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The Quantitative Analysis of Semi-Volatile Organic Compounds on the MDN™-5S Capillary Column

Katherine K. Stenerson and Leonard M. Sidisky

Supelco, Supelco Park, Bellefonte, PA USA

Abstract

United States Environmental Protection Agency (USEPA) Method 8270 is used routinely to analyze solid waste samples for the presence of analytes identified as environmental pollutants. This method requires GC/MS for positive identification and subsequent quantification of these compounds. The demands of the method make it necessary to use a column compatible with compounds of a variety of analyte functionalities. In addition, cost pressures associated with Method 8270 make it desirable to keep the analysis time as short as possible. Since the analysis of semi-volatiles requires that the column be brought to a final temperature in the range of 300°C, minimal column bleed at this temperature is imperative.

In this work, calibration data for 80 semi-volatile compounds is generated using a 30m x 0.32mm ID x 0.50µm MDN-5S capillary column. Split injection permits a calibration range from 10-180ppm. Constant flow using the GC's electronic pressure control (EPC) keeps run time under 25 minutes. Calibration data, including average relative response factors and %RSD values, are presented and the column's performance for key separations is examined. The data show that the 30m x 0.32mm ID x 0.50µm MDN-5S column performs key separations, and yields an 8270 calibration curve with good linearity and response. The low bleed characteristics of the column for GC/MS work are emphasized.

Introduction

To perform successfully for Method 8270, a column must have the following characteristics:

- Exhibit low bleed characteristics at temperatures in the range of 300°C**
- Ability to generate calibration curves in the range of 10-200ppm with percent relative standard deviation values (%RSD) of <15% for most compounds**
- Inertness towards compounds with a variety of analyte functionalities**
- Ability to resolve compounds of interest with common quantitation ions or interfering ions in their spectra**

The data which follows will demonstrate that the MDN-5S has all these characteristics and is a viable column choice for USEPA Method 8270.

Method 8270 is applicable to a total of 240 compounds. Many laboratories performing this method analyze for a much smaller subset of analytes. This subset is often derived from the USEPA's Priority Pollutant List and / or Target Compound List (TCL.) Both of these lists are used for regulatory purposes, with the latter being part of the special testing protocols described in the USEPA Statement of Work (SOW) being used by labs performing analyses as part of the Agency's Contract Lab Program (CLP.) The compounds analyzed in this work include those from both the Priority Pollutant and Target Compound lists. These compounds have a variety of functionalities, and are often referred to as two separate groups, *base-neutrals* and *acids*.

Run Conditions

Method 8270 allows standards and samples to be run for only a 12 hour time period after the successful analysis of a GC/MS tuning check standard. For this reason, shorter run times are critical to productivity. A 40 minute run time, plus 5 minute GC cycle time, allows an analyst to do approximately 16 runs per 12 hours. A 25 minute run time and 5 minute GC cycle time increases the throughput to approximately 24 runs per 12 hours.

The run conditions for the calibration were developed to complete the analysis in <25 minutes. With the run conditions described, the retention time of the last peak, benzo(g,h,i)perylene, was 22.97 minutes.

Run Conditions (cont.)

Column: 30m x 0.32mm ID, 0.50 μ m MDN-5S

Oven: 50°C/1 min. hold, 15°C/min. to 120°C, 20°C/min. to 280°C, 2°C/min to 300°C

Flow: 2.5mL/min. He, constant flow setting using electronic pressure control (EPC)

Injector Temp.: 280°C

MSD Interface Temp.: 290°C

Detector: HPTM5973 MSD, scan range 40- 450 amu, tuned to meet DFTPP criteria per Method 8270
source temp. = 240°C
quad. temp. = 160°C

Injection: 2 μ L, 10:1 split

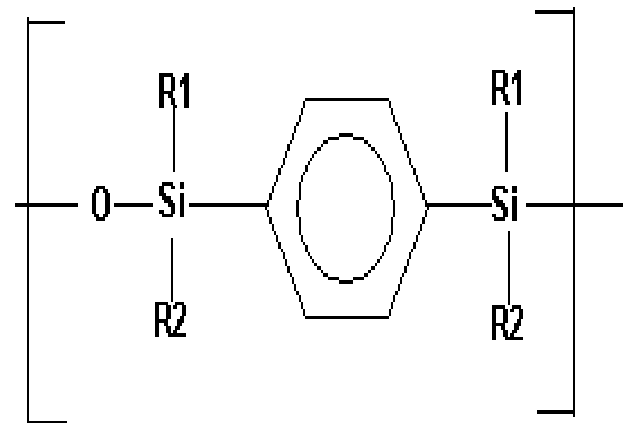
Standards: 10, 20, 50, 80, 133, 160 and 180ppm in methylene chloride

Bleed

Traditional polysiloxane phase chemistries are used for the preparation of the SPB™-5 and MDN-5 capillary columns. The MDN-5S chemistry is based on that of silphenylene phases, where a phenyl unit is incorporated into the polymer backbone. The figures below demonstrate the two different chemistries.



