Standard Operating Procedure for

the Collection of Carbonyl Compounds in Ambient Air for the Photochemical Assessment Monitoring Stations (PAMS) Network

Version 1.0

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1. **SCOPE AND APPLICABILITY**

This purpose of this standard operating procedure (SOP) is to describe the collection of carbonyl compounds for the EPA Photochemical Assessment Monitoring Stations (PAMS) network. This SOP describes the collection of carbonyl compounds onto silica gel sorbent cartridge media impregnated with diphenylhydrazine (DNPH) as described in EPA Compendium Method TO-11A.1 This SOP describes the procedures to be followed to collect three sequential 8-hour samples every third day, but does not describe the unique actions required to operate the specific sampling instruments. This SOP describes the handling, setup, collection, retrieval, and shipment of samples including field quality control samples, but does not describe the sample receipt, extraction, and analysis processes performed once the sample cartridges are received at the laboratory.

1. **SUMMARY OF METHOD**

A measured volume of ambient air is pulled by a vacuum pump through an ozone denuder to remove ozone, which interferes with both the collection and analysis of the carbonyls. The sampled air scrubbed of ozone is then passed through a silica gel sorbent cartridge impregnated with DNPH where carbonyls in the sampled air stream react with DNPH to form stable carbonyl hydrazones. These stable carbonyl hydrazones are maintained within the sorbent bed until extraction at the analysis laboratory. Carbonyl sampling for the PAMS program involves collecting three consecutive 8-hour samples on a 1-in-3 days schedule as required in 40 CFR Part 58 Appendix D, Section 5h.2 Cartridges are retrieved ideally within 48 hours (not to exceed 72 hours) of completion of the last of the three sequential samples and are stored and transported refrigerated and protected from light. Sample cartridges must be extracted for analysis within 14 days of collection. Extracts are then analyzed by high performance liquid chromatography (HPLC) and the carbonyl concentrations in the ambient air sample calculated from the measured concentrations in the sample extracts and the volume of air sampled through the cartridge.

