Analysis of Semivolatiles by GC/FID using the Ultra Inert Inlet Liners with Wool

Application Note

Environmental

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Abstract

With efficient deactivation on glass wool, the Ultra Inert liners with wool provide superior inertness for accurate analysis of semivolatile analytes by GC/FID, homogeneous sample mixing and evaporation, and maximum column and detector protection.

Agilent Technologies

Introduction

GC inlet liners are the centerpiece of the inlet system in which the sample is vaporized and mixed with the carrier gas, and then introduced to the capillary column. Inlet liners with wool have been used widely due to the benefits provided by glass wool. The wool inserted into liners can promote homogenous sample mixing and better quantitation. It provides a large surface area which aids the vaporization of liquid samples. It also acts as a trap to collect non-volatile residue in the sample, therefore protecting the GC column from the negative impacts of sample matrix. Liners with wool also prevent sample from hitting the bottom of the inlet before vaporization. However, the use of liners with wool has historically been greatly limited because of the high activity due to the large surface area and poor deactivations on glass wool, especially for the labile analytes, such as pesticides, active acidic and basic compounds. Traditional deactivation techniques usually cannot deactivate the glass wool surface area effectively. Active sites left on the wool can cause the degradation or adsorption of sensitive compounds in the liner before the analytes get to the column. This complicates quantitation, results in peak tailing or splitting, and can be particularly problematic for sensitive analytes. As a result, inlet liners with glass wool are usually not recommended for the analysis of active analytes.

USEPA Method 8270 has been used widely to determine the concentration of semivolatile organic compounds in the environment. Samples using this method usually contain a mix of acids, bases, and neutrals that must be measured concurrently. This test is a challenge for GC/MS instrumentation due to the interaction of the analytes with the surface of sample flow path, where the inlet liner can be a significant contributor to system activity. The active sites on the liner surface can cause unwanted absorption of these compounds and lead to the loss of system response. The most active compounds, the nitrophenols, showed lower response factors (RFs) at the low concentrations causing poor calibration curve linearity and low analytes sensitivity. This effect can be magnified when using liners with glass wool. With the wool liners, the responses for the sensitive analytes at lower levels (< 20 ppm) may completely disappear, which leads to very poor calibration curve linearity and failure of the run.

Agilent's Ultra Inert liner deactivation process significantly improves the efficiency and robustness of glass wool deactivation. The large glass wool surface area can be deactivated thoroughly. The Ultra Inert deactivation technique enables the use of Ultra Inert liners with wool for the analysis of sensitive semivolatile organic compounds using the EPA 8270 method. In this evaluation, the test mix includes representative difficult compounds in the 8270 method: N-nitrosodimethylamine, aniline, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-aminobiphenyl, pentachlorophenol, benzidine, 3,3-dichlorobenzidine, benzo[b]fluoranthene, benzo[k]fluoranthene. This test mix was used previously for the USEPA 8270 method improvements on the Agilent GC/MSD system. [1] All liner experiments were conducted using an FID to facilitate better comparisons because of the reproducibility of compound response over time. A calibration curve from 2 – 80 ng on column was used for linearity evaluation. In addition, the 10-day thermal stability at 330 °C and 100 injections repeatability was investigated.

Experimental

Standards and Reagents

EPA 8270 customized standard and internal standards were obtained from Ultra Scientific (North Kingstown, RI, USA). Ultra Resi-analyzed grade Methylene Chloride was from J. T. Baker (Phillipsburg, NJ, USA).

Solutions and Standards

The 8270 custom standard was purchased as 2000 µg/mL mixture in methylene chloride. Series calibration standards were prepared at 2, 5, 20, 40, and 80 µg/mL by appropriate dilution with methylene chloride. The 8270 semivolatile internal standard (IS) mixture at 4000 µg/mL in methylene chloride was spiked into standards with appropriate volume to generate constant 40 µg/mL IS concentration.

Instrumentation

All testing was done on an Agilent GC equipped with an Agilent 7683B autosampler and FID. Table 1 list the instrumental conditions used on this test and Table 2 lists flow path consumable supplies used in experiments.