SPB-5, MDN-5



MDN-5S

The addition of the silphenylene unit into the polymer backbone increases the overall stability of the stationary phase compared to the traditional polysiloxane-based phases. The silphenylene incorporation results in a more rigid backbone to the stationary phase preventing backbiting of the polymer and the generation of cyclic bleed fragments. This provides increased maximum temperature of these phases and more rapid stabilization of the column after conditioning runs and lower bleed and background spectra on GC/ MS analyses. A 10ppm calibration standard (2ng on-column) is presented in Figure A. Very little baseline rise was observed in the run.

The most predominant cyclic fragment encountered with bleed from both silphenylene and siloxane phases contains three siloxane units and is commonly referred to as “D3.” The mass of this fragment is 207 and its abundance in spectra of late eluting compounds can be used to assess a column’s performance with regards to bleed. High column bleed can interfere with proper spectral identification. The spectra of benzo(g,h,i)perylene (the last eluting peak) at 2ng on-column is presented in Figure B. The abundance of mass 207 is 15% relative to the base peak ($m/z=276$) and should not interfere with proper identification of this compound.

**Figure A: Low Level 8270 Calibration Standard, 10ppm
(2ng On-Column)**

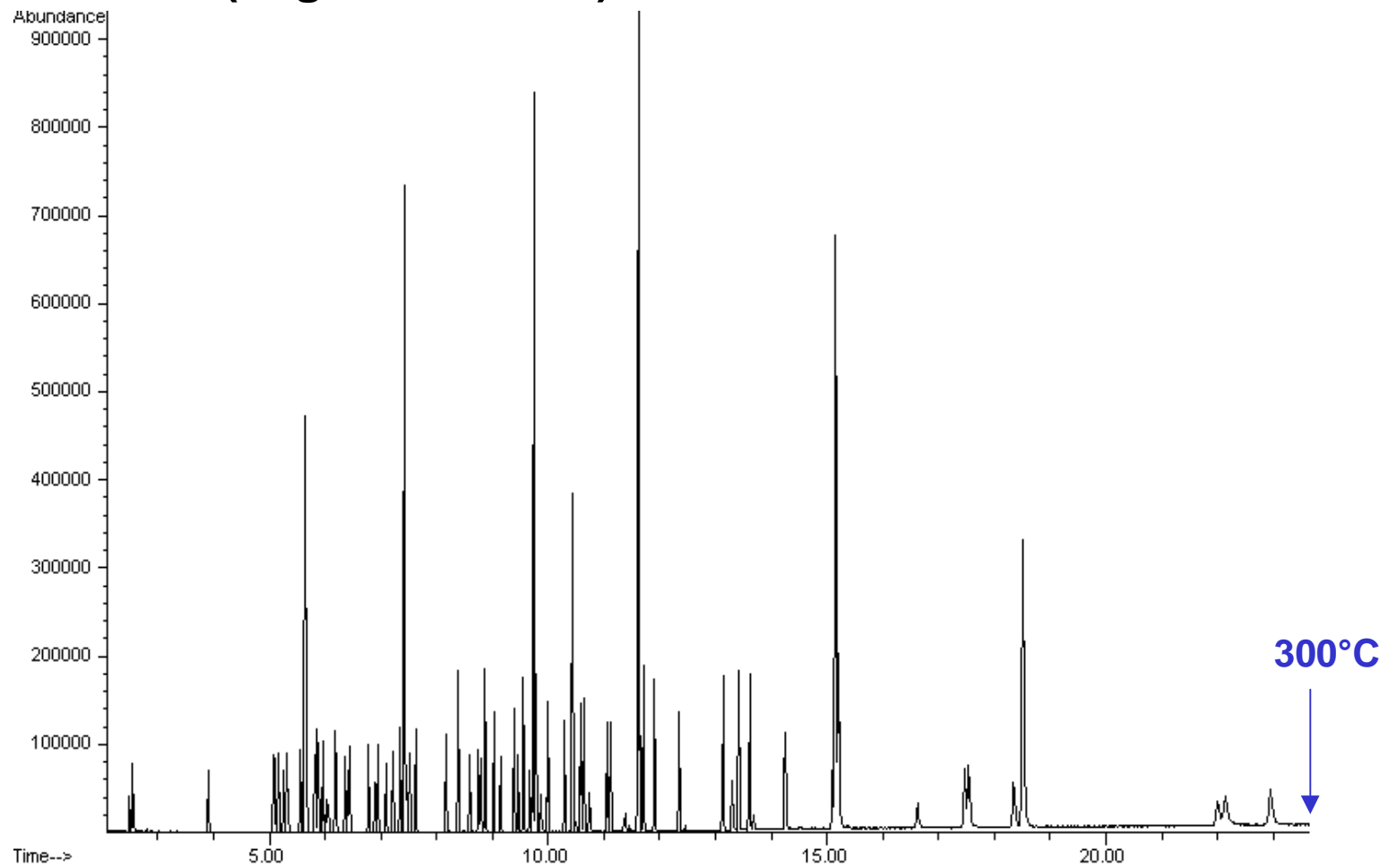
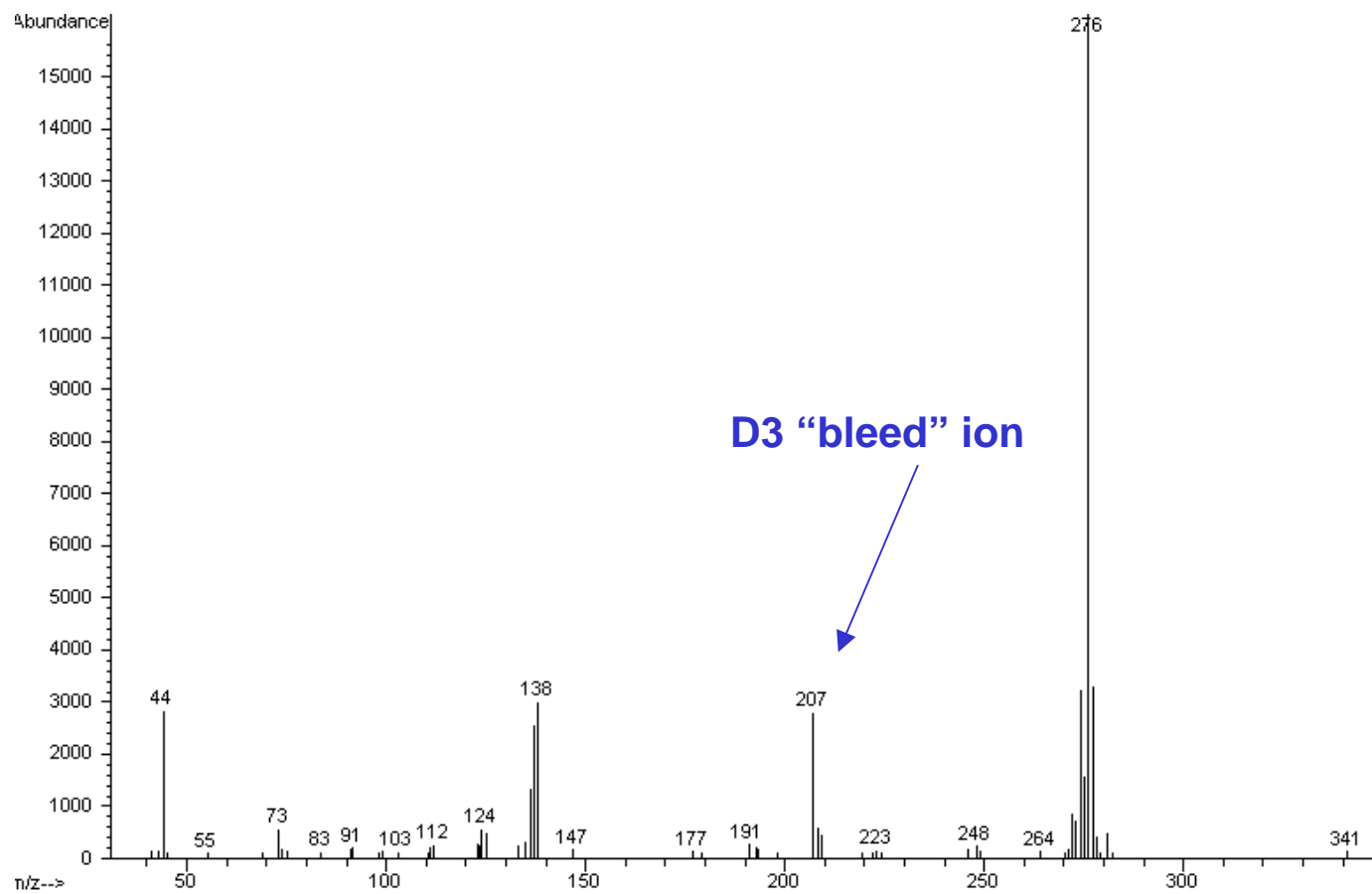


Figure B: Spectra of Benzo(ghi)perylene, 2ng On-Column



Calibration

The calibration standards contained a total of 80 analytes and 6 internal standards. The standards were prepared at 7 different levels, with all analytes being at the same level in each. The concentration of the internal standards in each calibration level remained constant at 50ppm. Response factors and percent relative standard deviation values (%RSDs) were calculated as described in Method 8270. A summary of the calibration results, the quantitation ions used, and compound retention times are presented in Tables 1a (acids) and 1b (base-neutrals.)

Method 8270 allows the average response factor from the initial calibration to be used for quantitative analysis of any compound provided the %RSD value for that compound was <15% in the initial calibration. If the value was >15%, then a first, second, or third order equation must be used. The majority of the compounds analyzed on the MDN-5S had %RSD values of <15%, indicating good linearity in the calibration range used.

