Semivolatile Organics Analysis Using an Agilent J&W HP-5ms Ultra Inert Capillary GC Column

Application Note

Environmental

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Abstract

Trace-level semivolatile organics analyses using methods such as USEPA Method 8270 are important tools for assessing environmental contaminants worldwide. The wide-ranging chemical diversity of target semivolatiles can prove chromatographically challenging. This application note demonstrates the benefits of using an Agilent J&W HP-5ms Ultra Inert Capillary GC column with electron impact single quadrupole scanning mass spectrometry for trace-level semivolatiles analysis.

Agilent Technologies has implemented new testing procedures to more effectively evaluate GC column inertness performance. These new testing procedures employ deliberately aggressive probes to thoroughly investigate column inertness and quality. These aggressive probes, including 1-propionic acid, 4-picoline, and trimethyl phosphate, are used to verify each column's inertness performance.

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Introduction

USEPA Method 8270 [1] is a commonly used method for detecting semivolatile organic compounds in environmental samples by GC/MS. This method encompasses several classes of analytes, including amines, alcohols, polycyclic aromatic hydrocarbons, and phenols. The acidic and basic nature of many of the analytes makes minimizing any column or instrument activity critical to good chromatography and reliable results.

Minimizing activity in the GC column is essential in maximizing an analyte's response. Nitrophenols are among the most active compounds in semivolatiles series. 2,4-Dinitrophenol in particular is notorious for showing low response through adsorption onto active sites in the flow path during analysis. At low concentrations, the response factor (RF) for 2,4-dinitrophenol can fall below the minimum average RF of 0.050 required by USEPA 8270 due to interaction between the analyte and sample flow path. Capillary GC column activity as a potential source of result uncertainty has been effectively eliminated with the Ultra Inert series of columns.

A custom standard containing an abbreviated list of analytes specific to USEPA Method 8270 was analyzed to evaluate column performance. This semivolatiles "short mix" contained n-nitrosodimethylamine, aniline, benzoic acid, 2,4-dinitrophenol, 4-nitrophenol, 2-methyl-4,6-dinitrophenol, pentachlorophenol, 4-aminobiphenyl, benzidine, 3,3'dichlorobenzidine, benzo[b]fluoranthene, and benzo[k]fluoranthene, along with the recommended internal standards. These target analytes were chosen based on their chemical activity, as well as their poor chromatographic behavior. The short mix is particularly useful for rapid evaluation of system performance for semivolatiles analysis. Challenging analytes from early-eluting nitrosoamines through late-eluting PAHs are represented in this mix and chromatographic performance can be assessed quickly.

A second "large mix" standard containing a broader selection of semivolatiles was also evaluated to show the Ultra Inert's performance when analyzing a more complex sample. This standard contained a variety of acidic, basic, and neutral groups, which ranged from very low-boiling components to high-boiling polycyclic aromatic hydrocarbons.

Experimental

An Agilent 6890N GC/5975B MSD equipped with a 7683B autosampler was used for this series of experiments. Table 1 lists the chromatographic conditions used for these analyses. Table 2 lists flow path consumable supplies used in these experiments.

Table 1. Chromatographic Conditions for EPA Method 8270 Calibration Standards

GC:	Agilent 6890N/5975B MSD
Sampler:	Agilent 7683B, 5.0-µL syringe (Agilent p/n 5181-1273) 1.0 µL splitless injection
Carrier:	Helium 30 cm/s, constant flow
Inlet:	Splitless; 260 °C, purge flow 50 mL/min at 0.5 min
	Gas saver 80 mL/min at 3 min
Inlet liner:	Deactivated dual taper direct connect (Agilent p/n G1544-80700)
Column:	Agilent HP-5ms Ultra Inert 30 m × 0.25 mm × 0.25 µm (Agilent p/n 19091S-433UI)
Oven:	40 °C (1 min) to 100 °C (15 °C/min), 10 °C/min to 210 °C (1 min), 5 °C/min to 310 °C, hold 8 min
Detection:	MSD source at 300 °C, quadrupole at 180 °C, transfer line at 290 °C, scan range 45 to 450 amu

