Agilent CrossLab
From Insight to Outcome

Advances in GC Column Selectivity for Environmental, Food Sample and Pharma Applications.

Gustavo Serrano, Ph.D.
Global Product Manager – GC Columns
Chemistries and Supplies Division
Agilent CrossLab Group

Agilent

Outline

- **Volatile Organic Compounds (VOCs)**

  Pharmaceutical and Environmental Applications
- **Polycyclic Aromatic Hydrocarbon (PAHs)**

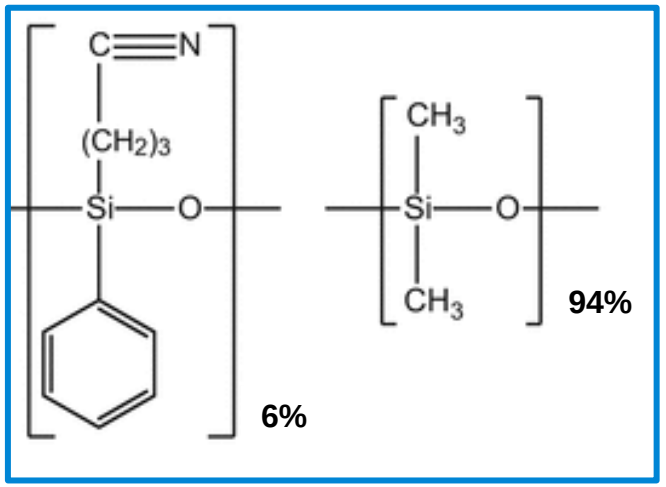
  Food and Environmental Applications
- **Polychlorinated Biphenyls (PCBs)**

  Environmental Application
- **Dioxins**

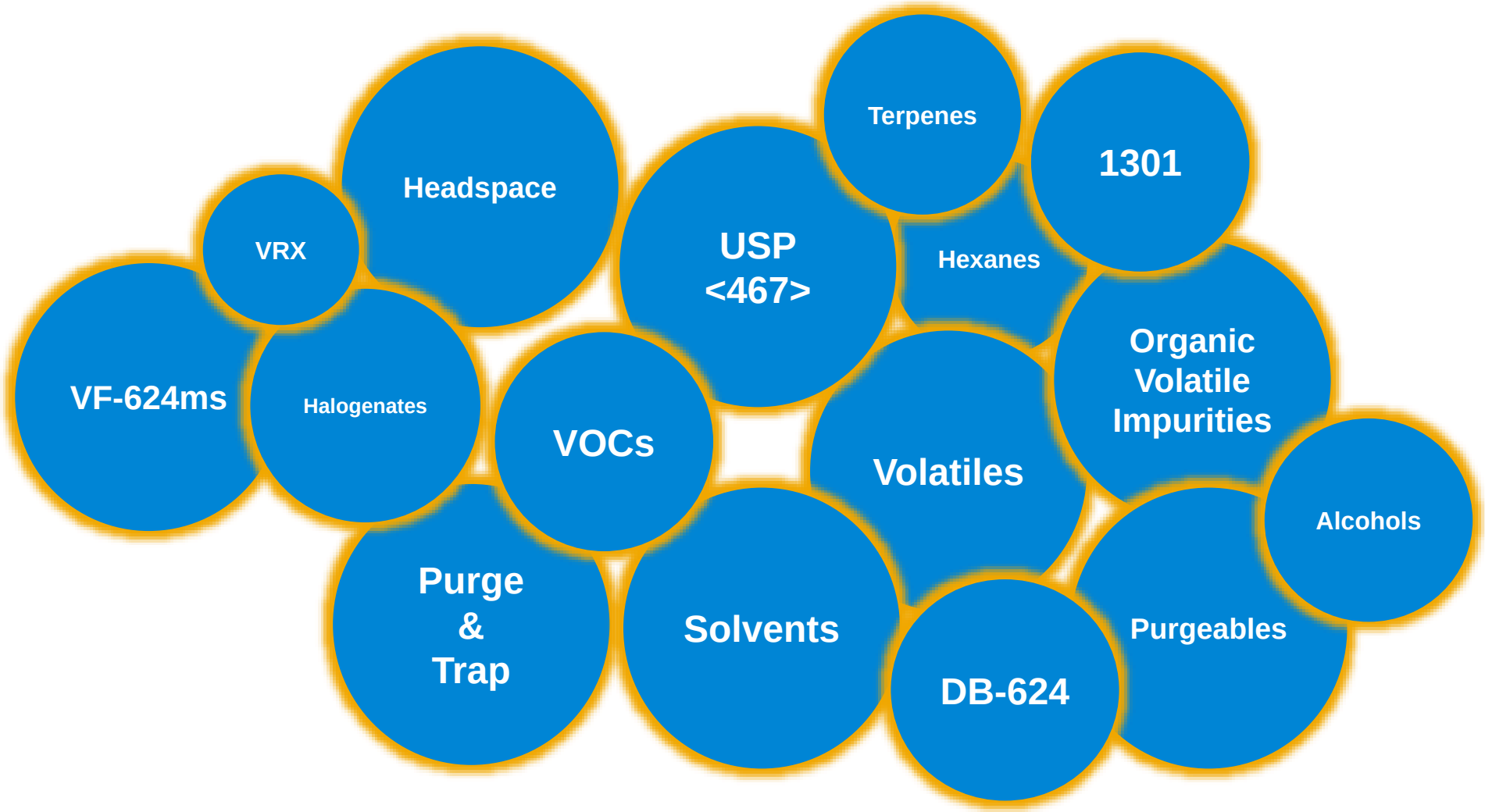
  Food and Environmental Applications

VOCs & Volatiles: Pharma and Environmental Applications

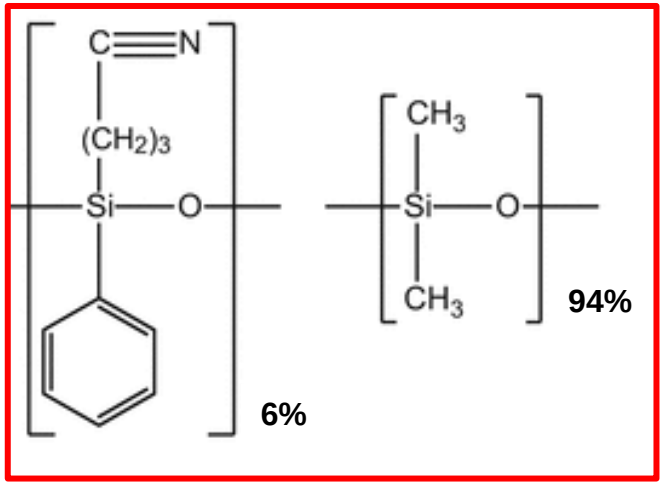
Agilent JW 624 GC Columns



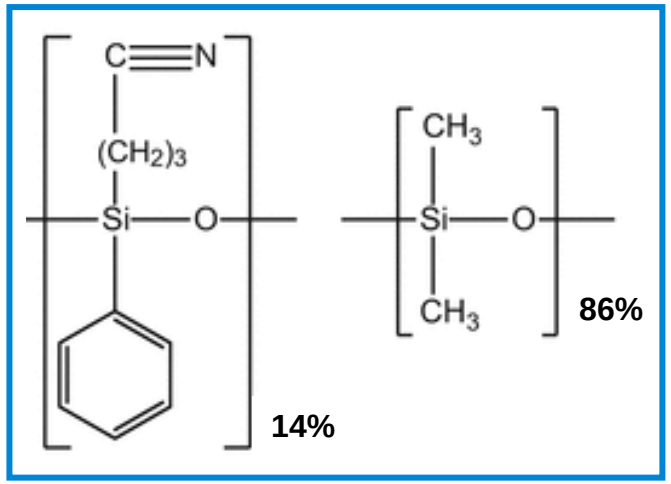
VOCs & Volatiles Analysis



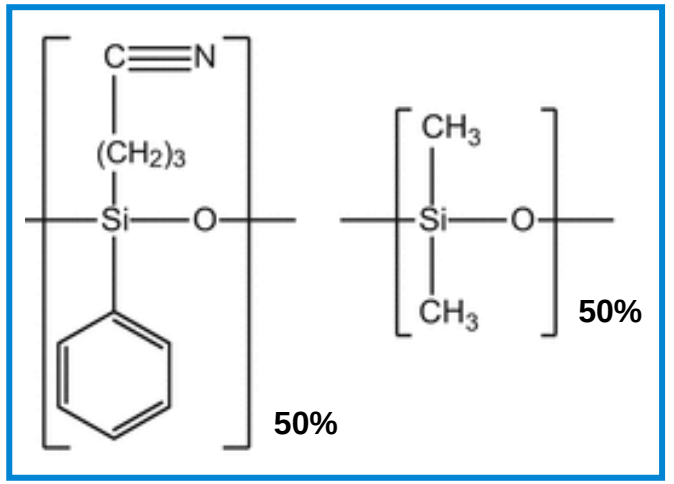
J&W Portfolio --- Cyanopropylphenyl Liquid Phases



6% cyanopropylphenyl 94% dimethylpolysiloxane



14% cyanopropylphenyl 86% dimethylpolysiloxane



50% cyanopropylphenyl 50% dimethylpolysiloxane

624-type phases

- DB-624 UI
- DB-624
- VF-624ms
- CP-Select 624 CB
- DB-Select 624 UI for <467>
- CP-Select for Hexanes

1701-type phases

- DB-1701
- DB-1701P
- VF-1701ms
- CP-Sil 19 CB

225-type phases

- DB-225
- DB-225ms
- CP-Sil 43 CB

1301-type phases

- DB-1301
- VF-1301ms

The 624 is the Most Popular Column Choice for Volatiles Analysis

$$R_s = {}^1/_4 \cdot \frac{\alpha - 1}{\alpha} \cdot \frac{k}{k+1} \cdot \sqrt{N_{th}}$$

N_{th} Plate count

k' Capacity factor

α Selectivity factor

Typical GC phases

DB-5ms, 30m x 0.25 mm i.d. x 0.25 µm

DB-624, 30m x 0.25 mm i.d. x 1.4 µm

Many VOCs & solvents have low BPs with therefore little retention/k
The thick-film *creates* higher retention/k and thus *improves separation*

VOCs and solvents contain various functional groups.
Cyano/phenyl/methyl mix of 624 provides different levels of interaction mechanisms: Dispersion, pi-pi stacking, dipole, H_2 bonding
This provides *excellent selectivity* with *improved separations* across many analytes

624 Applications & Workflows

Waters

VOCs / Purgeables
Nitrosamines

Soils

VOCs

Alcoholic Beverages

Alcohols & aromas

Air

Volatiles & Hydrocarbons
Halogenates / CFCs

Industrial

Solvents & Volatiles

Pharmaceuticals

Residual solvents

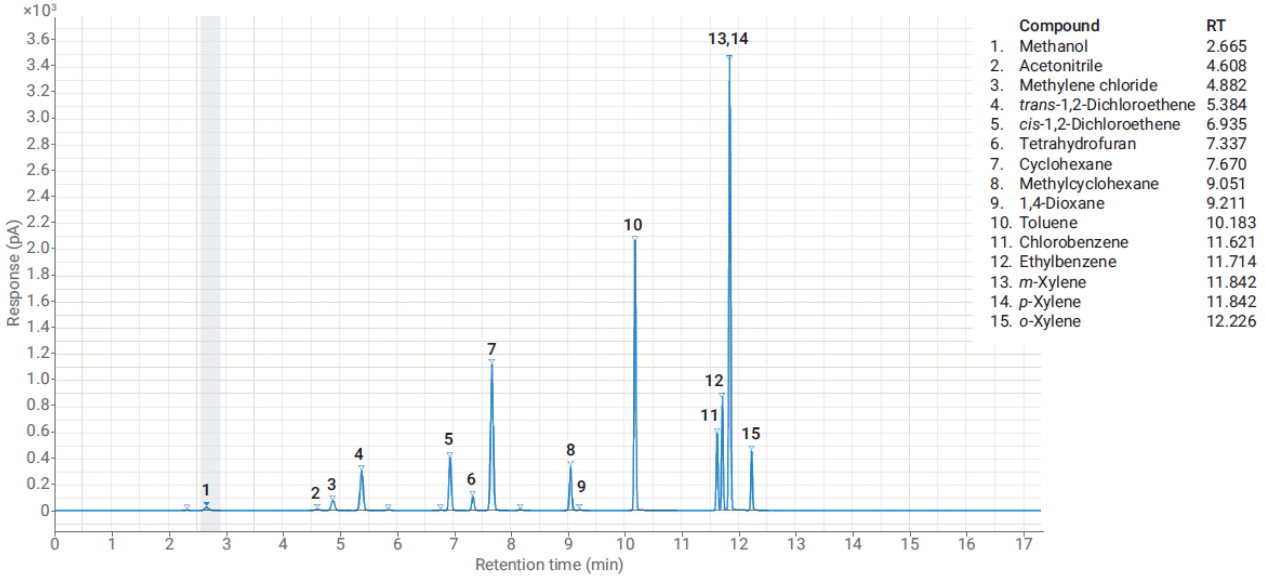
Residual Solvents

- Most are headspace applications
  - Hand sanitizer could also be done by headspace
- Can use FID or MSD
- There are Intuvo and 8890 applications
- Variety of columns (select and regular 624 UI) and dimensions
  - DB-624 UI
  - DB-Select 624 UI for 467

USP <467> Application Compares Select 624 to Innowax

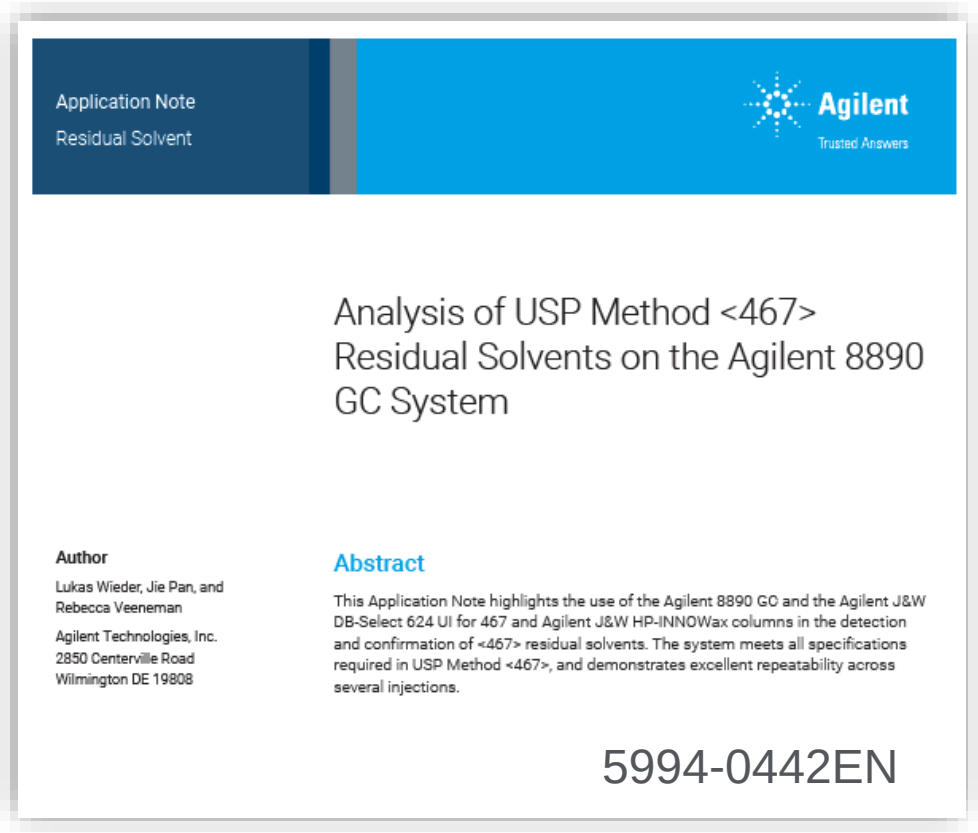
- HS/GC/dual FID
  - Split using CFT
- Class I and Class II (A & B) Residual Solvents

Class 2A solvents



	Compound	RT
1.	Methanol	2.665
2.	Acetonitrile	4.608
3.	Methylene chloride	4.882
4.	*trans*-1,2-Dichloroethene	5.384
5.	*cis*-1,2-Dichloroethene	6.935
6.	Tetrahydrofuran	7.337
7.	Cyclohexane	7.670
8.	Methylcyclohexane	9.051
9.	1,4-Dioxane	9.211
10.	Toluene	10.183
11.	Chlorobenzene	11.621
12.	Ethylbenzene	11.714
13.	*m*-Xylene	11.842
14.	*p*-Xylene	11.842
15.	*o*-Xylene	12.226

Figure 4. Chromatogram of the USP residual solvents class 2A standard solution resolved on a J&W DB-Select 624 UI for 467 GC column.


Application Note
Residual Solvent

Agilent
Trusted Answers

Analysis of USP Method <467> Residual Solvents on the Agilent 8890 GC System

Author

Lukas Wieder, Jie Pan, and Rebecca Veeneman

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Abstract

This Application Note highlights the use of the Agilent 8890 GC and the Agilent J&W DB-Select 624 UI for 467 and Agilent J&W HP-INNOWax columns in the detection and confirmation of <467> residual solvents. The system meets all specifications required in USP Method <467>, and demonstrates excellent repeatability across several injections.

