

## Standardization of Thermal Desorption GC/MS Analysis for Polycyclic Aromatic Hydrocarbons and Comparison of Recoveries for Two Different Sample Matrices

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### ABSTRACT

The analysis of PAHs in environmental samples involves sampling, extraction, concentration and final analysis using GC-MS. Traditional extraction of PAHs from a solid matrix, where much of the PAH reside, is a tedious and time consuming process. Thermal desorption (TD) can replace the traditional sample preparation step in the analysis scheme with a more efficient and direct method, which also eliminates the organic solvents used in the traditional extraction procedures, with the added advantage of significantly reducing the sample preparation time. This paper examines the recovery of standard PAHs solutions spiked on glass wool for different desorption times using TD techniques. Recoveries for desorption times ranging from 1 min to 20 min were studied. The peak areas obtained for individual PAHs increased as desorption time increased from 1 min to 15 min, while there was a decrease in peak areas as desorption times increased to 20 min. Therefore, the optimum desorption time for the highest recovery of PAHs was found to be 15 min. Coefficients of variation were calculated using the optimized desorption time for the PAH mix spiked on the glass wool substrate. It was found that low molecular weight and high molecular weight PAHs have high coefficients of variation (naphthalene 49%, Fluorene 24.2%, Dibenz(ah)anthracene 14.8%, Benz(ghi)perylene 15.5%), while the intermediate PAHs had much lower coefficients of variation (ranging from 0.5 % - 4.0%). The method response was tested for linearity by analyzing the glass wool spiked with five different concentrations of PAH mixtures, ranging from 0.01 to 20ng/ $\mu$ L.

The second part of the research examined the PAH recoveries from glass wool compared to Tenax spiked with PAH mixtures. This was performed by spiking the wool and 10 mg of tenax with 20ng/ $\mu$ L of the PAH mixture. The recovery of low molecular weight PAHs (having fewer numbers of rings) was larger in the case of Tenax than for the glass wool, whereas for the high molecular weight PAHs (having more rings), the recovery of PAHs from glass wool was larger than from the Tenax matrix.

Keywords: Toxic substances, Water quality, Methods, Sediments

### Introduction

Environmental contamination of natural resources with persistent organic pollutants (POP) is of great concern. Polycyclic aromatic hydrocarbons (PAHs) are an example of persistent organic pollutants of concern. As an example, some of the PAHs have been determined to be carcinogenic by several regulatory agencies (US Environmental Protection Agency (EPA), US Department of Health and Human Services (DHHS) and the International Agency for Research on

Cancer (IARC).

PAHs in urban runoff can occur in both particulate and soluble forms, although studies have identified the particulate forms as being the most predominate (Pitt et al. 1999). According to the Hwang and Foster (2005) study on urban stormwater runoff in Washington DC, particulate-associated PAHs account for 68-97% of total PAHs in the runoff.

The rapid and effective analyses of samples for toxicant contamination is very important to minimize their potential

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effects on the environment and on public health. The general analytical procedure for polycyclic aromatic hydrocarbons (PAHs) and other organic contaminants (such as pesticides) involves: sample collection, sample preparation and extraction, and final determination. In most cases, problematic PAH concentrations in water are typically low, emphasizing the extraction and concentration steps in the analytical process. Final detection of these contaminants is usually carried out with gas chromatography with a mass spectrophotometer detector.

Water or solid samples to be analyzed for PAHs contamination usually undergo solvent extraction prior to analysis. Liquid-liquid extraction by separatory funnel, or by continuous extraction, or by solid-phase extraction, are the most common extraction methods for liquid samples. Soxhlet, automated Soxhlet, and ultrasonic extraction methods are the common solvent extraction methods for PAHs from solid samples.

Solid-phase extraction (SPE) is the most common method used for the extraction and concentration of organic contaminants in liquid samples. EPA method 3535, under SW-846, explains the applicability, operation and limitations of the method. Organics from a known volume of liquid sample is extracted using a solid phase extraction device (a solid-phase sorption substrate in a filter stand) and then the targeted analytes are eluted from the solid-phase media using an appropriate solvent. However, suspended solids present in the sample can cause analytical and technical problems in sample concentration and final detection. Technical problems caused by suspended solids includes the plugging of the SPE cartridges and disks, which will cause the extraction to last for several hours, or even render it impossible, and difficulty in extracting the organics from the particulates, as SPE was developed to extract organics from filtered water samples. Continuous extraction of liquid samples for PAHs, as described in EPA method 3520, is more efficient (based on recovery) for samples containing particulates up to 1% (10,000 mg/L) that can cause emulsions. However, this method requires expensive glassware, uses fairly large volumes of solvents, and requires extraction times of 6 to 24 hours.

