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應用手冊

Routine Quantitation of PAHs in Sediments Using Electron Ionization GC-MS/MS

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This is an Application Brief and does not contain a detailed Experimental section.

Abstract

This application brief evaluates the Xevo TQ-GC as a fit for purpose electron ionization (EI) GC-MS/MS for the routine analysis of polycyclic aromatic hydrocarbons (PAHs) extracted from sediment samples.

Benefits

Xevo TQ-GC is a fit for purpose GC-MS/MS solution for routine analysis of PAHs in sediment samples.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common persistent organic pollutants (POPs) monitored by many agencies globally. PAHs can be generated naturally and anthropogenically through combustion of carbon-based fuels such as wood, coal, oil, and diesel, making them present in food, water, and soil samples worldwide. They are made up of fused aromatic rings and are classified as being carcinogenic or potentially carcinogenic. Although there are hundreds of native and substituted known PAHs, only a handful are typically focused on in regulatory methods. For example, Canadian Soil Quality Guidelines[1] recommend an analysis of 41 PAHs, Europe[2] follows the 15+1 list, and the United States[3] tends to follow a list of 16 priority EPA PAHs. Xevo TQ-GC is a fit for purpose GC-MS/MS solution for routine analysis of PAHs in sediment samples.

The goal of this evaluation was to expand the list of PAHs in one GC-MS/MS analysis to include the majority of the PAHs required in Canada, Europe, and the United States. Various sediment sample extracts previously extracted on site at Environment and Climate Change Canada Quebec Laboratory for Environmental Testing (QLET)[4] were used for this evaluation. A suite of approximately 50 PAHs (C9 through C24 PAHs as well as chlorinated and methylated isomers) were evaluated on the Xevo TQ-GC for routine performance criteria such as sensitivity, calibration range, and accuracy based on analysis of the extracted sediment samples.

Results and Discussion

Chromatographic performance was crucial for this analysis as the suite of PAHs included in the method contains three groups of critical isomer separations that need to be resolved; phenanthrene/anthracene, 2/3/4/5/6-methyl chrysene, and benzo(b)/(j)/(k)fluoranthene. Utilizing the Rxi-35Sil MS column, all the critical isomers were separated (Figure 1) sufficiently to achieve reliable quantitation.

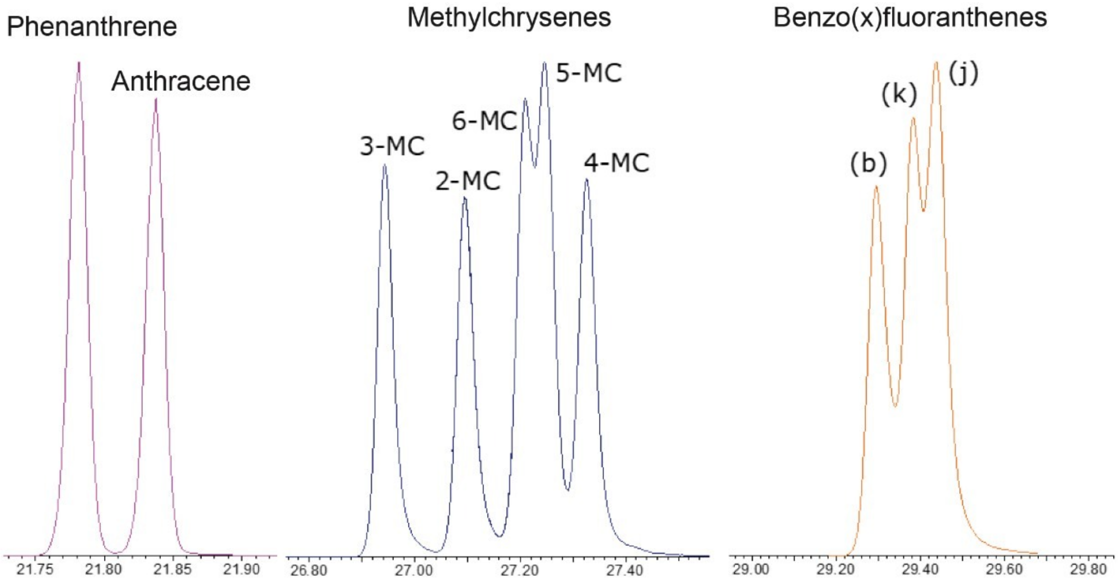

Figure 1. Three critical isomer pairs resolved using the Rxi-35Sil MS column. Full method details can be accessed and downloaded from the Xevo TQ-GC Quanpedia Database (marketplace.waters.com).

