Application Note

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Comparison of Fritted and Wool Liners for Analysis of Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry

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Abstract

Gas chromatography/mass spectrometry (GC/MS) is commonly used in the analysis of semivolatile organic compounds in environmental matrices. Selecting the correct liner for an analysis, such as environmental matrices with nonvolatile compounds, can lead to less downtime of the GC/MS system for maintenance by providing longer lifetimes. Typically, liners packed with glass wool or sintered frit liners are utilized for environmental analyses. This study shows that the Agilent Ultra Inert splitless low fritted liner is more resilient to a matrix challenge than splitless glass wool liners, as the sintered frit provided a significant barrier for matrix.

Introduction

Governmental regulatory authorities have established methods and performance criteria for the measurement of semivolatile organic compounds (SVOCs) identified as pollutants in environmental and industrial matrices, utilizing GC/MS systems.[1] The 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]

The GC inlet liner is an important consumable in maintaining a clean and inert GC/MS system. Deactivated liners help in preventing peak degradation in the inlet; furthermore, addition of a deactivated packing, such as glass wool or a glass frit, can provide surface area for better vaporization and a barrier to protect the GC column and MS source from complex matrices, such as soil. For these environmental analyses, injections are typically splitless injections to maximize analyte transmission to the column. Additionally, many of the analytes can be reactive to metal or active sites, which encourages the use of a single taper liner to minimize, or potentially eliminate, the interaction of the trace, active analytes with the gold seal. To maximize lifetime, minimize matrix on the head of the column, and minimize potential interaction of active analytes with metal surfaces, splitless single taper liners with glass wool or sintered glass fit are used for heavy matrix injections. This application note compares the Agilent Ultra Inert splitless low fritted liner, Agilent Ultra Inert splitless single taper with wool liner, and two other splitless single taper with wool liners with a focus on lifetime, DDT breakdown reproducibility for consistent deactivation, and the ability to re-use the calibration curve 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 nitrosamines to polyaromatic hydrocarbons (PAHs). An internal standard mixture of six deuterated PAHs was utilized 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 diluted to form calibration standards ranging from 0.1 to 100 µg/mL. Internal standards were added to each calibration standard at a concentration level of 40 µg/mL. The full list of the compounds, enumerated by retention order, can be found in a previous application note; the internal standards were listed at the end of the table out of retention order.[4]

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 prepared for method 8270 analysis, which is a representative matrix residue that is typically encountered in the lab, was procured from Pace Analytical (Mt. Juliet, TN).

Instrumentation

The Agilent 7890B GC was configured with a single MS flow path for interfacing with an inert EI ion source and 30 m Agilent J&W DB-8270D Ultra Inert column. The Agilent 5977A GC/MSD was installed with a 9 mm drawout plate. Table 1 summarizes the GC/MS instrumentation and consumables utilized in this study. Multiple liners were tested of the splitless single taper style with either glass wool or a sintered glass frit in the bottom of the liner above the taper; the specific liner styles are listed in Table 2. The GC and MSD method parameters (Table 3) have been optimized to provide an approximately 22-minute method, while retaining the required resolution for isomer pairs and following the EPA 8270 guidelines for parameters, such as scan range and scan rate.

Table 1. 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 G3440-20022)
Syringe	Agilent Blue Line 10 µL PTFE-tip plunger tapered syringe (p/n G4513-80203)
Column	Agilent J&W DB-8270D Ultra Inert, 30 m × 0.25 mm × 0.25 µm (p/n 122-9732)
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 Inserts	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)

Table 2. Liner styles and shortened names to be used in text.

