# Measurement of Carbonyl Compounds from Stationary Source Emissions by a PFBHA-GC-ECD Method

# 98-RP105A.04 (A227)

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# ABSTRACT

Carbonyl compounds have received increasing attention because of their important role in ground-level ozone formation. Currently, there is no validated stationary source emission test method for the measurement of carbonyl compounds, especially for the unstable carbonyls, such as acrolein. This paper presents a study in the development of a test method for the measurement of carbonyls from stationary source emissions. This method involves collection of carbonyls in midget impingers, derivatization of carbonyls with O-2,3,4,5,6-pentafluorobenzyl hydroxylamine hydrochloride (PFBHA), separation of carbonyl-PFBHA derivatives by gas chromatography (GC), and measurement of the derivatives with electron capture detection (ECD). Formaldehyde, acetaldehyde, acrolein, acetone, butyraldehyde, methyl ethyl ketone, methyl isobutyl ketone, and hexaldehyde were selected as candidates for the method evaluation.

The test gas containing the selected compounds was generated from either a certified gas cylinder or permeation tubes. The retention and recovery efficiencies for the selected compounds were tested using midget impingers filled with 20 mL of methanol or water. The retention in the upstream impinger was > 85% for all the compounds tested using methanol as the solvent, but the retention was < 70% for acetaldehyde and < 60% for acrolein, butyraldehyde, and hexaldehyde when collected in water. The recovery efficiency (total mass collected in upstream and downstream impingers) was > 80% for all the compounds tested using methanol as the collection solvent, but the recovery efficiency was < 75% for butyraldehyde and hexaldehyde using water as the solvent. Generally, larger variabilities of retention and recovery efficiencies were observed when water was used as the collection solvent. When tested under the humid condition (~10% water v/v), the presence of moisture appeared to have no effects on the retention and recovery efficiencies for carbonyl compounds.

The stability of selected compounds was tested in both water and methanol. Degradation of acrolein was observed in both solvents. In the presence of phenol, slow decay was also observed for formaldehyde, acetaldehyde, and hexaldehyde in water, but no decay was observed for these compounds in methanol. The addition of PFBHA stabilized acrolein in both water and methanol. Formaldehyde, acetaldehyde, and hexaldehyde also became stable with the addition of PFBHA in water with phenol presence. In addition, higher derivatization yields were obtained for ketones in methanol. Similar derivatization yields were obtained for aldehydes in both solvents; however, the aldehyde derivatives gradually dissociated in water after they formed.

Good detector response linearity was obtained for carbonyl-PFBHA derivatives ( $R^2 > 0.99$ ) over the range of 0.04 - 2.5 µg/mL when analyzed by GC-ECD. The analytical detection limit was ~10 pg. This detection limit equates to ~10 ng/L of carbonyls in a 20-L sample collected from stationary source emissions.

# INTRODUCTION

Carbonyl compounds have received increasing attention because of their important role in ground-level ozone formation.<sup>12</sup> These compounds are generated from both primary and secondary sources; they are directly emitted into the atmosphere from incomplete combustion<sup>3</sup> as well as being formed as an intermediate in the atmospheric photooxidation of hydrocarbons.<sup>12</sup> Because of their active roles in atmospheric chemistry, it is important to establish an accurate measurement technique for these compounds.

Currently, there is no validated stationary source emission test method for the measurement of carbonyl compounds, especially for the unstable carbonyl compounds, such as acrolein. This paper presents a study in the development of a test method for the collection and measurement of carbonyls from stationary source emissions. This method involves collection of carbonyl compounds in midget impingers, derivatization of carbonyls with O-2,3,4,5,6-pentafluorobenzyl hydroxylamine hydrochloride (PFBHA), separation of carbonyl-PFBHA derivatives by gas chromatography (GC), and measurement of the derivatives by electron capture detection (ECD)<sup>4-6</sup>. Both water and methanol were tested as the collection solvents, and the retention and recovery efficiencies for carbonyls were compared for both solvents.

