Column Evaluations for the Analysis of Polynuclear Aromatic Hydrocarbons

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Abstract

Polycyclic Aromatic Hydrocarbons (PAH) are compounds that are found just about everywhere in the environment: air, water and soil. Some PAHs are used in manufacturing processes while others are byproducts typically formed through the incomplete combustion of organic materials. PAHs are comprised of fused benzene rings. Naphthalene is the smallest of the PAHs with two fused benzene rings. The larger PAHs (those containing more than 6 or more benzene rings) tend to be extremely persistent in soil as their water solubility and mobility decreases substantially with their increasing molecular weight. Also, many PAHs are known or suspected carcinogens. The USEPA currently lists and mandates the determination of sixteen priority pollutant PAHs they deem the most hazardous as they are known or suspected carcinogens.

However, many analyses are being expanded beyond just these sixteen compounds. Compounds such as benzo(j)fluoranthene, dibenz(a,h)acridine and dibenzo(a,e)pyrene are being added to scans for monitoring purposes or due to increasing regulatory requirements but are difficult to analyze via conventional test conditions. In GC analyses employing a 5 % phenyl stationary phase, benzo(j)fluoranthene co-elutes with benzo(b)fluoranthene therefore its determination must be reported as a combined sum of isomers. Where regulations mandate uniquely reported concentrations for individual analytes this is obviously an ineffective technique.

In an attempt to achieve greater separation of these isomers we chose to investigate the potential of several commercially available stationary phases. The goal is to evaluate and optimize these stationary phases for the analysis of these extended PAH scans.

Routine PAH Analysis

The BPX5 (5 % Phenyl Polysilphenylene-siloxane) was first used to analyze the sixteen component priority pollutant PAH mixture. The temperature program was optimized to achieve the best separation of the critical isomer pairs in the analysis.

The resulting optimized temperature program was used as the initial program for subsequent columns. No internal standards or surrogates were used in these evaluations. As shown in Figure 1, the routine PAH analysis is relatively easy on a standard 5 % phenyl stationary phase. There are however, critical pairs that must be sufficiently resolved to ensure proper identification in GCMS analyses, since these pairs share the same quantitation ions. The separation of these critical pairs are shown in Figure 2.

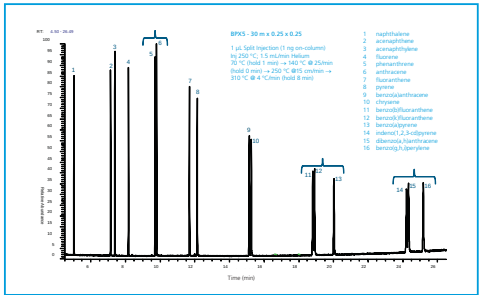

Figure 1. BPX5 30 m x 0.25 x 0.25
Routine Sixteen Component PAH Analysis – Total Ion Chromatogram (TIC)

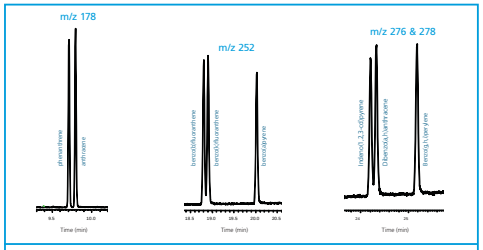

Figure 2. BPX5 30 m x 0.25 x 0.25
Routine Sixteen Component PAH Analysis– Critical Pairs

Expanded PAH Analysis

Three individual components were added to the routine sixteen component standard to mimic a typical expanded scan. 1-methylnapthalene, 2-methylnapthalene, and benzo(j)fluoranthene. We evaluated three phenyl containing stationary phases: BPX5, BPX35 and BPX50 as well as the carborane based HT8. As can be seen in Figures 3, the benzo(j)fluoranthene isomer is not completely resolved on the BPX5, which is a common problem for other equivalent 5 % phenyl stationary phase.

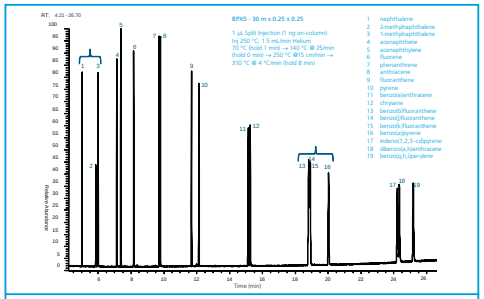

Figure 3. BPX5 30 m x 0.25 x 0.25
Expanded PAH Analysis , Nineteen Component – Total Ion Chromatogram (TIC)

The increase in phenyl functional groups in the BPX35 and BPX50 stationary phases should increase retention of these phenyl containing compounds. Ultimately through this increased interaction we hope to achieve resolution such that the quantitative and qualitative requirements can be met.

Unfortunately, the BPX35 (35 % Phenyl Polysilphenylene-siloxane) showed little improvement from the 5 % Phenyl phase, other than an increase in retention. The selectivity for the fluoranthene isomers showed no improvement and the indeno(123-cd)pyrene and dibenzo(a,h)anthracene pair showed a loss of resolution (Figure 4 and 5).

