Application Note

Environmental Analysis

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Analysis of Semivolatile Organic Compounds with Agilent Sintered Frit Liner by Gas Chromatography/Mass Spectrometry

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Abstract

Gas chromatography/mass spectrometry (GC/MS) is integral to the analysis of semivolatile organic compounds in environmental matrices. Depending on the complexity of the matrix, where some environmental matrices such as soil or wastewater matrices contain many nonvolatile compounds, the selection of the liner is crucial to longer lifetime of the GC/MS system and less downtime. The Agilent sintered frit liner offers extended lifetime of the GC/MS system before performing inlet maintenance, as well as excellent reproducibility.

Introduction

GC/MS is regarded as the select analytical technique for the analysis of semivolatile organic compounds (SVOCs).[1] Governmental regulatory authorities have established methods and performance criteria for the measurement of SVOCs identified as pollutants in environmental and industrial matrices. For example, United States Environmental Protection Agency (U.S. EPA) method 8270 (versions 8270D and 8270E) contains a list of over 200 compounds suitable for analysis by GC/MS in solid waste, soil, air, and water extracts.[2,3] Method 8270 contains SVOCs across several analyte class types from acids, bases, neutral compounds, and polyaromatic hydrocarbons (PAHs); this method also has detailed specifications and requirements for the quantitative analysis of SVOCs.

An important consumable in the GC/MS is the GC inlet liner. Maintaining a clean and inert GC/MS system starts at the inlet, specifically with the inlet liner. Using deactivated liners provides a good start for preventing peak degradation in the inlet. Choosing a liner with deactivated packing provides a large surface area for better vaporization and a barrier to protect the GC column and MS source from complex, nonvolatile matrices such as soil. One commonly used packing is glass wool; however, glass wool in liners can re-introduce active sites over the lifetime of the liner that can manifest as a decrease in peak response or degradation of sensitive compounds, such as 4,4'-DDT. A sintered frit liner offers the same vaporization space and protection from complex nonvolatile matrices such as glass wool liners, but does not suffer from possible loss of peak response due to wool breakage.

This Application Note demonstrates the ability of the sintered frit liner to extend the lifetime of the liner before replacement and retain excellent reproducibility across multiple liners. Thus, the same calibration curve can be used through several liner changes and column trims.

Experimental

A set of stock standards containing 97 target compounds and surrogates was selected to provide a representative mixture of acids, bases, and neutral compounds, as well as comprising various compound classes, from nitrophenols to PAHs. An internal standard mixture of six deuterated PAHs was used for recovery and calibration. The stock standards were combined and diluted in dichloromethane to make a working standard at 200 µg/mL. The working standard was then diluted to form the following nominal concentrations for the targets and surrogates for calibration standards: 0.1, 0.2, 0.5, 0.8, 1, 2, 5, 10, 20, 35, 50, 75, and 100 µg/mL. Internal standards were added to each calibration standard at a concentration level of 40 µg/mL. Table 1 lists the compounds that were used in the study. The compound numbers in Table 1 were assigned based on retention order of the targets and surrogates, with the internal standards listed at the end of the table out of retention order. These numbers were assigned to reduce the complexity of the graphs.

The tuning standard containing a mixture of benzidine, pentachlorophenol, 4,4'-diphenyltrichloroethane (4,4'-DDT), and decafluorodiphenyltrichloroethane (DFTPP) at 25 µg/mL was used to obtain the MS calibration and tuning settings.

A composite mixture of soils extracted with dichloromethane for method 8270 analysis, which was a representative matrix residue typically encountered in the lab, was procured from ESC Lab Sciences.

Table 1. Targets, surrogates, and internal standards.

No.	Compound
1	N-nitrosodimethylamine
2	2-Picoline
3	Methanesulfonic acid, methyl ester
4	2-Fluorophenol (surrogate)
5	Methanesulfonic acid, ethyl ester
6	Phenol-d_5 (surrogate)
7	Phenol
8	Aniline
9	*Bis*(2-chloroethyl) ether
10	2-Chlorophenol
11	1,3-Dichlorobenzene
12	1,4-Dichlorobenzene
13	Benzyl alcohol
14	1,2-Dichlorobenzene
15	2-Methylphenol (*o*-cresol)
16	*Bis*(2-chloro-1-methylethyl) ether
17	Acetophenone
18	*p*-Cresol
19	N-nitroso-di-*n*-propylamine
20	Hexachloroethane
21	Nitrobenzene-D_5 (surrogate)
22	Nitrobenzene
23	1-Nitrosopiperidine
24	Isophorone
25	2-Nitrophenol
26	2,4-Dimethylphenol
27	*Bis*(2-chloroethoxy)-methane
28	Benzoic acid
29	2,4-Dichlorophenol
30	1,2,4-Trichlorobenzene
31	Naphthalene
32	2,6-Dichlorophenol
33	*m*-Chloroaniline
34	Hexachlorobutadiene

No.	Compound
35	N-nitrosobutylamine
36	4-Chloro-3-methyl-phenol
37	2-Methylnaphthalene
38	Hexachlorocyclopentadiene
39	1,2,4,5-Tetrachlorobenzene
40	2,4,6-Trichlorophenol
41	2,4,5-Trichlorophenol
42	2-Fluorobiphenyl (surrogate)
43	1-Chloronaphthalene
44	2-Chloronaphthalene
45	*o*-Nitroaniline
46	Dimethyl phthalate
47	2,6-Dinitrotoluene
48	Acenaphthylene
49	*m*-Nitroaniline
50	Acenaphthene
51	2,4-Dinitrophenol
52	4-Nitrophenol
53	Pentachlorobenzene
54	2,4-Dinitrotoluene
55	Dibenzofuran
56	1-Naphthalenamine
57	2,3,4,6-Tetrachlorophenol
58	2-Naphthalenamine
59	Diethyl phthalate
60	Fluorene
61	4-Chlorophenyl phenyl ether
62	*p*-Nitroaniline
63	2-Methyl-4,6-dinitrophenol
64	Diphenylamine
65	Azobenzene
66	2,4,6-Tribromophenol (surrogate)
67	Phenacetin
68	4-Bromophenyl phenyl ether

No.	Compound
69	Hexachlorobenzene
70	Pentachlorophenol
71	4-Aminobiphenyl
72	Pentachloronitrobenzene
73	Pronamide
74	Phenanthrene
75	Anthracene
76	Dibutyl phthalate
77	Fluoranthene
78	Benzidine
79	Pyrene
80	*p*-Terphenyl-d14 (surrogate)
81	*p*-Dimethylaminoazobenzene
82	Benzyl butyl phthalate
83	3,3'-Dichlorobenzidine
84	Benz[a]anthracene
85	Chrysene
86	*Bis*(2-ethylhexyl) phthalate
87	Di-*n*-octyl phthalate
88	Benzo[b]fluoranthene
89	7,12-Dimethylbenz[a]anthracene
90	Benzo[k]fluoranthene
91	Benzo(a)pyrene
92	3-Methylcholanthrene
93	Dibenz[a,j]acridine
94	Indeno[1,2,3-cd]pyrene
95	Dibenz(a,h)anthracene
96	Benzo[ghi]perylene
97	1,4-Dichlorobenzene-d4 (internal standard)
98	Naphthalene-d_8 (internal standard)
99	Acenaphthalene-d_{10} (internal standard)
100	Phenanthrene-d_{10} (internal standard)
101	Chrysene-d_{12} (internal standard)
102	Perylene-d_{12} (internal standard)

Instrumental methods

The Agilent 7890B GC was configured with a single MS flowpath for interfacing with an Inert EI ion source and a 30 m DB-8270D Ultra Inert column. Previous work on EPA 8270 tested a 9 mm drawout plate.[4] Based on previous work, this study focused on using the 9 mm drawout plate. Table 2 summarizes the GC/MS instrumentation and consumables used. The GC and MSD method parameters (Table 3) have been optimized to provide an approximately 24 minute method, while retaining the required resolution for isomer pairs and following the EPA 8270 guidelines for method parameters, such as scan range and scan rate. The Agilent Ultra Inert splitless single-taper liner with frit was used for the EPA 8270 testing (Figure 1).

Instrumentation

Table 2. GC and MSD instrumentation and consumables.

