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Carbonyl Compounds - EPA Method TO-11A

1 Scope and Application

Method TO-11A is used to determine the concentrations of various Carbonyl compounds in ambient air samples collected on sorbent DNPH coated cartridges. Acetonitrile is used to extract Carbonyl compounds from the cartridges. The extract is injected in a high-pressure liquid chromatograph equipped with an ultraviolet absorbance detector. Identifications are obtained by analyzing a standard curve under identical conditions used for samples and comparing resultant retention times. Analytes are quantitated by relating the response produced for that compound to the standard curve response.

2 Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control definitions.

2.2 Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3 Second Source (SS) – A standard made from another manufacturer other than that of the primary source.

2.4 Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary sources calibration curve. The ICV is run a level equal to that of a Laboratory Control Sample (LCS) or that of a point on the calibration curve.

2.5 Collocated Sample Collection – Collocated samples are samples collected simultaneously using two completely separate sampling systems and then analyzing the samples and comparing the results obtained. This approach provides information on "Inter-system" variability.

2.5.1 The sample collectors designate which sample is "Primary" and which sample is "Collocated or QA." The EPD lab will follow this designation and label the first of these samples as the "Primary Sample" and the second as the "Collocated Sample or Duplicate."

2.6 Duplicate Sample Collection – Duplicate samples are samples collected simultaneously using one collection system (i.e., two separate samples through the same sampling system at the same time), and then analyzing the samples and comparing the results obtained. This simultaneous collection is typically

accomplished by teeing the line from the flow control device to the canisters, and then doubling the collection flow rate. This approach provides information on "Intra-system" variability.

2.7 Replicate Analysis – Replicate analyses is the analysis of one discrete sample multiple times. These are also known as "split" sample analyses. This approach provides information on "Analytical" variability.

3 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and chromatograms.

3.1.1 Glassware must be scrupulously cleaned with hot water and detergent followed by de-ionized water then rinsed with Acetonitrile and allowed to air dry.

3.1.2 The manifold is rinsed with Acetonitrile prior to sample analysis.

3.1.3 The use of high purity reagents and solvents helps minimize interference problems.

3.1.4 Plastics should never be used at any point in this analysis.

3.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes.

3.2.1 When contamination from one chromatography run to the next is suspected samples are reanalyzed employing the use of any necessary dilutions and solvent blanks to eliminate the problem.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample.

4 Safety

4.1 Refer to Laboratory Chemical Hygiene Plan, online revision.

5 Apparatus and Equipment

5.1 High Pressure Liquid Chromatograph (HPLC): HPLC system capable of injecting aliquots of a set volume and performing linear gradients at a constant flow

5.2 Chromatography software: Totalchrom or equivalent

5.3 Binary pump, flow rate 1-2mL/min

5.4 UV/Vis spectrophotometric detector, 360 nm

5.5 Auto Sampler

5.6 Deltabond AK 200 x 4.6 mm column or equivalent

5.7 Vacuum manifold: Waters sep pak

5.8 Cartridges: DNPH coated, Supelco or equivalent

5.9 Culture tubes: 8mL, 10mL and 30mL

5.10 Syringes: Various. Typically 50µL, 100µL and 1mL

5.11 Pipets: Disposable 5¼ inch or equivalent

5.12 Solvent squeeze bottles

5.13 Volumetric flasks, Class A: 10mL, 25mL

5.14 Autosampler vials: 2mL with snap caps

5.15 Centrifuge Tubes, Class A: 15mL, graduated

6 Reagents and Standards

6.1 Acetonitrile: HPLC grade or equivalent

6.2 Reagent water: HPLC grade or equivalent

6.3 Acetonitrile/Water: 60:40, v/v
6.4 Detergent: Steris Labklenz or equivalent
6.5 Stock standard solution: Stock standard solutions are prepared for EPA Method TO-11A using industry standards.
6.6 Calibration Standards: Dilutions made from the stock standard solutions.
6.7 Initial Calibration Verification Standard (ICV): A standard solution that is prepared from a second source vendor's standards. This standard is equivalent to a mid-point standard on the calibration curve.
6.8 All standards made for TO-11A analysis are to have an expiration date six months from the opening of the vendor stock ampule or the manufacturer's expiration date if less than six months from opening.
6.9 QC spiking Standard
6.9.1 To make the LCS/LCSD spike, dilute 1mL of vendor stock (see Table 6.10.3.1) in 5mL Acetonitrile final volume. The final concentration in LCS samples at 10mL is equivalent to Standard 2 in Table 6.10.3.6.
6.10 Calibration Standards
6.10.1 Do not assume that the vial that is marked as one milliliter actually contains a volume of 1mL.
6.10.1.1 All Stock Standards are stored separately from samples and protected from light at 4°C or less (not frozen).
6.10.2 Use a pipette or a syringe to accurately measure the amount that you intend to use.
6.10.3 Dilutions are used to produce a calibration curve in the following manner:
6.10.3.1 Calculations shown are in terms of Formaldehyde.

