Analysis of EPA Method 8270D Semivolatiles Using the Agilent J&W DB-UI 8270D Ultra Inert GC Column

Application Note

Environmental

Authors

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Abstract

A 29-component subset mix of basic, neutral, and acidic compounds (BNAs) was used to evaluate the Agilent J&W DB-UI 8270D Ultra Inert GC column, revealing acceptable peak shape, resolution, and response factors for this diverse analyte series. The column was compared to an alternative vendor's recommended premium column for EPA Method 8270D. The three main comparison points were tailing factor, resolution, and response factor. The average response factor for one particularly difficult component was included. Most laboratories running routine tests of BNAs use time-consuming extractions designed to recover every compound class in diverse sample types. By providing just one chromatographic assay, a laboratory can greatly simplify its work flow. Agilent has made column selection less complicated by specifically designing and testing a stationary phase that easily relates to the EPA method.

Introduction

EPA Method 8270D provides for the analysis of solid or liquid waste samples as well as air and particulate dust [1]. The list of priority pollutants published in the method monograph is quite extensive, numbering in excess of 250 compounds. One key element of the assay hinges on being able to generate defensible library matches, and to do that chromatographic separation becomes a critical piece of the analytical puzzle. Another factor that can detract from good spectral matching is poor peak shape, which leads to tailing components whose spectra can require subtraction or deconvolution to achieve reliable qualitative identification. Further complicating the matter is resolution efficiency, where co-eluting peaks cause match quality for

compound identification to suffer. Finally, EPA calibration guidelines call for minimum reporting limits (MRLs) to be referenced to the lowest calibration point, and the trend is always toward lower and lower MRLs.

The DB-UI 8270D Ultra Inert GC column was introduced to provide the needed resolution, inertness, and selectivity required to meet the demands of the assay while maintaining throughput [2]. A series of reactive compounds designed to elucidate problems related to column quality was developed as a subset to the EPA list. This smaller range of compounds exhibits a complete variety of reactivity and can be used to evaluate system performance quickly.

Materials and Methods

An Agilent 7890A Series GC was coupled to an Agilent 5975C GC/MSD with the Inert EI 350 non-coated source installed for this series of experiments.

GC conditions

Column:	Agilent J&W DB-UI 8270D, 20 m × 0.18 mm, 0.36 µm (p/n 121-9723) MSD Inlet transfer capillary Agilent J&W DB-UI 8270D, 1.5 m × 0.18 mm, 0.36 µm
Sample:	Agilent 8270 semivolatiles evaluation mix, 10 ng/µL (p/n 5190-0473)
Carrier:	Helium, 25 psi constant pressure mode, 1 psi during postrun
Oven:	40 °C (hold 3 min) to 300 °C at 25 °C/min (hold 3 min)
Injection:	Splitless, septum purge on at 1 min, 3 mL/min purge flow
Inlet temperature:	170 °C
Detector:	MSD transfer aux temp at 265 °C
PCM C-1:	1 psi with 5 mL/min bleed during run
Backflush:	Post run 3.5 min at 45 psi
GC:	Agilent 7890A Series GC
Automatic Sampler:	Agilent 7693, 0.5 µL injection in dichloromethane

MS conditions

Solvent delay:	2.5 min
MS temperature:	300 °C (source), 150 °C (quad)
Transfer line:	290 °C
Scan range:	30-550
MS:	Agilent 5975C with EI inert 350 source, tandem axis detector

Agilent flow path supplies

Vials:	Amber, screw cap (p/n 5182-0716)
Caps:	Blue, screw cap (p/n 5282-0723)
Vial inserts:	250 µL glass with polymer feet (p/n 5181-1270)
Ultimate Union Kit:	(p/n G3182-61580)
Siltite ferrules:	0.25 mm id (p/n 5188-5361)
Syringe:	5 µL (p/n 5181-1273)
Septum:	Advanced Green (p/n 5183-4759)
Inlet liner:	Dual taper direct connect (p/n G1544-80700)
Magnifier:	20x (p/n 430-1020)

Standard preparation

A 29-component checkout mix at 10 ng/µL in dichloromethane was used and diluted 1:5 in dichloromethane (J.T. Baker ultra-residue analyzed grade) to provide a 1 ng per component injection on-column in splitless mode. To make the solution water saturated at 0.15%, 15 µL of deionized water was added to vials containing 1 mL of the standard solution.

Sample preparation

Samples for analysis were extracted using Agilent High Flow Bond Elut C18 cartridges, as previously noted [4]. For seawater, a 20 mL wash with de-ionized buffer water was used to remove salt prior to elution. Laboratory control samples were prepared at 10 µg/L of each component in the checkout mix.