Parameter	Value
GC	Agilent 7890 GC
MS	Agilent 5977 GC/MSD with Inert EI source
Drawout Plate	9 mm (p/n G3870-20449)
Syringe	Agilent Blue Line 10 µL PTFE-tip plunger tapered syringe (G4513-80203)
Column	Agilent DB-8270D Ultra Inert, 30 m × 0.25 mm × 0.25 µm (p/n 122-9732)
Liner	Agilent Ultra Inert splitless single-taper liner with frit (p/n 5190-5112)
Inlet Septum	Agilent Advanced Green, nonstick 11 mm septum (p/n 5183-4759 for 50 pack)
Autosampler	Agilent 7650A automatic liquid sampler
Vials	Agilent A-Line certified amber (screw top) vials; 100/pk (p/n 5190-9590)
Vial Iserts	Agilent deactivated vial inserts; 100/pk (p/n 5181-8872)
Vial Screw Caps	Agilent screw caps, PTFE/silicone/PTFE septa, cap size: 12 mm; 500/pk (p/n 5185-5862)

Instrument conditions

Table 3. GC and MSD instrument conditions.

Parameter	Value
Injection Volume	1 µL
Inlet	Split/splitless 280 °C; Pulsed splitless 30 psi until 0.6 minutes; Purge 50 mL/min at 0.6 minutes; Switched septum purge 3 mL/min
Column Temperature Program	40 °C (hold for 0.5 minutes), 10 °C/min to 100 °C, 25 °C/min to 260 °C, 5 °C/min to 280 °C, 15 °C/min to 320 °C (hold 2 minutes)
Carrier Gas And Flow Rate	Helium at 1.30 mL/min, constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Scan	35 to 500 *m/z*
Gain Factor	0.4
Threshold	0
A/D samples	4

Figure 1. Ultra Inert splitless single taper liner with sintered frit.

Results and discussion

According to method 8270, the GC/MS must pass selected tests to determine suitability for quantitative analysis before samples can be analyzed, especially when data are used for regulatory reporting. Included in the suitability tests is the DFTPP tuning standard, which contains DFTPP, 4,4'-DDT, pentachlorophenol, and benzidine to validate the MSD tune and flowpath inertness. DFTPP is used to check the ionization capability and detection on the mass spectrometer. The breakdown, or lack thereof, of 4,4'-DDT to 4,4'-DDE and 4,4'-DDD is used to test flowpath inertness. Benzidine and pentachlorophenol compounds are also used to probe for system inertness, where benzidine peak tailing indicates basic activity, and acidic activity is identified by pentachlorophenol peak tailing. If the performance criteria of method 8270 are not met, the system is unsuitable for analysis, and maintenance must be performed.

Figure 2 displays a chromatogram of the tuning standard at 25 µg/mL. Method 8270 suggests a concentration of 50 µg/mL with a statement that a lower concentration may be used to accommodate more sensitive instruments. For this study, 25 µg/mL was chosen to avoid column overload and bias peak symmetry measurements. Table 4 lists the measured DFTPP ion ratios along with the specified ratios and ranges for method 8270D. In method 8270E, the number of ions reported changed to match the ions of EPA method 525, which is a smaller set of ions, and are shown in Table 4.[3] All measured ratios are well within the required limits. Tailing factor (TF) was used to check the acid/base activity of the system with the compounds pentachlorophenol and benzidine. Based on the method requirements, the TF, measured at 10% peak height for the extracted quantitation ion, should be no greater than 2.0. The TF for pentachlorophenol was 1.0, and for benzidine, 0.9, which are well within the requirements.

The breakdown percentage of 4,4'-DDT is used to test system inertness. The combined area sum of the extracted ions for 4,4'-DDD and 4,4'-DDE should not exceed 20% of the 4,4'-DDT area to pass system suitability. The percent breakdown was measured at 0.9% upon initial start-up of the system with the sintered frit liner.

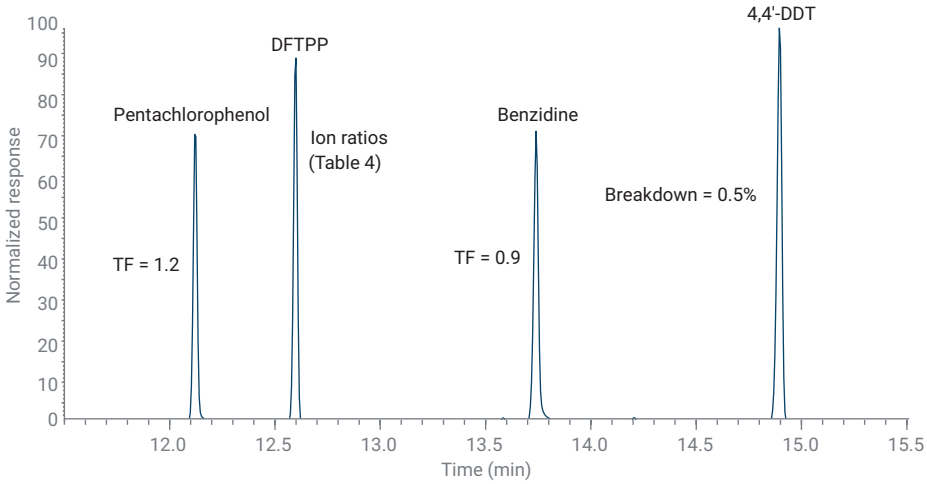

Figure 2. Total ion chromatogram of a method 8270 DFTPP tuning mixture on the Agilent Ultra Inert sintered frit liner with an Agilent 7890 GC coupled with a 5977 MSD.

Table 4. DFTPP tuning check.

Target Mass	Relative to Mass	Lower Limit %	Upper Limit %	Relative Abundance %	Pass/Fail
51	198	10	80	27.4	Pass
68	69	0	2	1.7	Pass
70	69	0	2	0.5	Pass
127	442	40	60	41.0	Pass
197	442	0	1	0.7	Pass
198	442	50	100	74.7	Pass
199	198	5	9	6.8	Pass
275	442	10	30	28.8	Pass
365	198	1	100	4.1	Pass
441	442	1	100	84.9	Pass
442	442	100	100	100	Pass
443	442	17	23	19.4	Pass

In addition to verifying system inertness and MSD tune, method 8270 states that chromatographic resolution must be shown for closely eluting structural isomer pairs, such as benzo(b)fluoranthene and benzo(k)fluoranthene. If these isomers are being reported, the valley between the two structural isomers cannot be greater than 50% of the average maximum height of the isomer peaks.

Benzo(b)fluoranthene and benzo(k)fluoranthene are generally selected as a measure of the system and method parameter ability to resolve isomers. Other structural isomers were also identified as closely eluting isomers and reviewed for resolution, specifically the pairs of benz[a]anthracene and chrysene, phenanthrene and anthracene, and 1-naphthalenamine and 2-naphthalenamine. Figure 3A illustrates the resolution achieved for benzo(b)fluoranthene and benzo(k)fluoranthene, where the valley is less than 25% of the average height, and passes the resolution criteria. Figures 3B–D display the separation of the other isomer pairs; all are baseline- or nearly baseline-resolved. After passing the system suitability tests, calibration data can be acquired. Figure 4 illustrates the separation of target compounds, surrogates, and ISTDs for the 24 minute method.

