Standard Operating Procedure for

the Analysis of Carbonyl Compounds in Ambient Air for the Photochemical Assessment Monitoring Station (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 receipt, extraction, and analysis of carbonyl compounds for the EPA Photochemical Assessment Monitoring Stations (PAMS) network. This SOP describes the laboratory analysis of carbonyl compounds collected 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 solvent extract derivatized carbonyl-hydrazones collected on the DNPH cartridge samples and to analyze the extracts by high performance liquid chromatography (HPLC) or ultra-high performance liquid chromatography (UHPLC) with ultraviolet detection, but does not describe the unique actions required to operate specific instruments or their associated software systems nor operation of HPLCs with mass spectrometer (MS) detection. The field collection instruments and procedures employed prior to receipt at the laboratory are not described in this document; however, are detailed in the companion Standard Operating Procedure for the Collection of Carbonyl Compounds in Ambient Air for the Photochemical Assessment Monitoring Station (PAMS) Network.

1. **SUMMARY OF METHOD (COLLECTION AND ANALYSIS)**

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 are extracted with acetonitrile (ACN) within 14 days of collection. Extracts are then analyzed by HPLC with ultraviolet detection (UV) at approximately 360 nm within 30 days of extraction. The carbonyl concentrations in the ambient air samples are calculated from the measured concentrations of the target analytes in the sample extracts and the volumes of air sampled onto the cartridges. The resulting in-air carbonyl concentrations of the collected samples are reported to the EPA Air Quality System (AQS) database. Quality control requirements are summarized in Table 6 at the conclusion of this SOP.

*Laboratories are required to measure and report the PAMS priority compounds formaldehyde and acetaldehyde and are encouraged to measure and report acetone and benzaldehyde. 3 The method described in this SOP may also be employed for measuring the additional carbonyls compounds listed in
Table 1.*

**Table 1. PAMS Priority and Optional Target Carbonyls**

|  |  |  |
| --- | --- | --- |
|  **Target Carbonyl** | **Chemical Abstracts Number** | **AQS Parameter Code** |
| acetaldehyde a | 75-07-0 | 43503 |
| acetone b | 67-64-1 | 43551 |
| benzaldehyde b | 100-52-7 | 45501 |
| formaldehyde a | 50-00-0 | 43502 |
| Additional Carbonyls That May Be Measured and Reported to AQS |
| butyraldehyde | 123-72-8 | 43510 |
| crotonaldehyde | 4170-30-3 | 43528 |
| 2,5-dimethylbenzaldehyde | 5779-94-2 | 45503 |
| heptaldehyde | 111-71-7 | 43950 |
| hexaldehyde | 66-25-1 | 43517 |
| isovaleraldehyde | 590-86-3 | 43513 |
| m&p-tolualdehyde | (m) 620-23-5/(p) 104-87-0 | 45506 |
| methyl ethyl ketone | 78-93-3 | 43552 |
| methyl isobutyl ketone | 108-10-1 | 43560 |
| o-tolualdehyde | 529-20-4 | 45505 |
| propionaldehyde | 123-38-6 | 43504 |
| valeraldehyde | 110-62-3 | 43518 |