Table 6.10.3.1 (Vendor Stock)

Formaldehyde-DNPH	1500µg/mL	Propionaldehyde-DNPH	500µg/mL
Acetaldehyde-DNPH	1000µg/mL	Butyraldehyde-DNPH	500µg/mL
Acetone-DNPH	500µg/mL	Benzaldehyde-DNPH	500µg/mL

6.10.3.2 The recommended preparation of the standards is as follows:

Stock Solution A:
150µg/mL = 1mL of Carbonyl vendor stock standard in 10mL of Acetonitrile
Stock Solution B:
60µg/mL = 4mL of 150µg/mL Carbonyl standard in 10mL of Acetonitrile
Stock Solution C:
15µg/mL = 1mL of 150µg/mL Carbonyl standard in 10mL of Acetonitrile

Standard Curve (as Formaldehyde derivative) in 100% Acetonitrile:
12.0µg/mL = 2.0mL of Stock A in 25mL of Acetonitrile
6.00µg/mL = 1.0mL of Stock A in 25mL of Acetonitrile
2.40µg/mL = 0.40mL of Stock B in 10mL of Acetonitrile
1.20µg/mL = 0.20mL of Stock B in 10mL of Acetonitrile
0.60µg/mL = 0.40mL of Stock C in 10mL of Acetonitrile
0.30µg/mL = 0.20mL of Stock C in 10mL of Acetonitrile

Table 6.10.3.2

	Formalde-Hyde	Acetalde-hyde	Acetone	Propion-aldehyde	Butyr-aldehyde	Benz-aldehyde
Std	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**
1	12.0	8.00	4.00	4.00	4.00	4.00
2	6.00	4.00	2.00	2.00	2.00	2.00
3	2.40	1.60	0.80	0.80	0.80	0.80
4	1.20	0.80	0.40	0.40	0.40	0.40
5	0.60	0.40	0.20	0.20	0.20	0.20
6	0.30	0.20	0.10	0.10	0.10	0.10

6.10.3.3 Standard Curve (as Formaldehyde derivative) in 60:40 ACN and H_2O:

6.00µg/mL = dilute 5mL of 12.0µg/mL ACN standard + 1mL 100% ACN with 4mL of reagent H_2O
3.00µg/mL = dilute 5mL of 6.00µg/mL ACN standard + 1mL 100% ACN with 4mL of reagent H_2O
1.20µg/mL = dilute 5mL of 2.40µg/mL ACN standard + 1mL 100% ACN with 4mL of reagent H_2O
0.60µg/mL = dilute 5mL of 1.20µg/mL ACN standard + 1mL 100% ACN with 4mL of reagent H_2O
0.30µg/mL = dilute 5mL of 0.60µg/mL ACN standard + 1mL 100% ACN with 4mL of reagent H_2O
0.15µg/mL = dilute 5mL of 0.30µg/mL ACN standard + 1mL 100% ACN with 4mL of reagent H_2O

6.10.3.4 These standards should be placed in clearly marked 10mL vials for storage in a refrigerator, away from samples and protected from light, at 4°C or less (not frozen). The concentrations of the standards as derivatives in 60:40 Acetonitrile and Water are:

Table 6.10.3.4

	Formalde-hyde	Acetalde-hyde	Acetone	Propion-aldehyde	Butyr-aldehyde	Benz-aldehyde
Std	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**
1	6.00	4.00	2.00	2.00	2.00	2.00
2	3.00	2.00	1.00	1.00	1.00	1.00
3	1.20	0.80	0.40	0.40	0.40	0.40
4	0.60	0.40	0.20	0.20	0.20	0.20
5	0.30	0.20	0.10	0.10	0.10	0.10
6	0.15	0.10	0.05	0.05	0.05	0.05

6.10.3.5 Standards as Carbonyls in 60:40 Acetonitrile and Water:
µg/ml Carbonyl = µg/mL Carbonyl Derivative
× (Molecular Weight Carbonyl/Molecular Weight Carbonyl Derivative)
For example: µg/mL Formaldehyde =
6µg/mL Formaldehyde DNPH × (30.0g/ (198.1-3+30-16g)) = 0.858µg/mL

Molecular Weight	DNPH	= 198.1
Molecular Weight	Formaldehyde	= 30.0
Molecular Weight	Acetaldehyde	= 44.05
Molecular Weight	Acetone	= 58.08
Molecular Weight	Propionaldehyde	= 58.08
Molecular Weight	Butyraldehyde	= 72.11
Molecular Weight	Benzaldehyde	= 106.12

Constants can be calculated from the second half of the equation, as there is no change in the equation for the exception of the concentration of the Carbonyl derivative. They are calculated for the seven analytes in the following manner:

Formaldehyde:
30.00g/ (198.1-3 + 30.00-16g) = **0.143**

Propionaldehyde:
58.08g/ (198.1-3+58.08-16g) = **0.244**

Acetaldehyde:
44.05g/ (198.1-3 + 44.05-16g) = **0.196**

Butyraldehyde:
72.11g/ (198.1-3+72.11-16g) = **0.287**

Acetone:
58.08g/ (198.1-3 + 58.08-16g) = **0.244**

Benzaldehyde:
106.12g/ (198.1-3+106.12-16g) = **0.372**

These can be used to calculate concentrations of standards as Carbonyls:
6.0µg/mL Formaldehyde DNPH × (0.143) = 0.858 µg/mL Formaldehyde

The concentrations of the standards as carbonyls in 60:40 Acetonitrile and Water are:

Table 6.10.3.5

	Formalde-hyde	Acetalde-hyde	Acetone	Propion-aldehyde	Butyr-aldehyde	Benz-aldehyde
Std	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**
1	0.858	0.784	0.488	0.488	0.574	0.744
2	0.429	0.392	0.244	0.244	0.287	0.372
3	0.172	0.157	0.0976	0.0976	0.115	0.149
4	0.0858	0.0784	0.0488	0.0488	0.0574	0.0744
5	0.0429	0.0392	0.0244	0.0244	0.0287	0.0372
6	0.0214	0.0196	0.0122	0.0122	0.0144	0.0186

The above concentrations should be used in the method producing a calibration curve in order to report the amounts found in samples, quality controls, Blanks, etc. in terms of µg/mL Carbonyl.

