CALIFORNIA AIR RESOURCES BOARD

Standard Operating Procedure for the Determination of Carbonyls in Ambient Air Analyzed by (Ultra) High Performance-Liquid Chromatography

MLD022
Revision 5.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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Standard Operating Procedure for the Determination of Carbonyls in Ambient Air Analyzed by (Ultra) High Performance-Liquid Chromatography

1. Scope

This method describes the procedures followed by Monitoring and Laboratory Division (MLD) staff for the determination of 2,4-dinitrophenylhydrazine (DNPH) derivatized carbonyls in ambient air by (Ultra) High Performance Liquid Chromatography [(U)HPLC] with ultraviolet/visible (UV/VIS) detection. A complete list of analytes that have been validated and approved by management may be found in Appendix 1. This standard operating procedure (SOP) was developed by the staff in the Organics Laboratory Section (OLS) of the Northern Laboratory Branch (NLB) and is based on the U.S. EPA Method TO-11A. This SOP is used in conjunction with the NLB's Quality Control Manual (QCM), as well as the instrument manufacturer's operation and software manuals.

2. Summary of Method

Carbonyls react with the DNPH to form stable hydrazone derivatives of corresponding aldehydes and ketones.The DNPH derivatives are eluted from the sampling cartridges using carbonyl free acetonitrile (ACN) and are quantified using reverse-phase (U)HPLC with UV absorption detection at 360 nm.

It should be noted that UHPLC methods should not be applied when using standard HPLC instrumentation. It is, however, acceptable to run standard HPLC methods on UHPLC instrumentation.

The DNPH-derivatized compounds in the sample are identified and quantified by comparison of their retention times and peak areas with those of external standard solutions. Though the reporting limit (RL) may vary upon request or between programs, the typical RL for routine ambient analysis of carbonyl compounds is 0.10 ppb. Appendix 2 lists the equivalent RL in terms of potential instrument units.

3. Acronyms

Acronym or Term	Definition
ACN	Acetonitrile
AQS	Air Quality System
CARB	California Air Resources Board
CAS	Chemical Abstracts Service
CCV	Continuing Calibration Verification
CS	Control Standard
DNPH	2,4-Dinitrophenylhydrazine
EBLK	Extraction Blank[1]
EPA	Environmental Protection Agency
H&SC	Health & Safety Coordinator
(U)HPLC	(Ultra) High-Performance Liquid Chromatography
LCS	Laboratory Control Spike (Blank Spike)
LIMS	Laboratory Information Management System
LOQ	Limit of Quantitation
LPM	Liters per Minute
MDL	Method Detection Limit
MEK	Methyl Ethyl Ketone (2-Butanone)
MLD	Monitoring and Laboratory Division
MW	Molecular Weight
NLB	Northern Laboratory Branch
OLS	Organics Laboratory Section
PPB	Parts per Billion[2]
PTFE	Polytetrafluoroethylene (TEFLON)
QC	Quality Control
QCM	Quality Control Manual
RL	Reporting Limit
RPD	Relative Percent Difference
SDS	Safety Data Sheet
SOP	Standard Operating Procedure
STP	EPA Standard Temperature and Pressure (1 atm and 25ºC)
UV/VIS	Ultraviolet/Visible

1. Extraction Blanks in this SOP are reflective of the same criteria of a Method Blank – as defined in the QCM. The nomenclature of “EBLK” or “Extraction Blank” will continue to be used through this SOP; however, will be reported to LIMS as a Method Blank.

2. The usage of “ppb” in this document reflects sampling volumes and molecular weights of the analytes.

4. Definitions

4.1. BATCH – An analytical batch is a set of samples (i.e. extracts) analyzed together as a group in an uninterrupted sequence. An extraction batch is a set of samples (no more than 20) which is processed all in one group, using the sample equipment and reagents.

4.2. BLANK – Sample media, solvent, or reagent that has not been exposed to the sample stream in order to monitor contamination during sampling, transport, storage, extraction, or analysis. The blank is subjected to the same analytical processes as samples.

