California Environmental Protection Agency

Air Resources Board

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF CARBONYL COMPOUNDS IN AMBIENT AIR

SOP MLD022
Revision 4.2

Northern Laboratory Branch
Monitoring and Laboratory Division

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DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedure are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used. This method is restricted to use by or under direct supervision of analysts experienced in the use of air sampling methods and analyses by high performance liquid chromatography (HPLC).

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SOP MLD022

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF CARBONYL COMPOUNDS IN AMBIENT AIR

1 SCOPE

This procedure describes the determination of formaldehyde, acetaldehyde, and methyl ethyl ketone (MEK) in ambient air utilizing 2,4-dinitrophenylhydrazine (DNPH) coated silica adsorbent followed by High Performance Liquid Chromatography (HPLC) with ultraviolet/visible (UV/VIS) detection. This method is based on the U.S. EPA Method TO-11A.[1]

2 SUMMARY OF METHOD

Ambient air is drawn through an acidified DNPH coated silica cartridge at a sampling rate of 0.7 liter per minute (LPM) for a 24-hour period (total volume sampled is 1 m^3 or 1000L +/- 10%). During sampling the formaldehyde, acetaldehyde, and methyl ethyl ketone react with the DNPH to form stable hydrazine 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 HPLC with UV absorption detection at 360 nm.

Formaldehyde and other carbonyl compounds in the sample are identified and quantified by comparison of their retention times and peak heights or peak areas with those of standard solutions. The limit of quantitation (LOQ) for carbonyl compounds is 0.1 ppbv.

3 INTERFERENCES AND LIMITATIONS

3.1 INTERFERENCES

Ozone reacts with the carbonyl compounds (aldehydes and ketones) and their derivatives causing lower detected results and chemical interferences. Therefore, ozone is removed during sampling using a pre-filter impregnated with potassium iodide (KI).

3.2 COELUTION

Possible interferences may be caused by the co-elution of other aldehydes and ketones. The HPLC column and solvent gradient used must be able to separate formaldehyde, acetaldehyde and methyl ethyl ketone from other closely eluting compounds.

3.3 CARTRIDGE IMPURITIES

Contamination or impurities in the sampling cartridge may cause elevated detection limits or concentrations. One cartridge from each lot must be analyzed to verify that the production batch meets the condition stated on the manufacturer's Certificate of Analysis and the laboratory blank criteria of less than the limit of detection (LOD).

3.4 PASSIVE SAMPLING

Passive sampling may take place if sampling cartridges are left exposed to ambient

conditions. DNPH cartridges come in sealed packaging from the manufacturer. After sampling, cartridges must immediately be returned to clean packaging and sealed to prevent exposure to sunlight which may produce artifacts and to prevent passive sampling. Samples must be kept refrigerated at 4°C until shipment to the laboratory.

Cartridges are shipped to the sample site with a cold pack at 4°C. Upon receipt at the sampling site the DNPH cartridges must be stored at 4°C until they are placed into the sampling apparatus just before the sampling event. The cartridges are allowed to equilibrate to ambient temperature for the sampling 24 hours prior to sample collection. The cartridges are removed and returned to the laboratory as soon as possible after sampling is complete. Upon receipt at the laboratory the cartridges are logged into the laboratory information management system (LIMS) and either extracted or held refrigerated at 4°C until extraction. The amount of time the sample DNPH cartridges are exposed to ambient temperature must be minimized. The DNPH cartridges are stable at ambient temperature for about 2 weeks according to vendor documentation.[2]

4 HEALTH, SAFETY AND CAUTIONS

The HPLC solvents have the highest potential for exposure to the chemist. The organic solvents used are acetonitrile, tetrahydrofuran, and methanol. The chemist performing this method must read the safety data sheets (SDS) to become familiar with the hazards before using these solvents in the laboratory. The aldehyde and ketone DNPH derivatives and DNPH contained in the cartridges are also potentially hazardous. SDS provided by the vendor for the chemical standard mixtures provide information on reactivity and toxicity. Safe laboratory procedures and personal protective equipment, (nitrile gloves, protective eye glasses or goggles, lab coat or protective apron) must be used when performing this method. A properly working hood and good laboratory practices (GLP) should be employed. The lab is equipped with an eyewash, shower, and spill kits to use if needed.