Table 1. Instrumental Conditions for Agilent GC/FID System used for Semivolatile Active Compounds Test

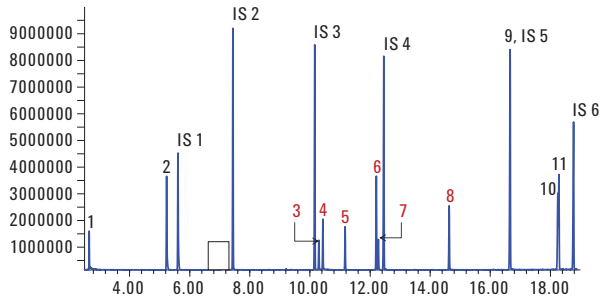
Autosampler	Agilent 7683B, 5 µL syringe (Agilent p/n 5181-5246), 1 µL injection volume. Preinj solvent A (methylene chloride) washes: 1 Sample pumps: 3 Postinj solvent B (methylene chloride) washes: 3
Carrier gas	Helium at 3 mL/min constant flow
Inlet	Splitless mode; 250 °C, 30 mL/min purge flow at 1.5 min
Analytical column	Ultra 2 column, 25 m × 0.32 mm, 0.52 µm, (p/n 19091B-112)
Oven profile	40 °C (1 min), 15 °C/min to 310 °C (0 min)
Detector	FID, 250 °C, H_2/Air/Makeup N_2: 40/450/45 mL/min

Table 2. Flow Path Supplies

Vials	Amber screw cap (Agilent p/n 5182-0716)
Vial caps	Blue screw cap (Agilent p/n 5182-0717)
Vial inserts	150 µL glass w/ polymer feet (Agilent p/n 5183-2088)
Septum	Advanced Green Non-Stick 11 mm (Agilent p/n 5183-4759)
Ferrules	0.5 mm id, 85/15 Vespel/graphite (Agilent p/n 5062-3514)
O-rings	Non-stick Flip-Top Liner O-ring (Agilent p/n 5188-5366)
Inlet liners	Agilent Ultra Inert deactivated single taper splitless wool liner (5190-2293)
Inlet seal	Gold plated inlet seal with washer (Agilent p/n 5188-5367)

Results and Discussion

The purpose of these tests is to evaluate the Ultra Inert liners with wool for the analysis of EPA 8270 semivolatile analytes. Although liners with wool can provide protection to the column and detector system from complicate environmental samples, they are usually not recommended for sensitive analytes analysis due to un-controlled activity of glass wool caused by large surface area and inefficient liner deactivation. The Agilent Ultra Inert deactivation process enables the application of Ultra Inert deactivated liners with wool for the analysis of sensitive semivolatile organic compounds. FID was used purposely as the detector to eliminate any activity contributed from the mass spectrometer. A previously established test mix [1] was used, which includes four phenols, several bases, and several neutral components. These compounds were selected to not only represent 8270 active analytes, but also to be resolved easily, and unambiguously detected by GC/FID. Figure 1 shows a sample chromatogram of the test mix. The feasibility of using Ultra Inert liners with wool was determined by the linearity of the practical calibration curve, the reproducibility among liners, the thermal stability at high temperature, and the precision of replicate injections. In parallel, competitor's equivalent liners with wool were tested for calibration curve linearity comparison.



1	N-Nitrosodimethylamine (N-NDMA)	7	Pentachlorophenol (PCP)	IS 1	Dichlorobenzene-d4
2	Aniline	8	Benzidine	IS 2	Naphthalene-d8
3	2,4-Dinitrophenol (2,4-DNP)	9	3,3-Dichlorobenzidine	IS 3	Acenaphthene-d10
4	4-Nitrophenol (2,4-DNP)	10	Benzo(b)fluoranthene	IS 4	Phenanthrene-d10
5	4,6-Dinitro-2-methylphenol (4,6-DN-2-MP)	11	Benzo(k)fluoranthene	IS 5	Chrysene-d12
6	4-Aminobiphenyl (4-ABP)			IS 6	Perylene-d12

Figure 1. A sample chromatogram of 8270 short test mix with peaks identification.