6.10.3.6 The adjusted amounts (µg/cartridge Carbonyls) used in the methods are:

Table 6.10.3.6

	Formalde-hyde	Acetalde-hyde	Acetone	Propion-aldehyde	Butyr-aldehyde	Benz-aldehyde
Std	**µg/cart**	**µg/cart**	**µg/cart**	**µg/cart**	**µg/cart**	**µg/cart**
1	8.58	7.84	4.88	4.88	5.74	7.44
2	4.29	3.92	2.44	2.44	2.87	3.72
3	1.72	1.57	0.976	0.976	1.15	1.49
4	0.858	0.784	0.488	0.488	0.574	0.744
5	0.429	0.392	0.244	0.244	0.287	0.372
6	0.214	0.196	0.122	0.122	0.144	0.186

6.11 Calibration Verification

6.11.1 Second Source Calibration Standard

6.11.2 A second source calibration verification standard (ICV) is run after every calibration curve in order to verify the concentration of the calibration standards. See Section 11.7, Calculations.

6.11.3 The ICV is made from a Second Source Stock A (see 6.10.3.2).

6.11.3.1 To make the 6µg/mL Second Source ICV standard, dilute 1mL of the Second Source Stock A in 25mL Acetonitrile final volume.

6.11.3.2 Dilute 5mL of the 6µg/mL ICV standard with 1mL ACN and 4mL of reagent water to make the ICV equivalent to Standard 2 (3.00µg/mL) on Table 6.10.3.4 in µg/cartridge.

6.11.3.3 The final concentration of the 3.00µg/mL ICV is equivalent in concentration to Standard 2 on Table 6.10.3.6 when analyzed on the HPLC.

6.11.4 Continuing Calibration Standard

6.11.4.1 To make the 3.00µg/mL Daily Calibration Verification Standard (CCC) at a concentration equivalent to Standard 2 on Table 6.10.3.4, dilute 1mL of Standard 1 on Table 6.10.3.2 (12µg/mL) into 1.4mL of Acetonitrile then add 1.6mL of reagent water totaling 4mL 60:40 Acetonitrile and Water and mix thoroughly.

6.11.4.2 The final concentration of the 3.00µg/mL CCC is equivalent to Standard 2 on Table 6.10.3.6 when analyzed on the HPLC.

6.12 MDL Spike

6.12.1 The MDL Spike concentration must be below the lowest point on the curve. Typically, the MDL spike is made by diluting curve Standard 4 on Table 6.10.3.2 by 1:10 and spiked at a volume of 100µL. The final MDL sample volume is 10 mL. See Table 6.12.1 for actual MDL spike concentrations.

Table 6.12.1

	Formalde-hyde	Acetalde-hyde	Acetone	Propion-aldehyde	Butyr-aldehyde	Benz-aldehyde
Std	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**
MDL	0.0858	0.0784	0.0488	0.0488	0.0574	0.0744

7 Sample Collection

7.1 Refer to Chapter 5 of the Georgia EPD Laboratory Quality Assurance Manual for sample container, sample preservation and sample holding times.

7.1.1 TO-11A samples are cooled and stored at 4°C or less (not frozen) from collection and have a 14 day hold time from the collection date to be extracted and a 30 day hold time for HPLC analysis from the extraction date.

8 Calibrations

8.1 Calibration Curve

8.1.1 A six-point calibration is performed for all single peak components. The calibration system uses traceable certified standards. The calibration is an external standard calibration with an "average of response factor linear curve fit" and should result in a percent relative standard deviation of less than 20% between calibration levels for each analyte or linear calibration using least squares regression with a correlation coefficient r of 0.999 (or r^2 of 0.998) or better. An alternate source standard is used to verify initial calibration of the measurement system.

8.1.2 The curve calibration must not pass through the origin.

8.1.3 Quadratic Fit (Second Order) is not a calibration curve option for this method.

8.2 Record Keeping

8.2.1 Documentation of an instrument calibration is reviewed for adherence to quality criteria and archived with the project records.

8.3 Daily Calibration Verification and Continuing Calibration

8.3.1 A continuing calibration standard ensures the instruments target compound retention times and quantitation parameters meet method performance criteria. Prior to sample analysis and after every 10 samples, a one-point daily continuing calibration verification is performed. Continuing calibration standards are analyzed during the analysis period to verify that instrument calibration accuracy does not exceed ±15% of the initial calibration.

8.4.1 Evaluation of the Linearity of the Initial Calibration

8.4.2 To evaluate the linearity of the initial calibration, calculate the mean response factor ($\overline{RF}$), the standard deviation (SD) and the relative standard deviation expressed as a percentage. If the RSD of the calibration or response factors is less than 20% over the calibration range, then linearity through the origin may be assumed, and the average calibration or response factor may be used to determine sample concentrations. See Section 11.9, Calculations

8.5 Verification of Linear Calibrations

8.5.1 Calibration verification for linear calibrations involves the calculations of % drift of the instrument response between the initial calibration and each subsequent analysis of the verification standard. The % drift may be no more than ± 20%. See Section 11.7, Calculations

8.6 Linear Calibration using First Order Least Squares Regression

8.6.1 Linearity through the origin cannot be assumed in a linear least squares fit. For this method the intercept of the calibration curve must not pass through the origin. The instrument responses versus the concentrations of the standards for the six points is done using the instrument data analysis software and the regression will produce the slope and intercept terms for a linear equation. The regression calculation will generate a correlation coefficient r that is a measure of "goodness of fit" of the regression line to the data. A value of 1.0 is a perfect fit. TO-11A requires a fit of 0.999 (or r^2 of 0.998) or better. See Section 11.4, Calculations

