DRAFT

Standard Operating Procedure for the Analysis of Photochemical Assessment Monitoring Station (PAMS) Volatile Organic Compounds (VOCs) in Ambient Air via the Consolidated Analytical Systems (CAS)/Chromatotec AirmOzone Auto-Gas Chromatograph with Flame Ionization Detection (Auto-GC-FID)

EPA Document Number

Effective Date: [DRAFT]

1. **SCOPE AND APPLICABILITY**

This standard operating procedure (SOP) describes the operation of the Consolidated Analytical Systems (CAS)/Chromatotec AirmOzone rack mounted automatic gas chromatography (auto-GC) system for the analysis of volatile organic compounds (VOCs) identified under the EPA’s Photochemical Assessment Monitoring Stations (PAMS) Program to be ozone precursors or relevant to atmospheric ozone formation. Procedures for the setup, calibration, operation, and shut-down are described herein. This SOP is intended to provide instruction for properly trained instrument operators. Monitoring requirements, training requirements, data validation and verification, and data reporting to AQS are outside the scope of this SOP.

1. **SUMMARY OF METHOD**

On an hourly cycle, the AirmOzone auto-GC system draws in ambient air from the inlet probe to collect and preconcentrate VOCs from the sampled atmosphere and subsequently separate the VOCs for detection via a flame ionization detector (FID). A new sample commences at the top of each hour. Ambient atmosphere is drawn into the auto-GC sampling inlet by the vacuum supplied by the system’s sampling pumps and routed through an air handling unit (AirmoCAL), which splits the sampled flow to two separate GC-FIDs, one for analysis of “light” VOCs with two to six carbon atoms (C2-C6), and the other for “heavy” VOCs with six to twelve carbon atoms (C6-C12). Sample flow is controlled via mass flow controller (MFC).

The sample flow for the C2-C6 compounds is routed through a Nafion® dryer to remove moisture prior to passing the sampled atmosphere through a three-phase sorbent trap cooled to approximately -10ºC by Peltier cooling for preconcentration. The permanent gases are unretained and VOCs of interest are captured. At the end of 20-minute collection period, the 40-minute analysis begins and the trap is desorbed by rapid heating to 300ºC for three minutes. The trap is then backflushed with carrier gas to sweep the desorbed VOCs onto the separation column.

The C6-C12 compounds are collected on a trap containing porous substances maintained at 20-25ºC by Peltier cooling for preconcentration. At the end of the 20-minute sample collection, the 40-minute analysis begins and the trap is desorbed by rapid heating to 300ºC for three minutes. The trap is then backflushed with carrier gas to sweep the trapped VOCs onto the separation column.

Target VOCs are separated via the GC columns (alumina PLOT column for C2-C6 and a BP-1 style column for C6-C12) contained in ovens whose temperatures are ramped according to specific programs to optimize compound separation. Compounds are detected by a flame ionization detector (FID) as the exit the column. Compounds are identified according to elution retention time (RT). The voltage response of the FID is converted to a concentration in parts per billion carbon (ppbC) based on the response factor (base sensitivity) according to the calibration based on the FID response of butane (C2-C6) or benzene (C6-C12) adjusted for a “substance factor” correcting for the individual compound FID response. System functions are controlled by an onboard personal computer integrated into the C6-C12 GC unit. In addition to the two GC units, the auto-GC system comprises a zero air generator (AirmoPURE), hydrogen generator (Hydroxychrom), sampling pumps (AirmoPUMP), and a standard gas and sampled atmosphere handling system (AirmoCAL).

PAMS target VOCs are listed below in Table 1. Priority compounds are those VOCs for which all PAMS sites must report concentrations. Optional compounds are those VOCs that ~~which~~ are of interest to the PAMS program but which concentrations are not required to be reported. Note there are two compounds in Table 1 that are not assigned by the PAMS program either as priority or optional compounds, but are nonetheless included in the 56-component retention time standard VOC mix typically analyzed for the PAMS program.

**Table 1: Priority and Optional VOCs for the PAMS Program**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **priority or optional \*** | **compound name** | **# carbons** |  | **priority or optional \*** | **compound name** | **# carbons** |
| o | carbon tetrachloride | 1 |  | o | 2,3-dimethylpentane | 7 |
| p | ethane | 2 |  | o | 2,4-dimethylpentane | 7 |
| p | ethylene | 2 |  | o | n-heptane | 7 |
| o | tetrachloroethylene | 2 |  | o | methylcyclohexane | 7 |
| o | acetylene | 2 |  | o | 2-methylhexane | 7 |
| o | ethanol | 2 |  | o | 3-methylhexane | 7 |
| p | propane | 3 |  | p | 2,2,4-trimethylpentane | 8 |
| p | propylene | 3 |  | p | ethylbenzene | 8 |
| o | 1,3-butadiene | 4 |  | p | m-/p-xylene | 8 |
| p | 1-butene | 4 |  | p | o-xylene | 8 |
| p | cis-2-Butene | 4 |  | p | styrene | 8 |
| p | isobutane | 4 |  | o | 2-methylheptane | 8 |
| p | n-butane | 4 |  | o | 3-methylheptane | 8 |
| p | trans-2-butene | 4 |  | o | n-octane | 8 |
| p | isopentane | 5 |  | o | 2,3,4-trimethylpentane | 8 |
| p | isoprene | 5 |  | p | 1,2,3-trimethylbenzene | 9 |
| o | cyclopentane | 5 |  | p | 1,2,4-trimethylbenzene | 9 |
| p | n-pentane | 5 |  | p | m-ethyltoluene | 9 |
| o | 1-pentene | 5 |  | p | o-ethyltoluene | 9 |
| o | cis-2-pentene | 5 |  | p | p-ethyltoluene | 9 |
| o | trans-2-pentene | 5 |  | o | isopropylbenzene | 9 |
| p | benzene | 6 |  | o | n-nonane | 9 |
| p | n-hexane | 6 |  | o | n-propylbenzene | 9 |
| o | cyclohexane | 6 |  | o | 1,3,5-trimethylbenzene | 9 |
| o | 2,2-dimethylbutane | 6 |  | o | n-decane | 10 |
| o | 2,3-dimethylbutane | 6 |  | o | m-diethylbenzene | 10 |
| x | 1-hexene | 6 |  | o | p-diethylbenzene | 10 |
| o | 2-methylpentane | 6 |  | o | a-pinene | 10 |
| o | 3-methylpentane | 6 |  | o | b-pinene | 10 |
| o | methylcyclopentane | 6 |  | o | n-undecane | 11 |
| p | toluene | 7 |  | x | n-dodecane | 12 |