Table 2. Flow Path Supplies

Vials:	Amber screw top glass vials (Agilent p/n 5183-2072)
Vial caps:	Blue screw caps (Agilent p/n 5182-0723)
Vial inserts:	100 µL glass/polymer feet (Agilent p/n 5181-8872)
Syringe:	5 µL (Agilent p/n 5181-1273)
Septum:	Advanced Green (Agilent p/n 5183-4759)
Inlet liners:	Deactivated dual taper direct connect (Agilent p/n G1544-80700)
Ferrules:	0.4 mm id short; 85/15 Vespel/graphite (Agilent p/n 5181-3323)
20x magnifier:	20x magnifier loupe (Agilent p/n 430-1020)

Sample Preparation

A 12-component custom semivolatiles mix was purchased from Ultra Scientific (Kingston, RI) and used to prepare a seven-level calibration standard set. The stock semivolatiles solution as delivered had a nominal concentration of 2,000 µg/mL. An internal standard mix as recommended by USEPA Method 8270 was purchased from AccuStandard (New Haven, CT). The internal/surrogate solution as delivered had a

nominal concentration of 4,000 µg/mL. The calibration standards were prepared with component and internal standard concentrations of 80, 40, 20, 10, 5, 2, and 1 µg/mL. All solutions were prepared in dichloromethane using class A volumetric pipettes and flasks. The dichloromethane used was Burdick and Jackson spectral grade purchased thorough VWR International (West Chester, PA). Dichloromethane was used as a reagent blank and syringe wash solvent.

The EPA 8270 Calibration Level 2 standard set was purchased from AccuStandard containing 83 semivolatile components and internal standards. The large mix calibration standard was prepared at an analyte concentration of 5 µg/mL.

Results and Discussion

Baseline Inertness Profile for Ultra Inert Columns

The basic approach for inertness verification for the Agilent J&W Ultra Inert series of capillary GC columns is testing with aggressive active probes at low concentration and low temperature. This is a rigorous approach that establishes consistent baseline inertness profiles for each column in the Agilent J&W Ultra Inert GC column series. The baseline inertness profile then serves as a predictor for successful analysis of chemically active species that tend to adsorb onto active sites, particularly at trace level like the semivolatiles in this application example. A more detailed description of the test mix and additional application examples can be found in references 2 through 7.

Semivolatiles Analysis (USEPA 8270)

In this application note a seven-level semivolatile calibration curve set was evaluated over the concentration range of 1 to 80 µg/mL on an Agilent J&W Ultra Inert HP-5ms 30 m × 0.25 mm × 0.25 µm (p/n 19091S-433UI). An example chromatogram of a 1-µL injection of the 1 µg/mL short mix calibration standard is shown in Figure 1. Scanning mode was used exclusively for this analysis.

Pentachlorophenol and benzidine are two components that are used to verify inlet and column inertness. Excessive peak tailing of these components would indicate column activity. Analysis of the short mix standard yielded sharp, symmetrical peak shapes for the problematic analytes as shown in Figure 2. Good separation was obtained in the analysis of the 5-ng on-column 8270 large mix standard for each of the semivolatiles, which is shown in Figure 3.

Semivolatile analysis by USEPA Method 8270 requires a minimum average RF of 0.050 for a system performance check compound such as 2,4-dinitrophenol. 2,4-Dinitrophenol is a highly active analyte that has proven to be one of the most challenging compounds, often yielding lower than expected