## **EXPERIMENTAL METHODS**

## Sampling

The sampling and analytical method for carbonyl compounds were evaluated in the laboratory. Formaldehyde, acetaldehyde, acrolein, acetone, butyraldehyde, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and hexaldehyde were selected as the candidate compounds for the method evaluation. A schematic diagram of the dynamic dilution system used for the test is shown in Figure 1. Acrolein, acetone, MEK, MIBK, and hexaldehyde were generated from a certified cylinder containing 14 - 21 ppm (v/v) of each compound (Scott Specialty Gases, Inc., Plumsteadville, PA), and butyraldehyde (~ 12 ppm) was generated from a 6-L stainless steel canister prepared in the laboratory. Formaldehyde and acetaldehyde were generated with calibrated permeation tubes heated in an oven at  $100 \pm 0.1$  °C and  $40 \pm 0.1$  °C, respectively. A dynamic dilution system with a 1-liter dilution flask was used for mixing carbonyls with diluent nitrogen. The flow rate of diluent nitrogen was 1.75 to 2.5 L/min, and the flow rate of the cylinder containing carbonyls was 20 to 40 mL/min. This mixture produced a continuous supply of gas containing carbonyl compounds at concentrations of 200 to 400 ppb. The retention and recovery efficiencies of carbonyls were also tested under humid condition. A test gas containing  $\sim 10\%$  (v/v) of water was generated by adding a humidified gas stream to the gases entering the dilution flask. Water condensation would be expected to occur in the impinger with test gas containing 10% (v/v) of water, and the effects of water condensation on the recovery efficiencies for carbonyl compounds could thus be tested.

The gas mixture was passed from the dilution flask to a three-port manifold, and the carbonyl compounds were collected in two midget impingers connected in series. A Teflon tube (1/4" OD) was used to connect the sampling port and the upstream impinger, and the Teflon line was wrapped with heating tape to prevent the condensation of the sample stream on the sampling line. Each impinger was filled with 20 mL of water (Milli-Q organic-free water) or methanol (Purge and Trap grade, Aldrich Chemical Co., Milwaukee, WI). The impingers were immersed in an ice bath during the sampling period. A drierite was connected between the downstream impinger

and the sampling pump to absorb water vapor in the sample stream. A schematic diagram of the sampling train is shown in Figure 2. The sampling flow rate was  $\sim 1.0$  L/min, and the collection time was 20 minutes. Tylan mass flow controllers were used to regulate the flow rate. After sample collection, the sample was diluted with water or methanol, as appropriate, to a 25 mL volume before derivatization.

## Sample Derivatization

Carbonyl compounds were derivatized by PFBHA (Aldrich Chemical Co., Milwaukee, WI) and measured by a GC-ECD. The PFBHA (5 mg/mL) was prepared in Milli-Q organic-free water. After sample collection, an aliquot (2-5 mL) was taken from the impinger and placed in a second vial. To determine reaction and extraction efficiency of the carbonyls, ten  $\mu$ L of 100  $\mu$ g/mL 2,3,5,6-tetrafluorobenzaldehdye (TFB) surrogate additive standard was added to the sample before derivatization. Subsequently, PFBHA was added in the amount of 0.1 mL of 5 mg/mL to the sample. The amount of PFBHA added to the sample was ~10-fold molar excess, which enhanced derivatization yields. The vial was sealed and shaken for ~ 30 seconds and the mixture was allowed to react for 24 hours at room temperature. Three drops of 37% hydrochloric acid were then added to acidify the mixture. Most of the unreacted PFBHA remained in the acidic aqueous phase during the subsequent extraction. The derivatives were extracted with 2 mL of optima grade hexane containing  $0.4 \,\mu g/mL$  of 1,2-dibromopropane as an internal standard. When methanol was used as the collection solvent, 1 mL of water was added to the mixture before extraction to obtain better separation between methanol and hexane. Also, a second extraction of the methanol fraction was performed with 1 mL of pure hexane. The top layer of hexane was transferred to another vial with a Pasteur pipet and analyzed by a GC-ECD.