a PAMS priority compound

b PAMS optional compound

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. **Carbonyl-Hydrazone:** Stable derivative formed from the reaction of DNPH with a given carbonyl compound.
5. **Chromatography Data System:** Computer software system that permits programming, control, data recording, and data processing for the HPLC.
6. **Continuing Calibration Verification (CCV):** Analysis of a carbonyl-hydrazone standard solution to demonstrate the HPLC calibration remains valid.
7. **DNPH:** diphenylhydrazine – derivatizing agent.
8. **Derivatized Standard:** Carbonyl compound that has been reacted with DNPH to form a carbonyl-hydrazone.
9. **Extraction Batch Quality Control (QC) Samples:** Laboratory-prepared samples that are processed in the laboratory in the same manner as field QC and field-collected samples. Extraction batch QC samples include: extraction solvent method blank (ESMB), method blank (MB), laboratory control sample (LCS), and LCS duplicate (LCSD). For extraction batch QC samples prepared on cartridge media, it is recommended that they be prepared from the same lot of cartridges as the associated field-collected samples.
10. **Extraction Solvent Method Blank (ESMB):** Aliquot of ACN extraction solvent taken through the extraction process to verify cleanliness of the extraction solvent and labware.
11. **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.
12. **High Performance Liquid Chromatograph (HPLC):** Instrument employed for the analysis of collected carbonyl compounds by separation and detection of derivatized carbonyl-hydrazones.
13. **Initial Multi-Point Calibration Curve (ICAL):** Standardization of the HPLC response to the target analytes by analysis of a series of standard solutions (minimally five or more) covering the concentration range of interest. The ICAL demonstrates the relationship between instrument response and analyte concentration. ICAL standard solutions are prepared from the primary stock standards.
14. **Laboratory Control Sample (LCS):** A DNPH cartridge that has been spiked with a known amount of target compound(s) and processed through the extraction and analysis procedure in the same manner as a field sample. The LCS assesses the recovery of the target analytes from the cartridge matrix through the extraction and analysis procedures as implemented during processing of the field-collected samples.
15. **LCS Duplicate:**  A cartridge prepared identically to the LCS. The LCSD assesses the precision of the laboratory preparation, extraction, and analysis procedures.
16. **Measurement Quality Objective (MQO)**: Criteria prescribed for a given measurement or set of measurements which may include bias, precision, completeness, frequency, and sensitivity.
17. **Method Blank (MB):** An unspiked DNPH cartridge that is extracted and analyzed to assess presence of background contamination through the extraction and analysis procedures.
18. **Method Detection Limit (MDL):** The laboratory MDL is determined as the larger of the MDL components determined from minimally 7 method blanks (MDLb) or from minimally 7 samples spiked with a known amount of target analytes (MDLsp) as detailed in 40 CFR Part 136 updated rule 82 FR 40836.4
19. **NIST:** National Institute of Standards and Technology.
20. **Ozone Denuder:** Device used to remove ozone from a sampled gas stream. For this method, the ozone denuder consists of a length of copper 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.
21. **PAMS:** Photochemical Assessment Monitoring Stations.
22. **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.
23. **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.
24. **PFA:** perfluoralkoxy copolymer resin (Teflon®).
25. **Photodiode array (PDA):** Detector that allows light covering a wide range of the ultraviolet and visible spectrum to be detected simultaneously. For this method, the wavelength of interest is approximately 360 nm.
26. **PTFE:** polytetrafluoroethylene (Teflon®).
27. **Pounds per square inch absolute (psia)**: Unit of pressure relative to absolute vacuum (0 psia).
28. **Proficiency Test (PT):** Sample with a known amount of target compounds blind to the laboratory. The PT is evaluates the laboratory’s performance to extract and analyze for the target analytes.
29. **Second Source Calibration Verification Standard (SSCV):** Standard solution prepared from a stock standard source procured from a provider (vendor) other than the primary standard employed to prepare the ICAL. The SSCV is prepared at a concentration(s) within the calibration curve and is analyzed to independently verify the calibration.
30. **Solvent Blank (SB):** Aliquot of ACN solvent analyzed to demonstrate that the analytical instrument is free of background contamination and potential interferences.
31. **Standard Temperature and Pressure (STP)**: 25°C and 760 mm Hg absolute pressure.
32. **Zero Air:** Synthetic air that has been scrubbed of carbonyls and water vapor.
33. **INTERFERENCES**
	1. Temperature effects:
		1. Carbonyl hydrazones degrade more quickly at ambient temperatures than at reduced (e.g. refrigerated) temperatures. Care should be taken to ensure sampled cartridges, prepared QC samples, and standard materials are maintained refrigerated at ≤ 4°C.
		2. Inability to maintain a stable separation column temperature may result in poor retention time stability which may make identifying target analytes difficult or impossible. Separation columns should be installed within a column heater set to a temperature several degrees above ambient laboratory temperature (e.g., 30°C) and the temperature maintained to within ±1°C, as practical.
	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 in the range of 360 nm and may be difficult or impossible to separate chromatographically from desired target compounds, particularly formaldehyde, resulting in overestimation or false positive detection of target compounds.5
	4. Contaminated solvents: Only high-purity grade, carbonyl-free solvents should be used for extraction, standard solution preparation, and mobile phase preparation. Solvents can adsorb carbonyl compounds from the ambient atmosphere, which will form carbonyl-hydrazones when introduced to DNPH extracted from sample cartridges and therefore should be stored tightly capped in sealed impermeable containers (e.g., amber glass bottles with PTFE-lined lids). Opening of solvent containers to ambient air should be minimized. Ambient air introduced to solvent containers by bottletop dispensers can be scrubbed of carbonyls by installing a blank DNPH cartridge onto the dispenser’s air inlet.
	5. Particulate build-up on separation column: Particulates commonly enter the HPLC system through materials washed into the solvent extracts during sample extraction. Particulates may include liberated silica gel and/or particulate matter residue collected on the cartridge filter during sampling. Over time, particulate build-up can substantially reduce or block flow through the separation column leading to reduced column life, shifting retention times, poor chromatographic performance (e.g., split chromatographic peaks), and/or over-pressurization and shutdown of the LC instrument. Installation of a guard column and/or frit upstream of the separation column can remove particulates from the injected sample aliquot and prevent damage to the separation column due to build-up. Separation columns exhibiting particulate build-up may be backflushed with can, methanol, and/or mobile phase to remove particulates.
	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. Acetone is included among the target analytes for this method; however, it is particularly difficult to analyze via this method due to the significant and variable concentrations in laboratory atmospheres and background levels on cartridge media. When measured concentrations of acetone are suspected to be elevated due to cartridge background and/or contamination, the associated sample data are to be qualified (flagged) and may require invalidation if, in the opinion of the analyst, the magnitude of the contamination is substantial. This SOP calls for solvent rinsing of labware; however, acetone should never be employed as a cleaning solvent for this method.
34. **SAFETY**

Analysts should take basic precautions for working in a wet chemistry laboratory by wearing personal protective equipment (PPE) such as solvent impermeable gloves, labcoat, safety glasses, and closed-toed shoes. Exposures to solvents should be minimized by working with these materials in a fume hood and complying with recommendations listed in safety data sheets (SDS).

1. **APPARATUS AND MATERIALS**
	1. HPLC System:
		1. HPLC system minimally consisting of an autosampler, solvent/mobile phase pump, degasser, column heater, and ultraviolet (UV) detector or PDA capable of wavelength operation at 360 nm.
		2. Analytical Separation Column: C-18 reversed phase column capable of meeting quality control (QC) and analytical acceptance criteria specified in Table 5 of this SOP. C-18 separation columns that perform chromatographically similarly for target analyte separation are available from a number of suppliers. Suitable columns will have inner diameters (IDs) of approximately 3 to 5 mm, lengths from 50 to 250 mm, particle sizes from approximately 2.5 to 5 µm, and pore sizes from approximately 50 to 100Å. EPA Method TO-11A allows for installing two such columns in series for separation of carbonyl compounds in addition to formaldehyde. Installation of a long column (e.g., > 350 mm) or an additional column in series improves separation of analytes but increases the sample run time.

Guard columns or stainless steel frits suitable for protecting the separation column are recommended available for typical HPLC systems. Guard columns with a pore size of approximately 5 µm are suitable for this application.

