DEVELOPMENT OF A NEW LOW BLEED COLUMN FOR GC-MS ANALYSIS

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Introduction

We have developed a low-bleed column for GC-MS use, the Supelco Low Bleed 5 ms (SLB™-5ms), that incorporates a combination of silphenylene polymer synthesis, a proprietary surface deactivation chemistry, and innovative manufacturing processes. The resulting column was found to be highly reproducible, have minimal MS bleed, adequate inertness, and to be stable for extended periods at high temperature. This work summarizes the bleed, inertness, and durability characteristics of this column.

Today's mass spectral detectors (MSDs) are designed for high sensitivity. High bleed columns can interfere with low level detection and proper peak identification. Excessive bleed can also contaminate the ion source, resulting in more frequent cleaning.

US EPA Method 8270 poses several special challenges. The widely varied compound list and calibration requirements of this method require a column with both low bleed characteristics and appropriate inertness. We used typical method 8270 run conditions and a low level standard containing many of the compounds analyzed by this method in assessing the performance of this column. Specifically, we measured column bleed detectable by MS, inertness for several problematic 8270 analytes, and column durability.

Materials and Methods

MS bleed was measured using two different methods. The first was a direct measure of the total ion current (TIC) at 325 °C, which was the maximum temperature of our 8270 analysis. The second method was a calculation of the percentage of m/z=207 to m/z=276 in the mass spectrum of benzo(g,h,i)perylene, which elutes at 325 °C. m/z=207 is an ion resulting from column bleed, while m/z=276 is the base peak in the mass spectrum of the benzo(g,h,i)perylene. This second method enabled us to determine the amount of spectral interference present from column bleed, and to take into account fluctuations in sensitivity of the MS system over the testing period.
All bleed testing was done using 30 m x 0.25 mm I.D. x 0.25 µm columns.

Results and Discussion

Figure A shows a comparison of the MS bleed as TIC between our new low bleed MS column, the SLB-5ms, and several other MS columns currently available on the market. The upper temperature limit of the analysis was 325 °C. Figure B is the spectrum of the late eluting peak benzo(g,h,i) perylene on the same SLB-5ms. This peak eluted at 325 °C. Note the low level of the bleed ion, m/z=207, compared to the analyte's ions m/z=276, m/z=138, and m/z=277. These later two ions, called qualifiers, are used to help identify the peak.
Figure C is a comparison between the percentage m/z=207 vs. m/z=276 in the MS spectrum of benzo(g,h,i)perylene on three different SLB-5ms columns, two older Supelco products, and the competitive MS columns from Figure A. The level of m/z=207 in the MS spectrum taken from competitive column A was actually higher than the qualifier ion m/z=138.