\* o = optional; p = priority; x = VOC contained in retention time standard but not of interest to PAMS program

1. **DEFINITIONS**

**Absolute pressure**: Pressure relative to complete vacuum, typically expressed in units of: psia, atm, mm Hg, kPa, or in Hg

**Analytical sequence**: List of sample analyses programmed into a sequence table within the CDS.

**Auto-GC**: Automatic gas chromatograph. Gas chromatograph capable of autonomous operation to collect an ambient air sample and to trap, separate chromatographically, identify, and quantitate the VOCs of interest.

**Baseline**: The instrument’s detector background signal in the absence of a substance.

**Base sensitivity**: The instrument area response to one unit of injected standard during instrument calibration. For example, when injecting 10 ppbC of butane, the resulting area response is divided by 10 and entered into the GC configuration table in VistaCHROM.

**Carrier gas**: The mobile phase in gas chromatography; the carrier gas is non-reactive to the target analytes. Carrier gas flows at a constant rate through the GC column to carry analytes to the detector. For the AirmOzone system, the carrier gas is hydrogen.

**Chromatographic peak**: The portion of a chromatogram recording the detector response when a compound is eluted from the column. To be considered a true peak for identification purposes, the signal-to-noise ratio must be ≥ 3:1.

**Chromatography Data System (CDS)**: The software program that controls the operation of the GC, acquires raw instrument data, and permits the operator to process collected data. The CDS allows programming of analysis sequences, generation of instrument calibration curves for target analytes, calculation of target analyte concentrations, and post-collection processing of raw instrument data. The CDS for the AirmOzone system is Chromatotec VistaCHROM software.

**Continuing calibration verification (CCV)**: Quality control sample consisting of a known concentration of target analytes, used to assess the ongoing suitability of the instrument calibration. CCVs are prepared by diluting a stock standard gas to a concentration within the calibration curve range (preferably within the lower 1/3 of the calibration curve range) and analyzed approximately every 24 hours of analysis. CCVs must recover within 30% of the nominal concentration for each analyte. CCVs may also serve as a reference for verifying analyte retention times.

**Data quality objectives (DQO)**: Metrics defined for a project or program which describe or quantify the desired criteria for collected data.

**Dilution factor (DF)**: The ratio of a standard gas to the corresponding diluent. Such is needed to calculate the concentration of diluted standard gases.

**Dynamic dilution**: Dilution of a standard gas or gases with a diluent gas by mixing gases together at known flow rates in an inert plenum.

**Flame Ionization Detector (FID)**: Detection device that responds to ions formed during combustion of organic compounds in a hydrogen flame. The production of ions and associated response within the FID is proportional to the concentration of organic compounds in the sample gas stream introduced to the detector. FIDs require a source of both hydrogen (fuel) and oxygen to produce the hydrogen flame.

**Gas chromatograph (GC)**: Analytical chemistry instrument that separates vaporized compounds according to physical or chemical properties by passing the sample through a separation column which serves as the stationary phase.

**Gauge pressure**: Pressure relative to ambient atmospheric pressure. Typically expressed in pounds per square inch gauge (psig). A measurement of 0 psig indicates ambient atmospheric pressure.

**Initial calibration (ICAL)**: Standardization of the instrument area response to known concentrations of a target analyte. Generation of an ICAL typically involves fitting response factors of analyses of several concentration levels via linear regression. The concentration of the target analyte can then be determined by translating its measured area response into a concentration via inversion of the linear regression equation determined from the ICAL.

**Inlet probe**: The opening of the analytical system inlet to the ambient atmosphere. The materials comprising, siting, and configuration of the inlet probe must comply with 40 CFR Part 58 Appendix E.

**Mass flow controller (MFC)**: Device that controls the flow a specific gas by adjusting a flow control valve based on thermal differences within a capillary tube between temperature sensors upstream and downstream from a heater. The difference in temperature between the sensors is translated to set the gas flow to a calibrated known flow via the flow control valve.

**Measurement quality objective (MQO)**: Criteria prescribed for a given measurement or set of measurements, which may entail bias, precision, completeness, frequency, and sensitivity.

**Part per billion carbon (ppbC)**: Concentration unit of measurement equivalent to a ppbv (defined below) multiplied by the number of carbon atoms in the molecule.