EPA method 3540 describes the Soxhlet procedure for

extraction of PAHs from solid matrices. As explained in EPA method 3540, a known amount of solid sample is mixed with anhydrous sodium sulfate and placed into an extraction thimble, or between two plugs of glass wool, and continuously extracted using an appropriate solvent. The extraction method may provide efficient extraction, but it requires about 16 to 24 hours for single samples and uses fairly large volumes of solvent. EPA method 3550, described under SW-848, outlines the detailed procedure of ultrasonic energy for extraction of semivolatile organic compounds from solid matrices. This method is comparatively efficient, requiring shorter times for extraction, but has less extraction efficiency. Ultrasonic extraction methods also use relatively large volumes of solvent, requires an expensive piece of equipment, and it requires large amounts of sample for samples having low concentrations of the analyte of interest.

Generally, PAHs are most effectively extracted from liquid samples at a neutral pH with methylene chloride. The commonly used solvents for extraction of PAHs from solid matrices are dichloromethane, cyclohexane, benzene, and methanol. Evaporation is usually employed to concentrate the solvents containing the extracted organics. The separation and detection methods are further described in EPA methods 8100 and 8310. These traditional approaches for extraction and evaporation are labor-intensive and time consuming. These methods are also prone to contamination introduced by impurities in the solvents, and also use large quantities of organic solvents in the process that could cause environmental contamination and hazards to the operators.

An alternative to the traditional approach of solvent extraction of organics in the presence of large amounts of particulates is thermal extraction. This method is becoming more popular and readily available, but has not been thoroughly tested. Thermal extraction, or thermal desorption, techniques use elevated temperatures as a means to transfer the analytes from solid sample matrices to the gaseous analytical system. The analytes desorbed from the solid sample matrices are concentrated in a cyrotrap at the head of a GC column. The concentrated analytes are then separated and detected using a standard GC column and MS detector which is similar to the analysis of liquid samples when con-

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centrated into a solvent. The research team at UA is continuing their work to develop an effective analysis procedure by incorporating thermal desorption techniques into effective analysis processes. The first part of this paper describes the general procedure employed in thermal desorption of PAHs. The second part of this paper provides the optimum operating conditions of the method followed by comparisons of the recoveries obtained for two different solid matrices. The two solid matrices used for study are glass wool and Tenax, and are spiked with a liquid standard mixer of PAHs.

## Analysis Procedure

### Tube Conditioning:

Prior to the use of the thermal desorption tubes for the analysis of samples, the thermal desorption tubes need to be conditioned at elevated temperatures. The conditioning of the tubes helps in removing all foreign materials which may cause sample cross contamination or memory peaks in the sample analysis. The tube conditioning is performed with the help of high purity nitrogen gas. Initially, the tubes are flow conditioned at room temperature for several minutes to get rid of oxygen from the interiors of the tubes. After initial purging of the tubes at room temperature, the tubes are heated up to 350 °C at a rate of 4 °/min while purging with nitrogen gas. The tubes are maintained at elevated temperatures of 350 °C for four hours. Throughout the conditioning process, the nitrogen flow is maintained at about 60 mL/min. At the end of the four hours at the elevated temperature, the tubes are removed from the conditioning oven and placed in the cooling rack at the rear of the oven and allowed to cool for 10 minutes. When the tubes are cooled, the tubes are immediately capped on both ends with the pre-conditioned steel caps. The same procedure is used for conditioning the needles.

### Tube Packing:

The thermal desorption tubes are made of stainless steel and are 4 mm in internal diameter and 100 mm long and threaded at both ends. Conditioned tubes are packed with the 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.

### Analysis:

The packed tubes, which are ready for analysis, are then loaded onto the system carousel. Once the analysis process is initiated with the help of the AutoDesorb™ software from the remote control system, the desorption tube is purged to remove oxygen, excess water, and volatile materials that are resident in the tube. The needle is then lowered into the GC inlet and the injection period starts, followed by purging. The injection time period is set based on the instrument response to allow the injection port pressures to equilibrate and the proper split flow to be reached before the injection time expires. At the end of the injection time, the heater blocks close around the desorption tube and the tube is heated at a rate specified in the method. Carrier gas transports the desorbed analytes into the inlet of the GC. The cryotrap then traps the analytes entering the GC inlet by condensing the organic gases and focus the analytes for their concentration. The cryotrap is then heated up ballistically to release the focused analytes instantaneously into the GC column, where the analytes are separated based on their volatility and are then detected by the MS, based on their charge to mass ratios.

