for future data analysis. 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 aim of reporting is to generate a database for electronic transfer to interested parties. The data was reviewed (verified) for errors, to assure that it meets DQOs and for adherence to other QA criteria such that the data represent the most accurate determinations possible, and is both defensible and suitable for MATES V use. The Laboratory made every effort to disseminate the data in a timely fashion to facilitate feedback.

III.4.2 Data Processing

Data was processed, reviewed, and reported routinely during the MATES V monitoring period. AQ Chemists processed data generated from Laboratory instruments using analytical software and uploaded data to the Laboratory Information Management System (LIMS). The data was then reviewed by peer AQ Chemists, followed by Senior AQ Chemist review, and finalized by Principal AQ Chemists.

The continuous BC and UFP data was also processed, reviewed, and reported routinely during the MATES V monitoring period. Air Quality Instrument Specialists processed and reviewed data acquired from DMS using analytical software, followed by Air Quality Specialist review, and finalized by a Program Supervisor.

III.4.3 Database Compilation

Data from the MATES V database was exported from the LIMS and stored in a MS Access database. The MATES V database is comprised of PM_{2.5} mass and its components (ions, metals, carbon, sugars), VOCs, carbonyls, TSP metals, and PAHs results for ten fixed sampling locations. The continuous BC and UFP data is stored in a separate MS Excel database. The database contains information regarding station names, station abbreviations (four letter acronyms), sampling dates, sample types, analyses, analytes, concentrations, units, MDLs, invalid qualifiers, and comment qualifiers.

APPENDIX III-A Air Contaminants Measured in MATES V Program

Pollutant Category		Measured Pollutants
Ultrafine Particles (UFPs)		UFPs
PM_{2.5}	Ions	Ammonium Ion, Chloride, Nitrate, Potassium Ion, Sodium, Sulfate
	Sugars	Galactosan, Levoglucosan, Mannosan
	Metals	Aluminum, Antimony, Arsenic, Barium, Cadmium, Calcium, Cesium, Chlorine, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Phosphorus, Potassium, Rubidium, Samarium, Selenium, Silicon, Strontium, Sulfur, Thallium, Tin, Titanium, Uranium, Vanadium, Yttrium, Zinc
	Other	PM _{2.5} mass, Black Carbon (BC), Elemental Carbon (EC), Organic Carbon (OC), Total Carbon (TC)
Total Suspended Particulate (TSP)	Metals	Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Cesium, Chromium, Cobalt, Copper, Cr ⁶⁺ (hexavalent chromium), Iron, Lead, Manganese, Molybdenum, Nickel, Potassium, Rubidium, Selenium, Strontium, Tin, Titanium, Uranium, Vanadium, Zinc
Volatile Organic Compounds (VOCs)	Carbonyls	2-Butanone (Methyl Ethyl Ketone), Acetaldehyde, Acetone, Benzaldehyde, Formaldehyde, Propionaldehyde
	Other	1,2-Dibromoethane, 1,2-Dichlorobenzene, 1,2-Dichloroethane, 1,2-Dichloropropane, 1,3-Butadiene, 1,4-Dichlorobenzene, 2-Butanone (Methyl Ethyl Ketone), Acrolein (2-Propenal), Acetone, Benzene, Bromomethane, Carbon Tetrachloride, Chloroform, Ethylbenzene, m+p-Xylene, Methyl tert-Butyl Ether (MTBE), Methylene Chloride, o-Xylene, Styrene, Tetrachloroethylene (Perchloroethylene), Toluene, Trichloroethylene, Vinyl Chloride
Polycyclic Aromatic Hydrocarbons (PAHs)		9-Fluorenone, Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(e)pyrene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysene, Coronene, Cyclopenta(c,d)pyrene, Dibenz(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-c,d)pyrene, Naphthalene, Perylene, Phenanthrene, Pyrene, Retene

APPENDIX III-B 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 III-C PAH (PUF) Chain of Custody (COC)



ERG
Eastern Research Group, Inc.