Calibration curve linearity and liner to liner reproducibility

A linear calibration curve for target analytes is critical to achieve accurate and reliable quantitative analysis results. The EPA 8270 method does not specify a calibration range, yet traditionally a dynamic range of 20 to 160 ng on column has been widely used in USEPA Contract Lab Program (CLP). With the increased sensitivity of newer GC/MS systems, users are moving toward lower detection limits. Therefore, a calibration range of 2 to 80 ng on column was chosen for this test. The 2 ng on column quantitation limit gave satisfactory response and peak shape on FID with S/N ratio greater than 20. In order to evaluate the compounds linearity over the calibration curve range, the response factors (RFs) at each calibration level were calculated as **Equation 1**. The overall RF values across the curve were used to calculate the relative standard deviation (RSD).

$$RF = \frac{Peak\ Area_{Analyte} \times Concentration_{Internal\ Standard}}{Peak\ Area_{Internal\ Standard} \times Concentration_{Analyte}} \qquad \textbf{(Equation 1)}$$

The higher the RF values, the higher the analyte responses and better peak intensity; and the lower the RSD value across the calibration range, the better the calibration curve linearity. According to USEPA 8270 method requirement [2], the RSD for each target analyte should be less than 20%. As an FID was used as the detector instead of a MSD, RFs are not identical for MSD and FID due to inherent response differences. Figure 2 shows the average FID RF values across the calibration range of 2-80 ng on column and RSDs for the selected representative active 8270 analytes. Each of the bars shows the average RF of seven tested liners for the corresponding analyte at each level as described in the legend in Figure 2. The order is 2 ng at the top increasing to 80 ng at the bottom. Above each bar is listed the average RF and RSD values across the calibration range of 2–80 ng on column. 3,3-Dichlorobenzidine data is not available due to its complete co-elution with IS peak 5, chrysene-d12 (Figure 1). It has to be mentioned that longer splitless time (1.5 min) with 30 mL/min of purge flow was used for the test. This longer splitless time allows a more complete transfer of target analytes onto the column at a fixed flow .

