Methodology for Qualitative and Quantitative Analysis of Polycyclic Aromatic Hydrocarbons (PAHs)

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ABSTRACT

Qualitative and quantitative analysis of polycyclic aromatic hydrocarbons (PAHs) were performed using a solid-phase micro-extraction (SPME) technique and gas chromatography-flame ionization detector (GC-FID) instrumentation. Several different extraction methods were tested to determine which method gave the most reproducible results. In order to determine how well the GC performed, commercial standards were used to determine the retention time and concentration of 16 PAHs. A 2-point calibration curve using 100 part per billion (ppb) and 20 ppb solutions was constructed for quantitative analysis. Future plans include analyzing river water samples on a regular basis over an extended period of time, and also Soxhlet extraction methods to study PAH levels in river sediments.

INTRODUCTION

PAHs are pollutants formed during the combustion of fossil fuels. Automobile emissions and coal-tar pavement[1] are common sources of PAHs. Because of this, PAHs can be commonly found deposited in sediment[2] near high-traffic areas, as well as in rain run-off areas and rivers. A method for both qualitatively and quantitatively analyzing these compounds would lead to a better understanding of how to prevent these contaminates from entering natural areas. The Concho River in downtown San Angelo is a prime location to collect samples as there is a large volume of automobile traffic and it collects a large source of rain run-off. A methodology was developed to qualitatively and quantitatively analyze PAH concentrations using SPME-GC-FID.

METHOD

- Purchased commercial PAH standards (Ultra Scientific); 1 mL of each individual PAH at 100 ppm, 3 mL of 100 ppm and 20 ppm standards composed of all 16 PAHs.
- GC Conditions (HP-5890 GC-FID); Pressures set for gas cylinders: 60 psi (He), 19.5 psi (H_2), 320 kPa (air)
  Column head pressure: 40 kPa
  Column type/dimensions: DB-5 column, 30 m (length) × 0.32 mm (diameter) × 0.25 µm (stationary phase thickness)
- Oven temperature program started at 50˚C, held for 5 min, then up to 160˚C at 20˚C/min, to 265˚C at 5˚C/min and finally to 300˚C at 3˚C/min and held for 15 min. The carrier gas was helium with a flow rate of 1.5 mL/min. The detector flow rates were 597 mL/min for air, 43.95 mL/min for hydrogen and 45.1 mL/min for helium (makeup gas). The detector was maintained at 320˚C. The injector was maintained at 250˚C.
- SPME technique implemented in order to test the extraction capabilities from controlled water samples.
- 30 µm PDMS SPME fiber used initially, while SPME allowed to soak in sample for 30 minutes, then injected on column for 5 minutes, finally removed and heated in second injector for 10 minutes to remove excess analytes.
- River water samples were taken from Concho River at same location twice per week. Samples were then filtered using a 0.45 micon cellulose nitrate filter to remove large colloids. Filtered samples were then qualitatively analyzed using same procedure as mentioned above.
- 100 µm PDMS SPME fiber used next based on literature[3] stating that 100 µm fiber has better reproducibility and adsorption over full molecular size range of PAHs.
- 100 ppb and 20 ppb standards created using commercial standards by diluting 200 µL of respective solution to 200 mL mark in volumetric flask.
- Calibration curves constructed for quantitative analysis of each PAH using results from above solutions.

RESULTS

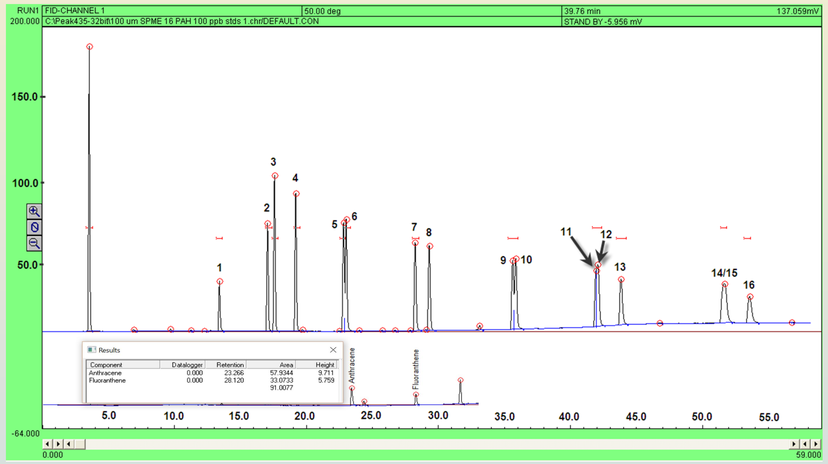

Figure 1- Chromatogram from 100 ppb solution of all 16 PAHs using a 100 µm SPME; inlay shows the results from a river water sample that showed the method was able to successfully detect PAHs in environmental samples using the 30 µm SPME fiber.

