# Improved Analysis of EPA Method 8270D on a Zebron™ ZB-SemiVolatiles Column

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*An improved method for EPA Method 8270D has been exhibited on a Zebron ZB-SemiVolatiles GC column. The benefits of this method include:*

- *Fast run times while still maintaining resolution of key compounds like benzo[b]fluoranthene and benzo[k]fluoranthene*
- *Great peak shape of typically poor performing compounds like phenols and amines*

## Introduction

EPA Method 8270D is a complicated method with one of the longest lists of analytes. A laboratory running a minimal list will still have over 80 compounds, and laboratories adding appendix mixes can have over 200 compounds in their calibration curves. This large number of compounds can lead to chromatographic challenges that must be addressed when choosing columns and developing methods.

*Chromatographic Coelutions and Shared Ions*

EPA Method 8270D employs mass spectrometry detection, which can discern co-eluting compounds of different masses. The large number of analytes run in this method commonly leads to coelutions. However, the method does not allow compounds to chromatographically coelute and also share ions for identification by MS. Any compounds that share ions must meet resolution requirements that are "achieved if the height to the valley between the two isomer peaks is less than 50 % of the average of the two peak heights."[1]

Specific pairs of notorious and sometimes overlooked compounds that both share ions as well as have similar retention times are listed in **Table 1**. It is therefore important to chromatographically resolve these compounds.

**Table 1.**
Traditionally coeluting compounds with shared ions.

| Critical Pair | Shared Mass |
|---|---|
| aniline / bis(2-chloroethyl)ether | 93 |
| 2,4,5-trichlorophenol / 2,4,6-trichlorophenol | 196 |
| benzo[b]fluoranthene / benzo[k]fluoranthene | 252 |
| indeno[1,2,3-cd]pyrene / dibenz[a,h]anthracene | 276 |

*The Solvent Effect*

Some analytes have very low boiling points and can co-elute with a tailing solvent, which contributes to instrument noise levels and also makes these peaks prone to the solvent effect. This can result in peak tailing. The most affected of these analytes is 1,4-dioxane, which is so problematic that some labs choose to run this compound in a separate and additional analysis. To improve the detection of this and other early eluting compounds, the conditions and column need to be precisely optimized.

*Reactive Compounds*

Active compounds include acidic phenols like pentachlorophenol and 2,4-dinitrophenol, basic amines like pyridine and benzidine, and thermally labile or reactive pesticides from commonly run appendix mixes. To consistently and accurately quantitate these compounds, a very inert system and column must be used. The smallest amount of activity can result and breakdown that will reduce response, produce tailing resulting in integration errors, or cause peak shape to deteriorate so that analytes begin to co-elute with neighboring compounds of similar masses.

## Experimental

The analytical conditions used are presented in **Table 2**. Instrumentation used was an Agilent® 6890 with 5973 MSD.

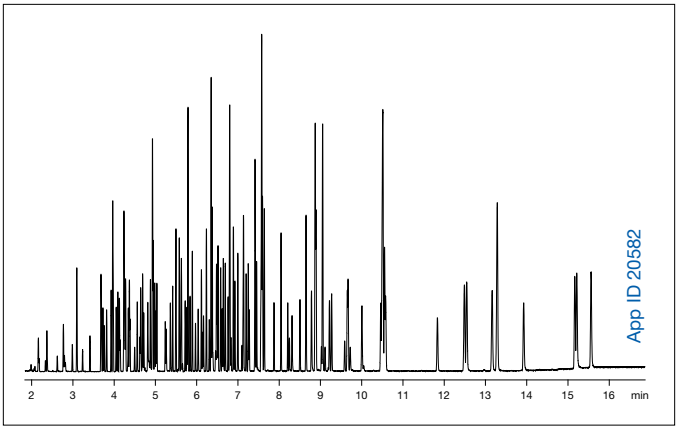
**Table 2.**
Analytical conditions used to collect EPA Method 8270D chromatograms on a Zebron ZB-SemiVolatiles column.