Liner Information	Name to be Used in Text
Agilent Ultra Inert Splitless Low Fritted Liner (p/n 5190-5112)	Agilent frit liner
Agilent Ultra Inert Splitless Single Taper With Wool Liner (p/n 5190-2293)	Agilent wool liner
Manufacturer A Deactivated Splitless Single Taper With Wool Liner	Wool A liner
Manufacturer B Deactivated Splitless Single Taper With Wool Liner	Wool B liner

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 min; Purge 50 mL/min at 0.6 min; Switched septum purge 3 mL/min
Column Temperature Program	40 °C (hold for 0.5 min), 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 min)
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	*m/z* 35 to 500
Gain Factor	0.4
Threshold	0
A/D Samples	4

Results and discussion

System suitability and calibration

According to method 8270, the GC/MS must pass selected tests to determine suitability for quantitative analysis before samples can be analyzed. The DFTTP tuning standard, which contains DFTPP, 4,4'-DDT, pentachlorophenol, and benzidine, is included in the suitability tests to validate the MSD tune and flow path inertness. DFTPP is used to check the ionization capability and detection of the mass spectrometer. The breakdown of 4,4'-DDT to 4,4'-DDE and 4,4'-DDD is utilized to test flow path inertness, as are the tailing factors of benzidine and pentachlorophenol, where pentachlorophenol peak tailing is related to acidic activity and benzidine peak tailing indicates basic activity. If the performance criteria of method 8270 are not met, the system is unacceptable for analysis and maintenance must be performed, such as liner replacement or column trimming. Method 8270 also 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.

The system suitability results and chromatographic resolution of closely eluting structural isomer pairs for the fritted liner have been described in a previous publication.[4] The chromatographic resolution of isomer pairs for the tested glass wool liners matched the Agilent frit liner results, as this resolution is more dependent on the oven temperature parameters. Related to the isomer pair verification, the total ion chromatograms (TICs) of the 97-target compound mixture were overlaid for each liner style to verify similar peak response and are shown in Figure 1. All of these liners have a glass material as a barrier at the base of the liner, just above the taper; therefore, similar peak response was expected and