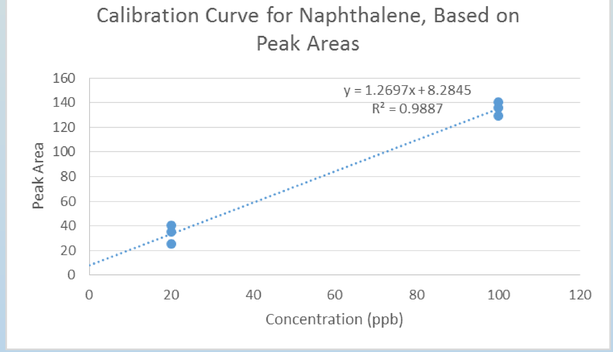

Figure 2- Calibration curve for naphthalene extracted from aqueous solutions using a 100 µm SPME fiber; similar curves were created for each PAH.

%RSD Values for 100 µm SPME Technique		
	20 ppb	100 ppb
Naph	18.0	3.5
AcPY	10.2	1.7
AcP	9.2	2.1
Flu	10.5	8.5
Phe	9.2	16.4
Ant	31.8	19.2
FL	12.5	25.5
Pyr	11.9	26.1
BaA	26.1	30.4
Chr	25.2	28.9
BbFL	----	31.6
BkFL	26.1	23.5
BaP	26.7	26.4
InP+DBA	27.0	25.4
BghiP	27.6	24.9

Table 1- RSD values showing precision and reproducibility of method based on peak areas for each PAH.

DISCUSSION

Method

After experimenting with a few different size SPME fibers, it was decided that a 100 µm PDMS fiber would be used for all analyses as it produced the largest signals. The other size fiber used for some analyses was a 30 µm PDMS fiber. This fiber was successfully able to extract several PAHs from river water samples (inlaid figure in Figure 1), but with varying degrees of reproducibility. Other conditions for the extraction technique that were settled upon included a 30 minute absorption time for the SPME fiber and then an injection time of the SPME fiber on the column for 5 minutes. It has been shown that varying the analyte absorption times as well as the SPME fiber injection time on the GC column[3] can have an impact on results, and these are some conditions that could be adjusted in future analyses to see if there is a statistically significant difference in the data obtained between the methods. As can be seen in Figure 1, the method settled upon for immediate analyses produces solid chromatographic data.

Data

The 100 µm SPME fiber was chosen as the fiber to move forward with because of its reproducible results at the concentrations being examined. At concentrations on the ppb level, it has been shown that RSD values of approximately 20% are acceptable results[4]. As can be seen in Table 1, the RSD values for peak areas fall within the accepted limits for most PAHs. Further analysis with the method could allow for all PAHs to be within accepted limits. In this preliminary analysis, the average detection limits for the PAHs were 4 ppb, and the average limits of quantitation were 11 ppb. 2-point calibration curves were also produced for each PAH using data from multiple 100 ppb and 20 ppb runs with the 100 µm SPME fiber. Early runs with the 30 µm fiber from 2/28/2016-3/22/2016 showed that we were able to identify anthracene, fluoranthene, and possibly benz[a]anthracene with concentrations approximately below 10 ppb. The 30 µm fiber became contaminated and based on literature[3] the 100 µm fiber was used next. River samples were analyzed using the 100 µm fiber from 4/4/2016-4/22/2016. During this time large amounts of rain were present. River samples were extremely diluted and PAHs were unable to be detected. However, lab prepared samples at 20 ppb showed significant peaks which supports that the method employed will be able to detect PAHs in future river water samples when river levels return to normal. The use of calibration curves created will allow for concentration determinations for each PAH present.

FUTURE ANALYSES

Using the calibration curves and method for analyzing river water samples, a periodic log of the environmental conditions, location of samples, and concentrations of PAHs detected will be kept in order to monitor the PAH levels in the river. Soxhlet extraction methods will also be employed by future students to analyze PAH concentrations in sediment beds rather than river water.

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