| | |
|---|---|
| Column | Zebron ZB-SemiVolatiles |
| Dimensions | 30 meter x 0.25 mm x 0.25 µm |
| Injection | 1.0 µL split 10:1 @ 280 °C |
| Oven Program | 40 °C for 0.5 min to 260 °C @ 40 °C/min to 295 °C @ 6 °C/min to 325 °C @ 25 °C/min for 2 min |
| Carrier Gas | Helium @ 1.4 mL/min, constant flow |
| Liner | Single Taper with Wool (AG0-8499) |
| Septum | PhenoRed™-400 (AG0-4697) |
| Inlet Seal | Easy Seals™ (AG0-8620) |
| Analytes | 25 ppm in dichloromethane |

## Results and Discussion

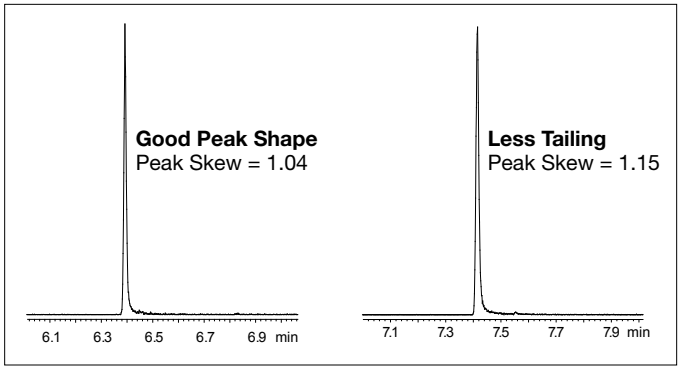
A chromatogram containing 137 analytes from the EPA Method 8270D list was collected and is shown in **Figure 1**. All 137 analytes elute within a 16 minute run. This short run time does not sacrifice performance, and the method still provides good response for active compounds and separation of key compounds which will follow. EPA 8270D recommended conditions result in runs over 35 minutes and typical optimized conditions are over 20 minutes. The conditions and column used in **Table 2** further reduce run times, allowing labs to run more samples per instrument per day, increasing revenue potential for the laboratory.

**Figure 1.**
Chromatogram of 137 EPA Method 8270D analytes at 25 ppm. A full list of these compounds can be found at www.phenomenex.com/GC.




One advantage is that the Zebron™ ZB-SemiVolatiles column has been well deactivated to give superb peak shape even for the most active compounds. **Figure 2** shows the peaks for 2,4-dinitrophenol and pentachlorophenol (PCP), two typically poor performing acidic compounds. These compounds show good peak shape and response with a peak skew of 1.04 for 2,4-dinitrophenol and a peak skew of 1.15 for PCP. The more symmetrical peak shape aids in peak integration and calibration, and peaks are higher and narrower for improved signal-to-noise ratios (S/N) and therefore lower limits of detection.

**Figure 2.**
2,4-dinitrophenol (left trace) and pentachlorophenol (right trace) peaks from the 8270D chromatogram.



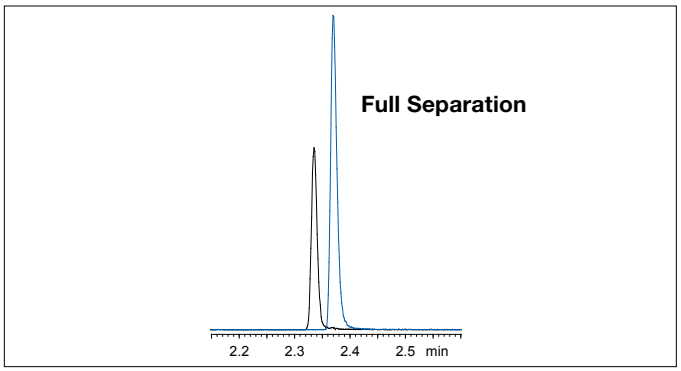

The ZB-SemiVolatiles column provides very good responses for both acidic and basic compounds, and does not sacrifice activity of bases to provide good response of acidic compounds. This is exhibited in the pyridine peak shape in **Figure 3** (blue trace). Pyridine is a very reactive amine that tails severely on other columns (See TN-2050). The ZB-SemiVolatiles column provides near Gaussian peak shape with tailing at 1.49, providing increased response and therefore improved signal-to-noise levels for this and other basic compounds.