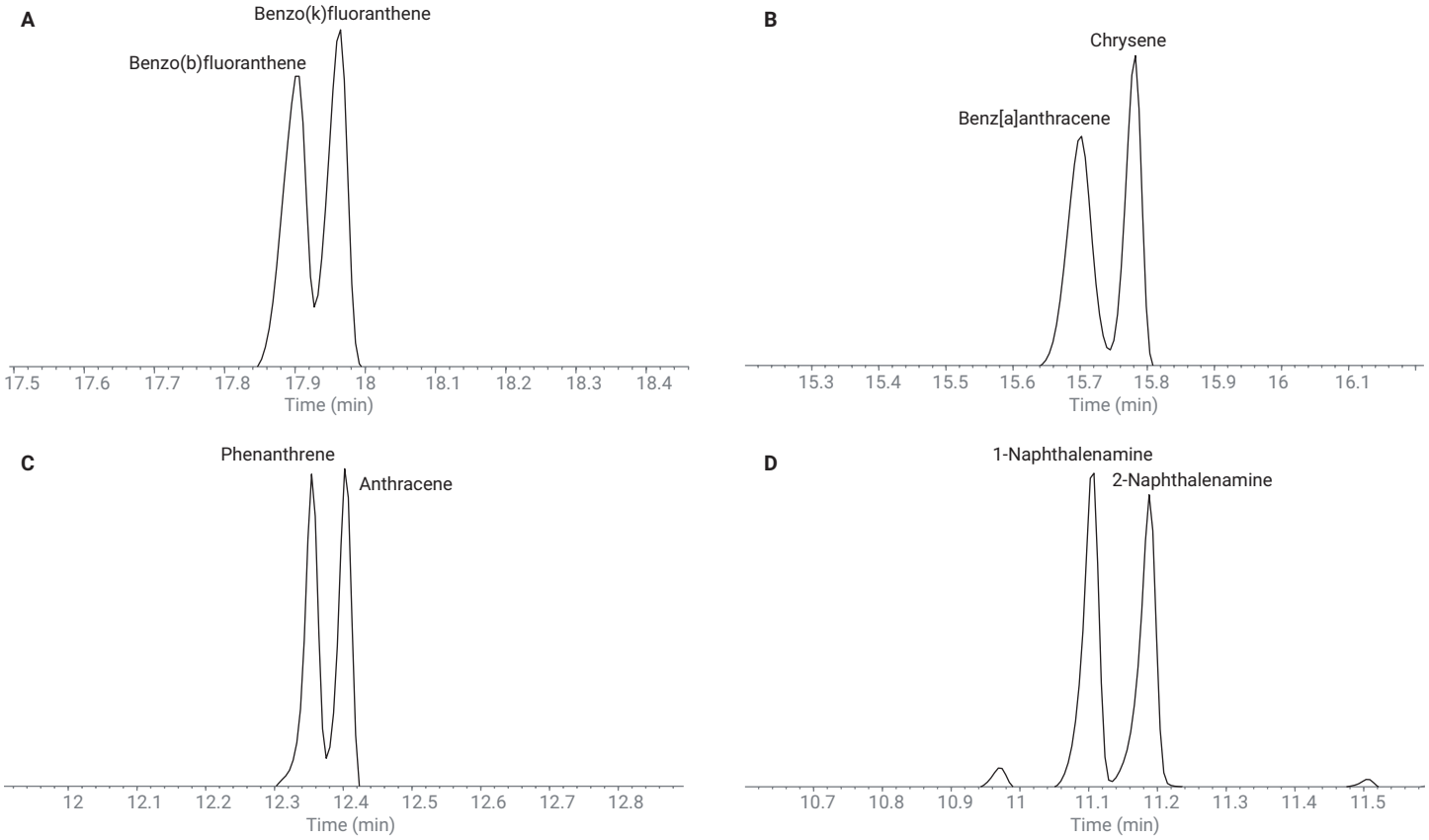

Figure 3. Extracted ion chromatograms for isomer pairs: (A) benzo(b)fluoranthene and benzo(k)fluoranthene, 252 *m/z*; (B) benz[a]anthracene and chrysene, 228 *m/z*; (C) phenanthrene and anthracene, 178 *m/z*, and (D) 1-naphthalenamine and 2-naphthalenamine, 143 *m/z*.

Calibration requirements

Calibration may be the most challenging requirement to achieve and maintain according to method 8270. The target list comprises a range of acidic, basic, and neutral molecules across various analyte classes. Figure 4 shows the chromatogram of the entire mixture. The type of calibration and calibration range for a specific analyte depend on the sensitivity of the GC/MS instrument and nature of the compound. Some compounds are more sensitive to surface activity, temperature, and detection efficiency, which results in several methods of calibration being used and accepted for quantitation. The easiest and most widely applied calibration uses average response factor. According to the method, a minimum of five standard levels must be evaluated and the relative standard deviation (RSD) in response factors should be within ±20%. Figure 5 shows the percent RSD achieved for 93 of the 97 compounds over a range of 0.1 to 100 µg/mL using 13 calibration levels. The average RSD for the 93 compounds was 10.25%.

Some compounds are active or labile, and tend to have response factors that vary as a function of concentration, especially the dinitrophenol compounds. For these analytes, method 8270 allows calibration to be achieved with curve fitting. The method stipulates that the correlation coefficient (R) must be greater than 0.99, and the calculated concentration of the lowest standard must be within ±20% of the actual concentration. Table 5 lists the calibration results for the remaining four of the 97 compounds using a weighted linear least squares regression with a 1/x weighting factor. In all cases, the specified calibration criteria were met, where the calibration ranges were selected to achieve the widest dynamic range and satisfy the criteria with a linear model. The percent deviation would be lower if the dynamic range were narrowed, or a higher-order calibration model were used.

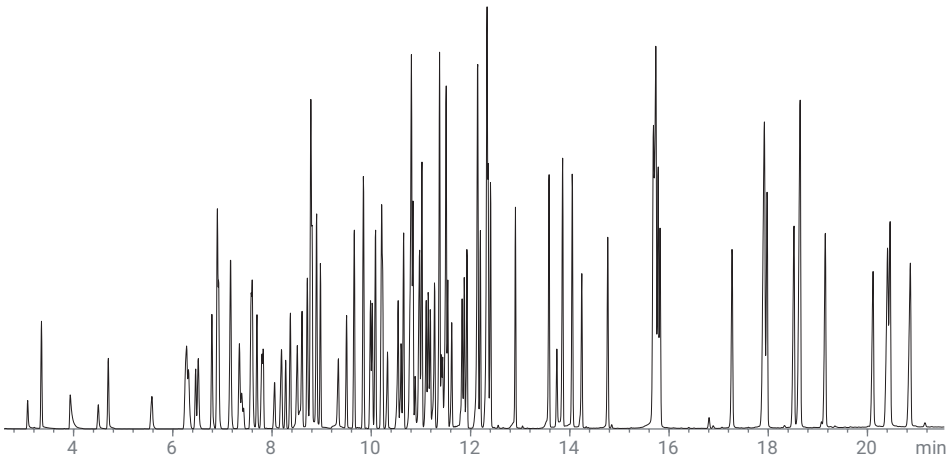

Figure 4. Total ion chromatogram showing separation of the target compounds and surrogates (10 ng/µL for target compounds and surrogates), and internal standards (40 ng/µL).

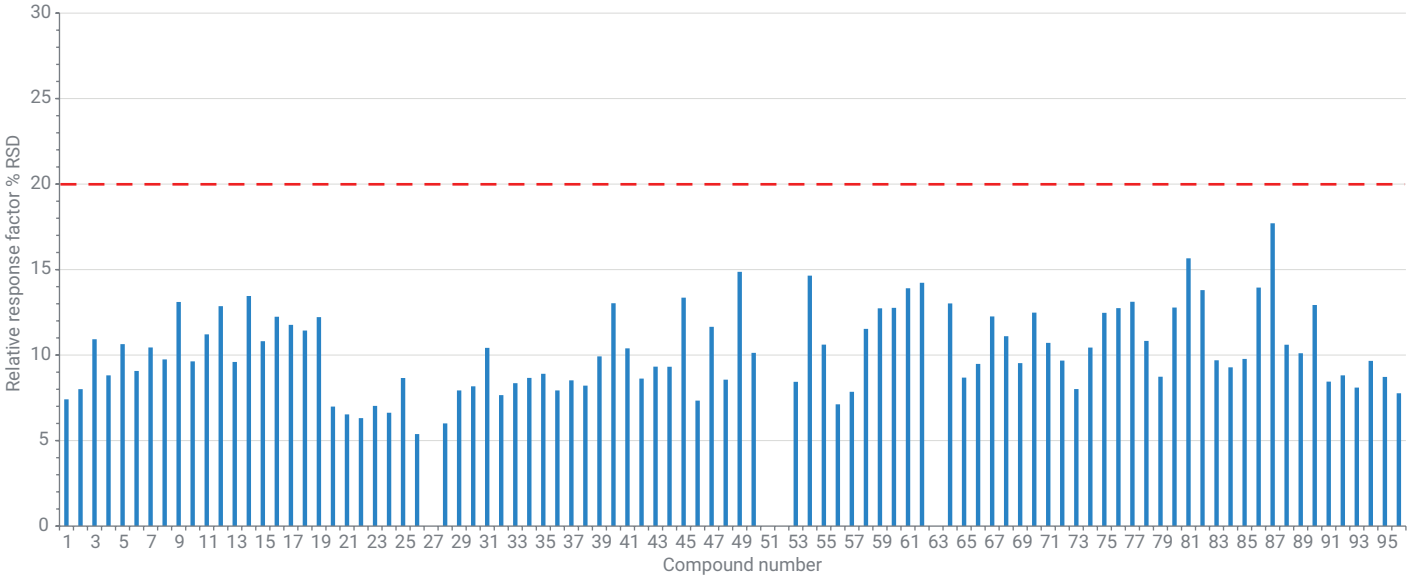

Figure 5. Percent RSD in average response factor for calibration from 0.1 to 100 µg/mL. The method 8270E limit on the %RSD for response factor is marked with the dashed red line. Detailed response factor information can be found in the Appendix.

Matrix study/repeatability of the sintered frit liner

To understand the durability of the sintered frit liner, an iterative cycle of matrix injections and performance checks was completed. Typically, environmental testing laboratories perform preventative maintenance, such as liner replacement or column trimming, at regular intervals to maintain system suitability and calibration integrity over time by avoiding column and source contamination. Comparatively, this study used a strategy whereby matrix samples were injected until suitability or calibration failure, then returned to acceptable performance with corrective maintenance, such as the liner change.

