

# TheReporter

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# Monitoring Aldehydes in Air, Using a New Adsorbent Cartridge and Reference Standard and HPLC

E. Doughty, I. DeGraff, D. Henderson, L. Nolan

*A new calibration standard containing fifteen 2,4-dinitrophenylhydrazine (DNPH)-aldehyde derivatives, a new air sampling cartridge containing DNPH-coated silica gel, and a SUPELCOSIL LC-18 column will enable industrial hygienists and others to monitor ozone precursors in air. Gradient analysis provides baseline resolution of all but two analytes. Two additional analytes coelute under isocratic conditions, but reequilibration time is eliminated. The new products meet the specifications described in US Environmental Protection Agency methods TO11 and IP-6A, American Society for Testing and Materials Method D5197, and the EPA's Technical Assistance Document for Sampling and Analysis of Ozone Precursors.*

In the uppermost atmosphere ozone (O<sub>3</sub>) is a vital barrier against dangerous solar radiation, but at lower and surface levels ozone is hazardous to human health. Under revisions to the Clean Air Act, photochemical assessment monitoring stations (PAMS sites) are established to monitor surface and upper air for aldehydes and volatile organic compounds which are known ozone precursors. Levels of these compounds contribute directly to the quality of ambient air. Of specific interest are formaldehyde and other carbonyl-containing compounds.

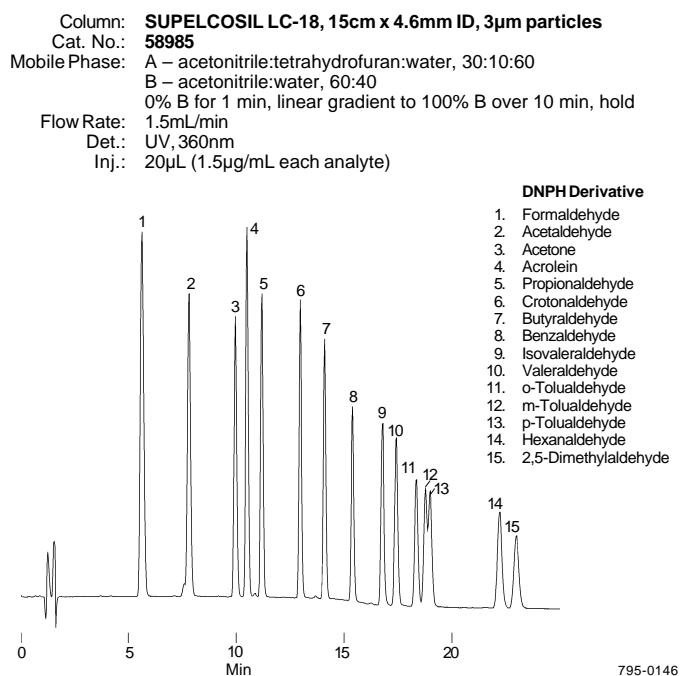
Historically, analysts have monitored carbonyl-containing compounds by following US Environmental Protection Agency (EPA) Toxic Organics Method TO5 or TO11. These methods are based on the conversion of carbonyl-containing compounds to 2,4-dinitrophenylhydrazine (DNPH) derivatives, or hydrazones, which then are analyzed by HPLC. The main difference between the two methods is that in Method TO5 a liquid impinger is used to convert the analytes to their DNPH derivatives, while in Method TO11 a DNPH-coated silica gel in a solid phase extraction tube is used to simultaneously trap and derivatize the analytes. EPA Method IP-6A and American Society for Testing and Materials (ASTM) Method D5197 are very similar to method TO11 and call for similar sampling and separation technology.

A major challenge to analysts monitoring aldehydes by any of these methods has been the lack of an appropriate reference standard. Supelco now introduces a calibration reference standard for use with EPA methods TO11 or IP-6A. TO11/IP-6A Aldehyde/Ketone-DNPH Mix contains DNPH derivatives of acetone and 14 aldehydes in acetonitrile (Figure A). While the amount of each derivative in the standard varies (from 105 µg/mL to 35.1 µg/mL), the equivalent amount of the underivatized molecules is uniform (15 µg/mL).

In addition to the new reference standard, we also introduce a new air sampling cartridge, produced to specifications outlined in the

EPA and other aldehyde monitoring methods. Supelclean™ LPD DNPH Cartridges are manufactured and produced for sampling aldehydes under EPA Method TO11, IP-6A, *Technical Assistance Document for Sampling and Analysis of Ozone Precursors*, and ASTM

**Figure A. Carbonyl-DNPH Standard on a 3 µm SUPELCOSIL LC-18 Column**



Method D5197. The new cartridges contain a 350mg bed of 150-250µm chrom-atographic grade silica gel coated with a 0.29% loading of DNPH. Each cartridge exhibits low background, and has a formaldehyde capacity of approximately 75µg. The estimated pressure drop across the cartridge is less than 7kPa (10psi) at a sampling flow of 1.5 liters/minute, hence the low pressure drop (LPD) designation.