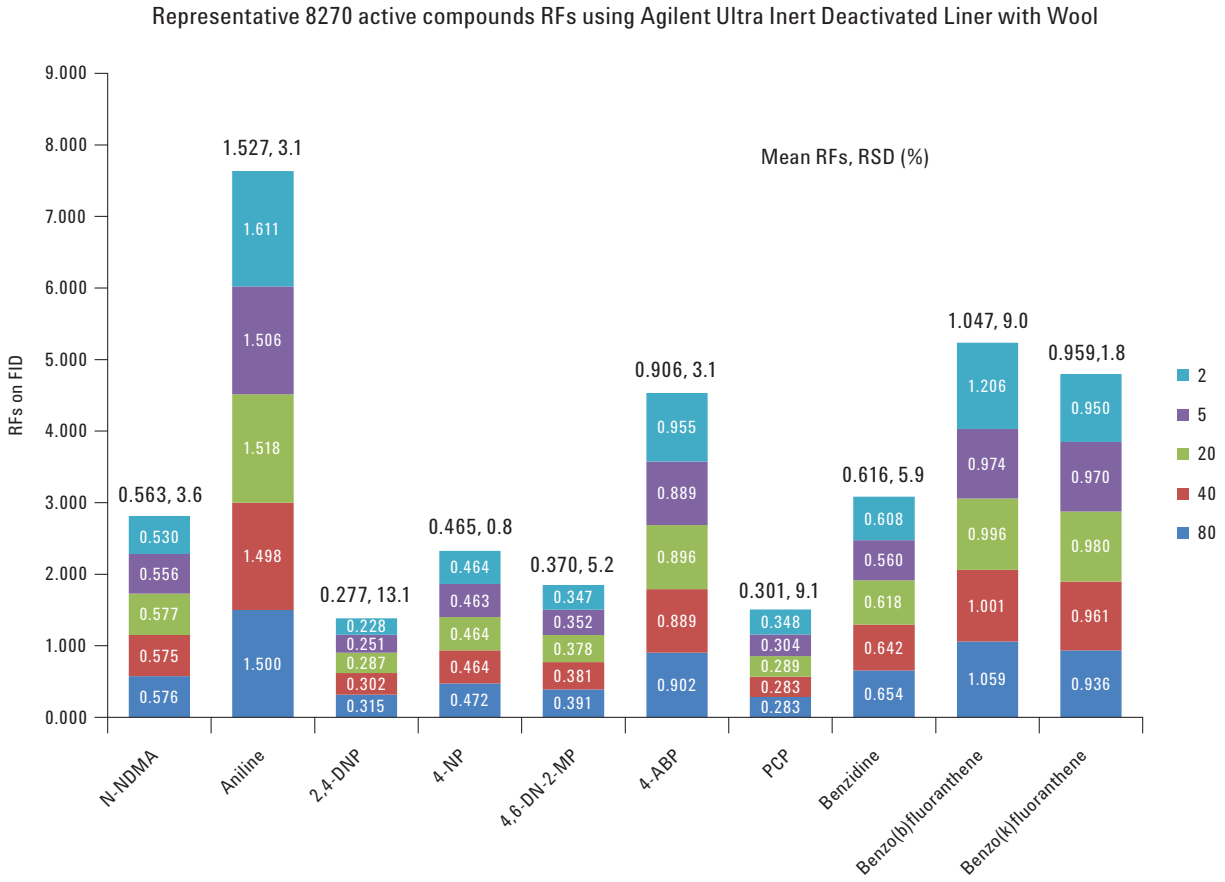


Figure 2. The 8270 representative active analytes RFs (FID) over calibration range (2-80 ng on column) using Agilent Ultra Inert deactivated liners with wool (p/n 5190-2293). (# liners = 7)

All compounds meet the EPA method requirement with less than 15% RSD, including the most problematic compound, 2,4-DNP which had an average RF value of 0.277 with 13.1% RSD, across seven of the Ultra Inert wool liners. The liner to liner performance is reproducible with excellent consistency.

Table 3. 2,4-DNP Average RF (on FID) and RSD Values for Seven Replicates of Agilent Ultra Inert Deactivated Liners with Wool (p/n 5190-2293) from Four Different Lots

Liner	Lot	Average RF over 2 – 80 ng on column	RSD (%)
UI wool liner 1	Lot 1	0.271	14.7
UI wool liner 2		0.266	13.8
UI wool liner 3	Lot 2	0.274	14.9
UI wool liner 4		0.279	10.3
UI wool liner 5	Lot 3	0.286	9.5
UI wool liner 6		0.283	11.8
UI wool liner 7	Lot 4	0.269	10.3

Table 3 shows the average RF and RSD values for seven replicates of Ultra Inert liners from four different lots.

Multi-injection repeatability and thermal stability at high temperature

Multi-injection repeatability was tested by continuously injecting 1 µL of 5 µg/mL standard samples for 100 injections. Data were collected and RF values were calculated after every 10 injections. Figure 3 shows repeatability over 100 injections with 5 ng on column. The results indicate that excellent repeatability can be achieved with Ultra Inert liners with wool, with less than 6% RSD RF values over 100 injections. Two calibration curves were run before and after 100 injections. The two curves match each other, and no curve diversion was observed for any target active compound. Figure 4 shows representative 2,4-DNP calibration curves before and after 100 injections.