1. **DEFINITIONS AND ABBREVIATIONS**
2. **Ambient Monitoring Technology Information Center (AMTIC)**: EPA website resource for information on ambient air monitoring programs and methods, quality assurance and control procedures, and federal regulations. <https://www.epa.gov/amtic>
3. **Carbonyl Compound**: Organic compound containing a carbon atom double-bonded to an oxygen atom, C=O. Classes of carbonyl compounds include, but are not limited to: aldehydes, ketones, carboxylic acids, and esters.
4. **DNPH:** diphenylhydrazine – derivatizing agent
5. **Field Quality Control (QC) Samples:** Samples additional to collected ambient air samples employed to characterize field bias, precision, or contamination. Such field QC samples include: field blank (FB), trip blank (TB), exposure blank (EB), duplicate, and collocated samples.
6. **High Performance Liquid Chromatograph (HPLC):** Instrument employed for the analysis of collected carbonyl compounds by separation and detection of derivatized carbonyl-hydrazones. For the purposes of this method ultra-high performance liquid chromatography (UHPLC) may meet the method performance specifications.
7. **Mass flow controller (MFC)**: Device that controls flow of a specific gas by adjusting a flow control valve by measuring 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.
8. **Measurement Quality Objective (MQO)**: Criteria prescribed for a given measurement or set of measurements, which may include bias, precision, completeness, frequency, and sensitivity.
9. **NIST:** National Institute of Standards and Technology
10. **Ozone Denuder:** Device used to remove ozone from a sampled gas stream. For this method, the ozone denuder consists of a length of copper (or stainless steel) tubing onto which potassium iodide (KI) has been deposited, covering all copper surfaces. Ozone in the sampled gas stream reacts with the KI and is eliminated from the sampled gas.
11. **PAMS:** Photochemical Assessment Monitoring Stations
12. **Part per billion carbon (ppbC)**: Concentration unit of measurement equivalent to a mixing ratio of 10-9 L (or moles) of carbon content of a trace gas in 1 L (or mole) of diluent. One ppbC is equivalent to 2.46 ×·1010 molecules cm-3 at 760 mm Hg pressure and 25°C multiplied by the number of carbon atoms in the molecule.
13. **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.
14. **Particulate matter (PM)**: a complex mixture of airborne small solid particles and liquid droplets.
15. **PFA:** perfluoralkoxy copolymer resin (Teflon®)
16. **PTFE:** polytetrafluoroethylene (Teflon®)
17. **Pounds per square inch absolute (psia)**: unit of pressure relative to absolute vacuum (0 psia)
18. **Standard Temperature and Pressure (STP)**: 25°C and 760 mm Hg absolute pressure
19. **Zero Air:** Synthetic air that has been scrubbed of carbonyls and water vapor
20. **INTERFERENCES**
    1. Temperature effects: Carbonyl hydrazones degrade more quickly at ambient temperatures than at reduced (e.g. refrigerated) temperatures. Care should be taken to ensure sampled cartridges are refrigerated to ≤ 4°C as soon as possible after completion of collection.
    2. Ozone: Ozone that is not removed from the sampled air stream may react directly with the DNPH reagent thereby making the DNPH unavailable for derivatizing carbonyl compounds. Ozone may also react with carbonyl-hydrazones on the sampled cartridge to degrade these compounds, leading to underestimation of sample carbonyl concentrations. These degradation byproducts may also be difficult or impossible to separate chromatographically from desired target compounds, resulting in overestimation or false positive detection of target compounds.
    3. Nitrogen dioxide: Nitrogen dioxide (NO2) is known to react with DNPH to form reaction products. These reaction products absorb light at 360 nm and may be difficult or impossible to separate chromatographically from desired target compounds, particularly the formaldehyde-hydrazone, resulting in overestimation or false positive detection of sample target compounds.
    4. Particulate build-up on particulate filters or inlet pathways: Particulate matter residues accumulated on particulate filters and/or inlet pathways can behave as sorbents and adsorb target carbonyls, releasing them later when the concentrations in the sampled air stream are lower. Thus, these residues may impart a negative bias for sampled gas streams with higher concentrations and a positive bias for those with lower concentrations.
    5. Catalytic surfaces: Materials such as copper tubing, brass fittings, or similar active metal materials in the sampling pathway serve as catalysts to degrade target carbonyls and result in underestimation of the measured target compound concentrations in ambient air. Wetted surfaces in the sampling pathway must consist of chromatographic grade stainless steel, borosilicate glass, or PTFE or PFA Teflon®.3
    6. Exposure to light may cause degradation and loss of the DNPH-carbonyl derivatives; therefore, DNPH-coated cartridges should be protected from light. Cartridges should be sealed into the foil pouch as soon as possible after sample retrieval to minimize exposure to light. Exposure to direct sunlight should particularly be avoided.
    7. Condensation of water in the inlet pathways can occur when warm humid sampled air is drawn into tubing within an air conditioned monitoring shelter. Condensation within the inlet flow path should be avoided and eliminated, where possible, to minimize the potential loss of carbonyls to dissolution in the water. Manifolds or sample line tubing within the monitoring shelter should be insulated and/or heated to eliminate condensation within the sampling lines.
21. **SAFETY**

Compressed gases – Care should be taken to follow established safety practices when working with compressed gases.

Instrument maintenance – Instrument operators should take precaution when working within the instrument chassis as contact with exposed wires and electrical connections can result in electrical shock. The ozone denuder is maintained at ≥ 50°C, therefore contact with the denuder oven should be avoided.

Glass manifolds – When cleaning, assembling, or installing glass manifolds, site operators should avoid use of excessive force, which can break or shatter the glass tubing resulting in lacerations.

1. **APPARATUS AND MATERIALS**
   1. Sequential Carbonyls Sampling Unit

Both sampling units listed below facilitate collection of three sequential samples and record sampling date, start time, stop time, average flowrate, minimum flowrate, maximum flowrate, total volume sampled, and sampling time duration for each sample channel.

