Quantification of Polycyclic Aromatic Hydrocarbons in Particulate Matter Using Thermal Desorption Extraction

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Abstract Traditional extraction methods for PAHs have some inherent disadvantages, such as requiring large amounts of samples and the use of organic solvents; they are time consuming and complex; and involve multi-step processes that are subject to errors. The thermal desorption based method for selected PAHs presented in this paper is rapid, requires no solvents, and is relatively easy to use. This method shows acceptable recoveries, repeatability, and linearity in response. Unfortunately, increased maintenance of the GC/MSD may be required when using this method, as fine particles may be transported into the injector, column, and detector. The application of TD/GC/MSD analytical technique is demonstrated by quantifying selected PAHs on size fractionated urban creek sediments from Alabama. The smaller and larger sized particulates were associated with higher concentrations of many PAHs, compared to the medium sized particulates.
Keywords Thermal Desorption, PAHs, Sediments, Extraction, GC/MSD, Stormwater

INTRODUCTION

PAHs are a class of frequently detected organic pollutants in urban stormwater runoff. PAH levels in urban freshwater sediments in North America have also increased over time (Metre, et al., 2000), indicating additional discharges associated with industrialization and urbanization, including increased use of vehicles, and wear and tear of asphalt (Kuklick, et. al, 1997; McCready, et.al 2000; Metre, et al., 2000). Prior studies (Pitt et al., 1999, Hwang et al., 2006) have shown that the significant particulate associations of PAHs affect their transport and fate in the aquatic environment.

Soxhlet (EPA method SW-848), automated soxhlet (EPA method 3540), and ultrasonic extraction (EPA method 3550) are the common solvent extraction methods for PAHs from solid samples. However, these methods have some inherent disadvantages, such as requiring large amounts of samples and organic solvents, they are time consuming and complex, and involve multi-step processes that are subject to errors (Zhang et al., 1994). Recently, there have been improved extraction techniques, such as supercritical fluid extraction, microwave digestion and solid phase micro extraction that have shown improved extraction recoveries and are less time consuming for PAHs analysis in solid matrices (Wong et al., 1999; King et al., 2003). However, these methods still require a separate extraction process prior to analysis and they also need large quantities of particulate samples which would require the filtration of very large quantities of typical water samples, if water sample particulates are to be tested.

Thermal extraction, or thermal desorption (TD), is an alternative PAH extraction technique which uses elevated temperatures as a means to directly transfer the analytes from solid sample matrices to the gaseous GC/MSD analytical system. The analytes desorbed from the solid sample matrices are concentrated in a cryotrap at the head of a gas chromatograph (GC) column. The concentrated analytes are then separated and detected using a standard GC column and mass spectroscopy detector (MSD), similar to the analysis of liquid samples when concentrated into a solvent. By this technique, pretreatment of the particulate samples is not necessary, avoiding the time consuming and expensive extraction step, and also this method avoids the use toxic solvents and hence the hazards and problems associated with proper disposal of used solvents. Only a few milligrams of particulate sample are needed for these analyses, requiring the filtration of relatively small water samples if water particulates are to be directly tested. Only a few applications of TD based extraction techniques for analysis of organic compounds associated with particulate matter have been published (Waterman et al., 2000; Ho et al., 2008). These applications refer to the analysis of PAHs in the National Institute of Standards and Technology (NIST) urban dust standard reference material (SRM1649A), but not on any stream or lake sediment standards or on broader ranges of environmental sediment samples.

This paper describes a modified and tested alternative PAH extraction procedure for urban creek sediment samples that used a SIS AutoDesorb^{TM} thermal desorption method. The particular TD unit used in this procedure mounts directly on the injection port and requires no modification to the GC instrument or to the transfer line. This paper demonstrates the reproducibility, efficiency, sensitivity and applicability of this TD/GC/MS method to quantify thirteen selected PAHs in NIST sediment standard reference material, 1941b. The paper also demonstrates the analytical technique by quantifying selected PAHs for size fractionated urban creek sediments collected from three urban creeks in central Alabama, USA.