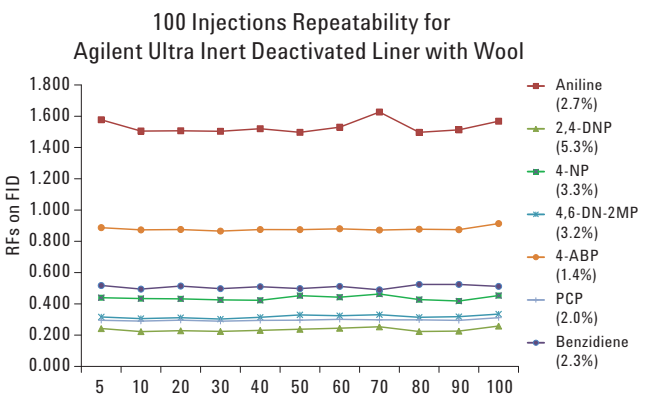


Figure 3. The 100 injections repeatability for Agilent Ultra Inert deactivated liner with wool (p/n 5190- 2293), less than 6% RSD achieved for all of active 8270 analytes over 100 injections with 5 ng on column.

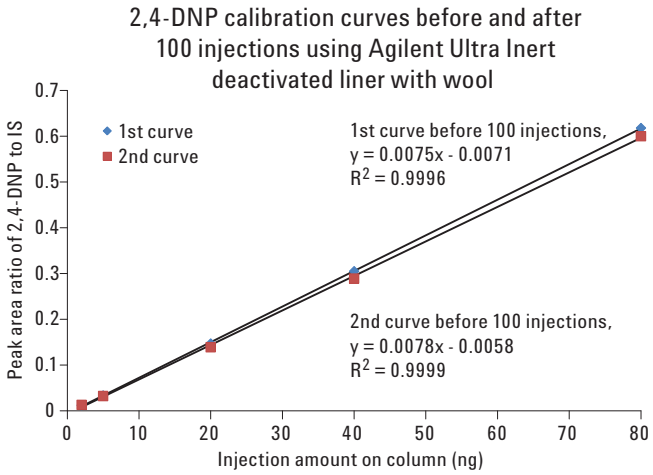


Figure 4, The 2,4-DNP calibration curve before and after 100 injections using Agilent Ultra Inert deactivated liner with wool (p/n 5190-2293).

The thermal stability of Ultra Inert wool liners was tested by keeping the liner in the inlet at 330 °C for 10 days. On each day, two 1 µL injections of 5 µg/mL standards were run, data were collected and RF values were calculated. Ten day RF variability for active analytes is shown in Figure 5. Results indicate that the Ultra Inert deactivated liner with wool is thermally stable at an inlet temperature of 330 °C with RSD less than 7% for active analytes.

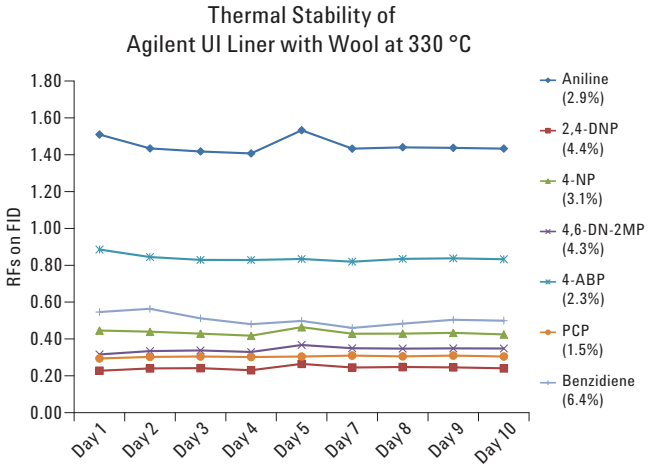


Figure 5. 10-day thermal stability at 330°C for Agilent Ultra Inert deactivated liner with wool (p/n 5190-2293), less than 7% RSD achieved for all of active 8270 analytes over 10-day test at 5ng on column.

The results of the multiple injections and thermal stability test demonstrate the excellent stability of Ultra Inert deactivated liner with wool allowing for more samples to be run over a longer time period, and reducing downtime for maintenance. With better protection to the analytical column and detector, the Ultra Inert liner with wool supports the longevity of the whole system for quantitative analysis.