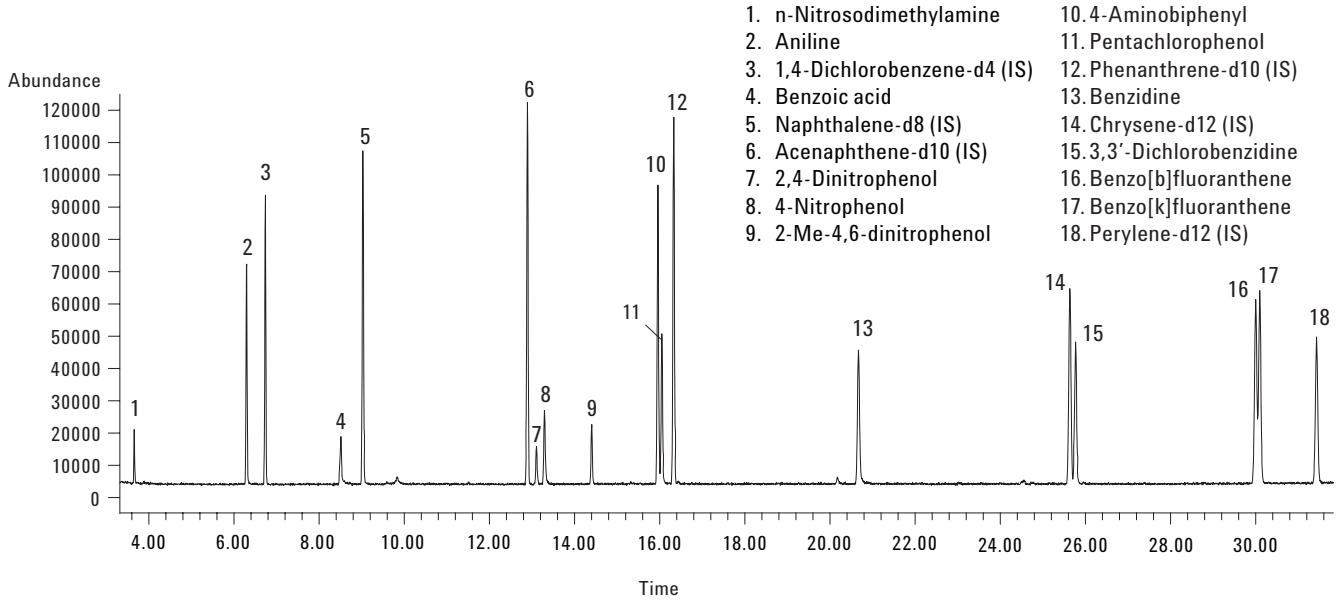

Figure 1. Total ion chromatogram (SCAN mode) of the 1-ng on-column EPA8270 short mix standard solution loading on an Agilent J&W HP-5ms Ultra Inert 30 m × 0.25 mm × 0.25 µm capillary GC column (p/n 19091S-433UI). Chromatographic conditions are listed in Table 1.

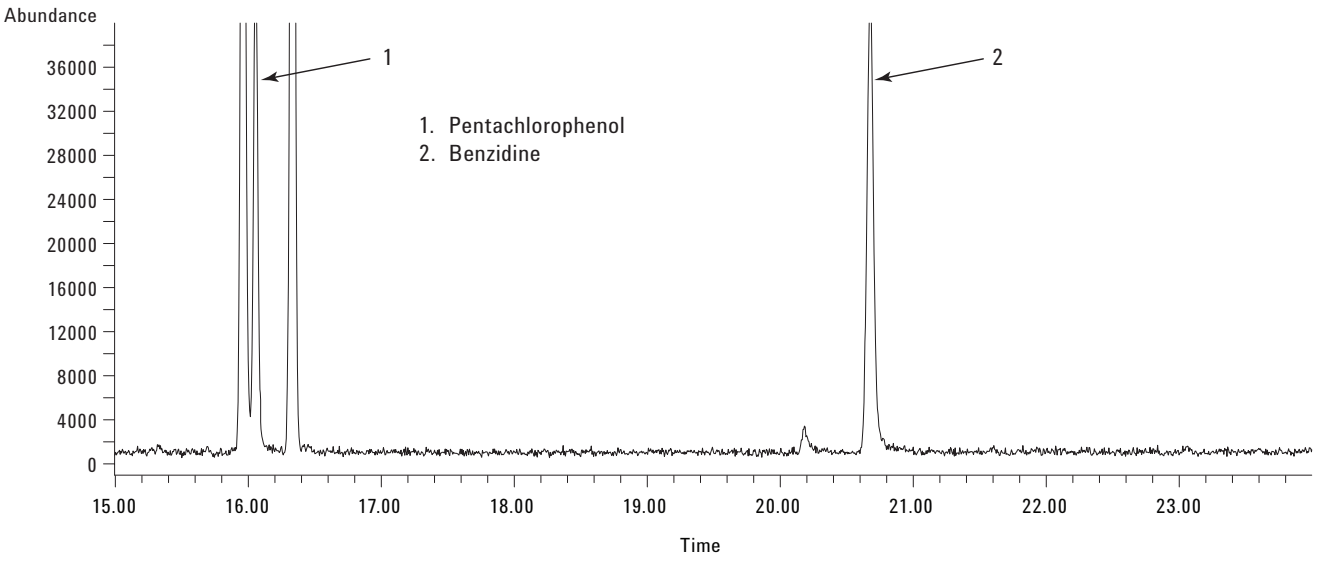

Figure 2. Enlarged section of the total ion chromatogram for a 1-µL injection of 1.0 µg/mL EPA 8270 short mix standard. The peaks of interest noted in the figure are two semivolatiles that are prone to peak tailing. Chromatographic conditions are listed in Table 1.

