EVALUATING A ROUTINE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FOR A NEW ELECTRON IONIZATION GC-MS/MS

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are abundant toxic environmental pollutants generated by the thermal decomposition of organic matter, primarily from human activity such as wood-burning or biofuel use. Their stable chemical properties make them very persistent and they can be found nearly everywhere around the globe. PAHs are monitored globally in both the environment and food with most monitoring regulations having been established for many decades. The European Food Safety Authority (EFSA), the US EPA, and others monitor up to 26 different PAHs due to their toxicity. Depending on the matrix analyzed and the regulatory requirements, Maximum Residue Limits (MRL) vary greatly. For example, the EU regulates PAHs in oily foods in the low µg/kg (ppb) range. The US EPA regulates benzo(a)pyrene to sub-µg/L (ppb) in water. Many regulations require the analysis be performed using a GC-MS system. Most established methods utilize electron ionization (EI) GC-MS. Furthermore, many highly utilized mass spectral libraries, such as NIST, are populated with EI data. This work evaluates a new EI GC-MS/MS instrument (Xevo TQ-GC) for the routine identification and quantification of a suite of approximately 50 PAHs in sediments.

Xevo TQ-GC

METHODS

Sample Preparation

Sediment samples were extracted in accordance with Environment and Climate Change Canada Quebec Laboratory for Environmental Testing (QLET) protocols. Briefly, samples were dried and ground before preparation. 5g of sediment sample were spiked with surrogates prior to Soxhlet extraction in toluene for 16 hours. Sample extracts were purified using copper (to remove sulfur) followed by a silica:alumina column clean up. The sample was dried under nitrogen and reconsitituted in iso-octane.

GC Conditions:

Column: Rxi-35Sil MS 30 m x 0.25 mm x 0.25 µm
Injection Type: Pulsed Splitless (32 psi for 1.2 min)
Inlet Temperature: 310 °C
Injection Volume: 1 µL
Flow Rate: 1.5 mL/min
Oven Program

Rate (°C/min)	Final Temperature (°C)	Hold Time (min)	Total Time (min)
-	65	0	-
5	155	0	-
25	275	0	-
2.5	330	7	51.8

Electron Ionization (EI) Conditions

System: Xevo™ TQ-GC
Ionization Mode: EI+
Electron Energy: 70 eV
Emission: 200 µA
Source Voltage: 4.5 V
Repeller Voltage: 44 V
Extraction Voltage: 44 V
Focus 1: 13.5 V
Focus 2: 153 V
Transfer Line Temperature: 320 °C
Source Temperature: 250 °C

RESULTS AND DISCUSSION

Method Performance

Among the approximately 50 PAHs included in the method, there are three groups of critical separations that needed to be achieved. The necessary resolution for two of the three groups of isomers could not be achieved using a common 5-phase column (**Figure 1A**). Only phenanthrene and anthracene could be resolved. Using an Rxi-35Sil MS column, the five methylchrysene isomers could be resolved and resolution was achieved for benzo(b)-, benzo (k)-, and benzo(j)fluoranthene (**Figure 1B**).

The TQ-GC demonstrated good linearity over the calibration range (1-200 pg/µL) used for sample analysis (**Figure 2**). The detection limits for most compounds analyzed were determined to be equal to or below the lowest point analyzed in the calibration range (1 pg/µL). **Table 1** highlights the detection limits for each compound in the analysis method.

