

Introduction

EPA method 8270D provides for the analysis of solid, liquid, and air/dust waste samples [1]. The list of priority pollutants published in the method monograph is quite extensive numbering in excess of 250 listed compounds. A key element of the assay hinges on being able to generate defensible library matches and in order to do that chromatographic separation becomes a critical piece of the analytical puzzle. High spectral match quality to library reference spectra can be accomplished when signal to noise is sufficient, which can only be accomplished if the component signal to noise is adequate. One factor that can detract from good spectral matching is poor peak resolution, this leads to co-eluting components and their spectra require subtraction or other algorithms to remove interfering non-qualifier ions. Further complicating the matter is signal to noise efficiency, once again possibly causing match quality for compound identification to suffer. The Agilent J&W 8270D column was introduced to provide the needed resolution, inertness, and selectivity required to meet the demands of the assay [2]. A series of reactive compounds designed to elucidate problems related to column quality has been developed as a subset to the EPA list. This smaller range of compounds exhibits a wide variety of reactivity with common column vulnerabilities such as peak tailing. A seawater sample from coastal New Jersey was spiked and caffeine was identified indicating human pollution sources are present.

Experimental

An Agilent 7890A GC was coupled to a 5975B Mass Spectrometer with the Inert EI 350 non-coated source installed for this series of experiments. Table 1 lists the chromatographic conditions used for these analyses.

GC conditions [3]

Column: Agilent J&W DB-UI 8270D 20m x 0.18mm x 0.36µm film (Agilent p/n 121-9723)

Sample: Agilent 8270 semi-volatiles Evaluation mix 10ng/uL diluted 1:2 for 1ng on-column

Carrier: Helium 1.0ml/min constant flow mode

Oven: 40 C (hold 3min), to 300 C at 25 C/min (hold 3min)

Inlet Temp: 275 C Ultra-inert splitless liner single taper no wool (p/n 5190-3162)

Splitless injector: Septum purge on at 1 min, 3ml/min purge flow

Detector: MSD transfer aux temp @ 265 C

MS: Agilent 5975B Conditions

Sampler: Agilent 7683B, 5uL Syringe 0.2uL injection in dichloromethane splitless

MS Conditions

MS: 5975B w/ EI inert 350 source

Solvent delay: 2.5min

MS temperature: 300 C (Source); 150 C (Quad)

Transfer Line 265 C

Scan Range: 30-550

Threshold: 50

Scan Rate: 6.3scans/sec

Experimental

Standard Preparation

A 29 component checkout mix at 10ng/uL nominal in dichloromethane (Agilent p/n 5190-0473) was used diluted 1:2 in dichloromethane (J.T. Baker Ultra-residue analyzed grade) in order to provide a 1ng per component injection on column in splitless mode. Calibration standards were prepared using an Agilent 7696A prep bench.

Sample Preparation

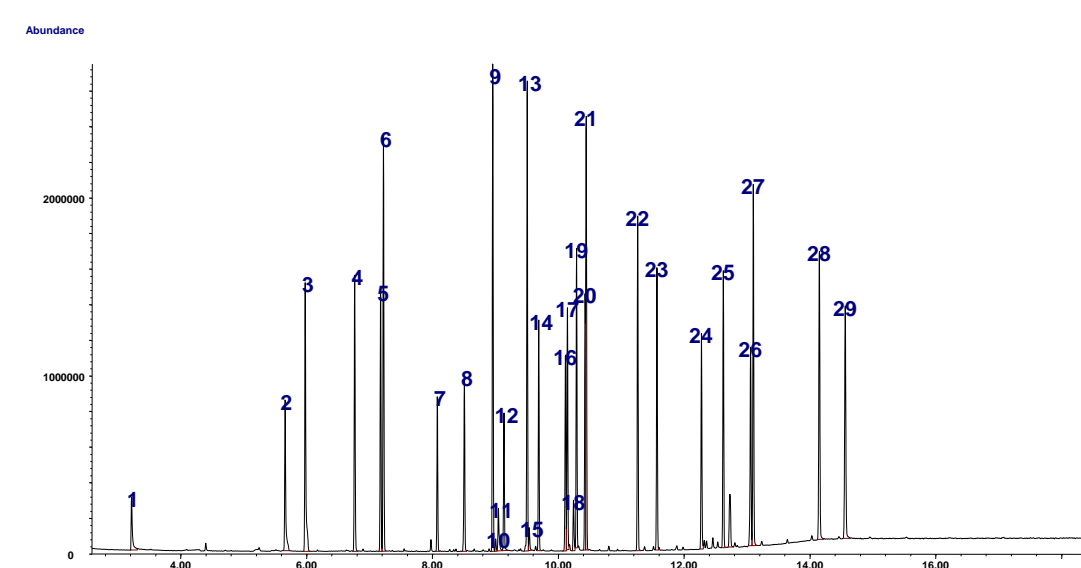
Samples for analysis were extracted using HF MEGA Bond Elut C18 (Agilent p/n 14256001) as previously noted [4]. For seawater, a 20ml wash with de-ionized buffer water was used to remove salt prior to elution. Laboratory control samples were prepared at 10ppb.