Performance comparison against competitors' equivalent liners

The performance comparison was conducted by comparing the Ultra Inert liners with wool with similar competitors liners and equivalent configuration, including Restek Siltek, Restek IP SemiVolatile, and Restek Sky liners. To show the liner performance differences, besides 2,4-DNP, several other compounds were compared in detail including 4,6-dinitro-2-methylphenol, 4-aminobiphenyl, pentachlorophenol, and benzidine. These compounds are problematic compounds mentioned in EPA 8270 method [2].

As shown in Table 4, the Ultra Inert liners with wool usually provide the lower RSD and higher average RF values through the calibration range, indicating the excellent linearity of calibration range and better system sensitivity. The Ultra Inert liners perform much better than Restek Siltek deactivated wool liner, and equivalent or slightly better than Restek IP deactivated SemiVolatile and Restek Sky wool liner.

Comparisons between UI deactivated liner with wool and liner without wool

It was demonstrated previously that the single taper splitless liners without wool showed excellent performance for the active semi-volatile compounds analysis.[1,3] The direct connect liners has been recommended for clean samples also with minimal inlet activity.[1] However, use of these liners potentially subjects the column to more degradation and the detector to more contamination from dirty samples. The addition of wool in the liner can efficiently protect the column and detector (MS source) by trapping the high boiling material and other interferences from sample matrix. However, the inertness of wool liners is always a concern due to the large surface area of glass wool and inefficient deactivation on wool. The Agilent Ultra Inert liner deactivation technique provides efficient and robust deactivation on the glass liner body as well as glass wool, enabling the use of wool liners for active compounds analysis. Figure 6 shows parallel comparison results between Ultra Inert liners with wool and liners without wool but with the same liner configuration (single taper, splitless). The results demonstrate that the Ultra Inert liners with wool provide equivalent performance as liners without wool to support quantitative analysis of active semivolatile analytes. With other benefits provided by wool liners such as homogeneous sample mixing and efficient liquid vaporization, and protection to column and MS source, Agilent Ultra Inert liners with wool can be the best choice for samples with complicated matrices.

Table 4. Liners Performance Comparison with Competitors' Equivalent Liners for Calibration Range of 2-80 ng on Column Using GC/FID

		Wool Liners			
Compounds		**Agilent Ultra Inert Deact. (n=7)**	**Restek Siltek Deact. (n=4)**	**Restek IP Deact. SV (n=4)**	**Restek Sky (n=3)**
2,4-DNP	Average RF	0.277	0.230	0.270	0.285
	RSD (%)	13.1	29.7	15.7	14.6
4,6-DN-2-MP	Average RF	0.370	0.342	0.375	0.377
	RSD (%)	5.2	14.6	6.8	7.6
4-ABP	Average RF	0.906	0.768	0.925	0.904
	RSD (%)	3.1	20.1	5.8	1.0
PCP	Average RF	0.301	0.320	0.323	0.300
	RSD (%)	9.1	13.7	15.3	6.9
Benzidine	Average RF	0.616	0.458	0.619	0.594
	RSD (%)	5.9	25.1	9.1	10.1