### Optimum Conditions:

Optimum conditions for thermal desorption were selected based on a series of experiments conducted to obtain good recovery of analytes from the solid samples and to have good separation of the analytical peaks. For this purpose, standard solid samples were prepared by spiking 10 µL of the 20 mg/L PAH mixed standard onto pre-treated glass wool. The thermal desorption unit was subjected to different desorption times and desorption temperatures. The final desorption temperatures were tested ranging from 250 °C to 375 °C. Final desorption temperatures of 350 °C produced higher peaks of individual PAHs. Similarly, different desorption times were tested to obtain maximum peak areas. A series of runs were made with different holding times for the final desorption temperature. The range of final temperature

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holding times tested ranged from 1 min to 20 min. It was found that the peak areas obtained for individual PAHs increased as the holding time increased from 1 min to 15 min, and 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. For three replicate runs, the coefficients of variation (COV) showed that low molecular weight and high molecular weight PAHs have high variations (naphthalene 49%, Fluorene 24.2%, Dibenz(ah)anthracene 14.8%, Benz(ghi)perylene 15.5%), while the intermediate PAHs had much lower variations (COVs ranging from 0.5% - 4.0%).

## Testing Method for Linearity:

The developed method was tested for linear responses for the different PAHs. For this purpose, solid matrices were prepared by spiking Tenax with 10, 50, 100, 200 and 400

ng of the PAH standard mix. Table 1 shows the regression index of determination ( $R^2$ ) values obtained for selected PAHs, which are all reasonable for this method.

## Comparison of Recoveries:

The second step of the research examined the PAH recoveries from glass wool compared to Tenax spiked with PAH mixtures. This was performed by spiking the wool and 10 mg of Tenax with 20 ng/ $\mu$ L of the PAH standard mixture. The recovery of low molecular weight PAHs (having fewer numbers of rings) was more in the case of Tenax than for the glass wool, whereas for the high molecular weight PAHs (having more rings), the recovery of PAHs from glass wool was greater than from the Tenax matrix. The comparative recovery calculations clearly showed that the recoveries of analytes vary depending on solid matrices. Tenax (an adsorbent resin) represents environmental solid sample more

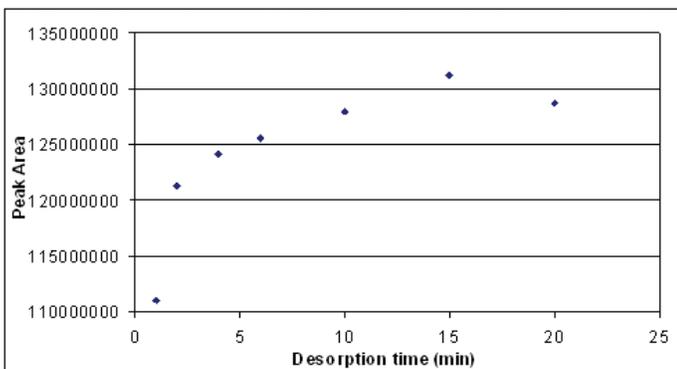


Figure 1. Desorption time versus peak areas for Pyrene

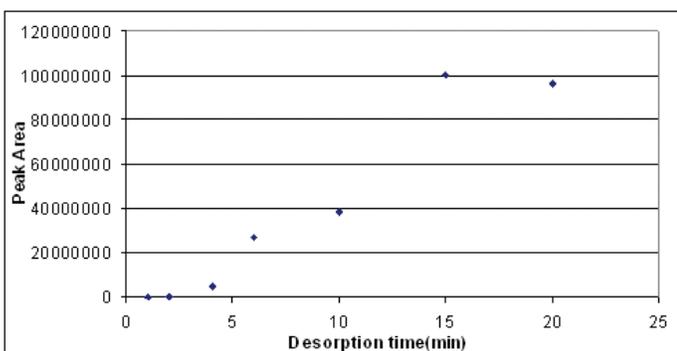


Figure 2. Desorption time versus peak areas for Benz(ghi)perylene

## Optimal conditions of thermal desorption system:

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
Cryo-trap:	enabled
Cryo cool temperature:	-40 °C
Cryo heat temperature:	300 °C
Cryo heat duration:	10.00 min
GC start time:	26.50 min