601 Keystone Park Drive, Suite 700, Morrisville, NC 27560

ERG Lab ID # _____

SVOC SAMPLE CHAIN OF CUSTODY

Lab Pre-Sampling	Site Code: <u>BUCA</u> City/State: _____ AQS Code: _____ Cartridge Certification Date: _____ Relinquished by: <u>RIC</u> Date: ^{RIC} <u>3/9/21</u>	Container #: <u>319</u> Collection Date: <u>4/22/21</u> Collocated Event (Y/N): _____ SUR ID: <u>1004005</u> XAD Lot: <u>BIC3101-K8</u> PUF Lot: <u>134597</u> Filter Lot: <u>17014295</u>																								
Field Setup	Received by: <u>MARQUEZ</u> Date: <u>04/20/21</u> Site Operator: <u>MARQUEZ</u> System #: <u>1001 081</u> Set-Up Date: <u>04/20/21</u> Elapsed Timer Reset (Y/N): <u>Y</u>																									
Field Recovery	Recovery Date: <u>04/27/21</u> <div style="text-align: center; border-bottom: 1px solid black; padding: 2px;"> Collection System Information: </div> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th></th> <th>Elapsed Time</th> <th>Temp. (°C)</th> <th>Barometric ("Hg)</th> <th>Magnehelic ("H₂O)</th> <th>Flowrate (std. m³/min)</th> </tr> </thead> <tbody> <tr> <td>Start</td> <td>00:00</td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>End</td> <td>24:00</td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>Average</td> <td></td> <td>14.4</td> <td>28.9</td> <td>34.7</td> <td>0.225</td> </tr> </tbody> </table> Total Collection Time (Minutes) <u>1440</u> Total Collection Volume (std. m ³) <u>323.45</u> Status: <input checked="" type="radio"/> Valid <input type="radio"/> Void (Circle one) Site Operator: <u>NMARQUEZ</u> Relinquished by: <u>NMARQUEZ</u> Date: <u>04/27/21</u>			Elapsed Time	Temp. (°C)	Barometric ("Hg)	Magnehelic ("H ₂ O)	Flowrate (std. m ³ /min)	Start	00:00					End	24:00					Average		14.4	28.9	34.7	0.225
	Elapsed Time	Temp. (°C)	Barometric ("Hg)	Magnehelic ("H ₂ O)	Flowrate (std. m ³ /min)																					
Start	00:00																									
End	24:00																									
Average		14.4	28.9	34.7	0.225																					
Lab Recovery	Received by: _____ Date: _____ Container #: _____ Status: <input checked="" type="radio"/> Valid <input type="radio"/> Void (Circle one) Uncorrected Temperature: _____ If void, why: _____ Corrected Temperature: _____ Thermometer: <input checked="" type="radio"/> IR1 <input type="radio"/> IR2 (Circle one) Samples stored in Refrigerator # 7																									

07-2017

Comments: _____

White: Sample Traveler

Canary: Lab Copy

Pink: Field Copy



South Coast Air Quality Management District
Tisch/Thermo Sampler for Ambient PAH Measurements
Field Work Sheet

Station:	RUCA		Location:	Rubidoux	<u>A</u>	B
Sampler Control #:	<u>1001-081</u>	1001-078	Property #:	33144		
Run Date:	4-22-2021		Day of Week:	M	T	W <u>Th</u> F Sat Sun

Filter Data

Filter Assembly ID #: ^{EL 4644} 13 15 Initial: PL

Placed on Sampler	Date: <u>04/20/21</u>	Time: <u>14:10</u>	Initial: <u>NM</u>
Removed from Sampler	Date: <u>04/27/21</u>	Time: <u>11:30</u>	Initial: <u>NM</u>
Returned to AQMD Lab	Date: <u>04/27/21</u>	Time: <u>13:00</u>	Initial: <u>NM</u>
Sent to ERG Lab	Date: <u>04/27/21</u>	Time: <u>14:35</u>	Initial: <u>PL</u>

Sampler Calibration Date: 08/13/20

Remarks:

Above Entries by: MARQUEZ

APPENDIX III-D MATES V Sample Chain of Custody (COC)



South Coast Air Quality Management District

MATES V Sample Log

Location: _____ Lab No: _____

Sample Type: _____

Sample Begin Date: _____ Retrieved By: _____

Sample End Date: _____ Retrieval Date: _____

Sample Load Date: _____

ATEC 8000 S/N:

Sample Type	Sample No.	Cartridge No.	Elapsed Time	Volume (L)	Comments
Carbonyls					

Xontech 924 S/N:

Sample Type	Sample No.	Cartridge No.	Elapsed Time	Volume (L)	Comments
Metals by ICP/MS					
Hexavalent Chromium					