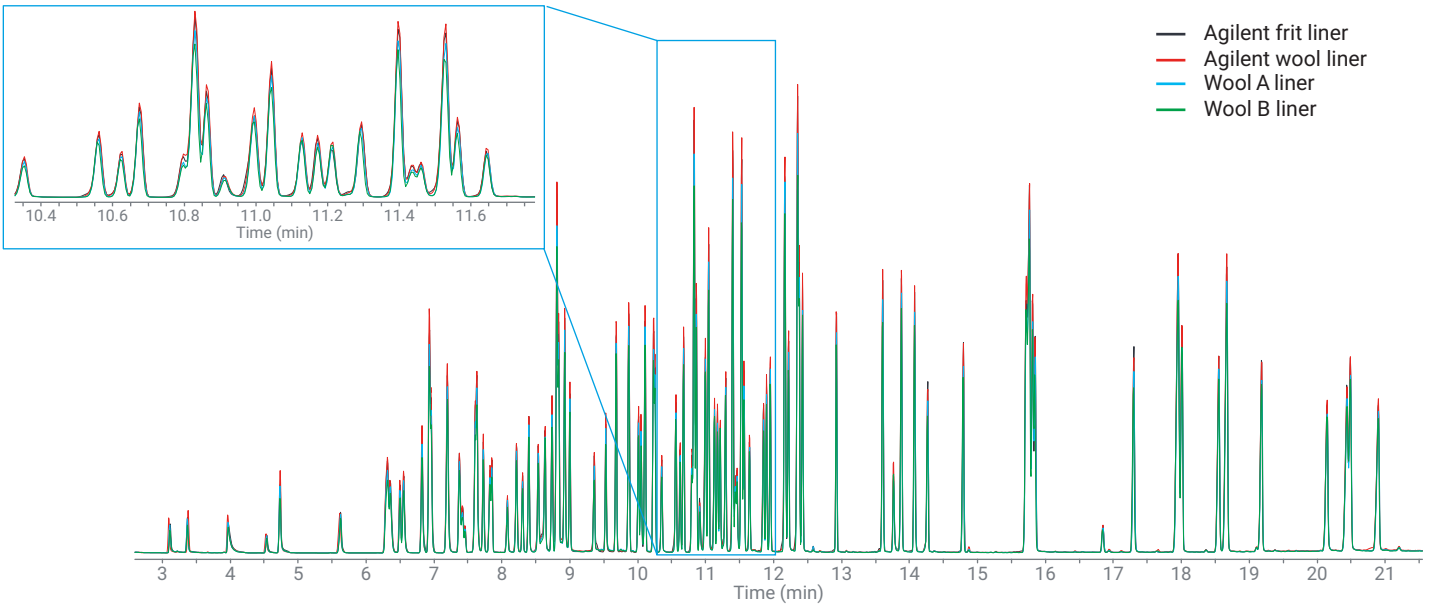

Figure 1. Total ion chromatograms (TICs) overlaid for Agilent frit liner (black trace), Agilent wool liner (red trace), Wool A liner (blue trace), and Wool B liner (green trace) at concentrations of 20 µg/mL for target compounds and surrogates and 40 µg/mL for ISTDs; inset is a magnification of the middle section of the TICs.

observed across the liners upon initial installation. The inset of Figure 1 displays the compounds eluting near the halfway point of the run to provide a closer look at the overlaid peak responses for the four liner styles.

The DFTPP tuning standard was assessed on all liners upon initial installation to verify suitability of the individual liner, and the liner style in general, for analysis. The initial DDT breakdown was averaged across five liners of each type; each liner had an initial DDT breakdown below 2.0%. The tailing factors (TF) for pentachlorophenol and benzidine were also averaged with values below 1.2 for the four liner styles, which are well below the limit of TF 2.0. Additionally, all DFTPP ion ratios passed for initial calibration (not shown here, but can be found in previous publication).[4] The average initial DFTPP tuning standard results of DDT breakdown and tailing factors are found in Table 4 for each liner style. Calibration curve data was collected on the Agilent frit liner and has been reported in a previous publication.[4] Only 4 of the 97 target compounds required linear regression to pass calibration criteria.

Matrix study

Typically, environmental testing laboratories perform preventative maintenance at regular intervals to maintain system suitability and calibration integrity. To compare the durability of the different liners, an iterative cycle of matrix injections and performance checks was completed. This study utilizes a strategy whereby matrix samples were injected until system suitability or calibration requirements failed; then, the system was restored to acceptable performance with corrective maintenance, such as a liner change. Additionally, the interchangeable use of glass frit and glass wool liners was evaluated to determine if a glass wool liner would also pass calibration criteria for a calibration curve generated on a frit liner.

The test study was gated by performance checks between 10 matrix injections, which consisted of three measurements related to specifications in method 8270E,[3] 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 90% of target compounds
- ISTD – Verify that the area of internal standard peak area drift is within a factor of 2

Prior to the first set of matrix injections for every liner, the GC/MS system was tested for system suitability and calibration verification, discussed in the previous section, using method 8270D parameters listed in Table 1. In the sequence, the QC and CCV checks were run before any matrix injections and then after every 10 matrix sample injections; the overall sequences were batched with 20 matrix injections for efficiency. After each sequence of 20 matrix injections, the QC and CCV results were reviewed. If the check runs passed, another sequence of 20 matrix runs was entered, until the QC and/or CCV checks failed. When the DDT % breakdown surpassed 20%, the inlet and turn-top were quickly cleaned with dichloromethane-soaked swabs and the liner and septum were replaced. Then, the system was retested with the QC and CCV check mixtures.

The Agilent frit liner was used to develop the first calibration curve and was the first liner subjected to matrix testing. Upon failure of QC (and/or CCV) criteria, this liner was replaced with an Agilent wool liner. Liner replacement was alternated between frit and glass wool liners to verify that the calibration curve was sufficient for the glass wool liner to pass the CCV criteria, even when the curve was generated with a glass frit liner of similar geometry. After five Agilent frit and Agilent wool liners were tested, Wool A and Wool B liners were added to the experimental set.

