

Optimizing Injection Port Conditions for the Analysis of Semivolatile Organics.

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Background

Split and splitless injections introduce the sample into a heated injection port as a liquid where it is rapidly and completely vaporized along with the analytes in the sample. The vaporized sample condenses at the head of the column along with the solvent. In split injection mode only a small amount of the vaporized sample is transferred onto the head of the column, the remainder of the sample and solvent is removed via the split vent line. The use of split injection minimizes analyte breakdown since compounds spend less time in the hot injection port, however, loss in sensitivity is observed since much of the sample exists the split vent line. In splitless injection the split valve is closed long enough to allow most of the vaporized sample and solvent in the injection port liner to be transferred to the analytical column which can take anywhere between 30 and 90 seconds. This work will demonstrate optimized conditions for a broad range of semivolatile compounds using methylene chloride as a solvent and feature the benefits of split injection for the analysis of semivolatiles.

Liner Deactivation

Inlet liners are made of borosilicate glass and contain active sites which can be identified as various forms of silanols including mono, geminal and vicinal. In addition, trace metallic impurities are commonly present. The goal of the liner deactivation is to provide an inert high-temperature coverage of these active sites. The liner used in this application is a Topaz liner which is deactivated using a chemical vapor deposition process with a proprietary deactivation reagents resulting in excellent coverage of active sites and high lot to lot reproducibility.

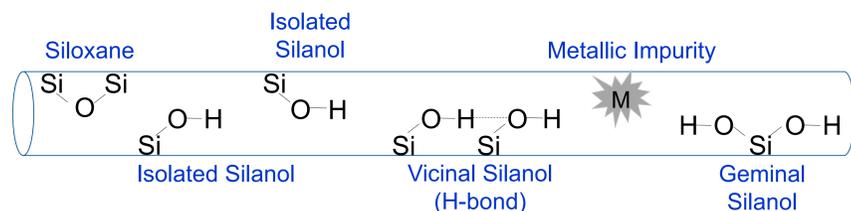


Figure 1: Examples of common surface sites found in the glass liner

Liner Glass Wool

Wool is recommended due to its high surface area which promotes vaporization, enhances mixing with the carrier gas reducing variability and protects the column from non-volatile matrix compounds. There are two types of glass wool: borosilicate and quartz, with quartz having less metal impurities. Topaz liners contain quartz wool which is placed in the liner prior to the deactivation process, which reduces the probability of broken fibers which exposes active silanols.

Liner Lot Testing

Each lot of liners are tested using Endrin, DDT (Figure 2), 2,4-Dinitrophenol and Carbaryl to ensure low breakdown for accurate and precise pg-levels of analysis.

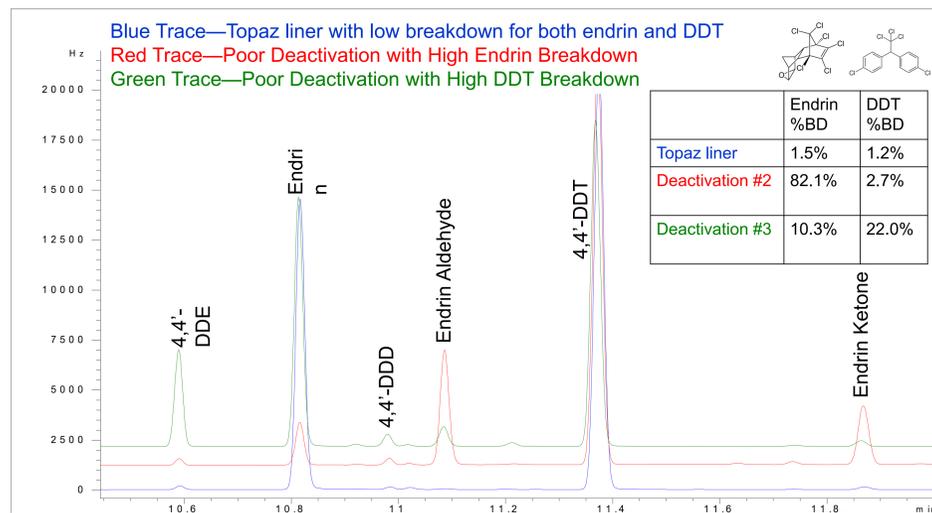


Figure 2: Example of the effect of deactivation quality using endrin and DDT as probes at 50 and 100 pg on-column concentration.