The test study was gated by performance checks between 10 matrix injections, which consisted of three measurements related to specifications in method 8270E, including:

- **QC:** Correct DFTPP tuning ratios, tailing factors for pentachlorophenol and benzidine less than 2.0, and percent breakdown for 4,4'-DDT less than 20%
- **CCV:** Midpoint calibration drift is within ±20% for more than 10% of target compounds
- **ISTD:** Verify the area of internal standard peak area drift is within a factor of 2

Prior to the first set of matrix injections, the system and fritted liner were tested for system suitability, discussed in the previous section, and calibrated using the compounds in Table 1 and the method 8270D parameters listed in Table 2.

Table 5. Calibration results using weighted least squares regression.

Compound No.	Compound	R^2	Calibration Range (µg/mL)	Percent Difference of Lowest Level Standard (±30% Required)
27	Benzoic acid	0.9983	0.5 to 100	20.0
51	2,4-Dinitrophenol	0.9989	0.5 to 100	8.0
52	4-Nitrophenol	0.9958	0.2 to 100	–5.0
63	2-Methyl-4,6-dinitrophenol	0.9964	0.5 to 100	–14.0

Study results

QC results

Ten liners were tested over the course of the study with a total of 260 matrix injections and 370 injections overall, including solvent blanks and QC checks. In the sequence, the QC and CCV checks were run before any matrix injections. QC and CCV checks were also completed after every 10 matrix sample injections, the overall sequences were batched with 20 matrix injections, for efficiency. After each sequence of 20 matrix injections, and the QC and CCV results were reviewed. If the checks passed, another sequence of 20 matrix runs was entered, until the QC and/or CCV checks failed. When the DDT % breakdown surpassed 20%, the liner and septum were replaced and the inlet and turn-top were quickly cleaned with dichloromethane-soaked swabs. Then, the system was retested with the QC and CCV checks. After each liner replacement, the percent breakdown dropped below 20% to an average breakdown of 0.9%, where the highest initial breakdown was 1.7% and lowest was 0.4%. On average, 23 matrix injections were completed before the DDT % breakdown limit (20%) was reached or surpassed for the sintered frit liners. Residue build-up in the liner is likely the cause of the 4,4'-DDT breakdown because replacement of the liner restored breakdown to values well below the 20% limit (Figure 6). Column trims are noted on the graph, and were generally performed after three frit liner data sets.

The QC sample also contains pentachlorophenol and benzidine to track tailing factors. Figure 7 displays the tailing factors for pentachlorophenol and benzidine, measured after a liner installation and each set of 10 matrix injections. From matrix injections 50 to 80, the pentachlorophenol tailing factor increased from 1.1 to 1.6, which is getting closer to the limit of 2.0. The column was trimmed, and a new liner was installed, after which the tailing factor returned to 1.0. The column was trimmed after an increase in pentachlorophenol tailing factor around matrix injections 220 to 240. The tailing factor dropped to 0.8 after the liner replacement and column trim. On average, the tailing factor for pentachlorophenol was 1.06, and the tailing factor for benzidine was 0.94.

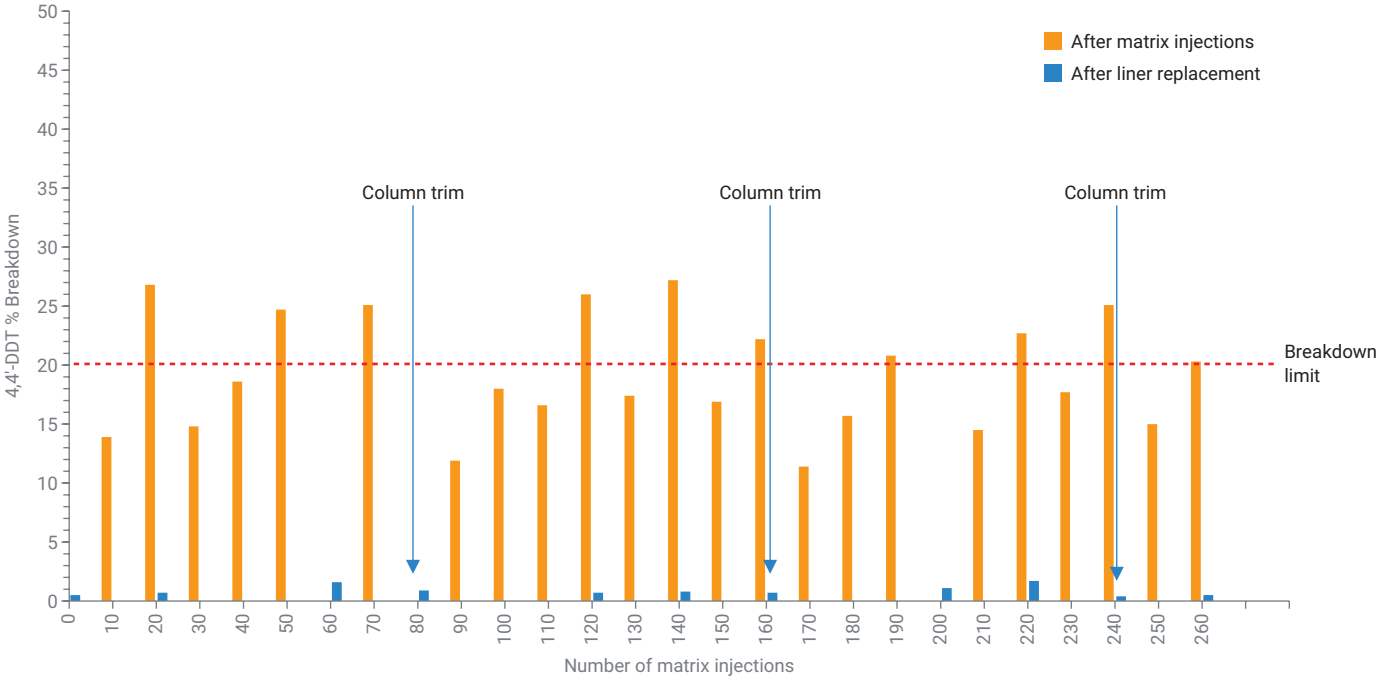

Figure 6. Breakdown and recovery of 4,4'-DDT after liner change (blue) and after matrix injection (orange). The breakdown limit of method 8270E is indicated with the dashed red line. Column trims are indicated with an arrow at each appropriate matrix injection number.

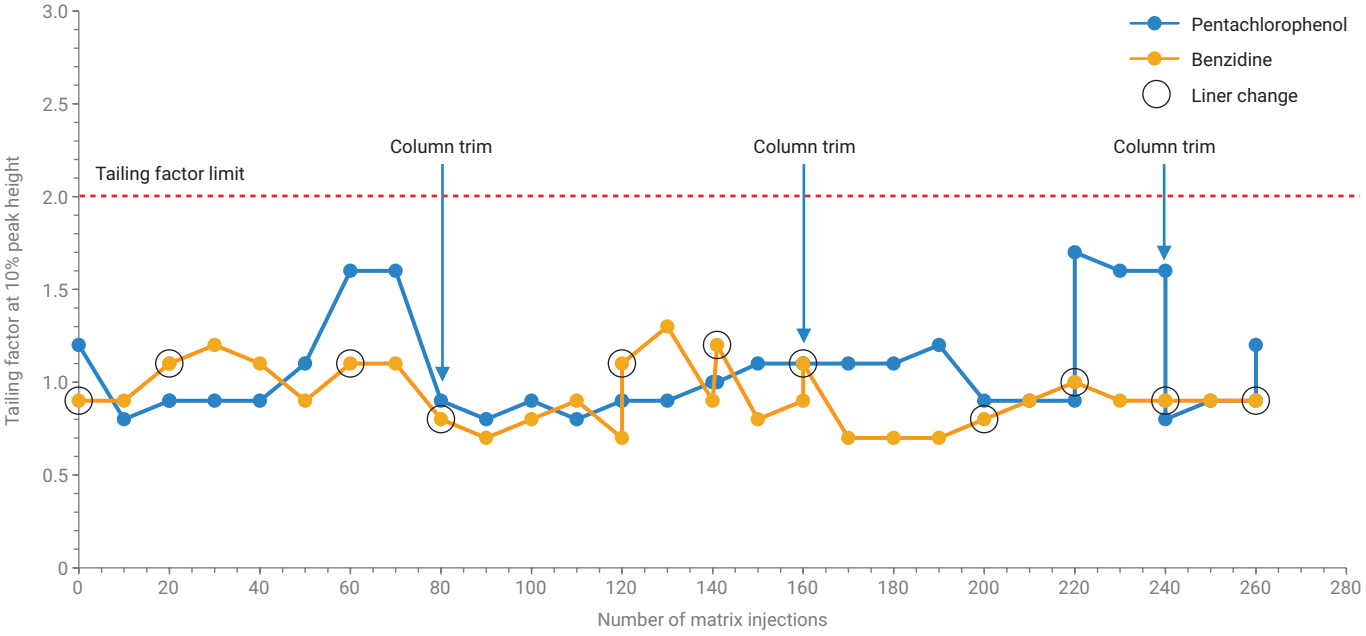

Figure 7. Tailing factor measurements after liner replacements and column trims for pentachlorophenol (blue) and benzidine (orange). The tailing factor limit for method 8270E is indicated with the dashed red line. Each liner change is indicated by a black, open circle, and sits over the benzidine tailing factor measurement for a simplified view of liner changes across the number of matrix injections. Column trims are indicated with an arrow at the corresponding matrix injection number.