**Part per billion volume (ppbv)**: Concentration unit of measurement equivalent to a mixing ratio of 10-9 L (or moles) of a trace gas in 1 L (or mole) of diluent. One ppbv is equivalent to 2.46·1010 molecules cm-3 at 760 mm Hg pressure and 25°C.

**Precision**: The reproducibility of a measurement. Auto-GC precision is determined by evaluating the similarity of the measured concentrations of successive analyses of a CCV on a weekly basis. The relative percent difference of the measurement pair is calculated by taking the absolute difference of the two measurements and dividing by the measurement pair average, expressed as a percentage.

**Raw instrument data**: Signals generated and recorded by the instrument in the process of making measurements. Such data may include instrument area responses, timestamps, flow rates, and other associated recorded instrument events such as valve switching, temperature changes, etc.

**Recovery**: The measured concentration of a target analyte divided by the nominal concentration, expressed as a percentage.

**Relative standard deviation (RSD)**: The standard deviation of a given sample of measurements divided by the mean of the sample measurements, expressed as a percentage.

**Response factor (RF)**: The ratio of the instrument response in area counts to the nominal concentration of the target analyte. The concentration of a given target analyte can be calculated by multiplying the area measured area response?by the response factor determined in the initial calibration.

**Retention time (RT)**: Duration of time following injection of the desorbed trap onto the GC column that a given target analyte takes to reach the detector. Retention times are assigned as the apex of the chromatographic peak.

**Retention time window**: Assigned time range during which a given target analyte is expected to elute from the separation column and reach the detector. Compound identification is determined by whether it elutes within a specified retention time window.

**Retention time standard (RTS)**: A 56-component or 59-component VOCs mixture containing target analytes. This standard is analyzed to confirm the retention times of target analytes.

**Sample**: Aliquot of atmosphere introduced to the inlet of the GC system that is trapped for subsequent separation by the GC. The volume of sample is determined by multiplying the sampling flow rate by the duration of sample collection.

**Second source quality control standard (SSQC)**: A standard gas purchased from a supplier different than the primary standard from which the ICAL is prepared. The standard gas is diluted to within the calibration curve and analyzed immediately following the ICAL. The SSQC independently verifies the quality of each analyte’s calibration curve.

**Signal-to-noise**: The ratio of the detector response to a known substance to the detector response in the absence of the substance.

**Standard temperature and pressure (STP)**: 25ºC and 760 mm Hg absolute pressure

**Static dilution**: Preparation of a standard gas dilution by addition of a standard gas or gases and diluent gas to an evacuated vessel. The absolute pressure of the vessel is measured after the addition of each gas and the dilution factor calculated by dividing the final vessel pressure by the partial pressure of each standard gas.

**System blank (SB)**: Analysis of a humidified zero air blank provided to the instrument through the instrument sampling inlet to ensure the instrument is sufficiently free of contamination.

**Thermal desorption (TD)**: The freeing of molecules from a sorbent by heating the sorbent to a temperature sufficient to release the molecules of interest from the sorbent

**Volatile organic compound (VOC)**: Carbon containing compounds with vapor pressure greater than 10-1 Torr at 25ºC and 1 atmosphere pressure

**Zero air**: Ambient air or synthetic air that has been scrubbed of hydrocarbons to achieve a total hydrocarbon content of nominally ≤ 0.05 ppmC.

1. **INTERFERENCES**

Prior to beginning collection of data with the auto-GC system for data reporting, it is strongly recommended that the system be installed and operated for a minimum of two months to ensure proper calibration, stable operation, and that operators are familiarized with the functions and troubleshooting of the instrument. PAMS requirements for Required Network sites as of the time this SOP was written require reporting of PAMS data to AQS for a three-month period annually, starting June 1 and ending August 31. If instruments experience significant downtime between PAMS seasons, there is potential for degradation or failure of components. For example, the Hydroxychrom hydrogen generator must be activated and run for a minimum of 5 minutes each month to ensure proper operation when needed for sampling season.

Collection and analysis of PAMS VOCs via auto-GC is subject to several interferences. GC/FID identifies compounds solely by retention time, and can be subject to compound misidentification or incomplete chromatographic separation when chromatograms show peaks co-eluting with target analyte peaks. Changes in humidity can impact the trapping efficiency for some of the light hydrocarbon target analytes, and may result in shifts in analyte retention time and subsequent misidentification of analyte peaks.

Higher molecular weight VOCs are susceptible to losses to wetted surfaces of the flow path, whether for sample introduction or connections to standard gases. Where possible, materials comprising the flow path for sample atmospheres and standard gases should consist of chromatographic-grade stainless steel. Where available, it is recommended that the chromatographic-grade stainless steel tubing be deactivated by silica lining.

Operators must be aware of the large amount of data produced by the auto-GC system and the need for frequent contact with the instrument to ensure proper operation. QC sample failure and system failure due to malfunction or power outage, etc. can jeopardize the validity of large amounts of data, which could lead to inability to meet the completeness MQO. Operators are encouraged to check in on the system frequently, daily if possible, whether at the site or via remote login, to verify the system is online and collecting data, that QC samples have been analyzed and meet criteria, and that future sample collections are scheduled and queued properly.