4.2.1. EXTRACTION BLANK – An unexposed sample DNPH cartridge that is extracted at the same time as samples and is taken through the entire sample analysis process. An extraction blank is used to monitor the laboratory preparation and analysis systems for interferences and contamination from glassware, reagents, sample manipulations, and the general laboratory environment.

4.2.2. SOLVENT BLANK - An aliquot of solvent analyzed with each batch of samples to indicate any contamination or artifacts that may come from the reagents and analytical steps.

4.3. CALIBRATION CURVE – Consists of at least five concentrations of a calibration standard that span the monitoring range of interest to determine instrument sensitivity and the linearity response for the target compounds.

4.4. CARRYOVER – Contamination from an adjacent sample causing false or inaccurate results in the subsequent sample(s).

4.5. CONTROL STANDARD – A midpoint standard analyzed after the calibration curve. The control standard is prepared with stock standards from a source different from those used to prepare the calibration standards. If a secondary source is not available, then a second analyst may prepare the control standard. The control standard must be analyzed at a minimum of once per batch, but is typically ran with every CCV.

4.6. CORRELATION COEFFICIENT – Typically expressed as ‘r’, it measures the linear relationship between two variables, with a value range of -1 to 1. A value close to 1 indicates a strong positive linear correlation between two variables; that is, when one variable increases so does the other. A value close to -1 indicates a strong negative linear correlation; that is,

when one variable increases the other decreases. A value close to 0 indicates a non-linear, or random, correlation.

4.7. DILUTIONS – Dilution is the process of reducing the concentration of a solute in solution, usually by adding more solvent. Dilutions are required when any sample concentration exceeds the calibrated linear range by more than ten percent. After diluting, the concentration should fall within the calibrated linear range. Additional dilutions are sometimes necessary.

4.8. HOLD TIME – The maximum amount of time a sample or extract may be stored prior to performing an operation. Extraction hold time is from sample collection to extraction. Analytical hold time is from sample extraction to analysis.

4.9. INTERFERENCE – Ozone reacts with the carbonyl compounds (aldehydes and ketones) and their DNPH derivatives causing lower results and chemical interferences. Discrete artifacts or elevated baselines from solvents, reagents, glassware, and other sample processing hardware that may cause misinterpretation of the chromatographic data. Chemical interferences are matrix effects that may cause the target compound to recover higher or lower than the expected value.

4.10. METHOD DETECTION LIMIT – A statistically derived value that is defined as being the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix (including sample media) containing the analyte. The procedure used to determine the MDL is documented in the NLB's Laboratory QCM.

4.11. REPLICATE – A second analysis of a randomly chosen sample within an analytical batch.

4.12. REPORTING LIMIT – A number which data is not typically reported below. The RL may or may not be statistically determined, and may be established by regulatory requirements or in conjunction with client or program needs. The RL is equivalent to or greater than the LOQ and should be at a concentration greater than or equal to the lowest calibration standard.

4.13. SPIKE – A quality control sample employed to evaluate the accuracy of a measurement. The spike is prepared by adding a known amount of the target analyte(s) to an aliquot of the solvent, media, or sample. The recovery of a spike provides an indication of the efficiency of analytical

procedures. Spikes can be added at any point in the sampling and analytical process such as field, laboratory, matrix, trip, etc.

5. Interferences and Limitations

5.1. Interferences may be caused by contaminants in the filters, sampling media, solvents, sample extraction apparatus, filtration apparatus, and glassware. An extraction blank is extracted and analyzed with each set of samples to monitor these possible sources of contamination.

5.2. The analytical system may become contaminated when samples containing high compound concentrations are analyzed. If there is suspected carryover from a high concentration sample, additional blanks should be analyzed to clean the system prior to reanalyzing the succeeding sample(s) to verify results.