* + 1. ATEC 8000 sequential cartridge sampler (8 channels) – various configurations are available with options for duplicate sample channels
    2. Tisch TE-423 sequential cartridge sampler (3 channels)
  1. DNPH-impregnated silica gel cartridge media
     1. Supelco LnDNPH S10 cartridges, 1 mg DNPH/cartridge, 150-250 µm particle size, or equivalent, catalog number 21026-U; 4 or
     2. Waters Sep-Pak cartridges, 350 mg sorbent per cartridge, 55-105 µm particle size, part number WAT037500 5
  2. NIST-traceable certified flow transfer standard – capable of accurately measuring flows from approximately 0.5 to 1.5 standard L/min with accuracy to within ± 1%
  3. USB drive (e.g., jump drive or thumb drive) with sufficient capacity to download sample collection data from the sampling unit (only applicable to the ATEC 8000-series sampling unit)
  4. PTFE or PFA Teflon® tubing – ¼″ outer diameter (OD)
  5. Cooler and freezer packs for transport of cartridge media
  6. Powder-free nitrile or equivalent gloves for handling cartridge media

1. **REAGENTS AND CHEMICALS**
2. Carbonyl-free air, which may be provided by:
   * 1. Zero air generator (< 0.01 ppm total hydrocarbons)
     2. Compressed cylinder of zero air (< 0.01 ppm total hydrocarbons)
     3. Air stream scrubbed of carbonyls with a fresh DNPH cartridge
   1. Deionized water – ASTM Type II or equivalent – used to clean the sampling inlet flow path surfaces
3. **SAMPLING INLET AND CARTRIDGE HANDLING**
   1. Sampling Inlet Probe

The sampling inlet probe must be constructed of borosilicate glass, chromatographic grade stainless steel, or PTFE or PFA Teflon®. The sampling inlet line can be extended to the exterior of the monitoring shelter or can be connected to an inlet manifold with a probe to the ambient atmosphere. Consideration must be given to the length of the sampling inlet line to ensure that the residence time is kept to 20 seconds or less.3 Consideration should also be given to minimize intrusion of particulate matter (PM) and water into the sampling line, which can effectively be reduced by inverting the inlet and installing a rain shield (such as inverted funnel) on the inlet probe. For connections to an inlet manifold, the sampling unit inlet can be connected to any port on the manifold. Connections must be leak-free to ensure that sampled air is from the ambient atmosphere entering the inlet probe.

1. Sample Cartridge Handling

New cartridges are to be stored refrigerated at ≤ 4°C upon receipt. New Waters cartridges are typically shipped from the vendor at ambient temperature and Supelco cartridges are typically shipped from the vendor at refrigerated temperatures. Cartridges are typically provided individually sealed in a foil pouch. To maintain cartridge integrity, the sealed foil cartridge storage pouch should not be opened until the cartridge is to be used in the field.

* + 1. Cartridges should only be handled with gloved hands (chemicals from hand sanitizers, lotions, etc., can contaminate sample cartridges).
    2. Markers containing volatile solvents (e.g. permanent markers such as Sharpie®) should be avoided for marking on foil storage pouches.
    3. Cartridge storage areas should be free of carbonyls. Cartridge refrigeration units should not be used for storage of solvents or items containing carbonyl compounds.

1. Chain of Custody

Blank cartridge media may originate at the analysis laboratory, if provided by the analysis laboratory; therefore, chain of custody (COC) procedures may be prescribed by the analysis laboratory. Regardless of the origin of the new cartridge media, each sample cartridge, whether an ambient sample or field QC sample (such as a trip blank, field blank, or exposure blank) must be listed on a COC form, which serves to document the transfer of the sample cartridges from their origin, through collection, and transport to the analysis laboratory. The following information will minimally be recorded on the chain of custody form:

* Origin of cartridges (e.g. analysis laboratory or field office)
* Transfer of cartridges between individuals (this includes signatures and dates for receipt and relinquishing cartridges)
  + Relinquishing cartridges to site operator (either by handoff or shipment with courier)
  + Receipt of cartridges by site operator
  + Relinquishing of sampled cartridges by site operator following retrieval (for handoff to analysis laboratory or shipment with courier)
  + Receipt of sampled cartridges by analysis laboratory
* Individual cartridges in the shipment listed with a unique tracking identifier
* Storage of cartridges at each point during transfer between individuals, including during shipment (e.g. stored at ≤ 4°C in onsite refrigerator, shipped with freezer packs, etc.)

Note that the convention for recording custody information for the samples can include recording transfers and storage on the field collection data sheet; however, it may be more convenient to include a separate COC form for each shipment that encompasses all samples in the shipment. A separate dedicated COC form reduces the number of instances where staff transferring cartridge custody are required to sign.

1. **QUALITY CONTROL**

Quality control and operational parameters and their associated frequency and acceptance criteria are summarized at the end of this SOP in Table 4.