8.6.2 Quadratic Fit (Second Order) is not a calibration curve option for this method.

8.7 Retention Time Windows

8.7.1 The width of the retention time window for each analyte, surrogate and major constituent in multi-component analytes is defined as 3 times the standard deviation of the mean absolute retention time established over a 72 hour period. See Section 11.5, Calculations

8.8 Daily Retention Time Update

8.8.1 Retention Times (RT) are updated once per analytical sequence when ran on an HPLC for TO-11A analysis at the beginning of the analytical sequence then again after each 24 hour period. The initial daily CCC is processed using Totalchrom software. The new RTs are saved in a copy of the Totalchrom method used for analyzing this batch of samples. To the existing Totalchrom method an extension is added by using "Month-Day-Year." Then hard copies of the calibration parameters are added to the data package for that batch of samples. (NOTE: If an analytical sequence is stopped for any reason longer than a typical work shift, a new retention time update is necessary for the next sequence.)

8.9 Sample Concentration

8.9.1 Sample results are expressed in µg/cartridge, see Section 11.1, Calculations

9 Quality Control

9.1 Refer to Appendix A – MDLs and RLs for Method TO-11A, Table 14.1 for MDLs and RLs.

9.1.1 A Method Detection Limit study for all analytes must be performed initially, after major instrument repairs or changes to extraction procedures. MDL studies performed for these purposes can be done by the extraction and analysis of 7 samples and 7 blanks over 3 separate days.

9.1.2 The 7 MDL sample study is performed by extracting 7 spiked DNPH cartridges, MDL_{Spike}, spiked below the lowest point of the curve and extracted along with 7 Blank DNPH cartridges, MDL_{Blank}. These sets of spiked and blank DNPH cartridges are extracted over 3 separate days and analyzed over a period of 3 separate days. There is a non-analysis day between each of the 3 days. A total of 14 DNPH cartridges are extracted, 7 spiked and 7 blank.

9.1.3 **On a continuous basis,** MDLs are performed by extraction and analysis of one DNPH cartridge spiked as an MDL_{Spike}, below the lowest point of the curve and extracted with every batch of samples along with the method blank DNPH cartridge, MDL_{Blank} per each batch of samples. The results of the MDL_{Spike} and MDL_{Blank} will be entered into LabWorks using the blank test code $B_TO11A, and the MDL test code, $MLTO11A, and the MDL Spiked Amount, $MATO11A. The MDL and MDL Blank analysis will be selected by using the highest values between instruments PE HPLC 01 and PE HPLC 02. MDL reports

will be pulled from LabWorks at a minimum of once per year (See SOP reference 13.6).

9.1.4 Tier 1 NATTS compounds Formaldehyde and Acetaldehyde must meet 10^{-6} Cancer Risk MDL MQO, See Table 9.1.4

Table 9.1.4 NATTS MDL MQO

Analyte	Cancer Risk 10^{-6} µg/m^3	MDL MQO µg/m^3	MDL µg/cartridge
Formaldehyde	0.08	0.08	See Appendix A
Acetaldehyde	0.45	0.45	See Appendix A

9.1.5 The higher value of the 2 MDLs, MDL_{Blank} or MDL_{Spike} will be used as the reporting MDL.

9.1.6 If the MDL_{Spike} is used the following must be true for the MDL to be valid: MDL < Spike Amount < 10 x MDL

9.2 Refer to Table 14.2 for Quality Assurance criteria.

9.3 Refer to Table 14.2.1 for Primary/Co-Location and Replicate criteria.

9.4 Refer to Reference 13.4 for training and certification procedures.

9.5 Refer to Reference 13.6 for annual MDL procedures.

10 Procedure

NOTE: To avoid acetone contamination, carbonyl samples are extracted in a dedicated hood.

10.1 Remove the sample DNPH-silica cartridges, blank QC cartridges, standards, and reagents from cold storage and allow them to equilibrate to room temperature prior to sample preparation and/or analysis, approximately 30 minutes.

10.1.1 Analysts must wear vinyl or nitrile gloves while handling DNPH cartridges.

10.1.2 Ink must not be used to label any part of the cartridge or cartridge envelope.

10.2 The manifold and culture tubes are cleaned and rinsed with acetonitrile prior to extraction. See Sections 3.1.1 and 3.1.2, Interferences

10.3 A DNPH-silica cartridge is used to collect an ambient air sample in the field.

10.4 A Blank, LCS/LCSD and MDL, using new cartridges, are extracted with every batch of 20 samples or less. (Batches are open for a 24 hour period.)

10.4.1 The LCS, LCSD and MDL will be spiked 30 minutes prior to sample extraction.

10.5 The LCS/LCSDs are both spiked with 100µL of a known concentration spiking solution equivalent to Standard 2 in Table 6.10.3.2 and allowed to sit on the manifold for 30 minutes prior to extraction. The cartridges must be re-capped with the cartridge plug during the 30 minute standing time.

10.6 The MDL is spiked with 100µL of a known concentration spiking solution equivalent to 1:10 Standard 4 in Table 6.10.3.2 and allowed to sit on the manifold for 30 minutes prior to extraction. The cartridge must be re-capped with the cartridge plug during the 30 minute standing time.

10.7 A Primary sample and Collocated Duplicate sample as well as a Replicate of the Collocated Duplicate sample will be analyzed with for 10 samples or less if available.