5.3. Compounds trapped on the column may cause baseline shifting, or the appearance of broad, extraneous “ghost” peaks. The column should be rinsed with extra acetonitrile or back-flushed to remove these contaminants prior to analyzing samples.

6. Personnel Qualifications and Training

Prior to performing this method, new personnel must be trained by staff with expert knowledge of this method. Personnel must be trained to understand the program’s requirements per any applicable State and Federal regulations and guidance, and this SOP. Personnel will also be trained to safely and properly operate the equipment needed to perform the method, the quality assurance components, waste disposal, and LIMS functionality pertaining to the program. Personnel should provide an initial demonstration of capability prior to performing this method on real-world samples (i.e. data for record). Training will be documented and maintained by the laboratory supervisor.

7. Safety Requirements

All personnel must follow the general health and safety requirements found in NLB’s Chemical Hygiene Plans.

7.1. The analyst should refer to the SDS of all chemicals used in this method for additional information regarding chemical properties and precautions.

7.2. The handling and preparation of samples, extracts, and standards must be conducted in a hood. Analysts should ensure that engineering and air quality controls are active and operating properly. Proper personal protective equipment must be worn, including nitrile gloves, safety glasses, and a laboratory safety coat.

8. Hazardous Waste

All solvent waste is collected into 4L bottles directly off the instrument and must have a hazardous waste label appropriately filled out – indicating the contents and start date of accumulation. Once full, the waste is disposed into the organic waste barrel in the chemical waste collection area. Old sample vials are to be deposited into buckets that also contain appropriate hazardous waste labels. The NLB H&SC will provide a new bucket for the satellite collection area upon analyst request.

9. Equipment and Supplies

9.1. Thermo Scientific Vanquish UHPLC system

9.2. Column: Acclaim Carbonyl C-18 (2.2 um, 2.1 x 150 mm) or equivalent

9.3. Disposable Syringes: 10 mL volume Luer-Lok tip such as BD disposable syringes part# 309604

9.4. 4 mL glass autosampler vials with Teflon lined screw caps

9.5. 12x32 mm autosampler vials with pre-slit silicone/PTFE septum.

9.6. 5.00 mL, Class A, Volumetric Flasks.

9.7. Eppendorf electronic pipettes: 15 - 5000 µL volume ranges

9.8. 1.5 mL disposable Pasteur pipettes

9.9. Sample rack used to hold sample cartridges and syringe bodies during extraction.

9.10. Disposable nitrile gloves to handle organic solvents.

9.11. 3.7 cm ashless cellulose filter for use as a KI ozone scrubber.

9.12. Ring clamps are used to hold the 3.7 cm cellulose filter.

9.13. Petri dishes to hold the ring clamps for the ozone filter assembly for shipping.

10. Reagents

10.1. Acetonitrile HPLC carbonyl free or better, CAS No 75-05-8 such as Burdick & Jackson

10.2. Water HPLC grade, such as that produced by Barnstead Nanopure water purification system Model # D11951, >16 MΩ–cm, 0.2 µm filter. HPLC mobile phase.

10.3. Methanol HPLC grade, CAS No 67-56-1, such as Burdick & Jackson

10.4. Isopropyl Alcohol (IPA) HPLC grade, CAS No 67-63-0, such as Burdick & Jackson

10.5. Formic Acid ≥97% A.C.S reagent grade, CAS No 64-18-6, such as Sigma-Aldrich

10.6. Potassium iodide (KI) – A.C.S reagent grade.

11. Standards Preparation

11.1. All standard solutions are stored at approximately <4°C until used. The standard solutions are removed from the refrigerator and allowed to equilibrate to room temperature before use. Standards should be returned to the refrigerator at the end of the work day. All standards used in this SOP are DNPH derivatized. The DNPH derivatized standards are corrected for equivalence and concentrations based on the unreacted ketone. Working standards are good for up to 120 days from preparation date, or as indicated by the performance of the standard, but are not to exceed the expiration date of the parent solution.