5 APPARATUS

5.1 Sampling system

A XonTech Module 920 or equivalent multi-media sampler fitted with a sampling head configured to hold the DNPH-silica cartridges and capable of sampling at a flow rate of between 0.5 and 2.0 LPM.

5.2 Analytical system

A gradient HPLC system consisting of mobile phase reservoirs; high pressure pumps; an injection valve or automatic sampler; a C-18 column (3.9 mm x 15 cm); a variable wavelength UV detector operating at 360 nm; and a data system.

5.3 Glass vials (4.0 ml) with Teflon lined screw caps to store extracts.

5.4 Auto sampler vials (1 ml) with polyethylene cap septum.

5.5 A sample rack used to hold cartridges during extraction.

5.6 5.0 ml volumetric flasks, Class A with etched serial numbers

5.7 A graduated cylinder used to mix HPLC solvents.

5.8 Nitrile gloves to handle the treated cartridges.

5.9 3.7 cm ashless cellulose filters for use as KI ozone scrubber.

5.10 Polypropylene syringe bodies (10 ml) and plungers to be used as solvent reservoirs during sample extraction.

5.11 Ring clamps used to hold the 3.7 cm cellulose filter KI ozone scrubber. Provided by XonTech for the 920 air sampler.

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

6 REAGENTS

6.1 Acetonitrile

Carbonyl-free HPLC grade acetonitrile pre-filtered by the manufacturer through a 0.1 µm filter. Used for sample extraction, standards, and HPLC mobile phase.

6.2 Tetrahydrofuran UV

For HPLC, GC, and spectrophotometry. Burdick & Jackson. HPLC mobile phase.

6.3 Methanol

Analytical grade, best source for HPLC, GC, pesticide residue analysis and spectrophotometry. Burdick & Jackson. HPLC mobile phase.

6.4 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.

6.5 Helium

Grade 5 or equivalent used as a HPLC mobile phase sparge gas.

6.6 Waters DNPH-coated silica cartridges.

6.7 Calibration Standards solutions containing mixtures of DNPH-derivatized carbonyl compounds (formaldehyde, acetaldehyde, and MEK).

6.8 Potassium iodide (KI) - A.C.S. reagent grade used as coating solution for ozone scrubber.

7 PREPARATION OF DNPH-CARBONYL STANDARDS AND OZONE SCRUBBER

7.1 Standard Preparation and Storage

7.1.1 Custom stock solutions are purchased from Cerilliant or other vendors.

7.1.2 Working standards are prepared by diluting the stock solutions with acetonitrile. The working standards should be between 0.05 µg/mL and 2 µg/mL for the initial calibration.

7.1.3 All stock solutions used for primary calibration standards have an expiration date provided by the vendor for unopened ampules. All working standards, controls, and spiking solutions prepared from the stock solutions must be replaced after 120 days from preparation.

7.2 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 twice and then letting the filter air dry. The filter is then placed in the filter holder assembly. The filter and holder assembly are stored in a petri dish at room temperature prior to shipment to the sampling site.[2]

7.3 DNPH Cartridge Preparation and Shipping

Purchased DNPH-silica cartridges are verified contaminant free by analyzing one from each manufacturing lot prior to being shipped to sampling sites. All cartridges must be stored in sealed packaging at 4°C until used for sampling. Cartridges must be used within six months from receipt by the laboratory based on manufacturer's recommendations.[2]

Prior to shipment, the cartridges are given a serial tracking number and an expiration date. The cartridge is shipped with a KI filter (ozone trap) under chain of custody (COC). The cartridge is shipped cold using cold packs ("blue ice") and stored at 4°C at the sampling site until installed in the sampler. Cartridges may not be used after the expiration date and must be returned to the laboratory for disposal.