5994-0442EN

5994-0442EN Instrument Conditions	
Column	**J&W DB-Select 624 UI for 467,** 30 m × 0.32 mm, 1.8 µm **(p/n 123-0334UI)**
Carrier Column 1	**Helium, constant flow, 2.0 mL/min**
Oven	**40 °C (5.0 min), ramp 18 °C/min to 180 °C (3.0 min)**
Inlet	**Split mode, 140 °C, split ratio 5:1**

Class I, II, & III RSA

- GC/FID/MS
- Headspace for 624 UI
- Liquid injection on Wax

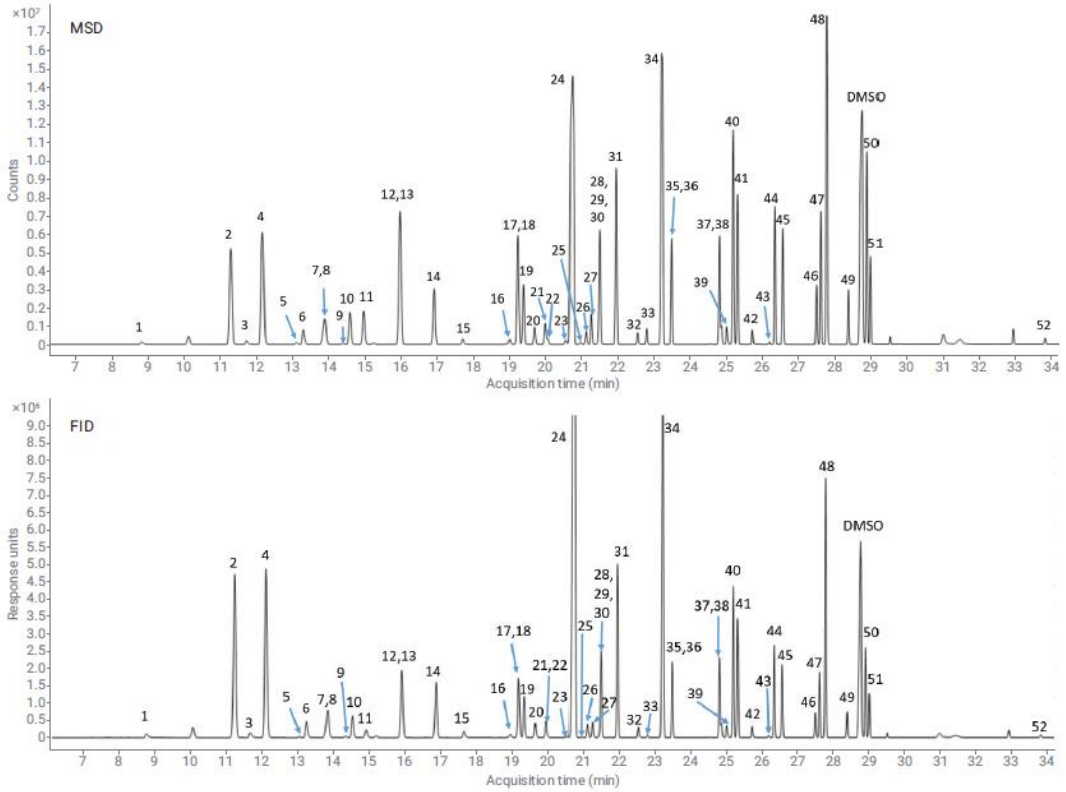
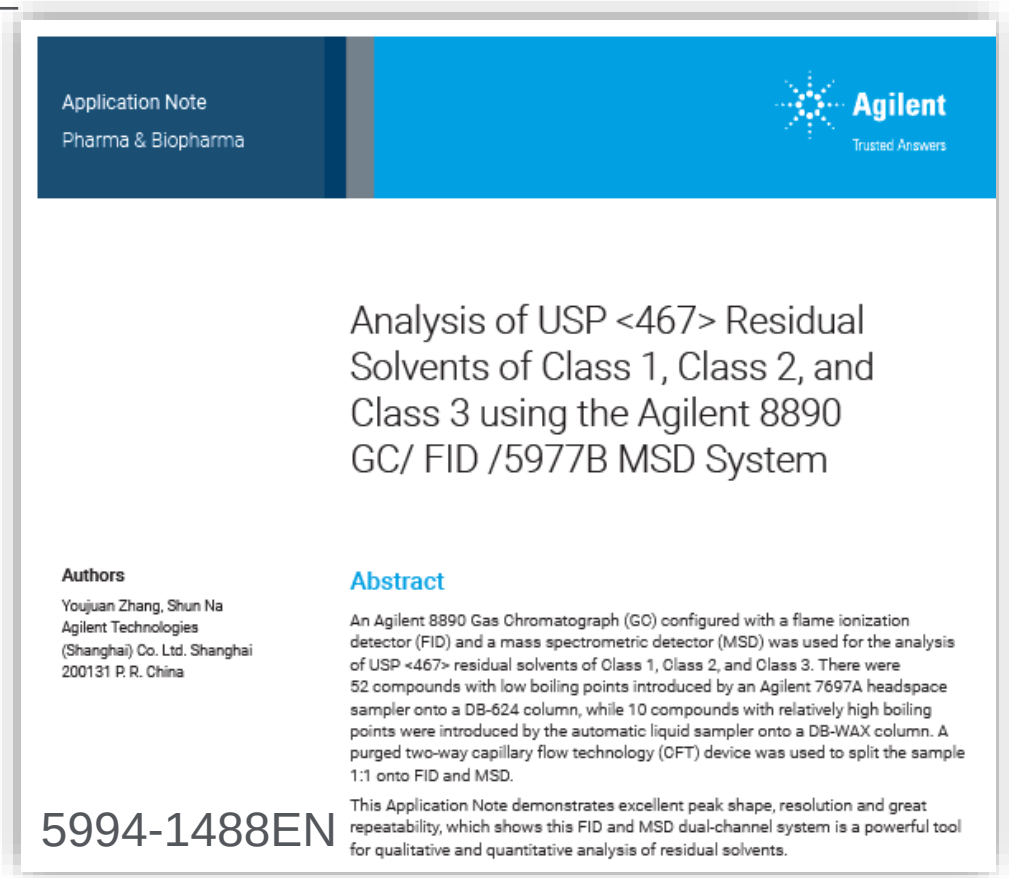


Figure 2. GC/MS-SCAN and FID Chromatogram of 52 compounds of standard solution (Level 7) on an Agilent DB-624 column. The effluent split ration is MSD: FID= 1:1.

No.	Name
1	Methanol
2	Pentane
3	Ethanol
4	Ethyl ether
5	1,1-Dichloroethene
6	Acetone
7	Isopropanol
8	Ethyl formate
9	Acetonitrile
10	Methyl acetate
11	Methylene chloride
12	tert-Butylmethyl ether
13	trans-1,2-Dichloroethene
14	Hexane
15	1-Propanol
16	Nitromethane
17	cis-1,2-Dichloroethene
18	2-Butanone
19	Ethyl acetate
20	2-Butanol
21	Tetrahydrofuran
22	Chloroform
23	1,1,1-Trichloroethane
24	Cyclohexane
25	Carbon tetrachloride
26	2-Methyl-1-propanol
27	1,2-Dimethoxyethane
28	Benzene
29	1,2-Dichloroethane
30	Isopropyl acetate
31	Heptane
32	1-Butanol
33	Trichloroethylene
34	Methylcyclohexane
35	1,4-Dioxane
36	Propyl acetate
37	4-Methyl-2-pentanone
38	Isoamyl alcohol
39	Pyridine
40	Toluene
41	Isobutyl acetate
42	1-Pentanol
43	2-Hexanone
44	Butyl acetate
45	Tetrahydrothiophene
46	Chlorobenzene
47	Ethylbenzene
48	m,p-Xylene
49	o-Xylene
50	Isopropylbenzene
51	Anisole
52	1,2,3,4-Tetrahydronaphthalene



Application Note
Pharma & Biopharma

Agilent
Trusted Answers

Analysis of USP <467> Residual Solvents of Class 1, Class 2, and Class 3 using the Agilent 8890 GC/ FID /5977B MSD System

Authors

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Abstract

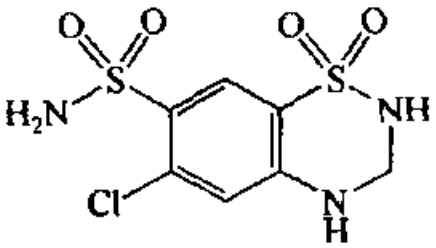
An Agilent 8890 Gas Chromatograph (GC) configured with a flame ionization detector (FID) and a mass spectrometric detector (MSD) was used for the analysis of USP <467> residual solvents of Class 1, Class 2, and Class 3. There were 52 compounds with low boiling points introduced by an Agilent 7697A headspace sampler onto a DB-624 column, while 10 compounds with relatively high boiling points were introduced by the automatic liquid sampler onto a DB-WAX column. A purged two-way capillary flow technology (CFT) device was used to split the sample 1:1 onto FID and MSD.

This Application Note demonstrates excellent peak shape, resolution and great repeatability, which shows this FID and MSD dual-channel system is a powerful tool for qualitative and quantitative analysis of residual solvents.

5994-1488EN

5994-1488EN Instrument Conditions	
Column	**J&W DB-624 UI for 467,** 60 m × 0.25 mm, 1.4 µm **(p/n 122-1364UI)**
Column 1	**Helium, constant flow, 1.0 mL/min**
Oven	**40 °C (10 min), ramp 5 °C/min to 80 °C (0 min), ramp 12 °C/min to 200 °C (10 min)**
Inlet	**Split mode, 250 °C, split ratio 10:1**

Hydrochlorothiazide



C7H8ClN3O4S2 MW 297.74

HS:

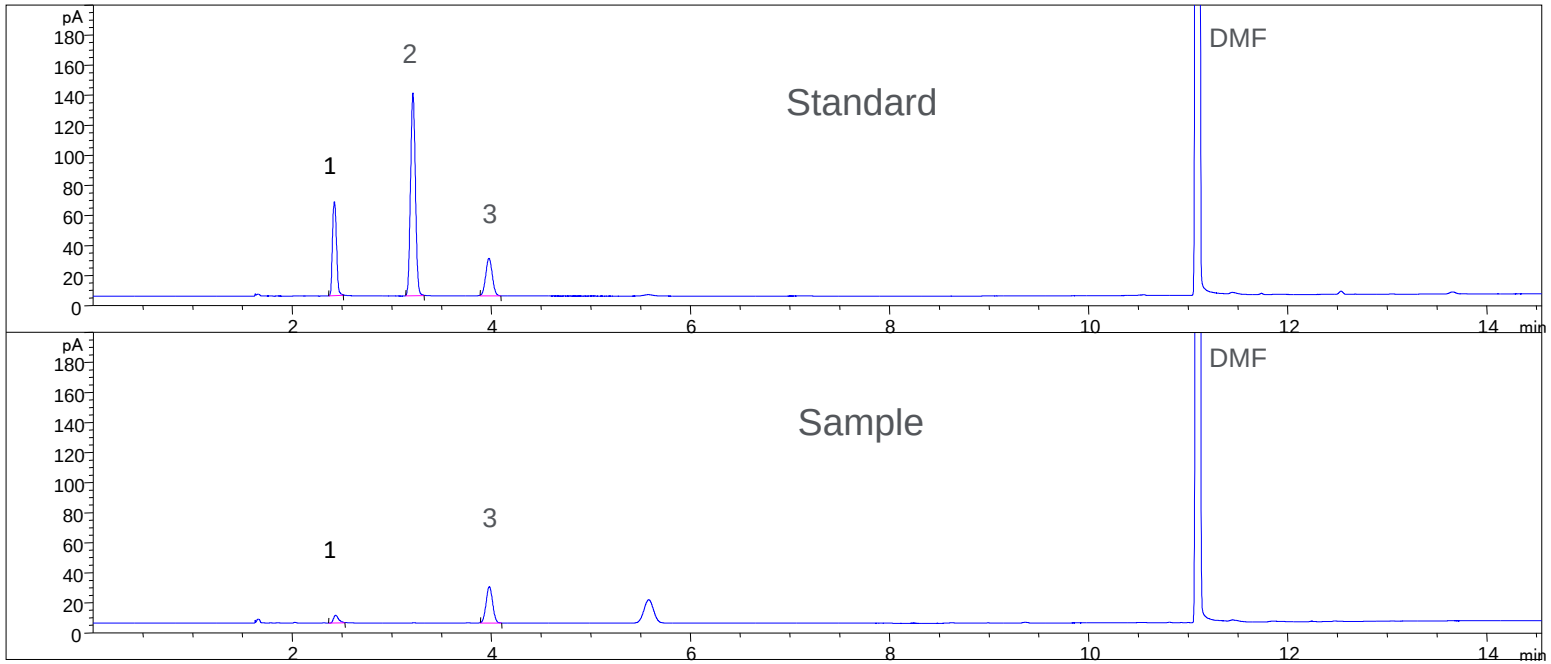
Oven Temperature:	80 °C
Loop Temperature:	100 °C
Transfer Line Temperature:	120 °C
Vial Equilibration (min):	30
Sample Loop :	1mL

Standards: 0.075mg/mL MeoH, 0.125mg/mL EtoH, 0.02mg/Ml isopropanol(ISTD)
Sample :25mg/mL Hydrochlorothiazide

GC:

Column:	**DB- select 624 UI**
	30 m x 0.530 mm x 3 µm, P/N125-0334UI
Carrier :	He, constant flow mode, 4.5mL/min
Inlet:	200 °C, split ratio 5:1
OVEN:	40 °C for 8 min
	45 °C/min to 200 °C
	200 °C for 1 min
Detector:	FID 250 °C

Hydrochlorothiazide

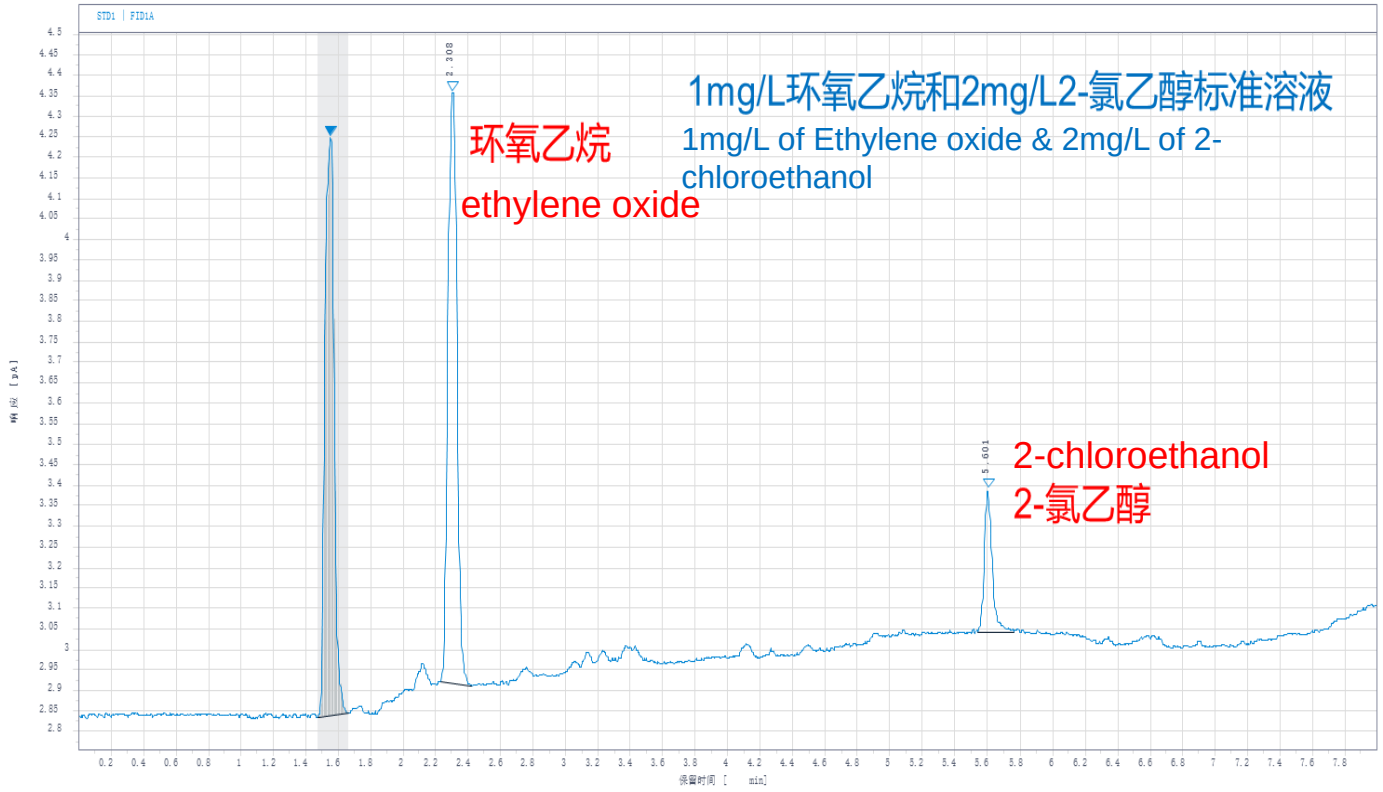


NO。	Compound	Retention time (min)		Area (mAU*s)		Theoretical Plate (N)	Resolution (Rs)	USP Tf
		RT	RSD（%） (n=6)	Area	RSD（%） (n=6)			
1	Methanol	2.43	0.05	165.75	1.60	15848	/	1.14
2	Ethanol	3.21	0.05	446.8	0.43	19565	9.47	1.05
3	Isopropanol（IS）	3.98	0.04	112.85	0.96	16902	7.28	1.02

Ethylene oxide sterilization residuals in PPE

DB-Select 624 UI，30m x 0.53mm x 3um (P/N 125-0334UI)

- Engineered to optimize pharmaceutical residual solvents analysis per USP Method <467>
- Ultra inertness and low bleed
- Recommended columns for ethylene oxide detection



Headspace:

Oven：80℃

Loop：90℃

Transfer Line：100℃

Equilibration time：30min

GC:

Inlet：200℃，split ratio：3:1

Inlet liner: Ultra Inert, splitless, straight, 2mm id (p/n 5190-6168)

Column：DB-Select 624UI，30mx0.53mmx3um (p/n125-0334UI)

Carrier gas：Nitrogen，5mL/min

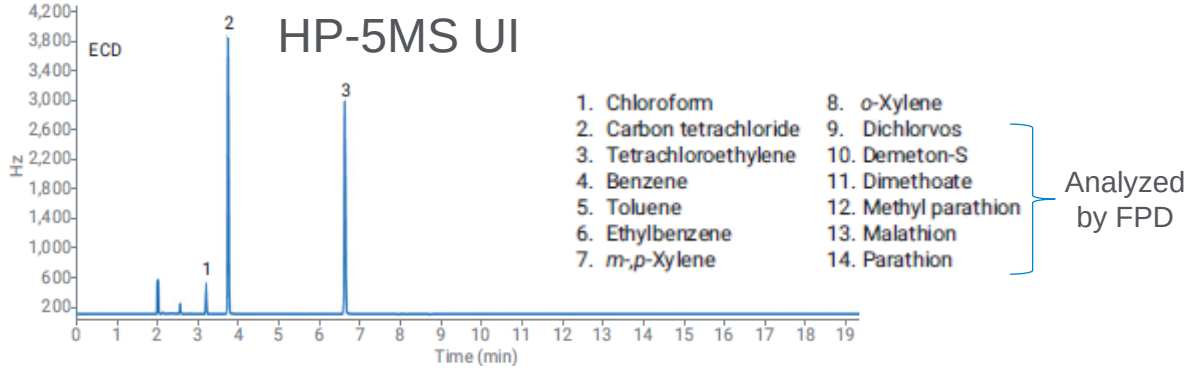
Oven：40℃(1min)，15℃/min to 130℃(1min)