## Instrumentation and Analytical Methods

Carbonyl-PFBHA derivatives were analyzed on a Hewlett Packard 5890 GC equipped with an ECD. The GC column used for derivatives separation was a 60-m length, 0.32-mm ID, 1.0- $\mu$ m film thickness, SPB-1 fused silica column (Supelco, Inc., Bellefonte, PA). The column carrier gas flow rate was 2 mL/min. A split/splitless injector was used for this study, and the split ratio was 1:35. The injector temperature was 250 °C, and the detector temperature was 280 °C. Initial oven temperature was held at 60 °C for 1 minute, then increased to 180 °C at the rate of 5 °C/min, and ramped to 250 °C at the rate of 20 °C/min, and held at the final temperature for 5 minutes.

## RESULTS

## Gas chromatography and detection

All the target compounds were well separated by the selected column and temperature program (Figure 3). One derivative compound was formed for symmetrical formaldehyde, acetone, and TFB, and two geometrical isomers of the derivatives were formed for the rest of the compounds. Good detector response linearity was obtained for carbonyl-PFBHA derivatives generated from the reaction in both water and methanol and analyzed by a GC-ECD. The correlation coefficient ( $R^2$ ) was larger than 0.99 over the calibration range of 0.04 - 2.5 µg/mL for all of the compounds tested. The precision of the instrument was tested by injecting the same concentrated carbonyl-PFBHA standard over a two-weeks period. The response was reproducible and the retention time did not change significantly within two weeks ( $\pm$  0.1 min). The relative standard deviation of response was less than 10% for the target compounds during the two weeks (with 7 replication injections). The analytical detection limit was about 10 pg for the carbonyl-PFBHA derivatives.

The detection limit is equivalent to ~10 ng/L of carbonyl compounds in a 20-L sample collected from stationary source emissions.

## Derivatization yields of carbonyls with PFBHA in water, in methanol, and in acetonitrile

The derivatization yield of carbonyl with PFBHA in different solvents was studied. Samples with the same concentrations of carbonyls and PFBHA were prepared in water, methanol, and acetonitrile. These samples were allowed to react for 10, 20, 30, 60, and 90 minutes, and 2, 4, 8, 16, 20, and 24 hours. Duplicate samples were prepared for each time period. Samples were extracted with 2 mL of hexane containing 1,2-dibromopropane after the designated reaction time, and extracts were analyzed by a GC-ECD.

Aldehydes seemed to react faster than the ketones with PFBHA in each of the three solvents. The reactions of aldehydes with PFBHA were more than 90% completed after 2 hours, but the reactions of ketones with PFBHA required more than 8 hours for completion. The aldehyde-PFBHA derivatives were stable in both methanol and acetonitrile; however, they gradually dissociated in water after they formed (Figures 4a to 4c). Higher derivatization yields were obtained for the ketones in both methanol and acetonitrile than in water. Thus, a better sensitivity was obtained using methanol or acetonitrile as the solvent rather than using water as the solvent. For the subsequent tests, methanol was chosen as the solvent due to the toxicities of acetonitrile.

## Stabilities of carbonyls dissolved in water and in methanol

A two-week stability study was conducted for aldehydes and ketones in both water and methanol. Known amounts of carbonyls were spiked in both solvents. Phenol is often present in some industrial emissions that contain carbonyl compounds; therefore, the effect of phenol on the stability of carbonyls was also tested. Carbonyl mixtures plus phenol were prepared in water and methanol, and carbonyls were also added into a condensate field sample that contained phenol. The field sample was collected during an unrelated field test at a wood products plant press and dryer, and was obtained from the Paper Industry's National Council for Air and Stream Improvement (NCASI). The stability of carbonyls in water and in methanol with the addition of PFBHA was tested as well. Samples with addition of PFBHA were split into two sets. One set was stored in a refrigerator, and another set was stored at room temperature.