Xontech 910S/N:

Sample Type	Sample No.	Canister No.	Start Vacuum		End Pressure	
			Sampler	Canister	Sampler	Canister
TO-15 NATTS						

Comments: |

Chain of Custody:

Relinquished By _____ Received By _____ Section/Group _____ Date/Time _____

Relinquished By _____ Received By _____ Section/Group _____ Date/Time _____

APPENDIX III-E 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 III-F Method Description for Sampling and Analysis of Carbonyls by UHPLC at the South Coast AQMD Laboratory

Sampling - Ambient air is drawn through an acidified dinitrophenylhydrazine (DNPH) coated silica cartridge mounted on an ATEC 8000 sampler. The samplers are located inside South Coast AQMD monitoring stations. A denuder is located upstream of the ATEC 8000 sampler and DNPH cartridge to eliminate or reduce ozone which interferes with carbonyl determination. The sampling cartridges are coated with a minimum of 300 mg of DNPH on Waters Sep-Pak silica cartridges. A volume of air is pulled through the cartridge at approximately 0.7 lpm for 24-hour sampling (1008 liters). Before and after sampling, each cartridge is kept capped and refrigerated at $\leq 4^{\circ}\text{C}$ in a foil envelope to prevent loss of captured carbonyls or contamination.

Laboratory Analysis - The laboratory currently uses a Thermo Vanquish ultra high-performance liquid chromatograph (UHPLC) with autosampler. After elution of the Sep-Pak cartridge with three milliliters of acetonitrile, the samples are placed in an autosampler. Samples are analyzed using a gradient mode starting with 42% acetonitrile and 58% water at a flow rate of 0.6 ml per minute on an Acclaim Carbonyl RSLC 2.2 μm , 2.1 mm by 150 mm column. One microliter of each sample is injected onto the column by the autosampler.

MATES V carbonyl samples from 2018 were analyzed using a Waters Millennium HPLC with autosampler and Waters C-18, 5 μm , 4.6 mm by 250 mm column. A Thermo Vanquish UHPLC was used starting with 2019 carbonyl samples.

Quantification - A six-point calibration curve is created from triplicate injections of standards from 0.4 ug/ml to 10.0 ug/ml range. A second set of standards is obtained from a separate source and used to verify the calibration. PAMS/NATTS compounds, acetaldehyde, formaldehyde, and acetone (along with methyl ethyl ketone, propionaldehyde, and benzaldehyde) are quantified by comparison to the calibration curve. The concentrations are reported as ug/m³ based on approximately 1000 L of air volume collected.

QA/QC – The Method Detection Limit (MDL) is determined according to EPA Appendix B to Part 136, 40CFR Ch.1 and Technical Assistance Document for the National Air Toxics Trends Stations Program, Revision 3, Chapter 4.0 Collection and Analysis Methods. A mid-level and a low-level control standard are added every 10 samples within each set, or batch, of analyses. For each set, or batch of 20 or less samples, an extraction solvent blank, a cartridge method blank, and a sample replicate injection are added. A duplicate sample from a second sampler is collected and analyzed every other month. For MATES V, duplicates were collected at Central Los Angeles and Rubidoux. A field blank is analyzed each month.

APPENDIX III-G Method Description for Sampling and Analysis of Elements by Energy Dispersive X-ray Fluorescence (ED-XRF) Spectrometry at the South Coast AQMD Laboratory

Sampling - Ambient air is drawn through a 47-mm Teflon filter loaded in a PM_{2.5} sampler. Typically, 24-hour sampling at about 20 liters per minute provides sufficient sample mass on the filter for analysis. The sampler must collect a homogeneous sample across the surface of the filter.

Laboratory Analysis - The Panalytical Epsilon 5 ED-XRF spectrometer is used to analyze 44 elements collected on a filter sample. Sample preparation involves bringing the filters to room temperature. Each filter is loaded onto an autosampler, placed in a sample chamber kept under vacuum and a small cross section of the filter near the center is scanned under eight different analytic conditions. Each condition is optimized for certain groups of elements. After spectral acquisition, an identification and deconvolution process extracts the net contributions to the counts for each of the 44 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 46 single and dual element standards. These calibration standards are verified using an NIST multi-element thin 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 reported in accordance with data reporting and analysis requirements. Finally, all runs are checked in duplicate for precision. Collocated samples are collected at specified sites and times to verify sampling and analytical precision.