MATERIALS AND METHODS

Chemicals and Materials

Standard solutions of PAHs were prepared by dilution (in 99.9% optima grade dichloromethane) of standard mix (1 mL, 47930-U QTM PAH Mix, Supelco®, PA, USA) containing each PAH at 1000 ng/mL. A carrier gas of ultra-high purity (99.9999%) helium and liquefied carbon dioxide (cylinder with dip tube) for cryo trap were obtained from Airgas, Tuscaloosa, AL. The equipment used during the method development and testing activities included the AutoDesorb^{TM} unit (Scientific Instrument Services, Inc. Ringoes, NJ, USA) coupled to a gas chromatograph (Agilent 6890) with a mass spectroscopic detector (Agilent 5973N). The TD unit consists of thermal desorption tubes which are 100mm long with 4mm internal diameters, and injection needles. TD tubes are heated to the required temperatures with heating blocks and the desorbed analytes are concentrated in a cryo trap mounted around the capillary column below the injection port. A TD tube conditioning oven was obtained from Scientific Instrument Services, Inc. (Ringoes, Nj, USA). A HP-5ms capillary column (30m x 0.25mm x 0.25µm, J&W Scientific, USA) was used in the GC. Untreated glass wool was obtained from Supelco® (PA, USA) as a sediment trap and to fill the desorption tubes. SRM1941b sediment standard material (described below) was obtained from NIST (Gaithersburg, MD, USA).

TD/GC/MS Methodology

The AutoDesorb^{TM} unit uses desorption tubes to contain the samples during the thermal desorption process. Prior to their use, the thermal desorption tubes and needles are conditioned in the tube conditioning oven at 350°C for 4 hours to eliminate all foreign volatile contamination. The conditioned tubes are packed with a known amount (depending on the expected PAH concentrations) of the solid sample to be analyzed. Both ends of the tubes are plugged with glass wool to hold the sample in place and to reduce the loss of fine particulates into the analytical stream that would plug the needle and accelerate contamination of the MS.

The packed tubes are loaded onto the system carousel and the analysis process is initiated using the AutoDesorb^{TM} software. Each desorption tube is purged to remove oxygen, excess water, and volatile materials that may be present in the tube. Injection starts following the purging and once the needle is lowered into the GC inlet. The injection time period was set based on instrument response and was sufficient to allow the injection port pressures to equilibrate and the proper split flow to be reached. At the end of the injection period, the heater blocks close around the desorption tube and the tube is heated at the specified rate. The carrier gas transports the desorbed analytes into the GC inlet. The cryotrap then traps the analytes exiting the GC inlet by condensing the organic gases and focusing the analytes for concentration. The cryotrap is heated ballistically to release the focused analytes instantaneously into the GC column, where the analytes then are separated based on their volatility. They are detected by the MSD based on their charge to mass ratios. The GC is operated with 20:1 split ratio with a column flow rate of helium carrier gas of 0.9mL/min. The programmed conditions of the GC are.

Initial temperature:	50ºC, hold for 1min
Final temperature:	300ºC hold for 20 min
Ramp 1:	20ºC/min from 50ºC to 140ºC
Ramp 2:	6ºC/min from 140ºC to 300ºC
Injector temperature:	300ºC
Carrier gas:	Helium at 35 cm/sec
Mode:	Constant flow

Thermal Desorption Method Optimization

The selected conditions for the thermal desorption extraction were determined based on a series of experiments conducted to obtain optimal recoveries of the analytes from the solid samples and to have good separation of the analytical peaks. Standard samples were prepared by spiking 10µL of the 20 mg/litre PAH standard onto pre-conditioned glass wool. The thermal desorption unit was subjected to different desorption times ranging from 1 to 20 minutes, and final desorption temperatures ranging from 250ºC to 375ºC.

Analysis of NIST SRM1941b Standard Sample

An urban harbor sediment standard, NIST SRM1941b, was tested using the developed TD extraction method. The standard was certified for 119 different constituents including PAHs, PCBs, and chlorinated pesticides. The sample was ground and sieved to a size finer than 150µm. This standard NIST sediment sample was subjected to TD/GC/MSD analyses to verify the optimized extraction conditions, and to measure method recovery and method sensitivity by testing the response linearity of the method.