Agilent Bond Elut C18 cartridges, 1 g, 6 mL (p/n 14256001)

Vacuum manifold processing station (p/n 5982-9110)

Manifold stopcocks (p/n 5982-9102)

60 mL reservoirs (p/n 12131012)

Adapters (p/n 12131001)

Sodium sulfate drying cartridges (p/n 12131033)

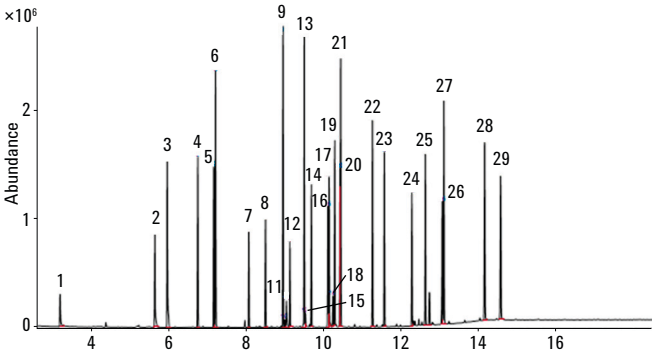
A measured volume of a water sample, 250 mL, was pH adjusted with HCl (pH 2), extracted with sorbent and dichloromethane, and concentrated and combined with another separate 250 mL sample adjusted with NH_4OH (pH 8). It was then extracted and concentrated to a final volume of 500 µL. This yielded a final 1,000-fold concentrated extract. Caffeine can be detected at µg/L levels, indicating human sources of pollution [5] are likely to be present, as seen in Figure 6. The High Flow cartridges have a 150-µm particle size, allowing for extractions with gravity feed for non-turbid samples. This reduces the need to apply vacuum and make iterative flow rate adjustments. Recovery of *n*-nitrosodimethylamine (NDMA) from tap water or other chlorinated sources would require dechlorination of sample containers prior to collection with 100 mg of sodium thiosulfate per liter of water. The seawater sample was not dechlorinated, and NDMA is absent in the spiked seawater, as shown in Figure 5.

Results and Discussion

Performance comparison of Agilent J&W DB-UI 8270D Ultra Inert GC columns and alternative vendor columns

To show the subtle variation in column quality, the lowest point in the calibration curve was used for these evaluations [6]. DB-UI 8270D columns from differing manufacturing lots were compared to various lots from another vendor's premium recommended column. The average tailing factor, selectivity, and response factor were determined for statistical purposes. These values were calculated for 5-point smoothed TIC traces, as reported by the Agilent MSD ChemStation performance reporting feature (ver. E.02.00.493). Once the averages were determined, their values were compared to the non-Agilent columns using the same GC/MS conditions and column dimensions. Three components were deemed to be the most problematic from the standpoint of tailing factor [7], namely NDMA, aniline, and 1,4-dichlorobenzene. The remaining 26 components in the mix all gave better tailing factors and were well behaved chromatographically. The critical pair used to evaluate column selectivity was chlorthalonil and phenanthrene. According to the National Center for Food and Agricultural Policy (NCFAP), chlorthalonil is the third most used fungicide, behind only sulfur and copper [8]. Phenanthrene can be found in cigarette smoke and is stable in the environment. All other components in the test mix gave better selectivity and match qualities. Of particular interest was 2,4-dinitrophenol (DNP), which gave the lowest average signal-to-noise response. Analytically, DNP is considered the most problematic compound in the Method 8270D target list. It must exhibit a minimum average response factor (RF) of 0.05. If any compound fails to meet the Method 8270 response factor criterion, system maintenance must be performed to bring a response factor to passing before samples can be analyzed. The average RF was calculated in the comparison and determined to be close to the assay limits with all columns.

Figure 1 demonstrates that the chromatographic peak shape is visually acceptable for all components in the mix using the DB-UI 8270D column. Table 2 highlights the observable differences between the Agilent and non-Agilent columns. One of the most active basic compounds in semivolatiles methods is NDMA. Figure 2 shows an overlay of NDMA chromatograms from Agilent and non-Agilent 8270D columns. This early eluting compound can give poor performance in the injection port and on the column, and many currently available columns deliver a poor peak shape for NDMA.