Table 1. Equipment and Consumables

Description	Part Number
HF MEGA Bond Elut C18 cartridges 1g	14256001
Vacuum manifold processing station	5982-9110
Manifold stopcocks	5982-9102
60ml Reservoirs	12131012
Adapters	12131001
Sodium sulfate drying cartridges	12131033

Chromatogram Comparison

Figure 1 TIC of 29 component Semi-volatiles evaluation mix



Peak Identification

- N-Nitrosodimethylamine
- Aniline
- 1,4-Dichlorobenzene-d4
- Isophorone
- 1,3-Dimethyl-2-nitrobenzene
- Napthalene
- Hexachlorocyclopentadiene
- Mevinphos
- Acenaphthene-d10
- 2,4-Dinitrophenol
- 4-Nitrophenol
- 2,4-Dinitrotoluene
- Fluorene
- 4,6-Dinitro-2-methylphenol
- Trifluralin
- Simazine
- Atrazine
- Pentachlorophenol
- Terbufos
- Chlorthalonil
- Phenanthrene-d10
- Aldrin
- Heptachlor epoxide
- Endrin
- 4,4'-DDT
- 3,3'-Dichlorobenzidine
- Chrysene-d12
- Benzo[b]fluoranthene
- Perylene-d12

Table 1 Comparison of performance criteria comparing Agilent(Green) to other vendor(Red)

Compound	Avg. T _F	Compound	Avg. T _F
N-Nitrosodimethylamine	1.45	N-Nitrosodimethylamine	2.14
Aniline	1.22	Aniline	1.30
1,4-Dichlorobenzene	1.02	1,4-Dichlorobenzene	1.28
	Resolution		Resolution
Chlorthalonil	1.40	Chlorthalonil	6.80
Phenanthrene	0.20	Phenanthrene	0.70
	Avg. RF		Avg. RF
2,4-Dinitrophenol	0.05	2,4-Dinitrophenol	0.03