10.7.1 If there is not enough Primary or Collocated samples for each 10 samples, a NATTS sample will be analyzed with a Replicate.

10.7.2 The percent RPDs between the LCS and LCSD, the percent RPDs between the Primary and Collocated samples and the percent RPDs between the Collocated sample and its Replicate and the Primary sample and the Replicate will be calculated using approved and secured spreadsheets found on the S: Drive and included with the associated data package. They will also be entered and calculated in the laboratory LIMS, LabWorks.

10.8 The DNPH-silica cartridge is extracted with 3-5mL of Acetonitrile using a Sep Pak vacuum manifold, using a gentle vacuum until the Acetonitrile is pulled through the cartridge.

10.9 Add Acetonitrile up to 6mL then add 4mL of reagent grade water to the sample to bring the final volume to 10mL mixing thoroughly. Note: It is best to not add the water to the Acetonitrile extract until shortly before the HPLC analysis of the samples. Experience has shown that samples can produce reliable data up to 3 days after water is added to the Acetonitrile extract.

10.9.1 Note: Analysts may mix smaller aliquots of extracted samples in Acetonitrile and Water at 60:40 ratio Acetonitrile and Water to preserve the sample volume in Acetonitrile to run later than 3 days if necessary but within the 30 day hold time. *However, the EPD Laboratory requires samples to be analyzed within 14 days.*

10.9.1.1 Example: Add 0.6mL sample extract and 0.4mL Water directly into the auto sampler vial and mix thoroughly prior to analysis.

10.10 Transfer about 1-1.5mL of sample into autosampler vials and secure with snap caps.

10.11 Samples are then ready for analysis by liquid chromatography.

10.12 For all samples requiring manual integrations during processing after analysis, a copy of an original, un-altered chromatogram will be included with each data set. The analyst may elect to print chromatograms of all samples prior to processing and include them with the data set.

10.13 Dilutions: Upon analysis of the extract, if a target compound response is greater than that of the highest standard of the calibration curve, the sample must be diluted with the final extraction solvent (Acetonitrile/Water: 60:40, v/v) so that, upon analyzing the dilution (in a valid analytical sequence), the target response is between the lowest concentration standard and the highest concentration standard.

10.14 Store the remaining extract in the sample refrigerator, protected from light, at 4°C or less (not frozen) for the remaining hold time, then dispose in the proper waste stream.

10.15 Qualifiers to be used for TO-11A samples are extracted from of the Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program manual, Section 3: Table 3.3-2 and Table 3.3-3. Null qualifier flags listed in the table below are applied to samples or individual compounds that are voided. Null codes are entered in the "!VOID" test code result as the two letter flags from the table unless otherwise noted for a specific flag. If a Null code is applied to a single compound, the Null code alone is entered in the result field(s). Only one null flag is to be applied to a given sample. See Table 10.15

Table 10.15 - Null Qualifier Flags

Qualifier Flags	Description
AG	Sample time out of limits
AH	Sample flow rate out of limits
AJ	Filter Damage
AL	Voided by operator
AM	Miscellaneous void (comment required)

Table 10.15 - Null Qualifier Flags

Qualifier Flags	Description
AN	Machine malfunction
AO	Bad weather
AP	Vandalism
AQ	Collection Error
AR	General lab error
AV	Power failure
AS	Poor quality assurance results
BA	Maintenance / routine repairs
BB	Unable to reach site
BE	Building site repair
BH	Interference / co-elution
BJ	Operator error
TS	Holding time or transport temperature is out of specs.

10.16 Quality Control and Detection Flags to be used for TO-11A results are extracted from of the Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program manual, Section 3, Table 3.3-2 and Table 3.3-3. If a Null qualifier from the Null Qualifier Flags table above is entered, no Quality Control or Detection Flags are to be entered. If no Null flags are entered, up to six Quality Control or Detection Flags may be entered for a single TO-11A result. QA flags are entered in the Qualifier field in LabWorks. See Table 10.16

Table 10.16 - Quality Control and Detection Flags + Laboratory Generated Flags

Qualifier Flags	Description
DI	Sample required dilution for analysis
EH	Estimated; exceeds upper range
FB	Field blank value above acceptable limit
LB	Lab blank value above acceptable limit
LJ	Identification of analyte is acceptable; reported value is an estimate
LK	Analyte identified; reported value may be biased high
LL	Analyte identified; reported value may be biased low
MD	Detected value at or below the MDL
MX	Matrix effect
ND	No value detected (Reported as “Not Detected” due to LIMS limitations)
QX	Does not meet QC criteria
SQ	Values between PQL and MDL

Table 10.16 - Quality Control and Detection Flags + Laboratory Generated Flags

Qualifier Flags	Description
TB	Trip Blank value above acceptable limits
TT	Transport temperature is out of specs

11 Calculations

11.1 Sample Concentration

Sample results are expressed in µg/cartridge

Eq. 11.1 $$Concentration(ug/cartridge) = \frac{(A_s)(D)(V_T)}{(RF)(V_i)}$$

11.1.1 Where:

A_s = Area of the peak for the analyte in the sample
D = Dilution factor
RF = Mean response factor (Area per μg)
V_i = Volume of sample injected in microliters
V_T = Total volume of the concentrated extract

11.2 Response Factor, RF, for a peak

Eq. 11.2 $$RF = \frac{Area_{Analyte}}{Concentration_{Analyte}}$$

11.2.1 Where:

RF = Response Factor
$Area_{Analyte}$ = Area of the peak of the analyte of interest
$Concentration_{Analyte}$ = Concentration of the analyte of interest in µg/ml

