Waters Integrity System Applications

The Analysis of DNPH Derivatives Using the Integrity LC/MS System

Highlights: Detection and identification of aldehydes as DNPH derivatives by combined PDA/MS detection.

Aldehydes and ketones in ambient outdoor and indoor air are monitored according to EPA Method TO-11. This method typically requires that high volumes of air samples be collected using DNPH cartridges and extracted using solvent prior to HPLC analysis. Aldehydes are easily analyzed as extracted DNPH derivatives. Rather than using single detector HPLC analysis, the combined PDA/MS technique eliminates the effects of interferences from sample matrices. MS also affords positive identification of these DNPH derivatives while the PDA detector is used to check for peak purity which yields greater confidence in data.

Analytical Conditions

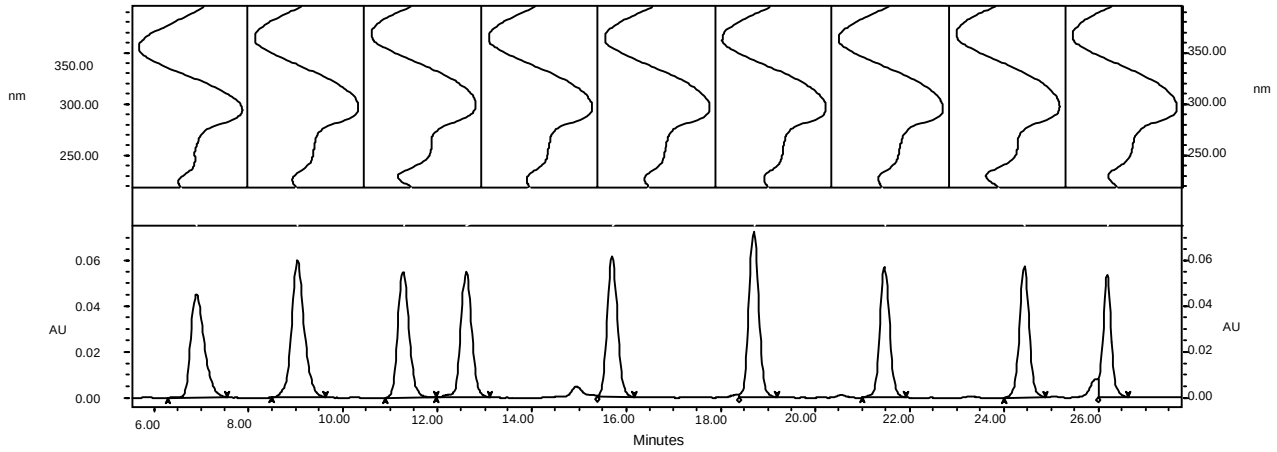
- Column: Symmetry C18 2 mm x 15 cm
- Eluent: A = H2O, B = THF, C = CH3CN

#	Time	Flow	% A	% B	% C	% D	Curve
1	0	0.3	60	10	30	0	0
2	1	0.3	60	10	30	0	6
3	11	0.3	40	0	60	0	6
4	21	0.3	20	0	80	0	6
5	25	0.3	10	0	90	0	6
6	30	0.3	60	10	30	0	6

- UV settings: 195-400 nm, resolution: 1.2 nm
- MS setting: scan 60 - 350 AMU, scan rate: 1
  source temperature: 215 °C
  nebulizer temperature: 56 °C

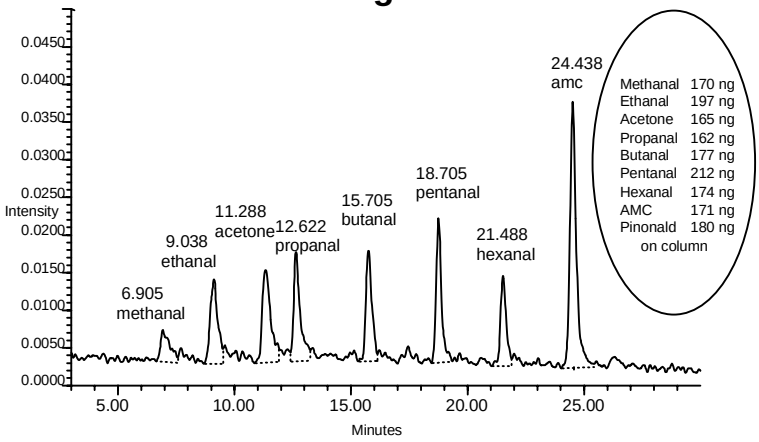
Derivatizations are done using Si DNPH derivative Sep Pak cartridges for air samples. Aqueous samples are derivatized using bulk DNPH.