8 SAMPLE COLLECTION

A XonTech Model 920 sampler, or equivalent, is used to draw the ambient air through the cartridges at a rate of 0.7 liters per minute for 24 hours. See the sampling Standard Operating Procedure produced by Air Quality Surveillance Branch (AQSB SOP 801 MLD DEC 2006).[3]

After sampling, the cartridges are removed from the sampler, capped (the end caps are snuggly pressed onto the exposed cartridges to prevent passive sampling), and shipped to the laboratory using cold packs. When received by the laboratory the sample cartridges are kept under refrigeration at 4°C until extraction. The KI filters are returned to the laboratory for disposal and are not reusable.

9 SAMPLE EXTRACTION AND ANALYSIS

9.1 Sample Extraction

9.1.1 Cartridges must be extracted within two weeks (14 calendar days) from the sampling date. The sample cartridges are removed from the refrigerator and allowed to equilibrate to ambient temperature for at least one hour but no more than eight hours prior to extraction. Each cartridge is removed from the sealed packaging and connected to a clean syringe body solvent reservoir.

9.1.2 The cartridge attached to a syringe body is placed in the syringe rack and extracted by gravity by adding 5 mL of acetonitrile to the syringe body. The extract is collected in a 5 mL volumetric flask. If the sample cartridge is not eluting by gravity a syringe plunger may be used to push the acetonitrile through the sample cartridge slowly at a rate of 1 mL per minute to avoid channeling. The carbonyl-DNPH analytes are very soluble in acetonitrile and are removed from the cartridge with the first few milliliters of solvent during the extraction process. Excess solvent ensures quantitative elution of all the analytes.

9.1.3 The extract is brought up to the 5 mL mark on the volumetric flask with additional acetonitrile, if needed. The volumetric flask is capped and inverted three times to mix the sample extract. The sample extract is transferred to an autosampler vial and stored at 4°C until sample analysis. The sample extract should be analyzed within 30 days from extraction.

9.2 Sample Analysis

The HPLC has been installed by the vendor in accordance to specifications provided by the manufacturer. Analysis of target compounds uses Empower software and connections to import data to the laboratory information system (LIMS) database. Refer to the manufacturer's manual for specifics of instrument operation.[4,5,6,7] Preventive maintenance is performed routinely by laboratory personal and annually by the instrument manufacturer under contract for this service. Routine diagnostics of the chromatography and sensitivity of the HPLC are performed before every analytical run and may require changing the guard column, replacing the analytical column or reagents, service visits or telephone technical support from the manufacturer.

9.2.1 The mobile phase for the HPLC is prepared as described in the work instructions associated with this SOP. Mobile phase may be premixed into separate solvent reservoirs or blended using the HPLC pump. The mobile phase is degassed before use with a helium sparge or by an inline vacuum degasser depending on the HPLC system.

9.2.2 A column heater may be used to stabilize retention times on the analytical column. The column heater should be set at least 5°C above ambient temperature. The column is equilibrated for 30 minutes at the flow rate of 1 ml/minute before the first analysis. A solvent blank is analyzed to check for interferences.

9.2.3 Daily instrument calibration is done using three different standards (0.25, 2.50, and 10.0 µg/5 ml). Linearity is indicated by a correlation coefficient (r) of at least 0.999.[8]

9.2.4 The calibration of the instrument is verified for each run by analyzing a control standard (5 µg/5mL). A new control standard is prepared from stock solutions every 120 days and when result biases indicate degradation or systematic changes in the procedure.

The analyzed concentration of the control standard must fall within the Upper Control Limit (UCL) and Lower Control Limit (LCL) of the control sample value (± 3X calculated Relative Standard Deviation or ± 15% whichever is greater).[8] Control limits are reviewed annually. New control limits are established when a new control standard is prepared and put into use.

9.2.5 A typical analytical run sequence consists of the following:

Blank (Solvent blank)
0.25 µg/ml standard
2.5 µg/ml standard
10.0 µg/ml standard
Control standard
Samples 1-10
Duplicate sample or replicate injection
Matrix spike
Control standard
Blank
(Sample runs should also include other QC samples such as field blanks, trip blanks, cartridge blanks, extraction blanks, reagent blanks, etc.)

See work instructions for operating parameters for the HPLC and preparation of mobile phase.