11.3 Average Response Factor

Eq. 11.3 $$\overline{RF} = \sum \frac{RFi}{n}$$

11.3.1 Where:

$\overline{RF}$ = Mean Response Factor
RF_i = Response factor of compound at each level *i*
n = Number of calibration standards

11.4 Alternate Sample Concentration Calculation using first order linear regression

The regression's slope and intercept terms for the linear equation is in the form:

Eq. 11.4 $y = a x + b$

11.4.1 Where:
y = Instrument response
a = Slope of the line
x = Concentration of Sample
b = Intercept

To use the equation to calculate sample concentrations, the equation is rearranged:

$$x = \frac{y - b}{a}$$

Note: In method TO-11A, the cartridges are extracted with 3-5m**L** of ACN then ACN is added up to 6mL then 4mL of water is added to make a final volume of 10mL. This factor is used in the curve values in the data acquisition software.

11.5 Average Retention Time, $\overline{RT}$

Eq. 11.5 $\overline{RT} = \sum \frac{RT}{n}$

11.5.1 Where:
$\overline{RT}$ = Mean retention time for target compound
RT = Retention time for the target compound
N = number of values

11.6 Sample Standard Deviation (n - 1) (σ_{n-1}) of response factors

Eq. 11.6 $\sigma_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(RF_i - \overline{RF})^2}{n-1}}$

11.6.1 Where:
σ_{n-1} = Sample Standard Deviation
$\overline{RF}$ = Mean response factor
RF_i = Response factor of compound at each level i
n = Number of calibration standards

11.7 Percent Drift, %Drift

Eq. 11.7 $$\%Drift = \frac{(Concentration_{Calculated} - Concentration_{Expected})}{Concentration_{Expected}} * 100$$

11.7.1 Where:
Concentration $_{Calculated}$ = Concentration calculated from result
Concentration $_{Expected}$ = Theoretical concentration of the standard

11.8 Quality Control Calculations

11.8.1 LCS Recovery and Precision:

Eq. 11.8.1 $$\text{LCS/LCSD/ICV \% Recovery} = \frac{R_{spike}}{\text{Expected Result}} X\,100$$

Eq. 11.8.2 $$\%\,\text{RPD(precision)} = \frac{\left|R_{sample} - R_{duplicate}\right|}{\left(\frac{R_{sample} + R_{duplicate}}{2}\right)} X\,100$$

11.8.2 Where:
R_{spike} = % recovery of spiked sample
R_{sample} = % recovery of sample
$R_{duplicate}$ = % recovery of duplicate sample

11.9 Calibration Calculations

Eq. 11.9.1 $$RF = \frac{Peak\ area\ of\ the\ compound\ standard}{micrograms\ of\ the\ compound\ injected}$$

Eq. 11.9.2 $$\overline{RF} = \sum \frac{RFi}{n}$$

Eq. 11.9.3 $$RSD = \frac{SD}{\overline{RF}}$$

Eq. 11.9.4 $$SD = \sqrt{\sum_{i=1}^{n} \frac{(RF_i - \overline{RF})^2}{n-1}}$$

Where:

RF = Response Factor

RF_i = Response Factor for compound at each calibration level
n = Number of calibration standards
$\overline{RF}$ = Mean Response Factor
SD = Standard Deviation
RSD = Relative Standard Deviation

11.10 To ensure data quality and obtain quantitative Carbonyl compound concentrations, the collection of Blanks is necessary. For national air toxics monitoring three types of Blanks are used to ensure data quality: certification Blanks, Field Blanks and Method Blanks.

11.10.1 Certification Blanks consist of three commercially prepared DNPH-coated, pre-packed cartridges that are eluted with ACN/Water using the same procedure as used for samples and analyzed to verify the acceptability of a specific cartridge lot from the vendor. Certification blanks are analyzed for each specific lot used for sampling. Alternatively, a "Certificate of Analysis" accompanying each lot may be used for certification as long as it meets the blank acceptance criteria.

11.10.1.1 A "Certificate of Analysis" accompanying each lot of DNPH-coated, pre-packed cartridges may be used for certification as long as the analysis meets the Blank acceptance criteria. If the values reported in the "Certificate of Analysis" do not meet acceptance criteria, three Laboratory Blanks from that lot must be analyzed and must meet blank acceptance criteria. If the mean mass ± 3 standard deviations (± 3 s) for the group of three Laboratory Blanks meet the criteria, no further certification of Laboratory Blanks is required for that particular cartridge lot. If large differences are observed for the three Laboratory Blank samples, additional Laboratory Blanks should be analyzed to obtain values for the mean and standard deviation. If the certification blanks or the "Certificate of Analysis" do not meet the specified blank acceptance criteria, the Carbonyl tubes should be shipped back to the manufacturer and a new lot requested.

11.10.1.2 For certification Blanks or the "Certificate of Analysis" to be acceptable, the following criteria must be met:

Formaldehyde:	< 0.15 µg/cartridge
Acetaldehyde:	< 0.10 µg/cartridge
Acetone:	< 0.30 µg/cartridge
Other Individual Compounds:	< 0.10 µg/cartridge

11.10.2 Field Blanks are blank cartridges that are sent to the field, connected to the sampling system and treated identically to the samples except that no air is drawn through the cartridge. Field Blanks are used to assess the background Carbonyl levels for cartridges used during the ambient sample collection process.