An aliquot was removed from each sample prepared above at designated storage times (0, 1, 2, 5, 7, 10, 14 days). Samples containing carbonyls only were allowed to react with PFBHA for 24 hours and then extracted with hexane containing 1,2-dibromopropane. Samples containing carbonyls and PFBHA were extracted directly with hexane containing 1,2-dibromopropane. The sample extracts were analyzed by a GC-ECD, and the response of each compound was compared with the data from Day 0. The results of the carbonyl stability studies are listed in Table 1.

All the compounds tested except acrolein were stable over the testing period in both water and methanol. Degradation of acrolein was observed in both solvents. In the presence of phenol (~25  $\mu$ g/mL), formaldehyde, acetaldehyde, and hexaldehyde decayed slowly in water, but not in methanol. The effect of phenol on acrolein degradation was further tested by preparing acrolein solutions (15  $\mu$ g/mL) with different phenol concentrations (5 - 50  $\mu$ g/mL) in both water and methanol. In water, the acrolein decay rate increased along with the increase of phenol concentration, but the decay rate observed for acrolein in methanol appeared to be the same regardless of the phenol concentrations. In both solvents, the phenol concentration did not

decrease over time. The results show that phenol probably promoted the dimerization of acrolein in water,<sup>5</sup> but this effect was not significant in methanol.

The addition of PFBHA stabilized carbonyls in both solvents. In methanol, carbonyl-PFBHA derivatives were stable over the testing period stored at room temperature and in the refrigerator. In water, formaldehyde, acetaldehyde, acrolein, and hexaldehyde were stabilized by PFBHA; however, as observed in the derivatization yield study, the derivatives of acrolein, hexaldehyde, and MIBK gradually dissociated in water stored either at room temperature or in the refrigerator. These results suggest that methanol is a better preservative for carbonyl compounds. In addition, carbonyl-PFBHA derivatives in hexane stored in a refrigerator were stable for 7 days but then started to decay. This was probably due to the dissociation of PFBHA derivatives in hexane.

### Comparison of the Retention and Recovery Efficiencies of Carbonyl Compounds Collected in Water and in Methanol

The retention and recovery efficiencies for the selected compounds were tested using midget impingers filled with 20 mL of methanol or water. The retention in the upstream impinger was > 85% for all the compounds tested when collected in methanol, but the retention was < 70% for acetaldehyde and < 60% for acrolein, butyraldehyde, and hexaldehyde when collected in water (Table 2). The recovery efficiency (total mass collected in upstream and downstream impingers) was > 80% for all the compounds tested using methanol as the collection solvent. When water was used as the solvent, the recovery efficiency was > 80% for acrolein, MEK, and MIBK but < 75% for butyraldehyde and hexaldehyde (Table 3). Also, larger variabilities of retention and recovery efficiencies were observed when water was used as the collection solvent versus using methanol as the collection solvent. When tested under the humid condition (~10% water v/v), the presence of moisture appeared to have no effects on the retention and recovery efficiencies for carbonyl compounds.

The retention and recovery efficiencies of carbonyls were also tested using water with the addition of PFBHA as the collection solvent. The retention in the first impinger was slightly higher for acrolein and hexaldehyde, but the recovery efficiency of hexaldehyde was still less than 75%.

#### CONCLUSIONS AND RECOMMENDATIONS

A test method has been developed in the laboratory for the collection and measurement of carbonyls from stationary source emissions. Carbonyls are more stable in methanol than in water, and higher retention and recovery efficiencies for carbonyls were obtained using methanol as the collection solvent. The derivatization yield of carbonyl-PFBHA was higher in methanol than in water; thus, a better sensitivity was obtained using methanol as the solvent. The preliminary laboratory evaluation indicates that this method can be applied to the collection and analysis of carbonyls, especially unstable carbonyl compounds such as acrolein, in stationary source emissions; however, field tests are needed to further test and evaluate this method.

