

# Polycyclic aromatic hydrocarbons (pahs)



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**Introduction**

Polycyclic aromatic hydrocarbons (PAHs) are made of two or more fused aromatic rings, where PAHs with two or three rings have low molecular weight and acute toxicity whereas PAHs with high molecular weight (4 or more rings) have shown high carcinogenic potential.

These compounds are often products of incomplete combustion reactions where there is a lack of oxygen, there are two types of PAH; natural and anthropogenic which can be found in many different kinds of samples . However, the ratio of natural processes to anthropogenic processes is very low.

PAHs can form due to a variety of anthropogenic sources the main one is believed to be atmospheric decomposition, other sources include thermal combustion processes, vehicular emissions and biomass burning [3]. PAHs caused from incomplete combustion reactions reach the sea via the atmosphere and rivers .

Due to the causes listed above the United States Environmental Protection Agency (EPA) and other agencies formed regulations for the detection and monitoring of PAHs in the human environment, with new analytical methods being produced with better sensitivity and selectivity . Overall the EPA has selected sixteen PAHs as priority pollutants [4].

To verify different PAHs in seawater is difficult as the overall solubility of PAHs in water is low, and continues to decrease as molecular weight increases, the low solubility in turn effects the hydrophobic nature (between

3 and 8) and therefore the concentration of PAHs dissolved in seawater is very low .

There are a variety of methods used to analyse the PAHs in seawater and other types of water. High Performance Liquid Chromatography (HPLC) is the most widely used analytical technique in analysing PAHs in seawater samples; in this document HPLC will be discussed along with other analytical methods such as Gas Chromatograph-Mass Spectrometer (GC-MS).

**This document focuses on data and results from the following papers:**

1. “ Determination of polycyclic aromatic hydrocarbons in seawater by high-performance liquid chromatography with fluorescence detection following micelle-mediated preconcentration” V. Pino et al.
2. “ Polycyclic Aromatic Hydrocarbons in Water and Sediment of the Baltic Sea”
3. “ GC-MS Analysis of Total Petroleum Hydrocarbons and Polycyclic Aromatic Hydrocarbons in Seawater Samples after the North Cape Oil Spill” Christopher M. Reddy and James G. Quinn

Each paper will be individually introduced and the sample preparation, analytical method and any results significant to the separation will be discussed. The methods will then be compared, giving the advantages and disadvantages of each technique.

**“ Determination of polycyclic aromatic hydrocarbons in seawater by high-performance liquid chromatography with fluorescence detection following micelle-mediated preconcentration” V. Pino et al.**

This paper looked at how non-ionic surfactant polyoxyethylene-10-lauryl ether (POLE) can be used for extraction of PAHs in seawater and compared cloud-point extraction (CPE)-HPLC and liquid-liquid extraction (LLE)-GC-MS.

### **Sample Preparation**

The sample was prepared by shaking fuel-oil with natural seawater for one hour, and then allowed to settle and age overnight, until phase separation. The aqueous layer was removed and mixed with POLE until a final solution of 1% (w/v) was reached in the surfactant. Following this 3.0 ml of aliquots in the presence of the 1% surfactant solution dissolved in artificial seawater were administered to CPE. In order to test the reliability of the method used for preconcentration and separation of PAHs, the PAHs were analysed from spiked and un-spiked seawater samples.

The method was evaluated by using LLE and GC-MS, overall determination was processed using the mass values which related to the molecular ions of the different PAHs .

### **Analysis**

Once the two phases had been separated, 25 µl of the surfactant-rich phase was injected into the system. The HPLC method used in this instance to determine and separate the PAHs consisted of gradient elution with a fluorescence detector. The mobile phase was a mixture of acetonitrile and water with a linear gradient from 55 to 100% acetonitrile for 30 minutes and

100% acetonitrile for 10 minutes. The column used for the analysis was a reversed phase C18 column (Table 1) with a  $\mu$ Bondapak C18 guard column.