* 1. Sample Inlet Probe Siting: Inlet probe siting must be compliant with the siting criteria specified in 40 CFR Part 58 Appendix E3, details of which are described in Section 3.3.1.2 of the PAMS TAD Revision 2.6
  2. Positive Bias Check: Prior to deployment and annually thereafter prior to PAMS season, the sampling unit is to be challenged with humidified zero air and a sample collected to demonstrate the sampling unit does not contribute to positive bias in measured concentrations. The positive bias check is preferably performed following instrument maintenance, which would include recharging or replacing the denuder, replacing particulate filter(s), replacing sample cartridge connection tubing, and calibrating the MFC(s). Additional details for the bias check are given in the PAMS TAD Revision 2 Section 5.7.1.1.6
  3. Flow Calibration: Prior to the PAMS season or following failure of a flow verification check, the MFC(s) in the sampling unit are calibrated by standardization against a NIST-traceable flow transfer standard covering flows that bracket the desired flow range of the sampling unit as described in Section J.3.
  4. Flow Calibration Verification: Minimally monthly, the flow of the sampling unit is verified by comparison to a NIST-traceable certified flow transfer standard. The measured flow must be within ±10% of the flow indicated by the sampling unit or recalibration is necessary. Site operators should immediately notify the agency QA representative of the failed flow calibration check to ensure that previously collected sample data are appropriately qualified (flagged).
  5. Field QC Samples:
     1. **Field Blank (Required Twice Monthly):** Field blank cartridges should remain in their sealed foil pouch until removed for exposure at the monitoring site. Field blanks characterize the contribution of contamination due to field handling activities and installation in the sampling unit, and do not characterize the contamination that occurs due to the exposure of the cartridge between cartridge installation and retrieval. To collect the field blank sample, install the cartridge in the sampling unit on an active sampling port employed for field sample collection, maintain the cartridge in the sampling unit for five to ten minutes, and retrieve as would be done for an ambient sample. Place the caps on the field blank cartridge inlet and outlet, seal the capped cartridge into the foil pouch, and store the field blank under refrigeration (≤ 4°C) as soon as possible (*note – Refrigerated storage may not be possible until retrieval of ambient samples)* until shipped to the laboratory.
     2. **Trip Blank (OPTIONAL):** Trip blank cartridges should remain in the sealed foil pouch until removed for exposure during associated field sample handling. The purpose of a trip blank is to characterize the contamination that occurs due to field sample handling during transport to the field site and to the analysis laboratory following retrieval. To collect the trip blank sample, open the foil pouch and remove the caps momentarily from the cartridge and replace the caps. Seal the capped cartridge into the foil pouch and store refrigerated (≤ 4°C) as soon as possible (*note – Refrigerated storage may not be possible until retrieval of ambient samples)* until shipped to the laboratory.
     3. **Exposure Blank (OPTIONAL):** Exposure blanks are similar to field blanks and trip blanks, where their purpose is to characterize potential contamination of ambient field samples; however, the purpose is to characterize the contamination contribution from exposing the cartridge to the same ambient conditions (minus flow) that an ambient sample experiences. To collect an exposure blank sample, install the exposure blank cartridge into a dedicated channel on the sampling unit (if so equipped) through which air is not permitted to flow. For multi-channel sampling units with unused channels, the exposure blank may be installed in a channel not activated for sample flow. For sampling units that have neither a dedicated blank channel nor unused channel available, remove the exposure blank cartridge from the foil pouch, install it in the sampling unit for five to ten minutes, uninstall the cartridge and replace the endcaps, place the cartridge (outside of the foil pouch) near the sampling unit for the duration of the sequential sampling event, and the retrieve the cartridge at the time the ambient field samples are retrieved. Seal the exposure blank cartridge in the foil pouch and store refrigerated (≤ 4°C) with the co-collected ambient field samples until shipped to the laboratory.
     4. **Duplicate Sample (OPTIONAL):** A duplicate sample is separate discrete ambient air sample collected concurrently with a primary sample. The sample inlet pathway including the ozone denuder is common to both the primary and duplicate sample; however, the duplicate sample is connected to a separate channel on the sampling unit with a flow controller independent of the primary sample. The duplicate sample is collected for 8 hours ± 20 minutes concurrently with one of the primary 8-hour sequential samples.
     5. **Collocated Sample (OPTIONAL):** A collocated sample is similar to a duplicate sample in that it is a separate discrete ambient air sample collected concurrently with a primary sample, but differs in that the entire sampling flow path - the inlet probe, ozone denuder, and sampling unit - are independent of the primary sample. The collocated sample is collected for 8 hours ± 20 minutes concurrently with one of the primary sequential 8-hour samples.  
        Field blanks are required to be collected twice per month (once every two weeks). Trip blanks, exposure blanks, duplicate samples, and collocated samples are not required; however, if these field QC samples are required by the monitoring agency, the frequency of collection is to be prescribed in the monitoring agency’s PAMS QAPP.
  6. Cartridge Lot Blank Determination and Acceptance: Prior to use in the field for sample collection, each lot of DNPH cartridges will be tested to ensure the background contamination is acceptably low. Minimally 3 cartridges per lot or 1% of the received lot, whichever is greater, should be extracted and analyzed to determine the average background concentration. Each tested cartridge will meet the criteria in Table 1:

**Table 1. DNPH Cartridge Lot Blank Acceptance Criteria**

|  |  |
| --- | --- |
| **Carbonyl Compound** | **Acceptance Limit (µg/cartridge)** |
| Acetaldehyde | < 0.10 |
| Formaldehyde | < 0.15 |
| Acetone | < 0.30 |
| Other Individual Target Carbonyl Compounds | < 0.10 |

If the criteria in the table are not met, the lot of media should not be used for sampling and should be returned to the vendor.

1. **SAMPLING UNIT SETUP AND CONFIGURATION**
   1. Sampling Unit Receipt and Inspection

Per the manufacturer instructions, unpack the instrument and inspect that the sampling unit is in good physical condition and that there are not missing components or loose fasteners. It is recommended that the sampling unit be purged with humidified zero air for a minimum of 24 hours prior to qualification for positive bias.

* 1. Required Verifications Prior to Sampling Unit Field Deployment (prior to PAMS season):
     1. Positive Bias Check (Refer to Section I.2)
     2. MFC Flow Calibration (Refer to Section J.3)
  2. Sampling Unit Flow Calibration: Prior to each PAMS season and following failure of a flow verification check, the MFC(s) in the sampling unit is calibrated by standardization against a NIST-traceable flow transfer standard covering flows that bracket the desired flow range of the sampling unit. MFCs are to be calibrated at flows corrected to standard conditions of 760 mmHg and 25°C. (Note that some sampling units default to standard conditions of 760 mmHg and 0°C as provided from the factory and may revert following power outages. The temperature reference must be corrected to 25°C.). The flow rate slope and intercept are set according to the manufacturer’s procedures for calibrating the sampling unit flows. Once the calibration is established, the flow at the desired setting is measured with the flow transfer standard and will be within ±10% of the flow setting.
  3. Installation of the sampling unit at the field site (following positive bias check and MFC flow calibration):
     1. Connect the sampling unit to AC power as specified in the instrument manual and power on the unit.
     2. Program the sampling unit calendar and clock timer to reflect the current date and accurate (within ± 5 minutes) local standard time (not corrected for daylight saving time).
     3. Connect the sampling inlet line to the sampling unit inlet port following the instructions in the instrument manual. Refer to Section H.1 for compatible sampling line materials.
     4. To eliminate dust or contaminants from entering the sampling unit flow path, connect each cartridge sampling port tubing inlet and outlet fittings together to close the pathway or install a placeholder cartridge in the port.

If the MFC calibration was performed at a location other than the field site, a flow verification check should be performed on each channel to be used for sample collection. If the verification measurement reading differs from the flow setting by more than ±10%, recalibration is necessary.

1. **SAMPLE COLLECTION PROCEDURE**
   1. Sample Setup

Site operators should transport sample cartridges under refrigeration to the field site in a cooler with freezer packs. COC forms will accompany the sample cartridges at all times to and from the field site and to the analysis laboratory.