Detector：FID，250℃

Capabilities of 8860 and HP-5ms UI/DB-624 UI for Environmental Applications

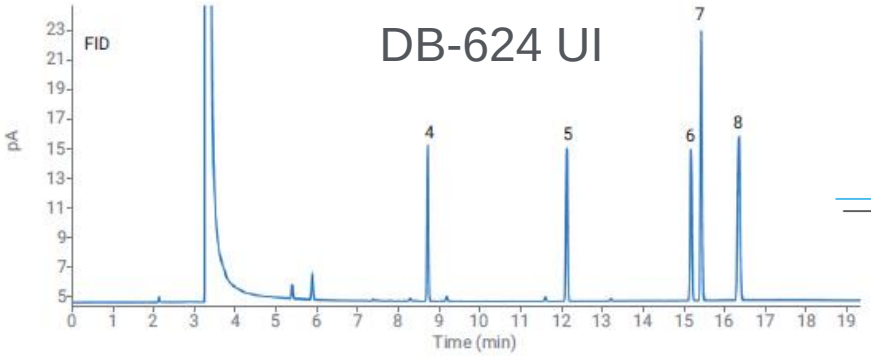
- Volatile halogenated and aromatic hydrocarbons
- Flexibility of 8860
  - Allows three detectors on one system
  - FID, ECD, FPD

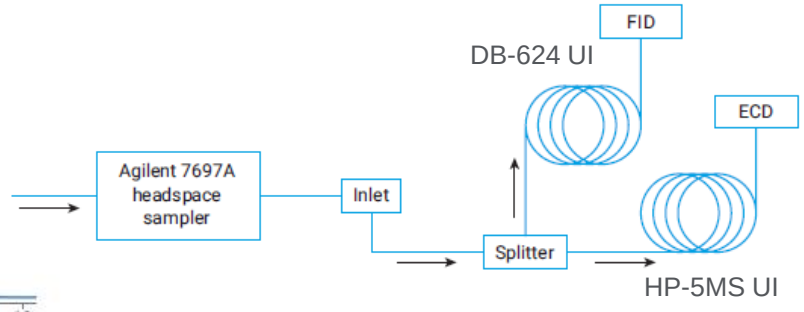
HP-5MS UI



Analyzed by FPD

DB-624 UI





Application Note
Environmental

Agilent
Trusted Answers

Analysis of Drinking Water with the Agilent 8860 GC and 7697A Headspace Sampler

Authors

Ian Eisele
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Abstract

The flexibility of the Agilent 8860 GC is demonstrated by an analysis requiring multiple types of detection and sample introduction. Volatile halogenated and aromatic hydrocarbons in water are sampled by headspace for detection by FID and ECD, and organophosphorus pesticides are detected by FPD. A single 8860 GC can be configured to run both analyses.

5994-1239EN

5994-1239EN Instrument Conditions	
Column	**J&W DB-624 UI for 467,** 30 m × 0.25 mm, 1.4 µm **(p/n 122-1334UI)**
Column 1	**Helium, constant flow, 1.0 mL/min**
Oven	**40 °C (2.0 min), ramp 6 °C/min to 120 °C (4.0 min)**
Inlet	**Split mode, 250 °C, split ratio 50:1**

VOC and the stability of the 8890 with the DB-624 UI GC Column

- The Chinese Ministry of Environmental Protection
  - HJ642-2013
- Demonstrates performance using a difficult matrix
  - Soil

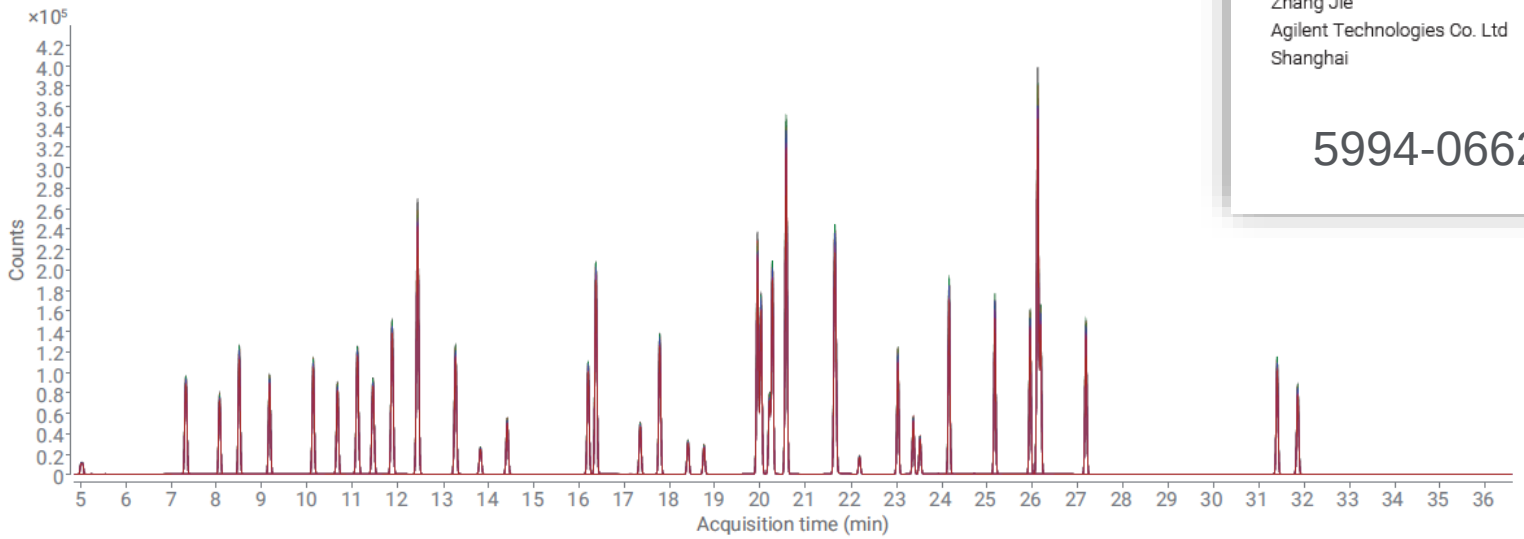

Figure 1. Overlaid TIC SIM traces for six replicates of 20 µg/L samples.

Application Note
Environmental

Agilent
Trusted Answers

Determination of Volatile Organic Compounds in Soil and Sediments

Using an Agilent 7697A Headspace Sampler, 8890 GC, and 5977B GC/MSD combined platform

Author

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5994-0662EN

Abstract

The accurate detection of volatile organic compounds (VOCs) in contaminated soil and sediment is of particular importance. The Chinese Ministry of Environmental Protection has produced a headspace GC/MS method, HJ642-2013, for the analysis of VOCs in soil and sediments. This Application Note has followed China method HJ642-2013 and demonstrated the excellent instrument performance of Agilent 7697A headspace, 8890 GC, and 5977B MSD combined platform for the targeted analysis.

5994-0662EN Instrument Conditions	
Column	**J&W DB-624 UI for 467,** 60 m × 0.25 mm, 1.4 µm **(p/n 122-1364UI)**
Column 1	**Helium, constant flow, 1.2 mL/min**
Oven	**40 °C (2.0 min), ramp 8 °C/min to 90 °C (4.0 min), ramp 6 °C/min to 200°C (10 min)**
Inlet	**Split mode, 250 °C, split ratio 10:1**

Recent 624 Phase Applications

5994-1926EN
Novel Residual Solvents Analysis of Cannabinoid Products with the Agilent Headspace-GC/MS System

5994-0442EN
Analysis of USP Method <467> Residual Solvents on the Agilent 8890 GC System

5994-1488EN
“Analysis of USP <467> Residual Solvents of Class 1, Class 2, and Class 3 using the Agilent 8890 GC/ FID /5977B MSD System”

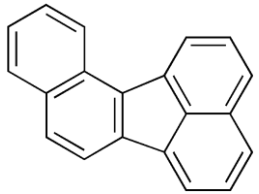
5994-1239EN
“Analysis of Drinking Water with the Agilent 8860 GC and 7697A Headspace Sampler”

5994-0662EN
“Determination of Volatile Organic Compounds in Soil and Sediments:
Using an Agilent 7697A Headspace Sampler, 8890 GC, and 5977B GC/MSD combined platform”

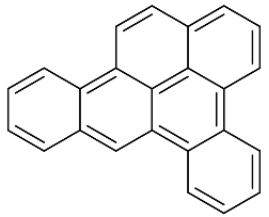
5994-1923EN
“Analysis of Ethanol and Isopropanol in Alcohol based hand sanitizers by direct injection GC/FID”

Food and Environmental Applications: PAHs

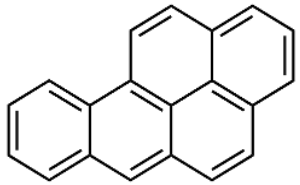
GC Column Updates & Solutions



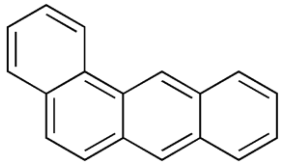
Benzo[j]fluoranthene



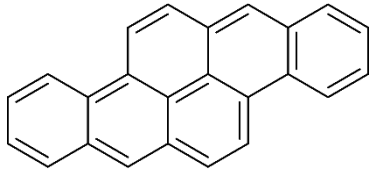
Dibenzo[a,e]pyrene



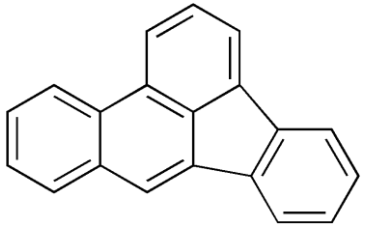
Benzo[a]pyrene



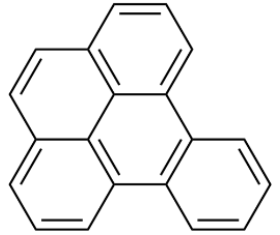
Benz[a]anthracene



Dibenzo[a,h]pyrene

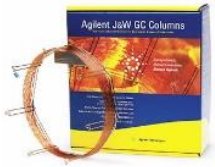
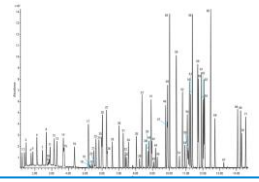
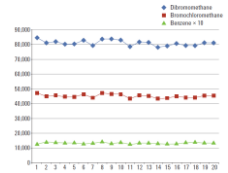


Benzo[b]fluoranthene



Benzo[g,h,i]perylene

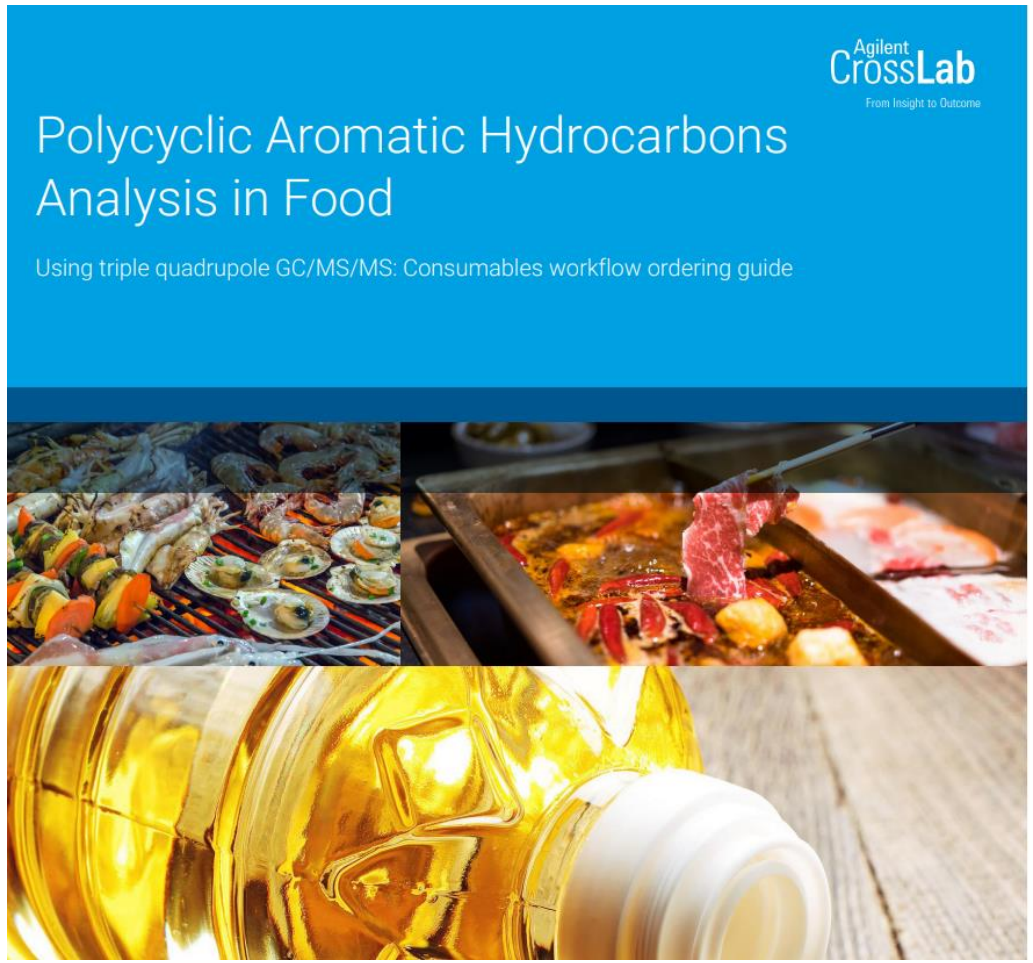
Agilent GC-PAH Solutions

Sample Containment	Sample preparation	Standards	Inlet Supplies	Separation	System Supplies	Application Notes
			 			
			 			
	EMR-Lipids	EPA 610 EPA 8270		DB-5ms UI DB-EUPAH Select PAH		

Consumables Selection Toolkit for PAHs in Food Workflow

5994-2016EN

Includes Checkout Standards, Column, Liners, Unions, Vials, Caps, filament, gas filters etc. needed to get started with PAH testing with suggested Agilent methods and compatible with PAH Workflow Kits

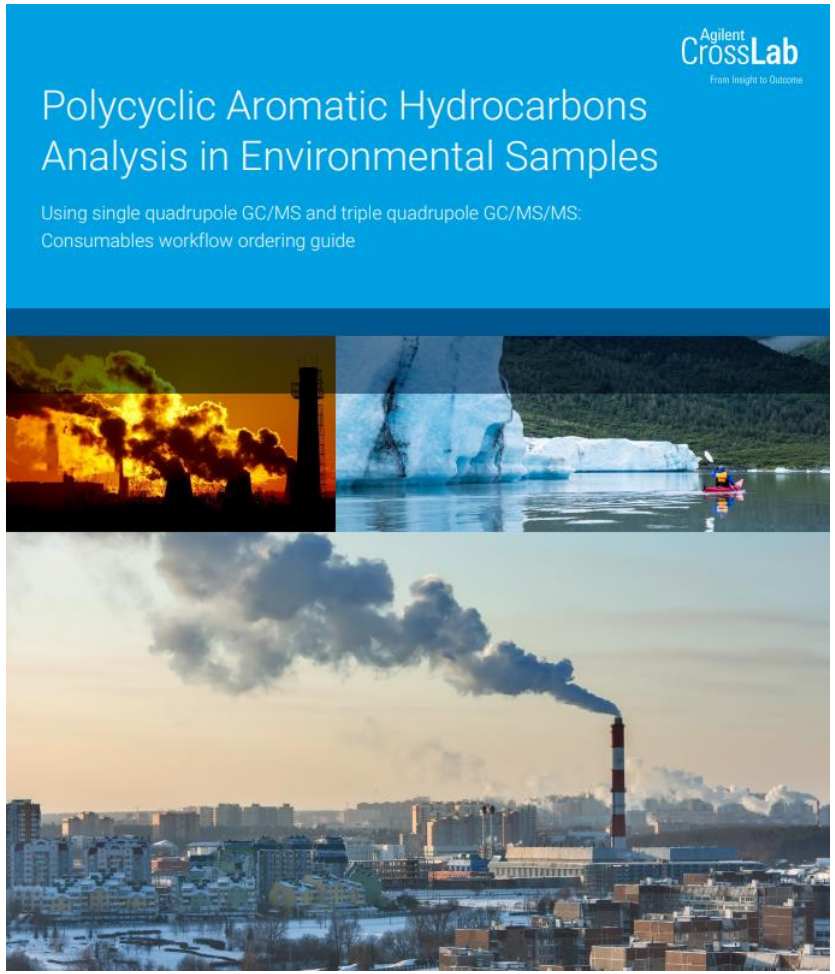


Item	Part Number
View MyList of sample preparation supplies	
Captiva EMR-Lipid cartridge, 3 mL, 300 mg	5190-1003
Ceramic homogenizers	5982-9312
Agilent positive pressure manifold processor (PPM-48)	5191-4101
Captiva EMR-Lipid cartridge, 6 mL, 600 mg	5190-1004
Bond Elut Jr PSA, 500 mg	12162042B
View MyList of standards	
EU PAH(15+1) standard kit; 250 µg/mL	5190-0487
EPA PAH standard (calibration standard); 500 µg/mL	8500-6035
Please go to www.agilent.com/chem/standards for additional volume and concentration standard options	
View MyList of Inlet Supplies	
Inlet septa, Advanced green, nonstick, 11 mm, 50/pk	5183-4759
Inlet septa, Advanced green, nonstick, 11 mm, 100/pk	5183-4759-100
Ultra Inert Splitless, single taper, glass wool	5190-2293
Ultra Inert splitless single-taper liner with glass frit	5190-5112
Ultra Inert Gold seal, with washer, 1/pk	5190-6144
Ultra Inert Gold seal, with washer, 10/pk	5190-6145
Self-Tightening column nut, collared, inlet	G3440-81011
Self-Tightening column nut, collared, MSD	G3440-81013
Replacement collar for self tightening nut	G3440-81012
15% Graphite / 85% Vespel Ferrules, 0.4 mm i.d., 10/pk	5181-3323
5 µL ALS syringe, fixed needle, 23-26s/42/cone	5181-1273
5 µL ALS syringe, fixed needle, 23-26s/42/cone 6/pk	5181-8810
10 µL ALS syringe, fixed needle, 23-26s/42/cone	5181-1267
10 µL ALS syringe, fixed needle, 23-26s/42/cone 6/pk	5181-3360
20x magnifier loop	430-1020
View MyList of GC Columns- 7890, 8890 and 8860	
Agilent J&W DB-EUPAH, 20 m x 0.18 mm, 0.14 µm	121-9627
Agilent J&W DB-5ms 20 m x 0.18, 0.18 µm	121-5522UI
Agilent J&W Select PAH, 30 m x 0.25 mm, 0.15 µm	CP7462