Split versus Splitless Injection for Low Level Testing

Split analysis, not surprisingly, produces good peak shapes and lower response when compared to the splitless injections. Since the boiling point of methylene chloride is 40°C it is not possible to perform solvent focusing by starting the oven temperature at 20°C below the boiling point of the solvent without cryogenic cooling. Performing a classical splitless injection with a 0.5-minute hold time results in split and tailing peak shapes for pyridine, 1,4-dioxane & N-nitrosodimethylamine. Only the splitless hold time of 0.15 minutes produced an acceptable peak shape with an area not much greater than that of the 10:1 split analysis. Using previously published optimized splitless pulse conditions produce the best results, however, Figure 4 illustrates the system can continue to pass continuing calibration verification checks (CCV) for a longer period of time when using split injection.

Semivolatile Compound	SPLIT (10:1)		SPLITLESS (0.5 min)	
	%RSD Area (n=5)	%RSD Area (n=5)	%RSD Area (n=5)	%RSD Area (n=5)
Pyridine	3.1	8.0		
Phenol	2.0	10		
N-Nitroso-di-n-propylamine	3.1	7.6		
2,4-Dichlorophenol	2.4	6.3		
Naphthalene	1.6	6.1		
Hexachlorocyclopentadiene	1.7	5.1		
2-Nitroaniline	2.7	4.0		
Acenaphthylene	1.3	5.4		
2,4-Dinitrophenol	6.8	9.5		
4-Nitrophenol	5.8	5.3		
4,6-Dinitro-2-methylphenol	5.7	6.4		
N-Nitrosodiphenylamine	2.2	5.3		
Pentachlorophenol	2.0	1.5		
Phenanthrene-d10	1.0	5.0		
Phenanthrene	1.2	6.2		
Perylene-d12	0.84	8.7		
Benzo(ghi)perylene	3.1	33		
Overall Average	2.6	7.5		

Figure 3: Average (n=5) relative response factors (RF) at 0.5 ng on-column illustrating better reproducibility using a split injection.

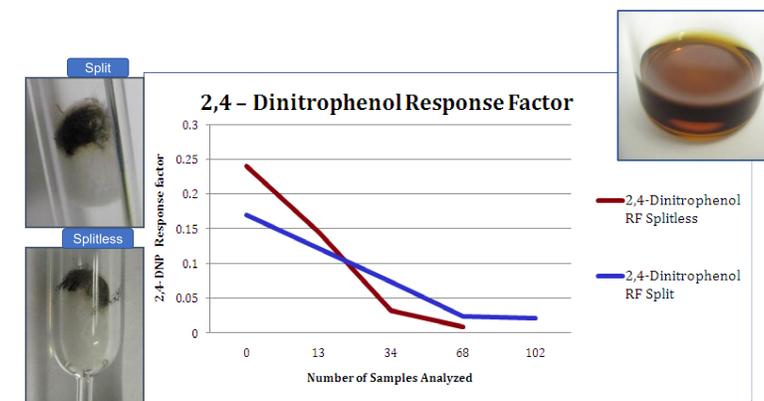


Figure 4: A soil extract from a leaking underground storage tank (LUST) was provided by Fairway Laboratories. Repeated injections of this standard demonstrates 2,4-dinitrophenol response remains higher using split injections.

Low-level Calibration for Sensitive Instruments

Split Method: Using a 10:1 Split: Sixty-three challenging acidic, basic, and neutral compounds were calibrated according to EPA method 8270E by GC-MS/MS at 0.5-5000 ppb. Linear (no-weighting) calibrations were fit to each compound to compare linearity at low levels. Peak symmetry was evaluated at 50 ppb, which served as a mid-range calibration point for most compounds. Linearity and peak shape was assessed on four additional 5-type (silarylene) columns, and linearity parameters (R2, RRF RSD) was assessed for each column. A suite of >150 semivolatiles (with surrogates and internal standards) was assessed on the RMX-5SiI MS to demonstrate peak shape and clarity at low-pg amounts on column to demonstrate versatility of the RMX-5SiI MS surface for challenging compounds.