APPENDIX III-H Method Description for Sampling and Analysis of Elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the South Coast AQMD Laboratory

Sampling - Ambient air is drawn through a 37-mm Cellulose filter loaded in a TSP sampler. Typically, 24-hour sampling at about 12 liters per minute provides sufficient sample mass on the filter for analysis.

Laboratory Analysis - A Perkin Elmer ICP-MS is used to analyze 38 elements collected on a 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 ICP-MS is calibrated daily using a certified calibration standard mixture containing all elements of interest. The standard is diluted to eight concentrations and a 9 point calibration curve is generated and used to determine the concentration of elements in samples. The elements in the sample solutions 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 - MDLs are performed annually to determine the analytical method sensitivity for the ICP-MS. A calibration check and blank analysis are required at the beginning and end of each analysis period and at intervals of ten samples to verify the calibration and check for contamination. Filter/ reagent blanks and filter/reagent spiked samples are digested and analyzed in each batch to examine the extraction efficiency and any matrix effects. Sample duplicates are performed for determining extraction and analysis precision. Interference check standards and serial dilutions are analyzed to insure matrix and instrument interferences are not present. Field blanks are taken at specified times depending on the frequency of sampling and reported in accordance with the data reporting and analytic requirements. Collocated samples are collected at specified sites and times to verify sampling and analytic precision.

APPENDIX III-I Method Description for Sampling and Analysis of Organic and Elemental Carbon by Thermal/Optical Carbon Analyzer at the South Coast AQMD Laboratory

Sampling - Ambient air is drawn through a 47-mm quartz filter loaded in a PM_{2.5} sampler. Typically, 24-hour sampling provides sufficient sample mass on a filter for analysis. The sampler must collect a homogeneous sample across the surface of the filter. A one-centimeter diameter punch from any sample portion 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. Sample preparation involves bringing the filters to room temperature. A small circular filter area is punched out from the quartz filter and loaded onto the carrier quartz tube. The filter is pushed into an oven whose temperature is raised in steps from ambient temperature to approximately 840 degrees Celsius. Helium is continuously passed over the filter until 480 degrees Celsius is attained, at which time a Helium/Oxygen mixture is then continuously passed over the punch until 840 degrees Celsius is reached to burn off elemental carbon. At the same time the surface of the filter is monitored with a laser beam to determine the 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 to identify the 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 determination of 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 consists of carbon containing gases (methane and carbon dioxide) in an inert gas. 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. 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, all samples are checked in duplicate and collocated runs are analyzed as a check of precision.

APPENDIX III-J Method Description for Sampling and Analysis of VOCs by GC/MS at the South Coast AQMD

Sampling - Ambient air is pumped through a properly sited probe and manifold into an evacuated Summa® polished and/or a silonite coated (Entech™) 6 liter canister using a Xontech 910A air sampler at the sample location. The sample is integrated over 24 hours to fill the canister to approximately 12 PSI, according to SOP00080 “Xontech 910 Canister Sampler/Multichannel Controller.” The canister is returned to the laboratory for analysis by Gas Chromatography with a Mass Spectrometer (GC/MS).

Laboratory Analysis - The Laboratory uses an Agilent 6890 Gas Chromatograph with an Agilent 5973 Mass Selective Detector. The sample is concentrated using an Entech 7200 cryo-concentrator then injected into a GC/MS. 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 removal of CO₂ collected with the sample. The concentrator loop is then heated and the contents cryo-focused at the head of a GC column for subsequent separation of the VOCs. The mass selective detector records the mass spectrum of each peak (compound) and the analyst uses certified standards to compare selected ions for each compound to determine its concentration according to SOP0008B “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 those for injected gas standards to determine concentration in parts per billion.

QA/QC - The Method Detection Limit (MDL) is determined for the GC/MS according to the method outlined in the EPA NATTS TAD (October 2016). Collocated samples may be collected on a scheduled frequency, depending on the program. All canisters from the canister cleaning system are batch verified by analysis of purified humidified nitrogen contained in the canisters for the presence of the compounds of interest. Presence of analytes of interest above 0.2 ppb is cause for corrective action.