Tuscaloosa Area Sediment Sample Collection and Processing

Fifteen separate sediment samples were collected from three different urban creeks (Cribbs Mill Creek, Hunter Creek and Carroll Creek) in and around Tuscaloosa and Northport, AL, USA. The sediment at the sampling point along Cribbs Mill Creek are mostly affected by runoff from single family medium density residential areas. The sediment at the sampling point along Hunter Creek are mostly affected by stormwater runoff from heavy road traffic next to the creek, commercial areas, and runoff from a trailer park residential area. Sediments at the sampling site from Carroll Creek are mostly affected by runoff from a high density residential area on one side of creek and forested lands on the other side of the creek.

All the samples were collected in pre-cleaned and autoclaved glass sample bottles using a manual dipper sampler made from polypropylene. The collected sediment samples were dried to remove moisture and were then sieved using a mechanical shaker and a set of stainless steel sieves with openings of 45, 90, 180, 355, 710, 1,400 and 2,800µm. PAH analyses were conducted on the material captured by these sieves, and on the pan (< 45µm). In addition, large organic materials (LOMs) (leaves and other debris) were manually separated from the largest particle fraction (>2,800µm) for separate analyses. Therefore, each of the 15 sediment samples had nine particle sizes that were analyzed for the PAHs.

RESULTS AND DISCUSSION

Thermal Desorption Method Optimization

The spiked glass wool solid matrices were subjected to different final desorption temperatures ranging from 250°C to 375°C. A final desorption temperature of 350°C produced the highest analytical peaks for the individual PAHs. Similarly, a series of runs was made with different holding times (1 to 20 min.) at the final desorption temperature. The peak areas obtained for individual PAHs increased as the holding time increased from 1 min to 15 min, but then decreased as the holding time further increased to 20 min. Therefore, the optimum desorption time for the highest recovery of PAHs was found to be 15 min. The coefficients of variation (COV) for triplicate analyses at these optimum times and temperatures showed that low molecular weight and high molecular weight PAHs have high variations in the peak areas (naphthalene 49%, fluorene 24%, dibenzo(a,h)anthracene 15%, benzo(ghi)perylene 16%), while the intermediate PAHs had much lower variations (COVs ranging from 0.5% - 4.0%). The final optimum conditions of the developed method are listed below.

Purge duration: 1.00 min
Injection duration: 1.00 min
Initial temperature: 50°C
Temperature ramp rate: 100°C
Final temperature: 350°C
Final temperature holding time: 15 min
Cryotrap: enabled
Cryo cool temperature: -40°C
Cryo heat temperature: 300°C
Cryo heat duration: 10.00 min
GC start time: 26.50 min

Analysis of NIST SRM1941b Standard Sample

Analysis of the NIST SRM 941b PAH sediment standard by TD/GC/MS was used to test the optimum conditions of the method described above. Most of the analytes present in the standard sample were detected and clear individual peaks were shown. However, there were two major problems identified during the analysis of this standard, as discussed below.

Presence of Sulfur Due to the presence of sulfur in the sediment sample, there were many unwanted sulfur-containing analytical peaks in the gas chromatogram (Figure 1). There is also a chance that the sulfur products of PAHs bond to particulates, making them difficult to extract. As copper forms copper sulfide when reacted with sulfur, the addition of small amounts of copper wire cuttings (about 4 – 5mg of copper wire cuttings for 30mg of sample) into the thermal desorption tube, along with the sediment sample, helped in preventing the formation of sulfur products of PAHs during the extraction process.

Moisture in the Sample Even after standard oven drying, the moisture content of the standard sample caused ice plugging in the GC column during the cryofocusing step and obstructed the flow of analytes through the column. This problem resulted in tremendous reductions in the peak areas obtained for the individual analytes, and in some cases there were no peaks observed (Figure 1). To further reduce the water content in the samples, they were also freeze-dried overnight before analysis.