Consumables Selection Toolkit for PAHs in Environmental Workflow

5994-2060EN

Includes Checkout Standards, Column, Liners, Unions, Vials, Caps, filament, gas filters etc. needed to get started with PAH testing with suggested Agilent methods and compatible with PAH Workflow Kits



View Mylist of GC column	
Agilent J&W DB-5ms UI 20 m x 0.18, 0.18 µm	121-5522UI
Agilent J&W Select PAH, 30 m x 0.25 mm, 0.15 µm	CP7462
Agilent J&W Select PAH, 15 m x 0.15 mm, 0.10 µm	CP7461
Agilent DB-UI8270D, 30 m x 0.25 mm, 0.25 µm	122-9732
Agilent DB-UI8270D, 20 m x 0.18 mm, 0.36 µm	121-9723
Agilent J&W DB-EUPAH, 20 m x 0.18 mm, 0.14 µm	121-9627
View Mylist of Intuvo GC columns	
Agilent J&W DB-5ms UI 20 m x 0.18, 0.18 µm	121-5522UI-INT
Agilent J&W Select PAH, Intuvo GC column, 30 m x 0.25 mm, 0.15 µm	CP7462-INT
Agilent J&W Select PAH, 15 m x 0.15 mm, 0.10 µm	CP7461-INT
Agilent DB-UI8270D INT, 30 m x 0.25 mm, 0.25 µm	122-9732-INT
Agilent DB-UI8270D INT, 20 m x 0.18 mm, 0.36 µm	121-9723-INT
Agilent J&W DB-EUPAH, Intuvo GC column 20 m x 0.18 mm, 0.14 µm	121-9627-INT
View Mylist of Intuvo Supplies	
Guard Chip, Intuvo Split/Splitless	G4587-60565
Intuvo inlet chip	G4581-60031
Flow Chip, Intuvo, D2-MS	G4581-60033
Flow Chip, Intuvo, swaged HES MS tall	G4590-60109
Inlet/MSD (Intuvo) Polyimide gasket	5190-9072
View Mylist of MS Supplies	
EI filament (for 7000A/B/C/D, 5977B Inert Plus, 5977A extractor, inert or stainless steel and 5975 systems)	G7005-60061
HES Filament for 7010 Triple Quadrupole GC/MS	G7002-60001
Drawout plate, 9 mm, inert source	G3440-20022
Drawout plate, 9 mm, extractor source	G3870-20449
View Mylist of Gas filters	
Gas Clean carrier gas Kit for 7890	CP17988
Gas Clean Carrier Gas Kit for 8890 and 8860	CP179880
Gas Clean carrier gas purifier replacement cartridge	CP17973
Gas Clean Filter Kit for Intuvo	CP17995
View Mylist of Vials and caps	
2 mL screw top amber, write-on spot, deactivated, certified, 100 pc	5183-2072
Screw caps, blue, certified, PTFE/silicone/PTFE septa	5182-0723
100 µL vial insert, glass with polymer feet	5181-8872

Priority PAHs in Food & Environment

	16 EPA	EU PAH (15+1)	EU PAH8	EU PAH4	AOAC	TEF
Napthalene	x				x	0.001
Acenaphthylene	x					0.001
Acenaphtene	x					0.001
Fluorene	x				x	0.001
Phenanthrene	x				x	0.001
Anthracene	x				x	0.01
Fluoranthene	x				x	0.001
Pyrene	x				x	0.001
Benzo[a]anthracene	x	x	x		x	0.1
Chrysene	x	x	x	x	x	0.01
Benzo[b]fluoranthene	x	x	x	x	x	0.1
Benzo[k]fluoranthene	x	x	x		x	0.1
Benzo[j]fluoranthene		x				0.1
Benzo[a]pyrene	x	x	x	x	x	1
Indeno[123cd]pyrene	x	x	x		x	0.1
Dibenzo[ah]anthracene	x	x	x	x	x	1
Benzo[ghi]perylene	x	x	x		x	0.01
Dibenzo[al]pyrene		x				10
Dibenzo[ai]pyrene		x				10
Dibenzo[ah]pyrene		x				10
Dibenzo[ae]pyrene		x				1
Cyclopenta[cd]pyrene		x				0.1
Methylchrysene		x				
Benzo[c]fluorene		x				

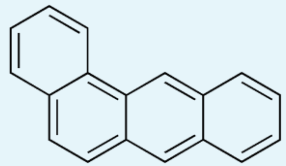
PAHs in high conc.
Low toxicity

PAHs in low conc.
High toxicity

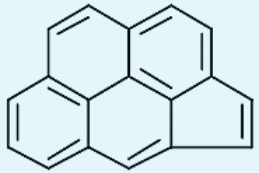
Gradual shift in focus from occurrence to toxicity & health risk → Changing analytical requirements

TEF = Toxicity Equivalence Factor

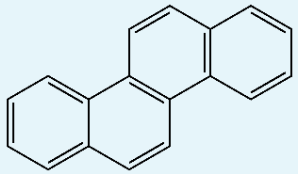
15+1 EU Priority PAHs & PAH4



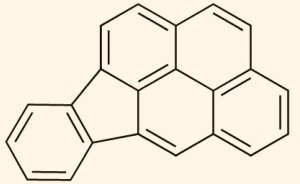
Benz[a]anthracene
MW: 228



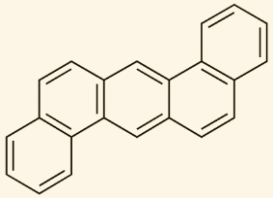
Cyclopenta[cd]pyrene
MW: 226



Chrysene
MW 228

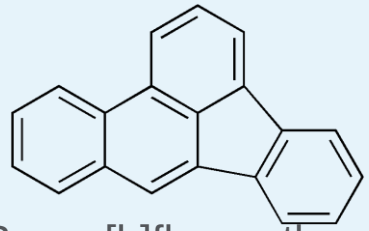


Indeno[1,2,3-cd]pyrene
MW 276

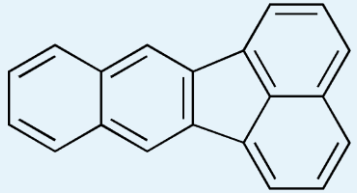


Dibenzo[a,h]anthracene
MW 278

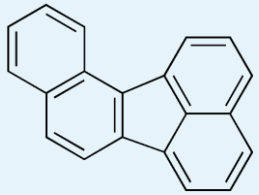
Isomeric PAHs



Benzo[b]fluoranthene
MW: 252

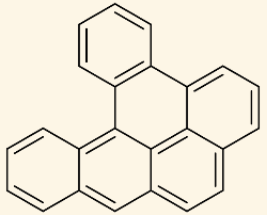


Benzo[k]fluoranthene
MW: 252

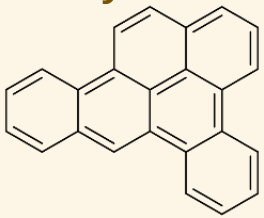


Benzo[j]fluoranthene
MW: 252

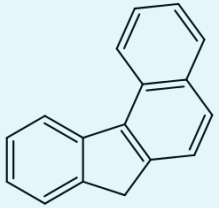
Late Eluters/Heavy PAHs



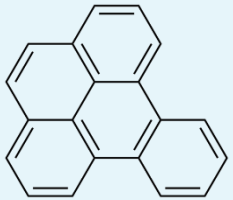
Dibenzo[a,l]pyrene
MW 302



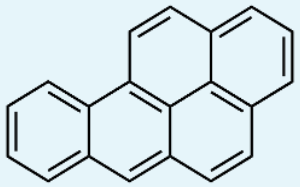
Dibenzo[a,e]pyrene
MW 302



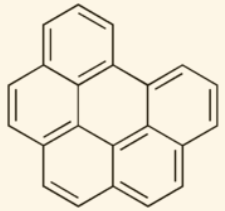
Benzo[c]fluorene
MW: 216



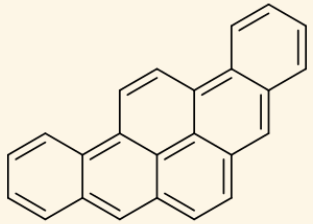
Benzo[e]pyrene
MW 252



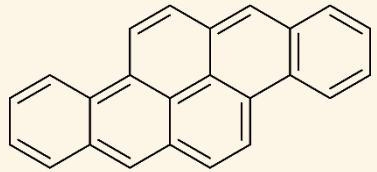
Benzo[a]pyrene
MW 252



Benzo[ghi]perylene
MW 276



Dibenzo[a,i]pyrene
MW 302



Dibenzo[a,h]pyrene
MW 302

Analytical Challenges & Solutions

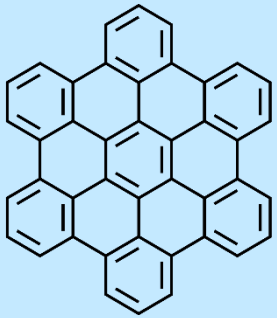
- Food related matrices:
  - Fats, oils, proteins → QuEChers + EMR Lipids
  - Inlet and column contaminating → Liner selection & preventive maintenance SOP
  - Increased background interferences → Sample prep & column backflush
- PAH isobars
  - Many PAHs have identical or quite similar Mw: no differentiation by Mass Spec
  - Chromatographic separation becomes essential
- GC column selectivity
  - Some PAHs with similar Mw are challenging to separate chromatographically
  - Dedicated, specially engineered GC liquid phases are required

Column Selection for PAHs -- Environmental and Food

Environmental Analysis

DB-5ms UI
DB-5ms

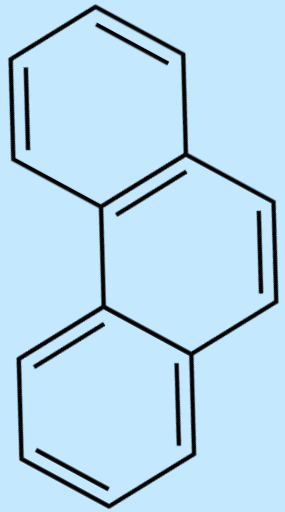
- 16 EPA PAHs 5ms is robust option
- DB-5ms UI in case polars are included



Food Analysis

DB-EUPAH
DB-17ms

- 16 EPA PAHs + Benzo b, k, j
- EUPAH for More separation detail
- 20 x 018 x 014 EUPAH optimized for Separation/ Speed/productivity



Select PAH

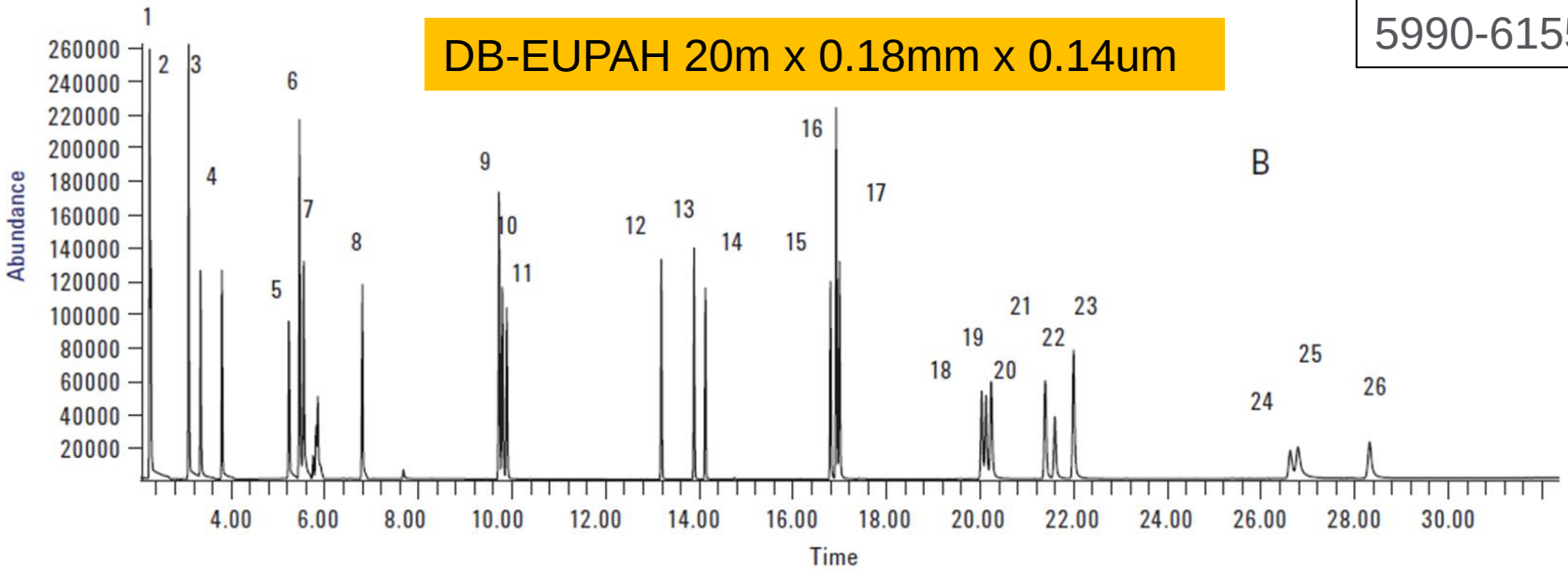
- 16 EPA PAHs + Benzo b, k, j
- 4 EUPAHs in Food
Benzo b, k, j & Chrysene/TriP
- 15m x 0.15mm for Speed/productivity

Agilent Specific-application GC column for PAH analysis

DB-EUPAH
- Mid-polar column that resolves benzo (b,j,k) fluroanthenes
- Resolution of 24 combined regulated PAHs can be achieved under 28 min

App Notes:
5990-5872EN
5990-6155EN

DB-EUPAH 20m x 0.18mm x 0.14um



1. Naphthalene-d8
2. Naphthalene
3. 2-methylnaphthalene
4. 1-methylnaphthalene
5. Acenaphthylene
6. Acenaphthene-d10
7. Acenaphthene
8. Fluorene
9. Phenanthrene-d10
10. Phenanthrene
11. Anthracene
12. Fluoranthene
13. Pyrene
14. p-Terphenyl-d14
15. Benzo(a)anthracene
16. Chrysene-d12
17. Chrysene
18. Benzo(b)fluoranthene
19. Benzo(k)fluoranthene
20. Benzo(j)fluoranthene
21. Benzo(e)pyrene
22. Benzo(a)pyrene
23. Perylene-d12
24. Indeno(1,2,3-cd)pyrene
25. Dibenzo(a,h)anthracen
26. Benzo(g,h,i)perylene

Agilent Specific-application GC column for PAH analysis

Select PAH
- Mid-polar column that optimize chrysene/triphenylene resolution
- Resolution of 54 PAHs under 40 min

App Notes:
SI-02232
SI-02263

Full resolution of benzo [b] fluroanthene

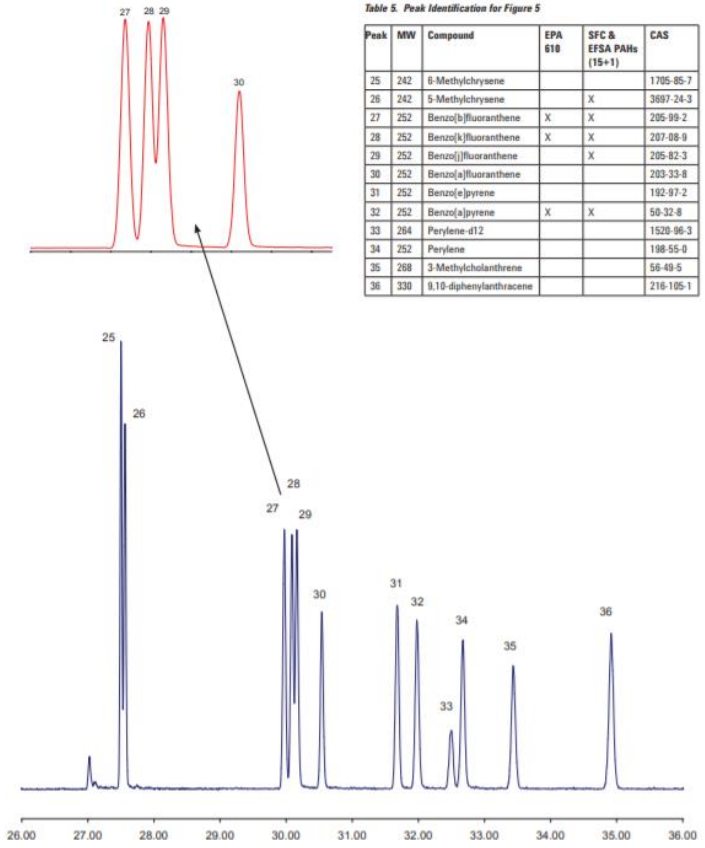


Table 5. Peak Identification for Figure 5

Peak	MW	Compound	EPA 610	SFC & EFSA PAHs (15+1)	CAS
25	242	6-Methylchrysene			1705-85-7
26	242	5-Methylchrysene		X	3697-24-3
27	252	Benzo[b]fluoranthene	X	X	205-99-2
28	252	Benzo[k]fluoranthene	X	X	207-08-9
29	252	Benzo[j]fluoranthene		X	205-82-3
30	252	Benzo[a]fluoranthene			203-33-8
31	252	Benzo[e]pyrene			192-97-2
32	252	Benzo[a]pyrene	X	X	50-32-8
33	264	Perylene-d12			1520-96-3
34	252	Perylene			198-55-0
35	268	3-Methylcholanthrene			56-49-5
36	330	9,10-diphenylanthracene			216-105-1