* + 1. Computer equipped with a Chromatography Data System (CDS): A computer system with installed CDS software compatible with the HPLC instrument and capable of automated control of the analytical instrument, online data acquisition, post-acquisition data manipulation, peak integration, and results presentation. Subsequent data manipulation and reduction may be performed with a commercially-available spreadsheet program or other suitable software.
	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;6 or
		2. Waters Sep-Pak cartridges, 350 mg sorbent per cartridge, (1 mg DNPH/cartridge) 55-105 µm particle size, part number WAT037500 7
	2. Apparatus for holding DNPH cartridges vertically to facilitate extraction
	3. Mechanical pipette with associated pipette tips, gastight syringe with PTFE-lined plunger, or combination of mechanical pipettes and syringes capable of accurately delivering 20 to 2000 µL – calibrated at the intended delivered volumes
	4. HPLC autoinjector vials compatible with the HPLC autosampler – amber glass with PTFE-sealed caps
	5. Class A volumetric flasks, TC: flasks labeled “TC” (to contain), various sizes, as needed, with stoppers (e.g. 2-mL, 5-mL, 100-mL, etc.)
1. **REAGENTS AND CHEMICALS**
	1. Acetonitrile (ACN): ACN must be high-purity HPLC grade, carbonyl-free quality.
	2. Reagent Water: Deionized water, ASTM Type I (resistivity ≥ 18MΩ·cm) or equivalent.
	3. Stock Standard Solutions: Single component or component mixtures of certified DNPH-carbonyl solution(s) in ACN may be purchased from a commercial vendor. This/these certified stock solution(s) is/are diluted in-house to prepare intermediate and working standards, as appropriate. Vendors typically provide certified concentration values of the DNPH-carbonyl compounds as both the concentration of the DNPH-carbonyl and free-carbonyl (or “functional”) compounds. Alternatively, high-purity neat solid carbonyl-DNPH standard materials may be sourced and stock standard solutions prepared by accurately weighing (to a minimum of three significant figures) an aliquot of neat material and diluting to a known volume with an appropriate solvent (e.g., ACN).
		1. Primary Stock Standard Solution(s): The ICAL standard solutions are prepared from the primary stock standard solutions.
		2. Secondary Source Stock Standard Solution(s): This stock standard material is procured from a different vendor than that of the primary stock standard(s), or, if not available from a different vendor, from a different lot than the primary stock standard(s).
2. **SAMPLE COLLECTION, MEDIA HANDLING, AND HOLDING TIMES**
	1. Field sample collection procedures are addressed in the companion Standard Operating Procedure (SOP) for the Collection of Carbonyl Compounds in Ambient Air for the Photochemical Assessment Monitoring Station (PAMS) Network.
	2. Sample Cartridge Handling
		1. New DNPH cartridge media are to be stored refrigerated at ≤ 4°C upon receipt.
			1. Waters cartridges are typically shipped from the vendor at ambient temperature.
			2. Supelco cartridges are typically shipped from the vendor at refrigerated temperatures.
		2. 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 or laboratory (e.g., for preparation of an extraction batch QC sample such as an MB or LCS).
		3. Cartridges should only be handled with gloved hands (chemicals from hand sanitizers, lotions, etc., can contaminate sample cartridges).
		4. Markers containing volatile solvents (e.g. permanent markers such as Sharpie®) should not be used for marking on foil storage pouches.
		5. Cartridge storage areas should be free of carbonyls. Cartridge refrigerated storage units should not be used for storage of solvents or items containing carbonyl compounds.
		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 2. 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. Holding Time and Storage Requirements
		1. Stock Materials: Unopened stock materials are appropriate for use until their expiration date provided they are stored per manufacturer requirements. Once opened, stock materials may not be used past the manufacturer recommended period or, if no time period is specified, not beyond six months from the opened date. To use the standard materials past this time period, standards must have been demonstrated to not be degraded or concentrated by comparison to freshly opened standards. Unopened stock materials must be stored per manufacturer recommendations. All stock and diluted working calibration standards must be stored at ≤ 4°C in a separate refrigeration unit from sample cartridges and sample extracts.
		2. Sample Holding Time and Storage Requirements

Results input to AQS must be appropriately qualified for failure to meet the following holding time and/or storage criteria.

* + - 1. All field-collected cartridges must be stored at ≤ 4°C and extracted within 14 days of the end of collection. These conditions similarly apply to laboratory-prepared QC samples, which must be stored at ≤ 4°C and extracted within 14 days of preparation.
			2. Extracts are to be stored at ≤ 4°C and must be analyzed within 30 days of extraction.
		1. Commercially-available DNPH cartridges are typically provided with an expiration from the manufacturer specifying storage conditions. Agencies are to comply with the manufacturer expiration, if given. Degradation of the DNPH reagent or silica gel sorbent bed which may reduce collection efficiency to unacceptable levels may occur after the assigned expiration date. Additionally, as DNPH cartridge media age, their levels of background contamination are likely to have increased, perhaps to unacceptable levels, due to passive sampling and uptake from the ambient atmosphere. For cartridges not assigned an expiration date or assigned an arbitrary expiration date (i.e., six months from time of receipt) by the manufacturer, agencies should work within this expiration period as practical. For such cartridges which have exceeded the arbitrary expiration period, they may be shown to be acceptable if, by performing another lot background assessment as described in Section H.2.vi, levels of contaminants meet the criteria in Table 2 and there remains sufficient DNPH to conduct sampling and ensure excess DNPH levels remain following sample collection. This level of DNPH on unsampled cartridges is recommended to be a reduction of DNPH area counts of no more than ~15% from the original lot acceptance analysis. *Note that both the Supelco S10 and Waters WAT037500 cartridges are impregnated with 1 mg of DNPH per cartridge, therefore a 15% reduction would indicate that 0.85 mg of DNPH are still available for sample collection.*
1. **LABWARE CLEANING**

Clean all associated labware by rinsing with ACN, washing with laboratory detergent, rinsing with deionized water, rinsing with ACN or methanol, and air drying or drying in an oven at no more than 80 to 90°C. Heated drying of volumetric labware at temperatures > 90°C voids the manufacturer volumetric certification. A best practice just prior to use is to rinse the labware several times with ACN and allow to air dry.

*Note that this labware cleaning process is the minimum recommended and that additional steps (e.g., additional rinses with deionized water and solvents) may be needed to remove silica gel residue, target analyte contamination, or interferences from laboratory soaps. Labware cleanliness will be demonstrated by evaluation of ESMB and MB and adjustments to the cleaning procedure should be made if contamination or interferences are observed in these negative QC samples.*

1. **LABORATORY EXTRACTION QUALITY CONTROL SAMPLES**

A best practice is to process field-collected cartridges in batches of no more than 20 at a time. All field-collected and laboratory extraction QC samples in a given extraction batch should be analyzed in the same analysis batch (an analysis batch is defined as all samples analyzed together within a 24-hour period).