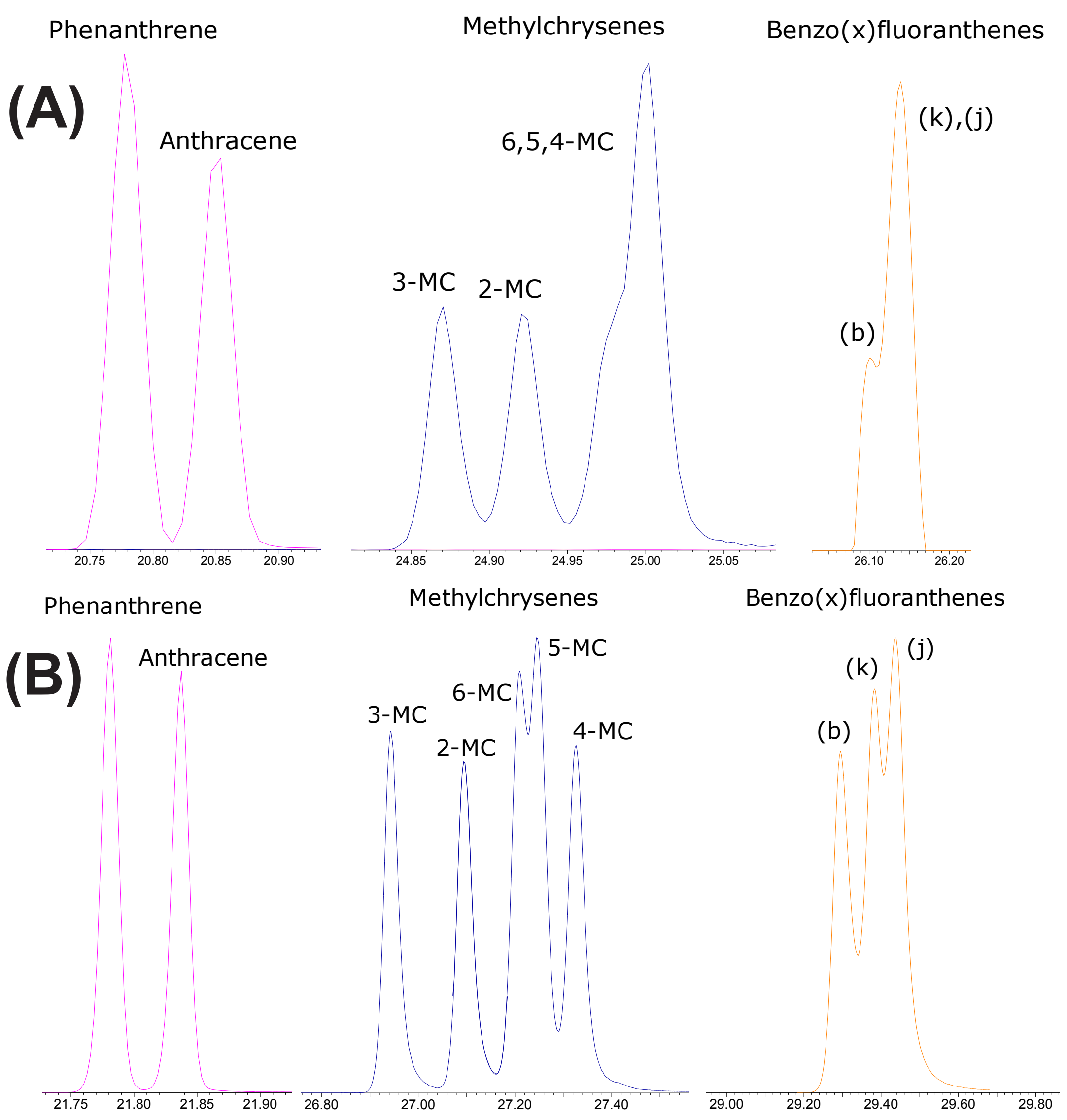

Figure 1. Resolution of critical PAH isomers using (A) Rxi-5MS and (B) Rxi-35Sil MS columns.