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PAH	R <sup>2</sup>
Naphthalene	0.9958
Fluorene	0.9848
Phenanthrene	0.9969
Anthracene	0.9944
Fluoranthene	0.9978
Pyrene	0.9975
Benz(a)anthracene	0.9934
Chrysene	0.9961
Benz(b)fluoranthrene	0.9925
Benz(a)pyrene	0.9881
Indeno (1,2,3-cd)pyrene	0.9819
Dibenzo (a,h)anthracene	0.9593
Benz(ghi)perylene	0.9657

closely then glass wool and hence the recoveries from Tenax matrix could give us a better idea about recovery of analytes from real environmental samples.

### Analysis of a Standard Sample using Developed Method:

A marine sediment standard, NIST1941b obtained from the National Institute of Standards and Technology (NIST), was tested using the developed method. This standard sample was collected from Chesapeake Bay at the mouth of Baltimore (MD) Harbor near the Francis Scott Key Bridge using a Kynar-coated grab sampler. The standard is certified for 119 different constituents of PAHs, PCBs and chlorinated pesticides. The sample was ground and sieved so the sediment particles were finer than 150 μm.

A 10 mg portion of NIST1941 was subjected to the analysis with the operational conditions determined during the method development. Most of the analytes present in the standard sample were detected and clear individual peaks were shown. There were two major problems identified during the analysis of the standard material using thermal desorption GS/MS analysis, as discussed below.

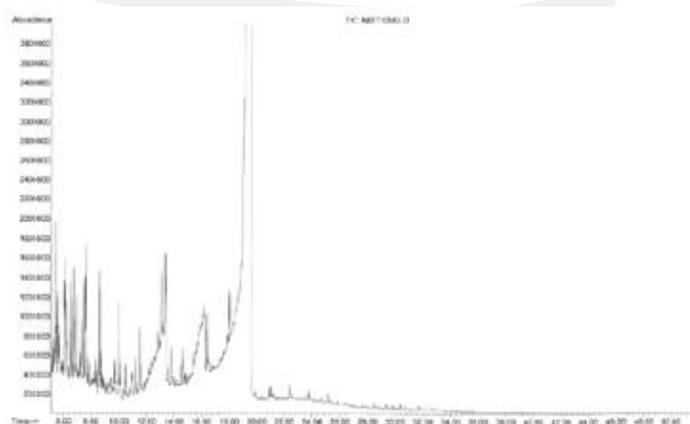


Figure 3. Chromatogram of NIST standard with dominant peaks of sulfur compounds

**Presence of sulfur:** Due to the presence of sulfur in the sediment sample, there were many unwanted sulfur-containing analyte peaks in the gas chromatogram. Sulfur products of PAHs bonds to particulate solids and makes them difficult to extract. As copper forms copper sulfide when reacted with sulfur, the addition of small amounts of copper into the thermal desorption tube along with the sediment sample helped in avoiding the sulfur products of PAHs. Figure 10 shows the chromatogram with unwanted peaks of sulfur products of PAHs.

### 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 has caused tremendous reductions in the peak areas obtained for the individual analytes, and in some cases there were no peaks observed. To reduce the water content in the sample, samples were further freeze dried before analysis.

### Recovery Calculations:

The percentage recovery of the developed method was tested by spiking environmental samples with 10 μL of the 20 ng/μL PAH standard mixture. An environmental runoff sample was collected from the University Mall parking lot in

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Figure 4. Chromatogram of NIST standard with ice plugging problem.



Figure 5. Chromatogram of freeze dried NIST standard with copper.