* 1. **Laboratory Extraction QC Samples Required with Each Extraction Batch** - The following laboratory extraction QC samples are prepared at 5% of the field-collected samples, which may include the various field QC samples such as those listed in Section C.10. For batch sizes of more than 20 field-collected cartridges, *n* such QC samples of each type are added to the batch, where *n* = batch size/20, and where n is rounded to the next highest integer. Thus, for extractions including 30 field-collected samples, two of each of the following QC samples would be included in each batch.
		1. Extraction Solvent Method Blank (ESMB): Negative QC sample prepared by transferring the extraction solvent for the extraction batch into a flask just as an extracted sample. The purpose of this negative control is to demonstrate that the extraction solvent is free of interferences and contamination and that the labware washing procedure is effective. All target analytes must be
		≤ MDLsp.
		2. Method Blank (MB): The MB is a blank unopened cartridge (that has not left the laboratory) and is extracted identically to field samples. The MB should not show target analytes above the laboratory MDL.
	2. **Laboratory Extraction QC Samples Required Quarterly** – The following laboratory batch QC samples are to be prepared, extracted, and analyzed minimally quarterly, but are recommended to be prepared as 5% of the field-collected sample load.
		1. Laboratory Control Sample (LCS): The LCS, also referred to as the laboratory fortified blank, is a positive control sample prepared by spiking a known amount of underivatized carbonyl target analyte or derivatized carbonyl-hydrazone onto a cartridge such that the expected target analyte concentration in the extract is in the lower third of the instrument calibration range. The LCS is then extracted with the same extraction solvent and method employed for field samples to assess bias in matrix of the extraction and analysis procedures. LCS recovery is to be within 80 to 120% of the theoretical concentration for formaldehyde and 70 to 130% of the theoretical concentration for all other target carbonyls.
		2. Laboratory Control Sample Duplicate (LCSD): The LCSD is prepared and extracted identically to the LCS. The LCSD assesses precision of the extraction and analysis procedures. LCSD recovery is to be within 80 to 120% of the theoretical concentration for formaldehyde and 70 to 130% of the theoretical concentration for all other target carbonyls. LCS and LCSD results must show precision as relative percent difference (RPD) of ≤ 20%.
1. **PROCEDURE**
	1. Sample Receipt

Field-collected (ambient and field QC samples) samples are to be transported under refrigeration to the laboratory (hand delivered by monitoring agency staff or delivered via courier) and arrive at the laboratory under refrigeration (cartridge shipments should arrive cold). Measuring the shipping temperature with a calibrated min-max type thermometer is a best practice to verify that the sample shipment remained cold (≤ 4°C) through the duration of transport.

* + 1. Upon opening the sample cooler, the temperature of the cartridge shipment should be measured and recorded. The temperature is ideally measured by aiming a calibrated handheld infrared (IR) thermometer gun at a foil pouch containing a sample cartridge in the shipment. Document the date and time of sample receipt in the sample receiving records (e.g., on the COC form).
		2. Verify that the correct number of cartridge samples expected is present in the shipment and verify that the unique identifiers on the chain of custody (COC) form and field data collection forms correlate to the samples in the shipment. Document any discrepancies for follow-up with field monitoring staff. Discrepancies such as missing samples, additional samples, or sample identifier mix-ups should be addressed as soon as possible with field staff.
		3. Review the COC form to ensure custody transfers (signatures with dates of sample transfer) and storage conditions information are complete. Document any discrepancies or deficiencies for follow-up with field staff.
		4. Sign and date the COC form to complete the custody transfer.
		5. Examine the foil pouches to ensure they are sealed and document any discrepancies or damage to the samples in the shipment.
		6. Log the samples into the laboratory tracking system such as a tracking database or laboratory information management system (LIMS) and assign unique laboratory identifiers as appropriate per the laboratory standard procedure for sample tracking.
		7. Store the samples under refrigeration at ≤ 4°C until extraction (no longer than 14 days from end of collection). Samples should be stored in a dedicated storage unit free of solvents and organic vapors that may contaminate the cartridge media and should not be stored with carbonyls standards materials or extracts.
	1. Sample Extraction

*Samples are extracted with ACN to final extract volumes of 2 to 5 mL and all cartridges are to be extracted with the same ACN volume. Complete extraction is accomplished with 2 mL of can. Additional solvent dilutes the final extract, resulting in reduced sensitivity at the HPLC. The collected extract volume must be known and accurately measured by a volumetrically certified method (e.g. Class A volumetric flask). To limit quantitative transfers and contact with potentially contaminated glassware, it is recommended to capture the extracted cartridge eluent into a Class A volumetric flask of the desired final volume.*

Powder-free nitrile or equivalent gloves should be worn for all standard, reagent, and cartridge handling steps.

* + 1. Determine the number of field-collected samples and laboratory extraction QC samples to be extracted. Gather the needed number of clean volumetric flasks (or other volumetrically-certified labware suitable for determining extraction volume), extraction solvent, and blank cartridges needed to prepare laboratory extraction QC samples. Label the flasks uniquely and record the sample identifiers in an extraction logbook, bench sheet, or similar record.

