

Alternative Analysis of Formaldehyde-DNPH and Other Carbonyl-DNPH Derivatives by Capillary GC

GC analysis of 15 carbonyl-DNPH compounds has some advantages over the HPLC analyses described in US EPA and other environmental methods. GC provides good resolution and reduces analysis time by almost 50%.

Key Words:

- cation exchange resin • carbonyl-DNPH
- formaldehyde

Determination of formaldehyde and 14 other carbonyls in air according to US Environmental Protection Agency Method TO11 and American Society for Testing and Materials Method D5197 calls for trapping the analytes on silica gel coated with 2,4-dinitrophenylhydrazine (DNPH), followed by HPLC/UV analysis. While sensitive, UV detection can be nonspecific, and is subject to many interferences. To obtain sufficient resolution using HPLC, analysis time can be long. Furthermore, some air monitoring laboratories are not equipped for HPLC analyses.

A recently developed capillary GC method provides an alternative to the accepted HPLC methodology. Resolution and sensitivity are good for many of the carbonyls evaluated. Analysis time is much shorter by GC than by HPLC (16 min vs. 30 min).

Over time, with high sample throughput, excess DNPH in sample extracts could have adverse effects on the column or detector, and could interfere with GC analysis of the carbonyl derivatives. A brief study was done to determine stability and ruggedness of the GC inlet, column, and detector systems when exposed to repeated injections of DNPH-derivatized extracts.

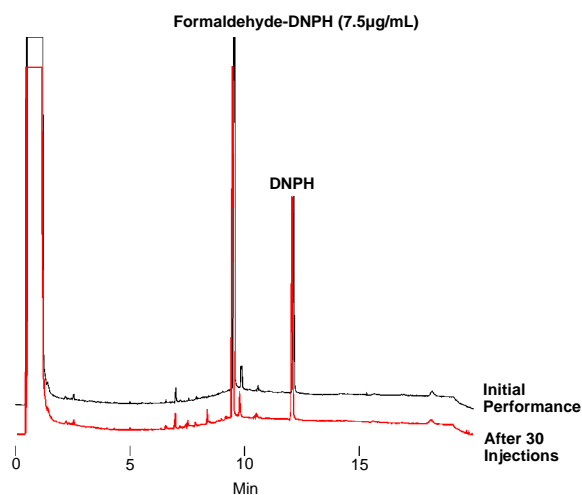
An LpDNPH S10 sampling cartridge was spiked with 75µg of formaldehyde standard, then eluted with 10mL of acetonitrile. A series of aliquots of the eluate were injected, without cleanup, into a capillary GC system. After 30 injections, there was no observable increase in background or decrease in sensitivity. Area counts and peak shape for formaldehyde-DNPH remained stable (Figure A).

For prolonged analysis, cleanup of the sample extracts may be necessary. Excess DNPH is easily removed by passing 4-5mL of extract through a 6mL cartridge containing 0.5g of specially cleaned cation exchange resin (1). Results are shown in Figure B. Recovery of formaldehyde-DNPH remained at an acceptably high level (96%) after cleanup.

A flame ionization detector (FID) can be used to analyze the carbonyl-DNPH compounds at concentrations of 0.15µg/mL or higher. An electron capture detector (ECD) offers greater sensitivity (<1.5ng/mL), but excess DNPH present in the sample extracts

Figure A. Capillary GC Column Is Stable in the Presence of Excess DNPH

Column: SPB-5, 15m x 0.53mm ID, 0.5µm film
Cat. No.: 25316
Oven: 50°C (1 min) to 250°C at 25°C/min, hold
Carrier: helium, 15mL/min
Detection: FID, 330°C
Injection: 1µL, splitless, 220°C



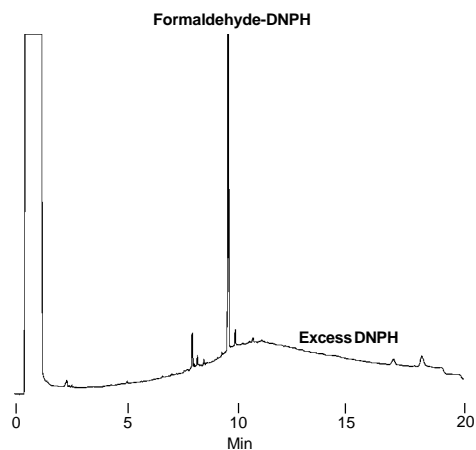
796-0090,0091

contains many detectable impurities, and has a large, interfering tail. If an ECD is being used, excess DNPH should first be removed by passing the extracts through a cleanup column as previously described. A nitrogen-phosphorus detector (NPD) is selective for the hydrazones, but the eluant — acetonitrile — would overload an NPD and cause interference.

An SPB™-5 column provides the best chromatography and the shortest analysis time. Figure C compares a calibration standard with a blank extract, showing the excess DNPH. Only two pairs of analytes coelute: acrolein and propionaldehyde, and o- and m-tolualdehyde. A rapid carrier gas flow rate is important. Slow flows produce excessive retention times and poor chromatography. Our investigation shows that faster flows can extinguish the FID flame when solvent reaches the detector. This is overcome by adjusting the hydrogen flow relative to carrier and make-up gas flows. Both split and splitless injections are acceptable.

Figure B. Cation Exchange Resin Removes DNPH from Sampling Tube Extract

Conditions same as Figure A.



