

## Determination of Formaldehyde in Ambient Air

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Waters Corporation



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### Abstract

This application note details how Waters sample preparation products, column chemistries and instrumentation meet or exceed the requirement to sample and quantitate carbonyl compounds.

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## Introduction

Carbonyl compounds are known to promote the formation of photochemical ozone. Short term exposure is known to cause irritation of the skin, eyes, and mucous membrane of the upper respiratory tract. For these reasons, regulatory agencies from around the world are interested in monitoring these compounds. Waters sample preparation products, column chemistries and instrumentation meet or exceed the requirement to sample and quantitate these analytes. The agencies include US EPA, NIOSH, ASTM, ISO, and JPMHLW. There are directives being drafted and testing going on in most countries in the world.



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## Results and Discussion

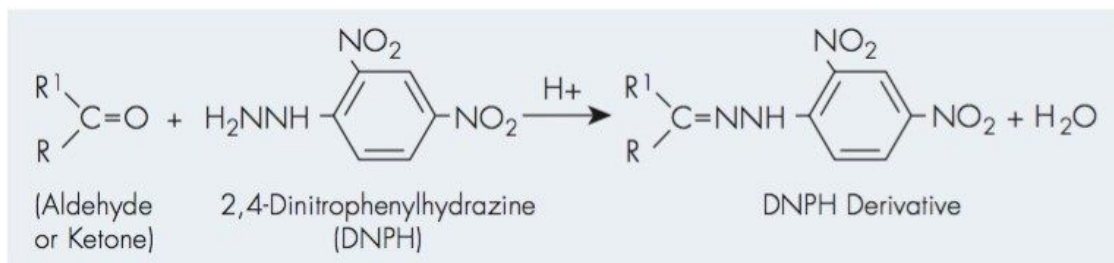
### Sep-Pak DNPH-Silica Cartridges for Analyzing Formaldehyde and Other Carbonyl Compounds in Air

Formaldehyde and other carbonyl compounds are receiving increasing attention both as toxic substances and as promoters in the photochemical formation of ozone in air. Source of aldehydes in residential buildings include plywood and particle board, insulation, combustion appliances, tobacco smoke and various consumer products. Aldehydes are released into the atmosphere in the exhaust of motor vehicles and other equipment in which hydrocarbon fuels are incompletely burned.

The most sensitive and specific method for analyzing aldehydes and ketones is based on their reaction with 2,4-dinitrophenylhydrazine (DNPH) and subsequent analysis of the hydrazone derivatives by HPLC. The hydrazones may be detected by absorbance in the ultraviolet region, with maximum sensitivity obtained

between 350 and 380 nm.

When carbonyl-containing compounds are adsorbed from air samples onto DNPH silica cartridges they are derivatized according to the following scheme:

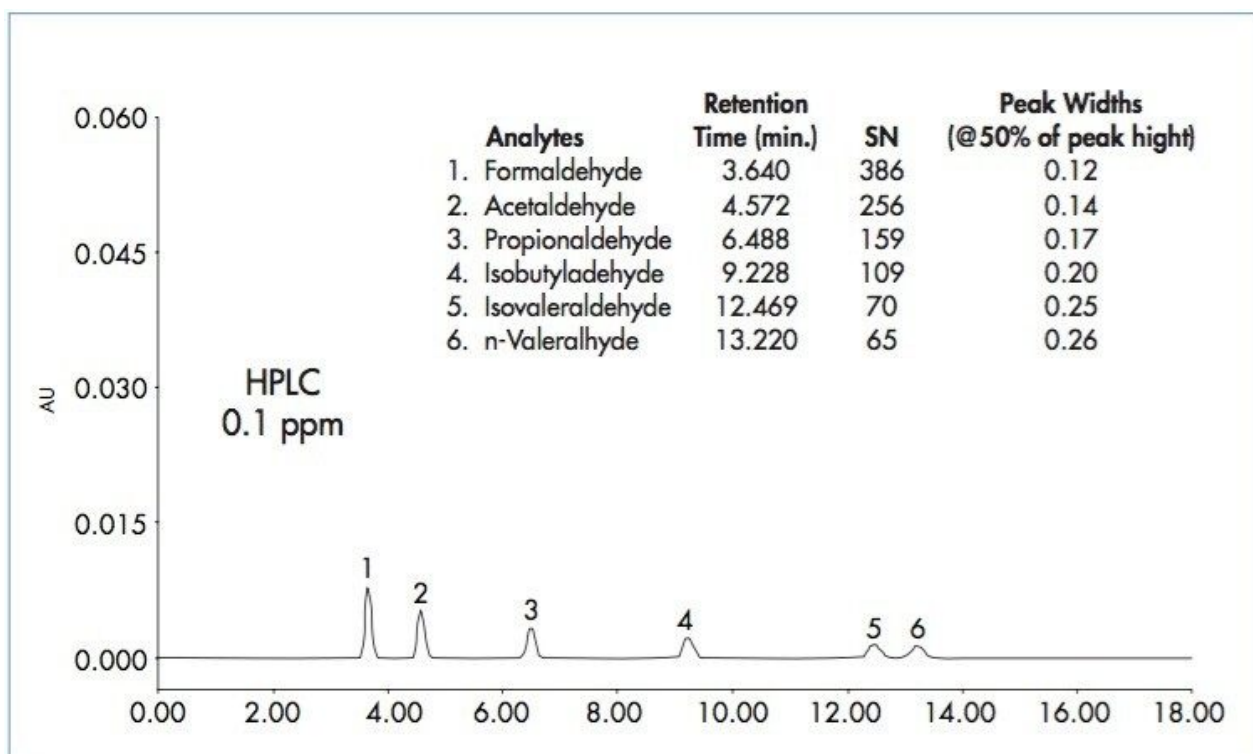


Sep-Pak DNPH-Silica cartridges meet the requirements of EPA Method TO -11A, JPM HLW and ISO 16000 providing a convenient device for sample collection. Using a vacuum pump, an air sample is drawn through the new Sep-Pak DNPH-Silica cartridge. The aldehydes and ketones react with the DNPH and form the hydrazone derivatives, which are retained on the cartridge. Later, the hydrazones are eluted from the cartridge with acetonitrile and analyzed by HPLC or Waters ACQUITY UPLC Technology. Detection limits can be as low as 3 ppbv for a 100 liter sample.

### Advantages of Waters Sep-Pak DNPH-Silica Cartridges

These cartridges provide you with significant advantages when compared to other techniques, such as liquid impingers, for the analysis of aldehydes and ketones. In addition, a new high speed, high resolution UPLC Technology application has been developed to provide excellent quantitation capability in the low parts-per-billion range.

## High-Level Example: HPLC Method: Aldehyde Profile from Diluted Auto Exhaust Emissions



- Sep-Pak DNPH-Silica cartridges meet the requirements of EPA Method TO-11A and ASTM-D-5791-1.
- Results from impingers and these cartridges are in excellent agreement.
- Solvent consumption, solvent exposure and hazardous waste disposal costs are reduced.
- Sep-Pak DNPH-Silica cartridges provide superior convenience and reproducibility, making them ideal for field sampling and process monitoring applications.
- Sep-Pak DNPH-Silica cartridges save time and increase productivity.
- Low background for higher sensitivity.

## HPLC Separation of DNPH Derivatives of Common Aldehydes and Ketones

Column: Nova-Pak® C<sub>18</sub> 3.9 x 150 mm  
Sample: Mixture of DNPH and DNPH derivatives in acetonitrile.