Five liners were tested for Wool A and Wool B liners and six liners were tested for Agilent frit and Agilent wool liners, for a total of 510 matrix injections and 788 injections overall, including solvent blanks, QC checks and CCV checks. Only the first five Agilent frit liner and first five Agilent wool liner data was utilized to calculate the averages for DDT breakdown, tailing factors, and liner lifetime. The sixth Agilent wool liner was run to check QC and CCV results after the third column trim and before running the next Wool B liner. Six Agilent frit liners were tested because a source cleaning and column replacement were required after 18 liners and 3 column trims; these factors necessitated verification of a new calibration curve on a frit liner.

Table 4. Average results for initial injections of the DFTPP tuning standard (QC check) and average lifetime by number of matrix injections for each liner style averaged across five liners.

Liner Type	Average Initial DDT % Breakdown	Average Initial Tailing Factor (TF) Pentachlorophenol	Average Initial Tailing Factor (TF) Benzidine	Average Lifetime (Number of Matrix Injections)
Agilent Frit	0.88%	1.10	1.00	24
Agilent Wool	1.94%	1.10	1.16	10
Wool A	1.06%	1.15	1.13	10
Wool B	1.02%	1.08	1.02	10

DDT breakdown was tracked to determine when the system was unsuitable for use, in which 20% breakdown was surpassed. After each liner replacement, the DDT breakdown dropped below 20% to less than 3% for all tested liners, as shown in Figure 2. Liners, and their respective DDT % breakdowns per initial and every 10 matrix injections, are displayed in the order of use in Figure 2. The average initial DDT breakdowns can be found in Table 4. Agilent frit liners had an average of 0.88% breakdown with a range of 1.10%; for Agilent wool liners, the average breakdown was 1.94%, with a range of 1.70%. For Wool A, the average was 1.06% with a range of 0.60%. For Wool B liner, the average breakdown was 1.02% with a range of 1.20%. Overall, the liners are deactivated well with few to no active sites, as shown by the consistently low initial breakdown values and narrow ranges. Residue build-up in the liner is the likely cause of 4,4'-DDT breakdown after repetitive matrix injections, since replacement of the liner restored breakdown to values well below the 20% limit (Figure 2).

DDT breakdown was the primary indicator of lifetime, where the system was no longer suitable for analysis, for each liner. Using the QC check data, specifically DDT breakdown, and CCV failures, the average lifetimes of each liner style were calculated and are summarized in Table 4. For all wool liners, 10 matrix injections were completed on average before the DDT breakdown limit of 20% was exceeded. Comparatively for the Agilent frit liners, an average of 24 matrix injections was achieved before passing the 20% breakdown limit, which is twice the glass wool liner lifetimes. The lifetime increase for glass frit liners over glass wool liners may be related to sintering the frit in place; nonvolatile matrix must permeate through the frit, rather than potentially traveling down the internal wall of the wool liners and into the head of the column.

While the EPA 8270E method states that the calibration must be verified by a midpoint standard on the calibration curve every 12 hours, this study tested the CCV standard after every 20 matrix injections, until failure by QC or CCV occurred. The calculated concentration must be within ±20% of the actual concentration for a valid calibration curve. If more than 20% of the compounds fail the 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, or more than nine compounds

