Semivolatile Analysis with Specially Designed Agilent J&W DB-UI 8270D Columns

Application Note

Environmental

Author

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Abstract

Excellent peak shapes and chromatographic performance for challenging semivolatile analytes are shown on 0.25 mm and 0.18 mm id Agilent J&W DB-UI 8270D columns. The utility of using a 29 semivolatile analyzer mix is demonstrated in less than 16 minutes on a 20 m × 0.18 mm, 0.36 µm DB-UI 8270D capillary GC column. The use of Agilent Ultra Inert liners with wool is also demonstrated on a high efficiency GC (0.18 mm id) column.

Introduction

There is a wide range of volatile and semivolatile contaminants finding their way into water sources around the world. In the United States (US), these contaminants are analyzed according to US-EPA Method 8270 for semivolatile organics [1]. In the European Union (EU), a large number of these same compounds are considered volatile with boiling points below 250 °C and are tested according to European Water Framework Directive 2000/60EC [2]. Though these analytes of interest are approached differently from a regulatory prospective, it is clear that water quality needs to be monitored on a global basis. Modern high sensitivity GC/MS instruments coupled with inertness verified consumable components provide a convenient and reliable means of monitoring these compounds.

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Many of the same compounds found on the US EPA 8270 list of analytes also appear in the European Water Framework Directive as Priority Substances or Chemicals of high concern [3]. These analytes are diverse in terms of their boiling points and chemical activity. A wide variety of active chemical moieties, including basic, acidic, and phosphorus-containing functional groups, can be challenging to chromatograph accurately [4]. Analytes with active functional groups may adsorb on active sites anywhere in flow path, resulting in tailing peak shape, higher detection limits, or in the worst case, nondetection of analyte.

GC columns specifically designed to meet the demands of these active and often problematic analytes are important in achieving consistent inertness performance. Inertness verification testing is necessary to deliver sharp peaks, low limits of detection, and the reliable system performance analysts seek [5]. Each Agilent J&W DB-UI 8270D GC column is factory tested with very active test probes to help assure the analyst that they will achieve sharp peaks and low detection limits for active semivolatile analytes.

Ultra Inert Testing

A semivolatiles Ultra Inert level test mix was designed specifically for the DB-UI 8270D column using demanding test probes relevant for semivolatile analysis. Probes used include propionic acid, pyridine, meta-xylene, para-xylene, and 1-chloro-2-flourobenzene. Acid and base behavior, aromatic isomer, and halogen selectivity are simultaneously evaluated with these probes. Testing is done under the particularly stringent conditions of both low concentration (5-10 ng/component on column) and low (45 °C) isothermal temperature to thoroughly probe for inertness. Figure 1 shows a typical test chromatogram for a DB-UI 8270D column. Test results from individual columns including test chromatograms provide proof of inertness performance with every column shipped.

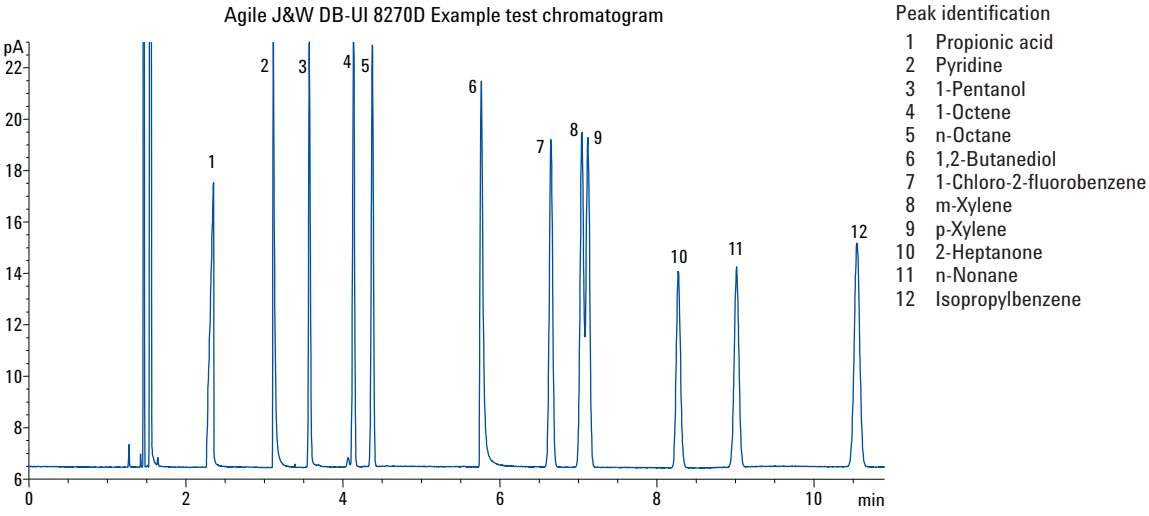


Figure 1. Example test chromatogram of semi-volatiles run on an Agilent J&W DB-UI 8270D column.