CCV results

According to method 8270, the calibration must be verified every 12 hours by injecting a standard at a midpoint on the calibration curve. The calculated concentration must be within ±20% of the actual concentration for a valid calibration curve. If more than 20% of the compounds fail this calibration check, the system is unsuitable for analysis, and corrective action must be taken. In this study, the corrective action limit was lowered to 10% failure rate for the 96 targets and surrogates, or more than nine compounds outside of the ±20% bounds. Figure 8 illustrates the CCV results, where the CCV failure was not achieved either before or at the same injection number as when the DDT % breakdown limit was passed. For liner 2, nine compounds fell outside of the method specification after 30 matrix injections, which was close to the study limit. Appendix Table 3 lists the compounds that were outside of the CCV bounds after liner installation and when each liner reached or passed the DDT % breakdown limit of 20%. After every liner change, the number of compounds failing calibration either dropped or remained below the 10% study limit. Note that in most cases, liner replacement would lower the number of compounds failing calibration, except for the liner replacements after more than 200 matrix injections. For these later liners and matrix injections, the failure rates are still well below the 10% study limit, but the rates may be higher than previous values because matrix has migrated onto the column. Column replacement dropped the CCV failure rate to two compounds, 4-aminobiphenyl and benzidine. Both compounds had higher responses than the initial calibration, indicating that the cause of the CCV failures was isolated to the column and not the flowpath or ion source.

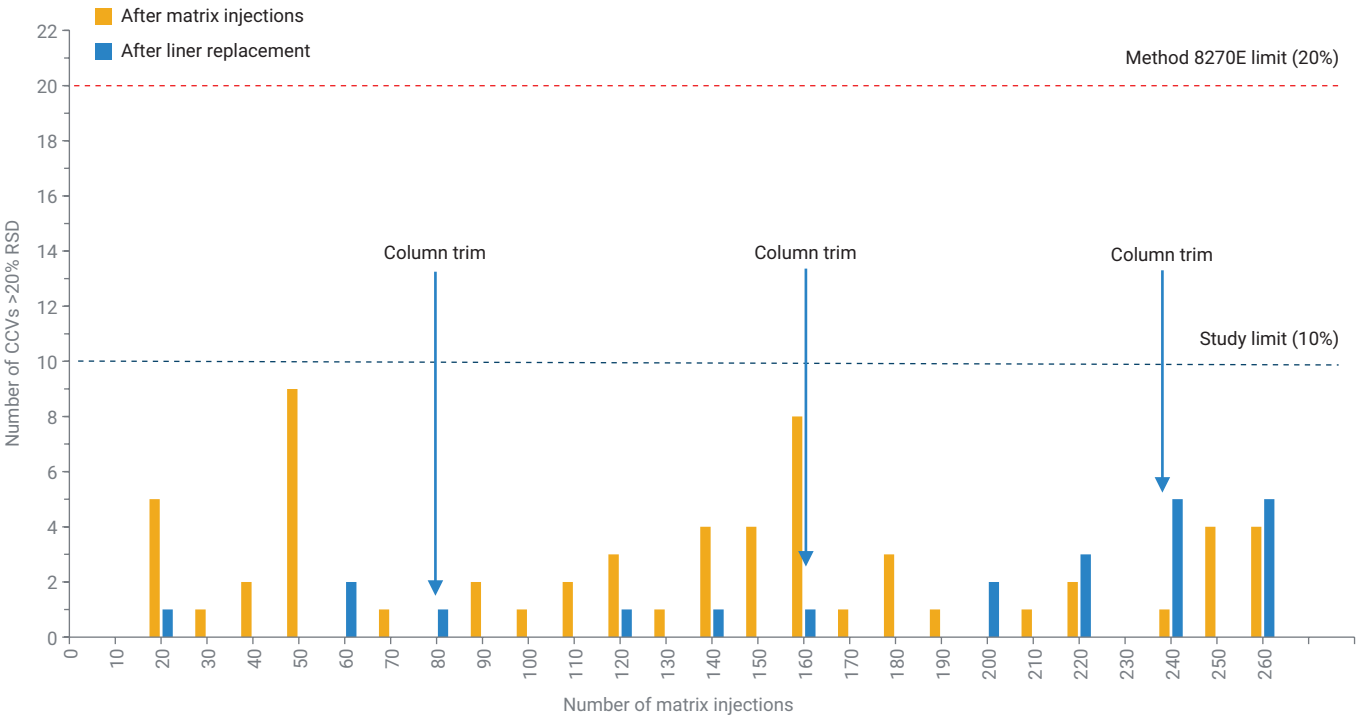

Figure 8. Number of CCV failures after liner change (blue) and after matrix injections (orange). The 8270E method limit is marked with a dashed red line, and the study limit is indicated with a blue dashed line. Column trims are indicated with an arrow at the corresponding matrix injection number.

ISTD results

Method 8270 states that the variability in area of internal standards should not exceed a factor of 2 (from 50% to 200%) when the areas are normalized. If this factor of the calibration area is exceeded, the system is unsuitable for analysis, and corrective action must be taken. Typically, the loss of response for internal standards is related to ion source contamination. Figure 9 displays the normalized area for the internal standards over 260 injections. Throughout the study, the internal standard area remained within the specified range. For liner 2 (matrix injections 20 to 50), there was a steady increase in the ISTD normalized area to 1.25 during the 30 matrix injections, at which point the DDT% breakdown passed 20% (Figure 6), and the number of CCV failures reached nine compounds (Figure 8 and Appendix Table A3). Upon installation of a new liner, the normalized area dropped slightly, but remained inside the ISTD area bounds. Over time, there was a downward trend in the normalized ISTD area, which is expected as the column and source become contaminated with continued soil matrix injections.

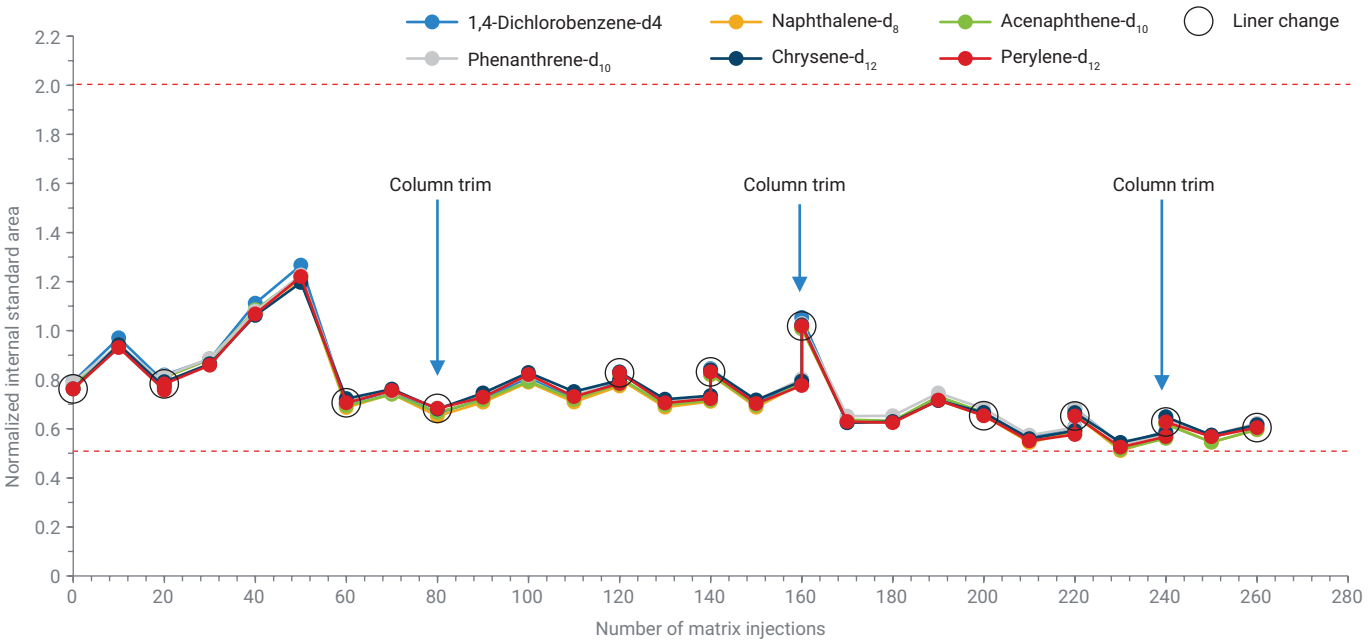

Figure 9. Normalized internal standard peak area across 260 injections for the six internal standard compounds. Each liner change is indicated by a black, open circle and sits over the normalized ISTD area measurement for a simplified view of liner changes across the number of matrix injections. Column trims are indicated with an arrow at the corresponding matrix injection number.