11.1.1. Typical calibration levels are prepared as shown in Table 1. Working calibration standards may be used for up to 120 days after preparation, or until degradation is observed (i.e. recoveries start to drift outside expected results) – whichever comes first.

Table 1. Typical Calibration Levels

Calibration Level	Std. Conc. (µg/mL)	Spiking Vol (µL)	Final Vol (mL)	Final Conc. (µg/mL)
Level 1	1.00	30	1.50	0.020
Level 2	1.00	75	1.50	0.050
Level 3	50.0	100	25.0	0.20
Level 4	50.0	250	25.0	0.50
Level 5	50.0	500	25.0	1.00
Level 6	50.0	1000	25.0	2.00

11.2. LCS and Control Standards

The control standard stocks and mix are prepared as described in section 11.1.1 for Level 4 (0.50 µg/mL). The control standard is prepared from a different standard lot or source of derivatized standards than what was used for the calibration standards.

12. Media and Sample Storage

12.1. Ozone Scrubber Preparation – Prepare a 0.6 M KI solution (4g/40mL) in deionized water. Fully soak each 3.7 cm cellulose filter in the KI solution by submerging each filter twice and the letting the filter air dry. The filter is placed in the filter holder assembly. The filter and holder are stored in a petri dish at room temperature prior to shipment to the sampling site.

12.2. Media storage – Prior to sampling, Sep-Pak DNPH-Silica Cartridges are stored and shipped at approximately <4°C.

12.3. Laboratory Sample Storage – The samples/QC are stored at approximately <4°C in a refrigerator until extraction.

13. Sample Extraction and Analysis

13.1. Sample Preparation and Extraction

13.1.1. Samples collected on Sep-Pak DNPH-Silica Cartridges are stored in a refrigerator at approximately <4°C until extraction. Remove the sample cartridges from the refrigerator and allow them to equilibrate at room temperature. All samples should be extracted within 14 days of the sampling date.

13.1.2. An extraction blank must be prepared with each batch of no more than 20 samples. The extraction blank should be from the same sample cartridge lot as the exposed sample cartridges. If the extraction blank is from another cartridge lot it will be noted on the extraction sheet.

13.1.3. A laboratory control spike (blank spike) must be prepared with each batch of no more than 10 samples. The LCS is prepared by spiking an aliquot of working standard into solvent. While this foregoes the extraction process, a separate study is to be performed annually that includes spiking through sample

cartridges from at least two different lots. This procedure may be found in Appendix 3.

13.1.4. Remove endcaps from exposed sample cartridge and attach to a 10 mL Luer-lock syringe body (solvent reservoir). Place in sample rack and have sample cartridge end inserted into a 5.00 mL Class A volumetric flask.

13.1.5. Add 5.00 mL acetonitrile using solvent auto dispenser and collect the eluent in the volumetric flask. Fill to mark with acetonitrile and invert three times to mix. Transfer the sample extract into a 4 mL sample vial to store at approximately <4°C until analysis.

13.1.6. All extracted samples should be analyzed within 30 days from extraction.

13.2. Sample Analysis

13.2.1. Analytical Sequence

Each analytical batch must include an opening calibration curve, a control standard and at least one extraction blank. Additional blanks may be ran if there is more than one cartridge lot associated with the samples, or if there are more than 20 samples. Every 10 or fewer samples must also include a replicate, LCS, matrix spike, CCV and Control standard. The same injection volume must be used for all standards and samples. The recommended order of analysis is as follows:

- Solvent blank
- Calibration standards
- Control standard
- Extraction blank
- Samples
- Replicate
- Laboratory Control Spike
- Matrix Spike
- CCV standard
- Control standard
- Solvent blank

13.2.2. Analytical Conditions

HPLC:

- Flow mode: Reverse Phase
- Column Flow: 0.6 mL/min
- Column: Acclaim Carbonyl C-18 (3.0 µm 3.0 x 250 mm)
- Column Oven: 35°C
- Injection Volume: 2.0 uL
- Detector Wavelength: 360 nm
- Detector Acquisition Rate: 5 Hz
- Total Run Time: 46 minutes (See Table 2A)