#### DISCLAIMER

The research described in this paper has been funded wholly or in part by the United States Environmental Protection Agency through Cooperative Agreement No. CR 823866-01 to Research Triangle Institute, Research Triangle Park, NC. It has been reviewed by the Agency and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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	Formaldehyde	Acetaldehyde	Acrolein	Acetone	MEK	Butyraldehyde	MIBK	Hexaldehyde
Water (4°C)	93.2	93.5	67.4	102.2	107.1	NA <sup>2</sup>	94.5	84.2
Water+phenol (4°C)	81.3	84.5	47.6	91.3	90.2	NA <sup>2</sup>	82.2	70.1
Field water sample (4°C) (Containing phenol)	92.1	78.2	65.3	92.3	95.1	NA <sup>2</sup>	97.5	NA²
Water+phenol+PFBHA (4°C)	107.2	103.2	86.2	117.1	115.1	NA <sup>2</sup>	87.5	83.5
Water+phenol+PFBHA (R.T.)	95.2	97.5	72.7	116.1	115.1	NA <sup>2</sup>	86.5	80.5
Methanol (4°C)	99.2	95.3	46.8	<b>95.2</b>	105.1	116.1	95.3	97.2
Methanol+phenol (4°C)	98.3	95.2	53.5	88.9	85.6	107.7	87.2	91.5
Methanol+phenol+PFBHA (4°C)	93.0	94.1	97.8	96.9	101.1	106.6	113.1	91.8
Methanol+phenol+PFBHA (R.T.3)	105.9	92.6	96.0	93.7	97.5	105.7	115.3	90.7
Carbonyls-PFBHA-Hexane <sup>4</sup>	111.3	NA <sup>2</sup>	116.2	114.5	115.4	118.5	119.2	116.8

Table 1. Comparison of stability of carbonyls in water and in methanol after two weeks.

Relative Response % (Day 14/Day 0)'

<sup>1</sup>The stability of carbonyls was represented as the response from each day over the response from Day 0 (average of two replicate samples).

<sup>2</sup>Not tested.

<sup>3</sup>Room temperature.

<sup>4</sup>These values are the relative response after one week.

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	Methanol		Wa	Water			
А.	Retention	Precision %RSD	Retention	Precision %RSD			
Formaldehyde	95.7%	0.8%	93.8%	0.4%			
Acetaldehyde	92.8%	5.6%	70.8%	12.0%			
Acetone	92.3%	3.2%	85.4%	4.9%			
Acrolein	85.7%	2.7%	59.6%	13.4% .			
MEK	94.8%	2.0%	84.4%	2.9%			
Butyraldehyde	94.8%	1.0%	58.4%	4.2%			
MIBK	98.2%	0.7%	82.5%	4.0%			
Hexaldehyde	97.7%	0.4%	57.8%	15.7%			
	Recovery	Precision	Recovery	Precision			
B.	Efficiency	%RSD	Efficiency	%RSD			
Formaldehyde	85.8%	3.6%	88.6%	7.5%			
Acetaldehyde	89.1%	5.9%	100.7%	14.3%			
Acetone	97.3%	13.1%	112.2%	12.1%			
Acrolein	94.5%	8.2%	<b>9</b> 6.0%	6.9%			
MEK	107.3%	6.8%	110.9%	10.9%			
Butyraldehyde	87.8%	2.2%	75.0%	2.7%			
MIBK	115.0%	9.3%	76.6%	13.2%			
Hexaldehyde	83.1%	3.1%	60.5%	16.4%			

Table 2. Retention (A) and recovery efficiencies (B) of carbonyls using water ormethanol as the collection solvent under dry condition.