Additional linearity criteria described by the method states that a specific set of compounds which are designated as “calibration check compounds” (CCCs) must have %RSD values <30% in order for the initial calibration to be considered valid. These compounds have been indicated in Tables 1a and 1b. The calibration generated on the MDN-5S met the 30% requirement for all CCCs.

Table 1a: Multi-level calibration results, acids

Compound	RT	Quant Ion	Avg. RRF	%RSD
2-Fluorophenol	3.90	112	1.247	1.8
Phenol (CCC)	5.10	94	1.809	3.6
2-Chlorophenol	5.33	128	1.426	2.9
Benzyl Alcohol	5.81	108	0.943	3.8
2-Methylphenol	5.96	108	1.285	4.1
4-Methylphenol	6.18	108	1.401	3.9
2-Nitrophenol (CCC)	6.89	139	0.187	9.4
2,4-Dimethylphenol	6.94	107	0.381	4.2
Benzoic Acid	7.03	105	0.262	22.6
2,4-Dichlorophenol (CCC)	7.21	162	0.297	4.9
4-Chloro-3-methylphenol (CCC)	8.17	107	0.348	5.2
2,4,6-Trichlorophenol (CCC)	8.75	196	0.399	8.2
2,4,5-Trichlorophenol	8.79	196	0.442	2.5
2,4-Dinitrophenol (SPCC)	9.81	184	0.152	19.8
4-Nitrophenol (SPCC)	9.87	109	0.248	14.8
2-Methyl-4,6-dinitrophenol	10.49	198	0.101	37.3
2,4,6-Tribromophenol	10.74	330	0.218	9.7
Pentachlorophenol (CCC)	11.37	266	0.129	26.9
Internal Standards:				
1,4-dichlorobenzene-d4	5.64	152		
Naphthalene-d8	7.43	136		
Acenaphthene-d10	9.74	164		
Phenanthrene-d10	11.62	188		
Chrysene-d12	15.15	240		
Perylene-d12	18.50	265		

Table 1b: Multi-level calibration results, base-neutrals.

Compound	RT	Quant Ion	Avg. RRF	%RSD	Compound	RT	Quant Ion	Avg. RRF	%RSD
N-nitrosodimethylamine	2.48	74	0.848	4.0	4-Chlorophenyl phenyl ether	10.44	204	0.740	8.1
Pyridine	2.54	79	1.540	4.2	4-Nitroaniline	10.45	138	0.381	4.7
Phenol-d6	5.09	99	1.760	3.1	N-nitrosodiphenylamine (CCC)*	10.58	169	0.506	6.8
Aniline	5.16	93	2.088	7.5	Azobenzene	10.64	77	0.752	8.3
Bis(2-chloroethylether)	5.26	95	0.436	3.4	4-Bromophenyl phenyl ether	11.06	248	0.215	3.6
1,3-Dichlorobenzene	5.56	146	1.429	5.2	Hexachlorobenzene	11.12	284	0.242	4.2
1,4-Dichlorobenzene (CCC)	5.67	146	1.466	4.9	Phenanthrene	11.65	178	1.028	7.8
1,2-Dichlorobenzene	5.88	146	1.388	4.6	Anthracene	11.71	178	1.045	6.4
Bis(2-chloroisopropyl)ether	6.02	45	1.214	4.1	Carbazole	11.90	167	1.022	6.4
N-nitroso-di-n-propylamine (SPCC)	6.21	70	1.082	4.2	Di-n-butyl phthalate	12.35	149	1.095	7.3
Nitrobenzene-d5	6.42	82	0.428	4.2	Fluoranthene (CCC)	13.13	202	1.232	5.2
Nitrobenzene	6.45	77	0.436	6.0	Pyrene	13.41	202	1.191	6.9
Isophorone	6.78	82	0.721	5.2	Benzidine	13.29	184	0.419	12.4
bis(2-Chloroethoxy)methane	7.09	93	0.429	5.4	Aramite #1	13.59	185	0.056	21.0
1,2,4-Trichlorobenzene	7.34	180	0.341	6.6	Aramite #2	13.68	185	0.075	19.7
Naphthalene	7.45	128	1.057	7.5	3,3'-Dimethylbenzidine	14.24	212	0.376	14.3
4-Chloroaniline	7.52	127	0.451	5.9	Butylbenzyl phthalate	14.26	149	0.477	6.0
Hexachlorobutadiene (CCC)	7.63	225	0.208	4.6	3,3'-Dichlorobenzidine	15.10	252	0.388	11.8
2-Methylnaphthalene	8.39	142	0.688	5.9	Benzo(a)anthracene	15.14	228	1.107	4.2
Hexachlorocyclopentadiene (SPCC)	8.60	237	0.377	10.9	Chrysene	15.00	228	1.028	6.1
2-Fluorobiphenyl	8.87	172	1.398	7.0	Bis(2-ethylhexyl)phthalate	15.21	149	0.603	9.4
2-Chloronaphthalene	9.02	162	1.170	7.0	Di-n-octyl phthalate (CCC)	16.62	149	1.089	22.6
2-Nitroaniline	9.15	65	0.423	5.0	Benzo(b)fluoranthene	17.47	252	1.217	8.1
Dimethyl phthalate	9.39	163	1.347	5.6	Benzo(k)fluoranthene	17.54	252	1.260	3.5
2,6-Dinitrotoluene	9.47	165	0.305	7.5	Benzo(a)pyrene (CCC)	18.35	252	1.124	7.8
Acenaphthylene	9.56	152	1.898	6.5	Indeno(1,2,3)cd-pyrene	22.00	276	1.010	12.0
3-Nitroaniline	9.68	138	0.357	4.8	Dibenzo(a,h)anthracene	22.14	278	1.059	6.4
Acenaphthene (CCC)	9.78	153	1.202	6.6	Benzo(g,h,l)perylene	22.95	276	1.174	3.3
2,4-Dinitrotoluene	9.98	165	0.427	8.1					
Dibenzofuran	10.00	168	1.788	7.4					
Diethyl phthalate	10.29	149	1.396	5.6					
Fluorene	10.44	166	1.290	8.2					