Inlet liner deactivation is another key issue in maximizing reliable system performance for semivolatile analysis. Agilent Ultra Inert liners are also tested with demanding test probes to provide consistently superior inertness performance and better peak shapes than traditionally deactivated inlet liners. New deactivation strategies enable the use of Ultra Inert liners with wool for successful analysis of active acidic, basic, and organophosphorus analytes.

Total Work Flow Solutions

Advanced software features such as simultaneous SIM/SCAN, retention time locking, backflush calculators, and the semivolatiles database are offered as tools to help speed semivolatile analysis to final results. Turnkey semivolatile analysis systems are available that are factory tested to deliver an up-and-running total work flow solution from day one.

Experimental

GC/MS System 1 consisted of an Agilent 7890 Series GC coupled to an Agilent 5975C Series GC/MSD with triple axis detector. The column used on this system was a 30 m × 0.25 mm, 0.25 µm DB-UI 8270D (Table 1). A 78 component mix with nominal analyte concentrations of 10 ng/µL per analyte was used to evaluate the chromatographic performance of the column on this system.

GC/MS System 2 was a 7890/5975C instrument GC and MS, but with a 20 m × 0.18 mm, 0.36 µm DB-UI 8270D, (Table 2). A 29 component mix at a nominal concentration of 10 ng/µL per analyte was used.

Table 3 lists the flow path supplies used with both GC/MS systems.

Table 1. Chromatographic conditions for System 1.

Column:	Agilent J&W DB-UI 8270D, 30 m × 0.25 mm, 0.25 µm (p/n 122-9732)
Carrier:	Helium, 1.2 mL/min constant flow, septum purge 3 mL/min, purge time on 0.7 min 50 mL/min, gas saver off
Oven:	30 °C (1.0 min), 15 °C/min to 100 °C, 20 °C/min to 240 °C (0.5 min), 15 °C/min to 325 °C (6.7 min)
Inlet:	MMI in nonpulsed splitless mode 1 µL at 275 °C
Inlet liner:	Dual taper direct connect liner (p/n G1544-80700)
MSD:	325 °C transfer line, 280 °C source, 150 °C quad, 35-500 AMU range
GC/MSD:	Agilent 7890 Series GC/5975C Series GC/MSD
Sampler:	Agilent 7693, 10.0 µL syringe (p/n G4513-80216)

Table 2. Chromatographic conditions for System 2.

Column 1:	Agilent DB-UI 8270D, 20 m × 0.18 mm, 0.36 µm (p/n 121-9723)
Column 2:	1.0 m × 0.15 mm id deactivated fused silica tubing (p/n 160-1625-10)
Carrier:	Helium, constant flow 1.58 mL/min set at 40 °C
Oven:	40 °C (2.5 min), 25 °C/min to 320 °C (4.8 min)
Inlet:	S/SL 1 µL pulsed splitless; 300 °C, 44 psi pulse to 1.4 min, purge flow 50 mL/min at 1.42 min, gas saver off
Inlet liner:	Agilent Ultra Inert single taper with wool (p/n 5190-2293)
MSD:	325 °C transfer line, 300 °C source, 150 °C quad, 30-550 AMU range
GC/MSD:	Agilent 7890 Series GC/5975C Series GC/MSD
Sampler:	Agilent 7683B, 5.0 µL syringe (p/n G4513-80206)
Aux EPC:	2 psi with 5 mL/min bleed during run
Backflush:	Post run 3.5 min at 75 psi Aux EPC, 2 psi inlet pressure

Table 3. Flow path supplies.

Vials:	Amber silanized screw top vials (p/n 5183-2072)
Vial caps:	Blue screw caps (p/n 5185-5820)
Vial inserts:	250 µL glass/polymer feet (p/n 5181-8872)
Syringe:	5 µL (p/n 5181-1273)
Septum:	Advanced Green (p/n 5183-4759)
Inlet liner:	Ultra Inert single taper (p/n 5190-3162)
Gold seal:	Gold plated inlet seal with washer (10/pk, p/n 5190-2209)
Ferrules:	0.4 mm id short; 85/15 Vespel/graphite (p/n 5181-3323)
CFT fittings:	Internal nut (p/n G2855-20530)
CFT ferrules:	SilTite ferrules, 0.25 mm id (p/n 5188-5361)
Magnifier:	20× Magnifier loop (p/n 430-1020)

Standard preparation

A 78 component EPA-8270 mix at a nominal concentration of 10 ng/µL in methylene chloride was obtained from AccuStandard (New Haven, CT), transferred to vials, and injected.