	Metl	nanol	Wa	Water		
А.	Retention	Precision %RSD	Retention	Precision %RSD		
Formaldehyde	90.7%	0.3%	95.3%	0.9%		
Acetaldehyde	94.8%	0.6%	70.0%	12.3%		
Acetone	<b>99.2%</b>	0.5%	86.2%	1.6%		
Acrolein	86.2%	0.8%	54.6%	5.3%		
MEK	95.0%	0.5%	83.7%	4.7%		
Butyraldehyde	93.7%	0.3%	62.9%	16.4%		
MIBK	98.7%	0.1%	85.9%	7.0%		
Hexaldehyde	92.5%	1.7%	41.3%	5.9%		
В.	Recovery Efficiency	Precision %RSD	<b>Recovery</b> Efficiency	Precision %RSD		
Formaldehyde	91.6%	4.5%	95.6%	2.1%		
Acetaldehyde	97.9%	0.9%	87.8%	4.7%		
Acetone	110.7%	5.4%	108.5%	2.4%		
Acrolein	105.8%	3.6%	113.1%	6.1%		
MEK	111.6%	6.8%	108.7%	4.7%		
Butyraldehyde	90.4%	3.0%	76.5%	5.2%		
MIBK	101.9%	10.2%	80.1%	3.7%		
Hexaldehyde	87.0%	2.0%	68.6%	7.1%		

Table 3. Retention (A) and recovery efficiencies (B) of carbonyls using water or methanol as the collection solvent under humid condition (10% water v/v).

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## Figure 2. Sampling train for carbonyl compounds

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TECHNICAL REPORT DATA						
1. REPORT NO. EPA600/A-98-049	2.			_		
4. TITLE AND SUBTITLE			5.REPORT DATE			
Measurement of carbonyl o	compounds from stat	ionary	March 18, 199	98		
source emissions using a PFBHA-GC/ECD method			6.PERFORMING ORGANIZATION CODE			
7. AUTHOR(S)			8.PERFORMING ORGA	NIZATION REPORT NO.		
Z. Fan, et.al., Research Research Triangle Park, M USEPA/ORD/HEASD, Research	, re, 27711					
9. PERFORMING ORGANIZATION NAME AND ADDRESS			10.PROGRAM ELEMENT NO.			
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			COOP CR823866			
12. SPONSORING AGENCY NAME AND	ADDRESS		13. TYPE OF REPORT AND PERIOD COVERED			
U. S. Environmental Prote	ection Agency		Meeting presentation			
NERL-RTP/HEASD/EMMB Research Triangle Park, N		14. SPONSORING AGENCY CODE				
15. SUPPLEMENTARY NOTES						
To be presented at the 91	l <sup>st</sup> annual AWMA Meet	ing, June 1	.4-19, 1998 in s	San Diego, CA		
16. ABSTRACT						
Carbonyl compounds have received increasing attention because of their important role in ground-level ozone formation. Currently, there is no validated stationary source method for the measurement of multiple carbonyl compounds containing unstable compounds such as acrolein. This paper presents the results for the laboratory development of a source method for the collection and analysis of eight carbonyl compounds (acetone, acrolein, acetaldehyde, butyraldehyde, formaldehyde, hexaldehyde, methyl ethyl ketone, and methyl isobutyl ketone). Samples are collected in two midget impingers, each containing 20 ml of methanol. The suggested sampling period is for 20 minutes and the sample rate is one liter per minute, resulting in a total collected sample of 20 liters. A two to five ml sample aliquot is removed, following completion of the sampling period, and stabilized with 0-2,3,4,5,6-pentafluorobenzyl hydroxylamine hydrochloride (PFBHA). The sample is reacted for a period of time, extracted with hexane and then analyzed by GC/ECD. The method is resistant to degradation of carbonyls from interference by phenols, has a detector response of $\mathbb{R}^2 \ge 0.99$ over the range of $0.04-2.5 \ \mu g/ml$ , and has an analytical detection limit of $\sim 10$ picograms. For a 20 minute field sample, this would equate to a source method detection limit of $\sim 10$ ng/ml.						
17.	KEY WORDS AND DOC	UMENT ANALYSIS	3			
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