		*It is a best practice to rinse clean labware several times with ACN and air dry just prior to use.*
		2. Remove the sample cartridges to be extracted from refrigerated storage and allow to warm to room temperature (approximately 30 minutes prior to extraction), maintaining the cartridges in the sealed foil pouches.
		3. Remove spiking solutions from refrigerated storage and allow to warm to room temperature (approximately 30 minutes).
		4. Prepare laboratory batch QC samples:
			1. **MB** (required as ≥ 5% of field-collected samples): The MB is an unspiked cartridge preferably of the same lot as the field-collected samples. Document the cartridge lot in the extraction records.
			2. **ESMB** (required as ≥ 5% of field-collected samples): Prepare the ESMB by adding extraction solvent to a volumetric flask and bringing the flask to the final extract volume.
			3. **LCS** (required quarterly, recommended as ≥ 5% of field-collected samples): The LCS is prepared with a new cartridge preferably of the same lot as the field-collected samples. Ensure the spiking solution(s) has warmed to room temperature prior to use. Examine the solution for precipitate or cloudiness which indicate incomplete dissolution of materials. Gentle warming in a water bath, manual agitation (e.g., shaking) and/or sonication may aid in dissolving precipitates. Using a calibrated mechanical pipette or gastight syringe, spike the cartridge with derivatized carbonyl-hydrazone or underivatized carbonyl standards in ACN. The selected LCS spiking concentration should result in concentrations of target analytes in the extract in the lower third of the calibration curves and recommended spiking volumes are ≤ 100 µL. (*For example, addition of 50 µL of a 15 µg/mL standard solution with a 5-mL extract volume will result in a theoretical concentration of 0.15 µg/mL.*) Allow the spiked solution to permeate the silica gel bed and the solvent to dry for approximately 30 minutes prior to extraction.
			4. **LCSD** (required quarterly, recommended as ≥ 5% of field-collected samples): Prepare this laboratory QC sample identically to the LCS.
		5. Remove each field-collected sample cartridge from its sealed foil pouch, remove the caps, and place in the extraction cartridge holding apparatus to orient the cartridges vertically. Position the field-collected and laboratory QC cartridge samples with the cartridge inlet facing down so that the cartridge is eluted in the reverse direction of sample collection. Use of a vacuum manifold is not necessary, but may reduce the time required to elute the cartridges. Position the catch flasks under the cartridges to capture the extracts and doublecheck that the sample identifiers match those on the catch flasks.
		6. Using a single lot of ACN for the extraction batch, add ACN extraction solvent to the cartridges to begin elution of the cartridges. As the solvent drains through the cartridge, add additional solvent taking care to not overfill the catch flasks. Note that the cartridge media will retain a small volume (approximately 0.5 mL) of solvent. Extraction solvent reservoir funnels or Luer-type syringe barrels are commercially available that can be connected to the top of the cartridge to speed up the extraction and provide an estimate for the volume of solvent. Note that Supelco S10 cartridges comprise an approximate 2-mL reservoir in the cartridge body for this purpose.
		7. Allow the solvent to drain into the catch flasks. Once elution is complete, dilute each flask to volume with extraction solvent as needed, stopper the flasks, and invert each flask several times to mix.
		8. Transfer an aliquot (e.g., approximately 500 µL) of each extract to a labeled amber autosampler vial for analysis and cap each vial tightly. It is recommended that a separate aliquot (e.g., a second autosampler vial) of the extract be stored as an archive to afford reanalysis should an error or problem occur during analysis. Any extract remaining after preparing the analysis vial and archive vial may be discarded or archived per the analyst’s discretion. Store extracts protected from light at ≤ 4°C in a dedicated storage unit.
	1. Analysis by HPLC
		1. HPLC Setup

Note that the following instrument settings are a suggested starting point for the analytical method and instrument setup. It is expected that experienced analysts will make modifications, as needed, to these parameters to optimize the analysis parameters for their specific instrument, separation column, and desired target analytes for quantitation. The method described below relates to HPLC; however, can be applied with little modification to UHPLC instruments.

* + - 1. Instrument Parameters
				1. Prior to beginning analysis, the analyst should ensure there are sufficient volumes of mobile phase reagents in the HPLC reservoirs to cover the needed volume to complete the analysis sequence(s) and that the waste reservoir has sufficient space.
				2. Begin pumping the starting mobile phase through the system and column minimally 30 minutes prior beginning an analytical sequence to ensure a stable chromatogram baseline. Instruments that have not been operated for several days or weeks may require extended conditioning pumping times to ensure gases, bubbles, and/or precipitates are eliminated.
				3. The simplest HPLC run method utilizes an isocratic method whereby the mobile phase remains a constant (e.g., 70:30) mixture of ACN:reagent water; however, adjustments to the mobile phase gradient program and addition of other reagents such as methanol may improve chromatographic performance and analyte separation depending on the desired suite of target analytes, column selected, flow rates, etc.
			2. Chromatography Data System Settings (example):
				1. UV or PDA detector wavelength: 360 nm

*Note: The target analyte carbonyl-hydrazones absorb light efficiently in the range of 340 to 380 nm for detection. Wavelengths selected within this range are typically suitable for this analysis.*

* + - * 1. Mobile Phase Flow Rate: 1.5 mL/minute
				2. Mobile Phase: isocratic 70:30 ACN:reagent water
				3. Injection Volume: 20 µL
				4. Column Temperature: 30°C, isothermal
				5. HPLC Run Time: formaldehyde, acetaldehyde, acetone, and benzaldehyde will typically elute within 20 minutes depending on the specific instrument configuration. Adjust run time to ensure complete elution of target analytes.

*Note: When first developing this method, analysts should analyze a calibration standard in the upper third of the expected calibration range to determine the elution order and approximate elution times. Vendors typically provide an example chromatogram with certified calibration stock solutions for assigning peaks to target analytes. A typical example chromatogram is shown below in Figure 1.*



**Figure 1: Example Carbonyls Analysis HPLC Chromatogram**

* + 1. Instrument Calibration
			1. To calibrate the HPLC instrument, a suite of calibration standard solutions containing the target carbonyl-hydrazones of interest covering the desired concentration range is analyzed. A minimum of five concentration levels is required, typically covering a range of 0.01 to 3.0 µg/mL of each free (underivatized) carbonyl. To avoid confusion, all concentration values should be determined in relation to the free (underivatized) carbonyl, and not the carbonyl-hydrazone. Standards are to be at room temperature prior to analysis. Prior to calibration, ensure the chromatograph baseline is stable and analyze a solvent blank (SB) to demonstrate the instrument is sufficiently clean. The SB will ideally show no or minor chromatographic peaks or baseline artifacts and all target analyte concentrations should be ≤ MDLsp.
			2. Prepare calibration standard solutions of target carbonyl-hydrazones at concentrations covering the desired calibration concentration range by diluting known volumes of stock and/or intermediate standard solutions in ACN to known volumes. Such dilutions are recommended to be performed by transferring stock standard volumes with calibrated mechanical pipettes or gastight syringes into Class A volumetric flasks and diluting to the desired final volume. An example calibration solution preparation scheme whereby stock standard solutions at 15 µg/mL are diluted in 2-mL Class A volumetric flasks is shown in Table 2.