1. n-Nitrosodimethylamine
2. Pyridine
3. 2-Fluorophenol
4. Phenol-d5
5. Phenol
6. Aniline
7. Bis(2-chloroethyl)ether
8. 2-Chlorophenol
9. 1,3-Dichlorobenzene
10. 1,4-Dichlorobenzene-D4
11. 1,4-Dichlorobenzene
12. Benzyl alcohol
13. 1,2-Dichlorobenzene
14. o-Cresol
15. Bis(2-chloroisopropyl)ether
16. p-Cresol
17. n-Nitroso-di-n-propylamine
18. Hexachloroethane
19. Nitrobenzene-d5
20. Nitrobenzene
21. Isophorone
22. 2-Nitrophenol
23. 2,4-Dimethylphenol
24. Benzoic acid
25. Bis(2-chloroethoxy)methane
26. 2,4-Dichlorophenol
27. 1,2,4-Trichlorobenzene
28. Naphthalene-d8
29. Naphthalene
30. 4-Chloroaniline
31. Hexachlorobutadiene
32. 4-Chloro-3-methylphenol
33. 2-Methylnaphthalene
34. Hexchlorocyclopentadiene
35. 2,4,6-Trichlorophenol
36. 2,4,5-Trichlorophenol
37. 2-Fluorobiphenyl
38. 2-Chloronaphthalene
39. 2-Nitroaniline
40. Dimethyl phthalate
41. 2,6-Dinitrotoluene
42. Acenaphthylene
43. 3-Nitroaniline
44. Acenaphthene-d10
45. Acenaphthene
46. 2,4-Dinitrophenol
47. 4-Nitrophenol
48. Dibenzofuran
49. 2,4-Dinitrotoluene
50. Diethyl phthalate
51. Fluorene
52. 4-Chlorophenyl phenyl ether
53. 4-Nitroaniline
54. 2-Me-4,6-dinitrophenol
55. n-Nitrosodiphenylamine
56. Azobenzene
57. 2,4,6-Tribromophenol
58. 4-Bromophenyl phenyl ether
59. Hexachlorobenzene
60. Pentachlorophenol
61. Phenanthrene-d10
62. Phenanthrene
63. Anthracene
64. Carbazole
65. Dibutylphthalate
66. Fluoranthene
67. Benzidine
68. Pyrene
69. p-Terphenyl-d14
70. Benzyl butyl phthalate
71. 3,3-Dichlorobenzidine
72. Benzo[a]anthracene
73. Chrysene-D12
74. Chrysene
75. Bis(2-ethylhexyl)phthalate
76. Di-n-octyl phthalate
77. Benzo[b]fluoranthene
78. Benzo[k]fluoranthene
79. Benzo[a]pyrene
80. Perylene-d12
81. Indeno[1,2,3,cd]pyrene
82. Dibenzo[a,h]anthracene
83. Benzo[g,h,i]perylene

