

Atmospheric Analysis & Consulting, Inc. Air Quality Laboratory

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## How To Test For Formaldehyde And Other Carbonyls In Air Using Regulatory Approved Methods

There are several decisions that must be made in order to determine which source testing method you should use to measure Formaldehyde and other Carbonyl emissions. Use the data presented in Table 1 to help you make those decisions and to find the most suitable testing method for your application.

Regulatory Mandate	• If your industry is listed in Table 1, you will most likely have to use the methods mandated by the regulatory agency in charge (Compliance or Engineering Test?). MACT standards and other regulatory mandates specify which sampling methods are allowed per industry.
Continuous or integrated	<ul> <li>Continuous methods exist for Formaldehyde and other carbonyls using FTIR (EPA 318 and 320).</li> <li>FTIR can have interferences from water vapor, so be careful with humid sources; also, FTIR typically has higher detection limits than most chemical testing procedures.</li> </ul>
sampling Moisture content	<ul> <li>Is isokinetic (for high moisture or saturated sources and high particulate) sampling required?</li> <li>As written, only EPA 316 and EPA 0011 are approved for isokinetic sampling. EPA 323 can easily be modified for isokinetic sampling and NCASI 105.01 allows modification for isokinetic sampling.</li> </ul>
Analytes	• Formaldehyde can be collected in water (EPA 316/323), Acetaldehyde and others not as well-need more water impingers or Silica Gel tubes or derivatization (DNPH or BHA).
NO <sub>2</sub> Levels (not NO or NOx)	• NO2 levels greater than 50-60 ppm may cause problems with DNPH, especially CARB 430. Use Water (EPA 316/323) or FTIR instead.
Range and Sensitivity	<ul> <li>Water has a higher range than DNPH (up to 2.3% Formaldehyde in EPA 316).</li> <li>Sensitivity order: DNPH &gt; BHA &gt; SPEC &gt; FID.</li> </ul>
	Come concorrect with DNDU methodes

#### Some concerns with DNPH methods:

\*High NO<sub>2</sub> Levels - Collect small sample volumes if the source has high analyte emission rates. \*Acetone contamination, especially for Method 5 rinses - Depletes the DNPH so analytes are not collected. \*DNPH is hazardous, so there are safety issues during shipping and collecting as well as hazardous waste disposal.

#### Vehicle Exhaust Methods

CARB 1004 uses impingers filled with DNPH solution in Acetonitrile or DNPH coated cartridges for sampling.

### **Ambient and Indoor Air Methods**

### Active Sampling Methods

- EPA TO-11A is the method most used for ambient and indoor air carbonyl measurements. Measurements are made using DNPH coated Silica Gel or C18 cartridges. This method can be used to analyze most gas-phase carbonyls with the exception of Acrolein and possibly other *a*, *β* unsaturated carbonyls. An ozone scrubber should be used upstream of the cartridge at all times. Typically, sampling is done at ~1 LPM for 3-4 hours with resulting reporting limits in the 0.05-0.15 ppbv range. NIOSH 2016/2018 and EPA IP-6A are the respective equivalent methods for industrial hygiene and indoor air applications.
- **EPA TO-5** is a DNPH impinger method that uses DNPH solution and iso-Octane to extract the hydrazones while sampling. This method may be preferable to TO-11 for Acrolein sampling or if really high concentrations are expected (larger capacity than TO-11 cartridges) or if sampling under really wet conditions.
- **EPA 8520** is a continuous chemical method that gives Formaldehyde readings every 1-2 minutes (5-500ppbv range) and is typically used as a screening tool for EPA SW-846 applications.

Passive Sampling Methods

• The DNPH coated filters/badges used in EPA IP-6C and OSHA 1007 are the preferred passive sampling method for most carbonyls with the exception of Acrolein.Flow rates are ~25-30mL/min.