UHPLC:

- Flow mode: Reverse Phase
- Column Flow: 0.4 mL/min
- Column: Acclaim Carbonyl C-18 (2.2 µm 2.1 x 150 mm)
- Column Oven: 28°C
- Injection Volume: 2.0 uL
- Detector Wavelength: 360 nm
- Detector Acquisition Rate: 20 Hz
- Total Run Time: 24.5 minutes (See Table 2B)

Table 2A. HPLC Run Parameters

Time (min)	Flow (mL/min)	Acetonitrile A (%)	Water B (%)
0.000	0.600	50.0	50.0
6.000	0.600	50.0	50.0
40.000	0.800	95.0	5.0
40.100	0.800	100.0	0.0
44.000	0.800	100.0	0.0
44.100	0.600	50.0	50.0
46.000	0.600	50.0	50.0

Table 2B. UHPLC Run Parameters

Time (min)	Flow (mL/min)	Acetonitrile A (%)	Water B (%)
0.000	0.400	45.0	55.0
8.300	0.400	45.0	55.0
17.000	0.400	100.0	0.0
20.000	0.400	100.0	0.0
20.000	0.400	45.0	55.0
24.500	0.400	45.0	55.0

14. Quality Control

Several types of samples are analyzed to ensure and assess the quality of the data. These samples, acceptance criteria, and corrective actions are described in Table 5. If QC results do not meet criteria, corrective action must be taken. All anomalies, corrective actions, and deviations from this SOP must be documented in the chemist's logbook, monthly QC report, and in the final data report.

Table 3. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Sample Hold Time (collection to extraction)	All samples	Store samples approximately <4°C until extraction. Extract within 14 days from collection date.	If hold time is exceeded, document and report.
Analytical Hold Time (extraction to analysis)	All sample extracts	Store extracts in cold storage until analysis. Analyze within 30 days from extraction.	If hold time is exceeded, document and report.

Table 3. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Extraction Blank	One per extraction batch at a minimum	All Analytes: <RL	If >RL check instrument and method materials for possible contamination, reanalyze extraction blank and all samples in batch. Evaluate sample results; when sample results are less than ten times higher than extraction blank results, results are invalidated for those samples associated with the blank.
Solvent Blank	One per analytical batch at a minimum	All Analytes: <RL	If > RL check instrument and solvent materials for possible contamination, reanalyze solvent blank and all samples in batch. Contact service engineer if contamination continues to persist.
Initial Calibration	Minimum of five calibration levels prior to analysis of each analytical sequence	$r \geq 0.98$	Reanalyze. Prepare new calibration standards if criteria still not met.
Carryover Check	After analysis of high concentration sample – At least 2.5 times greater than the upper calibration limit.	No target analytes detected with bias high results in subsequent sample(s) or <RL if analyzing blanks.	Reanalyze subsequent sample(s) to confirm results are not biased high due to contamination from analysis of preceding high concentration sample. If reanalysis results meet replicate criteria, report initial results. If not, analyze blanks or back-flush column to clean system. Reanalyze samples once system is clean.
Continuing Calibration Verification (CCV)	A midpoint calibration standard analyzed after ten or fewer samples and at end of analytical batch	Ending and bracketing CCV must be ±15% of the equivalent midpoint level concentration from the initial calibration.	Reanalyze the CCV that failed and all preceding/following samples that are not bracketed by a CCV that met criteria. Prepare a new CCV if criteria is still not met. Reanalyze all samples with new CCV.