The peak immediately prior to pyridine in **Figure 3** is n-nitrosodimethylamine (black trace). Though still an amine, it is less reactive than pyridine but still shows tailing on some columns. The peak shape for this amine on the ZB-SemiVolatiles column is so much improved that near baseline separation is achieved. Though these compounds do not share common main ions, the improved peak shape does make integration easier and integration from baseline more true and consistent. This has proven to be an advantage for some labs that wanted to increase reproducibility for these compounds.

*"We made the switch to the ZB-SemiVolatiles column for an increase in performance for separating pyridine and n-nitrosodi-methylamine. The improved peak shape has dramatically decreased the % RSD in our calibration curve."*

*Senior Organic Chemist*
*Phoenix Environmental Laboratories, Inc.*

**Figure 3.**
Peak shape and separation of n-nitrosodimethylamine (black trace) and pyridine (blue trace).




An additional advantage of a well-deactivated column with good peak shape for active compounds is that those compounds will perform more consistently, making calibration curves easier to pass. A more inert column can also provide longer lifetime because the column does not contribute to any initial degradation of analytes. Though the system may become contaminated from dirty samples, the column is not adding to the degradation due to contamination. Calibrations therefore hold longer and the system is more stable. This has been observed by labs running such routinely dirty spamples:

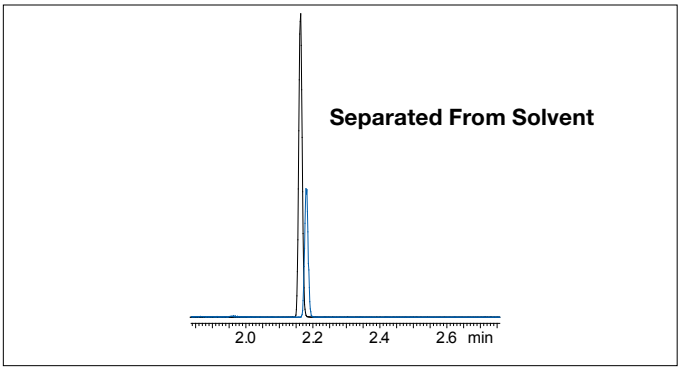
*"I have found the Phenomenex ZB-SemiVolatiles columns to be superior in quality and durability than any other columns we have previously used. The columns not only last longer, but the reproducibility of column is extraordinary. The column holds calibrations particularly well, even after multiple injections of samples with far less than desirable matrices. All of this equates to less downtime and maintenance and more productivity for TestAmerica."*

*Ryan McKernan, GC/MS Semi-Volatiles Analyst*
*TestAmerica Laboratories, Inc. Buffalo*

ZB-SemiVolatiles is also a high efficiency column with a stationary phase that is specifically suited for semivolatile analysis. This high column efficiency results in peaks that are higher and narrower than less efficient columns for improved signal. ZB-SemiVolatiles columns are also MS Certified for low bleed, which reduces noise. The combined increase in signal and decrease in noise gives improved signal-to-noise ratios for better sensitivity. It is therefore possible to add a small split to existing splitless programs which can greatly reduce the size of the solvent peak. This step allows for baseline separation of the dichloromethane solvent peak from

one of the earliest eluting compounds, 1,4-dioxane. This is shown in the very front of **Figure 1** and in greater detail in **Figure 4**. In addition, the small split will also reduce the amount of contamination that is introduced, further extending the lifetime of the analysis and the column.

**Figure 4.**
Extracted ion chromatograms for 1,4-dioxane D8 (black trace) and 1,4-dioxane (blue trace).




ZB-SemiVolatiles also provides separation for key pairs of analytes that may have similar ions in common. Aniline and bis(2-chloroethyl)ether share ions of mass 93 and are shown in **Figure 5**. Another critical separation is between the 2,4,5-trichlorophenol and 2,4,6-trichlorophenol isomers which share mass 196 as shown in **Figure 6**. Both sets of compounds here exhibit baseline separation on the ZB-SemiVolatiles column.