10 QUALITY CONTROL

10.1 Blanks and Spikes

Various blanks and spikes are used to assess the cleanliness and performance of laboratory and analytical systems as described below. See Table 1 for a summary of acceptance criteria.

~~10.1.1~~ Cartridge Blanks

The cartridge blank is an unused cartridge that is analyzed as a contamination check prior to using cartridges from a particular manufacturing lot. The cartridge blank is also used to verify the “Certificate of Analysis” from the manufacturer. One cartridge from each production lot must be analyzed for impurities prior to use. The cartridge blanks must not contain:

Formaldehyde	>0.15µg/cartridge
Acetaldehyde	>0.10µg/cartridge
Acetone	>0.30µg/cartridge
MEK	>0.10µg/cartridge

If the lot fails all cartridges will be returned to the manufacturer for replacement and a new lot of cartridges will be tested for use.

10.1.2 Extraction Blanks

The extraction blank is an unused DNPH cartridge retained in the laboratory and is from the same lot number as those shipped to the sampling sites. Extraction blanks also

confirm and verify the COA provided with each cartridge lot throughout its use. The extraction blank results are tracked to certify that the sample DNPH cartridges meet sampling criteria for background levels. An extraction blank is prepared and analyzed with each batch of samples and is treated just as all other samples. The extraction blank should have no target compounds that exceed:

Formaldehyde	>0.15µg/cartridge
Acetaldehyde	>0.10µg/cartridge
Acetone	>0.30µg/cartridge
MEK	>0.10µg/cartridge

If the extraction blank concentration exceeds these amounts it must be reanalyzed to confirm results and an investigation to find possible sources of contamination will be performed. Samples associated with this blank can be invalidated or have background correction performed.

10.1.3 Field Blanks

A field blank is an unused DNPH cartridge sent to the field and connected to the sampler but no air is drawn through the cartridge. This blank assesses any contamination that may have occurred during shipping and sample handling. Field blanks are collected on a rotating basis among network monitoring sites and should represent 10% of the sample sites. The field blank is extracted and analyzed just as all other samples. The field blank cartridges should not contain any analyte with concentrations greater than:

Formaldehyde	> 0.30µg/cartridge
Acetaldehyde	> 0.40µg/cartridge
Acetone	> 0.75µg/cartridge
Sum of other carbonyls	> 7.00µg/cartridge

If the concentrations exceed these levels an investigation is warranted. As corrective action, additional field blanks will be sent to the site and monitored until criteria are met. Field blank results will be compared to trip blank results to identify potential sources of sample contamination.

10.1.4 Trip Blanks

Trip blanks are unused DNPH cartridges sent to a field site and then returned without exposure. Trip blanks are collected on a rotating basis among network monitoring sites and should represent 10% of the sample sites. The blank cartridges should not contain any analyte with concentrations greater than:

Formaldehyde	> 0.15µg/cartridge
Acetaldehyde	> 0.10µg/cartridge
Acetone	> 0.30µg/cartridge
MEK	> 0.10µg/cartridge

If the concentrations exceed these levels an investigation is warranted and corrective actions will be taken. Sample shipping and handling practices will be examined for possible contributions to background contamination.
Trip blanks and field blanks are used to determine where contamination may be occurring in the sampling event. Comparing the results of trip blanks, field blanks, and extraction blanks may indicate problems in sampling and will be used to correct or resolve sample contamination issues.

~~10.1.5~~ Solvent Blanks

A solvent blank must be analyzed before any standard or sample is analyzed. The solvent blank must not contain formaldehyde, acetaldehyde, or MEK at concentrations greater than the LOD. The solvent blank is a check for interferences that may be detected by the UV detector at 360 nm. If the solvent blank fails, the HPLC solvents are discarded and replaced with fresh HPLC solvents from a new unopened bottle. The solvents are filtered and the solvent blanks are reanalyzed for interferences. If the solvent blank analysis fails again solvents from different lots are analyzed to verify contamination. The HPLC system is investigated for potential contributions to the solvent blank failure such as guard column, HPLC column, and other chromatographic issues. If warranted, based on instrument adjustments or other corrective actions, an initial calibration is analyzed before sample analyses resume.