* + 1. Field Blank: If scheduled for the particular sampling event, site operators should collect the field blank sample prior to installing the cartridges for field sample collection. Install the field blank cartridge in a position employed for active ambient sample collection for five to ten minutes and retrieve the sample, capping the cartridge, sealing the capped cartridge in the foil pouch, and storing under refrigeration   
       (≤ 4°C) until shipped to the analysis laboratory.
    2. Sample Cartridge Installation:
       1. Cartridge connections are tapered press-fit and are secured by applying sufficient pressure to the fittings to ensure an airtight seal.
          1. Supelco cartridges must be installed in the sampling unit such that the sampling flow matches the proper direction of flow. The cartridges are directional; the narrow opening is the cartridge inlet and the wider opening is the cartridge outlet. Adapter fittings (P/N 21018-U) are required on the outlet end to install Supelco cartridges.4
          2. Waters cartridges are bi-directional for flow, but should be installed such that the narrow diameter cartridge opening is connected to the sampling unit’s female Luer fitting and the wider diameter cartridge opening is connected to the sampling unit’s male fitting (narrower) from the sampling unit. The tubing configuration on the sampling unit will determine the cartridge orientation and only allows installation in one direction.5
    3. Install the cartridges in the sampling positions designated and programmed for sequential sampling. Minimally, three cartridges will be installed in the sampling unit for each sampling event, one for each of the 8-hour sequential samples for the sampling day. Exposure blanks or duplicate samples may also be installed as required by the monitoring agency.
    4. Program the sampling unit timer per the instrument manual to sample at a flow rate of 0.5 to 1.25 L/minute per the schedule in Table 2 once every three days per the national sampling calendar, which is available on EPA’s AMTIC website at the following link:

<https://www3.epa.gov/ttn/amtic/calendar.html>

**Table 2. PAMS Carbonyl Sampling Sequence Schedule**

|  |  |  |  |
| --- | --- | --- | --- |
| Sequential Sample | Start Time  (local standard time) | End Time (local standard time) | Sample Duration (hh:mm) |
| 1 | 04:00 | 12:00 (noon) | 08:00 |
| 2 | 12:00 (noon) | 20:00 (8:00 p.m.) | 08:00 |
| 3 | 20:00 (8:00 p.m.) | 04:00 | 08:00 |

* + 1. Leak Check: If the sampling unit is so equipped, a leak check routine is to be run once cartridges are installed to verify that the internal instrument flow path and cartridge connections are leak-free prior to the site operator departing the site (note that the Tisch TE-423 does not have a built-in leak check routine). If leak check fails (the default leak check acceptance criterion for ATEC 8000-series sampling units is < 0.03 L/minute flow – this criterion is user adjustable), recheck cartridge connections for tightness, tubing cracks, and loose fittings. Inspect cartridges to ensure there are not cracks in the cartridge housing which could cause a leak. If necessary, install cartridges on alternative channels that do not exhibit leaks. Repeated leak check failures following corrective steps may indicate a tubing failure inside the sampling unit such as may occur due to holes in tubing caused by vibration of tubing against an interior component. Document the leak check outcome on the sample collection form. The ATEC 8000-series sampling units automatically perform a leak check on each sample channel programmed for sample collection during the first 30 seconds of the collection and will flag samples that exceed the factory default criterion.7
    2. Prior to departing the monitoring site, verify the instrumental sampling program is correct and the instrumental sampling program is enabled.
  1. Sample Retrieval
     1. Cartridges are to be retrieved ideally within 48 hours (not to exceed 72 hours) of the completion of collection of the third (20:00 to 04:00) sequential sample. [Note that for sampling units with only 3 sampling channels, retrieval before 48 hours from the end of collection completion is necessary to ready the sampling unit for the next sampling event.]
     2. Site operators should ensure that there is immediate refrigerated storage available when retrieving samples. Onsite refrigerators must maintain temperatures of ≤ 4°C. If an onsite refrigeration unit is not available, site operators must utilize a cooler with cold freezer packs in which to store and transport samples. A best practice to minimize contamination is to transport the sealed foil pouch within a zipper-lock plastic bag containing approximately 0.5 to 2 grams of activated carbon, which will absorb contaminants.
     3. Prior to retrieving samples from the sampling unit, review the recorded sample collection data from the sampling unit display to ensure that sampling occurred according to the intended program. Record any discrepancies (e.g. low flow conditions, power failures, leak check failures, etc., as indicated by flags or error messages) on the sample collection form. For sampling units so equipped (e.g., ATEC 8000-series sampling units), it is highly recommended to transfer sample collection data to an external drive for later review and archive.
     4. Record the sample collection information from the sampling unit display on the field data collection form. Wearing clean powder-free gloves, retrieve each sample cartridge individually, install the cartridge caps, seal the capped cartridge in the associated foil pouch, and place the cartridge in refrigerated storage. On the sample collection form or COC form, record the date and time each cartridge was retrieved from the sampling unit.
     5. Transfer collected samples, sample collection forms, and associated COC forms to the laboratory, maintaining the collected samples at refrigerated temperatures. The laboratory has 14 days to extract the samples from the end of sample collection, therefore samples should be dispatched to the laboratory as soon as possible to provide sufficient time to extract the samples. If a shipping courier is employed for sample transport, overnight air shipments are recommended to ensure sample temperatures remain refrigerated upon receipt at the laboratory. Pack sufficient freezer packs and/or ice to ensure sufficient cooling capacity during shipment.