**Table 1: Vydac 201TP54 Reversed Phase C18 Column**

Column	
length x	250
internal	x 4.
diameter /	6
mm	
Particle	
size / $\mu$ m	5
Pore size /	
$\text{\AA}$	300

A flow rate of 1 ml / minute was used to elute the compounds.

## Results

Each PAH gave an acceptable retention time with a relative standard deviation between 0.64 and 0.83%.

The seawater contaminated with fuel-oil were analysed by both CPE-HPLC and LLE-GC-MS (Table 3). As can be seen the PAHs with fewer aromatic rings have similar results with both techniques where as the PAHs with more aromatic rings are different this could be due to the lower sensitivity in GC-MS.

## “ Polycyclic Aromatic Hydrocarbons in Water and Sediment of the Baltic Sea” G. Witt

During the years 1992 to 1994, 15 PAHs were analysed in seawater from the Baltic Sea during the different seasons. The method used is based on HPLC with fluorescence detection.

### Sample Preparation

156 seawater samples were collected from various depths, surface water (2-15m), bottom water (below the halocline) and surface micro layer (0-0.2 cm). The PAHs from the samples were separated and extracted via a HPLC column; three fractions were obtained using 9 ml pentane, 9 ml pentane/10% dichloromethane and 9 ml acetone as the eluents. The PAHs were contained into the second fraction and was evaporated down to 500 µl.

### Analysis

The HPLC column used to separate the sample in to fractions was a MERCK LiChrospher Si 100-5 (Table 4)

#### Table 4: MERCK LiChrospher Si 100-5

Column	
length x	250
internal	x 4
diameter	
/ mm	
Particle	5
size / µl	
Pore	60

diameter

/ Å

Matrix      Silica  
                 gel

The column used in the analysis of the PAHs was a GROM PAH using gradient elution (Table 5).

**Table 5: GROM PAH**

Column

length x      250

internal      x 4

diameter /

mm

A)

Wa

ter

Eluents

B)

CA

N

Flow rate /      1

ml min<sup>-1</sup>

Temperatu  
re / °C            20

A fluorescence detector was used, along with a wavelength programme for optimal detection of all PAHs (Table 6).

From the 16 PAHs listed as priority pollutants, acenaphthylene was the only one not detected as it does not show fluorescence activity.

### **Results**

It was seen that there were a greater amount of lower molecular weight PAHs varying in concentration from 1 to 4.5 ng/L-1 in relation to higher molecular weight PAHs which remained below ng/L-1.

The concentration of PAHs in different seasons was also compared, it was seen that autumn had the highest concentration this maybe because of low microbial degradation and photo-oxidation during the season; and summer had the lowest. During the winter months, the temperature of seawater is low which inhibits the microbial degradation of the PAHs. In spring the plankton are in abundance and thus cause a large amount of loose matter to be produced which may transfer the PAHs to the sea floor. This was mostly true for two/three ring PAHs, four to six rings however have a higher persistence to microbial degradation.

The amount of PAHs in the surface micro layer was 2-13 times higher than that of the water below; this can be due to the atmospheric input .



**“ GC-MS Analysis of Total Petroleum Hydrocarbons and Polycyclic Aromatic Hydrocarbons in Seawater Samples after the North CapeOil Spill”****Christopher M. Reddy and James G. Quinn [6]**

GC-MS was used to measure PAHs in seawater samples after the North Cape oil spill.

**Sample Preparation**

The samples were spiked with internal standards which consisted of the following: 10 to 25 µg docosane and 2 µg each of naphthalene-d8, biphenyl-d10, acenaphthene-d10, anthracene-d10 and perylene-d12. After the samples were spiked they were shaken and extracted once with 100 ml methylene chloride and twice more with 100 ml of hexane. The organic extracts were then combined and rotary-evaporated to 1 ml while being solvent-exchanged into hexane. Following this the hexane extract was chromatographed and the first fraction (obtained by eluting with 20 ml of a 70/30 mixture of hexane/methylene chloride) containing the aromatic hydrocarbons was rotary-evaporated to a small volume (100 µl) and spiked with an external recovery standard (1. 2 µg o-terphenyl in isooctane), and injected into the GC-MS detector.