Table 3. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Control Standard (CS)	Opening control after calibration and additional controls bracketing every ten or fewer samples.	At least one CS must be analyzed with every analytical batch. The CS must fall within established control criteria as described in QCM.	Reanalyze CS. Prepare new CS if criteria still not met. Reanalyze all samples with new CS.
Replicate	One per ten or fewer samples in analytical batch at a minimum	Evaluate when both primary and replicate are ≥5*RL RPD ±25%	Reanalyze replicate and all associated samples within bracketing standards. If still outside criteria, investigate and correct issues. Reanalyze. Invalidate all samples in batch if replicate fails again.
Collocated	Run when available	Evaluate when both primary and collocated are ≥5*RL RPD ±25%	Confirm results, report, and notify manager.
Laboratory Control Spike (LCS)	At least one per extraction batch	70-130% of expected value	Reanalyze LCS and all associated samples in the batch. If the LCS still does not meet criteria, prepare a new LCS and reanalyze analytical batch. If LCS still fails, perform routine maintenance or contact service technician.
Matrix Spike	At least one per extraction batch	70-130% of expected value	Check if LCS meets criteria. If so, a matrix effect will be noted and results reported. If not, follow LCS corrective action.
Storage Temperature	Keep samples and standards in cold storage until preparation for analysis	Approximately <4ºC	If the storage fridge/freezer performing anomalously (ice buildup, room temp, etc.), transfer standards and samples to a properly working fridge/freezer and repair or replace the old unit.

Table 3. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Retention Time	All samples and standards	±0.30 minutes relative to midpoint calibration standard	If retention times drift outside criteria, backflush the column and purge the pump. Check if times are stable by running a standard in replicate. If stable, re-run and report new results. If drifting still occurs, perform pump maintenance or contact service engineer.

15. Calculations

15.1. Relative Percent Difference (RPD) between two results:

$$RPD = \frac{|X1 - X2|}{(X1 + X2)/2}\ x\ 100\%$$

Where: X1 = First Value and X2 = Second Value

15.2. Matrix spike percent recoveries:

$$\left(\frac{\left(Concentration_{Matrix\ Spike} - Concentration_{Primary\ Sample}\right)}{Spiked\ Amount}\right) \text{x} 100\%$$

15.3. Laboratory Control Spike (Blank Spike) percent recoveries:

$$\left(\frac{LCS\ Concentration}{Spiked\ Amount}\right) \times 100\%$$

15.4. Unit Conversions

15.4.1. Raw Concentration (µg/mL) to Media Concentration (µg/cartridge):

$$\boldsymbol{Conc}_{\boldsymbol{\mu g/cart}} = \frac{\boldsymbol{Conc}_{\boldsymbol{\mu g/mL}}\ \boldsymbol{x}\ \boldsymbol{Extraction\ Volume}\ [\boldsymbol{mL}]}{\boldsymbol{1\ cartridge}}$$

15.4.2. Media Concentration (µg/cartridge) to Volumetric Concentration (µg/m^3):

$$\boldsymbol{Conc}_{\boldsymbol{\mu g/m^3}} = \boldsymbol{Conc}_{\boldsymbol{\mu g/cart}}\ \boldsymbol{x}\frac{\boldsymbol{1\ cartridge}}{\boldsymbol{Sample\ Volume}\ [\boldsymbol{L}]}\ \boldsymbol{x}\ \frac{\boldsymbol{1000\ L}}{\boldsymbol{1\ m^3}}$$

15.4.3. Volumetric Concentration (µg/m^3) to Volumetric Concentration (ppb):

$$\boldsymbol{Conc_{ppb} = Conc_{\mu g/m^3}\ x\ \frac{1\ mole}{Molecular\ Weight\ [g]}\ x\ \frac{24.46\ L}{1\ mole}}$$

16. Data Management and Reporting

Data management consists of samples logged into LIMS, documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are to be kept with the instrumentation at all times.

16.1. During data acquisition, the raw data files are processed by the analytical software to produce result files. The result files contain quantitation information such as peak areas and retention times, along with concentration and instrumentation information.

16.2. Peaks found in the chromatogram are verified by the chemist that they were identified correctly. Integration of each peak is evaluated to ensure the software processed the data appropriately.