UV Spectrum Index for DNPH Derivatives



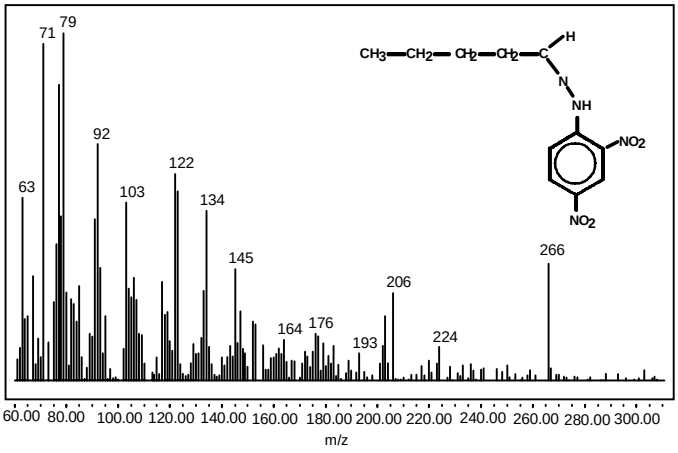
This Spectrum Index Plot displays UV spectra for each chromatographic peak. The UV spectra of all of the aldehyde derivatives is predictably the diphenylhydrazone derivative spectrum. The characteristics of this spectrum essentially overwhelms any individual nature offered by the original aldehyde thus making library reference matching difficult. Due to the fact that a hydrozone derivative is created via DNPH extraction, all of the UV spectra are the same (chemical similarity).

Mass Chromatogram at m/z = 122



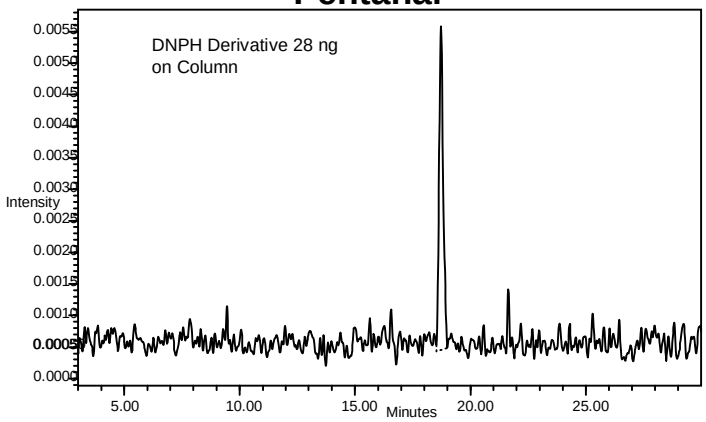
This is an extracted ion chromatogram at 122 m/z. Notice how little additional dispersion occurs when comparing this mass chromatogram to the UV chromatogram on page 1. This illustrates the extremely low dispersion characteristics of the system.

Mass Spectrum of Pentanal-DNPH



A pentanal DNPH spectrum with a prominent molecular ion is shown. The dinitrophenylhydrazone derivatives generally exhibit very prominent molecular ions indicating that the geometry of their M+ ions are quite stable. Automated MS (and UV) library search routines can be used to confirm the identification of chromatographic peaks

SIM Mode : Monitoring m/z 266 for Pentanal



For MS detection, the ability to extract single ion chromatograms adds another level of confirmation for targeted compounds. This is an extracted mass chromatogram at m/z 266 indicating sensitivity in the low ng range using SIM analysis. MS selectivity is a valuable tool for eliminating interferences from complex environmental matrices.

The Integrity System provides reliable qualitative and quantitative capabilities for the HPLC laboratory. This is the first system to offer integrated PDA and MS data in one unit. Reproducible, searchable MS data, peak homogeneity results, as well as efficient HPLC separation are all achieved using Integrity. Confidence in identification of DNPH derivatives based on PDA and MS data generated from a single injection is obtained.