*Note: Analysts are recommended to prepare two or more separate intermediate dilutions (e.g., the 3.0 and 1.125 µg/mL standards in Table 3) directly from a stock standard solution to ensure that dilution errors are noticed. Dilution errors for serial dilutions prepared from a single intermediate dilution will propagate to the subsequent dilutions and may not be discovered.*

**Table 3. Example Scheme for Preparation of Calibration Standards**

|  |  |  |  |
| --- | --- | --- | --- |
| **Calibration Standard Target Concentration (µg/mL) \*** | **Source Solution Concentration(µg/mL) \*** | **Volume of Source Solution (mL)** | **Final Volume (mL)** |
| 3.0 | 15.0 | 0.400 | 2.0 |
| 1.125 | 15.0 | 0.150 | 2.0 |
| 0.30 | 3.0 | 0.200 | 2.0 |
| 0.10 | 1.0 | 0.200 | 2.0 |
| 0.010 | 1.0 | 0.020 | 2.0 |

\* Concentration reflects free-carbonyl (underivatized).

* + - 1. Prepare a SSCV standard with target carbonyls at concentrations in the lower third of the calibration range by diluting a stock standard from the second source stock standard (a supplier different than the primary stock supplier) by following a dilution scheme similar to step 2 above.
			2. Calculate the theoretical concentrations of the calibration standard solutions according to the formulas in Section L corrected for purity and the analytical concentration listed on the certificate of analysis (COA), as appropriate. Enter these theoretical concentrations of the calibration standards into the CDS calibration table.

*Note: The stock standard COAs typically list a target, or nominal concentration; however, the analytical concentration, and not the target value, should be the source value for determining the theoretical concentration of each calibration standard solution.*

* + - 1. Analyze each calibration standard solution minimally once (it is recommended to analyze each calibration level in triplicate) to generate the calibration curve.
			2. Ensure the CDS has properly identified each target analyte peak and that the peak integration is appropriate and consistent for each concentration level and target analyte. Adjust CDS parameters for target analyte identification and for peak integration as needed.
			3. Establish the calibration curve for each target analyte using the CDS calibration linear regression function to plot the instrument response (area response units for each target analyte chromatographic peak) on the y-axis and the nominal concentration on the x-axis. The calibration curve correlation coefficient (r) for each target analyte must be ≥ 0.999 for linear fit and the curve must not be forced through the origin. Once the calibration curves are established, re-evaluate each calibration level against the curve (plug the area response into the regression equation) to ensure that the calculated concentration of each calibration solution is within ±20% of its theoretical concentration.

			*Calibration curves must include a minimum of five (5) calibration standard levels. Individual calibration standard levels may not be excluded from the calibration curve to improve the regression arbitrarily; a valid technical reason must be documented to justify the removal of a calibration standard level (e.g., known injection error, chromatographic interference with integration or identification, etc.).*
			4. Examine the linear regression intercept to ensure the absolute value of the concentration equivalent (|intercept/slope|) is less than the laboratory MDLsp. When this specification is not met, the analyst may establish the regression using weighted regression such as concentration-1 or concentration-2, which increases the influence of the lower concentration standards in the regression. If the intercept still does not meet the acceptance criterion, the source of the error, such as may occur from inaccurate dilution, contamination, or suppression, must be corrected and the calibration curve re-established before sample analysis may commence.
			5. Update the retention time (RT) windows in the CDS as the mean RT from the ICAL for each target analyte. For positive identification, the RT of a target analyte must be within three standard deviations (3*s*) or ± 2%, whichever is smaller, of its mean RT from the ICAL.
			6. Once the calibration criteria listed in steps 5 through 9 above are met, analyze an SSCV to verify the calibration for each target analyte. The SSCV measured concentration is to be within ± 15% of the theoretical concentration for each target analyte. Once verified, these calibration curves will be employed for determining the concentrations of all subsequent analyzed solutions until a new calibration is established. Depending on the instrument, the calibration curve may remain valid for six months or longer, as evidenced by analysis of a continuing calibration verification (CCV) standard.
		1. Sample Analysis
			1. Once calibration curves have been established for each target analyte and met the acceptance criteria as verified by analysis of the SSCV, the calibration is verified minimally every 12 hours of analysis by analyzing a CCV standard. The CCV typically consists of an analysis of a calibration standard with all target analytes at concentrations in the lower third of their calibration range. A best practice is to analyze two or more standard levels with concentrations representing different portions of the calibration curve range (e.g., one each in the lower third and middle third of the concentration range). The CCV may be diluted from the primary calibration stock material or the secondary source stock material. CCVs are to be within ±15% of the theoretical concentration and will verify target analyte RTs are within the established RT windows.
			2. On days when an ICAL is not performed, the analytical sequence should commence with an SB followed by a CCV. Once these two QC checks demonstrate that the system is sufficiently clean and the calibration remains valid (and RTs are stable), analyze laboratory QC samples, field QC samples, and field samples. The CCV, followed by an SB, is analyzed every 12 hours of analysis and at the conclusion of the analytical sequence. Analysts should verify the sample identifiers were entered correctly into the CDS sequence table prior to beginning the analysis sequence.
			3. With each analysis sequence of 20 or fewer field-collected samples, at least one field-collected sample extract should be selected for replicate analysis. For sequences containing more than 20 field-collected samples, *n* such replicates must be analyzed, where *n* = batch size/20, and where *n* is rounded to the next highest integer. Thus, for analytical sequences including 30 field-collected samples, two different field-collected samples would be analyzed in replicate. Replicate analysis precision should be ≤ 20% RPD for concentrations ≥ 0.5 µg/cartridge.
			4. Target analytes are identified by their RT and will have a signal-to-noise ratio of > 3:1, preferably > 5:1. 8
			5. Extracts of samples from DNPH cartridges (e.g., ambient field samples, field QC samples, MB, LCS, and LCSD) must have a DNPH peak present in the chromatogram. For DNPH cartridge extracts that do not contain a DNPH peak in the chromatogram, the sample sequence should be verified to ensure vials were not switched. Lack of a DNPH peak in the chromatogram indicates the depletion of the DNPH derivatizing agent for the associated cartridge (and potentially a negative bias in the reported carbonyls’ concentrations) or that the extract vial was mislabeled. DNPH elutes prior to target analytes and is typically the largest peak in the chromatogram for cartridge extracts.
			6. It is recommended that an SB be analyzed following analysis of a suspected high concentration sample or a high concentration standard to avoid carryover to the next sample extract in the sequence. These “cleanout” blanks should be labeled appropriately in the sequence and are required to meet blank acceptance criteria.
			7. Field QC Sample Acceptance Criteria

Analysts should review field QC sample results for compliance with the following criteria. Note that failure of these criteria does not necessarily indicate a problem with the extraction and analysis; however, implies an issue with the field collection and/or sample handling and should prompt the laboratory to notify field staff of the criteria failure(s) immediately.