Peak ID

1. *n*-Nitrosodimethylamine
2. Aniline
3. 1,4-Dichlorobenzene-d4
4. Isophorone
5. 1,3-Dimethyl-2-nitrobenzene
6. Naphthalene
7. Hexachlorocyclopentadiene
8. Mevinphos
9. Acenapthene-d10
10. 2,4-Dinitrophenol
11. 4-Nitrophenol
12. 2,4-Dinitrotoluene
13. Fluorene
14. 4,6-Dinitro-2-methylphenol
15. Trifluralin
16. Simazine
17. Atrazine
18. Pentachlorophenol
19. Terbufos
20. Chlorthalonil
21. Phenanthrene-d10
22. Aldrin
23. Heptachlor epoxide
24. Endrin
25. 4,4′-DDT
26. 3,3′-Dichlorobenzidine
27. Chrysene-d12
28. Benzo[b]fluoranthene
29. Perylene-d12

Figure 1. TIC of a 29-component semivolatiles evaluation mix on an Agilent J&W DB-UI 8270D Ultra Inert GC column.

Table 2. Comparison of observable differences between Agilent and non-Agilent columns.

	Agilent J&W DB-8270D Ultra Inert column	Non-Agilent column
Compound	**Avg. TF**	
n-Nitrosodimethylamine	1.28	1.42
Aniline	1.22	1.30
1,4-Dichlorobenzene	1.02	1.28
	Resolution	
Chlorthalonil		
Phenanthrene	0.90	0.75
	Avg. RF	**Avg. RF**
2,4-Dinitrophenol	0.05	0.03

Figure 3 shows an overlay of Agilent and non-Agilent chromatograms for the DNP peak. DNP is a source of soil contamination and has been difficult to recover and quantify at low levels in soil from contaminated waste sites. It has been used as a pesticide and a wood preservative [9].

Figure 4 shows the expanded view of the critical pairs. This pair resolution would be affected by slight changes in column geometry, such as length or internal diameter and slight film thickness variation from lot to lot.

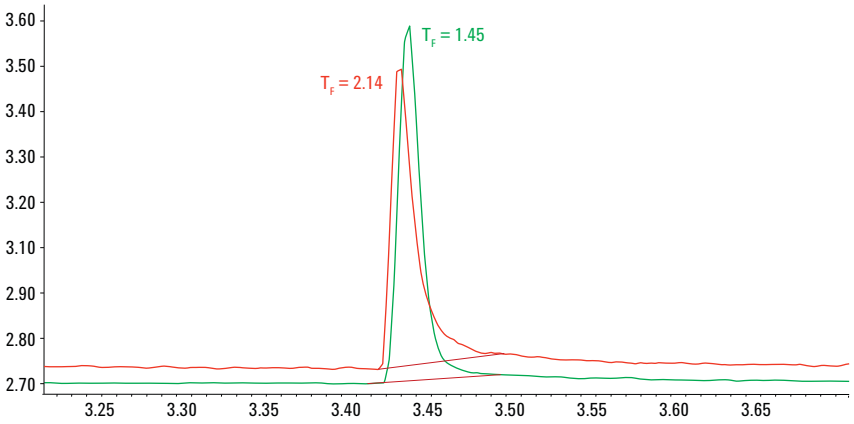


Figure 2. Comparison of *n*-nitrosodimethylamine peak tailing, due to extra-column effect, between an Agilent J&W DB-UI 8270D Ultra Inert GC column (green trace) and a comparative non-Agilent column (red trace).

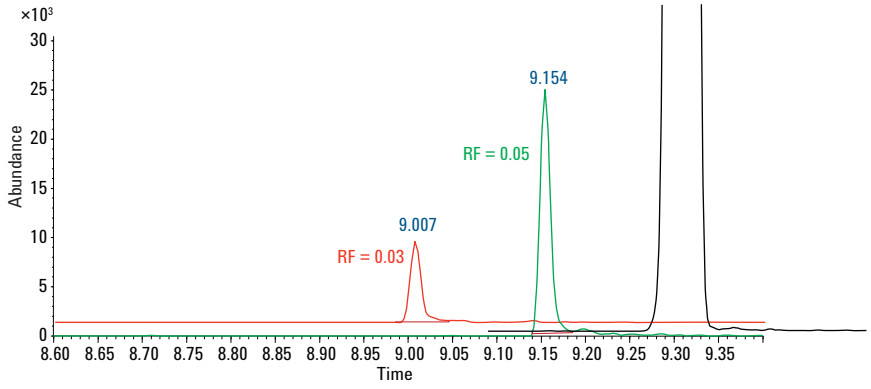


Figure 3. 2,4-Dinitrophenol response factors from an Agilent J&W DB-UI 8270D Ultra Inert GC column (green trace) and a comparative non-Agilent column (red trace) at 1 ng on-column with splitless injection.