16.3. The instrument method is calibrated for both retention time and concentration during data processing using the integrated calibration standard areas. The concentrations of target compounds are based on the peak areas and the known analyte concentrations in the standards. Concentrations are calculated using the instrument standardization routine for samples, blanks, controls, and spikes. Retention times are verified that the peaks are not shifting more than ± 0.30 minutes. If shifting occurs, maintenance may need to be performed and samples reanalyzed.

16.4. The final results will be adjusted by an appropriate dilution factor (only if the sample was diluted; otherwise, the dilution factor would be 1.00) and reported to LIMS in µg/mL.

16.5. Data from the analytical instrument are transferred into LIMS via a data transfer software (i.e., LIMSLink). LIMSLink is also programmed to check results against QC criteria in LIMS before data transfer. Post data transfer, the analyst will review the raw data and QC data transfer and apply corrective action(s) as needed.

16.6. Analyte concentrations will not be reported if below the RL

17. Maintenance and Repairs

Preventive maintenance is done on an annual basis on the HPLC and repairs are done as needed by an approved vendor under contract to MLD or by experienced staff. All maintenance and repairs are documented in a logbook.

18. Revision History

	Date	Updated Revision	Original Procedure
1.0	No Information Available	Not Applicable. Original SOP.	No Information Available
2.0	January 9, 1991	No Information Available	No Information Available
3.0	N/A	No Information Available	No Information Available
4.0	January 1, 1996	No Information Available	No Information Available
4.1	October 5, 1998	No Information Available	No Information Available
4.2	June 1, 2014	Addressed findings from 2011 EPA TSA Audit including: dilutions, holding times, field and trip blanks, standards and expiration dates.	No Information Available
4.2-A01	February 10, 2015	Gave detailed procedure of DNPH cartridges in relation to lot checks, extraction blanks and samples.	No Information Available
4.2-A09	October 28, 2015	• DNPH derivative nomenclature updated to “hydrazone" • Column temperature criteria updated to be 35^{o}C • Lot check frequency updated to one per lot or one per 40 cartridges • Updated control criteria to reflect ±15% if standard deviation is <5%	• Previously “hydrazine” • Previously 5^{o}C above ambient • Previously just one per production lot • Previously calculated only using standard deviations

5.0	December 23, 2020	• Updated reporting units to µg/mL • Added UHPLC instrumentation and specifications • Added five extra analytes • Added storage temp criteria (approximately <4°C) • Updated RT criteria to be absolute (±0.30 min) • Updated Collocated and Replicate QC criteria to ±25%	• Previously reporting in µg/cartridge • Previously only standard HPLC • Previously only three analytes • Previously no temp criteria • Previously relative RT criteria (3 sigma or ±2% mean calibration) • Previously 15% and 10%, respectively

19. References

19.1. Determination of Formaldehyde in Ambient Air Using Adsorbant Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology); EPA Compendium Method TO-11A. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Second Edition); EPA/625/R-96/010b; U.S. Environmental Protection Agency, Center for Environmental Research Information; Cincinnati, OH: January 1999

19.2. Waters Sep-Pak DNPH-Silica Cartridge [Care and Use Manual], WAT037506 Rev B, Waters Corporation, Milford, MA, March, 2009

19.3. Standard Operating Procedures for RM Environment Systems Inc. (REMSI) 924 Toxics Air Sampler, AQSB SOP 801, Second Edition; California Environmental Protection Agency, California Air Resource Board, Monitoring and Laboratory Division, Air Quality Surveillance Branch (AQSB), Air Monitoring-North Section, December, 2006

19.4. Thermo Scientific Vanquish *UHPLC System* Operating Manual, 4820.3601-EN, Revision 3.0a September 2017, ThermoFisher Scientific Inc., 168 Third Avenue, Waltham, MA 02451.

19.5. Thermo Scientific Vanquish *Pumps VH-P10-A-02* Operating Manual, 4820.44111-EN, Revision 1.0 October 2017, ThermoFisher Scientific Inc., 168 Third Avenue, Waltham, MA 02451.