Mobile Phase: A: Water/Acetonitrile/Tetrahydrofuran 60/30/10 v/v/v

B: Water/Acetonitrile 40/60 v/v 3 mL

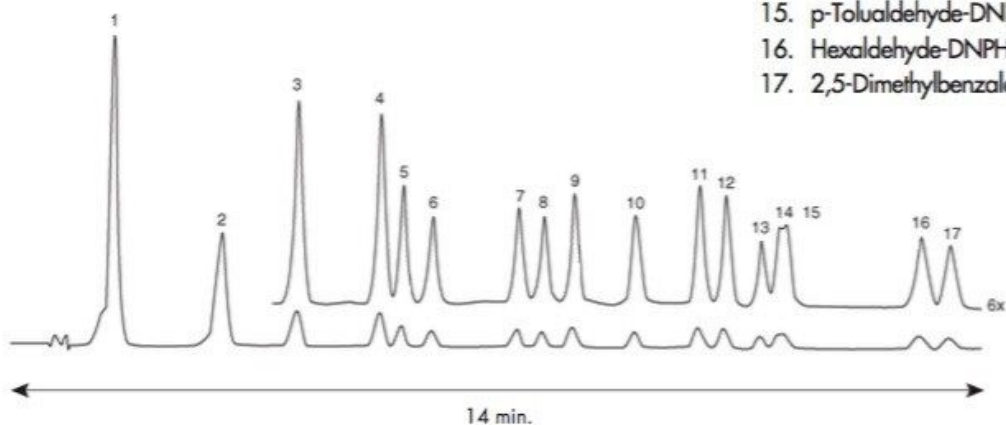
Gradient: 100% A for 1 minute, then linear gradient from 100% A to 100% B in 10 minutes

Flow Rate: 1.5 mL/min

Injection: 20 µL

Detection: 360 nm

1. DNPH
2. Formaldehyde-DNPH
3. Acetaldehyde-DNPH
4. Acetone-DNPH
5. Acrolein-DNPH
6. Propionaldehyde-DNPH
7. Crotonaldehyde-DNPH
8. Butanone-DNPH
9. Butyraldehyde-DNPH
10. Benzaldehyde-DNPH
11. Isovaleraldehyde-DNPH
12. Valeraldehyde-DNPH
13. o-Tolualdehyde-DNPH
14. m-Tolualdehyde-DNPH
15. p-Tolualdehyde-DNPH
16. Hexaldehyde-DNPH
17. 2,5-Dimethylbenzaldehyde-DNPH



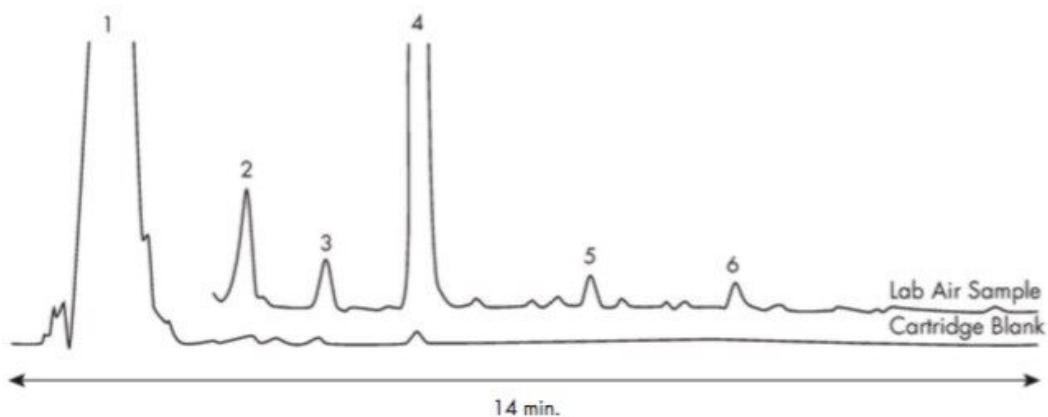
## Low-Level Example: Aldehyde Profile from Laboratory Air