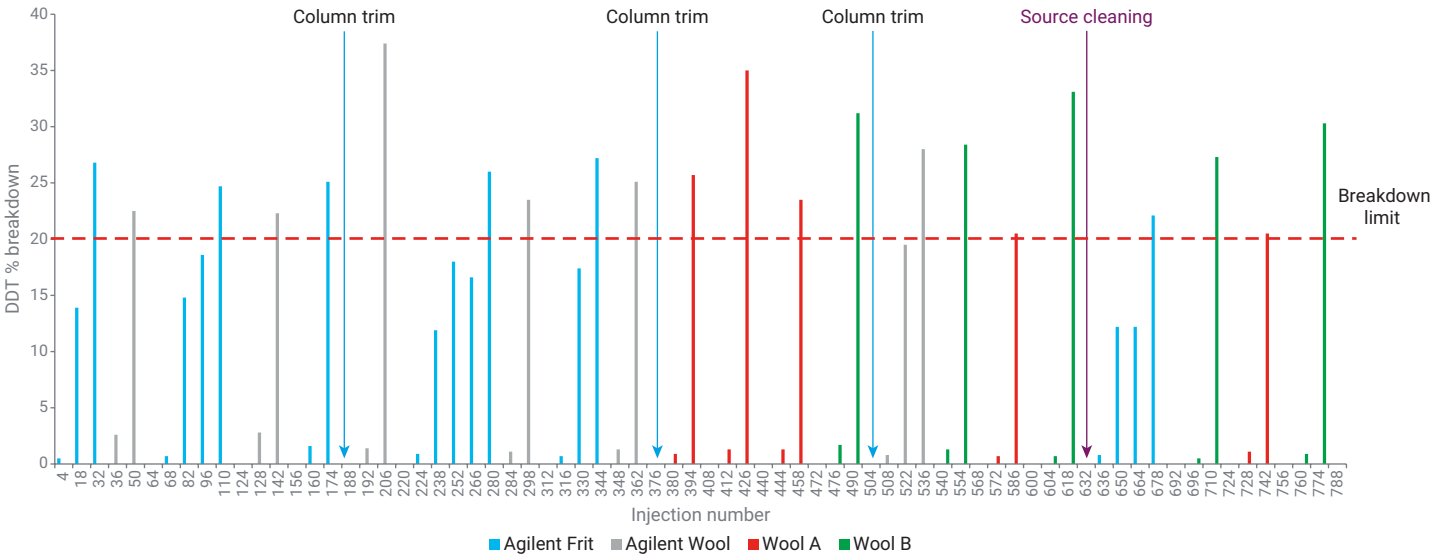

Figure 2. Breakdown and recovery of 4,4'-DDT displayed in order of use for each liner with the following colors: Agilent frit (blue), Agilent wool (gray), Wool A (red), and Wool B (green) liners. The breakdown limit of method 8270E is indicated with the dashed red line. Column trims and source cleaning are indicated with an arrow at each appropriate matrix injection number.

outside of the ±20% bounds. Figure 3 illustrates the CCV results with each liner displayed in order of use and the respective number of compounds failing for the initial QC check and after every 10 matrix injections. Based on the data, a calibration curve produced with a glass frit liner can be utilized for a glass wool liner of similar geometry. The initial CCV failures on glass frit and glass wool liners were typically less than four failing compounds, indicating that glass wool liners can be used with a frit calibration curve. After every liner change, the number of compounds failing calibration either dropped below, or remained below, the 10% study limit. In most cases, liner replacement would lower the number of compounds failing calibration, except for liner replacements after more than 376 total injections (250 matrix injections), where the number of failing compounds typically remained steady. Some liners had CCV compound failures close to the study limit; the higher number of failures occurred after matrix injections, such as nine compounds failing CCV criteria for the second frit liner after 30 matrix injections and the last Wool B liner after 10 matrix injections (at injection number 774). When the number of CCV failures increased significantly with more matrix injections or remained above four failing compounds for an initial CCV injection, a column trim was considered. CCV failure only occurred with the 18th liner overall, which was the second Wool B liner, with 11 CCV compounds failing the calibration check. Additionally, *m/z* 127 ion ratio of the DFTPP compound failed on the final QC check for this liner, resulting in the source cleaning. For most of the later liners and matrix injections, the failure rates remain below the 10% study limit, but the initial failure rates may be higher than previous values because matrix had migrated onto the column and reached the source. This explanation is probable, as the CCV failures dropped to zero and DFTPP ion ratios passed after the source was cleaned and the column and liner were replaced.