1. **SAFETY**

The auto-GC system includes an air compressor which stores air at high pressure in a ballast tank. Ruptures to the tank or connection lines can result in injury to persons in close proximity to the instrument. Instrument components are heavy and installed on roller bearing shelves that can be pulled out from the main rack. Operators should take precaution not to pinch fingers or have loose clothing caught between the shelf and rack. The auto-GCs and FIDs utilize hydrogen gas provided by the onboard hydrogen generator. Leaks in the hydrogen delivery system may result in hydrogen build up resulting in a fire or explosion. Instruments should not be operated near open flame and sources of sparks should be eliminated. The shelter in which the instrument is installed should have a hydrogen gas detection/warning system.

Standard gases are contained within high pressure cylinders. Staff working with high pressure cylinders must be properly trained on the proper handling and operating aspects.

Operators should exercise caution when working on interior components of the instruments as internal components operate at both high temperatures (GC oven, FID, trap during desorption) and very cold temperatures (Peltier cooler) which can cause burns to unprotected skin.

1. **APPARATUS AND MATERIALS**

The CAS/Chromatotec AirmOzone auto-GC system comprises a rack system with separate components. The footprint of the rack system is approximately 24” wide x 36” deep, but does not include additional space required for peripheral equipment such as a gas dilution system or calibration gas cylinders. The rack system components include a hydrogen generator, input selection system with scrubbing catalyst, pair of sampling pumps, compressor system to supply air for source air for the zero air generator and to provide pneumatic valve control, a light hydrocarbon (C2-C6) GC-FID unit, and a heavy hydrocarbon (C6-C12) GC-FID unit with an integrated personal computer controller. Note that to meet PAMS QC requirements, separate standard gases and a system to dilute standard gases will be necessary.

1. CAS/Chromatotec AirmOzone auto-GC system  
   1. AirmoCAL flow regulation unit with internal permeation tube gas generator
   2. AirmoVOC C2-C6 – Model A11000
      1. Three-phase trap containing Carbotrap C, Carbopack B, and Carboxen
      2. Separation column: Porous Layer Open Tubular (PLOT) Al2O3/Na2SO4, 50 m length, 0.53 mm inner diameter, 10 µm film thickness
      3. MFC: 0-20 ml/minute
      4. Critical orifice: 40 µm
      5. Nafion dryer – 1 foot length of Nafion® tubing contained within a plastic cylinder purged with dry air – vented to atmosphere
   3. AirmoVOC C6-C12 – Model A21022
      1. Integrated control PC - Supervisor
      2. Separation column: MXT30 CE capillary metallic, 60-m x 0.28 mm with 1-µm film thickness
      3. MFC: 0-20 ml/minute
      4. Critical orifice: 40 µm (verify)
   4. AirmoPURE zero air generator
   5. AirmoPUMP sampling pump – two are required
   6. Hydroxychrom-100 or Hydroxychrom-160 hydrogen generation system
      1. Deionization resin bag (part number)
   7. Uniterruptible power supply (UPS) – specs? 110V AC/15 A/battery capacity? Power conditioning?
   8. VistaCHROM software, version 1.49 or newer
   9. Windows compatible USB keyboard and mouse
2. High purity regulator – stainless steel construction with CGA350 connection fitting. Each standard cylinder will require such a regulator.
3. Gas dilution system – Standard gases may be diluted by either dynamic dilution or static dilution.  
   1. The dynamic dilution or gas blending system should provide a dilution factor of approximately 5000-fold. This can be accomplished with mass flow controllers capable of flowing at 5 L/minute and 1 mL/minute, respectively, or via a set of flow restrictions that permit flow calculations based on calibrated partial pressures and can provide such dilution factors.
   2. Static dilutions require a clean, evacuated vessel in which to prepare the dilution and an accurate, highly sensitive pressure gauge to measure the partial pressures of the added standard and diluent gases.
4. Stainless steel sampling canister(s) – Fused silica lined canisters are recommended over SUMMA deactivated canisters to maximize the transfer efficiency of higher molecular weight VOCs. Depending on need, fused silica lined canisters are available in 6-L, 15-L and 33-L from various suppliers.
5. Various lengths of 1/4”, 1/8”, and 1/16” chromatographic-grade stainless steel tubing and associated appropriate Swagelok fittings. It is recommended that all such stainless steel tubing be fused silica lined. Additionally, connections to standard cylinders or canisters should consist of 1/16” tubing to minimize dead volume and potential losses of higher molecular weight VOCs.
6. **REAGENTS AND CHEMICALS**
7. Zero air – Zero air, or hydrocarbon-free air, containing nominally ≤ 0.05 ppbC total hydrocarbons (THC) is provided by the AirmoPURE zero air generator and subsequently scrubbed via a catalyst heated within an oven within the AirmoCAL unit to 350ºC.
8. Calibration stock standard gas – NIST-certified or NIST-traceable certified multi-component blend standard gas containing the target compounds of interest listed in Table 1. Typically, this standard gas is purchased at a concentration of 1000 ppbv for each target compound.
9. Second source stock standard gas - NIST-certified or NIST-traceable certified multi-component blend standard gas containing minimally 15 of the target compounds of interest listed in Table 1. Typically, this standard gas is purchased at a concentration of 1000 ppbv for each target compound.
10. Retention time standard (RTS) – component gas mixture containing the target compounds of interest listed in Table 1. Concentrations of the target compounds range from approximately 8 ppbC to 60 ppbC. While not required, concentrations of propane and benzene, and other compounds may be NIST-traceable certified.
11. Deionized water (DI) – For use in the hydrogen generator and for humidifying the standard gases. CAS specifies deionized water with conductivity < 0.20 µS/cm, equivalent to resistivity of > 5 MΩ·cm. Most laboratory water polishing units provide ASTM Type I water capable of providing water with resistivity ≥ 18 MΩ·cm, which meets specifications.
12. CAS/Chromatotec specifies the use of permeation tubes for butane, benzene, and n-hexane for calibration verification. The AirmoCAL unit can provide a dilution of these compounds for analysis which the manufacturer cites for demonstrating continuing calibration acceptance and retention time stability. Operators may analyze such standards within their analytical sequences, however, they do not replace the CCV or RTS prescribed in the QC section of this SOP. Experience has shown that decreases in higher molecular weight VOC responses can occur while lighter VOCs, such as C6s, can be unaffected. In order to ensure issues with higher molecular weight compounds are identified quickly, a CCV will require a minimum of 15 compounds covering the C2-C10 spectrum.
13. **SAMPLE COLLECTION AND HANDLING**