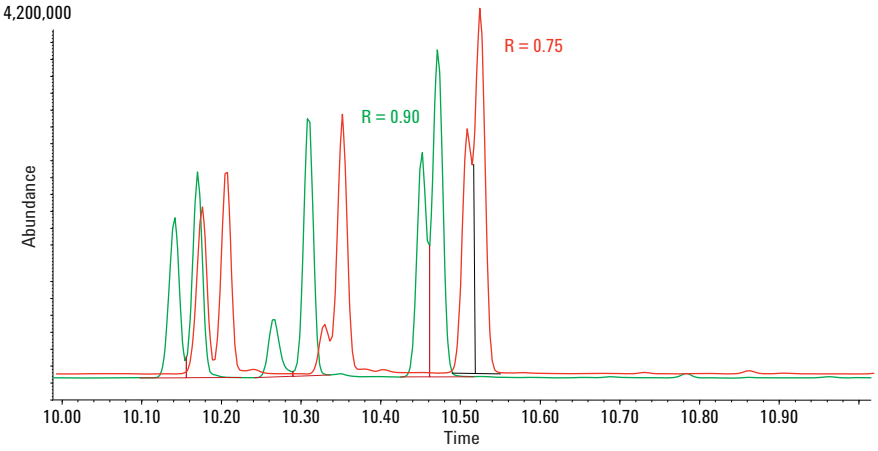
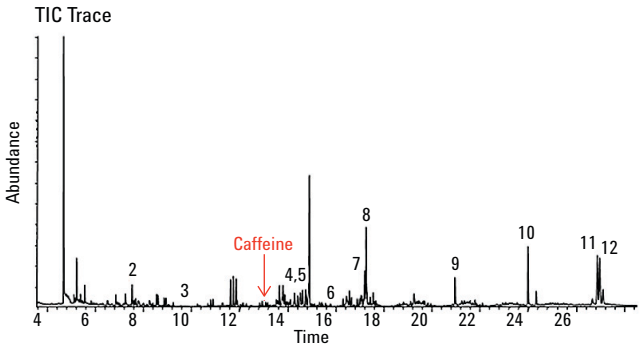


Figure 4. Separation of the critical pair chlothalonil and phenanthrene on an Agilent J&W DB-UI 8270D Ultra Inert GC column (green trace) and a comparative non-Agilent column (red trace).



Peak ID

2. Aniline
3. Benzoic acid
4. 2,4-Dintrophenol
5. 4-Nitrophenol
6. 2-Methyl-4,6-dinitrophenol
7. Pentachlorophenol
8. Dichloro-diamino-biphenyl
9. Benzidine
10. 1[1,1′-Biphenyl]-4,4′-dichloro-diamine
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene

Figure 5. Analysis of spiked seawater from coastal New Jersey, U.S., using an Agilent J&W DB-UI 8270D Ultra Inert GC column.

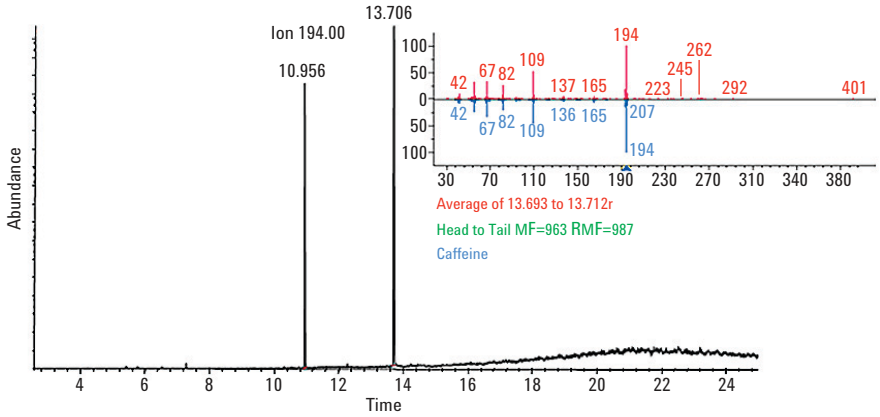


Figure 6. Presence of caffeine at 13.706 minutes indicating sources of human pollution.

Conclusions

The Agilent J&W DB-UI 8270D Ultra Inert GC column provides subtle but observable performance improvements for EPA 8270D compounds when compared to a non-Agilent premium column. When applying the varied criteria most critical to the long term success of the assay, namely response factor for DNP, tailing factor for NMDA, and separation of the aromatic pair chlorthalonil and phenanthrene, the DB-UI 8270D column exceeds the assay criteria and is best in class when measured against the most closely competitive premium alternative column.

Acknowledgement

The authors thank Joan Stevens for her fruitful discussions involving sample preparation using solid phase extraction cleanup to isolate compounds from seawater.

References

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