Application Note 92

Monitoring Carbonyls in Air Using the LpDNPH S10 Cartridge with Analysis by HPLC

Supelco has designed an adsorbent cartridge for use in sampling carbonyls from ambient and indoor air as described in US EPA and ASTM methods. The LpDNPH S10 cartridge is silica based and precoated with 2,4-dinitrophenylhydrazine derivatizing reagent. This sampling device was laboratory tested and results compared to those from other, commercially available products. Field test results also were obtained. The LpDNPH S10 cartridge meets method criteria for purity, stability, and for the recovery and capacity of formaldehyde.

Key Words:
- air monitoring • carbonyls • DNPH reagent
- low pressure drop

There has been a growing concern about carbonyls as air pollutants because of their toxic properties and their role as ozone precursors. In 1990 the Clean Air Act Amendments, which include the regulation of carbonyls in the atmosphere, were enacted. The methodology describes sampling and analysis of carbonyls: US Environmental Protection Agency (EPA) ambient air method TO11 (1), indoor air method IP-6A (2), Photochemical Assessment Monitoring Station (PAMS) site testing guidelines (3) , and American Society for Testing and Materials (ASTM) D5197 (4). Each method requires the capture of airborne carbonyls on a silica-based adsorbent cartridge that is coated with 2,4-dinitrophenylhydrazine (DNPH) derivatizing reagent. Using these methods as guidelines, the capabilities of the new LpDNPH S10 cartridge were tested in the lab and at field PAMS sites.

The LpDNPH S10 cartridge (Figure A) is a solid phase extraction (SPE) tube containing high purity silica, particle size range 150-250µm (60/100 mesh), that has been surface-coated with DNPH reagent. (Carbonyls react with DNPH to form the more stable hydrazone.) The reagent loading (0.29% or 1mg/cartridge) and bed weight of 350mg were designed to meet the method specifications for a maximum cartridge capacity of 75µg of formaldehyde. A sampling pump draws air samples through the device at flow rates from 0.5-1.5L/min. Following sample collection, the cartridges are desorbed with 5.0mL high purity acetonitrile using a vacuum manifold, in reverse direction of the air flow. The cartridge's built-in reservoir allows rapid desorption without the attachment of a syringe barrel. Analysis is by HPLC/UV using the DNPH-carbonyl derivatives for calibration. Figure B illustrates the separation of 15 carbonyl derivatives using a single LC-18 column.

Figure A. LpDNPH S10 Cartridge

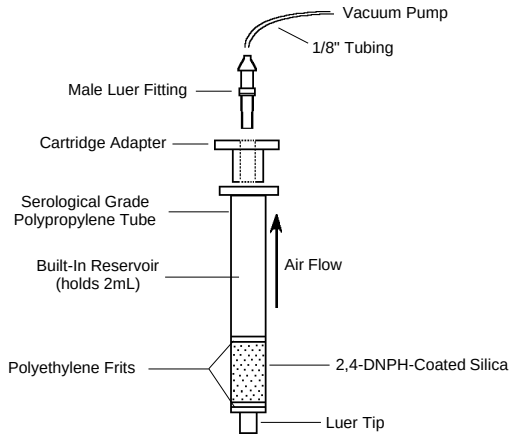

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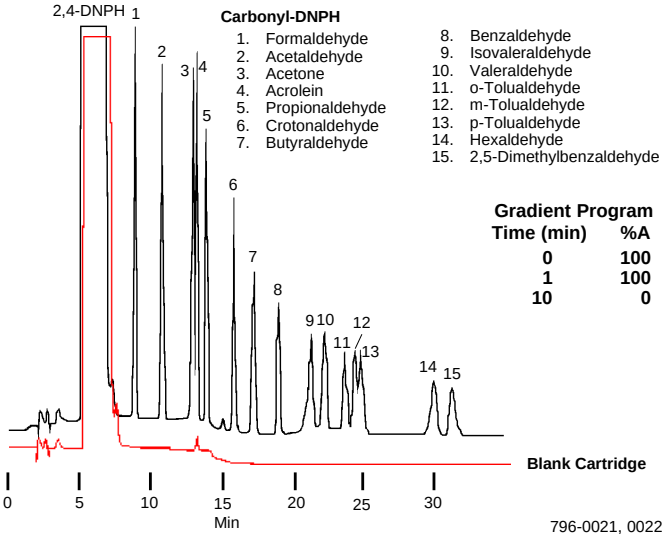
Figure B. Spiked Cartridge vs. Blank

Column: **SUPELCOSIL™ LC-18**, 25cm x 4.6mm ID, 5µm particles
Mobile Phase: A - water/acetonitrile/tetrahydrofuran (60/30/10)
B - water/acetonitrile (40/60)
Flow Rate: 1.5mL/min
Det.: UV, 360nm
Inj.: 25µL of extract

Spiked Cartridge
(~5µg each aldehyde/ketone-DNPH derivative)



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The combination of the large particle size silica and the syringe barrel cartridge design results in very low pressure drop across the sampling device: from 3.5 inches of water (0.9kPa) at 200cc/min to a high of only 34 inches of water (8.6kPa) at 1.9L/min. This pressure drop allows the use of a variety of sampling pumps, such as an automated sequential sampler used for PAMS monitoring and a personal sampling pump.