The Xevo TQ-GC demonstrated good calibration over the calibration range used (0.2–40 µg/kg) for sample analysis (Figure 2), with all R^2 values >0.998. As demonstrated in Figure 2, some PAHs produced a linear calibration curve while others had a slightly quadratic nature. The best fit was used for each compound in order to perform accurate quantitation. The detection limits for most compounds analyzed were determined to be below the lowest calibration point of 0.2 µg/kg (ppb). Table 1 highlights the detection limits for each compound in the analysis method.

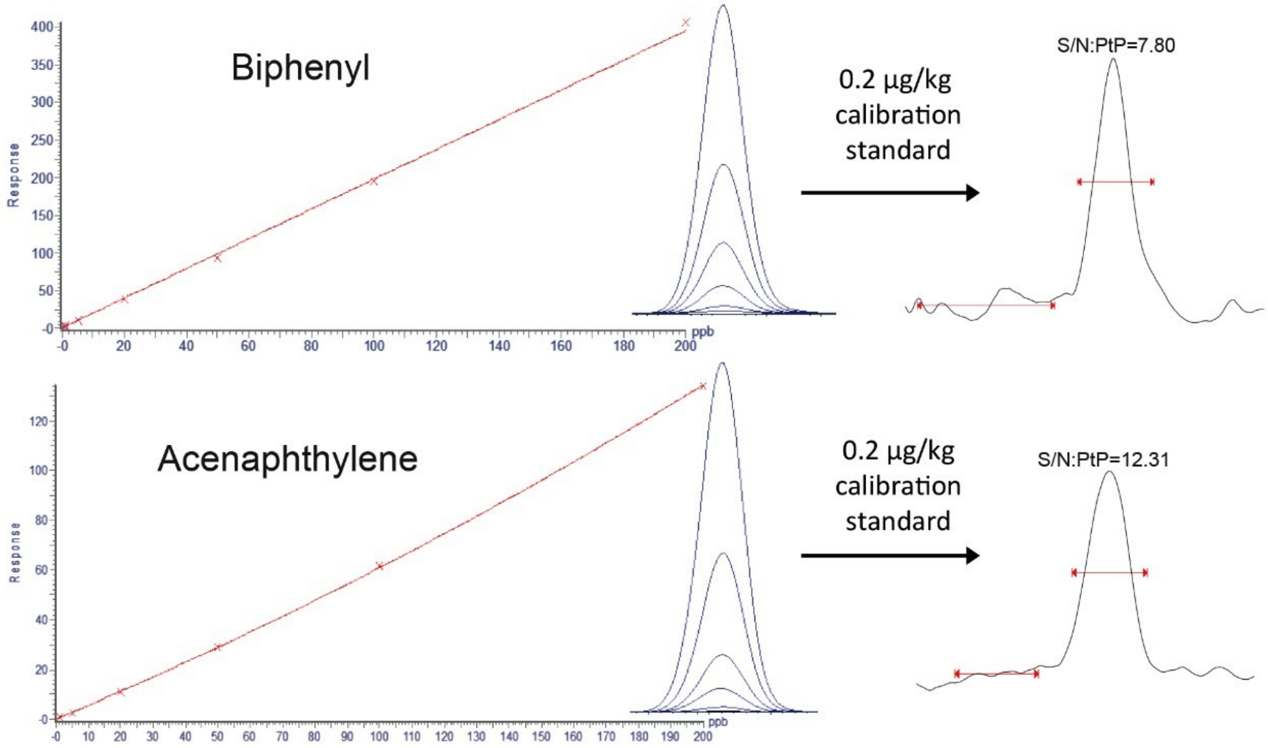

Figure 2. Calibration curves and peak overlays of each calibration point for biphenyl (top) and acenaphthylene (bottom).