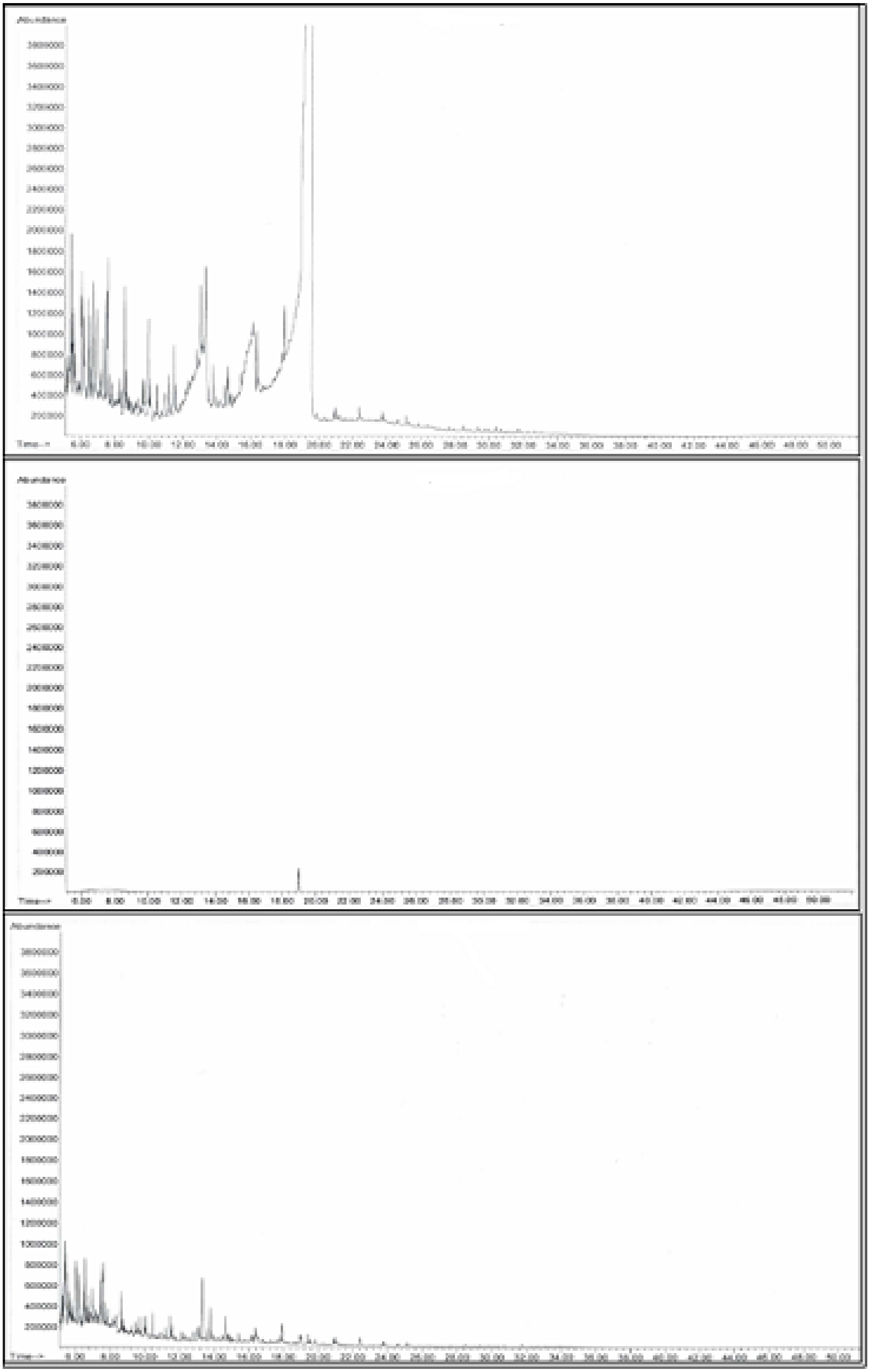

Figure 1. Chromatogram of NIST standard with dominant peaks of sulfur compounds (top), ice plugging problem (middle), with added copper cuttings (bottom).