Conclusion

This study demonstrates the suitability of the Agilent Ultra Inert splitless single taper frit liner for the analysis of semivolatile organic compounds. The liner can easily meet the performance requirements specified by US EPA method 8270E. In addition, repetitive injections of a soil extract illustrated the resilience of the frit liner to a matrix challenge, as the sintered frit provided a significant barrier for matrix. Also, the sintered frit liners have less risk of formation of new active sites from glass wool breakage, or movement of glass wool by pressure changes in the inlet. The sintered frit liners also showed that the Ultra Inert deactivation was consistent with the low 4,4'-DDT% breakdown (below 1% on average) upon liner changes, and the ability to use the same calibration curve over 10 liner changes.

References

1. Padilla-Sánchez, J. A.; Plaza-Bolaños, P.; Frenich, A. G. Applications and Strategies based on Gas Chromatograph-Low-Resolution Mass Spectrometry (GC-LRMS) for the Determination of Residues and Organic Contaminants in Environmental Samples. In *Comprehensive Analytical Chemistry*; Cappiello, A.; Palma, P., Eds.; Advanced Techniques in Gas Chromatography-Mass Spectrometry (GC-MS-MS and GC-TOF-MS) for Environmental Chemistry, Volume 61; Ferrer, I.; Thurman, E., Eds; Elsevier, Oxford, 2013, pp 181-199.
2. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method 8270D; *United Stated Environmental Protection Agency*, Revision 4, February **2007**.
3. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method 8270E; *United Stated Environmental Protection Agency*, Revision 4, June **2018**.
4. Analysis of Semivolatile Organic Compounds Using the Agilent Intuvo 9000 Gas Chromatograph, *Agilent Technologies*, publication number 5991-7256EN, **2016**.

Appendix A

Appendix Table A1. Retention times, response factors, average response factor, and % RSD for target and surrogate compounds from 0.1 to 100 µg/mL.

			Concentration level (µg/mL)														
No.	Compound	RT (min)	1 (0.1)	2 (0.2)	3 (0.5)	4 (0.8)	5 (1.0)	6 (2.0)	7 (5.0)	8 (10.0)	9 (20.0)	10 (35.0)	11 (50.0)	12 (75.0)	13 (100.0)	Average	% RSD
1	N-nitrosodimethylamine	3.079	0.346	0.317	0.345	0.376	0.359	0.403	0.341	0.375	0.347	0.361	0.336	0.323	0.311	0.349	7.41
2	2-Picoline	3.940	0.601	0.550	0.631	0.677	0.658	0.739	0.608	0.693	0.667	0.696	0.647	0.627	0.585	0.645	8.01
3	Methanesulfonic acid, methyl ester	4.486	0.364	0.287	0.328	0.347	0.340	0.366	0.351	0.361	0.301	0.309	0.289	0.277	0.268	0.322	10.93
4	2-Fluorophenol (surrogate)	4.684	0.587	0.576	0.662	0.716	0.688	0.791	0.650	0.702	0.717	0.729	0.674	0.651	0.623	0.674	8.81
5	Methanesulfonic acid, ethyl ester	5.556	0.628	0.514	0.570	0.583	0.596	0.612	0.596	0.612	0.514	0.528	0.488	0.473	0.455	0.551	10.64
6	Phenol-d_5 (surrogate)	6.224	0.890	0.790	0.889	0.939	0.922	1.003	0.929	0.985	0.870	0.886	0.814	0.777	0.742	0.880	9.07
7	Phenol	6.251	1.021	0.758	0.840	0.917	0.916	0.988	1.031	1.073	0.955	0.961	0.885	0.830	0.796	0.921	10.44
8	Aniline	6.299	1.233	1.035	1.152	1.206	1.203	1.281	1.224	1.278	1.084	1.099	1.011	0.967	0.993	1.136	9.75
9	Bis(2-chloroethyl) ether	6.443	0.876	0.722	0.803	0.830	0.830	0.859	0.830	0.842	0.713	0.720	0.663	0.626	0.560	0.759	13.11
10	2-Chlorophenol	6.497	0.883	0.752	0.864	0.900	0.898	0.961	0.901	0.933	0.830	0.841	0.770	0.737	0.700	0.844	9.63
11	1,3-Dichlorobenzene	6.780	1.067	0.929	0.998	1.074	1.050	1.124	1.009	1.040	0.958	0.945	0.864	0.806	0.760	0.971	11.21
12	1,4-Dichlorobenzene	6.920	1.139	0.963	1.052	1.089	1.075	1.136	1.027	1.051	0.961	0.944	0.856	0.792	0.739	0.986	12.86
13	Benzyl alcohol	7.133	0.586	0.493	0.556	0.580	0.578	0.619	0.620	0.651	0.549	0.556	0.512	0.495	0.478	0.559	9.60
14	1,2-Dichlorobenzene	7.160	1.108	0.913	1.001	1.045	1.033	1.082	1.000	1.026	0.909	0.890	0.808	0.751	0.708	0.944	13.46
15	2-Methylphenol (*o*-cresol)	7.326	0.762	0.607	0.697	0.752	0.751	0.797	0.762	0.794	0.675	0.686	0.629	0.607	0.581	0.700	10.81
16	*Bis*(2-chloro-1-methylethyl) ether	7.380	0.528	0.409	0.475	0.501	0.489	0.513	0.494	0.523	0.442	0.446	0.409	0.391	0.350	0.459	12.24
17	Acetophenone	7.556	1.310	1.064	1.187	1.260	1.275	1.330	1.297	1.328	1.119	1.129	1.032	0.983	0.938	1.173	11.77
18	*p*-Cresol	7.572	1.016	0.833	0.943	1.022	1.002	1.082	1.052	1.089	0.920	0.931	0.843	0.808	0.763	0.946	11.43
19	N-nitroso-di-*n*-propylamine	7.577	0.465	0.349	0.412	0.449	0.439	0.475	0.451	0.476	0.400	0.404	0.369	0.353	0.331	0.413	12.22
20	Hexachloroethane	7.690	0.149	0.146	0.155	0.161	0.165	0.177	0.162	0.168	0.161	0.165	0.153	0.148	0.135	0.157	6.99
21	Nitrobenzene-d_5 (surrogate)	7.775	0.326	0.277	0.313	0.336	0.336	0.361	0.345	0.358	0.323	0.337	0.319	0.322	0.323	0.329	6.53
22	Nitrobenzene	7.802	0.325	0.278	0.305	0.332	0.330	0.356	0.335	0.345	0.312	0.325	0.305	0.309	0.311	0.321	6.31
23	1-Nitrosopiperidine	8.032	0.161	0.141	0.155	0.171	0.171	0.185	0.175	0.186	0.167	0.175	0.166	0.169	0.171	0.169	7.03
24	Isophorone	8.166	0.573	0.485	0.551	0.589	0.590	0.633	0.611	0.635	0.570	0.597	0.566	0.567	0.573	0.580	6.63
25	2-Nitrophenol	8.267	0.192	0.159	0.188	0.198	0.202	0.221	0.218	0.227	0.203	0.216	0.205	0.213	0.211	0.204	8.66
26	2,4-Dimethylphenol	8.358	0.344	0.282	0.317	0.334	0.334	0.346	0.336	0.351	0.327	0.341	0.321	0.320	0.323	0.329	5.38
27	Bis(2-chloroethoxy)-methane	8.497	0.405	0.347	0.385	0.410	0.410	0.429	0.424	0.430	0.386	0.401	0.382	0.379	0.382	0.398	6.00
28	Benzoic acid	8.551	Linear Regression														
29	2,4-Dichlorophenol	8.594	0.310	0.261	0.296	0.321	0.327	0.350	0.344	0.358	0.323	0.334	0.312	0.310	0.307	0.319	7.93
30	1,2,4-Trichlorobenzene	8.706	0.414	0.356	0.383	0.397	0.399	0.415	0.398	0.404	0.361	0.369	0.343	0.331	0.328	0.377	8.17
31	Naphthalene	8.802	1.251	1.054	1.138	1.176	1.177	1.240	1.155	1.169	1.035	1.048	0.964	0.931	0.907	1.096	10.42
32	2,6-Dichlorophenol	8.888	0.329	0.280	0.315	0.325	0.329	0.354	0.338	0.344	0.308	0.316	0.294	0.288	0.281	0.316	7.66
33	*m*-Chloroaniline	8.888	0.445	0.374	0.427	0.452	0.459	0.486	0.472	0.488	0.431	0.442	0.413	0.397	0.386	0.436	8.36
34	Hexachlorobutadiene	8.973	0.246	0.209	0.229	0.239	0.237	0.248	0.236	0.240	0.213	0.220	0.202	0.196	0.192	0.224	8.67
35	N-nitrosobutylamine	9.321	0.195	0.149	0.182	0.194	0.198	0.216	0.208	0.219	0.201	0.209	0.198	0.201	0.203	0.198	8.90
36	4-Chloro-3-methylphenol	9.492	0.268	0.233	0.263	0.280	0.289	0.309	0.309	0.320	0.287	0.302	0.286	0.285	0.286	0.286	7.93
37	2-Methylnaphthalene	9.653	0.783	0.668	0.738	0.772	0.782	0.808	0.787	0.791	0.707	0.719	0.664	0.642	0.633	0.730	8.52
38	Hexachlorocyclopentadiene	9.835	0.262	0.208	0.238	0.251	0.259	0.268	0.270	0.280	0.250	0.254	0.240	0.227	0.224	0.249	8.21
39	1,2,4,5-Tetrachlorobenzene	9.840	0.434	0.371	0.393	0.407	0.411	0.425	0.410	0.412	0.365	0.368	0.342	0.327	0.316	0.383	9.92
40	2,4,6-Trichlorophenol	9.974	0.235	0.190	0.219	0.228	0.249	0.273	0.260	0.288	0.257	0.298	0.288	0.282	0.300	0.259	13.03
41	2,4,5-Trichlorophenol	10.011	0.246	0.213	0.235	0.271	0.257	0.277	0.286	0.269	0.248	0.221	0.288	0.282	0.300	0.261	10.39
42	2-Fluorobiphenyl (surrogate)	10.075	1.620	1.390	1.548	1.586	1.596	1.655	1.556	1.579	1.413	1.403	1.318	1.322	1.301	1.484	8.62