Compound	Limit of Detection (µg/kg)	Canadian Soil Quality Guidelines◊	EU 15+1 List*	EPA 16 List
Indene	0.04			
Naphthalene	0.12	x		x
1-Methylnaphthalene	0.07			
2-Methylnaphthalene	0.07			
1-Chloronaphthanlene	0.08			
2-Chloronaphthanlene	0.08			
Biphenyl	0.18			
1,3 Dimethylnaphthalene	0.06			
Acenaphthylene	0.04			x
Acenaphthene	0.1			x
2,3,5 Trimethylnaphthalene	0.1			
Fluorene	0.12	x		x
Phenanthrene	0.1	x		x
Anthracene	0.16	x		x
Carbazole	0.18	x		
1-Methylphenanthrene	0.12	x		
Fluoranthene	0.08	x		x
Pyrene	0.08	x		x
Retene	0.16			
2 Methylfluoranthene	0.1	x		
Benzo(c)phenanthrene	0.1	x		
Benzo(c)acridine	0.16	x		
Benzo(a)anthracene	0.1	x	x	x
Chrysene	0.04	x	x	x
2-Methylchrysene	0.14	x		
3-Methylchrysene	0.14	x		
4-Methylchrysene	0.14	x		
5-Methylchrysene	0.14	x	x	
6-Methylchrysene	0.14	x		
Benzo(b)fluoranthene	0.14	x	x	x
Benzo(k)fluoranthene	0.14	x	x	x
Benzo(j)fluoranthene	0.14	x	x	
7,12 dimethylbenzo(a)anthracene	0.12			
Benzo(a)pyrene	0.16	x	x	x
Benzo(e)pyrene	0.16	x		
Perylene	0.18	x		
3-Methylcholanthrene	0.18			
Dibenzo(ah)acridine	0.08	x		
Dibenzo(aj)anthracene	0.06	x		
Dibenzo(ac)anthracene	0.06	x		
Dibenzo(ah)anthracene	0.06	x	x	x
Indeno(1,2,3-cd)pyrene	0.04		x	x
7H Dibenzo(cg)carbazole	0.54	x		
Benzo(ghi)perylene	0.04	x	x	x
Anthanthrene	0.14	x		
Dibenzo(ae)fluoranthene	0.06	x		
Coronene	0.12			
Dibenzo(ae)pyrene	0.24	x	x	
Dibenzo(ai)pyrene	0.24	x	x	
Dibenzo(ah)pyrene	0.24	x	x	

Table 1. Limits of detection determined for each PAH included in the method. ◊Dibenzo(al) pyrene, Dibenzo(aj) acridine, Benzo(a)acridine, Benzo(ghi)fluoranthene, 1-methythchrysene, and Triphenylene were not included in this study. *Benzo(c)fluorene, Cyclopenta(cd)pyrene, and Dibenzo(a,l)pyrene were not included in this study.

A series of sediment sample extracts containing various levels of PAHs were evaluated on the Xevo TQ-GC. All samples were previously characterized for the same suite of PAHs using a validated method on another electron impact (EI) based GC-MS/MS system. Samples were quantified using the calibration range demonstrated in

Figure 3. High concentration samples that fell outside the calibration range were diluted and re-analyzed. The quantitative results compared very well with the expected concentrations determined on the alternate EI based GC-MS/MS system. 75% of the PAHs had a percent difference of calculated concentration of less than 15%. The remainder were all within 30% difference. A comparison between the two sets of results can be seen in Figure 3 for one of the sediment samples analyzed.