Method Recovery Calculations

Three samples of 27 mg of standard were analyzed using the TD/GC/MS in selected ion monitoring (SIM) mode of the MS and resulting concentrations were compared with certified concentration of the analytes for recovery calculations, as shown in Table 1. The acceptable range of extraction recoveries for PAHs from liquid samples using SPE methods are also shown in Table 1. The calculated recoveries ranged from 27 to 143 percent. In general, one would expect higher percentages of recovery of analytes from liquid samples compared to solid samples. Even though calculated recoveries for some of the analytes have low percentage values, they were still in the acceptable ranges of recoveries for aqueous samples.

Table 1. Calculated TD/GC/MS Method Recoveries

PAH	NIST Certified Concentrations, µg/kg, (95% C.I)			TD/GC/MS Measured Concentration µg/kg, (Standard Deviation)	% Recovery (based on average NIST concentration)	[1]Acceptable Range of % Recovery from EPA Methods (Aqueous Samples)	[2]Acceptable Range of % Recovery from *Standard Methods* (Aqueous Samples)
	Minimum	Maximum	Average				
Naphthalene	753	943	848	1064 (329)	125	*D – 122	21 – 133
Fluorene	70	100	85	121 (17)	142	D – 142	59 – 121
Phenanthrene	362	450	406	446 (112)	110	D – 155	54 -120
Anthracene	166	202	184	192 (37)	104	NG	NG
Fluoranthene	601	701	651	406 (64)	62	14 – 123	26 – 137
Pyrene	542	620	581	189 (33)	33	D – 140	52 – 115
Benzo(a)anthracene	310	360	335	365 (65)	109	33 – 143	33 – 143
Chrysene	260	322	291	407 (116)	140	17 – 168	17 – 168
Benzo(b)fluoranthrene	432	474	453	157 (107)	35	24 – 159	24 – 159
Benzo(a)pyrene	341	375	358	148 (74)	41	17 – 163	17 – 163
Indeno(1,2,3-cd)pyrene	284	398	341	116 (86)	34	NG	NG
Dibenz(a,h)anthracene	43	63	53	24 (15)	46	NG	NG
Benzo(g,h,i)perylene	262	352	307	133 (88)	43	NG	NG

*D: detected, result must be greater than zero

[1] acceptable range of recoveries for EPA method 610 for analysis of organic chemicals from municipal and industrial wastewater, as provided under 40 CFR part 136.1.

[2] acceptable range of recoveries for extraction of liquid samples as provided in *Standard Methods for the Examination of Water and Wastewater* (2005).

NG: Not given

Method Sensitivity Calculations

NIST sediment samples of different weights, ranging from 3mg to 60mg, were analyzed using the developed method. Linear regressions were performed between method estimated analyte weights and corresponding weights in the certified standard to test the method response for linearity. The standard error of the regression was used to estimate the detection limit (DL) and the limit of quantification (LOQ) of the method (McCormick and Roach 1987):

$\mathrm{DL} = Y_0 + S_y Z_\alpha$ (1)

$\mathrm{LOQ} = Y_0 + 2 S_y Z_\alpha$ (2)

Where, Y_0 is the intercept of the regression equation, S_y is the standard error of the regression, and Z_α is the area under the normal curve associated with a one-tail probability for a given confidence level (such as the 95% C.I.).

For the analytes indeno(1,2,3-cd)pyrene and dibenz(a,h)anthracene, the linear line was forced to pass through the origin, as the intercepts were found to be insignificant (p values for indeno(1,2,3-cd)pyrene and for dibenz(a,h)anthracene were 0.327 and 0.263, respectively). Table 2 shows the calculated DL and QL for this method. The residuals of the regression were found to be normally distributed according to the Duncan test in Minitab. The R^2 indices of determination for the tests indicate that the method showed good linearity of analyte mass to response within the tested weight range for all of the PAHs. The worst non-linearity was observed for Dibenz(a,h)anthracene indicating that the mass/response ratio for this PAH varied during the replicate tests more than for the other PAHs.