The HT8 (8 % Phenyl (equiv.) Polycarborane-siloxane) showed very poor selectivity for the fluoranthene isomers in the 16 component standard, so the analysis of the expanded scan with benzo(j)fluoranthene was not pursued. However, it should be noted that the HT8 showed baseline resolution of the late eluting PAHs, namely indeno(123-cd)pyrene and dibenzo(a,h)anthracene (Figure 6).

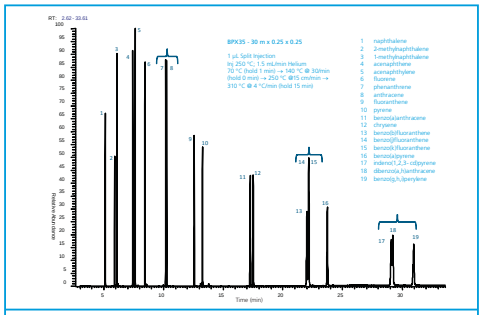

Figure 4. BPX35 30 m x 0.25 x 0.25
Expanded PAH Analysis , Nineteen Component – Total Ion Chromatogram (TIC)

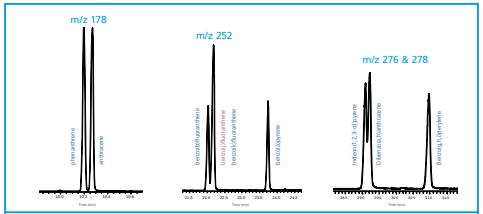

Figure 5. BPX35 30 m x 0.25 x 0.25
Expanded PAH Analysis , Nineteen Component – Critical Pairs

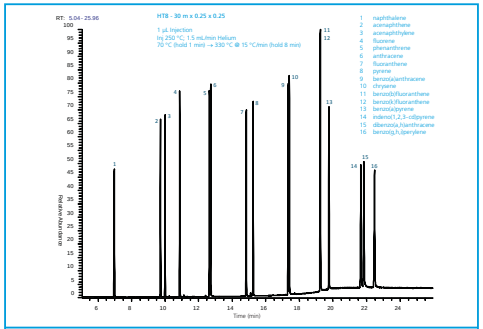

Figure 6. HT8 30 m x 0.25 x 0.25
Expanded PAH Analysis , Nineteen Component – Critical Pairs

The BPX50 results showed significant improvement for the fluoranthene isomers over the other stationary phases for the expanded scans as shown in Figure 7 and Figure 8. The benzo-fluoranthene isomers are nearly baseline resolved. The only drawback was a slight loss in resolution of phenanthrene and anthracene but it is still enough to qualify these compounds effectively.

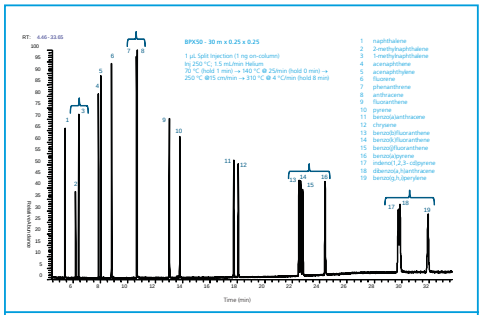

Figure 7. BPX50 30 m x 0.25 x 0.25
Expanded PAH Analysis , Nineteen Component – Total Ion Chromatogram (TIC)

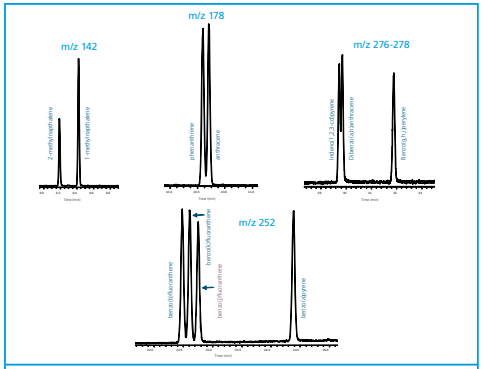

Figure 8. BPX50 30 m x 0.25 x 0.25
Expanded PAH Analysis , Nineteen Component – Critical Pairs

Conclusion

As shown in the previous chromatograms, simple changes in stationary phases can have a profound effect on selectivity for PAHs. The polycarborane based HT8 column showed a unique selectivity for indeno(123-cd)pyrene and dibenzo(a,h) anthracene compounds. Although these two compounds share separate quant ion (276 and 278 respectively) their co-elution can make identification difficult, therefore the ability to baseline resolve these compounds could prove beneficial in some assays. The BPX50 is an excellent solution for the analysis of expanded PAH scans, specifically the benzo-fluoranthene isomers. These isomers are nearly baseline resolved and can easily be quantitated as distinct peaks. The drawback is the slight loss in resolution of the phenanthrene / anthracene isomers. Analysts will have to be aware of this affect especially when performing the analysis via GC/MS SIM mode.

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