A 29 component GC/MS semivolatile Analyzer Checkout Mix at a nominal concentration of 10 ng/µL was obtained from Agilent Technologies, Inc. (Santa Clara, CA) (p/n 5190-0473). This mixture was transferred to vials and used as is or diluted with Ultra Resi-analyzed grade dichloromethane (J. T. Baker, Phillipsburg, NJ). Ultra Resi-analyzed grade dichloromethane was also used as the syringe wash solvent.

Results and Discussion

Figure 2 shows the injection of 1 µL of a 78 component semivolatiles component mixture at a nominal concentration of 10 ng/µL for each component. At this loading level, (10 ng on column) peak shapes can be viewed clearly and there is sufficient SCAN signal for spectral library identification. In an analysis of less than 24 minutes, all peaks of interest are identified and quantified, with excellent peak shapes. The acidic component pentachlorophenol gave excellent peak shape under these conditions with USP peak tailing factors below 1.3.

Figure 3 displays an expanded section of the total ion chromatogram from Figure 2 where benzo-b-fluoranthene and benzo-k-fluoranthene positional isomers elute. The resolution between these peaks is 1.20, indicating excellent resolution.

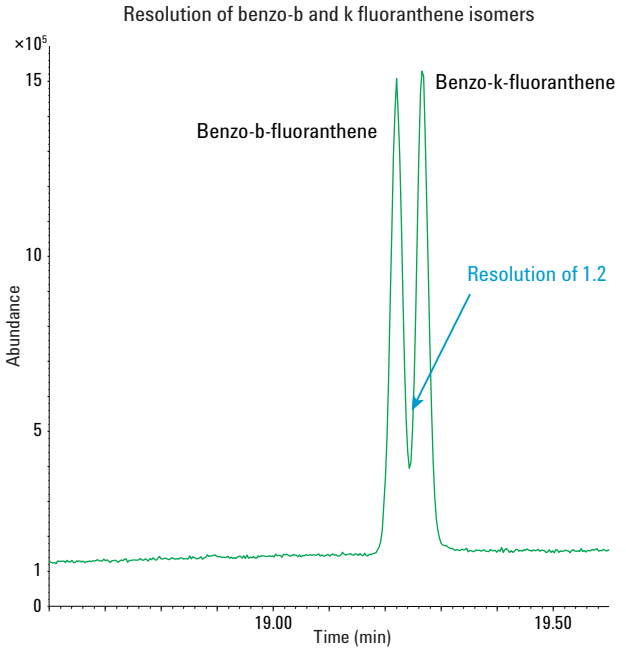


Figure 3. Separation of benzo-b and k fluoranthene isomers. Conditions as in Table 1.