Table 2. Thermal Desorption Method Sensitivity Calculations

PAH	Y-intercept (p Value)	Slope (P Value)	Standard Error	% R^2	Detection Limit (ng)	Lower Quantification Limit (ng)
Naphthalene	6.09 (0.013)	1.24 (0.000)	2.15	98.5	9.63	13.17
Fluorene	0.58 (0.012)	1.53 (0.000)	1.24	96.4	2.62	4.66
Phenanthrene	4.47 (0.002)	0.85 (0.000)	1.16	97.1	6.37	8.27
Anthracene	3.2 (0.001)	0.42 (0.001)	0.38	94.1	3.83	4.47
Fluoranthene	1.78 (0.002)	0.33 (0.000)	0.54	98.8	2.67	3.55
Pyrene	7.34 (0.000)	0.43 (0.000)	1.5	93.2	9.81	12.28
Benzo(a) anthracene	1.77 (0.000)	0.22 (0.000)	0.29	96.8	2.25	2.73
Chrysene	0.31 (0.002)	0.25 (0.000)	1.41	96.5	2.63	4.95
Benzo(b) fluoranthrene	3.55 (0.000)	0.23 (0.000)	0.36	97.6	4.15	4.74
Benzo(a)pyrene	3.37 (0.002)	0.42 (0.000)	0.5	97.5	4.2	5.03
Indeno(1,2,3-cd) pyrene	0	0.32 (0.001)	0.62	93.1	1.34	2.36
Dibenz(a,h) anthracene	0	0.43 (0.051)	0.64	52.2	1.05	2.09
Benzo(ghi) perylene	0.13 (0.0482)	0.14 (0.000)	0.51	97.1	0.97	1.82

Creek Sediment PAHs Analyses

Figure 2 shows the observed particle size distribution of the sediment represented by the fifteen samples. Overall, most of the particles were distributed in the range of 90 to 710µm, with only about 10%, on average, greater than 1,000µm. The lack of small particles in the sediment samples reflects the transport of these fines during high creek flows. Cribbs Mill Creek had more of the large particles and Carroll Creek had more of the small particles.

All sediment fractions were analyzed for PAHs using the TD/GC/MS methods described in this paper. Average concentrations of selected PAHs associated with sediment sizes, and the associated standard deviations, are shown in Table 3. Generally, smaller sized and larger sized particles (especially LOMs) were associated with higher concentrations of PAHs, compared to medium sized particles. This trend is similar to results previously reported by Rushton, 2006. Prior fugacity modeling by Bathi, et al (2009) showed that urban stormwater PAHs are strongly associated with the organic matter content of the particulates. It is no surprise then that leaf fractions were found to have the highest concentrations of some of the PAHs. However, most of the mass of the PAHs are associated with the smaller and intermediate sized creek sediment particles, as very little of the sediment was associated with the large organic matter (0.6%).

