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 DS197 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.

For a flame ionization detector (FID) to 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 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.
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**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
  2. Acetaldehyde
  3. Acetone
  4. Acrolein
  5. Propionaldehyde
  6. Butyraldehyde
  7. Isovaleraldehyde
  8. Crotonaldehyde
  9. Valeraldehyde
  10. Hexaldehyde
  11. Benzaldehyde
  12. p-Tolualdehyde
  13. m-Tolualdehyde
  14. o-Tolualdehyde
  15. 2,5-Dimethylbenzaldehyde

- **Reference not available from Supelco.**
- SPB is a trademark of Sigma-Aldrich Co.
- Fused silica columns manufactured under HP US patent no. 4,293,415.

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

**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.