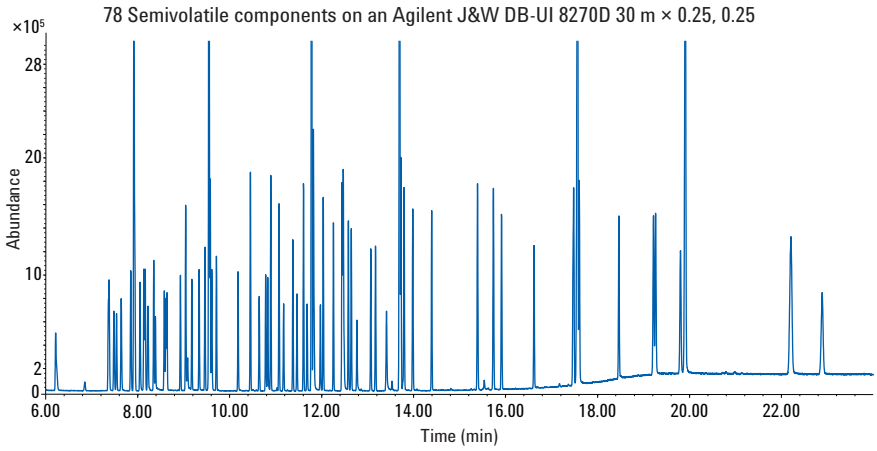


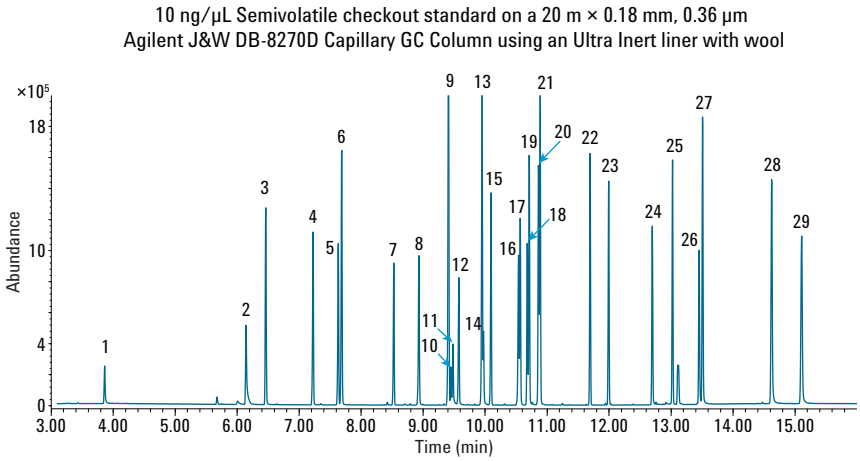
Figure 2. Example total ion chromatogram of a 78 component semi-volatile standard injection with a 10 ng on column loading for each component. Conditions as in Table 1.

Figure 4 shows the resolution of a 29 component mix of semivolatiles with excellent peak shapes for all components. These results were obtained in less than 16 minutes using an Agilent J&W DB-UI 8270D, 20 m × 0.18 mm, 0.36 µm column. This mix represents a wide cross section of analytes in terms of boiling point ranging from N-nitrosodimethylamine to perylene-d 12. Sharp symmetrical peaks were observed for both the early eluting N-nitrosodimethylamine and the late eluting perylene-d 12.

The 29 component mix contains a wide range of chemically active analytes including acidic phenols, organic bases, and organophosphorus and organochlorine pesticides. 2,4-Dinitrophenol, 4 nitrophenol, and pentachlorophenol all show excellent peak shape and response on this system using a DB-UI 8270D, 20 m × 0.18 mm, 0.36 um capillary GC column and an Agilent Ultra Inert liner with wool. Base analyte response and peak shapes were excellent for N-nitrosodimethylamine, aniline, and 3,3′ dichlorobenzidine.

Organochlorine pesticides like DDT and endrin are known to break down in response to surface activity, particularly in the inlet. Endrin and DDT breakdown products were below 1.5% of the total area for the endrin and DDT peaks, respectively, after a series of 100 plus solvent blank and standard injections. Organophosphorus pesticides, such as mevinphos, simazine, atrazine, and terbufos, can also show peak tailing due to interactions in the liner. Excellent peak shapes were observed even for these challenging pesticides with an Ultra Inert liner with wool.

From a regulatory standpoint, this 29 component mix represents a cross section of target analytes important in the European Union that are listed in either List 1 Annex to Directive 76/464/EEC or Annex II to Directive 2008/105/EC and in the US-EPA Method 8270D for semivolatile analysis. Water quality is a truly worldwide concern that requires careful monitoring with robust analyses.



Peak identification

1	N-Nitrosodimethylamine	11	4-Nitrophenol	21	Phenanthrene-d10
2	Aniline	12	2,4-Dinitrotoluene	22	Aldrin
3	1,4-Dichlorobenzene-d4	13	Fluorene	23	Heptachlor epoxide
4	Isophorone	14	4,6-Dinitro-2-methyl phenol	24	Endrin
5	1,3-Dimethyl-2-nitrobenzene	15	Trifluralin	25	4,4'-DDT
6	Naphthalene	16	Simazine	26	3,3'-Dichlorobenzidine
7	Hexachlorocyclopentadiene	17	Atrazine	27	Chrysene d-12
8	Mevinphos	18	Pentachorophenol	28	Benzo[b]flouranthene
9	Acenaphthene-d10	19	Terbufos	29	Perylene-d12
10	2,4-Dinitrophenol	20	Chlorothanlonil		

Figure 4. Example chromatogram of a 29 component mix on an Agilent J&W DB-UI 8270D 20 m × 0.18 mm, 0.36 µm capillary GC column (p/n 121-9723). Conditions as in Table 2.

Figure 5 shows an expanded view of the 9.3 to 9.8 retention time window from Figure 3. 2, 4 Dinitrophenol is a particularly challenging analyte, often displaying distorted peak shapes and poor response. In this case, a sharp symmetrical peak is observed with strong response.