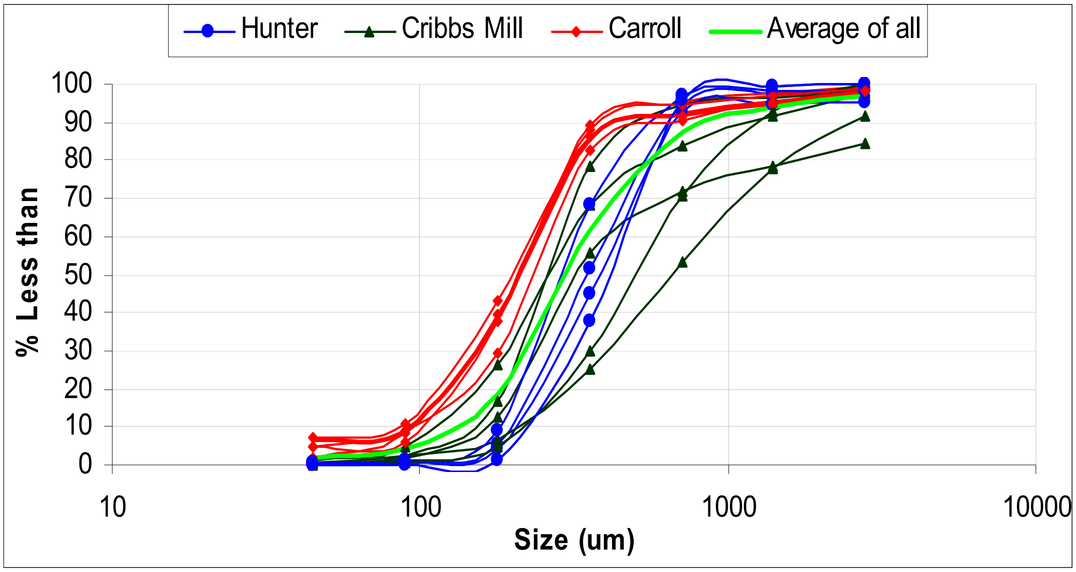

Figure 2. Observed creek sediment particle size distributions

Table 3. Observed PAH concentrations and associated standard deviations for urban creek sediment by size fractions

PAH	Mean Concentration (µg/kg) (Standard Deviation)								
	< 45 µm	45 – 90 µm	90 – 180 µm	180 - 355 µm	355 – 710 µm	710 - 1400 µm	1400 - 2800 µm	> 2800 µm (w/o LOM)	> 2800 µm LOM
Naphthalene	255 (275)	177 (156)	163 (224)	94 (87)	124 (131)	790 (2046)	891(2014)	124 (74)	2637 (2107)
Fluorene	257 (295)	189 (134)	225 (187)	125 (135)	139 (140)	196 (144)	293 (173)	216 (161)	1771 (945)
Phenanthrene	264 (278)	205 (211)	140 (158)	92 (92)	110 (85)	130 (136)	197 (230)	188 (164)	2007 (1422)
Anthracene	354 (397)	288 (273)	261 (253)	152 (150)	182 (182)	366 (314)	491(614)	218 (152)	2255 (1089)
Fluoranthene	650 (868)	624 (753)	345 (372)	202 (242)	247 (336)	259 (237)	237 (197)	191(173)	1520 (902)
Pyrene	653 (738)	519 (548)	412 (577)	175 (174)	240 (405)	207 (153)	192 (122)	172 (129)	2054 (954)
Benzo(a) anthracene	501 (595)	408 (537)	258 (286)	169 (171)	224 (229)	167 (134)	271 (252)	278 (371)	2164 (1045)
Chrysene	591 (618)	602 (689)	363 (363)	202 (199)	273 (268)	190 (125)	296 (242)	171 (130)	1810 (852)
Benzo(b) fluoranthrene	597 (522)	517 (598)	358 (389)	402 (671)	227 (150)	316 (262)	375 (369)	329 (375)	2179 (1425)
Benzo(a)pyrene	1474 (2210)	1524 (3079)	662 (459)	434 (513)	351 (210)	502 (533)	1119 (2086)	392 (255)	2330 (1866)
Indeno(1,2,3-cd) pyrene	787 (544)	657 (538)	942 (794)	258 (187)	332 (189)	576 (774)	706 (917)	357 (424)	1774 (933)
Dibenz(a,h) anthracene	1267 (1864)	787 (1022)	675 (545)	276 (234)	355 (226)	687 (511)	835 (1254)	286 (191)	1492 (775)
Benzo(g,h,i) perylene	706 (686)	465 (451)	591 (691)	199 (226)	174 (116)	551 (567)	396 (299)	348 (229)	2236 (1728)

CONCLUSIONS

The newly developed TD/GC/MS method is found to be a good alternative method for analyzing PAHs in sediments. This method may also be a good procedure for analyzing very small amounts of separated sediments from water samples. The estimated recovery, sensitivity and repeatability of the method was found to be acceptable and within the range of alternative methods currently being used. The method application for urban stream sediments was also successfully demonstrated as part of this research. Unfortunately, the method resulted in frequent maintenance on the GC inlet, the capillary column, and the MS detector, as the GC/MSD lost sensitivity due to fouling from the fine particles that escaped from the TD tubes. More work will be required in modifying the GC inlet and how the desorption tubes are mounted on the GC inlet to avoid this frequent sensitivity loss of the equipment.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant No. EPS-0447675. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

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