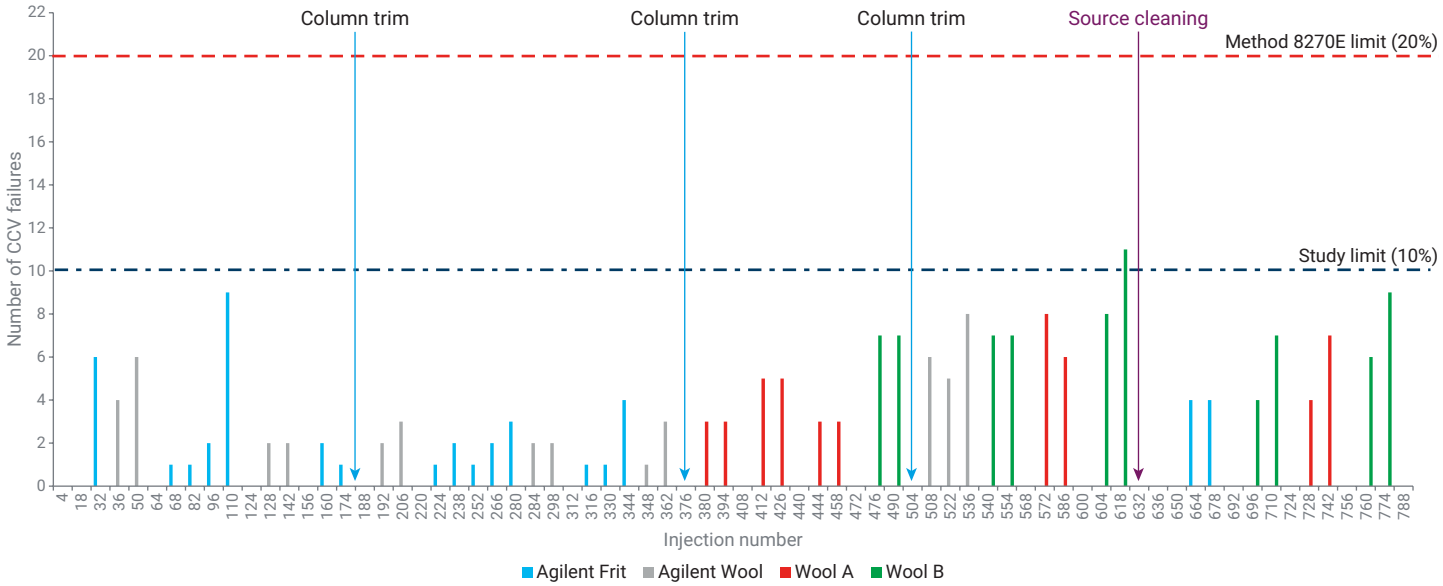

Figure 3. Number of CCV failures displayed in order of use of each liner with the following colors: Agilent frit (blue), Agilent wool (gray), Wool A (red), and Wool B (green) liners. The method 8270E limit is indicated with the dashed red line; the study limit of 10% is marked by the dot-dash blue line. Column trims and source cleaning are indicated with an arrow at each appropriate injection number.

Conclusion

This study shows that the Ultra Inert splitless low fritted liner is resilient to a matrix challenge, as the sintered frit provided a significant barrier for matrix. The fritted liner maintained the longest average lifetime of 24 matrix injections, which was more than twice the lifetimes of the glass wool liners. All splitless single taper liners with glass frit or wool show consistent deactivation, as all had low 4,4'-DDT % breakdown below 2% on average, with new liner installations. Liners of similar geometry and barrier material (e.g., glass frit and glass wool) have similar peak responses for this EPA 8270 analysis and can utilize the same calibration curve.

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