*Decomposes in the GC inlet to form diphenylamine, which is the method designated CCC.

Response

Method 8270 sets response criteria for a specific set of compounds. These compounds are called “system performance check compounds” (SPCCs.) These compounds are particularly susceptible to activity in both the column and the GC/MS system. In the initial calibration, these SPCCs must have average response factors of $>.05$ in order for the calibration to be valid. Compounds which are SPCCs have been indicated in Tables 1a and 1b. They have all met the response criteria described in the method.

In addition to the method designated SPCCs, pentachlorophenol and benzidine are routinely used to assess GC/MS performance for Method 8270. As illustrated in Figure C, both compounds were easily detected at 2ng on-column.

Column performance is also assessed by running a special “tuning standard” prior to the calibration. This standard contains DDT, benzidine, pentachlorophenol, and the tuning compound DFTPP, at 50ppm each. In an active system, DDT will degrade to DDD and DDE and benzidine and pentachlorophenol will exhibit decreased response. This tuning standard is illustrated in Figure D. DDT did not exhibit any degradation and both benzidine and pentachlorophenol exhibited acceptable response.

Figure C: Pentachlorophenol and Benzidine at 2ng On-Column on the MDN-5S

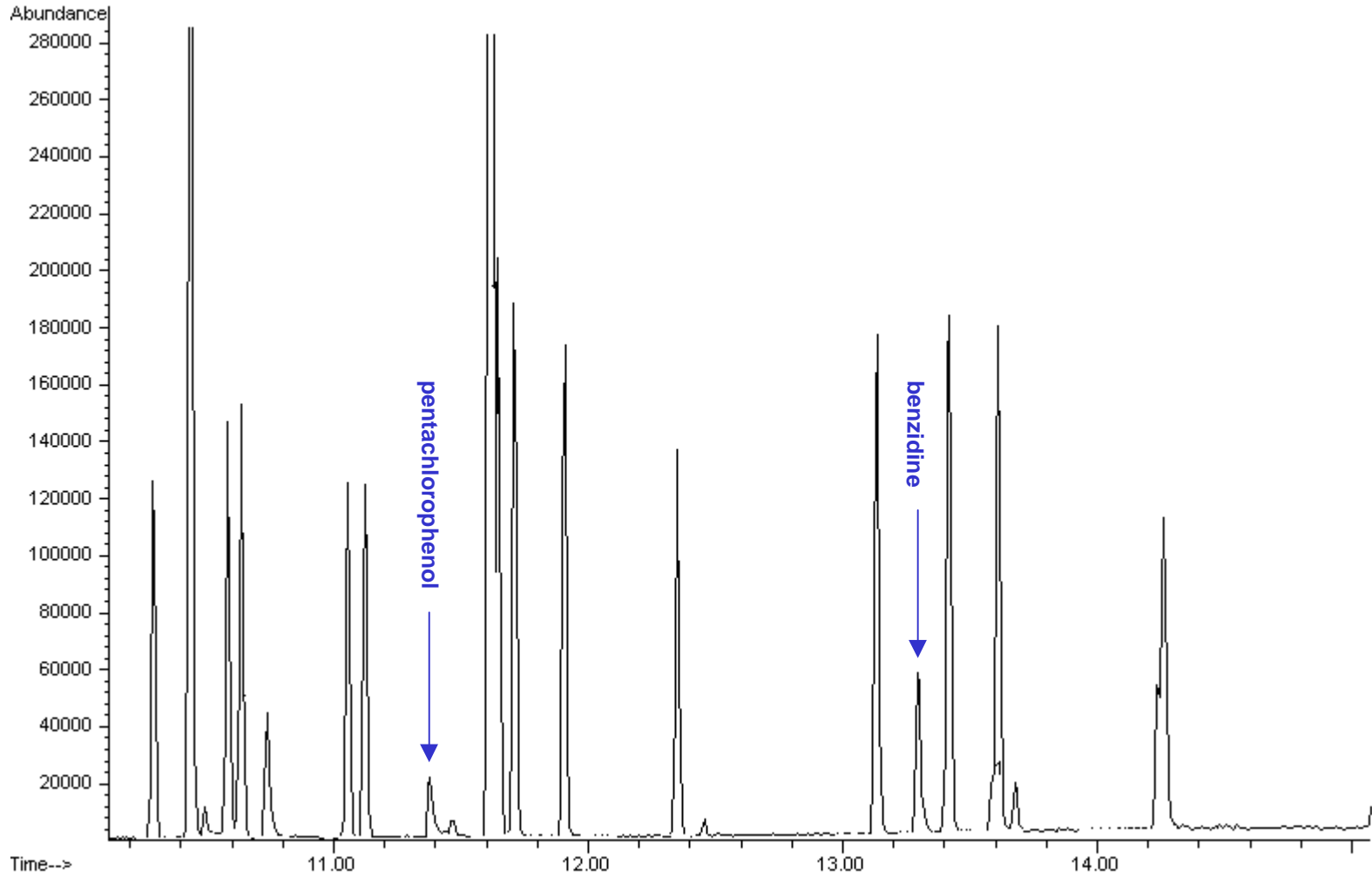
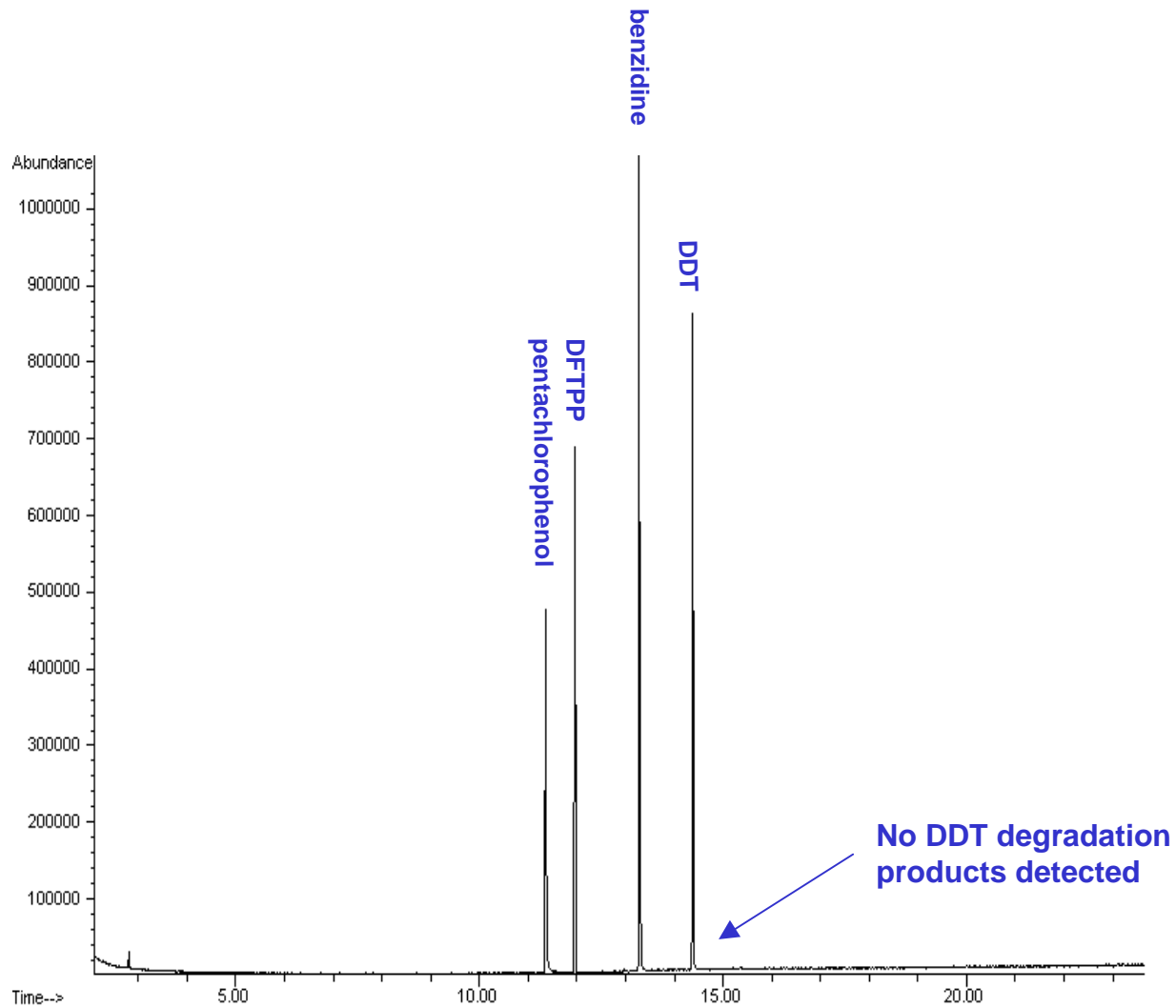


Figure D: 8270 Tuning Check Standard on the MDN-5S



Resolution

An MSD has the unique ability to resolve compounds with different masses, even if they are not separated chromatographically. Some 8270 analytes are isomers, and have the same mass spectra. Other compounds, while not isomers, have spectra containing common ions which are used for quantitation in one or both of the compounds. In these cases where the MSD cannot resolve the compounds, they must be resolved chromatographically. Examples of each of these scenarios are presented in Figures E and F.