### Lab Air Sample

1. DNPH	
2. Formaldehyde-DNPH	4.8 ppbv
3. Acetaldehyde-DNPH	1.2 ppbv
4. Acetone-DNPH	118.0 ppbv
5. Butanone-DNPH	0.8 ppbv
6. Isovaleraldehyde-DNPH	0.7 ppbv

### Cartridge Blank (calculated for 100 liter sample)

1. DNPH	
2. Formaldehyde-DNPH	0.35 ppbv
3. Acetaldehyde-DNPH	0.27 ppbv
4. Acetone-DNPH	0.34 ppbv



The sample was obtained in a chemical research laboratory using a portable sampling pump. One hundred liters of air was drawn through the cartridge at 0.65 L/min. The sample was found to contain low concentration of formaldehyde (4.8 ppbv), acetaldehyde (1.2 ppbv) and methyl ethyl ketone (0.8 ppbv), but a significant amount of acetone (118 ppbv). Significant concentrations of acetone are frequently found in laboratories because of its widespread use as a solvent.

## Ozone Scrubber Cartridge for Removing Ozone Interference When Monitoring Outdoor Air

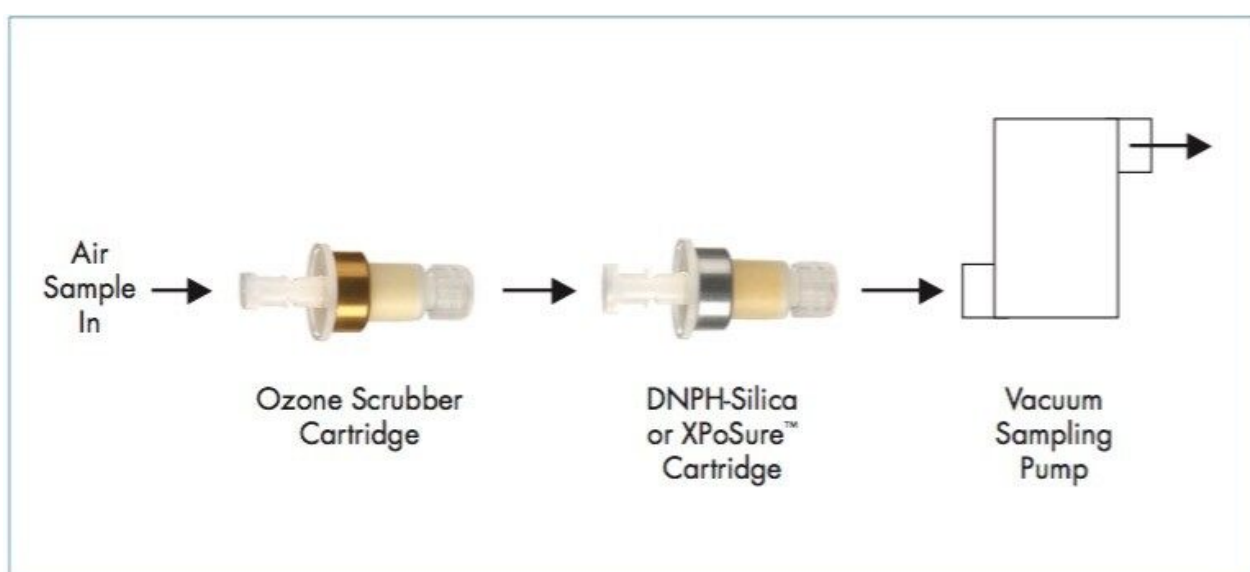
Ozone has been shown to interfere with the analysis of carbonyl compounds in air samples that have been drawn through cartridges containing silica-coated with 2,4-dinitrophenylhydrazine (DNPH). Waters Ozone Scrubber cartridges are designed to remove this ozone interference.

These disposable devices are intended for use in series combination with the Sep-Pak DNPH-Silica cartridges or XPoSure Aldehyde Sampler cartridges. One Ozone Scrubber cartridge replaces the 1/4" diameter by 36" long copper ozone denuder located in the heated zone of sampling systems used for outdoor air monitoring (PAMS program).