10.1.6 Spikes

A matrix spike sample and blank spike sample are analyzed with every ten field samples. A matrix spike sample is prepared by adding a known amount of standard to a sample extract. The sample to be spiked is chosen at random. A blank spike sample is an aliquot of solvent that is spiked with a known amount of standard. The blank spike will not have any sample matrix effects. The spiked samples are analyzed and spike recoveries are calculated. Recoveries must be between 70% and 130% to be valid. See section 10.8 for calculations. If the percent recovery is outside this range, the chromatogram is examined for chemical interferences. The matrix spike chromatogram results are compared to the blank spike analysis. If it is determined that the matrix is not affecting the recoveries, a new matrix spike must be prepared and analyzed along with a reanalysis of all samples following the last valid spike. Report and compare all results and flag the data as needed.

10.2 Initial Multipoint Calibration

A multipoint calibration must contain a minimum of five different concentrations that bracket the expected ambient levels. Each concentration level is analyzed a minimum of 3 times. The calibration curve is linear when the least-squares fit “r” is 0.98 or greater.

A multipoint calibration is required to be performed at least annually and under the following conditions:

a.) When the column is changed.
b.) When major instrument maintenance is performed.

c.) When there is a major modification to the instrumentation or standard operating procedure.
d.) When there is a change in the matrix or a reagent.

10.3 Dilutions

When a sample has an analyte concentration greater than 10% over the highest calibrated standard, the sample extract must be diluted and reanalyzed. The dilution should be greater than 50% of the upper calibrated range. The concentration must fall within the calibration range to be considered a valid analysis. Final results must take into account the dilution factor.

10.4 Limit of Detection (LOD) Verification

The LOD must be verified on an annual basis, and when the same conditions as listed under the multipoint calibration verification occur. The LOD is performed using criteria based on 40 CFR Part 136, Appendix B.[9] This is done by analyzing a minimum of seven replicates of a solution containing the target analytes at a concentration of 1 to 5 times the expected LOD.

The LOD is calculated using the following equation, as specified in the Northern Laboratory Branch's Quality Control Manual[8] and 40 CFR Part 136, Appendix B[9]:

LOD = t (n-1, 1-α = 99%) * S
t (n-1, 1-α = 99%) = student's T-distribution value at n-1 degrees of freedom
n is the number of replicates
n= at least 7
t= 3.143
s = standard deviation

Example Calculated LOD and LOQ

Target Compound	Calculated LOD	Calculated LOD	Limit of Quantitation (LOQ)	Limit of Quantitation (LOQ)
	(µg/cartridge)	(ppbv)	(µg/cartridge)	(ppbv)
Formaldehyde	0.0069	0.0054	0.1	0.1
Acetaldehyde	0.0048	0.0026	0.1	0.1
MEK	0.0094	0.0032	0.1	0.1

All subsequent LOD verifications should be at least 3 times less than the limit of quantitation (LOQ). The LOQ for target analytes is based on the LOD and is the lower level where measurements become quantitatively meaningful at the 99% probability level. LOQ = 10 x s where s is the standard deviation of the lowest standard.

Formaldehyde and acetaldehyde LOQ must be equal to or less than 0.1 ppbv. If the LOD does not achieve the required LOQ, examine the HPLC system and detector for hardware problems that require repair. Failing the LOD indicates that the HPLC system is

unsatisfactory for analysis. No further analysis may be performed on the HPLC until the system passes the LOD. Note that the sample size required is one cubic meter of air and the LOQ is dependent on the sample size.

10.5 Daily Calibration

A three-point calibration curve is calculated for each analytical run by analyzing calibration standards with concentrations 0.25, 2.50, and 10.0 µg/5 mL as aldehyde or ketone. Linearity is indicated if the correlation coefficient is 0.98 or greater. If the daily calibration fails corrective action must be taken. Inspection of the chromatography, instrument parameters, instrument operation, and preparation of fresh solvent mixtures or standards may need to be performed. All samples associated with the failed daily calibration must be reanalyzed under an acceptable daily calibration.