**Analysis**

The PAHs were first extracted with methylene chloride and hexane and then fractionated via HPLC using silica gel. The analysis was done using a Hewlett-Packard 5890 Series II GC with a Hewlett-Packard 5971 mass selective detector. After the sample was injected, the compounds were separated using a 30m J&W Scientific DB-XLB fused silica-capillary column (Table 7).

**Table 7: J&W Scientific DB-XLB fused silica-capillary column**

Column  
length x  
internal  
diameter /  
mm

30,  
000  
x 0.  
25

Film  
thickness  
/  $\mu\text{m}$

0.  
25

Temperat  
ure limit / -  
 $^{\circ}\text{C}$

340  
360

According to the website [7] this column has low polarity and is excellent for PAHs.

The oven was set at  $70^{\circ}\text{C}$  for 1.5 minutes, then ramped to  $320^{\circ}\text{C}$  at  $10^{\circ}\text{C}$  per minute, and then held for a further 10 minutes.

The detector was run in selected-ion monitoring (SIM) mode for ions that have an m/z of 50 to 550, PAHs usually range between 128 and 234 m/z.

## Results

A total of 54 seawater samples were collected and analysed were collected between day 4 and day 132 after the North Cape oil spill, results from a week after the oil spill showed that there were high concentration of PAHs, with the total sum coming too  $115 \mu\text{g L}^{-1}$ , these are some of the highest <https://assignbuster.com/polycyclic-aromatic-hydrocarbons-pahs-essay-samples/>

values for a marine oil spill. The relative percentage deviations for duplicate samples for total PAHs came to <3%.

The use of other GC detectors such as GC flame ionisation detector which is widely used may not be suitable for the detection of PAHs as often lower limits of detection are needed, which is why GC-MS would be used.

### **Comparison of analytical methods**

The most popular technique for the separation and determination of PAHs is HPLC however; a disadvantage of this is that gradient elution must be used opposed to isocratic elution due to the sample's complexity. Other factors include that HPLC is expensive, and that it requires large amounts of solvent especially when gradient elution is used.

The paper by V. Pino et al. and the paper by G. Witt both used HPLC reversed phase column with a fluorescence detector, however Pino et al. used a surfactant with a low retention time (POLE) which allowed for the determination of PAHs which were more polar. In Figure 2 the compounds eluted between ~7 and 40 minutes using the above method; whereas the method used by Witt produced a chromatogram (Figure 3) which shows the products eluted between ~7 and 23 minutes. The difference in retention times shows that the method used by Witt was more useful.

However, the samples of seawater used for analysis by each paper were from different sources, Pino et al. does not state where the seawater samples were taken, while Witt took the sample from the Baltic Sea. Pino et al. only extracted 14 PAHs but Witt extracted all 16 PAHs listed by the EPA.

From the data listed in Tables 2 and 6 it can be seen that there are

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comparable results such as Phenanthrene which eluted in 13.9 minutes for Pino et al. and 12.2 minutes for Witt, the emission wavelengths measured were identical at 370 nm and that the excitation wavelength only differed by 2 nm between Pino (248 nm) and Witt (246 nm).

Overall, the HPLC methods used by both papers shows that it is a reliable method for determining PAHs in seawater, a fluorescence detector was used as the filters select the excitation and emission wavelengths and it reduces the complexity of the chromatogram which provides orthogonal information.

Even though HPLC seems the most popular technique GC-MS is being used to analyse the PAHs after they have been separated by HPLC. This change could be because GC is faster than HPLC and that with a mass spectrometer (MS) detector it is possible to combine detection, quantification and identification. GC-MS is especially good for complex mixtures such as seawater where several analytes have similar retention times.