* + - * 1. Trip blanks (TB) will meet the lot blank acceptance criteria listed in
				Table 2.
				2. Field blank (FB) and exposure blanks (EB) will meet the following criteria in Table 4:

**Table 4. Field and Exposure Blank Acceptance Criteria**

|  |  |
| --- | --- |
| **Carbonyl Compound** | **Acceptance Limit (µg/cartridge)** |
| Acetaldehyde | < 0.40 |
| Formaldehyde | < 0.30 |
| Acetone | < 0.75 |
| Sum of Other Target Carbonyl Compounds | < 7.0 |

* + - * 1. Duplicate samples will show precision of the in-air concentrations of
				≤ 20% RPD for samples with target analytes ≥ 0.5 µg/cartridge.
				2. Collocated samples will show precision of the in-air concentrations of
				≤ 20% RPD for samples with target analytes ≥ 0.5 µg/cartridge.
		1. Method Detection Limits (MDLs)

Prior to use of the extraction and analysis method to report ambient sample carbonyls measurement concentration data, the laboratory will determine the MDL for each target analyte to be reported. An in-depth description of MDLs is detailed in Sections 3.3.5.1 and 5.6 of Revision 2 of the PAMS Technical Assistance Document (TAD). 8

1. **CALCULATIONS AND DATA REPORTING**

#### Calculation of Free Carbonyl Concentration in Solution

The concentration of the free carbonyl portion of a carbonyl-hydrazone in solution is calculated based on the ratio of molecular weights of the free carbonyl to the carbonyl- hydrazone per the following formula:

$$C\_{free} =C\_{ch}\frac{MW\_{free}}{MW\_{ch}}$$

Where:

*Cfree* = concentration of free carbonyl (µg/mL)

*Cch* = measured concentration of carbonyl-hydrazone (µg/mL)

*MWfree* = molecular weight of free carbonyl (g/mol)

*MWch* = molecular weight of carbonyl-hydrazone (g/mol)

* 1. The free carbonyl concentration of each target carbonyl when preparing stock standard solutions from neat solid standard materials is determined according to the following formula:

$$C\_{ssfree}= \frac{M\_{neat}∙P\_{neat}∙MW\_{free}}{V\_{stock}∙MW\_{ch}}$$

Where:

*Cssfree* = free carbonyl concentration in stock solution (µg/mL)

*Mneat* = mass of neat carbonyl-hydrazone material (µg)

*Pneat* = purity of carbonyl-hydrazone compound in neat material, as a decimal

*MWfree* = molecular weight of free carbonyl (g/mol)

*MWch* = molecular weight of carbonyl-hydrazone (g/mol)

*Vstock* = final volume of stock solution (mL)

* 1. The free carbonyl concentration of each target carbonyl in a working level standard solution prepared by dilution of a stock standard solution is determined as:

$$C\_{ws}= \frac{C\_{ss}∙V\_{ss}∙MW\_{free}}{V\_{ws}∙MW\_{ch}}$$

Where:

*Cws* = free carbonyl concentration in working solution (µg/mL)

*Css* = stock standard solution carbonyl-hydrazone analytical concentration from the certificate of analysis (µg/mL)

*Vss* = volume of stock standard solution added (mL)

*Vws* = final volume of working standard solution (mL)

*MWfree* = molecular weight of free carbonyl (g/mol)

*MWch* = molecular weight of carbonyl-hydrazone (g/mol)

#### The concentration of the target analyte in the measured solution is calculated according to the following formula based on the established linear regression:

$$C= \left[A-b\right]/m$$

Where:

*C =* Concentration of target analyte in sample (µg/mL)

*A =* Integrated peak area of the target analyte in the sample extract (area counts)

*b =* Intercept of the calibration curve (area counts)

*m =* Slope of the calibration curve (area·mL·µg-1)

* 1. Target carbonyl concentrations measured in extracts are normalized to the total collected sample volume for reporting as the mass per sampled volume (e.g. µg/m3) per the following formula:

$$C\_{air}= \frac{C\_{extract}∙V\_{extract}∙DF}{V\_{air}}$$

Where:

*Cair =* concentration of target analyte in air (µg/m3)

*Cextract =* concentration of target analyte in the sample extract (µg/mL)

*Vextract =* volume of sample extract (mL)

*DF =* dilution factor (= 1 if no dilution performed on the extract)

*Vair =* volume of standard conditions sampled air for the cartridge (m3)

Example: An ambient sample cartridge collected at 1.00 L/minute for 480 minutes (0.480 m3) was extracted with 5.0 mL of ACN was diluted by a factor of 2 (e.g., 1 mL of extract was diluted to 2 mL final volume with ACN) measured 2.42 µg/mL of formaldehyde on the HPLC.

2.42 µg/mL · 5.0 mL · 2 = **50.4 µg/m3**

 0.480 m3

Measured concentrations of target carbonyls in field-collected samples (primary sequential 8-hour samples, duplicate samples, collocated samples) as well as FBs are to be reported to AQS in µg/m3 at standard conditions of 25°C and 760 mmHg.

Target analyte concentrations in FBs are to be normalized to the target standard conditions collected volume of an 8-hour sample at the typical designated flow rate.

Target analyte concentrations for TBs may be reported as the total measured mass/cartridge or may be normalized to the target standard conditions collected volume of an 8-hour sample at the typical designated flow rate.