19.6. Thermo Scientific Vanquish *Split Samplers VH-A10, VF-A10, VH-A40, VF-A40* Operating Manual, 4828.5001-EN, Revision 3.0 February 2018, ThermoFisher Scientific Inc., 168 Third Avenue, Waltham, MA 02451.

19.7. Thermo Scientific Vanquish *Column Compartments VH-C10* Operating Manual, 4827.3201-EN, Revision 2.0a September 2017, ThermoFisher Scientific Inc., 168 Third Avenue, Waltham, MA 02451.

19.8. Thermo Scientific Vanquish *Variable Wavelength Detectors VF-D40* Operating Manual, 4820.7701-EN, Revision 1.1a September 2017, ThermoFisher Scientific Inc., 168 Third Avenue, Waltham, MA 02451.

19.9. NLB Laboratory Quality Control Manual, Revision 4.0 2018

19.10. NLB Chemical Hygiene Plan, current version

20. Appendices

20.1. OLS-MLD022-A1: Target Compounds Validated by MLD022

20.2. OLS-MLD022-A2: Unit Equivalency of Target Analytes for MLD022

20.3. OLS-MLD022-A3: Annual LCS Verification Procedures

APPENDIX 1

OLS-MLD022-A1

Target Compounds Validated by MLD022

Compound	CAS Number (Raw)	CAS Number (DNPH-Derivatized)
Formaldehyde	50-00-0	1081-15-8
Acetaldehyde	75-07-0	1019-57-4
Propionaldehyde*	123-38-6	725-00-8
Methyl Ethyl Ketone (MEK)	78-93-3	958-60-1
n-Butyraldehyde*	123-72-8	1527-98-6
Benzaldehyde*	100-52-7	1157-84-2
Valeraldehyde*	110-62-3	2057-84-3
Hexaldehyde*	66-25-1	1527-97-5

**Indicates analyte is validated, but not reported to U.S. EPA's Air Quality System (AQS) database.*

APPENDIX 2

OLS-MLD022-A2

OLS-MLD022-A2: Unit Equivalency of Target Analytes for MLD022

Compound	MW (g/mole)	RL (ppb)	RL[a] (ug/m^3)	RL[b] (ug/sample)	RL (ug/mL)
Formaldehyde	30.03	0.10	0.12	0.12	0.025
Acetaldehyde	44.05	0.10	0.18	0.18	0.036
Propionaldehyde	58.08	0.10	0.24	0.24	0.048
Methyl Ethyl Ketone (MEK)	72.11	0.10	0.29	0.30	0.059
n-Butyraldehyde	72.11	0.10	0.29	0.30	0.059
Benzaldehyde	106.12	0.10	0.43	0.44	0.087
Valeraldehyde	86.13	0.10	0.35	0.35	0.071
Hexaldehyde	100.16	0.10	0.41	0.41	0.083

a – Reporting Limit in µg/m^3 assumes a constant flow of 0.7 L/min for 24 hours.

b – Reporting Limit in µg/sample uses a 5.0 mL extraction volume.

APPENDIX 3

OLS-MLD022-A3

OLS-MLD022-A3: Annual LCS Verification Procedures

1. Take the stock standard out of cold storage and place in work area. Allow it to warm to room temperature.
2. Obtain two unopened DNPH cartridges, ensuring that they are from two unique lots.
3. Attach a Luer-Lock syringe to each cartridge and place each setup over a clean, 5 mL, volumetric flask. It may be useful to have rack for holding the cartridge-syringe setup in place.
4. Spike 50 µL of stock standard into each syringe.
5. Flush each syringe with four 1 mL aliquots of solvent (ACN).
6. Fill each flask to the 5 mL line, stopper, and mix.
7. Place an aliquot from each flask into an autosampler vial for analysis.
8. Calculate the percent recovery (see section 15.3) to evaluate the validity of the results, using a ±30% criteria.