Each Ozone Scrubber cartridge contains 1.4 grams of granular potassium iodide. When air containing ozone is drawn through this packed bed, iodide is oxidized to iodine, consuming the ozone, according to the following reaction:



### Flow Schematic for Air Sampling System



The theoretical capacity of a single cartridge is 4.2 mmoles of ozone (200 µg). The particle size of the potassium iodide granules is optimized for good mass transfer and flow characteristics.

### XPoSure Aldehyde Sampler Cartridges for Monitoring Aldehydes in Indoor Air

Based on an extension of our DNPH coating technology, XPoSure Aldehyde Sampler cartridges are the most sensitive active samplers available today.

#### Highest Sensitivity

Compared to existing sampling tube technology which have high and variable backgrounds, XPoSure™ cartridges are guaranteed to give consistent low aldehyde backgrounds, cartridge-to-cartridge, lot-to-lot.

#### High-Collection Efficiencies

You can achieve > 95% collection efficiencies for all aldehydes at flows of up to a liter per minute. And, you only need to use one cartridge - no breakthrough bed is necessary.

Low Pressure Drop - Use with Portable Personal Sampling Pumps

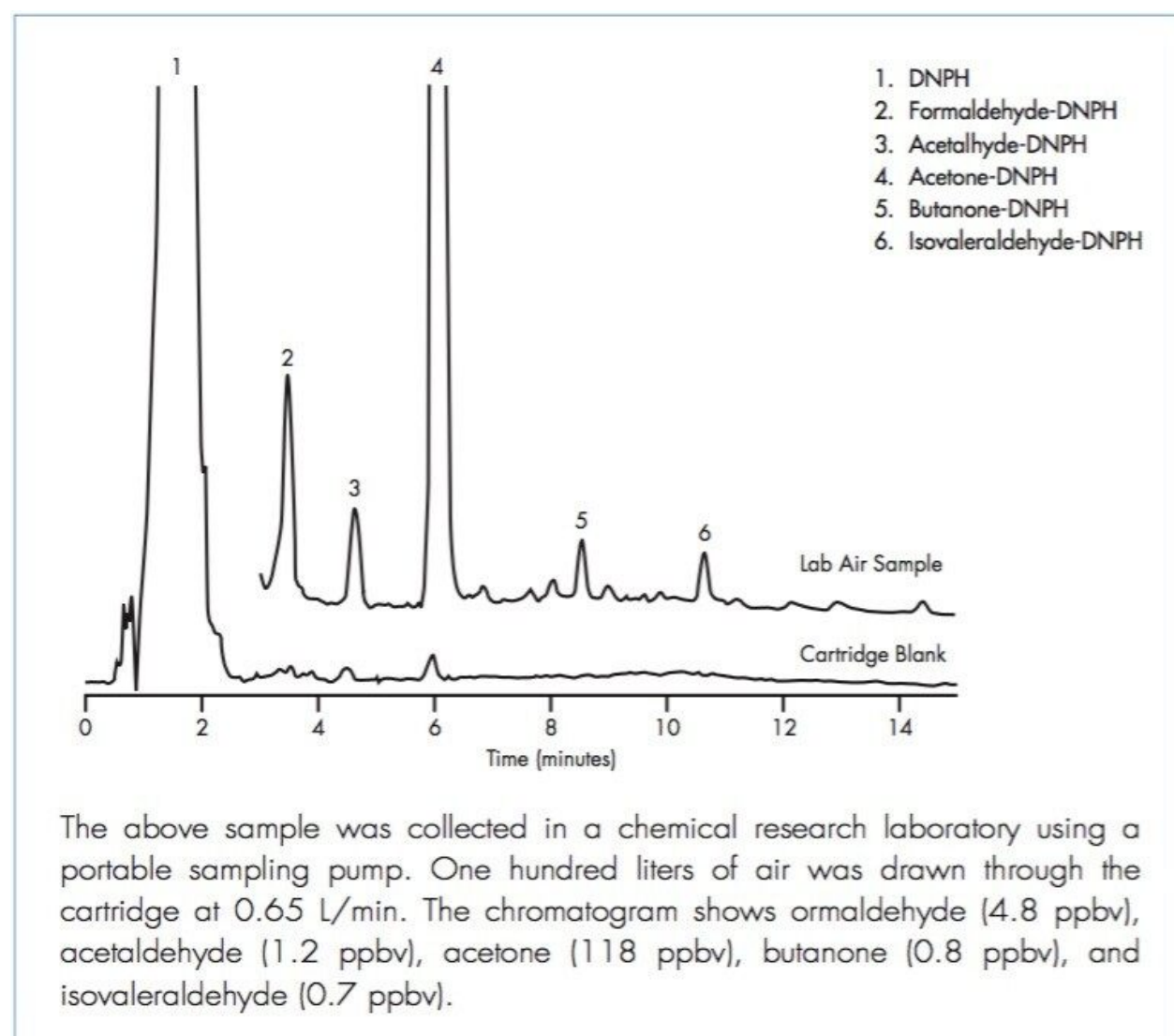
Large particle size and higher porosity frits make this new XPoSure cartridge compatible with personal sampling pumps.