Figure A. GC-MS Bleed as TIC, 5 ng Method 8270 Standard

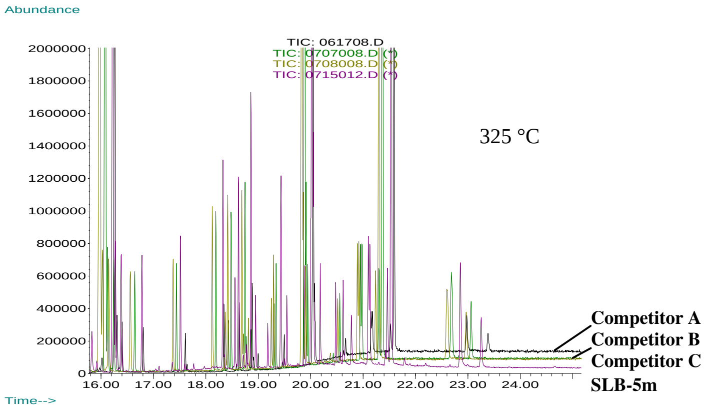


Figure B. MS Spectra of Benzo(g,h,i) perylene, 5 ng, 325 °C; SLB-5ms

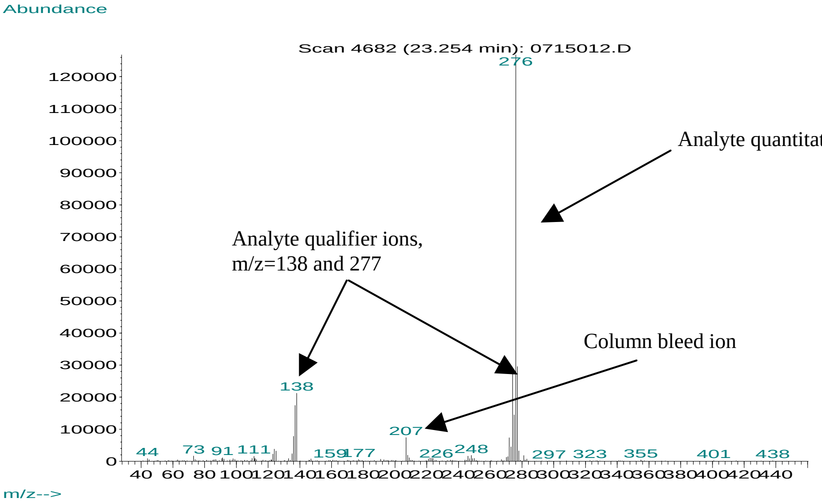
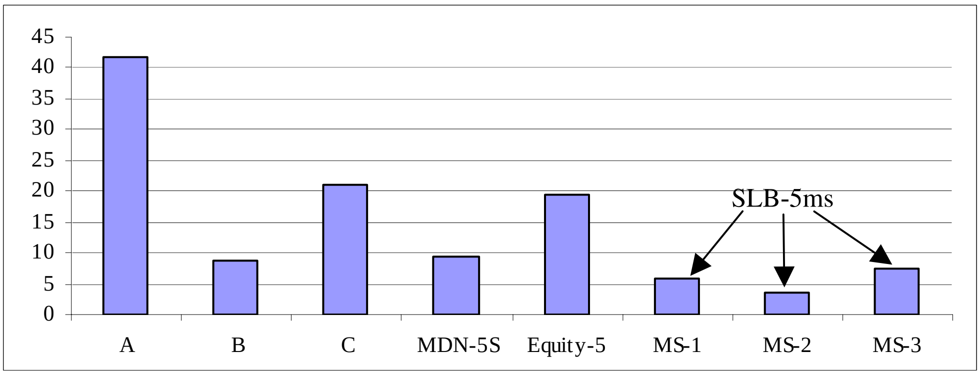


Figure C. GC-MS Bleed as %m/z=207 vs. m/z=276 in the Spectrum of Benzo(g,h,i)perylene



A,B,C: Competitor Columns

US EPA Method 8270 encompasses the analysis of a broad range of compounds, including bases, acids, and neutrals. From the initial calibration, and in every subsequent 12-hour sample analysis sequence, the method requires that a set of compounds known as system performance check compounds, or SPCCs, meet a minimum response criteria before samples can be analyzed. These compounds are identified in the method as being difficult to analyze due to low response. To evaluate the inertness of the SLB-5ms vs. other MS columns, we compared the response of the SPCCs and several other compounds known as low responders. Table 1 compares the response of these compounds at 5 ng,

Table 1. Comparison of response at 5 ng on-column, 30 m x 0.25 mm I.D. x 0.25 µm MS Columns

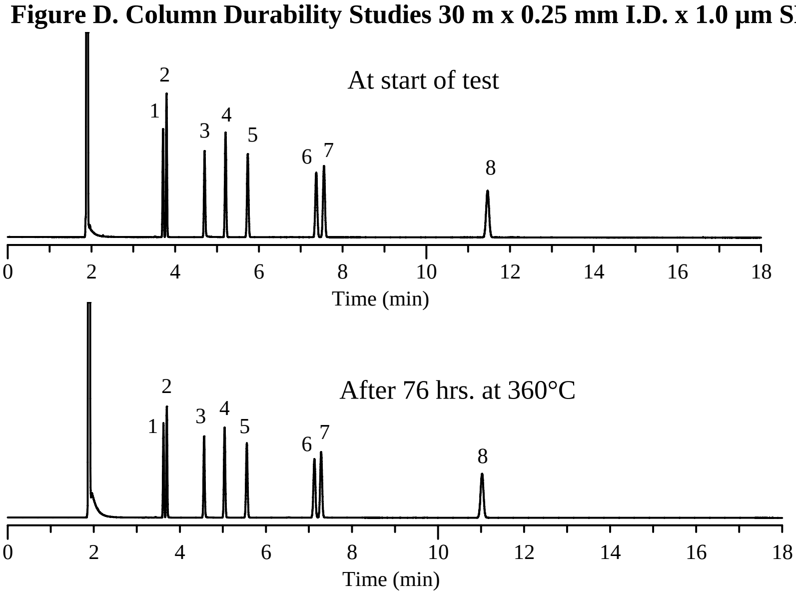
Column	Competitor A	Competitor B	Competitor C	SLB-5ms #1	SLB-5ms #2
	Response Factors at 5 ng on-column				
benzyl alcohol	0.84	0.85	0.67	0.65	0.72
n-nitroso-di-n-propylamine	0.90	0.84	0.78	0.92	0.92
benzoic acid	0.16	0.10	0.11	0.11	0.14
4-chloroaniline	0.40	0.40	0.40	0.42	0.45
4-chloro-3-methylphenol	0.32	0.30	0.32	0.33	0.36
hexachlorocyclopentadiene	0.35	0.30	0.52	0.41	0.36
2-nitroaniline	0.35	0.31	0.29	0.31	0.29
3-nitroaniline	0.30	0.29	0.25	0.27	0.29
2,4-dinitrophenol	0.10	0.07	0.12	0.10	0.11
4-nitrophenol	0.19	0.18	0.18	0.16	0.17
2-methyl-4,6-dinitrophenol	0.10	0.07	0.11	0.10	0.11
pentachlorophenol	0.09	0.07	0.13	0.13	0.15
benzidine	0.46	0.40	0.49	0.63	0.84