10.6 Control Standard

A control standard is a standard obtained from a second source whose analytical results are recorded and used to generate control charts. The upper and lower control limits are set at ± 3 times the calculated standard deviation (s) from the average. The upper and lower warning limits are set at ± 2 times the calculated s from the average. This provides minimum upper and lower control limits of ± 15% and upper and lower warning limits of ± 10%. Control standard results must be within the established upper and lower control limits for the analytical run to be valid. If the control limits are exceeded, then the problem must be investigated and resolved. All samples in an analytical run must be bracketed by control standards that meet the control limits or must be reanalyzed. Control standards are charted to monitor for trends. If 7 consecutive control results are trending in a single direction, new control standards must be made and new control limits must be established.

10.7 Method Precision

Sample precision is measured by the replicate analysis of ambient samples. Replicates must be analyzed at a rate of 10%. The maximum allowable percent difference (PD) for the replicate results is ± 15% for formaldehyde, acetaldehyde, and MEK. If the replicate analysis fails to meet criteria repeat the replicate analysis and all samples associated with the replicate. Chromatograms must be reviewed for possible chemical interference and sample injection problems.

10.8 Method Accuracy

Method accuracy is determined by measuring the recovery of a spiked sample (see 10.1.6 spikes). A spiked sample is prepared by placing 950 µL of an extracted sample into an autosampler vial and adding 50 µL of the spiking standard. The concentration of the spiking standard is 10 µg/mL. The percent recovery is calculated as follows:

$$\text{Percent Recovery} = \frac{(M1 - M2) * 100}{C}$$

M1 = Measured conc. of spiked sample (ug/5 mL)

M2 = Measured sample conc. (ug/5mL)
C = Actual conc. of spike (2.5 µg/5 mL)

For a valid spike analysis, the percent recovery must be between 70 and 130 percent. If the percent recovery is outside this range, prepare a new spiked sample and analyze along with all samples following the last valid spike.

11 CALCULATIONS

Concentrations are reported as parts per billion by volume (ppbv) and are calculated as follows:

$$ppbv = \frac{(24.46\ L/mole * 10^9) * G}{MW * V}$$

G = Net mass of carbonyl in grams (g)
V = volume of air collected in liters (L)
MW = molecular weight of carbonyl (grams/mole)

Molecular Weights

Formaldehyde	30.03 g/mole
Acetaldehyde	44.05 g/mole
MEK	72.11 g/mole

When G is expressed in micrograms (µg) it simplifies the conversion of PPBC to PPBV as follows:

G = (Sample concentration as µg/mL) * (extract volume in mL)

$$PPBC = \frac{(G\ \mu g) * (1000\ L)}{(\text{sample volume in L}) * (m^3)} = \mu g/m^3$$

$$PPBV = \frac{(PPBC\ in\ \mu g/m^3) * R\ (L/mole)}{MW\ (g/mole)} * 1{,}000{,}000{,}000 = \frac{PPBC * 24.46}{MW}$$

Example Calculation for Formaldehyde

Where:
R = gas constant at standard temperature and pressure = 24.46 L/mole
(Temperature = 25°C and Atmospheric Pressure = 1 atm)[10]
Extract Volume = 5 mL
Sample Volume = flow rate /sampling time = 0.7 L/min for 24 hours = 1008 L
Molecular Weight MW = 30.03 g/mole

G = (1.783 µg/~~mL~~) * (5 ~~mL~~) = 8.915 µg

$$PPBC = \frac{(8.915\ \mu g) * (1000\ L)}{(1008\ L) * (1\ m3)} = 8.844\ \mu g/m3\ \text{(PPBC) Formaldehyde}$$

$$PPBV = \frac{(8.915\ \mu g)*(1000\ L)*(24.46\ L/mole\ (\ 1mg\ )*(1\ g)*(1m3)\ *\ \cancel{1000000000}}{(1008\ L)\ *(1\ m^3)\ (30.03\ g/mole)*(\cancel{1000}\ \mu g)*(\cancel{1000}mg)*\ (\cancel{1000}\ L)}$$

= 7.20 PPBV Formaldehyde

OR

$$PPBV = \frac{PPBC * R}{MW} = \frac{8.8442\ PPBC * 24.46}{30.03} = 7.20\ PPBV\ Formaldehyde$$

12 DATA MANAGEMENT AND REPORTING

All results are verified by peer and management review. The results are then sent to the Laboratory Information Management System (LIMS) for archive and reporting. Data for the ambient toxics program are transferred from LIMS to the US EPA Air Quality System (AQS) database for public access.