Optimal resolution of triphenylene/chrysene

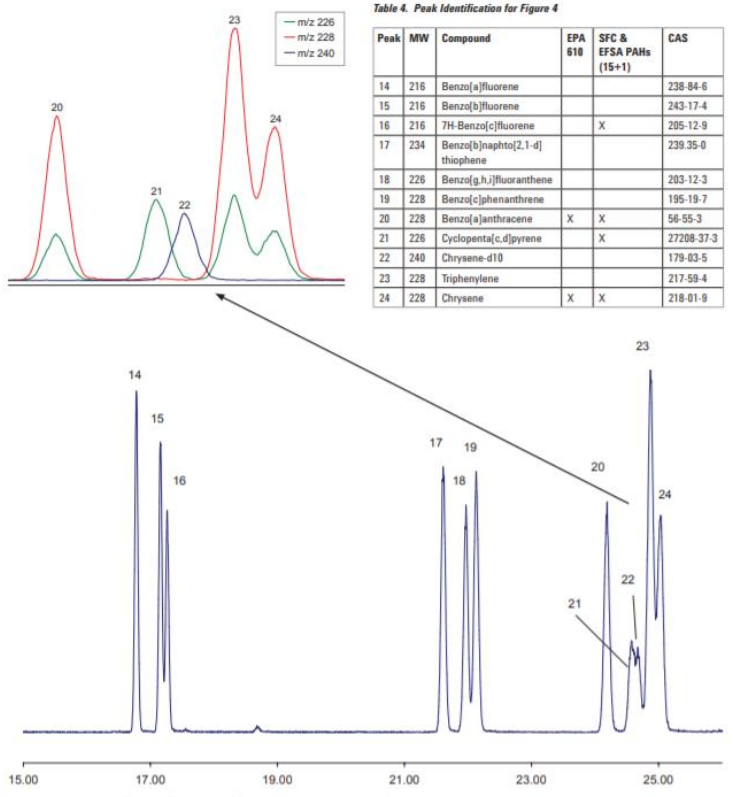


Table 4. Peak Identification for Figure 4

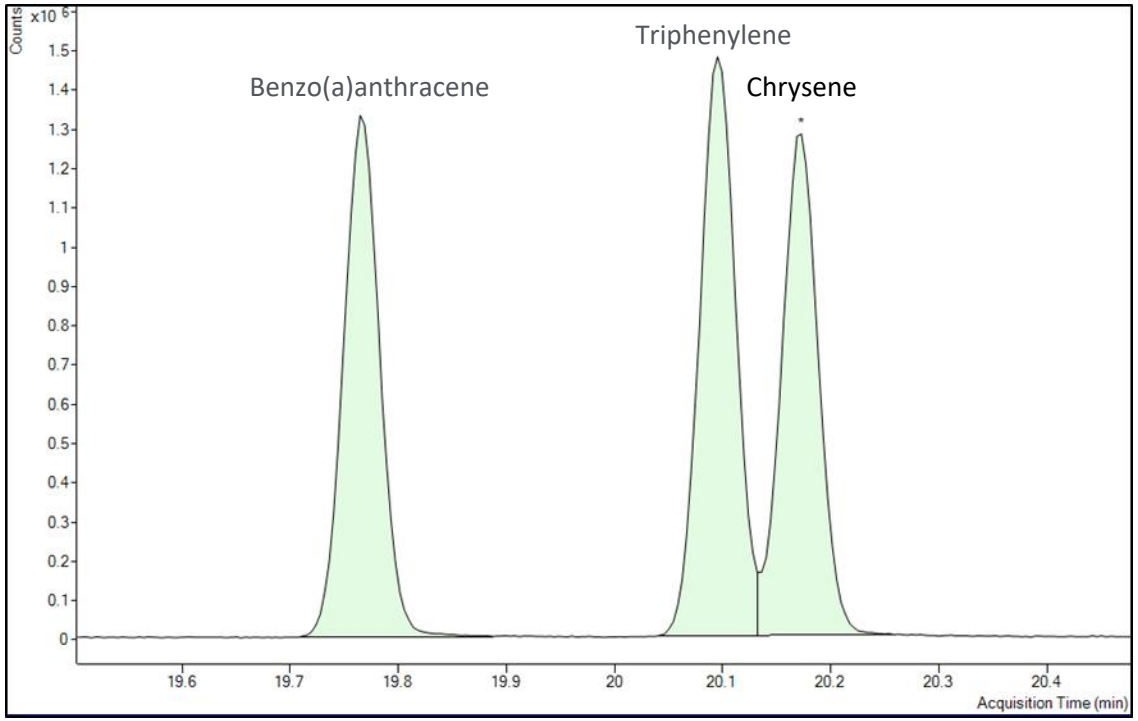
Peak	MW	Compound	EPA 610	SFC & EFSA PAHs (15+1)	CAS
14	216	Benzo[a]fluorene			238-84-6
15	216	Benzo[b]fluorene			243-17-4
16	216	7H-Benzo[c]fluorene		X	205-12-9
17	234	Benzo[b]naphto[2,1-d] thiophene			239.35-0
18	226	Benzo[g,h,i]fluoranthene			203-12-3
19	228	Benzo[c]phenanthrene			195-19-7
20	228	Benzo[a]anthracene	X	X	56-55-3
21	226	Cyclopenta[c,d]pyrene		X	27208-37-3
22	240	Chrysene-d10			179-03-5
23	228	Triphenylene			217-59-4
24	228	Chrysene	X	X	218-01-9

What happens if we increase the column aspect ratio?

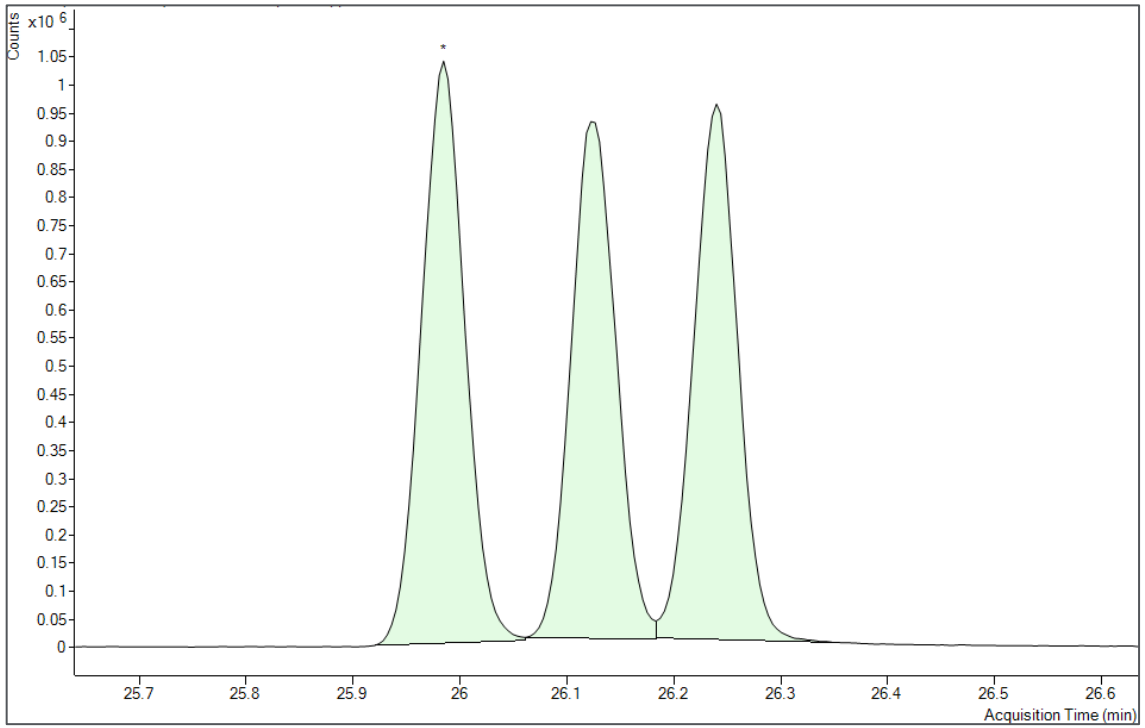
Custom Select PAH

- 40m x 0.18mm i.d. x **0.07** µm df
- Full resolution of chrysene/triphenylene and benzo [b,j,k] fluoroanthenes
- Keep in mind limitations of thin-film phases (column lifetime, loading capacity)

Best resolution of triphenylene/chrysene



Full resolution of benzo [b,j,k] fluroanthene



*Courtesy of Carlos Bueno – Application Scientists, Agilent Spain

Factors to consider in optimizing EU 15+1 and US-EPA PAH analyses

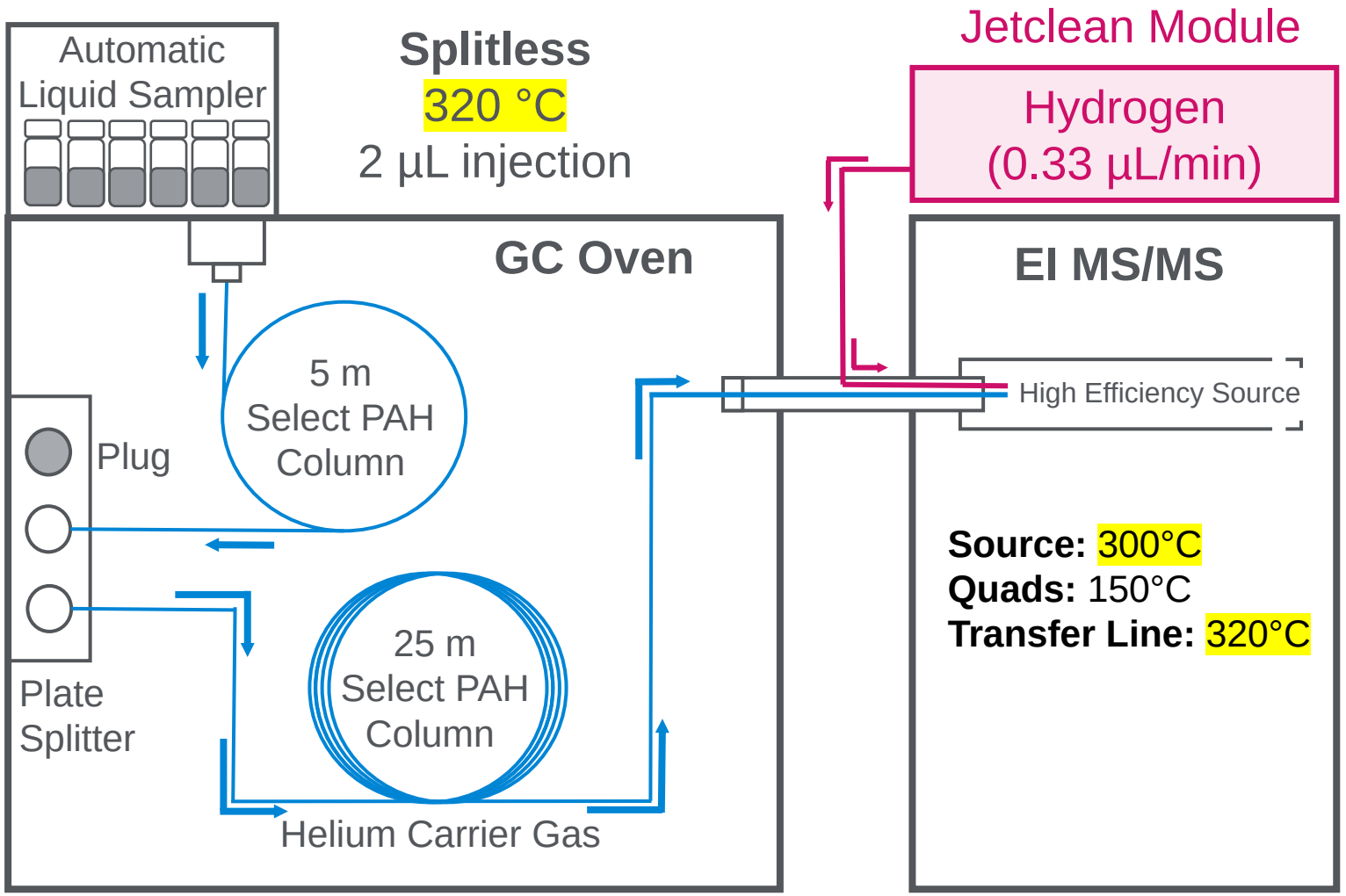
- Choose Agilent J&W DB-EUPAH when resolution of benzo (b,j,k) fluoroanthene isomers required.
- Select an Agilent J&W Select-PAH when Triphenylene is presented as an interference.

  Offers the best resolution value between Triphenylene and Chrysene
- Choose an Agilent J&W DB-5ms Ultra Inert when benzo (b,j,k) fluoroanthene isomers can be reported as a sum of the isomers.

  DB-5ms Ultra Inert resolves 23 of 24 regulated PAHs in 27% faster cycle time than DB-EUPAH
- Consider use of retention gaps and inlet backflushing to reduce cycle time and maintenance
- Achieve faster analysis times with no loss of resolution using 0.18mm i.d. GC columns
- Optimize injection volume, temperature, purge time, and solvent focusing for best results
- Minimize inlet and system dwell time with higher linear velocities

A typical customer setup for PAHs in Food samples

GC/MS/MS Configuration with Backflush, Jetclean and RT Locking



Liner

- 4-mm single-tapered liner with **glass wool**

Column

- Select PAH
- 30 m x 250 µm x 0.25 µm
- Column 1 Flow at 1.2 mL/min
- Column 2 Flow at 1.5 mL/min

Oven program

- Initial: 80 °C (0.5 min)
- Ramp at 120 °C/min to 120 °C
- Ramp at 40 °C/min to 180 °C
- Ramp at 3 °C/min to 280 °C
- Ramp at 120 °C/min to 325 (18 min)

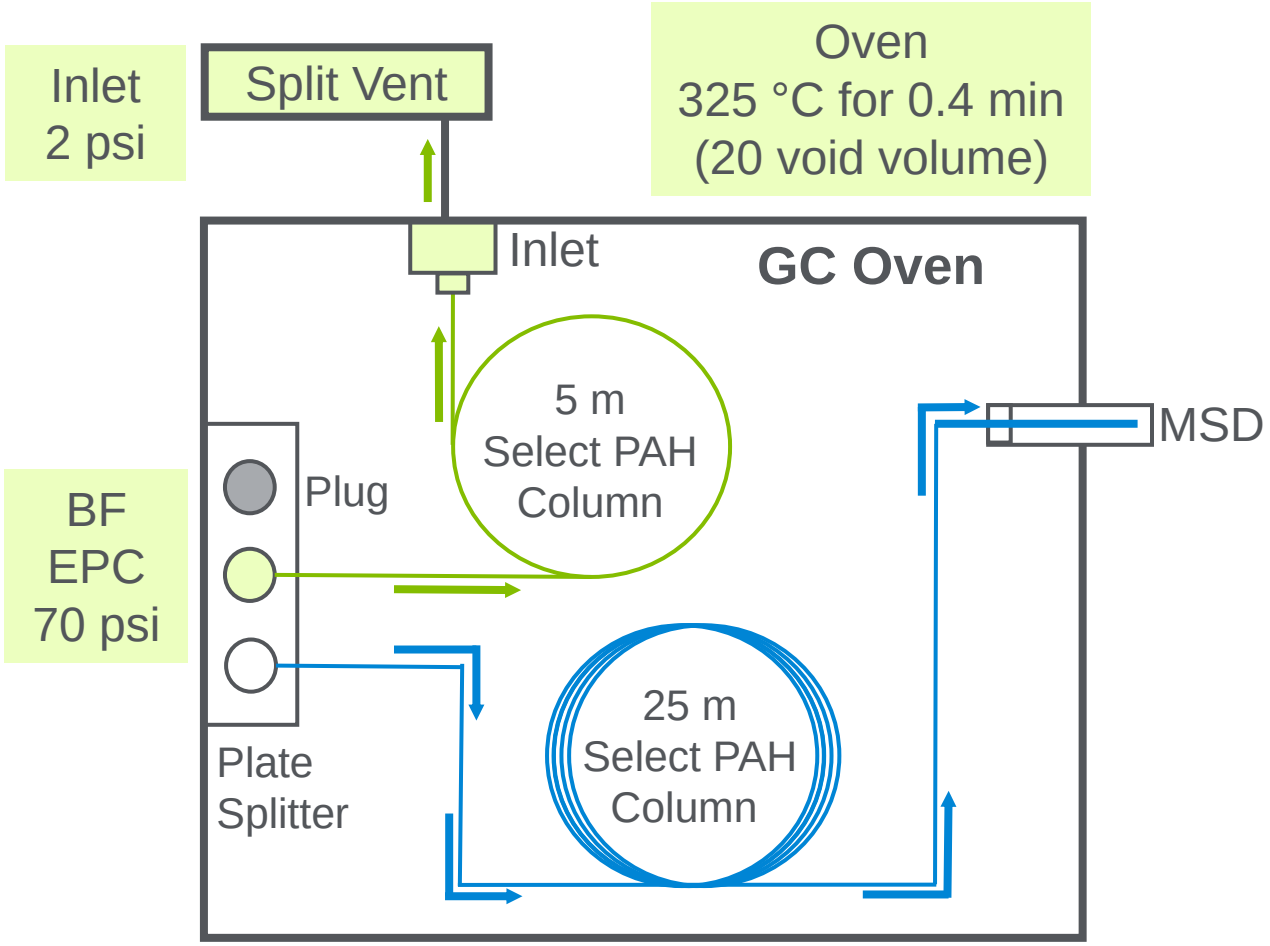
Modifications

- Backflush (BF)
- JetClean
- Retention Time Locking (RTL)

