

**Ashland Specialty Chemical Company  
Modified Impinger Method for Acrolein in Air**

**Background**

This procedure is based on dinitrophenylhydrazine (DNPH) chemistry similar to Method CARB 430 to capture acrolein in air (and other selected carbonyl containing air toxics) and form a stable hydrazone derivative for the quantification of the acrolein. The acrolein reacts with DNPH in the acidic solution and is continuously extracted out of the aqueous phase by the toluene. The sampling train usually has three impingers connected in series. Two impingers may be inadequate to capture all of the acrolein in some sources. This was evident where two impingers were used to sample a two cylinder gasoline fueled lawn tractor engine. Each impinger contains 10 mL of water, two mL of DNPH-HCl acidic solution and two mL of toluene. The bubbling action of the air sampling breaks up the toluene layer into small droplets that performed a liquid-liquid extraction of the aqueous phase continuously during sampling. The toluene is an effective co-solvent for the acrolein which increases the capture efficiency of the acrolein. Acrolein has low water solubility compared to formaldehyde and purges out of a deionized water impinger. The tendency for acrolein carry-over requires more impingers for acrolein than for formaldehyde. The sampling flow is achieved with a rotary vane vacuum pump with a critical orifice in line. Recommended sample flow rates are 0.2 to 0.4 liters per minute. This sampling rate provides desirable extraction performance.

Impinger methods using DNPH have historically given low recovery for acrolein. The acidic solution is believed to be responsible for the loss of the hydrazone formed in the reaction of DNPH and the aldehyde. Nitrogen oxides in the sample appear to accelerate the loss of the hydrazones. Field extraction with organic solvents immediately following sampling has improved recoveries, but this is often difficult to perform in the field and recoveries were still lower than desired. Sampling times have been reduced to minimize the loss of the hydrazones. This also raises the method detection limit (MDL). The continuous toluene extraction employed in this procedure has provided stable and consistent recovery of acrolein. Field spike recovery average for 14 spiked samples was 94.2%. The field spikes were stable for two weeks at ambient conditions.

**1. PURPOSE:**

This procedure describes the sampling and analysis of short chain aldehydes in air.

**2. SCOPE:**

This procedure can be used for ambient air, industrial hygiene surveys, process engineering surveys, or in accordance with Code of Federal Regulations, Volume 40, Part 60, Appendix A, Method 18.

This method can be used to analyze the aldehydes listed in Table 1 in a single chromatogram that are collected in ambient air, work place air, combustion sources, vehicle emissions, or hot wet process emissions.

**TABLE 1**  
**Analytes**

	<b>Boiling Point (°C)</b>	<b>Density (g/mL)</b>	<b>MW (g/mole)</b>	<b>Range (mg/m<sup>3</sup>)</b>
formaldehyde	-21	0.815	30.03	0.002-1000
acetaldehyde	20.8	0.783	44.05	0.005-1000
acrolein	52.5	0.863	56.06	0.002-1000

**3. APPARATUS and REAGENTS:**

- 3.1 Midget impingers using a removable six-dram threaded vial, available from Supelco, part number 64712-U.
- 3.2 6mm glass tube impinger connectors secured with 3/16 inch ID silicone tubing.
- 3.3 Sampling pump suitable to provide sample flow at 0.2 to 0.4 liters per minute.
- 3.4 Gas chromatograph equipped with a nitrogen phosphorus detector (NPD).
- 3.5 Column - see instrument parameters for specific analyte.
- 3.6 Syringe - 10  $\mu$ L
- 3.7 DNPH-HCl solution. Place 4 grams of recrystallized DNPH in a one-liter Erlenmeyer flask (see Method CARB 430 for recrystallizing details) and add 500 mL 2N HCl. Add 4mL 85% phosphoric acid. Heat with stirring to dissolve. Blanket with nitrogen. When the yellow-orange solution is clear, remove from heat and allow it to cool to room temperature. Maintain a nitrogen blanket. Some precipitate may form. Check the blank level for the compounds of interest. Extract the DNPH solution with toluene if the blank levels are too high. Pour the solution into a glass bottle and cap with an airtight closure. Maintain a nitrogen blanket every time the bottle is opened. Impinger vials may be prepared by adding two mL of the DNPH-HCl solution, 10 mL D. I. water and two mL of toluene. For large batches of impingers, pre-dilute the DNPH-HCl solution and add 12 mL to each vial.

**4. SAMPLING PROCEDURE:**

- 4.1 Prepare three impingers connected in series using the 6mm glass tube connectors.
- 4.2 Attach the impinger vials filled with DNPH-HCL solution to the impinger stems. Place the impingers in a rack inside a small cooler. Add ice and maintain the ice bath during sampling. Connect the impingers to the sampling pump and turn on the sampling pump prior to connecting the impinger train to the sample probe.
- 4.3 Sample at 0.2 to 0.4 liters per minute for as long as necessary to collect adequate mass for desired detection level. Samples were collected for up to one hour without any problems. Ambient sampling may require two to three hours to collect adequate mass for desirable quantification.
- 4.4 When sampling is complete, disconnect the sampling probe prior to stopping the sampling pump. This will prevent loss of sample if the stack has positive or negative pressure. Remove and cap each impinger vial and transport the vials to the analytical laboratory.

**5. SAMPLE ANALYSIS**

- 5.1 Remove the toluene layer with a graduated pipette and measure the volume. Another option is to make up the toluene layer to the original 2.0 mL. Place the toluene fraction in labeled vials or autosampler vials for analysis by GC/NPD.
- 5.2 Analyze according to Ashland Chemical Method CA4618.

6. **REFERENCES**

<u>Analyte</u>	<u>Reference</u>
Formaldehyde	CARB 430
Acetaldehyde	CARB 430
Acrolein	CARB 430

**APPENDIX A**

**INSTRUMENT PARAMETERS**

<b>Formaldehyde, Acetaldehyde, Acrolein</b>	
<b>Instrument:</b>	Varian 3800
<b>Column:</b>	
length, m	30.0
I.D, mm	0.53
OD, in	0.8
material	fused silica
<b>Stationary Phase:</b>	
type	DB-17 ( J&W Scientific or equivalent)
thickness (µm)	1.0
<b>Temperature:</b>	
injector	230°C, on-column
detector	280°C
Oven:	
initial	200°C for 10 min
final	230°C
program rate	5.0°C/min
<b>Carrier Gas:</b>	
type	helium
rate	7-10 mL/min (8psig)
	20 mL/min make-up at detector
<b>Sample:</b>	
injection volume	2.0 µl
solvent	toluene
<b>Detection:</b>	
type	NPD
sensitivity	1 X 10 <sup>-11</sup> a/MV