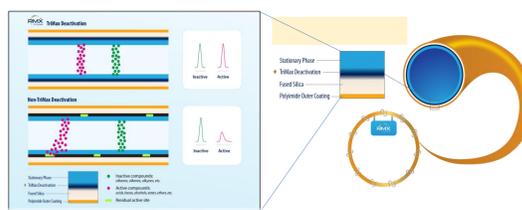


Figure 5: Highly effective deactivation protects analytes from surface interactions, improving peak shape for a wide range of compound chemistries.

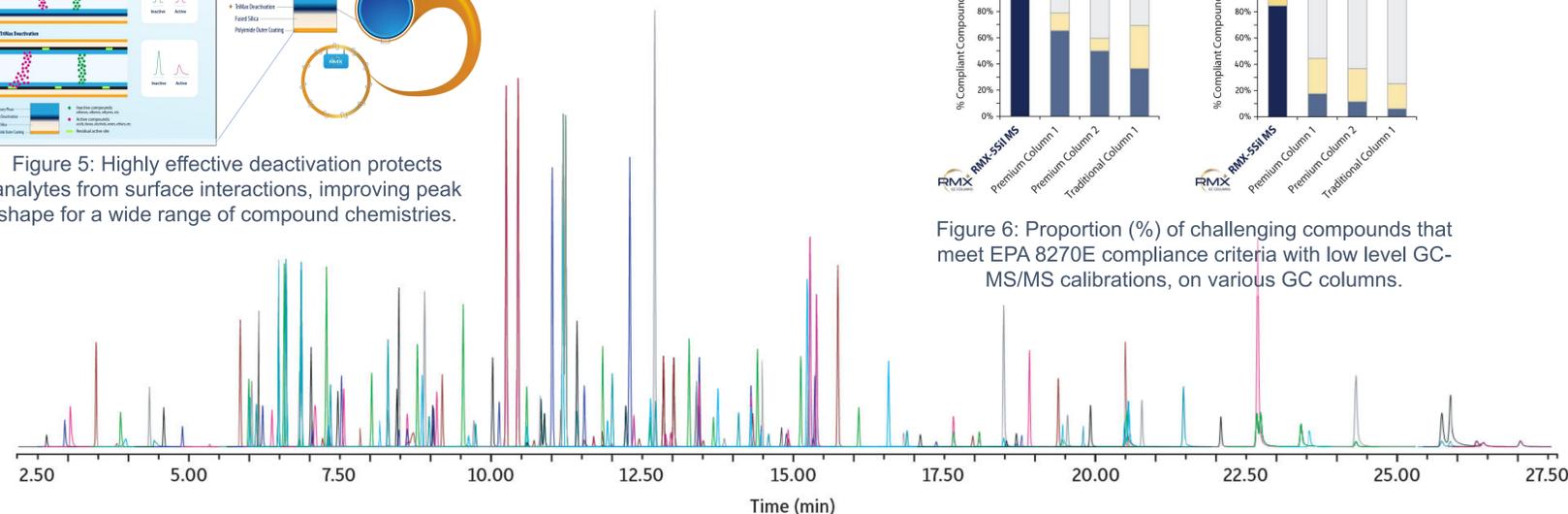


Figure 7: GC-MS/MS of over 150 semivolatiles (10 pg on column) using a 10:1 split injection, comprised of acidic, basic, and neutral compounds with a variety of functionalities.

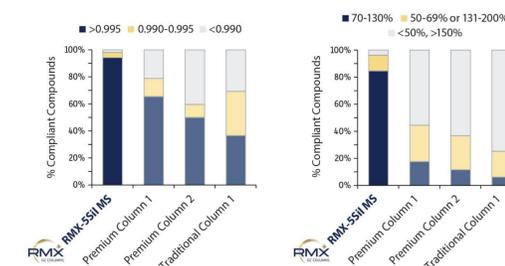


Figure 6: Proportion (%) of challenging compounds that meet EPA 8270E compliance criteria with low level GC-MS/MS calibrations, on various GC columns.

Conclusions

Analyzing picogram levels of semivolatile compounds requires optimized conditions, a highly inert sample pathway and instrumentation capable of trace detection. The use of a properly deactivated wool liner in split mode combined with a highly inert column produces excellent peak shape, increase response, and good reproducibility.