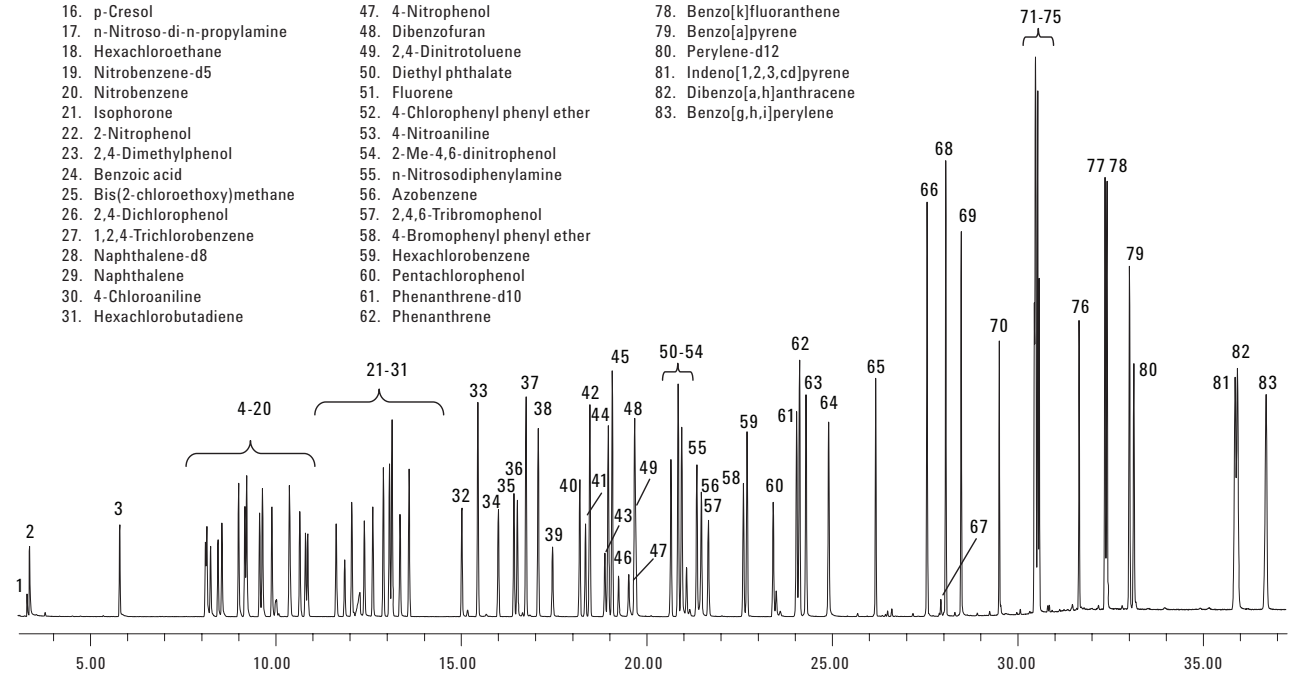

Figure 3. Total ion chromatogram (SCAN mode) of 5-ng on-column loading of EPA 8270 calibration (large mix) standard solution on an Agilent J&W HP-5ms Ultra Inert 30 m × 0.25 mm × 0.25 µm capillary GC column (p/n 19091S-433UI). Chromatographic conditions are listed in Table 1.

response factors at lower concentrations. In the analysis of the short mix calibration standard, the response for 2,4-dinitrophenol was greater than 0.1 at the 1-ng level. The average response was 0.15 over the concentration range studied. An example chromatogram for the signal-to-noise ratio for a 1-ng on-column loading of 2,4-dinitrophenol is shown in Figure 4. The signal-to-noise ratio for this difficult analyte was greater than 16 to 1. This demonstrates the excellent performance of the HP-5ms Ultra Inert GC column.

Linearity was excellent across the range studied, giving R^2 values of 0.990 or greater for even the more difficult phenols. Figure 5 indicates the correlation coefficients for several of the more active analytes.