Ideally, sample collection begins at the beginning of the hour. Sample collection must commence no earlier than 5 minutes before the top of the hour and no later than 45 minutes after the top of the hour. For example, for sample collection of the 10:00 hour, sample collection must commence between 9:55 and 10:45 for the sample to be valid for that hour. This ensures that at least 15 of the 20 minutes, or 75%, of sample collection occurs during the hour.

The auto-GC permits near real-time analysis of ambient air. Ambient atmosphere is routed through either a standalone inlet dedicated to the auto-GC or to a manifold inlet to which the auto-GC sampling inlet is connected. For the standalone inlet, a length of 1/8” or 1/16” inner diameter (ID) chromatographic stainless steel tubing extends from the instrument sampling inlet through the shelter wall or roof to the inlet probe. Manifold inlets consist of a glass or stainless steel inlet probe outside the shelter extending inside the shelter and connecting to a glass manifold with multiple ports for instrument connections. A blower fan is connected to the manifold to pull ambient air into the manifold at a known rate exceeding two-fold the combined flow demand of all connecting instruments. The blower exhaust is routed outside the shelter away from the inlet probe. The auto-GC sample inlet is connected to the glass manifold via a short length of 1/8” or 1/16” ID chromatographic stainless steel tubing. The length and inner diameter of the stainless steel tubing is selected to ensure the residence time of the sampled atmosphere is 20 seconds or less. The total sampling demand of the AirmOzone instrument is approximately 29 mL/minute. To maintain a residence time of 20 seconds or less at this sampling rate, the lengths of 1/18” or 1/16” ID tubing must be no more than 122 cm or 488 cm, respectively. It is recommended that manifolds and inlet tubing be heated or insulated to prevent condensation as the warmer, more humid ambient air is cooled within sampling line inside the shelter.

All portions of the inlet pathways must consist of chromatographic-grade stainless steel, glass, PTFE Teflon, or equivalent. Use of rubber, Tygon, or similar materials is prohibited as these materials may behave as sorbents or sources for VOCs, resulting in the loss of VOCs in the sampling train or offgassing VOCs, which can contaminate the sampled air stream. The use of copper, brass, or non-chromatographic-grade stainless steel is also prohibited, as such materials contain active sites that can act as catalysts for destructive reactions of target analytes. Sample inlet lines should be cleaned or replaced on a prescribed frequency as particulate matter build-up on the wetted surfaces may also behave as a sink or source of VOCs, biasing measured concentrations.

1. **QUALITY CONTROL**

Quality control (QC) requirements and acceptance criteria are discussed in further detail within the PAMS Technical Assistance Document (TAD) and are summarized in Table 2.

When initially placed into service and prior to reporting data from the system, the method detection limit (MDL) must be determined for each target analyte. The MDL is determined following the procedure described in the PAMS TAD, which is an adaptation of the method update rule (MUR) to the 40 CFR Part 136 Appendix B procedure. The MDL is an estimate of the concentration at which a given analyte can be detected above background 99% of the time. The MDL must be determined initially, following changes to the instrument or method that can reasonably be expected to significantly change the sensitivity of the instrument or method, such as: replacement of the FID, replacement of the trap(s), or change of carrier gas (i.e. from He to H2). Determined MDLs must meet the criteria specified in the PAMS QAPP and TAD. Refer to the PAMS TAD for further instruction for determining MDLs.

QC samples are to be analyzed routinely following the initial calibration (ICAL) to demonstrate continued suitability of the instrument calibration, acceptable levels of target analyte contamination, acceptable reproducibility of measurements, and proper identification of analytes by the chromatography data system. Refer to Section X.C for more information on initial calibration. The frequency for QC sample measurements will be either approximately daily or weekly, depending on the check. Note that such frequency requirements are draft and may be subject to change.

The most frequent QC checks consist of a system blank (SB) and continuing calibration verification, which are to be analyzed approximately daily. These QC checks should be scheduled in the analytical sequence to occur successively (SB followed by CCV) to begin nightly between the hours of 20:00 and 02:00. It is recommended that the starting time for the SB analysis rotate through the hours of 20:00 through 02:00. If the SB/CCV begin at the same time every night, for example, 22:00, no ambient sample data will be collected for the two-hour period between 22:00 and 0:00. An example rotation schedule is included in Figure 1, which demonstrates that the rotation allows approximately four days of ambient collections for each hour each week.