Benzo(b)fluoranthene and benzo(k)fluoranthene are isomers and are both quantitated using $m/z=252$. For this reason, the two must be sufficiently resolved to allow for accurate analysis. The pair was 81% resolved in the 80ppm mid-level calibration standard. This is illustrated in Figure E.

Indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene have different quantitation ions, 276 and 278 respectively. However, the two contain both of these ions in their spectra. In cases where these two compounds must be resolved, the MDN-5S allows the analyst to use run conditions which will result in sufficient resolution of the two without a lengthy run time. The pair was 60% resolved in the 80ppm mid-level calibration standard while still maintaining a run time of <25 minutes. This is illustrated in Figure F.

Figure E: Resolution of Benzo(b)fluoranthene and Benzo(k)fluoranthene in the Mid-Level Calibration Standard (80 ppm), shown at $m/z=252$

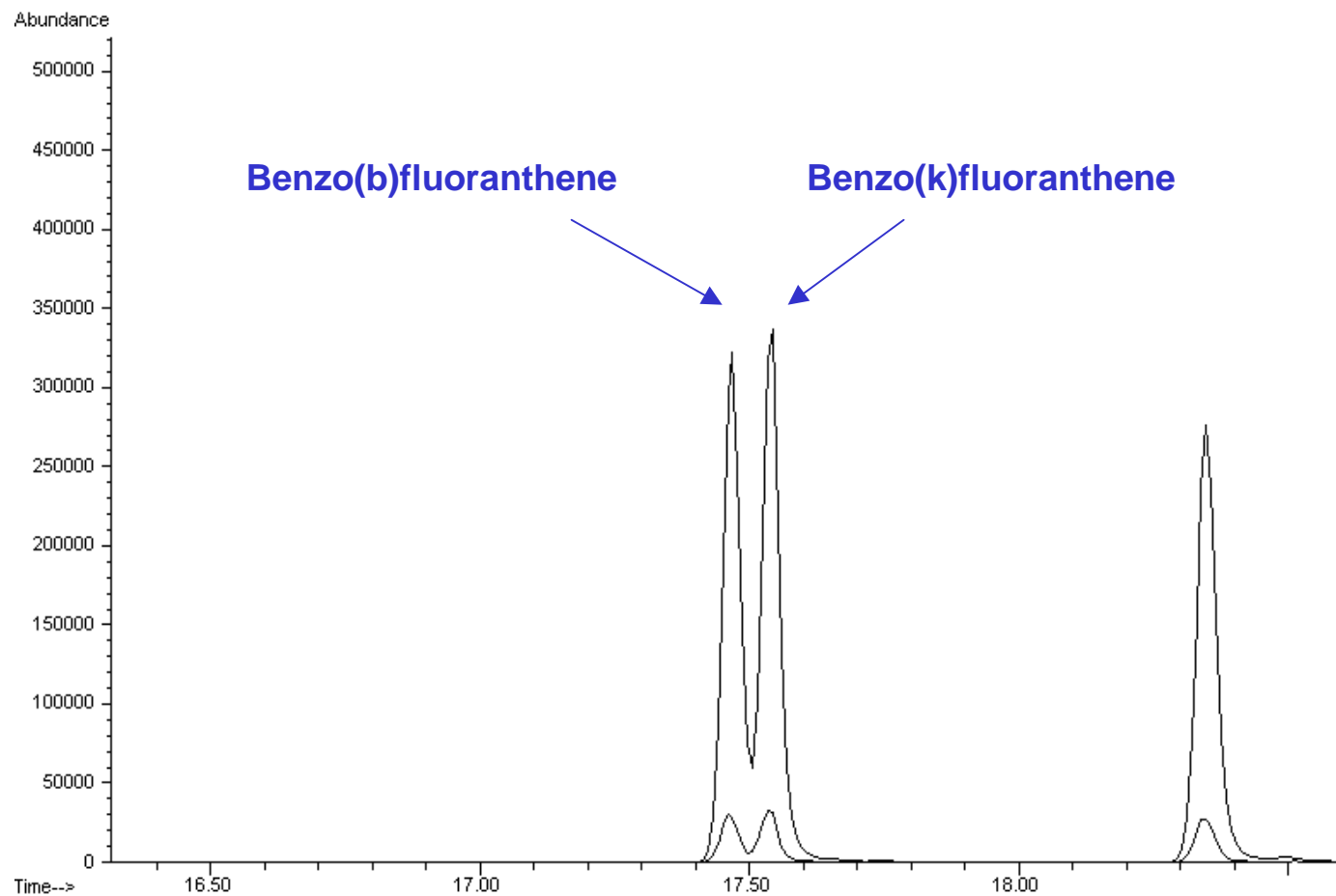
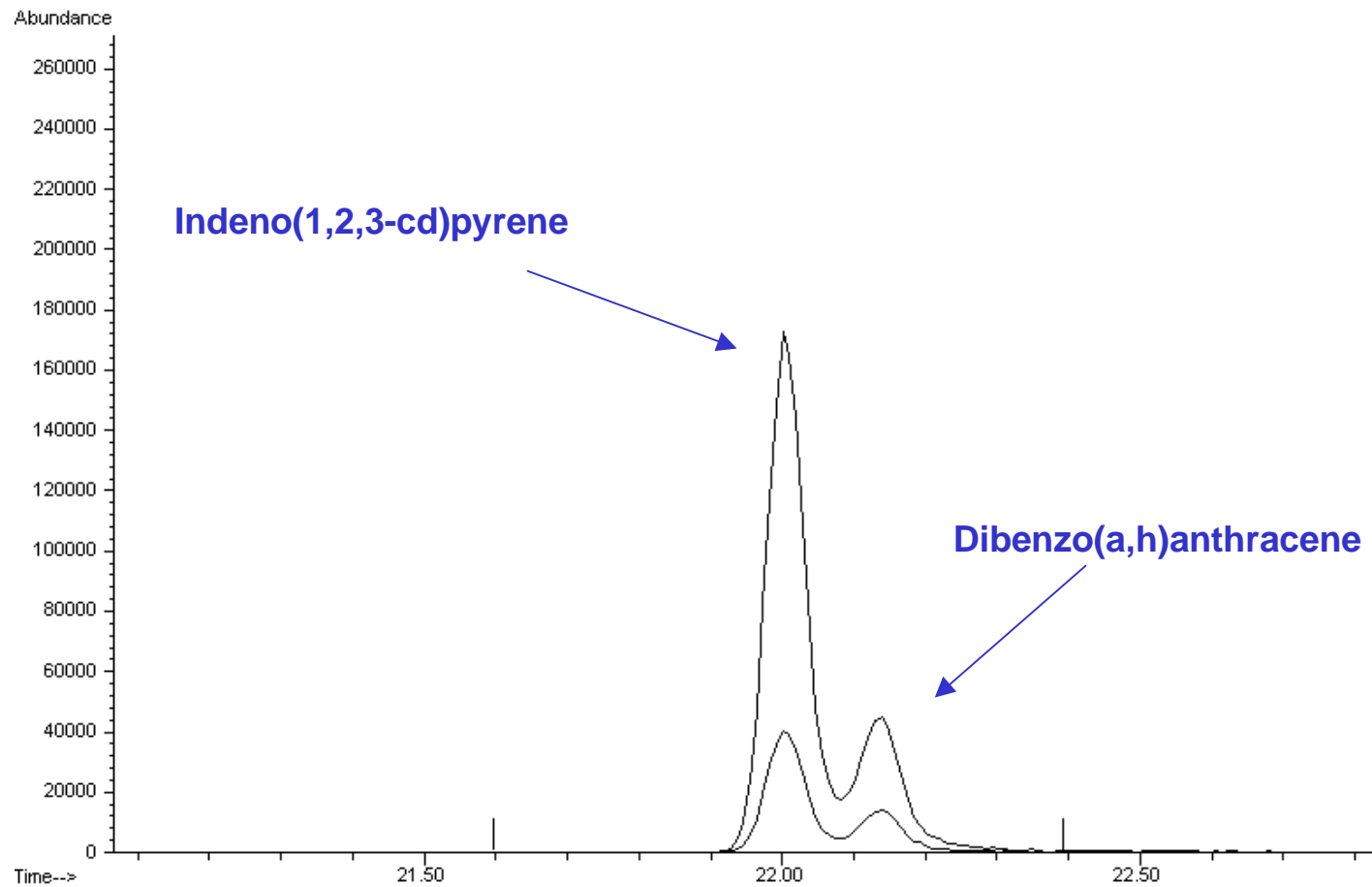


Figure F: Indeno(1,2,3-cd)pyrene and Dibenzo(a,h)anthracene in the Mid-Level Calibration Standard (80ppm), shown at m/z=276



Conclusion

The 30m x 0.32mm ID, 0.50 μ m MDN-5S can be used to quantitatively analyze semi-volatile compounds. Specifically, the column can meet criteria which are vital to successful use for USEPA Method 8270:

- **Low bleed at temperatures in the range of 300°C**
- **Linearity in a wide working range, as defined by %RSD values of <15% for the majority of compounds in a multi-level calibration**
- **Compatibility with compounds of a variety of analyte functionalities**
- **Sufficient resolution of non-mass resolved pairs**