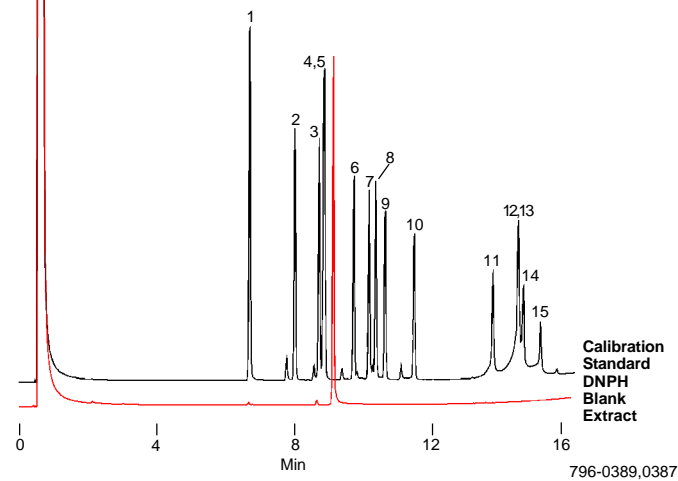
96-0169

Figure C. Carbonyl-DNPH Mix by GC/FID

Column: **SPB-5, 30m x 0.53mm ID, 0.5µm film**
 Cat. No.: **25317**
 Oven: 150°C (2 min) to 300°C at 10°C/min
 Carrier: helium, 12.5cc/min
 Detection: FID, 320°C
 Injection: 1µL, direct injection, 220°C

Carbonyl-DNPH (at 15µg/mL)

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



796-0389,0387

Ordering Information:

LpDNPH S10 Adsorbent Cartridge Starter Kit

10 cartridges plus adapters for various air sampling pumps **21024-U**

SPB-5 Fused Silica Capillary Columns

15m x 0.53mm ID, 0.5µm film **25316**
 30m x 0.53mm ID, 0.5µm film **25317**

TO11/IP-6A Aldehyde/Ketone-DNPH Mix

15 DNPH derivatives at 15µg/mL as carbonyl in acetonitrile, 1mL **47285-U**

Other mixes are available — please inquire.

SPB is a trademark of Sigma-Aldrich Co.

Fused silica columns manufactured under HP US patent no. 4,293,415.

Reference

1. Dalene, M., P. Persson, G. Skarping, *J. Chromatogr.*, 626: 284-288 (1992).
 Reference not available from Supelco.

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.

Note 107

For more information, or current prices, contact your nearest Supelco subsidiary listed below. To obtain further contact information, visit our website (www.sigma-aldrich.com), see the Supelco catalog, or contact Supelco, Bellefonte, PA 16823-0048 USA.

ARGENTINA · Sigma-Aldrich de Argentina, S.A. · Buenos Aires 1119 **AUSTRALIA** · Sigma-Aldrich Pty. Ltd. · Castle Hill NSW 2154 **AUSTRIA** · Sigma-Aldrich Handels GmbH · A-1110 Wien
BELGIUM · Sigma-Aldrich N.V./S.A. · B-2880 Bornem **BRAZIL** · Sigma-Aldrich Quimica Brasil Ltda. · 01239-010 São Paulo, SP **CANADA** · Sigma-Aldrich Canada, Ltd. · 2149 Winston Park Dr., Oakville, ON L6H 6J8
CZECH REPUBLIC · Sigma-Aldrich s.r.o. · 186 00 Praha 8 **DENMARK** · Sigma-Aldrich Denmark A/S · DK-2665 Vallensbaek Strand **FINLAND** · Sigma-Aldrich Finland/YA-Kemia Oy · FIN-00700 Helsinki
FRANCE · Sigma-Aldrich Chimie · 38297 Saint-Quentin-Fallavier Cedex **GERMANY** · Sigma-Aldrich Chemie GmbH · D-82041 Deisenhofen **GREECE** · Sigma-Aldrich (o.m.) Ltd. · Ilioupoli 16346, Athens
HUNGARY · Sigma-Aldrich Kft. · H-1067 Budapest **INDIA** · Sigma-Aldrich Co. · Bangalore 560 048 **IRELAND** · Sigma-Aldrich Ireland Ltd. · Dublin 24 **ISRAEL** · Sigma Israel Chemicals Ltd. · Rehovot 76100
ITALY · Sigma-Aldrich s.r.l. · 20151 Milano **JAPAN** · Sigma-Aldrich Japan K.K. · Chuo-ku, Tokyo 103 **KOREA** · Sigma-Aldrich Korea · Seoul **MALAYSIA** · Sigma-Aldrich (M) Sdn. Bhd. · Selangor
MEXICO · Sigma-Aldrich Química S.A. de C.V. · 50200 Toluca **NETHERLANDS** · Sigma-Aldrich Chemie BV · 3330 AA Zwijndrecht **NORWAY** · Sigma-Aldrich Norway · Torshov · N-0401 Oslo
POLAND · Sigma-Aldrich Sp. z o.o. · 61-663 Poznań **PORTUGAL** · Sigma-Aldrich Quimica, S.A. · Sintra 2710 **RUSSIA** · Sigma-Aldrich Russia · Moscow 103062 **SINGAPORE** · Sigma-Aldrich Pte. Ltd.
SOUTH AFRICA · Sigma-Aldrich (pty) Ltd. · Jet Park 1459 **SPAIN** · Sigma-Aldrich Quimica, S.A. · 28100 Alcobendas, Madrid **SWEDEN** · Sigma-Aldrich Sweden AB · 135 70 Stockholm
SWITZERLAND · Supelco · CH-9471 Buchs **UNITED KINGDOM** · Sigma-Aldrich Company Ltd. · Poole, Dorset BH12 4QH
UNITED STATES · Supelco · Supelco Park · Bellefonte, PA 16823-0048 · Phone 800-247-6628 or 814-359-3441 · Fax 800-447-3044 or 814-359-3044 · email: supelco@sial.com

H

Supelco is a member of the Sigma-Aldrich family. Supelco products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product for a particular use. Additional terms and conditions may apply. Please see the reverse side of the invoice or packing slip.

BT0