* 1. Masses of target carbonyls per sampled air volume units can be converted to ppbv through reports generated by AQS (e.g., AMP501 or by the following formula:

$$C\_{A ppbV}= C\_{A µg/m3 }∙C\_{f}$$

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 and associated conversion factors for the PAMS target carbonyls are shown in Table 5.

**Table 5. Molecular Weights and Conversion Factors of
PAMS Target Carbonyls**

|  |  |  |  |
| --- | --- | --- | --- |
| Target Carbonyl | Molecular Weight(g/mol) | *Cf* (µg·m-3·ppbv-1) | Number of Carbon Atoms/molecule |
| 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.

* 1. For failures of field QC sample criteria (e.g. FBs or TBs exceeding criteria) or laboratory QC acceptance criteria (e.g. exceeding holding time, method blank exceedance, etc.), associated sample results are qualified (flagged) by addition of the appropriate QA qualifier or null code qualifier code when data are reported to AQS. These qualifiers will be defined with the monitoring agency program QAPP.

**Table 6. Summary of Quality Control and Operational Parameters**

|  |  |  |  |
| --- | --- | --- | --- |
| **Parameter** | **Detail** | **Required Frequency** | **Acceptance Criteria** |
| Chain of Custody Completed | Custody transfers between individuals and storage conditions documented | Documented for each field-collected sample (ambient and field QC sample) | Documentation, signatures, and dates complete without gaps |
| Solvent Blank (SB) | Analysis of acetonitrile solvent to demonstrate the HPLC is sufficiently clean, free of chromatographic interferences, and has a stable chromatographic baseline | Prior to ICAL, prior to daily CCV, and after each CCV | Target analyte concentrations ≤ MDLsp |
| Initial Calibration (ICAL) | Analysis of five or more different concentration calibration standard solutions covering the concentration range of interest | Initially, after failed continuing calibration verification, and after changing instrument components or maintenance that impact calibration response | R ≥ 0.999, backcalculated concentration of each standard level within ±20% of theoretical, |intercept/slope| ≤ MDLsp |
| Retention Time (RT) Windows | Assignment of time range when target analytes elute from column and reach detector | RT windows for each target analyte are established with each ICAL | RT window established as ± 3*s* or ± 2% of its mean RT from ICAL |
| Second Source Calibration Verification Standard (SSCV) | Analysis of a known standard prepared from a stock solution sourced from a vendor independent of the primary calibration stock standard; verifies the quality of the ICAL | Immediately following successful ICAL | Target analyte concentrations within ±15% of theoretical |
| Continuing Calibration Verification (CCV) | Analysis of known standard solution(s) to verify the instrument calibration remains valid – recommended in the lower 1/3 of the calibration range | After every 12 hours of analysis, at the beginning of each day’s analysis when an ICAL is not performed | Target analyte concentrations within ±15% of theoretical |
| Holding Times | Maximum duration from end of sample collection for sample extractionMaximum duration from sample extraction to analysis | Each field collected sample, field QC sample, and laboratory QC sampleAll extracts | ≤ 14 days from end of sample collection to extraction≤ 30 days from sample extraction to analysis |
| Method Blank (MB) | Blank cartridge from the lot of co-extracted field-collected samples – extracted to assess cleanliness of media and reagents | As 5% of field collected samples. One per extraction batch of 20 or fewer field-collected samples | Target analyte concentrations ≤ MDL |

**Table 6. Summary of Quality Control and Operational Parameters (continued)**

|  |  |  |  |
| --- | --- | --- | --- |
| **Parameter** | **Detail** | **Required Frequency** | **Acceptance Criteria** |
| Laboratory Control Sample (LCS) | Blank cartridge spiked with a known amount of target analytes and extracted | Minimally quarterly, recommended as 5% of field collected samples (one per extraction batch of 20 or fewer) | Formaldehyde recovery within 80 to 120%, all other target analyte recoveries within 70 to 130% |
| Laboratory Control Sample Duplicate (LCSD) | Duplicate blank cartridge spiked with a known amount of target analytes and extracted to assess precision of the extraction and analysis method | Minimally quarterly, recommended as 5% of field collected samples (one per extraction batch of 20 or fewer) | Formaldehyde recovery within 80 to 120%, all other target analyte recoveries within 70 to 130%; precision as RPD ≤ 20% |
| Extraction Solvent Method Blank (ESMB) | Aliquot of solvent lot used for extraction dispensed into a volumetric flask used for extraction | As 5% of field collected samples. One per extraction batch of 20 or fewer field-collected samples | Target analyte concentrations ≤ MDLsp |
| Field Blank (FB) | Blank cartridge installed in an actively used sampling channel for five to ten minutes – no air is sampled through the cartridge | As submitted to the laboratory by field site(s) | Compounds must meet criteria in Table 4 |
| Exposure Blank (EB) | Blank cartridge installed in an actively used sampling channel for the duration of an ambient air sample – no air is sampled through the cartridge | As submitted to the laboratory by field site(s) | Compounds must meet criteria in Table 4 |
| Trip Blank (TB) | Blank cartridge accompanying collected samples to and from the field site | As submitted to the laboratory by field site(s) | Compounds must meet criteria in Table 2 |
| Sample Storage | Cartridges stored refrigerated and protected from light in dedicated storage without extracts, standards, or solvent vapors | All samples | Storage in sealed foil pouch at ≤ 4°C |
| Extract Storage | Sample extracts stored refrigerated and protected from light in dedicated storage without standard solutions or solvent vapors | All extracts | Storage in amber vials with PTFE lids at ≤ 4°C |
| Duplicate Sample | Sample cartridge collected concurrently with a primary 8-hour sample through a common inlet probe  | As submitted to the laboratory by field site(s) | RPD ≤ 20% for compounds ≥ 0.5 µg/cartridge |
| Collocated Sample | Separate sample cartridge collected concurrently with a primary 8-hour sample through an independent inlet probe | As submitted to the laboratory by field site(s) | RPD ≤ 20% for compounds ≥ 0.5 µg/cartridge |
| Target Analyte Identification | Evaluation of signal-to-noise (S/N) ratio and analyte retention time (RT) | All target analytes in all analyzed solutions | For positive identification S/N ≥ 3:1 and RT within assigned window |

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