Method	Industry	Analytes	Media	Iso	High Moisture	Impinger	Analysis	Misc
EPA 316	Mineral Wool Wool fiberglass	Formaldehyde Only	Water	Yes	Yes	2*100 GS (2*200 etc) M5 Train	Spec	
EPA 323 / NCASI 98.01	Natural Gas Stationary Sources / Wood Product Mills	Formaldehyde Only	Water	No (?)	?	1-2*20 M	Spec	OA2
EPA 0011	Stationary Sources Incinerators	For, Acet,Pro, Iso, Acetop	DNPH	Yes	Yes	1*200+2*100 GS M5 Train	HPLC	OA1
CARB 430	Stationary Sources	For, Acet	DNPH	No	No	2*10M	HPLC	
CARB 430M*	Stationary Sources	For, Acet, Acr	DNPH/ Toluene	No	No	2*10M	HPLC	AAC
NCASI 94.02	Pulp and Paper Mills	For, Acet, Act, MEK	Water/SG	No	No	1*20M F/B SG Tubes	Spec (For) GC-FID (others)	OA2
NCASI 99.02	Wood Product Facilities	For, Acet, Act, Acr, MEK, MIBK, Pro	Water/ Canister	No	<60% Moisture	3*25 M/Can	Spec (For) GC-FID (others)	OA2
NCASI 105.01	Pulp and Paper	For, Acet, Acr, Pro	Water/BHA	No (?)	No	M/ GS	Spec (For) GC-NPD (others)	OA1 OA2

### Table 1. Source Testing Methods for Formaldehyde and other Carbonyls

For-FormaldehydeImpAcet-AcetaldehydeM-MAcr-AcroleinGS-Act-AcetoneF-FnPro-PropanalB-BaMEK-Methyl Ethyl KetoneSG-MIBK-Methyl Isobutyl KetoneCarrIso-IsophoroneIso-Acetop-AcetophenoneSpeOA1-Other carbonyl analytes possible per methodAcetop-OA2-Method can also be used for methanol or other analytes\*A

Impinger 2\*100= Two 100 mL impingers M-Midget impinger GS-Greenburg-Smith full size impinger F-Front B-Back SG-Silica Gel Canister-Summa Canister Iso-Isokenitic Sampling Spec-Spectrophotometer

\*AAC Method



METHOD	STORAGE CONTAINER	PRESERVATION	MAX HOLDING TIME				
EPA 0011	Amber Glass Bottle/Teflon Liner	Cool, 4°C, dark	Use solution within 5 days of prep 30 days FCTE/FCTA				
EPA 316	Polyethylene bottles	Cool, 4°C, dark	14 days from collection				
EPA 323	Amber 40mL VOA Vial/Teflon Liner	Cool, 4°C, dark	14 days from collection				
CARB 430	25mL Glass Vial/Teflon Liner	Cool, 4°C, dark	Use solution within 2 days of prep 7 days FCTE/30 days FETA				
NCASI 94.02	Liquid-Glass Jar/Bottle Silica Gel Tube	Cool, 4°C, dark	Stable for 21 days Stable for 10 days				
NCASI 98.01	VOA vial	Cool, 4°C, dark	Stable for 28 days				
NCASI 99.02	Liquid VOA/Poly Canister	Cool, 4°C, dark Cool	2 weeks 3 weeks				
NCASI 105.01	Glass Jar/Bottle	Cool, 4°C, dark	BHA-21 days FCTE-14 days FETA, aqanalyze within 21 days				
EPA TO-11A	Foil bag etc.	Cool, 4°C, dark	14 days FCTE 30 days FETA				
EPA TO-5	Glass Vial/Teflon Liner	Cool, 4°C, dark	Use solution within 2 days of prep				

# Table 2. Containers, Storage and Holding Times for Carbonyl Methods

FCTE-From Collection to Extraction | FETA-From Extraction to Analysis | FCTA-From Collection to Analysis

# **Table 3. Reporting Limits**

Method	Analytical Range (ug/mL)	SRL (ug/mL)	Liquid Volume (mL)	SRL (ug/sample)	Flow Rate (LPM)	SRL (ppbV) Formaldehyde
EPA 316	.25-3.0	.25	200	50	~15	40.7 (30t^3)
EPA 323	.20-7.5	.20	20	8	.24	271 (24L)
EPA 0011	.005-10	.025	250	6.25	~15	5.87 (30t^3)
CARB 430/430M	.005-10	.025	10	.25	.15	3.4 (60L)
NCASI 105.01 NPD	.5-100	.50	25	12.5	~0.4	423 (24L)
NCASI FID (not Formaldehyde)	.5-1000	.50	90	45	0.4	1530 (24L)
EPA TO-5	.005-10	.025	10	.25	.1-1.0	3.4 (60L)
EPA TO-11A	.005-10	.025	1.5	.0375	.1-1.0	.17 (180L)
OSHA 1007	.005-10	.025	2.0	050	.30	.5-5.6 (72L)

Please contact AAC for additional sampling information such as the method required number of runs, spike & blank requirements, recommended sampling volumes, required solution volumes per test, analytical detection limits and reporting limits, etc. - **Email**: info@aaclab.com



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