1. **CALCULATIONS AND DATA REPORTING**
   1. Total Collected Sample Volume

The total collected sampled standard conditions air volume may be accessible from the sampling unit during sample retrieval and is equal to the total sampling duration for the cartridge multiplied by the average flow rate for the sample duration as follows:

Where:

*Vs* = sampled air volume at standard conditions (L)

*Ds* = sample duration (minutes)

*Qavg* = average standard conditions flow rate during sample collection (L/minute)

* 1. Target Carbonyl Compound Concentration

Details for calculation of the carbonyl compound concentrations are described in the associated carbonyls analysis SOP. Briefly, measured carbonyls are normalized to the total sampled standard conditions air volume and the concentrations reported as µg/m3.

Conversion to ppbv can be performed by generation of reports in AQS or by the following formula:

Where:

*CAppbv* = molar concentration in air at standard conditions (ppbv)

*CAµg/m3* = mass concentration in air at standard conditions (µg/m3)

*Cf* = conversion factor (µg·m-3·ppbv-1) = molecular weight/(0.082059 × 298.15)

Molecular weights (g/mol) for the PAMS priority and optional target carbonyl compounds8 are shown in Table 3:

**Table 3. Carbonyl Molecular Weights and Conversion Factors**

|  |  |  |  |
| --- | --- | --- | --- |
| Carbonyl | Molecular Weight (g/mol) | *Cf*  (µg·m-3·ppbv-1) | Number of Carbon Atoms |
| formaldehyde | 30.026 | 1.2273 | 1 |
| acetaldehyde | 44.0526 | 1.8006 | 2 |
| acetone | 58.0791 | 2.3739 | 3 |
| benzaldehyde | 106.124 | 4.3376 | 7 |

To convert the concentration in air from ppbv to ppbC, the concentration in ppbv is multiplied by the number of carbon atoms in one molecule of the target analyte.

**Table 4. Quality Control and Operational Parameters**

|  |  |  |  |
| --- | --- | --- | --- |
| **Parameter** | **Detail** | **Required Frequency** | **Acceptance Criteria** |
| Sampling Inlet Line Cleaning or Replacement | Clean particulate residue from inlet line or install new | Prior to the beginning of each PAMS season | None |
| Positive Bias Check | Collection of a sample of humidified zero air to investigate contamination contributed by the sampler | Prior to the beginning of every PAMS season and following instrument maintenance (ozone denuder recharge, particulate filter change, etc.) | All target compounds < 0.2 µg/cartridge greater than  co-collected reference sample |
| Mass Flow Controller Calibration | Establishment of the MFC slope and intercept by comparison to a flow transfer standard | At the beginning of each PAMS season and when flow verification checks fail criteria | Flow verification immediately following calibration measured with a flow transfer standard must be within ±10% of the flow setting |
| Mass Flow Controller Calibration Verification | Verify sampling flow of each channel at the sampling flow setting | Minimally monthly during active monitoring | Flows measured by flow transfer standard within ±10% of flow setting |
| Ozone Denuder Recharge or Replace | Recoat denuder with fresh KI | Every other PAMS season | None. Recommended to challenge sampling unit with ozone at 120% of the maximum site-measured ozone concentration and measure < 10 ppb or  < 5% of the challenged concentration. |
| Particulate Filter Replace | Replace inline PTFE particulate filter | Beginning of each PAMS season or more frequently if flows decrease | None |
| Clock Accuracy | Verify clock accuracy against a known accurate time standard | Minimally monthly, recommend each sampling event | Within ±5 minutes of the time standard |
| Field Blank | Blank cartridge installed in a sampling channel for five to ten minutes | Every other week during active monitoring | Compounds must meet criteria in PAMS TAD Revision 2 Table 5-4 |
| Trip Blank | Blank cartridge accompanying collected samples to and from the field site | Not required, recommended monthly during active monitoring | Compounds must meet criteria in PAMS TAD Revision 2 Table 5-2 |
| Ambient Sample Collection | Collection of ambient air at a known flow | Three sequential 8-hour samples every 3rd day per national sampling calendar | Sample collection must be for 8 hrs ± 20 minutes |
| Sample Storage | Cartridges stored refrigerated and protected from light | All samples | Storage and transport in foil pouch at ≤ 4°C |