Tuscaloosa AL, and particulate matter in the water sample was separated by sieving the sample through a 90  $\mu\text{m}$  sieve. The collected particulate matter was oven dried overnight at 100oC. Triplicate samples of dried particles of 10 mg each were subjected to TD-GC/MS analysis and resultant areas of the selected PAHs peak areas measured. Another triplicate sample of dried particles of 10 mg each were spiked with

the 10  $\mu\text{L}$  of the 20  $\text{ng}/\mu\text{L}$  PAH standard mixture and were subjected to TD-GC/MS analysis and the resultant peak areas measured and compared to the first batch results. The percentage recoveries of the spiked PAHs were calculated by comparing the differences in average peak areas obtained from the spiked and un-spiked environmental samples with average peak areas obtained by analyzing triplicates of the

**Table 2. Comparison of peak areas for two solid matrices.**

PAH	Mean area		Ratio of area
	Glass wool	10 mg Tenax	Glass wood/Tenax
Naphthalene	22788021.50	61202757.00	0.37
Fluorene	63267375.50	71902289.33	0.88
Phenanthrene	93644340.75	98973950.67	0.95
Anthracene	97919751.75	99626677.33	0.98
Fluoranthene	114127323.50	116877318.33	0.98
Pyrene	112801392.50	113481063.00	0.99
Benz(a)anthracene	125345520.00	122965363.00	1.02
Chrysene	127764095.00	127548616.00	1.00
Benz(b)fluoranthrene	137369218.50	137484565.00	1.00
Benz(a)pyrene	129740976.50	115008191.67	1.13
Ideno(1,2,3-cd)pyrene	128386541.00	90639700.67	1.42
Dibenz(a,h)anthracene	77365639.00	47015167.33	1.65
Benz(ghi)perylene	83206184.00	50522238.00	1.65

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**Table 3. Spike recovery of developed method.**

PAH	Mean area			
	Environmental Sample	Liquid Standard (1000 µg/L)	Spiked Sample	% Recovery
Naphthalene	76379564	44635222	90154097	31
Phenanthrene	29615669	40529498	58078570	70
Anthracene	15669946	43013765	40612935	58
Fluoranthene	69663919	62594052	96248625	43
Pyrene	82927225	68914168	109785364	39
Benz(a)anthracene	53005722	54253782	70200141	32
Chrysene	98286258	56073172	116817543	33
Benz(b)fluoranthrene	114019177	69394215	142837284	42
Benz(a)pyrene	125545124	54748760	152641922	50
Ideno(1,2,3-cd)pyrene	92514576	68144887	119386641	39
Dibenz(a,h)anthracene	89867981	63016083	117948321	45

**Table 4. Acceptable recoveries for selected analytes**

PAH	<sup>1</sup> Acceptable range of % recovery from EPA methods (aqueous samples)	<sup>2</sup> Acceptable range of % recovery from <i>Standard Methods</i> (aqueous samples)
Naphthalene	*D - 122	21 - 133
Fluorene	D - 142	59 - 121
Phenanthrene	D - 155	54 - 120
Fluoranthene	14 - 123	26 - 137
Pyrene	D - 140	52 - 115
Benz(a)anthracene	33 - 143	33 - 143
Chrysene	17 - 168	17 - 168
Benz(b)fluoranthrene	24 - 159	24 - 159
Benz(a)pyrene	17 - 163	17 - 163

\*DA: detected, result must be greater than zero  
<sup>1</sup>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.  
<sup>2</sup>acceptable range of recoveries for extraction of liquid sample as provided in the standard methods for the examination of water and wastewater (2005)>

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20 ng/ $\mu$ L of liquid PAHs standard.

The calculated recoveries ranged from 30 to 70 percent, as shown on Table 3. Table 4 shows the acceptable range of extraction recoveries for PAHs from liquid samples using SPE methods. 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 are still in the acceptable ranges of listed recoveries.

## Conclusions:

The suspended solids portion of PAH contamination is very important and needs to be considered when analyzing environmental samples. The traditional methods for liquid samples for PAHs analyses may not be effective when large portions of the PAHs are associated with particulates. Traditional methods for sediment analyses of PAHs are labor intensive, time consuming, and also involves large amounts of solvents which may cause environmental contamination. The newly developed thermal desorption technique for sample preparation is very effective for analyzing particulate-bound PAHs. This sensitive method is also suitable for analyzing particulates that have been separated from water samples by standard filtration. This research is also examining particulate-bound PAHs for many separate particulate sizes, separated by fine filters and sieves. The method showed good linearity over a wide range of analyte concentrations and the calculated recoveries of the method are within acceptable ranges. The method requires less preparation time and effort and produces final analysis results in much shorter periods of time. The new technique also doesn't involve the use of any solvents. However, this technique doesn't restrict unwanted analytes from entering the capillary column and the final detector. This additional material hastens the contamination of the MS detector, requiring more frequent instrument maintenance.

## Acknowledgements:

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 author(s) and do not necessarily reflect the views of the National Science Foundation.

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