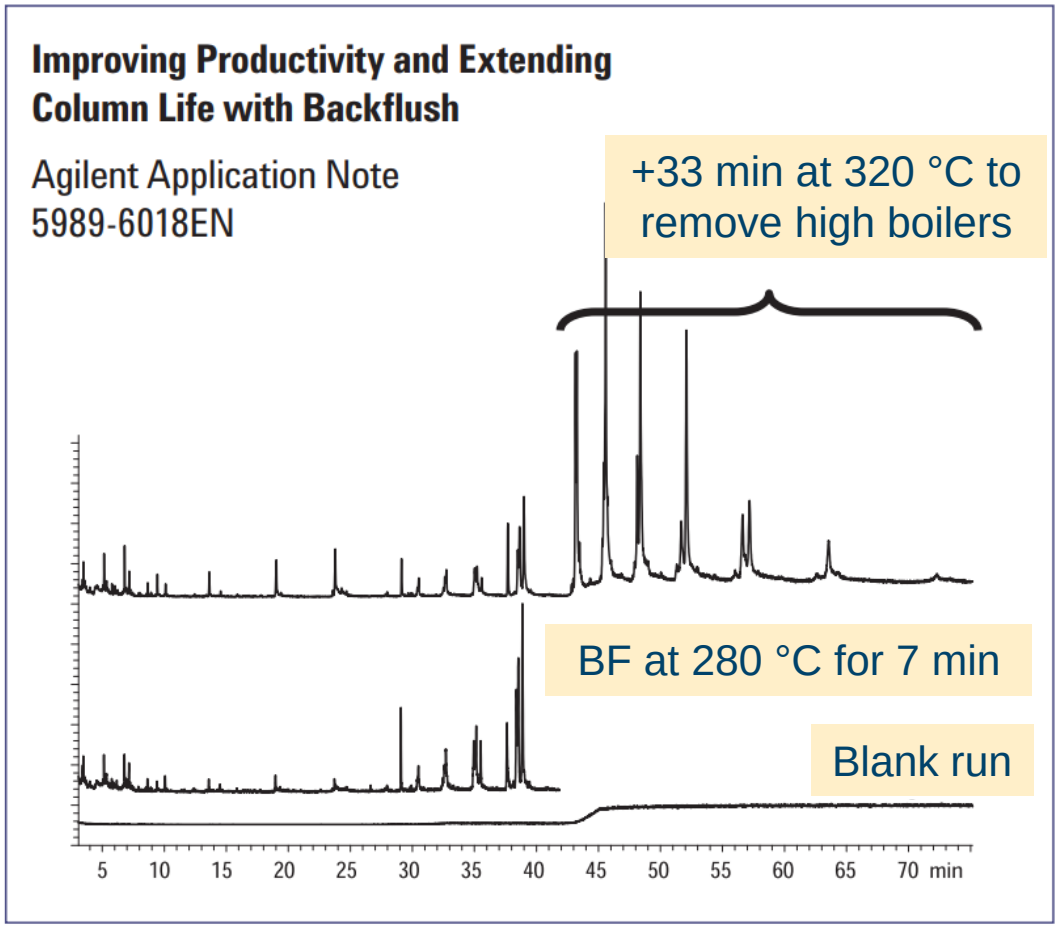
BackFlush

To maintain column lifetime

How it works? At the end of every run…



Reduce cycle time and eliminates carryover



Key PAH App Notes incl. Sample Prep

PAHs in Salmon
SI-02424: https://www.agilent.com/cs/library/applications/SI-02424.pdf
Sample prep: 7.8 x 300 mm PLgel 100A
Column: J&W Select PAH, 15m x 0.15mm x 0.10µm

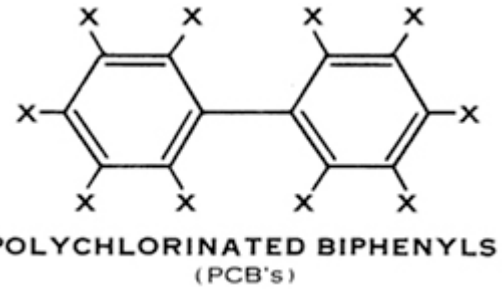
PAHs in Peanuts and chocolate with Select PAH column
5991-2299EN: https://www.agilent.com/cs/library/applications/5991-2299EN.pdf
Sample prep: Bond-Elut Si
Column: J&W Select PAH, 15m x 0.15mm x 0.10µm

PAH Analysis in Salmon with Enhanced Matrix Removal
5991-6088EN: https://www.agilent.com/cs/library/applications/5991-6088EN.pdf
Sample prep: Bond-Elut EMR Lipids & Bond-Elut Polish
Column: DB-5ms UI, 20m x 0.18mm x 0.18µm

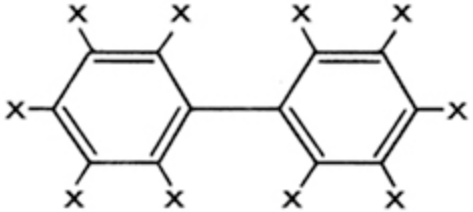
Determination of 19 Polycyclic Aromatic Hydrocarbon Compounds in Salmon and Beef
5994-0553EN: https://gcms.cz/labrulez-bucket-strapi-h3hsga3/paper/application-pahs-salmon-beef-5994-0553en-agilent.pdf
Sample prep: 2 step SoLE using 20:80 EtOAc/ACN and EMR Lipids
Column: DB-EUPAH, 30m x 0.25mm 0.25µm

Environmental applications: Polychlorinated Biphenyls (PCBs)

Column Updates & Solutions



Polychlorinated biphenyls



- A polychlorinated biphenyl (PCB) is an organic chlorine compound with the formula $C_{12}H_{10-x}Cl_x$. They were widely used as dielectric and coolant fluids in electrical apparatus, carbonless copy paper and in heat transfer fluids
- Around 209 PCB's
- List of reported PCB congeners are determined by different organizations. Examples of PCB congener lists include:
  - 7 Indicator Congeners (marker PCB's) in Europe: 28, 52, 101, 118, 138, 153, 180, indicate presence/absence of PCB's. Related to PCB occurrence in Aroclors 1242, 1248
  - 12 Most Toxic Congeners (WHO), 77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167, 189
  - 18 NOAA Status & Trend Congeners
  - 36 CDC PCB congener list (found in biological sample)
  - 159 Congeners Quantified in Aroclor mixes

Polychlorinated Biphenyls (PCBs) analysis by GC

Aroclors

- 'Old' way to measure PCBs. Chromatographic 'fingerprint' indicative of one of Aroclors mixture. No concentration/identification of specific PCB
- 9 common PCB Aroclor mixtures (1221, 1232, 1242, 1016, 1248, 1254, 1260, 1262, 1268), each with distinctive GC pattern.
- **Method:** GC/ECD, SW-846, EPA 8082A, GC column: **DB-5ms, 30m x 0.25mm x 1 um**, DB- 608, 30m x 0.25mm x 1 um

Homologs

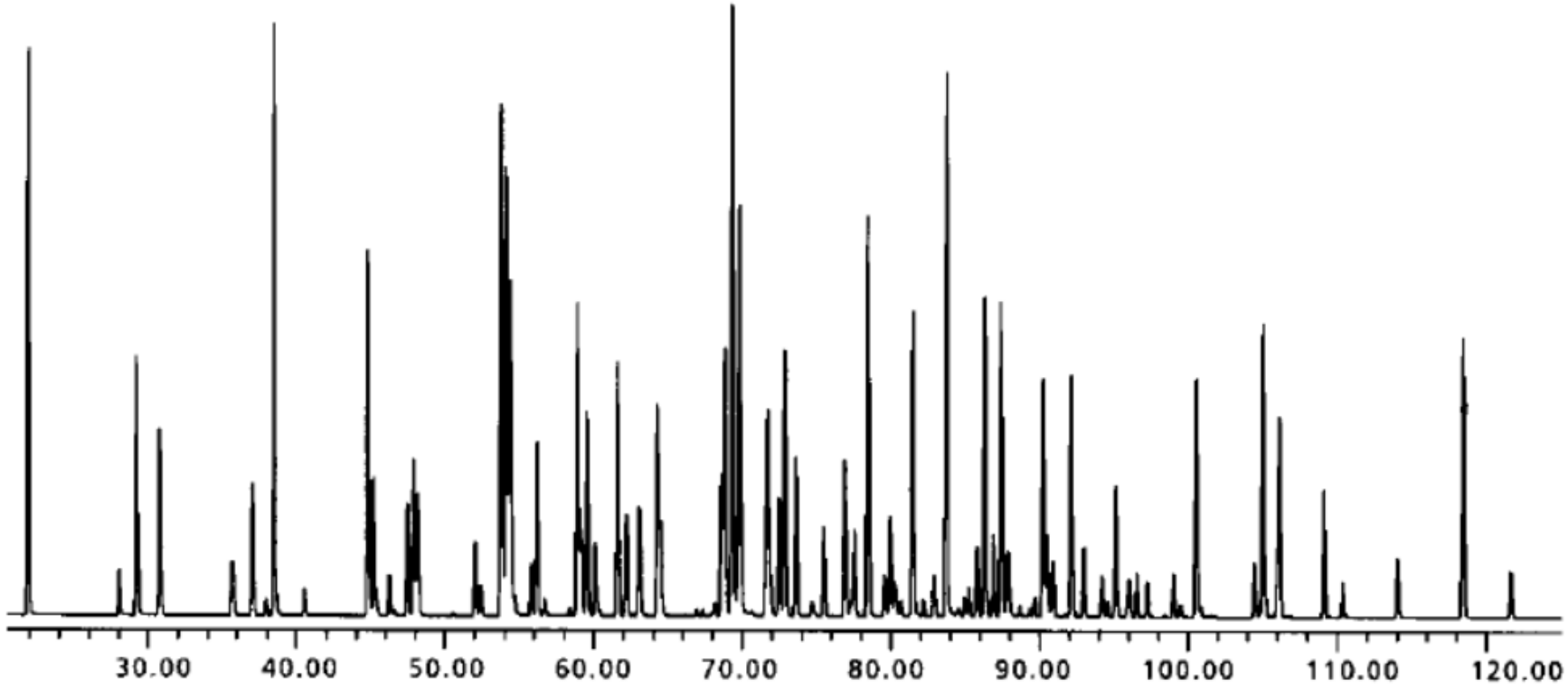
- Grouping PCB congeners by number of chlorine atoms, this can vary from one to ten. All PCBs with same number of chlorine atoms belong to same homolog group. Testing for PCB homologs provides more reliable results than the Aroclor method
- Laboratory results for PCB homologs will list the amount of PCB present in the sample by the number of chlorine atoms.
- **Method:** GC/MS, EPA Methods 8270D, 625, and 8081 A/B, GC Column: **DB-UI 8270D 30m x 0.25mm x 0.25 um**, DB-5ms UI, 30m x 0.25mm x 0.25 um

Congeners

- More congener detail can be needed, generally a subset of full 209 PCB congeners.
- NOAA PCB congener method cites 20 congeners , SW-846 8082 method cites 19 congeners. WHO list cites 12 congeners.
- **Method:** GC/MS EPA Method 1668C, GC column: **DB-XLB 30m x 0.18mm x 0.18 um meets method requirements**. Column must resolve congeners 34/23, and 187/182. Congener 156/157 must co-elute within 2 seconds at peak maximum

Analysis of Aroclors 1016-1268 (without 1221) with DB-XLB

GC System:	Agilent 7890
Column	**DB-XLB**, 30m x 0.18 mm i.d. x 0.18 um df (121-1232)
Carrier	Helium at 37 cm/sec, measured at 150 ºC
Oven	100 ºC (1 min), 1.2 ºC/min to 265 ºC
Injector	Hot on-column, 250 ºC, 1 µL in isooctane, 12.5 ppm
Detector	MSD, SIM, 340 ºC transfer line



IUPAC	Retention time
PCB 23	55.54 min
PCB 34	55.33 min
PCB 156	105.3 min
PCB 157	105.72 min

Other GC columns:

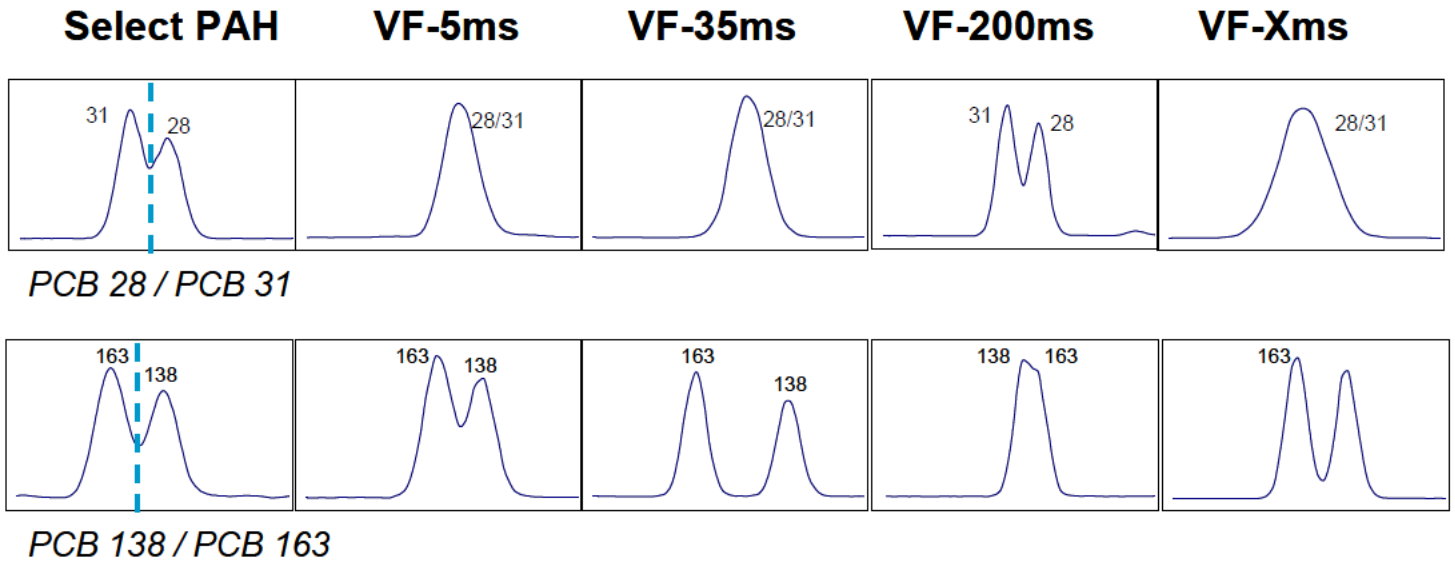
- DB-5ms UI, DB-8270D UI
- DB-35ms UI
- CP-Sil 8 for PCB
- CP-Sil 8/C18 CB for PCB

Source: https://www.agilent.com/cs/library/chromatograms/361.pdf

Analytical Challenges & Solutions for PCBs

- For PCB's, -5 type columns can be used to quantify PCB homologs, **but polarity is too low to resolve key PCB congeners.**

Key PCB separations using GC columns with different selectivity

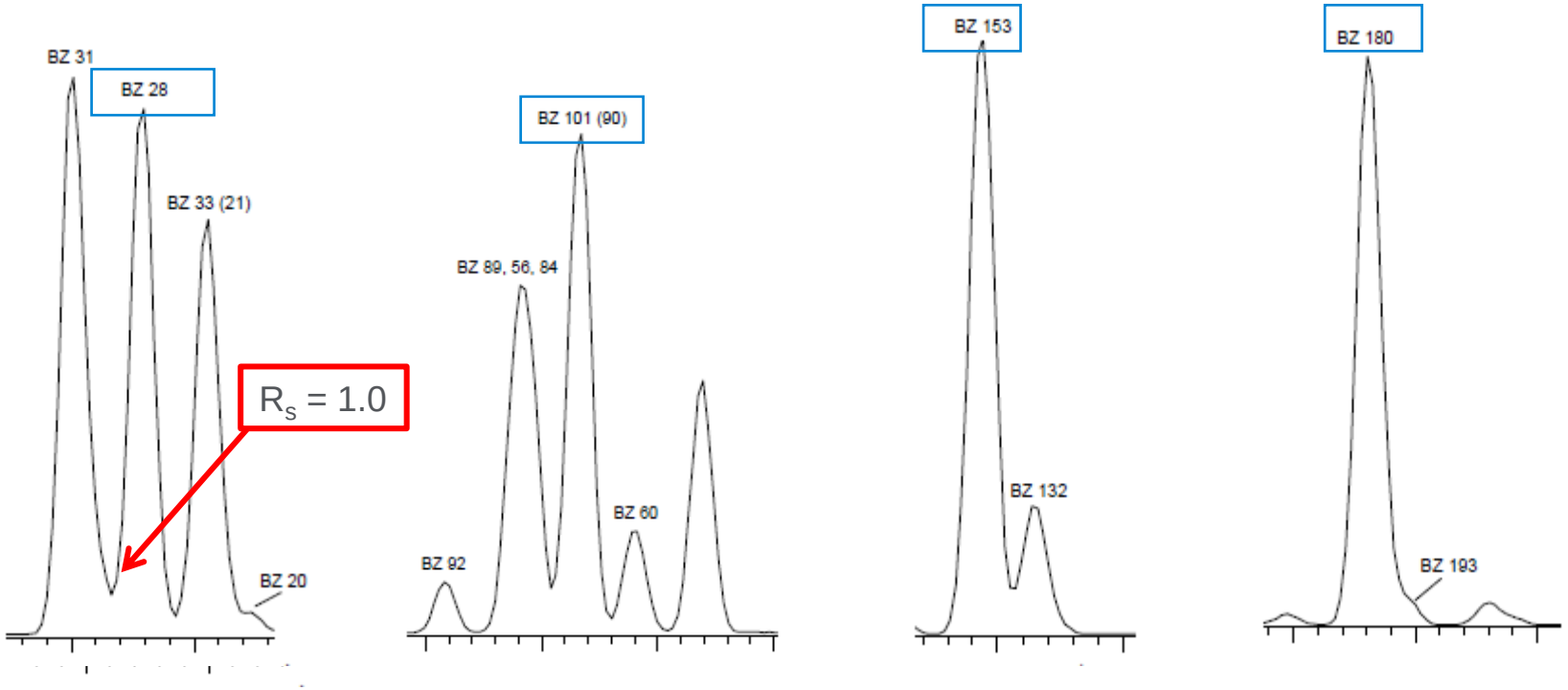


Select PAH can partially separate 28/32 and 138/163 PCB pairs, making it a good option for multi-residue analysis

How about DB-XLB?