			Concentration level (µg/mL)														
No.	Compound	RT (min)	1 (0.1)	2 (0.2)	3 (0.5)	4 (0.8)	5 (1.0)	6 (2.0)	7 (5.0)	8 (10.0)	9 (20.0)	10 (35.0)	11 (50.0)	12 (75.0)	13 (100.0)	Average	% RSD
43	1-Chloronaphthalene	10.198	2.674	2.248	2.509	2.578	2.573	2.679	2.560	2.597	2.310	2.276	2.134	2.109	2.063	2.408	9.32
44	2-Chloronaphthalene	10.198	2.673	2.249	2.509	2.578	2.573	2.679	2.559	2.597	2.310	2.276	2.134	2.109	2.063	2.408	9.32
45	*o*-Nitroaniline	10.316	0.323	0.263	0.334	0.371	0.378	0.416	0.421	0.443	0.401	0.421	0.407	0.420	0.425	0.386	13.36
46	Dimethyl phthalate	10.525	1.387	1.180	1.407	1.473	1.457	1.527	1.483	1.493	1.361	1.381	1.335	1.226	1.372	1.391	7.34
47	2,6-Dinitrotoluene	10.589	0.257	0.220	0.275	0.295	0.305	0.331	0.339	0.347	0.330	0.310	0.293	0.302	0.297	0.300	11.65
48	Acenaphthylene	10.642	1.980	1.718	1.991	2.052	2.056	2.176	2.105	2.099	1.893	1.874	1.774	1.711	1.705	1.933	8.56
49	*m*-Nitroaniline	10.755	0.208	0.188	0.236	0.275	0.279	0.307	0.312	0.323	0.296	0.303	0.285	0.276	0.264	0.273	14.87
50	Acenaphthene	10.835	1.545	1.272	1.360	1.385	1.386	1.434	1.354	1.350	1.229	1.213	1.153	1.111	1.110	1.300	10.13
51	2,4-Dinitrophenol	10.867	Linear Regression														
52	4-Nitrophenol	10.931	Linear Regression														
53	Pentachlorobenzene	10.963	0.706	0.595	0.645	0.676	0.672	0.694	0.661	0.665	0.606	0.598	0.557	0.564	0.557	0.631	8.43
54	2,4-Dinitrotoluene	11.001	0.317	0.280	0.346	0.402	0.413	0.459	0.459	0.467	0.429	0.429	0.413	0.362	0.361	0.395	14.65
55	Dibenzofuran	11.011	1.956	1.664	1.830	1.895	1.879	1.977	1.865	1.819	1.665	1.628	1.539	1.471	1.430	1.740	10.61
56	1-Naphthalenamine	11.092	1.148	1.019	1.139	1.184	1.200	1.236	1.035	1.113	1.000	1.047	1.005	1.073	1.077	1.098	7.12
57	2,3,4,6-Tetrachlorophenol	11.140	0.329	0.299	0.345	0.362	0.362	0.390	0.392	0.403	0.371	0.376	0.354	0.348	0.341	0.359	7.85
58	2-Naphthalenamine	11.177	1.231	0.987	1.212	1.257	1.215	1.230	0.846	1.084	0.948	1.072	1.031	1.068	1.077	1.097	11.53
59	Diethyl phthalate	11.257	1.763	1.370	1.631	1.502	1.518	1.588	1.501	1.499	1.377	1.372	1.224	1.184	1.131	1.435	12.74
60	Fluorene	11.364	1.515	1.239	1.418	1.468	1.471	1.528	1.453	1.432	1.297	1.250	1.149	1.065	1.042	1.333	12.76
61	4-Chlorophenyl phenyl ether	11.370	0.749	0.635	0.718	0.723	0.735	0.750	0.713	0.705	0.641	0.614	0.561	0.507	0.486	0.657	13.91
62	*p*-Nitroaniline	11.380	0.251	0.223	0.287	0.313	0.323	0.352	0.361	0.372	0.340	0.286	0.281	0.305	0.283	0.306	14.23
63	2-Methyl-4,6-dinitrophenol	11.418	Linear Regression														
64	Diphenylamine	11.493	2.231	1.880	2.185	2.239	2.271	2.379	2.257	2.244	2.013	1.955	1.790	1.635	1.550	2.048	13.02
65	Azobenzene	11.530	0.647	0.556	0.629	0.666	0.679	0.715	0.695	0.806	0.726	0.708	0.685	0.656	0.638	0.678	8.68
66	2,4,6-Tribromophenol (surrogate)	11.610	0.167	0.140	0.163	0.175	0.173	0.189	0.191	0.193	0.173	0.179	0.164	0.152	0.150	0.170	9.48
67	Phenacetin	11.803	0.283	0.240	0.287	0.319	0.322	0.359	0.365	0.370	0.336	0.347	0.302	0.302	0.280	0.316	12.26
68	4-Bromophenyl phenyl ether	11.867	0.261	0.228	0.254	0.266	0.268	0.276	0.274	0.273	0.243	0.242	0.227	0.199	0.196	0.247	11.10
69	Hexachlorobenzene	11.921	0.336	0.294	0.316	0.327	0.334	0.345	0.335	0.333	0.299	0.296	0.279	0.263	0.258	0.309	9.53
70	Pentachlorophenol	12.124	0.158	0.139	0.164	0.179	0.185	0.205	0.213	0.216	0.193	0.191	0.178	0.168	0.165	0.181	12.48
71	4-Aminobiphenyl	12.129	0.781	0.682	0.779	0.805	0.786	0.836	0.755	0.834	0.751	0.742	0.687	0.603	0.589	0.741	10.71
72	Pentachloronitrobenzene	12.140	0.104	0.091	0.107	0.116	0.114	0.125	0.126	0.126	0.112	0.112	0.105	0.102	0.100	0.111	9.68
73	Pronamide	12.188	0.352	0.300	0.362	0.387	0.394	0.420	0.407	0.394	0.357	0.358	0.338	0.321	0.309	0.361	10.44
74	Phenanthrene	12.348	1.451	1.198	1.219	1.211	1.248	1.285	1.227	1.218	1.100	1.059	1.021	0.925	0.958	1.163	12.47
75	Anthracene	12.391	1.296	1.120	1.190	1.261	1.272	1.293	1.230	1.169	1.042	0.999	0.917	0.925	0.958	1.129	12.75
76	Dibutyl phthalate	12.899	1.503	1.172	1.285	1.318	1.341	1.435	1.427	1.372	1.225	1.193	1.099	1.013	0.968	1.258	13.12
77	Fluoranthene	13.573	1.281	1.155	1.248	1.315	1.317	1.399	1.370	1.311	1.170	1.146	1.072	1.028	0.993	1.216	10.83
78	Benzidine	13.734	0.467	0.433	0.482	0.438	0.394	0.452	0.368	0.438	0.350	0.427	0.427	0.437	0.451	0.428	8.74
79	Pyrene	13.846	1.415	1.300	1.397	1.447	1.476	1.540	1.502	1.432	1.276	1.233	1.102	1.053	1.062	1.326	12.78
80	*p*-Terphenyl-d_{14} (surrogate)	14.044	1.000	0.876	0.968	1.028	1.018	1.111	1.036	1.051	0.963	0.981	0.924	0.863	0.854	0.975	8.01
81	*p*-Dimethylaminoazobenzene	14.231	0.224	0.188	0.246	0.277	0.274	0.319	0.311	0.333	0.311	0.331	0.322	0.311	0.318	0.290	15.66
82	Benzyl butyl phthalate	14.755	0.445	0.394	0.472	0.517	0.511	0.599	0.598	0.629	0.591	0.627	0.609	0.583	0.600	0.552	13.80
83	3,3′-Dichlorobenzidine	15.665	0.419	0.355	0.404	0.448	0.458	0.495	0.476	0.503	0.473	0.488	0.456	0.426	0.403	0.446	9.69
84	Benz[a]anthracene	15.686	1.535	1.610	1.409	1.407	1.393	1.487	1.365	1.395	1.258	1.341	1.263	1.185	1.188	1.372	9.28
85	Chrysene	15.761	1.254	1.134	1.220	1.228	1.257	1.325	1.230	1.220	1.098	1.131	1.073	1.012	0.920	1.162	9.78
86	*Bis*(2-ethylhexyl) phthalate	15.814	0.666	0.571	0.689	0.783	0.809	0.882	0.895	0.939	0.890	0.908	0.863	0.784	0.715	0.799	13.95
87	Di-*n*-octyl phthalate	17.253	0.948	0.867	1.044	1.185	1.234	1.393	1.439	1.559	1.454	1.535	1.493	1.441	1.448	1.311	17.71