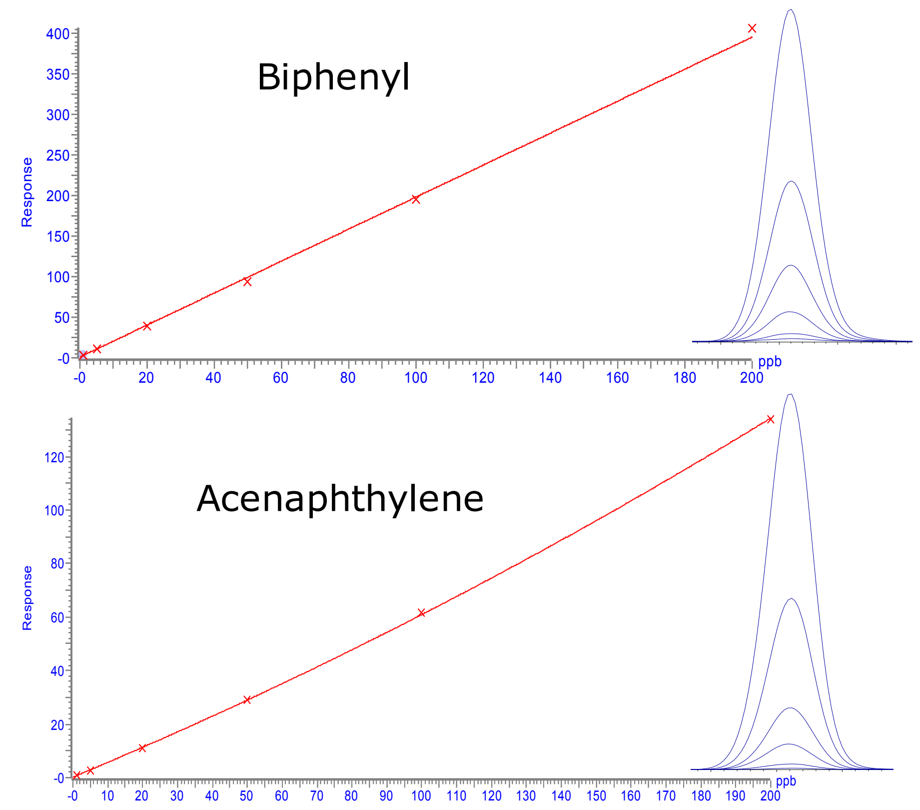

Figure 2. Calibration curves and overlaid chromatograms for examples of two PAHs analyzed in method.

Sediment Sample Analysis

A series of sediment sample extracts containing various levels of PAHs were evaluated on the TQ-GC. All samples were previously characterized for the same suite of PAHs using another EI based GC-MS/MS system. Samples were quantified using the calibration range demonstrated in Figure 2. High concentration samples that fell outside the calibration range were diluted and re-analyzed. The resulting quantitative results compared very well with the expected concentrations determined on the different EI based GC-MS/MS system. A comparison between the two sets of results can be seen in **Figure 3** for one of the sediment samples analyzed.