Easy-to-Use

Sample, elute and shoot, it's that easy. You'll never have to break open and manipulate a glass tube again.

And because the cartridges are made from high density polyethylene (HDPE), breakage is not a concern.

### Low-Level Example: Aldehyde Profile from Laboratory Air



## Fast Analyses of Aldehydes and Ketones by ACQUITY UPLC Technology

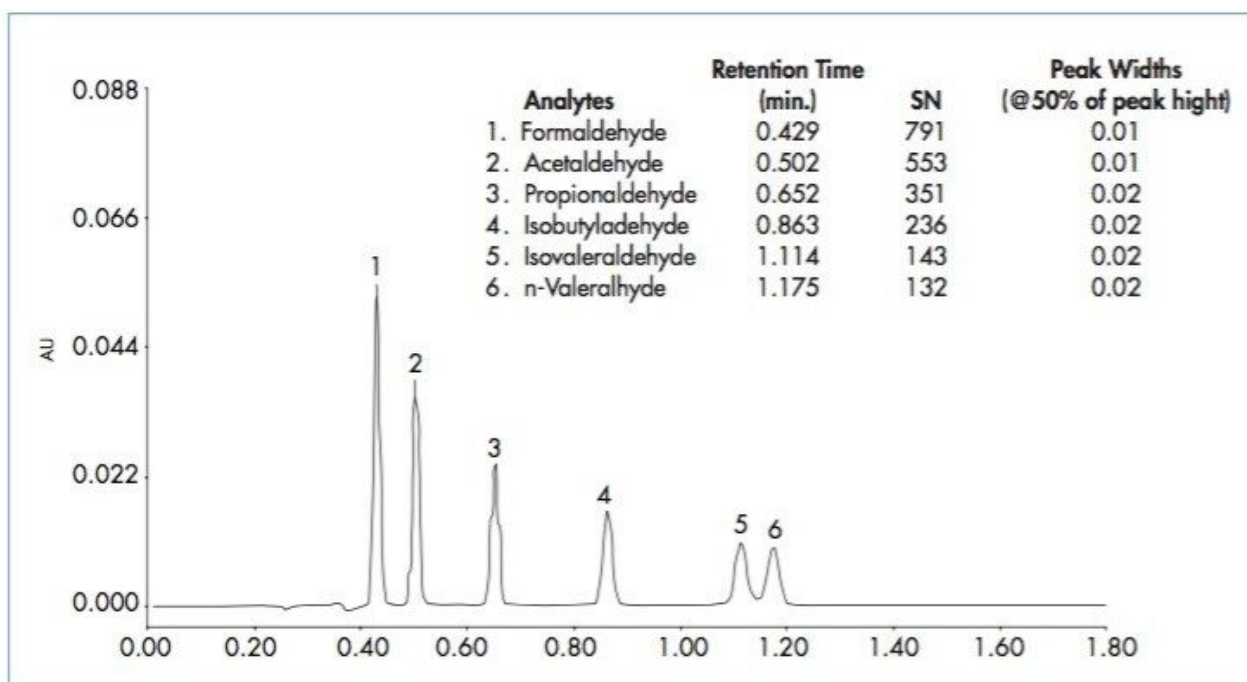
Aldehydes and ketones can be analyzed as DNPH derivatives rapidly and efficiency using Waters ACQUITY UPLC Technology. Results can be obtained several times faster than conventional HPLC technologies.