Weekly checks will include the SB/CCV but will also include a precision check consisting of an additional CCV and will be followed by analysis of the SSQC and retention time standard (RTS). Note that if the RTS contains the appropriate target compounds at certified concentrations, this may be analyzed as the SSQC or the CCV. It is recommended that weekly checks be analyzed on weekend (Saturday or Sunday) nights (22:00 to 02:00) in order to maximize the collection of data during the workweek when concentrations are generally higher (and thus have more impact on ozone formation) due to increased traffic and higher traffic density.

The following QC samples are required. Acceptance criteria and additional information are included in Table 2.

1. System blank (SB): This blank sample consists of humidified zero air and is analyzed approximately every 24 hours to demonstrate contamination levels of target analytes are sufficiently low. All target analytes must analyze less than the determined MDL or 0.5 ppbC, whichever is greater (note this specification is subject to change).

2. Continuing calibration verification (CCV): The CCV is analyzed approximately every 24 hours to demonstrate the instrument calibration remains within specification. Target compound response must be within ± 30% difference from the expected nominal concentration.

3. Retention time standard (RTS): The RTS is analyzed weekly to verify the retention time windows assigned to each target analyte are appropriate. If there are shifts in retention times which result in the CDS mis-identifying or missing peaks, the retention time window(s) must be adjusted in the substance table.

4. Second Source Quality Control Standard (SSQC): The SSQC is analyzed weekly to independently verify the quality of the calibration. Target compound response must be within ± 30% difference from the expected nominal concentration.

1. Precision check: A replicate of the CCV is analyzed weekly to assess the precision of the replicate measurement. Replicate measurements must show precision of ≤ 25% (note this specification is subject to change) relative percent difference (RPD).

**Table 2: Quality Control Parameter and Acceptance Criteria**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **QC Parameter** | **Description** | **Required Frequency** | **Acceptance Criteria** | **Suggested Corrective Action** |
| Initial calibration (ICAL) | Multi-point calibration of the auto-GC with each compound of interest. Minimum of three concentrations covering approximately 0.5 to 50 ppbC for each compound. | Initially at the beginning of PAMS season, after maintenance to the instrument expected to alter the instrument response, following failing continuing calibration checks, and at the end of PAMS season | For linear regression, must show r2 of ≥ 0.995 and have an x-intercept within ± 0.2 ppbC of the origin. Each standard level evaluated against the calibration curve must be within 30% of the nominal concentration. | Prepare new calibration. It may be necessary to investigate for system contamination or interferences resulting in suppression or enhancement of analytes. May require preparation of new calibration standards. |
| System blank (SB) | Analysis of humidified zero air to ensure the system is sufficiently clean for continued analysis. | Prior to ICAL, and approximately daily | All target VOCs must be < the determined MDL or 0.5 ppbC | Analyze another blank, if possible, to investigate potential carryover from high concentration sample. Investigate system for contamination. Potentially qualify all samples for affected compounds since the last passing SB. |
| Continuing Calibration Verification (CCV) | Analysis of a known standard prepared within the calibration curve to demonstrate the instrument calibration remains within tolerance. | Approximately daily following the SB | All target VOCs must recover within 30% of the expected nominal concentration. | Investigate chromatogram for retention time shifts which may result in peak misidentification. Investigate for instrument contamination resulting in co-eluting peaks. Investigate for system leaks or trap malfunction resulting in low recovery. Potentially qualify all samples for affected compounds since the last passing CCV. |
| Second Source Quality Control Standard (SSQC) | Analysis of a known standard prepared from a stock gas from a supplier different from the stock gas for preparing the ICAL. This check independently verifies the quality of the ICAL. | Immediately following ICAL and weekly thereafter | All target VOCs must recover within 30% of the expected nominal concentration. | Investigate for discrepancy between ICAL and SSQC. Investigate chromatogram for retention time shifts which may result in peak misidentification. Investigate for instrument contamination resulting in co-eluting peaks. Investigate for system leaks or trap malfunction resulting in low recovery. Potentially qualify all samples for affected compounds since the last passing CCV. |
| Retention Time Standard (RTS) | Analysis of a 56-component blend of VOCs in the ~10-60 ppbC range to verify established retention time windows | weekly | All target VOCs must be within the established retention time windows. | Review previous week’s ambient and QC check samples to evaluate events resulting in retention time shift. May require reassignment or adjustment of retention time windows and reprocessing of data collected since the most recent RTS. |
| Precision check | Replicate analysis of the CCV to evaluate the reproducibility of the analysis | weekly | Absolute relative percent difference for each target VOC must be ≤ 25% on a week-to-week basis. | Investigate system for contamination, leaks, or suppression, as indicated by trends in compound behavior. Potentially qualify all samples for affected compounds since the last passing precision check. |
| Method Detection Limit (MDL) | Determination of the estimated concentration where the analyte is detected above the background level 99% of the time. The MDL is an estimate of this concentration and is to be determined following the method update rule (MUR) of the 40 CFR Part 136 Appendix B procedure as described in Section XX of Revision X of the PAMS Technical Assistance Document | Annually or following significant change to the instrument or method which would reasonably be expected to result in a significant change to the instrument sensitivity; such as detector replacement, trap replacement, change in carrier gas (i.e. from He to H2) | MDLs must be determined per the prescribed procedure and be ≤ 0.5 ppbC for each target VOC. | Investigate instrument for carryover or contamination. Verify spiking level for the MDL procedure is appropriate. Adjust spiking level and repeat procedure. |

1. **PROCEDURE**
2. Installation of the auto-GC rack system

The manufacturer will typically install the instrument and perform setup when newly purchased. The instrument system must be installed in a shelter maintained between 10 to 35ºC. This required temperature range should be attainable for instruments installed in shelters that also house criteria pollutant monitoring equipment, as the shelter must be maintained within 15 to 33ºC. Note that temperature fluctuations or extended excursions beyond temperature limits may lead to retention time shifts or potential extended GC oven cooling times which may result in failure to begin a sample sequence at the assigned time.