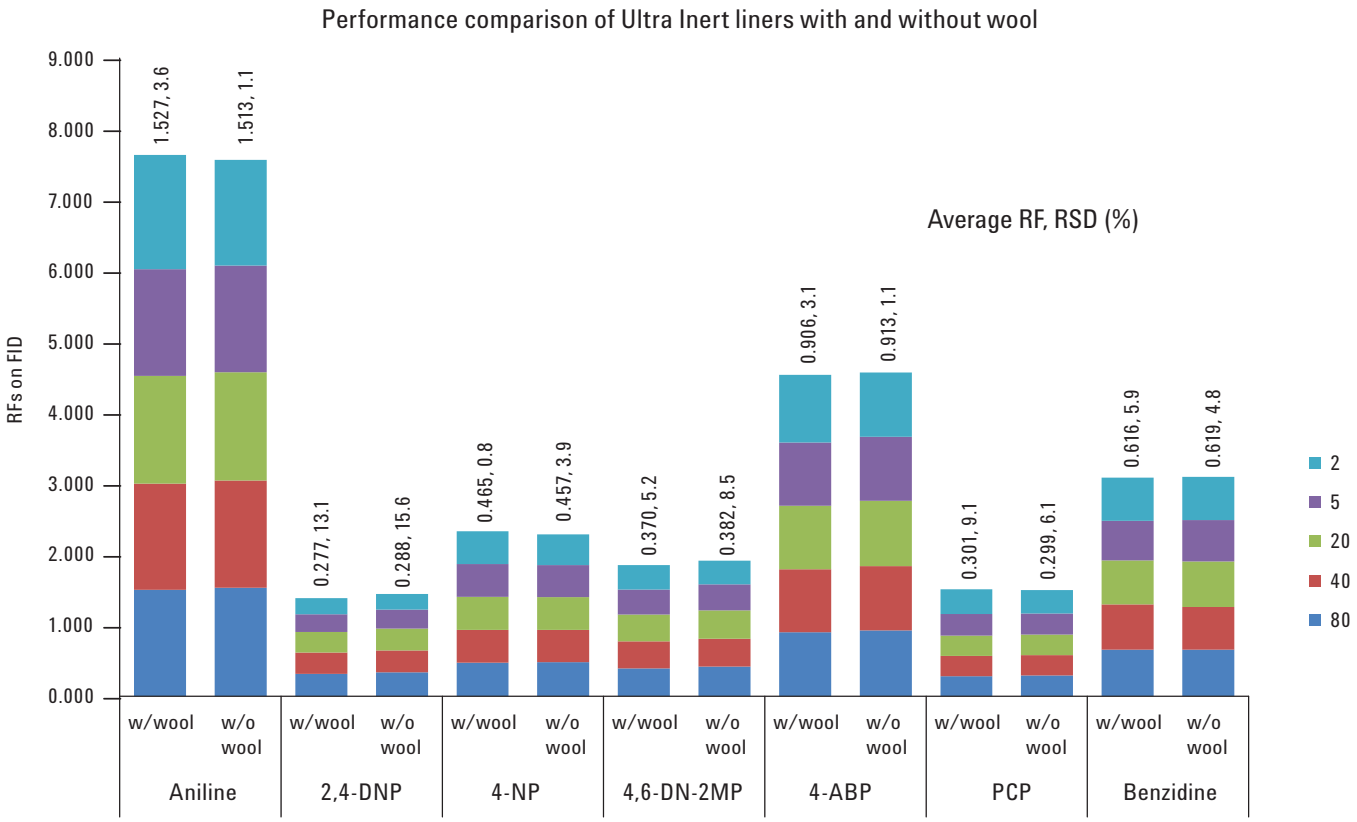


Figure 6. Performance comparison of Agilent Ultra Inert deactivated liner with wool (p/n 5190-2293) and Ultra Inert deactivated liner without wool (p/n 5190-2292).

Conclusion

Agilent Ultra Inert liners with wool have shown excellent inlet inertness to support the quantitative analysis of EPA 8270 semi-volatile active analytes. The linearity of the calibration curve meets the EPA method requirement of <20% RSD for all of active analytes even down to 2 ng on column. The thermal stability at 330 °C of the deactivated wool liner was evaluated with great consistency over 10 days. Multi-injection repeatability over 100 injections for all active compounds was excellent with less than 6% RSD. With efficient and robust deactivation of the wool, Agilent Ultra Inert liners with wool provide excellent inertness for accurate quantitative analysis of semi-volatile active analytes. Because liners with wool provide other benefits like homogeneous sample mixing and evaporation, non-volatile residue trapping, and column and detector protection, Ultra Inert liners with wool are the best choice for the analysis of active compounds in dirty sample matrix.

References

1. M. Szelewski, B. Wilson, P. Perkins, "Improvements in the Agilent 6890/5973 GC/MSD system for Use with USEPA Method 8270." Agilent Technologies publication 5988-3072EN.
2. USEPA 8270D method, http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8270d.pdf
3. L. Zhao, A. Broske, D. Mao, "Evaluation the New Agilent Ultra Inert No Wool Liners for Active Compounds Analysis by GC." Agilent Technologies pubilication 5990-7380EN.

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