- As mentioned earlier, DB-XLB offers the best resolution for PCB congeners
- Rs = 1.0 for PCB 31/28, and baseline resolution for other key PCBs

EU Monitor PCBs on DB-XLB

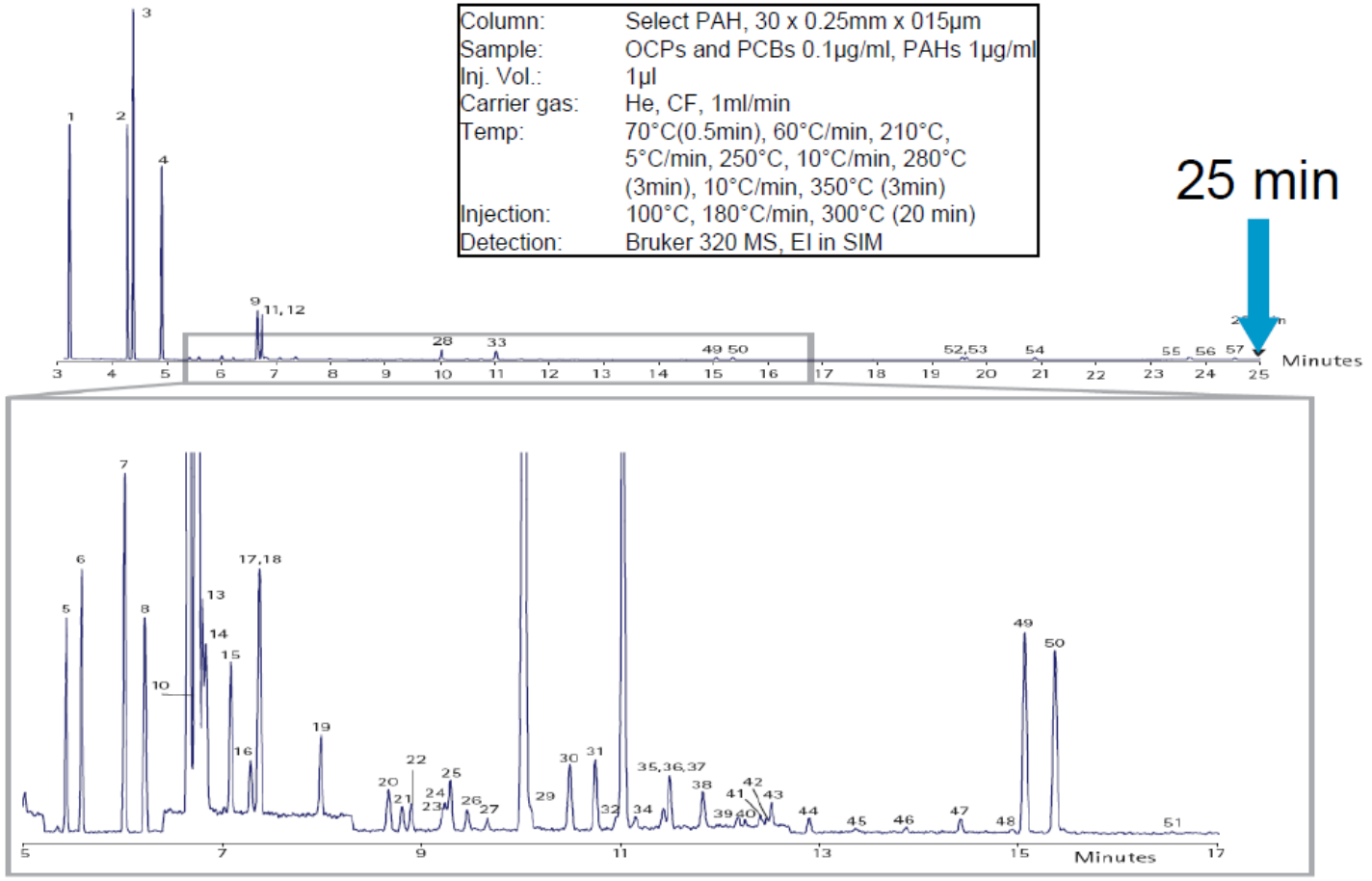


Column: **DB-XLB**
30 m x 0.25 mm I.D., 0.5 µm
1 m x 0.53 mm I.D. Retention Gap
J&W P/N: **122-1236**
Carrier: Helium at 34.2 cm/sec, measured at 150°C
Oven: 100°C for 1 min
100-320°C at 5.6°/min
Injector: Hot On-column, 250°C, Split Flow
100 mL/min
2 µL dilute Aroclor mixture
Detector: MSD, SIM of 221.9, 255.9, 291.9, 325.8, 359.8, 395.8, 429.7, 463.7
300°C transfer line

Agilent offers the only one-column solution for OCPs, PAHs and PCBs congeners: Select PAH

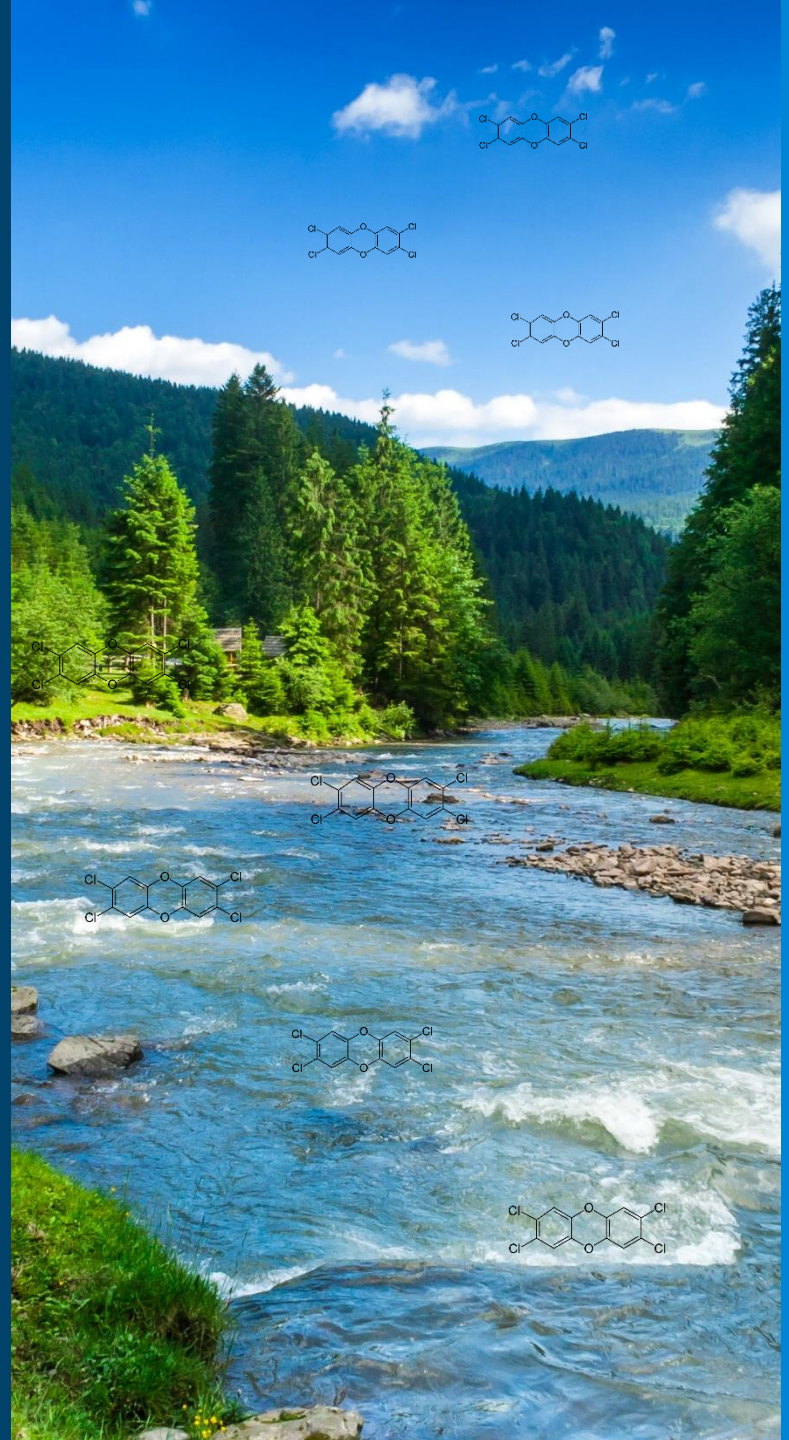
GC/MS analysis of 16 PAHs, 17 PCBs, 24 OCPs with Select PAH GC Column

Column:	Select PAH, 30 x 0.25mm x 015µm
Sample:	OCPs and PCBs 0.1µg/ml, PAHs 1µg/ml
Inj. Vol.:	1µl
Carrier gas:	He, CF, 1ml/min
Temp:	70°C(0.5min), 60°C/min, 210°C, 5°C/min, 250°C, 10°C/min, 280°C (3min), 10°C/min, 350°C (3min)
Injection:	100°C, 180°C/min, 300°C (20 min)
Detection:	Bruker 320 MS, EI in SIM



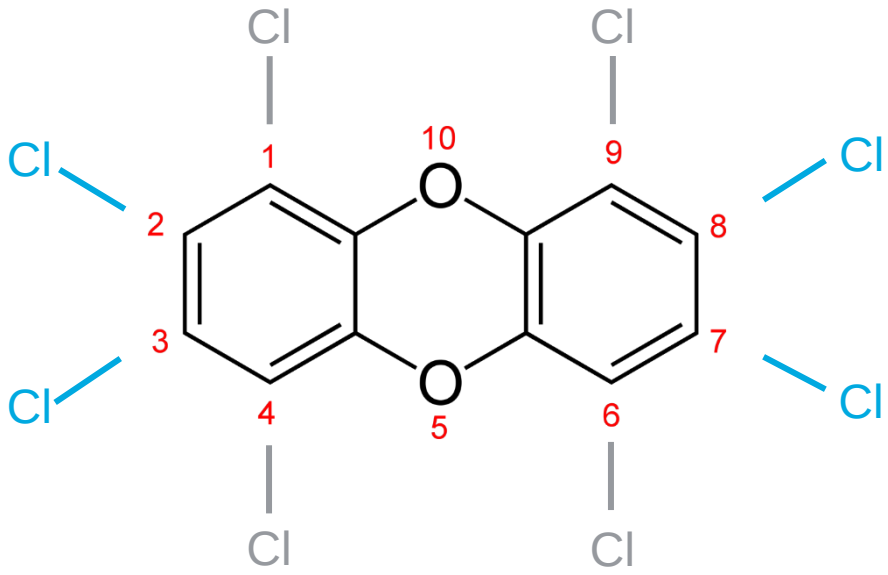
App Note: SI-02438

Environmental applications: Dioxins and Furans by GC/MS/MS and a DB-5ms UI



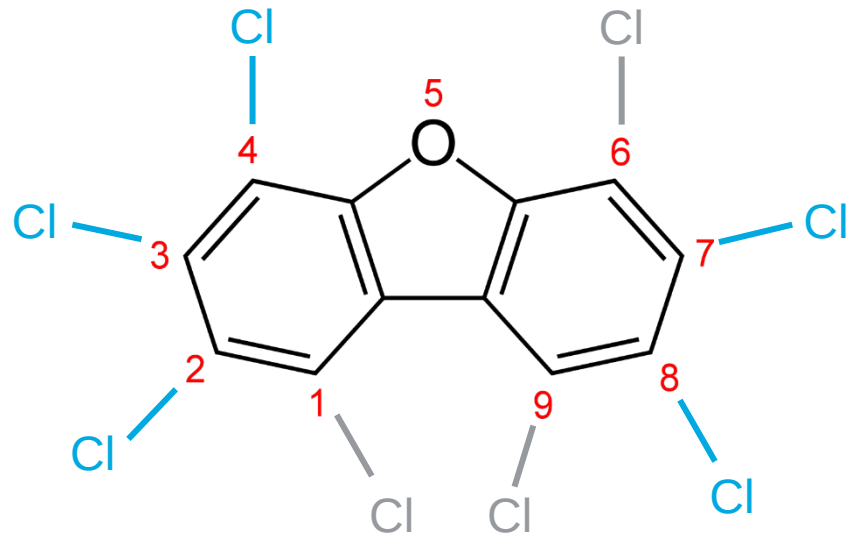
PCDD and PCDF Nomenclature and Isomers

Dioxins
Polychlorinated dibenzodioxin (PCDD)



2,3,7,8 – TCDD
(2,3,7,8-Tetrachlorinated dibenzodioxin)

Furans
Polychlorinated dibenzofurans (PCDF)



2,3,4,7,8 – PCDF
(2,3,4,7,8-Pentachlorinated dibenzofurans)

Chlorine Atoms	PCDD Isomers	PCDF Isomers
1	2	4
2	10	16
3	14	28
4	22	38
5	14	28
6	10	16
7	2	4
8	1	1
Total	**75**	**135**

75 total PCDD isomers

135 total PCDF isomers

17 toxic isomer

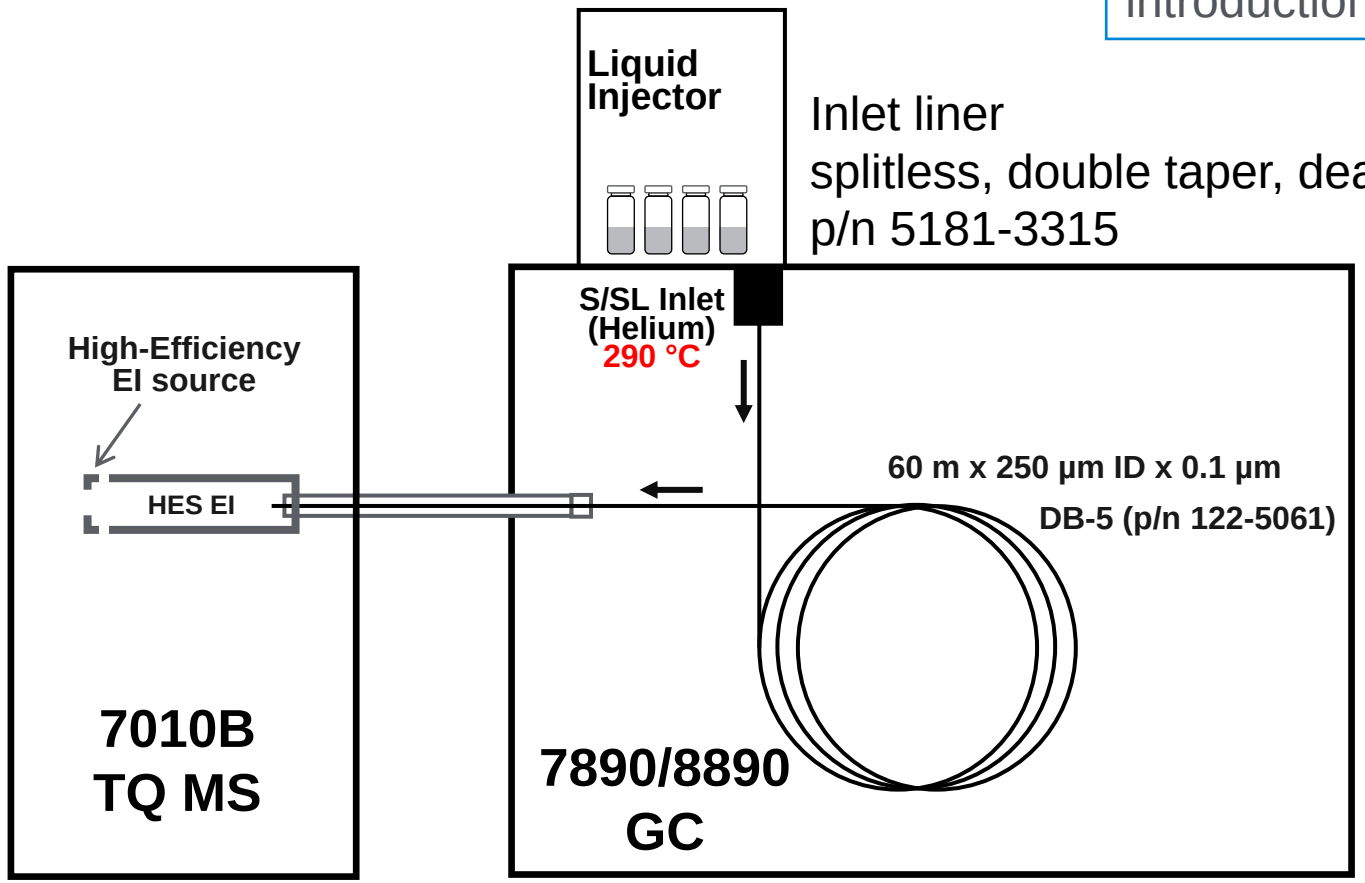
EPA has accepted GC/TQ as an equivalent Technology to analyze dioxins in Environmental Samples

This method meets all requirements for measurements of 2,3,7,8 substituted tetra-Octa CDDs and CDFs in wastewater… The performance of this method is substantially similar to methods listed in 40 CFR Part 136 for measurement of PCDDs/PCDFs in wastewater… EPA will recommend this method be included in list of approved methods at 40 CFR Part 136

-EPA Office of Water

System Configuration Used in the Application 5994-3029EN (16130 Method)

Most labs use CTC PAL for sample introduction (1 mL vial)



Inlet liner
splitless, double taper, deactivated
p/n 5181-3315

Source: 290 °C
Quads: 150 °C
Transfer Line: 290 °C

He Quench Gas:
2.25 mL/min
N_2 Collision Gas:
1.5 mL/min

Oven program:
90 °C (2 min)
22 °C/min to 200 °C
1 °C/min to 215 °C (10 min)
5.2 °C/min to 300 °C (2.7 min)