**Table 4. Quality Control and Operational Parameters (continued)**

|  |  |  |  |
| --- | --- | --- | --- |
| Sample Retrieval | Samples are retrieved, capped, protected from light, and stored refrigerated | Each sampling event | within 72 hours of end of 3rd sequential sample (20:00 to 04:00) |
| Duplicate Sample Collection | Collection of a separate sample cartridge concurrently through a common inlet probe with a primary 8-hour sample | Optional – recommended as 10% of primary sampling events | Relative percent difference ≤ 10% for compounds ≥ 0.5 µg/cartridge |
| Collocated Sample Collection | Collection of a separate sample cartridge concurrently through an independent inlet probe with a primary 8-hour sample | Optional – recommended as 10% of primary sampling events | Relative percent difference ≤ 10% for compounds ≥ 0.5 µg/cartridge |
| Sample Retrieval | Duration from end of sample collection to sample retrieval | Each field collected sample and QC sample | Preferably within 48 hours and not to exceed 72 hours from the end of collection |
| Sample Holding Time | Duration from end of sample collection to extraction | Each field-collected sample and QC sample | 14 days from end of collection to extraction |

1. **REFERENCES**
   1. U.S. EPA. Compendium Method TO-11A, Determination of Formaldehyde in Ambient Air using Adsorbent Cartridge followed by High Performance Liquid Chromatography (HPLC). EPA/625/R-96/010b. Available at (accessed December 2019): <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>
   2. 40 CFR Part 58 Appendix D. Available at (accessed December 2019): <https://ecfr.io/Title-40/pt40.6.58#ap40.6.58.0000_0nbspnbspnbsp.d>
   3. 40 CFR Part 58 Appendix E. Available at (accessed December 2019): <https://ecfr.io/Title-40/pt40.6.58#ap40.6.58.0000_0nbspnbspnbsp.e>
   4. Supelco LpDNPH S10, S10x, S10L Cartridges Product Specification Sheet T495028B, Sigma-Aldrich 1997. Available at (accessed December 2019): <https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Supelco/Product_Information_Sheet/4727.pdf>
   5. Waters Sep-Pak DNPH-Silica Cartridge Care and Use Manual, WAT037506 Rev B, Waters Corporation, March 2009. Available at (accessed December 2019): <https://www.waters.com/webassets/cms/support/docs/wat037506.pdf>
   6. U.S. EPA. Technical Assistance Document for Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Stations Program, Revision 2, April 2019. EPA-454/B-19-004. Available at (accessed December 2019): <https://www.epa.gov/amtic/pams-technical-assistance-document-tad>
   7. Model 8000 Automated Sampler Operations and Maintenance Manual Version 20.00, March 19, 2014, ATEC. Available at (accessed December 2019): <http://www.atec-online.com/linked/8000_manual_freescale.pdf>
   8. U.S. EPA. Additional Revisions to the Photochemical Assessment Monitoring Stations Compound Target List. October 2, 2017. Available at (accessed December 2019):  
      <https://www3.epa.gov/ttnamti1/files/ambient/pams/targetlist.pdf>
   9. Tisch 3 Channel Carbonyl Sampler Operation Manual, Revision 1, February 8, 2008. Available at (accessed December 2019):  
      <https://tisch-env.com/wp-content/uploads/2015/07/TE-423-Carbonyl-Sampler.pdf>
   10. ASTM D5197-16, Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology), ASTM International, West Conshohocken, PA, 2016. Available at (accessed December 2019): <http://www.astm.org/cgi-bin/resolver.cgi?D5197>
   11. ISO Guide 31:2015 Reference materials — Contents of certificates, labels and accompanying documentation. Geneva: International Organization for Standardization. 2015.