APPENDIX III-K 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) which is received by the Laboratory in a cold pack. The received modules are refrigerated at $\leq 4^{\circ}\text{C}$ until needed and then constructed for sampling by a Laboratory Technician for use by the field Instrument Technician. The Instrument Technician installs the filter with PUF/Tenax collection module onto the Hi-Vol sampling unit and collects the sample after sampling completion. The Instrument Technician returns the sample immediately after sampling and places it in the laboratory refrigerator which is at $\leq 4^{\circ}\text{C}$. 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 approximately 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 South Coast AQMD Project Manager and U.S. 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 U.S. EPA approved QAPP, under the contract for NATTS."

QA/QC- The South Coast AQMD portion of 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 III-L Method Description for Sampling and Analysis of Hexavalent Chromium by Ion Chromatography at the South Coast AQMD 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 are refrigerated at $\leq 4^{\circ}\text{C}$ to minimize the reduction of hexavalent chromium to trivalent chromium.

Laboratory Analysis – Thermo Fischer Scientific ICS-5000 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 20 mM sodium bicarbonate solution via ice bath sonication for one hour. The extract is then filtered to remove solids/particles and analyzed by 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 using a visible light lamp emitting at a wavelength of 530 nm 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 2000 part per trillion (ppt). The hexavalent chromium sample concentrations are quantified by area comparisons to the area obtained for the calibration standards. 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 (Liters) and dividing by the air volume (m³).

QA/QC – MDLs are performed annually to determine the analytical method sensitivity for the IC. The IC is calibrated weekly to achieve a minimum correlation coefficient of 0.9990. Blank and check standard analyses are performed every 10 samples to verify the precision of the analytical data. 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 and trivalent chromium concentrations to verify the accuracy of the method. A duplicate (DUP) injection of the first sample is analyzed at the end of the sequence to check for instrument drift and Cr^{III}/ Cr^{VI} conversion. Field blanks are taken at specified times depending on the frequency of sampling and reported in accordance with the data reporting and analysis requirements. Collocated samples are collected at specified sites and times to verify sampling and analytical precision. Detailed procedures are described in SOP00046, *The Analysis of Hexavalent Chromium in Ambient Air by Ion Chromatography*.

APPENDIX III-M Method Description for Sampling and Analysis of Levoglucosan and Related Monosaccharide Anhydrides at the South Coast AQMD Laboratory

Sampling - Fine particulate matter (PM_{2.5}) is collected by ambient air filtration onto 47 mm quartz fiber filters using Met One Instruments SASS™ samplers. Each sampler is programmed to sample approximately 9.8 m³ of air over 24 hours. Levoglucosan and associated monosaccharide anhydrides (mannosan, galactosan) are analyzed by extraction of whole filters.

Laboratory Analysis – Monosaccharide anhydride concentrations in filter samples are determined with a Thermo Trace 1310 Gas Chromatograph (GC) coupled to an ISQ LT single quadrupole mass spectrometer (MS). Filters are spiked with an isotopically labeled internal standard (¹³C₆-levoglucosan) and extracted by ultrasonication in acetonitrile. An aliquot of each extract is derivatized by a silanizing reagent to convert monosaccharide anhydrides to trimethylsilyl (TMS) derivatives suitable for GC/MS analysis. Samples are analyzed by GC/MS within 24 hours of derivization.

Speciation and Quantification – Samples are analyzed by GC/MS using a simultaneous selective ion monitoring (SIM)/full scan method. Each compound is positively identified by three characteristic mass fragments and quantified using the response of a primary fragment relative to the isotopically labeled internal standard. Using air volume data gathered during sampling, instrument concentrations (µg/filter) are converted to µg/m³ of air.

QA/QC - Calibration curves for all compounds of interest are constructed with authenticated standards referenced to the isotopically labelled internal standard. The levoglucosan calibration curve is confirmed with a secondary authenticated standard. Instrument stability is verified by injection of low- and mid-level calibration standards following every 10 sample injections and at the close of each sequence. Due to the instability of TMS-derivatives, all calibration and secondary standards are prepared and derivatized in parallel to each sample batch. Blank contributions are assessed with instrument blanks run at the beginning of each sequence and after every 10 sample injections, a filter blank extracted as part of each sample batch, and monthly field blanks. Extraction efficiency is assessed with one filter blank spike sample per sample batch. Results from replicate injections and collocated samples are used to characterize instrument and sampling variability, respectively.