13 WASTE DISPOSAL

KI filters used as an ozone trap in series with a DNPH silica cartridge are discarded as solid lab waste.

The expired or unused DNPH cartridges are extracted with 5 mL acetonitrile to remove unreacted DNPH. The extract is disposed in the lab solvent waste stream. The extracted DNPH cartridges are disposed as solid lab waste.

1 Table 1: CARB MLD022 Summary of Carbonyl Quality Control Procedures

Parameter	QC Check	Frequency	Acceptance Criteria	Corrective Action
HPLC Column Efficiency	Analyze Control sample	At setup and 1 per sample batch	Resolution between acetone and propionaldehyde, 1.0 Column efficiency >5000 plate counts	Eliminate dead volume, back flush or replace the column: repeat analysis
Linearity Check	Run a 5-point calibration curve	At setup, annually, and when calibration check is out of acceptance	Correlation coefficient, 0.999, relative error for each level against calibration curve +/- 20% or less relative error	Check integration, reintegrate or recalibrate
Retention Time	Analyze Control	Once per 12 hours or less	Acetaldehyde within retention time window established by determining 3 sigma or +/- 2% of the mean calibration and midpoint standards, whichever is greater	Check system for plug, regulate column temperature; check gradient and solvents
Calibration Check	Analyze Control	Once per 12 hours or less	84 to 115% recovery	Check integration, recalibrate or prepare standard, reanalyze samples not bracketed by acceptable standard
Calibration Accuracy	Analyze Control	Once after calibration in triplicate	85 to 115% recovery	Check integration, recalibrate or prepare standard, reanalyze samples not bracketed by acceptable standard
Sensitivity	LOD study	Determined annually, or after any major instrument change. Minimum of 7 low level cartridge standards analyzed over a 2-day period (minimum)	Formaldehyde: 0.100 ug/m3 Acetaldehyde: 0.100 ug/m3	
System Blank	Analyze acetonitrile	Bracket sample batch,1 at beginning and 1 at end of batch	Measured concentration, less than LOQ	Locate contamination and document levels of contamination in file
Lot Blank Check Certificate of Analysis	Analyze blank cartridge for new lots	Every lot received and at least one per batch of 20 samples	Compounds must be less than values listed: Formaldehyde <0.15 ug/cartridge Acetaldehyde <0.10 ug/cartridge Acetone <0.30 ug/cartridge Others <0.10 ug/cartridge	Analyze another cartridge. Notify vendor if lot blank continues to fail. Failed lots are not used for sampling
Extraction Blank	Analyze extraction blank	Extraction Batch	Compounds must be less than values listed: Formaldehyde <0.15 ug/cartridge Acetaldehyde <0.10 ug/cartridge Acetone <0.30 ug/cartridge Others <0.10 ug/cartridge	Perform blank correction for extraction batch for concentrations greater than values listed.

Replicate analysis	Replicate injections	Every ten samples	<10% RPD for concentrations greater than 0.5 ug/cartridge	Check integration, check instrument function, reanalyze duplicate samples an check for matrix effects or bad injections
Matrix spike	Analyze MS, using calibration standard	One MS per batch of 20 samples	70 to 130% recovery for Formaldehyde, Acetaldehyde, and MEK	Check calibration, check extraction procedures
Precision	Collocated Samples	Every sampling event	<15% CV (Coefficient of Variation)	Notify site operator

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3 SOP MLD 022 REVISION HISTORY

Revision Number	Revision Date	Effective Date	Revisions Made
1.0			
2.0	January 9, 1991	April 4, 1991	
3.0			
4.0	January 1, 1996	March 27, 1996	
4.1	October 5, 1998	January 1, 2001	
4.2	June 1, 2014	June 1, 2014	Addressed findings from 2011 EPA TSA Audit including dilutions, holding times, field and trip blanks, standards and expiration dates.