**Figure 5.**
Separation of aniline (first peak) and bis(2-chloroethyl)ether (second peak) which share mass 93.

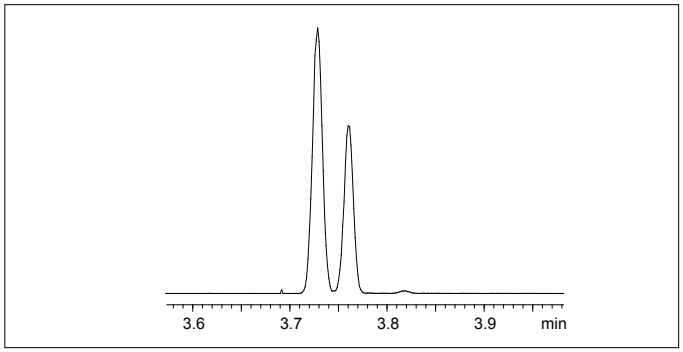
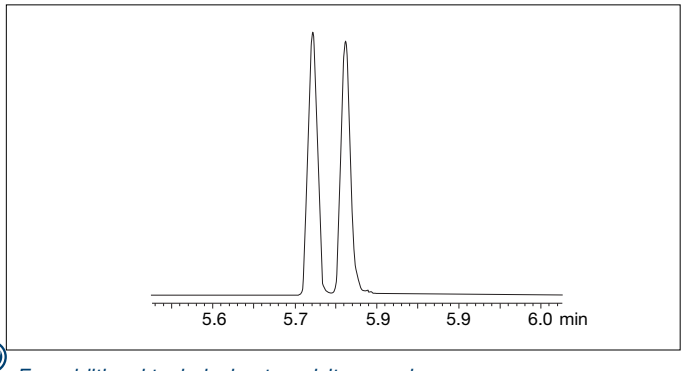
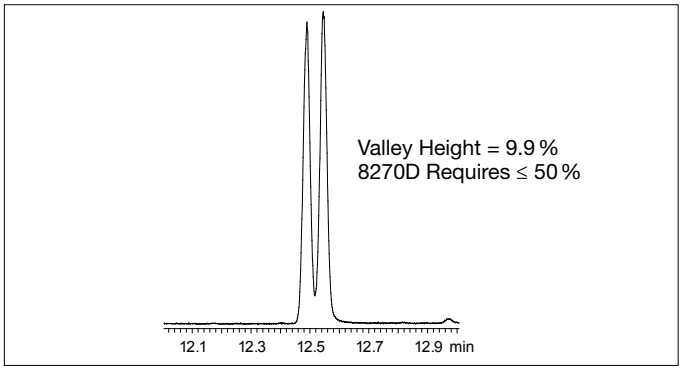



**Figure 6.**
Separation of 2,4,5-trichlorophenol and 2,4,6-trichlorophenol isomers with mass 196.




The resolution and optimized selectivity of the ZB-SemiVolatiles column is most evident when analyzing hard to separate PAH isomers like benzo[b]fluoranthene and benzo[k]fluoranthene. These two analytes have identical mass spectra and must be separated chromatographically to meet the 50 % resolution requirements stated in EPA 8270. The resolution achieved by the ZB-SemiVolatiles column results in valley height less than 10 % as shown in **Figure 7**. This is well below the required value of 50 % required by the method.

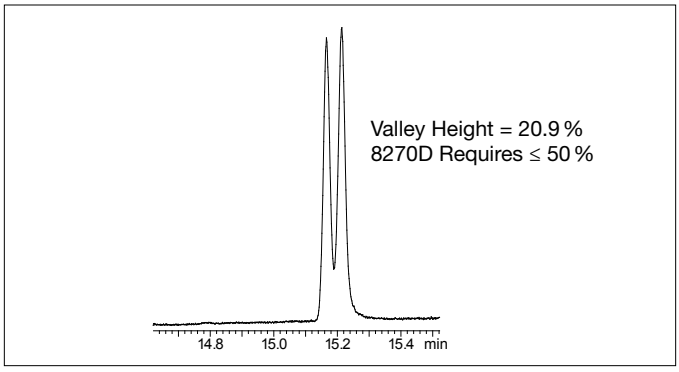
**Figure 7.**
Separation of benzo[b]fluoranthene (first peak) and benzo[k]fluoranthene with a resolution of 9.9 %.