Results and Discussion

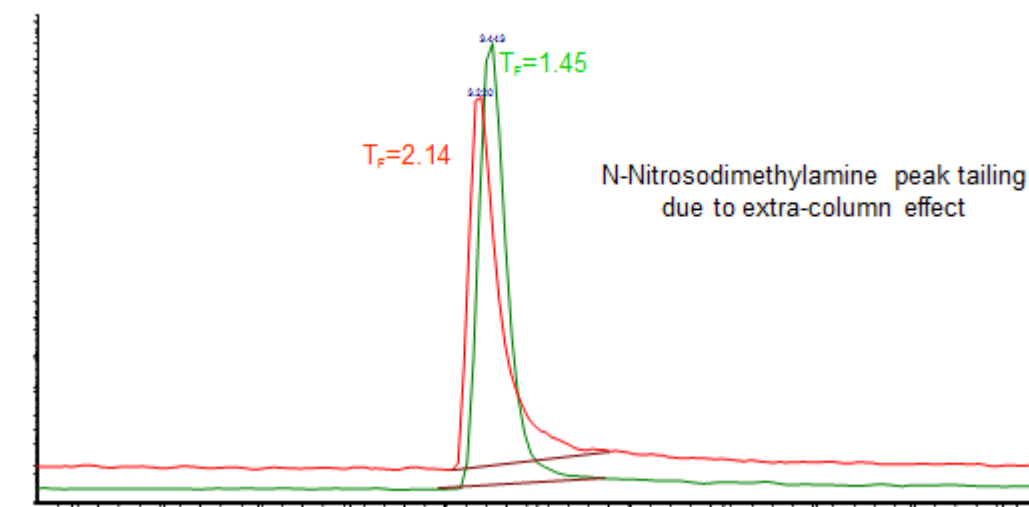


Figure 2 Comparing Agilent(green) vs Competitor(Red)peak tailing effect for basic components

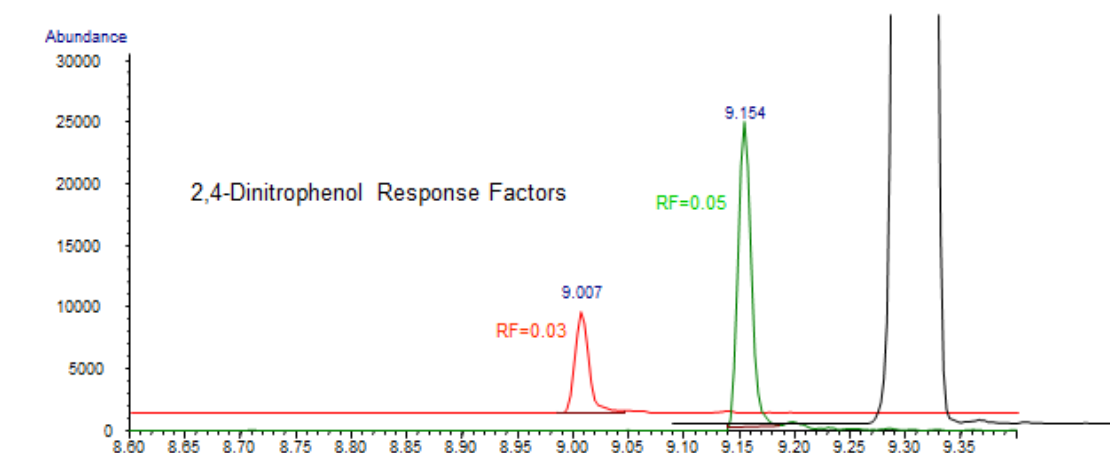


Figure 3 Response factors for DNP among various vendors at 1ng on column splitless.