According to methodology, linearity of the analytical system is established by a five-point calibration curve using standard solutions of the DNPH derivative of the monitored carbonyls . A ten-point calibration curve for formaldehyde-DNPH, covering a standard concentration range of 0.005 to 15.0µg/mL, yielded a correlation coefficient of 0.999. In addition, eight-point curves for acetaldehyde and acetone-DNPH, for the range of 0.005 to 7.5µg/mL, resulted in correlations of 0.9999.

The average background level in five different lots of the cartridge and a comparison of other sampling devices can be found in Table 1. Field test results from a California PAMS site showed blanks of 0.00µg/cartridge for formaldehyde, acetaldehyde, and methyl ethyl ketone (MEK), and 0.22µg/cartridge for acetone. When kept refrigerated, the blanks remained at <0.1µg/cartridge for formaldehyde for the duration of the 12-month stability study.

Recovery studies were done by dynamically spiking the sampling device. Dilute, liquid standards of formaldehyde, acetone, and acetaldehyde were spiked into a glass midget impinger, which was warmed to a uniform temperature of 60°C. A sampling pump was then attached and air drawn from the impinger through the cartridge at 1.5L/min.

Table 2 is a summary of the recovery study. While recoveries for formaldehyde and acetaldehyde were 100% and exhibited good reproducibility, results for acetone varied and exhibited reduced recoveries at the higher concentration levels. Comparison of recovery efficiencies with other sampling devices are included in Table 2. Test results obtained from this method were confirmed using a calibrated formaldehyde permeation device to assure that no sampling biases were introduced. Field test results agreed with our findings. Spiked cartridges stored at 4°C were found to be stable (≥96% recovery) after 8 weeks, exceeding method requirements.

The LpDNPH S10 sampling device meets all criteria required by EPA and ASTM methods. The versatility of the cartridge makes it convenient to use in the field and in the laboratory. Because of low pressure drop and low background interference, sensitivity and validity of sampling results are enhanced.

Table 1. Carbonyl Background Comparison

Cartridge	µg/Cartridge Formaldehyde	Acetaldehyde	Acetone
Supelco LpDNPH, avg. 5 lots	0.036	0.008	0.082
Supplier #2, type A, avg. 2 lots	0.063	0.023	0.061
Supplier #2, type B, 1 lot	0.043	0.167	0.118

Table 2. Carbonyl Recovery Comparison

Cartridge	Total Carbonyls µg/cart.	Recovery (%) Formaldehyde	Acetaldehyde	Acetone
Supelco LpDNPH, avg. 2 lots, n=3	0.6	103	127	103
	6.0	104	135	93
	60.0	106	120	69
Supplier #2, type A, 1 lot, n=1	0.6	90	103	160
	6.0	104	120	98
	60.0	108	124	88
Supplier #2, type B, 1 lot, n=1	0.6	160	139	111
	6.0	106	123	78
	60.0	104	113	59

Cartridges were spiked dynamically, ambient temperature 74 -80°F, humidity range 22-50%. Recoveries were background corrected.

Contact our Technical Service Department (phone 800-359-3041 or 814-359-3041, FAX 800-359-3044 or 814-359-5468) for expert answers to your questions.

Ordering Information:

Description	Cat. No.
LpDNPH S10 Cartridge Starter Kit (10 cartridges, adapters)	**21024-U**
LpDNPH S10 Cartridges (10 cartridges)	**21026-U**
LpDNPH S1050 Cartridges (5 packs of 10 cartridges)	**21014**
SUPELCOSIL LC-18 HPLC column 25m x 4.6mm ID, 5.0µm particles	**58298**
TO11/IP-6A Aldehyde/Ketone-DNPH Mix 15µg/mL each of carbonyl equivalent in acetonitrile, 1mL	**47285-U**

References

1. *Method for the Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC),* US EPA Method TO11, Revision 1.0, June 1987.
2. *Determination of Formaldehyde and Other Aldehydes in Indoor Air Using a Solid Adsorbent Cartridge,* US EPA Method IP-6A, revised September 30, 1989.
3. *Technical Assistance Document for Sampling and Analysis of Ozone Precursors,* EPA/600-8-91/215, Section 5 "Methodology for Determining Carbonyl Compounds in Ambient Air."
4. *Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology),* ASTM D 5197-92, 1916 Race St., Phila., PA 19103.

References not available from Supelco.

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