11.10.2.1 For Field Blanks to be acceptable, the following criteria must be met:

Formaldehyde:	< 0.30 µg/cartridge
Acetaldehyde:	< 0.40 µg/cartridge

Acetone:	< 0.75 µg/cartridge
Sum of other compounds:	< 7.00 µg/cartridge

11.10.3 Method Blanks are blank cartridges that never leave the laboratory and are extracted with every batch of samples. Method Blanks are used to assess possible laboratory contamination.

11.10.3.1 The following criteria must be met for Method Blanks:

Formaldehyde:	< 0.15 µg/cartridge
Acetaldehyde:	< 0.10 µg/cartridge
Acetone:	< 0.30 µg/cartridge
Other Individual compounds:	< 0.10 µg/cartridge

11.10.3.2 If the Method Blank fails to meet acceptance criteria, that Method Blank should be re-run on the HPLC once. If the Method Blank still fails to meet acceptance criteria, flag all associated samples within the batch. Check the laboratory for signs of possible contamination.

11.10.3.3 If the ACN Solvent Blank and/or the ESMB fail to meet criteria for Acetone due to trace amounts present in the ambient atmosphere, the Corrective Actions in Table 14.3 will be followed for the affected QC Blank(s). If the re-run(s) still do not meet criteria, the affected QC Blank(s) will be flagged on the chromatogram and any associated data will be used as Acetone is an unregulated compound for NATTS.

12 Waste Management

12.1 See GA EPD Laboratory SOP6-015, EPD Laboratory Waste Management Standard Operating Procedures, online revision.

13 References

13.1 EPA Method TO-11A, January 1999
13.2 Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, October 2016 or later.
13.3 National Air Toxics Trends Station Work Plan, March 2015 or later.
13.4 GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision or later and Continuing Demonstration of Capability SOP 6-002, online revision.
13.5 GA EPD Laboratory SOP – EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.6 GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.
13.7 GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charting and Control Limits SOP, SOP 6-025, online revision.
13.8 GA EPD Laboratory Quality Assurance Plan, online revision.
13.9 GA EPD Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.

14 Practical Quantitation Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 14.1 MDLs & RLs* for EPA Method TO-11A

		Matrix (AIR)		
Parameter/Method	**Analyte**	**MDLs**	**RL**	**Unit**
TO-11A	Acetaldehyde Acetone Benzaldehyde Butyraldehyde Formaldehyde Propionaldehyde	See Appendix A for current MDLs	See Appendix A for current RLs	µg/cartridge µg/cartridge µg/cartridge µg/cartridge µg/cartridge µg/cartridge

* RLs are determined by multiplying the calculated MDL value for each compound by 3.18.

Table 14.2 LCS/LCSD* Acceptance Criteria for EPA Method TO-11A

Method	Analyte	Accuracy (%R)	Precision (RPD)
TO-11A	Acetaldehyde	70 - 130	20
	Acetone	70 - 130	20
	Benzaldehyde	70 - 130	20
	Butyraldehyde	70 - 130	20
	Formaldehyde	80 - 120	20
	Propionaldehyde	70 - 130	20

*LCS/LCSD recovery and precision limits are static based on the default limits in the Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, Oct. 2016. Annual Control Charts will be generated for this method. They will be used for trend monitoring of analytical systems.
Field Matrix Spikes are stated as not required by the TAD, Rev. 3, Oct. 2016.

Table 14.2.1 Acceptance Criteria for EPA Method TO-11A Primary/Co-Location and Replicates

Method	Analyte	Primary/Collocation + Primary/Replicate Precision (RPD)*	Collocation/ Replicate Precision (RPD)*
TO-11A	Acetaldehyde	20	10
	Acetone	20	10
	Benzaldehyde	20	10
	Butyraldehyde	20	10
	Formaldehyde	20	10
	Propionaldehyde	20	10

*RPDs may exceed given limits if analyte concentrations are < 0.5 µg/cartridge

Table 14.3 Summary of Calibration and QC Procedures for Method EPA TO-11A

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
TO-11A	Carbonyls	A six-point initial calibration for all analytes	Initial calibration prior to sample analysis	RSD for all analytes ≤ 20% linear-least squares regression r ≥ 0.999 (or $r^2 \geq 0.998$)	Correct problem then repeat initial calibration	
		Second-source Calibration verification (ICV)	Once per initial calibration	All analytes within ± 15% of expected value (85-115%)	Correct problem then repeat initial calibration	
		Retention time window calculated for each analyte	Once per year or after major maintenance of the instrument	± 3 times standard deviation for each analyte retention time from 72-hour study	Correct problem then reanalyze all samples analyzed since the last retention time check. Redo retention time window study	
		Retention time window update	First CCC of each sequence and the first CCC of each 24 hour period	Must be done for every batch		
		Calibration verification (CCC)	Beginning each analysis sequence prior to the analysis of samples for every 12 hour shift or every 10 samples (whichever is sooner) and at the end of the analysis sequence	All analytes within ± 15% of expected value (85-115%)	Correct problem then repeat initial calibration verification and reanalyze all samples since last successful calibration verification	
		IDC – Initial Demonstration of Capability - Generate acceptable accuracy and precision using four cartridge analyzes of a QC check sample, a blank and a blind sample.	Once per analyst	QC acceptance criteria Table 14.2	Locate and fix problem then re-run or re-extract demonstration	
		CDC – Continuing Demonstration of Capability using same criteria as IDC or 2 consecutive batch QC or a Blank and a Blind sample	Required every six months after IDC for each analyst	QC acceptance criteria Table 14.2	Locate and fix problem then re-run or re-extract demonstration	
		Certification Blank(s)	Checked once per lot of cartridges	Acceptance criteria listed in 11.10.1.2 using 4 cartridges per lot (minimum 3 cartridges or 1% or samples)	Re-extract 4 cartridges. If the re-extracts do not meet criteria, return lot to vendor	