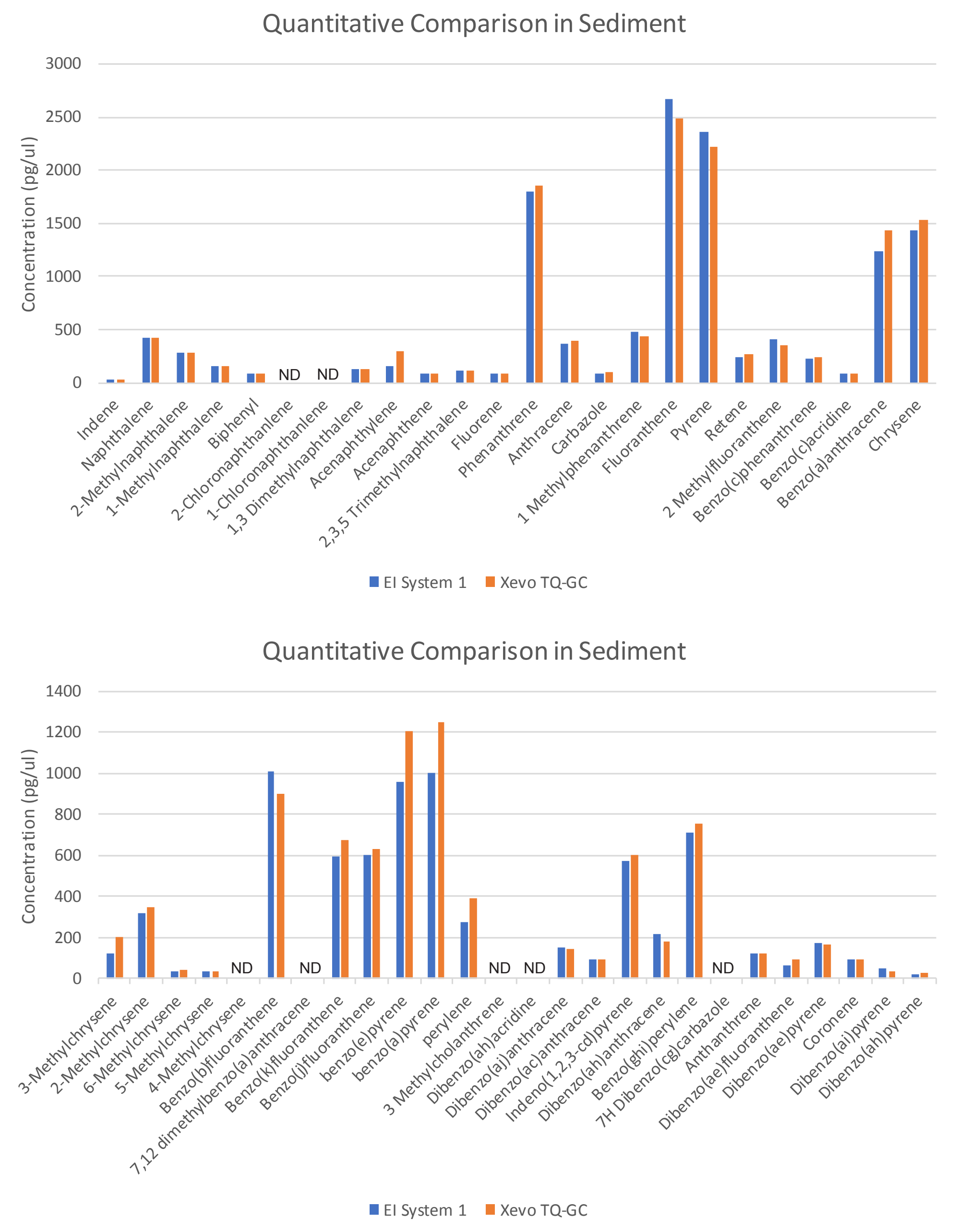

Figure 3. Comparison of the calculated concentrations of PAHs in extracted sediment sample. Orange bars represent data from Xevo TQ-GC and blue bars represent data from previous analysis of sample on a different EI based GC-MS/MS system. (ND) not detected

Compound	Limit of Detection (pg/µL)
Indene	< 1
Naphthalene	< 1
Methylnaphthalene (1- and 2-)	< 1
Chloronaphthanlene (1- and 2-)	< 1
Biphenyl	< 1
1,3 Dimethylnaphthalene	< 1
Acenaphthylene	< 1
Acenaphthene	< 1
2,3,5 Trimethylnaphthalene	< 1
Fluorene	< 1
Phenanthrene	< 1
Anthracene	< 1
Carbazole	< 1
1-Methylphenanthrene	< 1
Fluoranthene	< 1
Pyrene	< 1
Retene	< 1
2 Methylfluoranthene	< 1
Benzo(c)phenanthrene	< 1
Benzo(c)acridine	1
Benzo(a)anthracene	< 1
Chrysene	< 1
Methylchrysene (2-,3-,4-,5-,and 6-)	1
Benzo(b),(k), and (j)fluoranthene	1
7,12 dimethylbenzo(a)anthracene	1
benzo(a) and (e)pyrene	1
perylene	< 1
3-Methylcholanthrene	1
Dibenzo(ah)acridine	1
Dibenzo(aj), (ac), and (ah) anthracene	1
Indeno(1,2,3-cd)pyrene	1
7H Dibenzo(cg)carbazole	1
Benzo(ghi)perylene	1
Anthanthrene	1
Dibenzo(ae)fluoranthene	1
Coronene	1
Dibenzo(ae),(ai), and (ah)pyrene	5

Table 1. Limits of detection based on calibration range used for sediment analysis. The lowest calibration point was 1 pg/µL (ppb). An LOD of < 1 indicates the LOD was determined to be below the lowest calibration point run.

CONCLUSIONS

- **The Xevo TQ-GC provides the benefits of electron ionization (EI) GC-MS/MS analysis.**
- **Resolution of critical PAH isomers was achieved using the Rxi-35Sil MS column.**
- **The method demonstrated the required linearity and sensitivity for routine PAH analysis.**
- **Detection limits for the PAHs studied were mostly at 1 pg/µL (ppb) or below.**
- **The Xevo TQ-GC has been demonstrated to be a robust EI GC-MS/MS for routine analysis of a large suite of PAHs in sediments.**