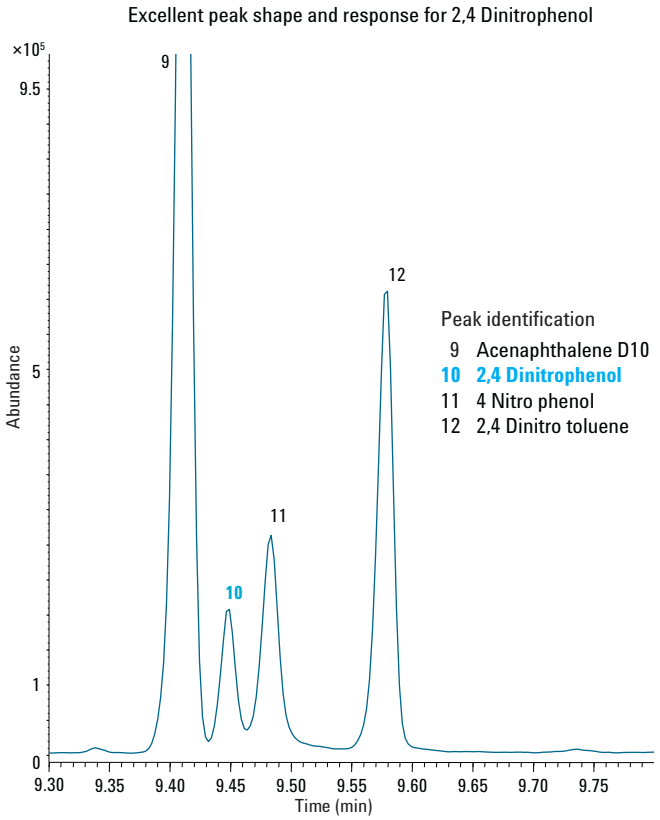


Figure 5. 2,4 Dinitrophenol expanded view. Conditions as in Table 2.

Conclusions

This application note shows the effective use of Agilent J&W DB-UI 8270D columns for semivolatile analyses in both 0.25 mm and 0.18 mm id formats. Excellent peak shapes for active analytes, including acidic phenols, organic bases, endrin, DDT, and organophosphorus pesticides were observed on both columns. In the example on the 0.18 mm id column, an Ultra Inert liner with wool was used and showed very low endrin, DDT breakdown, while yielding sharp symmetrical peaks for the organophosphorus compounds, in the 29 component semivolatiles analyzer mix.

The 29 component semivolatiles analyzer mix was shown to be quite useful for assessing system performance for water quality testing for both EU and US regulated laboratories. The mix contains analytes specifically called out by both regulatory bodies. Many of these analytes are challenging chromatographically, and the mix as a whole serves as a rapid and convenient way to assess system performance.

Customer Testimonial

"In my 30 years of experience in running virtually every USEPA semivolatile method...like Methods 608, 625, 508, 525.2, and of course, 8270x...the performance of the Agilent J&W DB-UI 8270D GC column has raised the bar for semivolatile analysis. With both conventional inlet technologies (Split/Splitless and LVI inlets) and on-column introduction, the DB-UI 8270D has demonstrated:

- Superior chromatographic resolution (PAHs specifically are phenomenal!)
- Superior inertness (reactivity of acid-fraction components like 4-Nitrophenol and 2,4-Dinitrophenol, which have low pKa values, is minimal)
- Superior breakdown characteristics (4,4'-DDT and Endrin breakdown is well below all method requirements and in many examples <5%!)
- Superior peak tailing performance of Pentachlorophenol and Benzidine (Benzidine, for example is Gaussian in peak shape)

As a result of my continued research and work with clients, the Agilent J&W DB-UI 8270D GC column will be the column of choice for my continued work and the recommended GC column to my clients analyzing under the core set of USEPA methods for semivolatile analysis."

Jeffery S. Hollis
Owner/Consultant
AnalySense - Sacramento, CA

References

1. US-EPA Method 8270D Revision 4 (February 2007).
2. Directive 2000/60EC of the European Parliament and of the Council Establishing a Framework for Community Action in the Field of Water Policy (23 October 2000).
3. Priority Substances and Certain Other Pollutants Annex 2 of Directive 2008/105/EC (2008).
4. D. Rood. *The Troubleshooting and Maintenance Guide for Gas Chromatographers*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany (2007).
5. J. Luong, R. Gas, W. Jennings. *J. Sep. Sci*. 30, 2480 (2007).

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