			Concentration level (µg/mL)														
No.	Compound	RT (min)	1 (0.1)	2 (0.2)	3 (0.5)	4 (0.8)	5 (1.0)	6 (2.0)	7 (5.0)	8 (10.0)	9 (20.0)	10 (35.0)	11 (50.0)	12 (75.0)	13 (100.0)	Average	% RSD
88	Benzo[b]fluoranthene	17.874	1.270	1.076	1.203	1.300	1.342	1.438	1.385	1.488	1.469	1.535	1.480	1.518	1.588	1.392	10.60
89	7,12-Dimethylbenz[a]anthracene	17.879	0.517	0.439	0.507	0.546	0.556	0.607	0.598	0.630	0.598	0.623	0.614	0.610	0.628	0.575	10.11
90	Benzo[k]fluoranthene	17.933	1.215	1.089	1.217	1.303	1.284	1.428	1.311	1.375	1.237	1.145	1.087	0.938	0.924	1.196	12.93
91	Benzo(a)pyrene	18.489	1.119	0.945	1.072	1.176	1.159	1.298	1.240	1.319	1.223	1.275	1.216	1.194	1.214	1.189	8.45
92	3-Methylcholanthrene	19.120	0.529	0.475	0.545	0.575	0.588	0.644	0.637	0.665	0.615	0.633	0.603	0.599	0.591	0.592	8.82
93	Dibenz[a,j]acridine	20.077	0.838	0.738	0.842	0.887	0.909	0.997	0.960	1.018	0.937	0.955	0.906	0.905	0.890	0.906	8.10
94	Indeno[1,2,3-cd]pyrene	20.355	1.065	0.935	1.021	1.071	1.097	1.208	1.172	1.238	1.158	1.215	1.314	1.289	1.244	1.156	9.66
95	Dibenz(a,h)anthracene	20.414	1.067	0.945	1.050	1.108	1.130	1.232	1.196	1.245	1.134	1.111	1.034	0.998	0.968	1.094	8.72
96	Benzo[ghi]perylene	20.810	1.089	0.956	1.039	1.106	1.005	1.210	1.137	1.177	1.084	1.069	0.996	0.977	0.956	1.061	7.76

Table A2. Retention times and calculated concentrations for targets using linear regression.

			Concentration Level (µg/mL)												
No.	Compound	RT (min)	1 (0.1)	2 (0.2)	3 (0.5)	4 (0.8)	5 (1.0)	6 (2.0)	7 (5.0)	8 (10.0)	9 (20.0)	10 (35.0)	11 (50.0)	12 (75.0)	13 (100.0)
28	Benzoic acid	8.551	NA	NA	0.6	0.68	0.86	NA	4.3	8.8	19	37	51.7	77.1	97.3
			$y = 0.004829x - 0.002393$, weighting 1/x, $R^2 = 0.9983$												
51	2,4-Dinitrophenol	10.867	NA	NA	0.54	0.82	0.99	1.8	4.8	10.6	18.8	36.5	50.5	76.5	102.2
			$y = 0.00522x - 0.001372$, weighting 1/x, $R^2 = 0.9989$												
52	4-Nitrophenol	10.931	NA	0.19	0.4	0.68	0.85	1.9	4.9	9.6	18.5	30.2	45.1	76.4	99.7
			$y = 0.007200x - 8.818888 \times 10^{-4}$, weighting 1/x, $R^2 = 0.9958$												
63	2-Methyl-4,6-dinitrophenol	11.418	NA	NA	0.43	0.74	0.96	2.2	5.7	11.9	21.5	34.8	46.9	77.8	96.5
			$y = 0.005832x - 2.620849 \times 10^{-4}$, weighting 1/x, $R^2 = 0.9964$												

Table A3. Compound names, in the continuing calibration verification mixture (CCV), that failed the CCV check (±20% average RF from calibration curve) per liner, when the liner was installed and when the liner reached 20% breakdown for 4,4'-DDT.

	CCV failed compounds	
Liner number	**Liner installation/replacement**	**Compounds Failing CCV When Liner/System Reaches >20% DDT Breakdown**
Liner 1	–	Bis(2-chloro-1-methylethyl)ether 2,4-Dinitrophenol *p*-Nitroaniline *Bis*(2-ethylhexyl)phthalate Di-*n*-octyl phthalate
Liner 2	2-Methyl-4,6-dinitrophenol	2,4,6-Trichlorophenol *o*-Nitroaniline 2,6-Dinitrotoluene Pentachlorophenol Benzidine *p*-Dimethylaminoazobenzene Benzyl butyl phthalate Di-*n*-octyl phthalate Indeno[1,2,3-cd]pyrene
Liner 3	2-Methyl-4,6-dinitrophenol Benzidine	2,4-Dinitrophenol
Liner 4	2-Methyl-4,6-dinitrophenol	Benzoic acid Pentachlorophenol 2,4,6-Tribromophenol
Liner 5	2-Methyl-4,6-dinitrophenol	2,6-Dinitrotoluene *p*-Nitroaniline 2,4,6-Tribromophenol Pentachlorophenol
Liner 6	2-Methyl-4,6-dinitrophenol	*o*-Nitroaniline 2,6-Dinitrotoluene 2,4-Dinitrotoluene 2,3,4,6-Tetrachlorophenol *p*-Nitroaniline 2,4,6-Tribromophenol Pentachlorophenol Benzidine
Liner 7	2-Methyl-4,6-dinitrophenol	Benzoic acid
Liner 8	2-Methyl-4,6-dinitrophenol Benzidine	*p*-Nitroaniline 2,6-Dinitrotoluene
Liner 9	Benzoic acid 2,4-Dinitrophenol 2-Naphthylamine	Hexachlorocyclopentadiene
Liner 10	Benzoic acid *p*-Nitroaniline 2-Methyl-4,6-dinitrophenol 2,4,6-Tribromophenol Pentachlorophenol	2,4-Dinitrotoluene *p*-Nitroaniline 2,4,6-Tribromophenol Pentachlorophenol

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