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*Waters ACQUITY UPLC System*

High-Level Example: UPLC Method: Aldehyde Profile from Diluted Auto Exhaust Emissions



## Sep-Pak DNPH-Silica Cartridge

	Description	Part Number	Mass/ Volume/Type	Chemistry
<b>DNPH Short</b>	<p>DNPH and XPoSure™ contains acidified dinitrophenylhydrazine reagent coated on a silica sorbent. Used for the collection of air samples and subsequent quantitation of aldehydes and ketones by reaction to form the hydrazone derivative, and analysis by HPLC.</p> <p>DNPH-Silica is specified in several EPA procedures for the analysis of carbonyl compounds in air.</p>	WAT037500 Box of 20	350 mg / 0.7 mL / Plus Short	<ol style="list-style-type: none"> <li>1. Particle Size - 55-105 µm</li> <li>2. Pore Size 125Å</li> <li>3. Coating 14 µmoles/g or 5 µmoles/cartridge</li> </ol>
<b>DNPH Long</b>	<p>DNPH and XPoSure™ contains acidified dinitrophenylhydrazine reagent coated on a silica sorbent. Used for the collection of air samples and subsequent quantitation of aldehydes and ketones by reaction to form the hydrazone derivative, and analysis by HPLC.</p> <p>DNPH-Silica is specified in several EPA procedures for the analysis of carbonyl compounds in air.</p>	WAT039550 Box of 20	800 mg/ 1.6 mL/ Plus Long	<ol style="list-style-type: none"> <li>1. Particle Size - 55-105 µm</li> <li>2. Pore Size 125Å</li> <li>3. Coating 14 µmoles/g or 10 µmoles/cartridge</li> </ol>

## Ozone Scrubber

	Description	Part Number	Mass/Volume/Type	Chemistry
Ozone Scrubber Potassium / Iodine	For removing ozone interference with the analysis of carbonyl compounds. Use in series with Sep-Pak® DNPH or XPOSure™ cartridge.	WAT054420 Box of 20	1.4 g / 1.6 mL / Plus Short	1. 1.4 g of potassium iodide 2. capacity 4.2 mmoles of ozone/cartridge
	Description	Part Number	Mass/Volume/Type	Chemistry
XPOSure™	Larger particle dinitrophenyl-hydrazine coated silica for use with personal air monitors.	WAT047205 Box of 20	350 mg / 0.7 mL / Plus Short	1. Particle size 500 - 1000 µm

## HPLC/UPLC™ Columns Recommended for Separation of DNPH Derivatives

Description	Dimensions	Particle Size	Part Number
Nova-Pak® C <sub>18</sub>	3.9 x 150 mm	4 µm	WAT086344
Symmetry® C <sub>18</sub>	3.9 x 150 mm	5 µm	WAT045905
ACQUITY UPLC® BEH Phenyl	2.1 x 100 mm	1.7 µm	186002885
ACQUITY UPLC® BEH Phenyl (3 pk)	2.1 x 100 mm	1.7 µm	186002885

## Featured Products

ACQUITY UPLC System <<https://www.waters.com/514207>>

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