Time segment
MRM mode

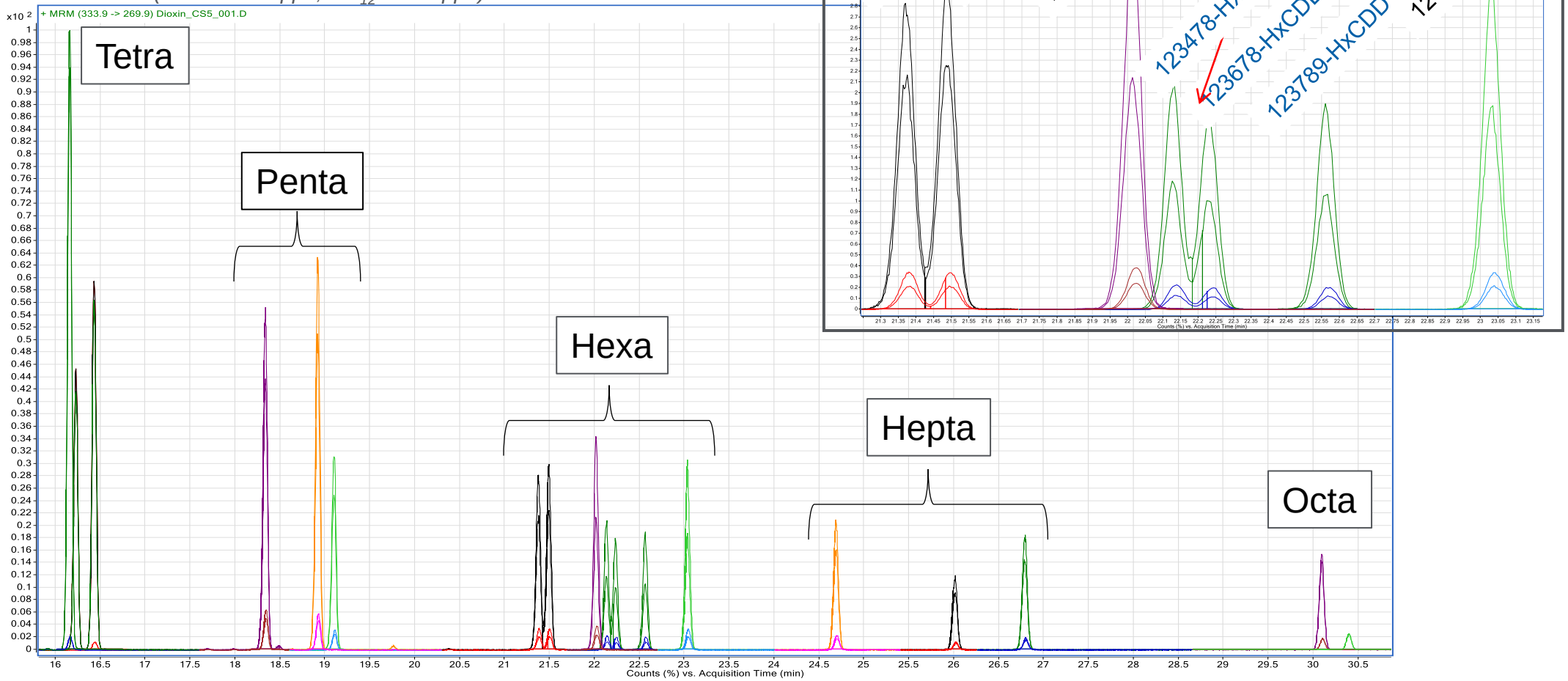
Total run time
51.05 min

Dioxins/Furans – Chromatogram

Excellent separation of the difficult *hexa*-dioxin/furan isomers

GC Column – DB5MS UI (*60m x 0.25mm x 0.25 µm*)

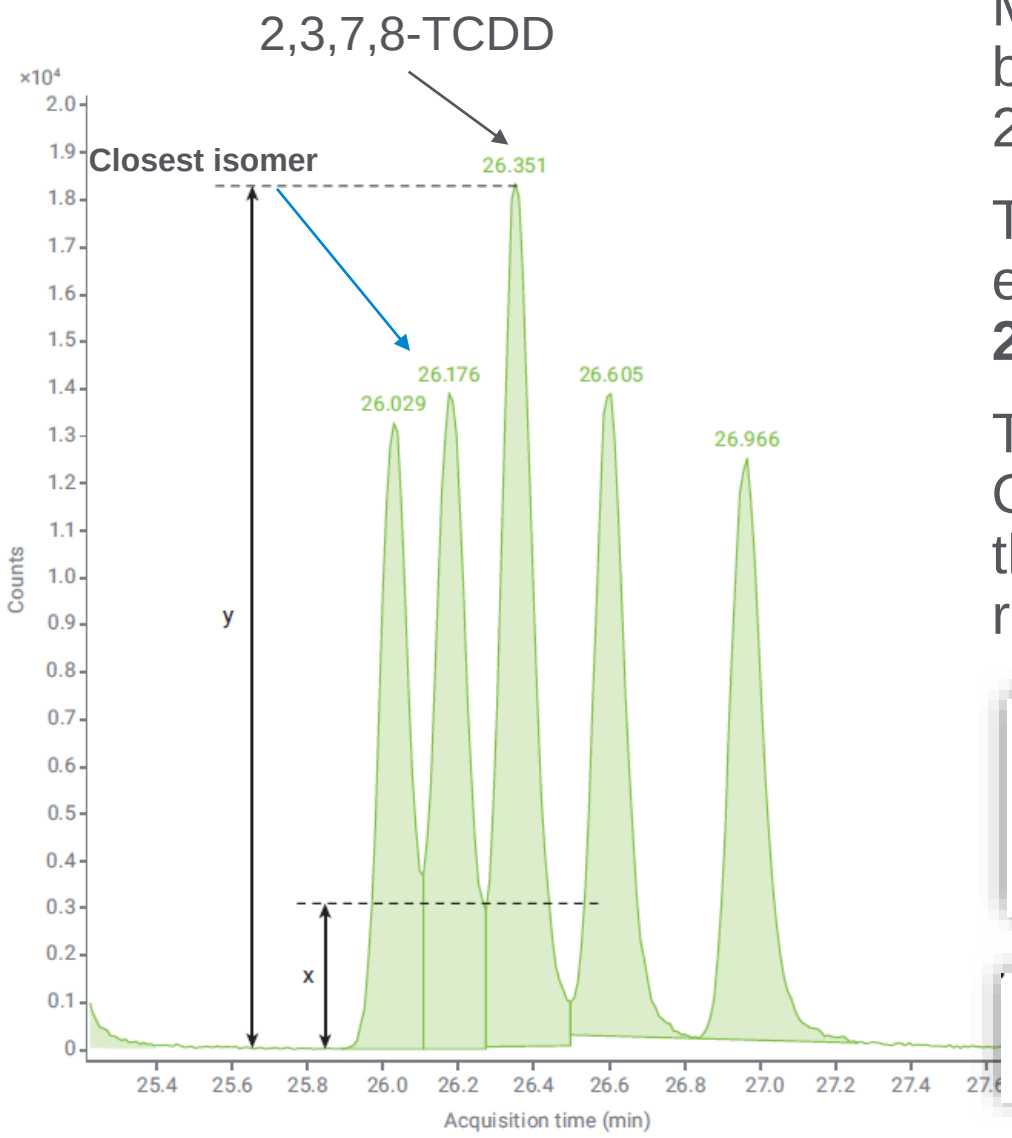
Level CS5 (TCDD = 2.0 ppb; $^{13}C_{12}$ = 100 ppb)



Resolution = 0.64
Peak to Peak Valley = 14.1%

Resolution = 0.69
Peak to Peak Valley = 23.5%

TCDD Isomer Specificity



Method 1613B calls for calculation of the percent valley between the GC peaks that elute most closely to the 2,3,7,8-TCDD and TCDF isomers.

The height of the valley between the isomers most closely eluting to the 2,3,7,8-TCDD labeled **“x” does not exceed 25% of the 2,3,7,8-TCDD peak height “y”.**

This parameter can be set as an outlier in the MassHunter Quantitative Analysis method. If the valley exceeds 25%, the analytical conditions need to be adjusted or the analysis repeated using a different GC column.

Method Table

Time Segment: <All> Compound: 2,3,7,8-TCDD Reset Table View

Quantifier

Name	TS	Transition	Scan	Type	Resolution Calculation Type	Resolution Limit
2,3,7,8-TCDD	1	319.9 -> 256.9,...	MRM	Target	Valley Height/Peak Heig...	25.0

Sample							2,3,7,8-TCDD Results						
Name	Data File	Type	Level	Vial	Acq. Date-Time	Acq. Method File	RT	Resp.	MI	Calc. Conc.	Accuracy	S/N	Resolution F.	Resolution R.
DX041D-CAL,,/01-73	DX9Z0444.D	Cal	CS3	7	8/22/2019 2:31 AM	TQEI_DB5_DX_11	26.351	221151		9.0183	90.2	2339.21	20.4	7.8

Method detection Limits (MDLs) with 7890/7010 GC/TQ Far Surpassed Method 1613B MDLs

The GC/TQ MDL results for the aqueous (1 L), solid (10 g), and tissue (10 g) samples:

Compound	Aqueous	Solid	Tissue
	MDL and (MRL) in pg/L	MDL and (MRL) in pg/g	MDL and (MRL) in pg/g
2,3,7,8-TCDD	1.1 (10) *	0.029 (1)	0.057 (0.5)
1,2,3,7,8-PeCDD	1.39 (50)	0.037 (5)	0.051 (2.5)
1,2,3,4,7,8-HxCDD	1.05 (50)	0.042 (5)	0.061 (2.5)
1,2,3,6,7,8-HxCDD	1.08 (50)	0.045 (5)	0.033 (2.5)
1,2,3,7,8,9-HxCDD	1.78 (50)	0.064 (5)	0.067 (2.5)
1,2,3,4,6,7,8-HpCDD	1.19 (50)	0.070 (5)	0.032 (2.5)
OCDD	9.4 (100)	0.311 (10)	0.085 (5)
2,3,7,8-TCDF	0.56 (10)	0.60 (1)	0.056 (0.5)
1,2,3,7,8-PeCDF	1.0 (50)	0.037 (5)	0.046 (2.5)
2,3,4,7,8-PeCDF	1.25 (50)	0.039 (5)	0.033 (2.5)
1,2,3,4,7,8-HxCDF	0.89 (50)	0.032 (5)	0.029 (2.5)
1,2,3,6,7,8-HxCDF	1.11 (50)	0.031 (5)	0.046 (2.5)
1,2,3,7,8,9-HxCDF	1.22 (50)	0.048 (5)	0.084 (2.5)
2,3,4,6,7,8-HxCDF	1.26 (50)	0.026 (5)	0.034 (2.5)
1,2,3,4,6,7,8-HpCDF	0.92 (50)	0.255 (5)	0.064 (2.5)
1,2,3,4,7,8,9-HpCDF	1.35 (50)	0.028 (5)	0.043 (2.5)
OCDF	2.81 (100)	0.365 (10)	0.113 (5)

MDL ~ 1.1 ppt for 2,3,7,8-TCDD

*The current MDL for 2,3,7,8-TCDD with the GC/HRMS 1613B is 4.4 pg/L.
The MDL achieved with GC/TQ is 4 times better.

Dioxin Analysis Method for Food & Feed

Validation of a Confirmatory GC/MS/MS Method for Dioxins and Dioxin-like PCBS to Meet the Requirements of EU Regulation 709/2014

Application Note

Food

Author

Joerg Riener
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Abstract

Using the Agilent 7890B GC and the Agilent 7000C Series Triple Quadrupole GC/MS System, a GC/MS/MS method has been developed and fully validated to meet the requirements of EU Regulation 709/2014 for the monitoring of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) in animal feedstuffs. It provides similar performance to GC/HRMS, the analytical platform required by previous EU regulations, in spite of the difference in mass analyzer technologies.

Determination of Polychlorinated Dibenzo-p-dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF) in Foodstuffs and Animal Feed using the Agilent 7000 Triple Quadrupole GC/MS System

Application Note

Food Safety

Authors

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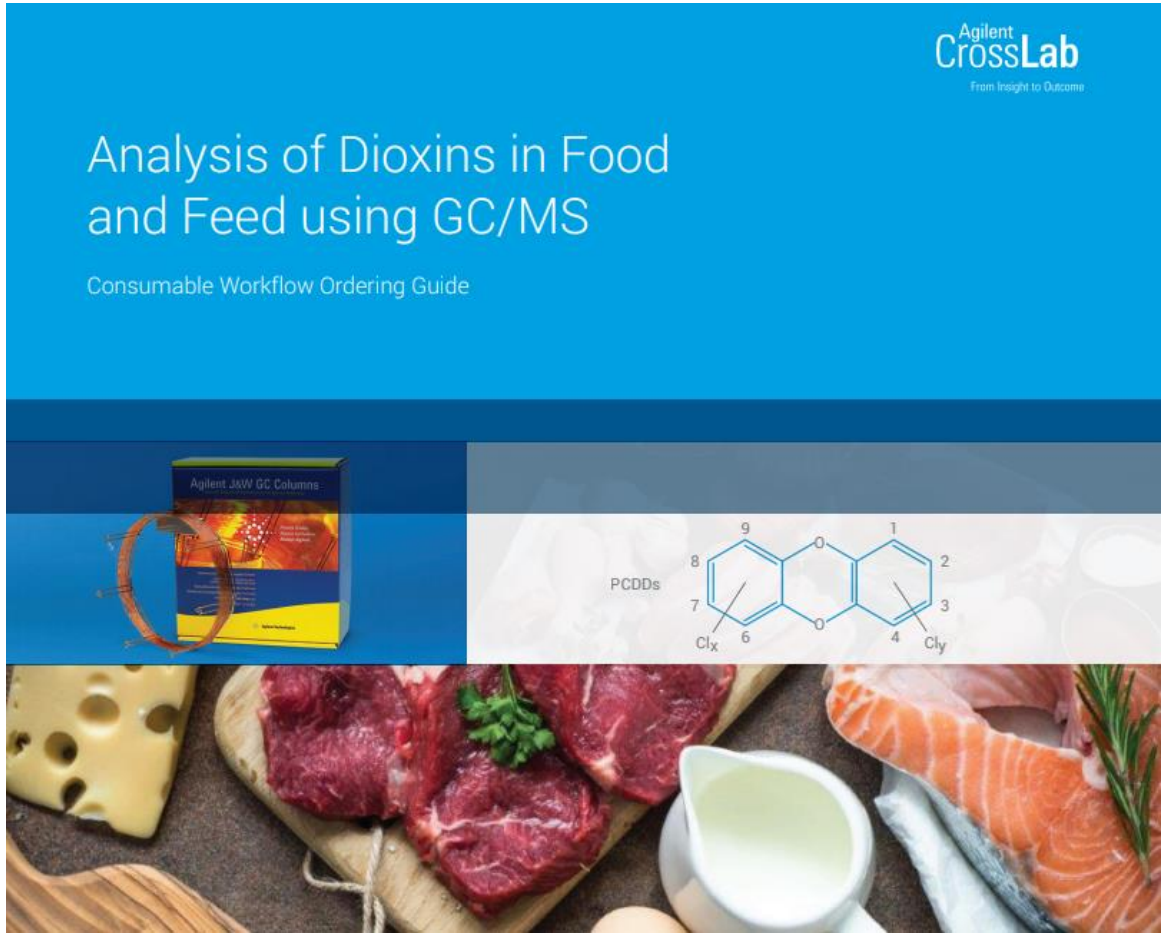
Abstract

A method has been developed on the Agilent 7000 GC Triple Quadrupole GC/MS system for the analysis of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in foodstuffs and animal feed. The method was shown to give linear response over the required concentration range, good repeatability of response and quantitation down to low pg TEQ/g levels.

Consumables Selection Toolkit for Dioxins Workflow

5994-3649EN

Includes Checkout Standards, Column, Liners, Unions, Vials, Caps, filament, gas filters etc. needed to get started with Dioxin testing with suggested Agilent methods and compatible with Dioxin Workflow Kit



MyList of Chemical Standards	
Dioxin Analyzer Checkout Standard Kit	G3440-85039
Chlorinated Dibenzo-p-dioxin Mixture, 10 µg/mL, Toluene, 1 mL	RPE-065M-1
Chlorinated Dibenzofuran Mixture, 10 µg/mL, Toluene, 1 mL	RPE-045M-1
2,3,7,8-Tetrachlorodibenzo-p-dioxin, 50 µg/mL, Toluene, 1 mL	RPE-029S-1
Octachlorodibenzo-p-dioxin, 50 µg/mL, Toluene, 1 mL	RPE-017S-1
2,3,7,8-Tetrachlorodibenzofuran, 50 µg/mL, Toluene, 1 mL	RPE-037S-1
1,2,3,7,8-Pentachlorodibenzofuran, 50 µg/mL, Toluene, 1 mL	RPE-042S-1
1,2,3,4,7,8-Hexachlorodibenzofuran, 50 µg/mL, Toluene, 1 mL	RPE-043S-1
Octachlorodibenzofuran, 50 µg/mL, Toluene, 1 mL	RPE-019S-1
MyList of GC Column and retention gap	
DB-5ms Ultra Inert, 60 m x 0.25 mm, 0.25 µm	122-5562UI
Ultimate Plus Deactivated fused silica tubing, 5 m, 0.25 mm*	CP802505
MyList of GC Supplies	
Purged Ultimate Union**	G3186B
Liner, Ultra Inert, splitless, single taper, glass wool (4 mm id)	5190-2293
Inlet Septa Non-Stick Adv Green, 11 mm, 50/pk	5183-4759
Ultra Inert Gold seal, with washer, 1/pk	5190-6144
Ultra Inert Gold seal, with washer, 10/pk	5190-6145
Self-Tightening column nut, collared, inlet	G3440-81011
Self-Tightening column nut, collared, MSD	G3440-81013
ALS syringe, Blue Line, 10 µL, fixed needle, 23/42/cone, PTFE-tip plunger	G4513-80220
15%Graphite/85% Vespel Ferrules, 0.4 mm id, 10/pk	5181-3323
QuickPick preventative maintenance kit, for split vent trap, includes 1 cartridge**	5181-6495
Ceramic scribe column cutter, 4/pk	5181-8836
Column installation tool	G1099-20030
MyList of Vials and Caps	
Vial, screw top, amber, silanized, write-on spot, certified, 2 mL, 100/pk	5183-2072
ALS Vial Cap, screw, green, PTFE/red silicone septa, 100/pk	5182-0718
Vial insert, 250 µL, glass conical with polymer feet, deactivated, 100/pk Insert size: 5.6 x 30 mm	5181-8872
MyList of MS supplies	
EI Filament (for 7000A/B/C/D, 5977B Inert Plus, 5977A Extractor, Inert or Stainless steel and 5975 systems)	G7005-60061

This guide provides recommendations for Agilent products used in this analysis, so you can find what you're looking for quickly. Click the MyList* links in the header to add items to your "Favorite Products" list at the Agilent online store. Then, enter the quantities for the products you need. Your list will remain under "Favorite Products" for your use with future orders.

Conclusions

- **Agilent have the most complete portfolio of GC columns for general purpose and specific applications**
- Agilent is committed to continue innovation that provides better lab productivity and economic value to our customers
- Agilent continues to develop new technical notes to solve the toughest challenges in gas chromatography

We are here to help!

Thank you!

Agilent CrossLab
From Insight to Outcome

Agilent