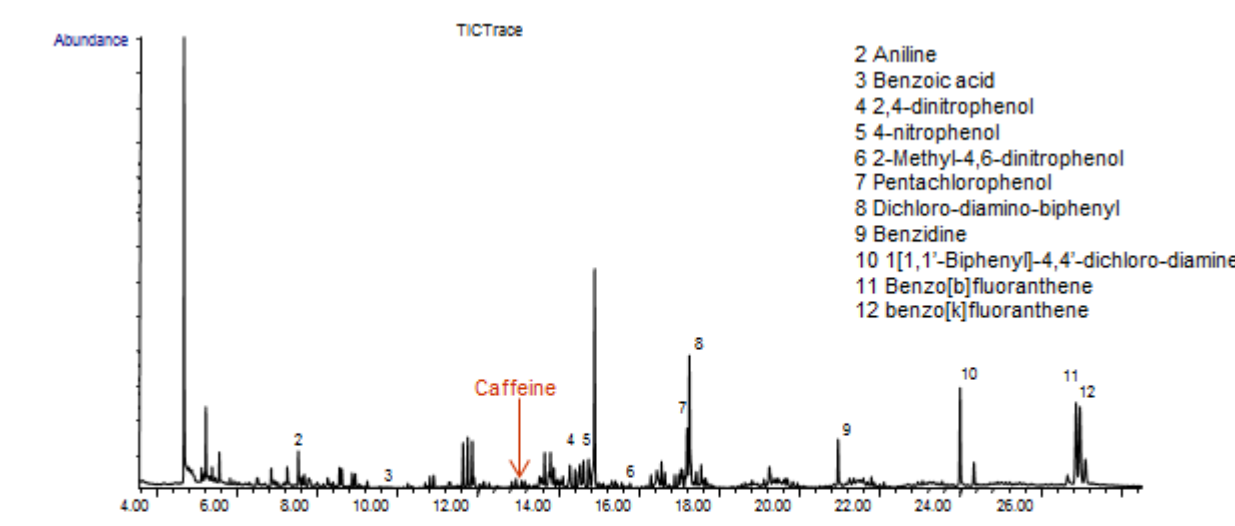


Figure 5 Spiked seawater from Coastal New Jersey

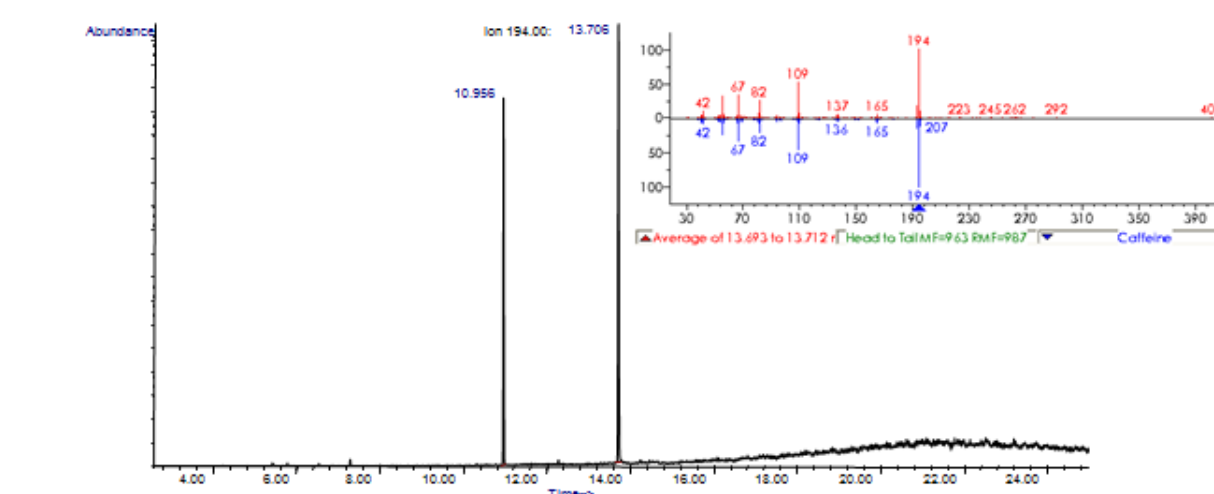


Figure 6 Presence of caffeine indicating human sources of pollution

Results and Discussion

Performance Comparison of Agilent DB-8270D GC column and alternate vendor

In order to make comparisons, DB-8270D columns from differing manufacturing lots were evaluated and compared to various lots of a competing vendor's recommended column.

Figure 1 demonstrates that chromatographic peak shape is acceptable for all components in the mix. Table 1 highlights the subtle but observable differences between vendors. One of the most active basic compounds listed in semi-volatiles methods is N-nitrosodimethylamine.

Figure 2 shows a comparison between vendors. This early eluting compound can give poor performance in the injection port and on the column, and many currently available columns give a poor peak shape for it. Systems pre-conditioned by injecting a slightly basic solvent can perform well with this basic component, but might then perform poorly with the acidic compounds, such as DNP.

An overlay of the various vendor chromatograms for the DNP peak is included in Figure 3. It has been used as a pesticide and a wood preservative.

Caffeine can be detected in ppb levels indicating human sources of pollution are likely to be present as seen in Figures 5 & 6.

The seawater sample was not dechlorinated at time of collection, therefore peak#1 N-NDMA is absent.

Conclusions

The analysis of effluents for BNA's offers challenges that Ultra Inert columns meet and exceed, even for matrices with high salinity, effective sample prep and column robustness work in sync.

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

Further details for this poster can be found by accessing application note 5991-0250EN on the Agilent Literature Library Site.
<http://www.chem.agilent.com/Library/applications/5991-0250EN.pdf>