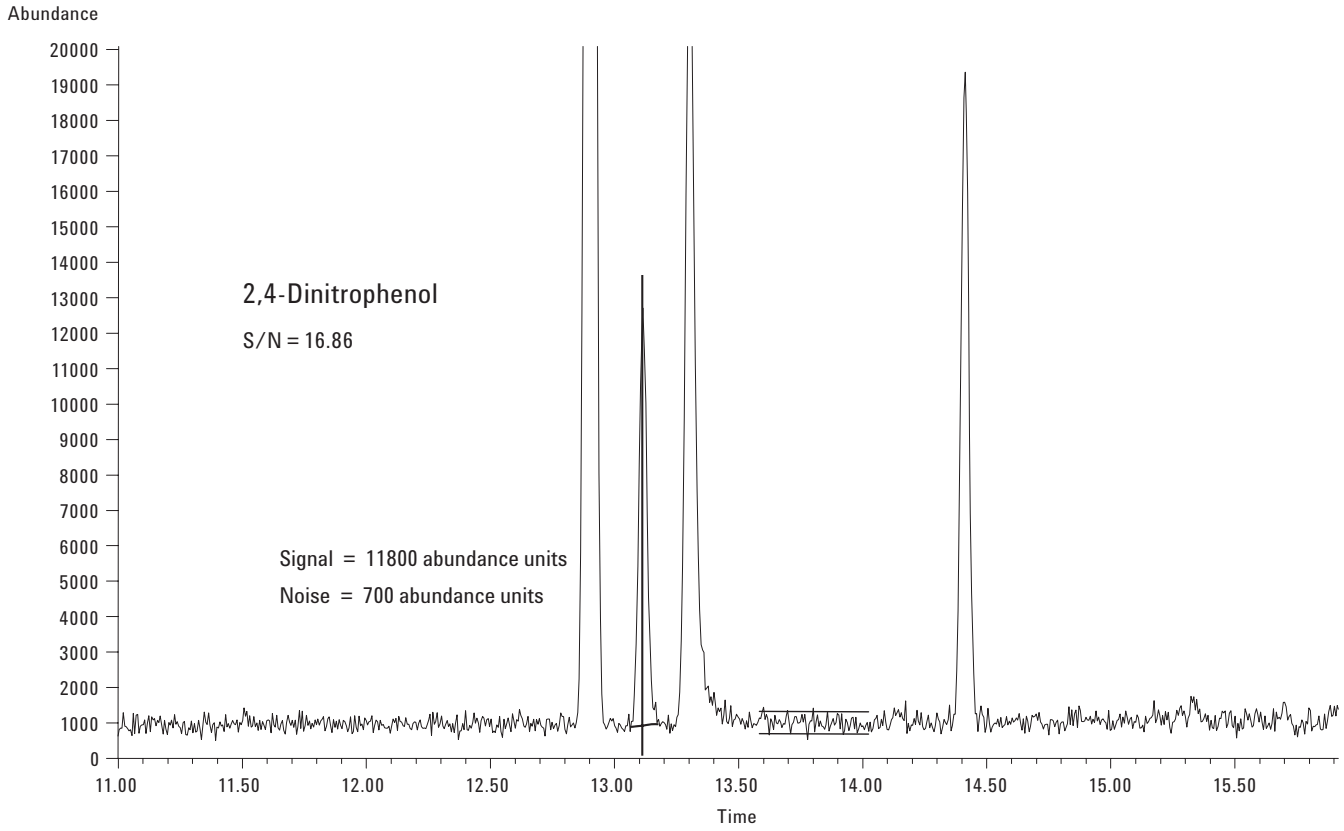

Figure 4 . Enlarged section of the total ion chromatogram (scan mode) for a 1-µL injection of 1 µg/mL EPA Method 8270 short mix standard on an Agilent J&W HP-5ms Ultra Inert 30 m × 0.25 mm × 0.25 µm capillary GC column (p/n 19091S-433UI). The peak in the figure is 2,4-dinitrophenol, one of the more demanding semivolatiles. This injection represents an on-column loading of 1 ng per component. Chromatographic conditions are listed in Table 1.

	R^2
n-Nitrosodimethylamine	0.995
2,4-Dinitrophenol	0.990
4-Nitrophenol	0.995
Pentachlorophenol	0.995
Benzidine	0.995

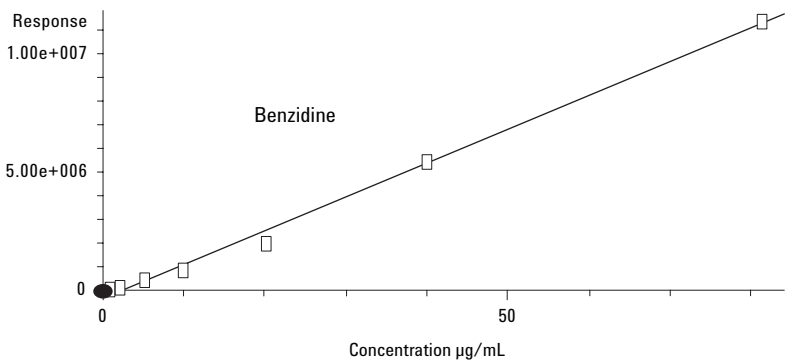

Figure 5. Correlation coefficients for some of the more challenging analytes in the EPA Method 8270 short mix standard over the 1 to 80 µg/mL range of this study and an example linear regression plot for benzidine.

Conclusions

This application successfully demonstrates the use of an Agilent J&W HP-5ms Ultra Inert capillary GC column for low-level semivolatile organics. Linearity was excellent for all semivolatiles studied, yielding 0.99 or greater R^2 values down to a 1-ng column loading of each component. One of the reasons for excellent linearity and high R^2 values is the highly inert surface of the column. The lack of chemically active sites makes these columns an excellent choice for semivolatiles analyses.

This study was done using SCAN mode on an Agilent 6890N/5975B GC/MSD equipped with an inert electron impact source. The signal-to-noise ratio for a 1-ng on-column loading of 2,4-dinitrophenol was greater than 16 to 1 with this system. This result clearly shows the power of using an Agilent J&W HP-5ms Ultra Inert column for low-level semivolatile organics analysis. Lower limits of quantification are expected when using one of Agilent's latest GC/MS offerings, such as the 7890A/5975C GC/MSD Triple-Axis Detector coupled with an Agilent J&W HP-5ms Ultra Inert GC capillary column.

References

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