The required power supply for the instrument is a 20A 110V AC circuit (manual shows 220 VAC but our instrument ran on 110V). All components should be connected to the UPS unit to ensure power is conditioned to 110V and is continually available. The UPS permits the instrument to run uninterrupted during short power outages, the duration of which is dependent on the UPS unit. Note that for instruments connected to a manifold inlet, if the blower motor power is cut during an electrical outage, the instrument will be sampling stale air from the manifold, and not fresh ambient air. In such cases, the associated data must be invalidated.

1. Initial Startup (Insert figures and diagrams)

The following steps are a basic outline. Refer to the instrument manuals for further information, diagrams, and instructions.

* 1. Connect the hydrogen lines from the “Output H2” port on the back of the Hydroxychrom unit to the “H2 inlet ports on the back of the C2-C6 and C6-C12 GC-FID units (these are 1/16” Swagelok fittings).
  2. Hydroxychrom hydrogen generator
     1. Disconnect the tube assembly between the water inlet and outlet (installed for transport).
     2. Fill the external DI water reservoir approximately 1/3 full with deionized water.
     3. Connect the tube from the external DI reservoir to the “Zerowater inlet” port on the back of the instrument.
     4. Provide electrical power to the unit. It will automatically prime the pump and fill the internal DI reservoir. Once filled, the unit will begin electrolysis and supply hydrogen.
  3. Connect zero air lines from the “Air out” port on the AirmoPURE unit to the “Valve Air” inlet ports on the back of the C2-C6 and C6-C12 GC-FID units and to the “air inlet” port on the back of the AirmoCAL unit (these are 1/8” Swagelok fittings).
  4. Connect the zero air lines from the “Air outlet” port on the AirmoCAL unit to the “Air” inlet ports on the back of the C2-C6 and C6-C12 GC-FID units.
  5. Connect vacuum pump lines to the “Vacuum” ports on the back of the C2-C6 and C6-C12 GC-FID units (these are ¼” Swagelok fittings).
  6. Connect the sample transfer lines to the “sample out” port on the back of the AirmoCAL to the “Sample” ports on the back of the C2-C6 and C6-C12 GC-FID units (these are ¼” Swagelok fittings).
  7. Connect tubing for a vent external to the shelter to the “purge” port on the back of the AirmoCAL.
  8. Connect the sample inlet line from the inlet probe or inlet manifold to the “sample in” port on the back of the AirmoCAL unit.
  9. Connect the RS232 cable between the COM1 port on the back of the C6-C12 GC-FID and the “RS232” port on the back of the C2-C6 GC-FID.
  10. Plug in the USB mouse and keyboard to the front USB ports on the C6-C12 GD-FID unit.
  11. Connect all electrical plugs to the UPS unit, plug the UPS power supply into an appropriate wall socket, and power on the UPS.
  12. Switch on each individual component as needed via switches on the backs of the instruments. Each component should power on.
  13. Remove the top cover of the C2-C6 GC-FID unit and adjust the Peltier controller setting (in left front of unit) to 5ºC. Allow this setting to maintain for a minimum of three hours prior to adjusting the setting to -10ºC. This conditioning at 5ºC allows the sweeping of moisture from the Peltier box to ensure icing does not occur.
  14. Log in to the computer with the access credentials provided by the manufacturer.

*Note: Instrument manuals are available on the desktop of the control PC of the C6-C12 GC unit.*

* 1. Set the PC clock to the local standard time (not adjusted for Daylight Savings Time) following the clock adjustment procedure in the instrument manual.
  2. Open the VistaCHROM software
  3. Log in to the VistaCHROM software with the access credentials provided by the manufacturer.
  4. Double-click on the icon for each analyzer to open a VistaCHROM control panel for each instrument.
  5. In each instrument control panel window, click the “Log ON” button in the upper left corner to connect the PC to the GC unit (refer to Figure XX).
  6. In each instrument control panel window, double-click the GC clock to synchronize the GC clocks to the PC clock.
  7. Verify the following instrument conditions on the C2-C6 GC-FID unit:
     1. Column head pressure: 155 hPa
     2. Ambient pressure: 1017 hPa
     3. Critical pressure: 10 hPa less than the ambient pressure (during sampling)
     4. FID temperature: 170ºC
  8. Verify the following instrument conditions on the C6-C12 GC-FID unit:
     1. Column head pressure: 469 hPa
     2. Ambient pressure: 1017 hPa
     3. Critical pressure: 10 hPa less than the ambient pressure (during sampling)
     4. FID temperature: 170ºC

1. Calibration (More to be added to this section once calibration conventions are established with the workgroup)  
   1. CAS/Chromatotec provides the instrument with a factory calibration. This calibration consists of analyzing a zero air sample and a 100 ppbC standard that is NIST-traceable certified. The base sensitivity assigned to each GC-FID unit is determined during the factory calibration and entered into the GC settings table. This base sensitivity value is the FID response normalized to 1 ppbC of either butane (C2-C6) or benzene (C6-C12). Subsequent concentration measurements of target analytes are calculated from this base sensitivity value through an equation that applies a factor to the base sensitivity. Chromatotec recommends that users not adjust this value (however, we will be working with CAS/Chromatotec over the coming months to ensure that operators can perform system calibration as needed following CCV failures or other failures, and these processes will be described in the final approved SOP).
2. Analysis of Ambient Air  
   1. Creating Sequence Tables  
        