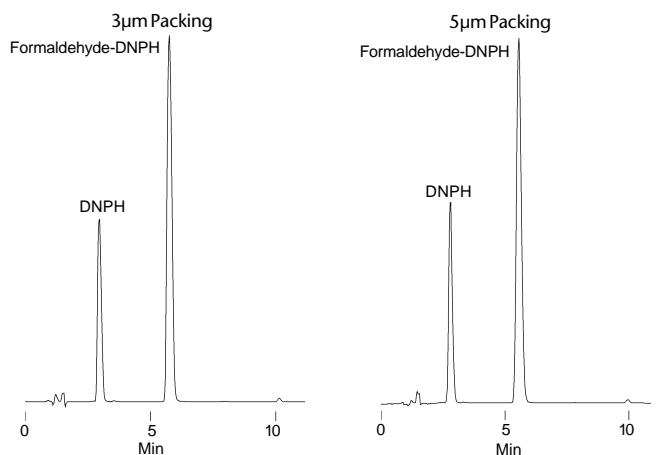
Samples collected on Supelclean LPD DNPH cartridges are eluted with acetonitrile and analyzed by reversed phase HPLC, in isocratic or gradient mode, on a SUPELCOSIL™ LC-18 HPLC column. Analysts in our laboratories have separated the 15 DNPH compounds on 15cm x 4.6mm columns containing 3µm and

5 $\mu$ m silica-based packings. Figure A demonstrates the gradient separation. All peaks except meta and para tolualdehyde-DNPH are resolved to baseline – a separation superior to other published separations of these analytes. We also analyzed a sample containing DNPH and formaldehyde-DNPH under the gradient conditions, to demonstrate that underivatized DNPH reagent, which is present in all analyzed samples, can be resolved from formaldehyde-DNPH. On either SUPELCOSIL LC-18 column, DNPH elutes well before formaldehyde-DNPH (Figure B), making either column suitable for this analysis.

When we separated the DNPH-aldehydes under isocratic conditions, we obtained sharp peaks from both 5 $\mu$ m (Figure C) and 3 $\mu$ m

### Figure B. DNPH and Formaldehyde-DNPH Resolved

Columns: SUPELCOSIL LC-18, 15cm x 4.6mm ID  
 Cat. Nos.: 58985 (3 $\mu$ m particles), 58230-U (5 $\mu$ m particles)  
 Mobile Phase: A – acetonitrile:tetrahydrofuran:water, 30:10:60  
 B – acetonitrile:water, 60:40  
 0% B for 1 min, linear gradient to 100% B over 10 min, hold  
 Flow Rate: 1.5mL/min  
 Det.: UV, 360nm  
 Inj.: 20 $\mu$ L (1.5 $\mu$ g/mL each analyte)



columns. Under these conditions, however, two pair of analytes coelute: meta and para tolualdehyde-DNPH and acetone-DNPH and acrolein-DNPH. Increased throughput and the solvent conservation associated with eliminating equilibration time can offset these coelutions, particularly if these aldehydes are not present in your samples. A 25cm x 4.6mm column (5 $\mu$ m packing) improves the resolution of acetone-DNPH/acrolein-DNPH, but the best resolution is still that obtained by using the gradient conditions.

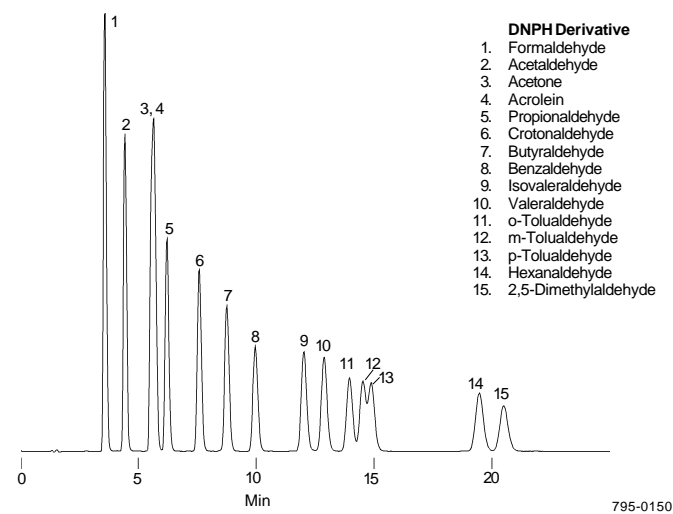
In addition to the new reference standard, the new sampling cartridge, and SUPELCOSIL HPLC columns, we also offer a sequential air sampler specifically designed for air sampling as described in the EPA's *Technical Assistance Document for Sampling and Analysis of Ozone Precursors*. The sampler (Model 2210, Cat. No. 24649)

is described in product specification sheet 494117 (available on request).

If you must monitor aldehydes in indoor or ambient air, we highly recommend our new TO11/IP-6A Aldehyde/Ketone-DNPH Mix, new Supelclean LPD DNPH Adsorbent Cartridges, and a SUPELCOSIL LC-18 column.

### Figure C. Isocratic Analysis of Carbonyl-DNPH Compounds

Column: SUPELCOSIL LC-18, 15cm x 4.6mm ID (5 $\mu$ m particles)  
 Cat. No.: 58230-U  
 Mobile Phase: acetonitrile:water, 60:40  
 Flow Rate: 1mL/min  
 Det.: UV, 360nm  
 Inj.: 20 $\mu$ L (1.5 $\mu$ g/mL each analyte)



### Ordering Information:

TO11/IP-6A Aldehyde/Ketone-DNPH Mix	47285-U
Supelclean LPD DNPH Adsorbent Cartridges pk. of 10	21024-U
SUPELCOSIL LC-18 Columns	
15cm x 4.6mm, 3 $\mu$ m particles	58985
15cm x 4.6mm, 5 $\mu$ m particles	58230-U
25cm x 4.6mm, 5 $\mu$ m particles	58298
Sequential Air Sampler	24649

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