Table 14.3 Summary of Calibration and QC Procedures for Method EPA TO-11A

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
TO-11A	Carbonyls	Solvent Blank	Prior to ICAL or Daily CCC and samples	All target analytes < MDL value	Correct problem then re-run solvent blank and any affected samples	Manually flag chromatograms and use data
		Extraction Solvent Method Blank (ESMB)	Once per batch. After initial daily CCC and prior to Method Blank and samples	All target analytes < MDL value	Correct problem then re-run ESMB and any affected samples	Manually flag chromatograms and use data
		Field Blank	One per sample collection location	Acceptance criteria listed in 11.10.2.1	For all samples from same location, flag failing compound(s)	"FB" for Field Blank issue
		Method Blank	One per analytical batch of 20 samples or less	Acceptance criteria listed in 11.10.3.1	For all samples in batch, flag failing compound(s)	"LB" for Method Blank issue
		LCS/LCSD for all analytes	One LCS/LCSD per analytical batch of 20 samples or less	QC acceptance criteria Table 14.2	Rerun LCS/LCSD once within 24 hours of original. If not, correct problem and rerun entire batch once. Flag all samples in batch with the AS qualifier if reruns fail	"AS" for Quality Assurance issue
		Primary Sample and Co-Located Sample %RPD	Once every batch of 20 samples or less if available	20% RPD for Primary and Collocation results unless sample concentrations are < 0.5 µg/cartridge	Re-run Primary and Collocated samples	
		Primary Sample and Collocated Replicate %RPD	Once every batch of 20 samples or less if available	20% RPD for Primary and Collocation results unless sample concentrations are < 0.5 µg/cartridge	Re-run Primary and Collocated samples and Co-Located Replicate	
		Collocated Sample and Replicate %RPD	Once every batch of 20 samples if available	10% RPD for Collocation and Replicate results unless sample concentrations are < 0.5 µg/cartridge	Re-run Collocated sample and Replicate	
		Replicates	Minimum frequency of 10% samples. One replicate per batch of 1-10 samples. Two replicates per batch of 11-20 samples.	RPD for all analytes < 10% unless sample concentrations are < 0.5 µg/cartridge	Re-run Primary and Collocated samples and Collocated Replicate	
		Second-column confirmation	Each batch is analyzed on a second column	Same as for primary column analysis	Same as for primary column analysis if used for quantitation	

Table 14.3 Summary of Calibration and QC Procedures for Method EPA TO-11A

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
TO-11A	Carbonyls	MDL study	Once per year or after major maintenance of the instrument	All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall be < the RLs in Table 14.1	Re-do MDL Study	None
		MDL analysis	Once per batch or as needed to acquire data points per SOP 6-007, online revision	All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e. Surrogate Spike or Internal Standard, etc. if included) must meet established criteria	Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data	None
		Results reported between MDL and RL	Yes	none	none	Use "SQ" qualifier.
		Results reported below MDL	Yes	none	none	Use "MD" qualifier.
		Results reported at 0.0 µg/cart or less	Yes	none	none	Use "ND" qualifier. (Manually enter "ZD" for "ND" result)

15 Associated LabWorks Test Codes

15.1 Parent Test Code
15.1.1 $TO11A – Analysis Results
15.2 Extraction Test Code
15.2.1 TO11E – Cartridge Extraction
15.3 QC Test Codes
15.3.1 $B_TO11A – Extraction Blank Results
15.3.2 $LATO11A – LCS/LCSD Spike Amount
15.3.3 $LSTO11A – LCS Results
15.3.4 $LDTO11A – LCSD Results
15.3.5 $LRTO11A – LCS Percent Recovery
15.3.6 $L2TO11A – LCSD Percent Recovery
15.3.7 $LPTO11A – LCS/LCSD Precision
15.3.8 $MATO11A – MDL Spike Amount
15.3.9 $MLTO11A – MDL Results
15.4 NATTS Primary, Collocated and Replicate Test Codes
15.4.1 $XATO11A – Collocated Sample Results (or Sample Results when using Sample Duplicates)
15.4.2 $XBTO11A – Primary Sample Results
15.4.3 $XXTO11A – Replicate Results
15.4.4 $XPTO11A – Collocated Sample/Replicate Precision (or Sample/Replicate Precision with Sample Duplicates)
15.4.5 $XQTO11A – Primary Sample/Collocated Sample Precision
15.4.6 $XZTO11A – Primary Sample/Replicate Precision

Appendix A – MDLs and RLs for EPA Method TO-11A

Table A.1 MDLs and RLs for EPA Method TO-11A

		Matrix (AIR)		
Parameter/Method	**Analyte**	**MDLs***	**RLs****	**Unit**
TO-11A	Acetaldehyde	0.163	0.518	µg/cartridge
	Acetone	0.281	0.894	µg/cartridge
	Benzaldehyde	0.138	0.439	µg/cartridge
	Butyraldehyde	0.099	0.315	µg/cartridge
	Formaldehyde	0.102	0.324	µg/cartridge
	Propionaldehyde	0.155	0.493	µg/cartridge

* MDLs are based on MDL baseline studies from 01/01/2019 to 12/27/2020.
** RLs are determined by multiplying the calculated MDL value for each compound by 3.18.

Updates:
Updated for online revision. Added Appendix A.