The power to separate PAHs also extends to the last pair of PAHs, indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene. Though the main ions of these compounds are different, dibenz[a,h]anthracene contains a strong mass 276 which is the main ion for indeno[1,2,3-cd]pyrene. It is therefore desirable to chromatographically separate these compounds to meet the method requirements for compounds with similar masses.

The separation of these two compounds is shown in **Figure 8**. The separation shown here is 20.9 %, which again is well below the method requirements of 50 %.

**Figure 8.**
Separation of indeno[1,2,3-cd]pyrene (first peak) and dibenz[a,h]anthra-cene (second peak) with a resolution of 20.9 %.



# APPLICATIONS

## Conclusions

The ZB-SemiVolatiles column is an efficient and well-deactivated column specifically designed to overcome the challenges of semi-volatile analyses like EPA Method 8270D. The improved peak shape of both acids and bases can provide more reproducible and accurate results. The lack of contributed activity can also extend column lifetime and reduce maintenance. This in combination with the superb resolution of key compounds can result in faster run times, increasing overall lab productivity and reducing downtime for maintenance.

## References

1. EPA Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2007.

## Ordering Information

### Zebron™ ZB-SemiVolatiles GC Columns

| ID (mm) | df (µm) | Temperature Limits (°C) | Part No. |
|---|---|---|---|
| **15 Meter** | | | |
| 0.25 | 0.25 | -60 to 325/350 | 7EG-G027-11 |
| 0.25 | 0.50 | -60 to 325/350 | 7EG-G027-17 |
| **20 Meter** | | | |
| 0.18 | 0.18 | -60 to 325/350 | 7FD-G027-08 |
| 0.18 | 0.36 | -60 to 325/350 | 7FD-G027-53 |
| **30 Meter** | | | |
| 0.25 | 0.25 | -60 to 325/350 | 7HG-G027-11 |
| 0.25 | 0.50 | -60 to 325/350 | 7HG-G027-17 |
| **30 Meter with 5-Meter Guardian™ Integrated Guard** | | | |
| 0.25 | 0.25 | -60 to 325/350 | 7HG-G027-11-GGA |
| **30 Meter with 10-Meter Guardian Integrated Guard** | | | |
| 0.25 | 0.25 | -60 to 325/350 | 7HG-G027-11-GGC |
| **60 Meter** | | | |
| 0.25 | 0.25 | -60 to 325/350 | 7KG-G027-11 |

### Include Phenova® CRMs With Your 8270D Analysis

| Part No. | Product Description | Standard Type |
|---|---|---|
| AL0-101232 | 8270 Calibration Standard (1000 µg/mL in Methylene Chloride) | Calibration |
| AL0-101233 | PAH Plus Methylnaphthalenes (2000 µg/mL in Methylene Chloride) | Calibration |
| AL0-101234 | 8270 Phenols Standard (2000 µg/mL in Methylene Chloride ) | Calibration |
| AL0-101235 | Appendix IX Mix 1 (2000 µg/mL in Methylene Chloride) | Calibration |
| AL0-101237 | Appendix IX Mix 2 (2000 µg/mL in Methylene Chloride) | Calibration |
| AL0-101238 | SV Internal Standard Mix (4000 µg/mL in Methylene Chloride) | Internal |
| AL0-101250 | 2-Fluorobiphenyl (1000 µg/mL in Methylene Chloride) | Surrogate |

Phenova CRMs available only in USA and Canada. Order these standards and others for 8270D at www.phenomenex.com/standards.

guarantee

If Zebron columns do not provide at least an equivalent separation as compared to any other GC column of the same phase and comparable dimensions, return the column with comparative data within 45 days and keep the column for a FULL REFUND. If you are not satisfied with Phenova CRMs for any reason, simply let us know and keep the products for FREE!*

* Limit US $300, CAD $345

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