Method 8270 system performance check compounds (SPCCs)

Typical low responding compounds

30 m x 0.25 mm I.D. SLB-5ms columns of two different film thicknesses, 0.25 and 1.0 µm, were evaluated for key performance parameters after extended holds at an elevated temperature. The listed isothermal maximum for these two dimensions is 340 °C, however 360 °C was used for the durability test in an attempt to expedite degradation in olumn performance. Minimal change in retention, selectivity, response, and efficiency was exhibited by both dimensions after a total of 76 hours at 360 °C. In addition, no increase in bleed was observed, indicating good phase stability. Figure D illustrates the change in performance of the 1.0 µm column after 76 hours at 360 °C. As expected, there was some decrease in retention, but no change in peak shape, response, or resolution.

Figure D. Column Durability Studies 30 m x 0.25 mm I.D. x 1.0 µm SLB-5ms

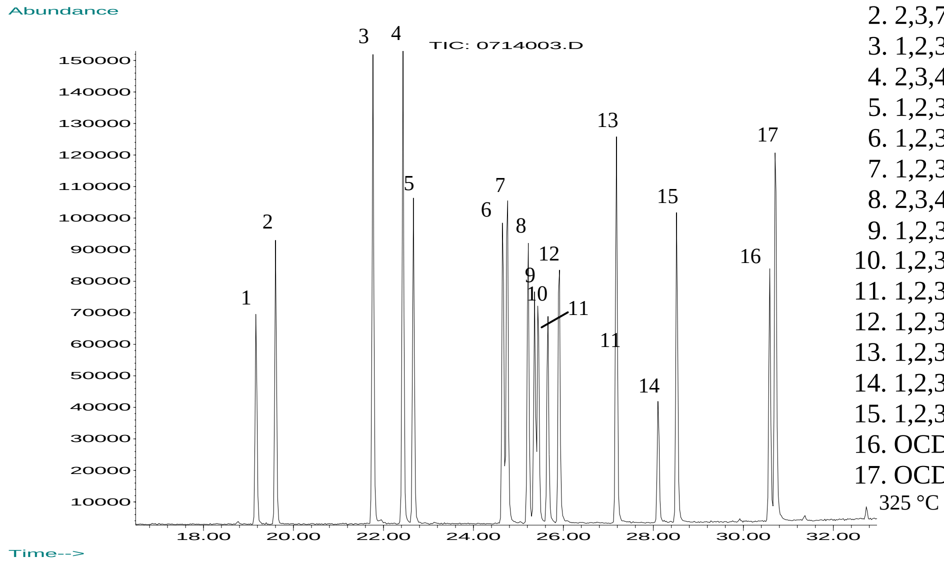


1. Peak List
2. Octanone
3. Decane
4. Octanol
5. Undecane
6. 2,6-Dimethylphenol
7. 2,6-Dimethylaniline
8. Dodecane

Figure E illustrates the separation of a 17-component mix containing the 2,3,7,8-substituted tetrachlorinated dibenzofuran and dibenzodioxin species (PCDFs and PCDDs).

Figure F illustrates the separation of a mix containing the 14 most common polybrominated diphenyl ethers. These compounds are used as flame retardants and are of concern due to their increasing presence in environmental and biological samples.