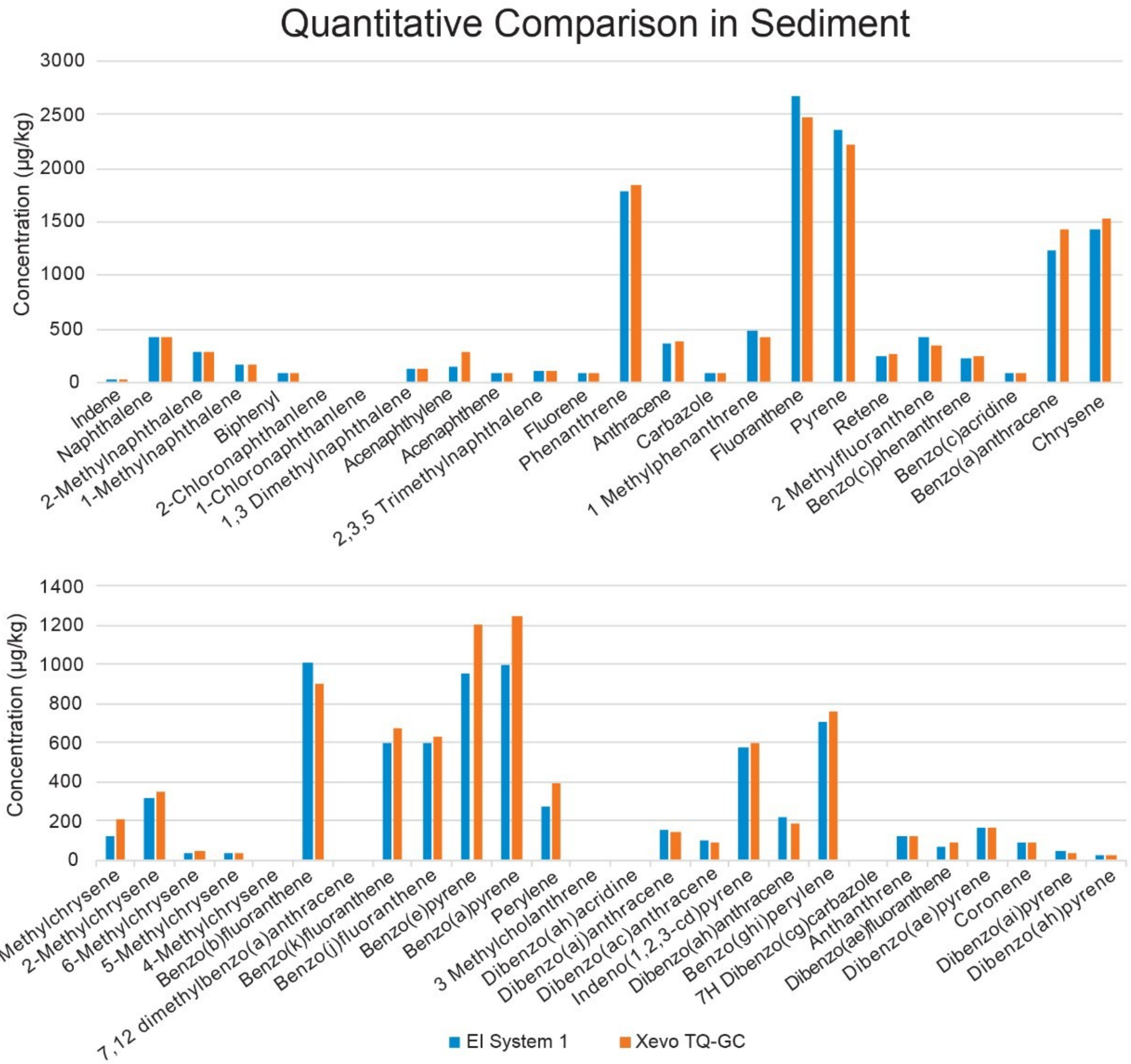

Figure 3. Quantitative comparison of the concentrations of each PAH detected in a sediment sample. Alternative EI based GC-MS (blue) and Xevo TQ-GC (orange).

Conclusion

The Xevo TQ-GC is suitable for the routine and accurate analysis and quantitation of a large suite of PAHs in sediment samples. All PAHs had limits of detection well below 1 µg/kg, ranging from 0.04 to 0.54 µg/kg. The utilization of tandem quadrupole technology (MRMs) allows enhanced selectivity to methods that typically would utilize single quadrupole analysis (SIM or SIR). This allows the Xevo TQ-GC to meet and exceed global regulatory methods. While this evaluation was on sediment samples, with proper sample preparation, this GC-MS/MS method could easily be applied to other types of environmental and food samples requiring routine PAH testing.

References

1. CCME (Canadian Council of Ministers of the Environment), 2010. Canadian Soil Quality Guidelines for Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (Environmental and Human Health Effects). Scientific Criteria Document (revised). 216 pp.

2. Joint Research Center (JRC) Technical Notes, Polycyclic Aromatic Hydrocarbons (PAHs) Factsheet, 4th edition, 2011.

3. EPA Method 8310, Revision 0, September 1986, Third Edition of the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846.

4. Method: Q0510S0. Analyse des hydrocarbures aromatiques polycycliques dans des solides-technique pas GC-MS. Environment and Climate Change Canada Quebec Laboratory for Environmental Testing.

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