      Creating a sequence table requires entry of a list of “methods” into the CDS. Due to the two GC-FIDs operating independently, a sequence table must be created for each GC-FID in the respective control window. Depending on the firmware version of the VistaCHROM software, up to 23 method lines may be entered into a sequence table. Note that this limit of 23 method lines permits entry of a full week’s worth of analytical sequences into the sequence table if the approximately daily and weekly QC samples currently proposed are to be analyzed. Please refer to Figure 1 for an example sampling schedule including QC samples for a one week period. Note that QC samples are suggested to occur between 20:00 and 02:00 hours (and are highlighted in blue). Ambient samples are noted as “amb” in the figure. Refer to Figure 2 for an example sequence table covering the sampling schedule detailed in Figure 1.



**Figure 1: Example sampling schedule for a 7-day period including approximately daily and weekly QC samples**



**Figure 2: Example VistaCHROM sequence table for a 7-day sampling period**

In general, the instrument conditions for the individual method designations entered in the sequence table will be identical in most respects with the exception being the instrument port assigned to the various gas streams. The analysis parameters for the collection duration, desorb duration and temperature, and GC temperature program will be identical across these methods.

* 1. Once the sequence tables have been created and saved for each GC-FID, the sequences can be manually started from the VistaCHROM control windows of each GC instrument or can be loaded into the CDS and set to automatically start at the end of a given sequence table cycle (cycle refers to completion of the entire sequence table including repetitions). When manually starting a sequence, the sequence will begin at the top of the next minute, therefore it is important to click the start button for both instruments within the same minute to ensure the GC operations are synchronized.

1. Evaluating Collected Data (add figures and screenshots to this section)  
   1. Collected sample data may be viewed via the Chromatotec PeakViewer software. This software allows creating overlays of chromatograms in several different viewing configurations. Sample chromatograms can be overlaid with standard or blank chromatograms to investigate retention time shifts, baseline shifts, or carryover of target compounds or interferences.
   2. Post-processing of data is permitted through the PeakViewer software interface. To make adjustments to retention time windows or to calibration factors, the operator must update these items in the method substance table and select the files for reprocessing. Once reprocessed, users may need to make further adjustments to the values in the substance table to fine tune peak integration or retention time windows. Please refer to the VistaCHROM manual for specific information regarding adjustments to the method substance tables.
2. **CALCULATIONS AND DATA REPORTING**
   * + 1. Measured concentrations are to be reported in units of ppbC. These are the units to be entered into the system for calibration, therefore the instrument provides results in ppbC and reporting of the concentrations is straightforward. Consult the PAMS TAD and the AQS reporting guide for specific AQS reporting parameters and conventions.
       2. Calculations
   1. Standard dilution concentration via dynamic dilution:

Cd = (Fs·Cs)/(Fs + Fd)

Where:

Cd = diluted concentration (ppbC)

Cs = stock standard concentration (ppbC)

Fs = flow of stock standard gas (standard mL/minute)

Fd = flow of diluent gas (standard mL/minute)

* 1. Standard dilution concentration via static dilution:

Cd = Ps·Cs

Pf

Where:

Cd = diluted concentration (ppbC)

Cs = stock standard concentration (ppbC)

Ps = partial pressure of stock standard gas (mm Hg)

Pf = final pressure of vessel (mm Hg)

* 1. Quantitation of Sample Using Linear Regression:

C = (A – b)/m

Where:

|  |  |  |
| --- | --- | --- |
| C | = | concentration of compound measured in ppbC |
| A | = | integrated peak area of the compound being measured in the sample |
| b | = | intercept of the calibration curve |
| m | = | slope of the calibration curve |

* 1. Measured concentration (for linear mode calibration in VistaCHROM):

C = F·(A + Aoffset)

BS

Where:

C = measured concentration (ppbC)

F = factor (assigned for each compound according to

relationship to butane or benzene)

A = area response of target analyte in sample

Aoffset = area offset

BS = base sensitivity (assigned during instrument calibration)

* 1. Relative Standard Deviation (RSD):

RSD = standard deviation x 100

mean

* 1. Absolute Relative Percent Difference (RPD) is calculated as:

RPD = |result A – result B| x 100

mean of results A & B

* 1. Absolute Percent Difference (APD) is calculated as:

APD = |result measured – result expected| x 100

result expected

* 1. Percent Recovery is calculated as:

% recovery = concentration measured x 100

concentration expected

* 1. Total collected sample volume

Vs = Fs·Ds·106

Where:

Vs = collected sample volume (m3)

Fs = sample flow rate (standard mL/minute)

Ds = duration of sampling (minutes)

* + - 1. Data Validation and Verification

During review of the ambient concentration data, operators and data reviewers will invariably encounter situations where compounds exhibit interferences, QC checks fail acceptance criteria, and target compound responses are questionable as to the presence or absence. Monitoring organizations must have prescribed procedures to address such issues to ensure they are handled consistently and the decisions are technically justifiable. Refer to the PAMS TAD and PAMS QAPP for further information regarding data validation and validation.

1. **REFERENCES**  
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