Figure E. 2,3,7,8-Substituted PCDDs and PCDFs

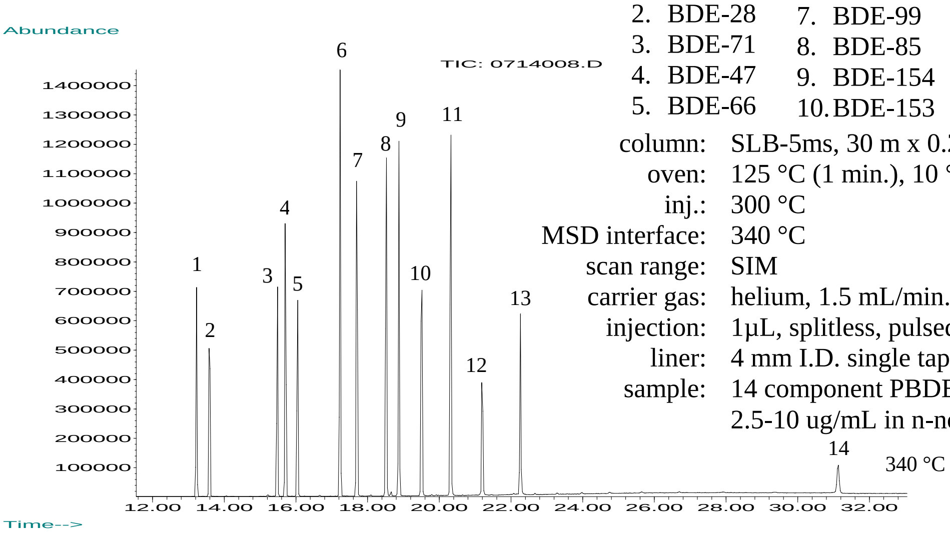


1. 2,3,7,8-TCDF, 100 ppb
2. 2,3,7,8-TCDD, 100 ppb
3. 1,2,3,7,8-PCDF, 250 ppb
4. 2,3,4,7,8-PCDF, 250 ppb
5. 1,2,3,7,8-PCDD, 250 ppb
6. 1,2,3,4,7,8-HxCDF, 500 ppb
7. 1,2,3,6,7,8-HxCDF, 500 ppb
8. 2,3,4,6,7,8-HxCDF, 250 ppb
9. 1,2,3,4,7,8-HxCDD, 500 ppb
10. 1,2,3,6,7,8-HxCDD, 500 ppb
11. 1,2,3,7,8,9-HxCDD, 250 ppb
12. 1,2,3,7,8,9-HxCDF, 250 ppb
13. 1,2,3,4,6,7,8-HpCDF, 250 ppb
14. 1,2,3,4,6,7,8-HpCDD, 250 ppb
15. 1,2,3,4,7,8,9-HpCDF, 250 ppb
16. OCDD, 500 ppb
17. OCDF, 500 ppb

column: SLB-5ms, 30 m x 0.25 mm I.D. x 0.25µm
oven: 150 °C (1 min.), 5 °C/min. to 325 °C (2 min.)
inj.: 250 °C
MSD interface: 325 °C
scan range: SIM
carrier gas: helium, 37 cm/sec., constant
injection: 1 µL, splitless (1 min.)
liner: 4 mm I.D., single taper
sample: 17-component 2,3,7,8-substituted dioxin/furan standard, 100-500 ppb in n-nonane

TC=tetrachloro
PC=pentachloro
HxC=hexachloro
HpC=heptachloro
OC=octachloro
DD=dibenzodioxin
DF=dibenzofuran

Figure F. Polybrominated Diphenyl Ethers



1. BDE-17
2. BDE-28
3. BDE-71
4. BDE-47
5. BDE-66
6. BDE-100
7. BDE-99
8. BDE-85
9. BDE-154
10. BDE-153
11. BDE-138
12. BDE-183
13. BDE-190
14. BDE-209

column: SLB-5ms, 30 m x 0.25 mm I.D. x 0.25 µm
oven: 125 °C (1 min.), 10 °C/min. to 340 °C (15 min.)
inj.: 300 °C
MSD interface: 340 °C
scan range: SIM
carrier gas: helium, 1.5 mL/min., constant
injection: 1µL, splitless, pulsed (30 psi until 0.2 min.)
liner: 4 mm I.D. single taper
sample: 14 component PBDE standard, 2.5-10 ug/mL in n-nonane