HSLU Hochschule Luzern

Practical 3:

Analysis of PAHs in Plastics by GC-MS

Environmental Chemistry and Biology HS2024

Dr. Macarena San Martín Ruiz
Lecturer

Team 4
Matteo Frongillo
Ramadhan Nura
Folagbade Popoola
Jonathan Lawrence Boms
Kron Xhemajli

Contents

1 Introduction

The purpose of this experiment is to analyze and quantify polycyclic aromatic hydrocarbons (PAHs) in plastics using Gas Chromatography-Mass Spectrometry (GC-MS). PAHs are a group of organic compounds consisting of multiple aromatic rings and are commonly found as contaminants in the environment due to incomplete combustion of organic matter. Since PAHs pose significant risks to human health and the environment, their detection and quantification are critical in environmental chemistry.

This experiment introduces key analytical techniques, such as chromatographic separation based on molecular properties (e.g., boiling points and hydrophobicity) and mass spectrometric detection of characteristic ion fragments. Calibration curves and internal standards are also employed to ensure accurate quantification of the detected PAHs.

1.1 PAHs

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of organic compounds composed of multiple aromatic rings made up of carbon and hydrogen atoms. They are primarily formed as byproducts of incomplete combustion of organic matter. PAHs are widespread in the environment and can be found in air, soil, water, and food sources. Common sources include vehicle emissions, industrial processes, and natural events like wildfires.

The detection of PAHs is of great importance due to their potential adverse effects on human health and the environment. Many PAHs are known to be carcinogenic, mutagenic, and toxic, posing serious risks through prolonged exposure. They can accumulate in the food chain, contaminating water supplies and agricultural produce. As a result, monitoring and quantifying PAHs in various matrices, such as plastics, soil, and water, are essential for assessing pollution levels, mitigating environmental contamination, and ensuring public health safety. Analytical techniques like GC-MS allow for accurate identification and quantification of PAHs, providing critical data for regulatory purposes and environmental management.

2 Materials and Methods

2.1 Materials

- Gas chromatograph – Mass spectrometer
- Helium (carrier gas)
- Standard PAH kit
- Chloroform (solvent)
- Vials
- Pipettes

2.2 Procedure

In this experiment, a standard solution of PAHs was initially prepared by diluting the stock solution to achieve a concentration ratio of 1:10 in chloroform. To ensure accuracy and precision during the preparation process, calibrated syringes were used to carefully measure the required volumes. For the subsequent dilution to 1:100, 0.9 mL of the 1:10 solution was precisely transferred into a clean vial using a syringe, minimizing any possible errors in volume measurement. The remaining volume was then filled with chloroform to achieve a final solution volume of 1 mL, ensuring consistent and accurate preparation of the diluted sample. The proper use of syringes and sealing techniques contributed to the reliability and reproducibility of the experimental results.

Once the dilution process was complete, the vial was tightly sealed using specialized caps to prevent contamination or solvent evaporation, which could affect the sample integrity and analysis. These sealed vials were then carefully handled and introduced into the Gas Chromatography-Mass Spectrometry (GC-MS) system for analysis.

2.3 Preparation of diluted solutions for a calibration curve

2.3.1 Legend

- $\mathbf{C_i}$: Initial stock concentration (μg/mL)
- $\mathbf{C_t}$: Target concentration (μg/mL)

- $\mathbf{V_s}$: Volume of stock solution required (mL)
- $\mathbf{V_t}$: Target volume (mL)
- $\mathbf{V_c}$: Volume of chloroform required (mL)

2.3.2 Formulas

- Amount of volume of stock solution required $\mathbf{V_s}$:

$$V_s = \frac{C_t \cdot V_t}{C_i}$$

Equation 1: Stock solution volume

- Volume of chloroform required $\mathbf{V_c}$:

$$V_c = V_t - V_s$$

Equation 2: Solvent volume

2.3.3 Ratios

Table 1: Diluted solution ratios

Dilution	$\mathbf{C_i}$	$\mathbf{C_t}$	$\mathbf{V_s}$	$\mathbf{V_t}$	$\mathbf{V_c}$
1:10	10	1	0.1	1	0.9
1:100	10	0.1	0.01	1	0.99
1:1000	10	0.01	0.001	1	0.999

3 Results

3.1 Chromatogram

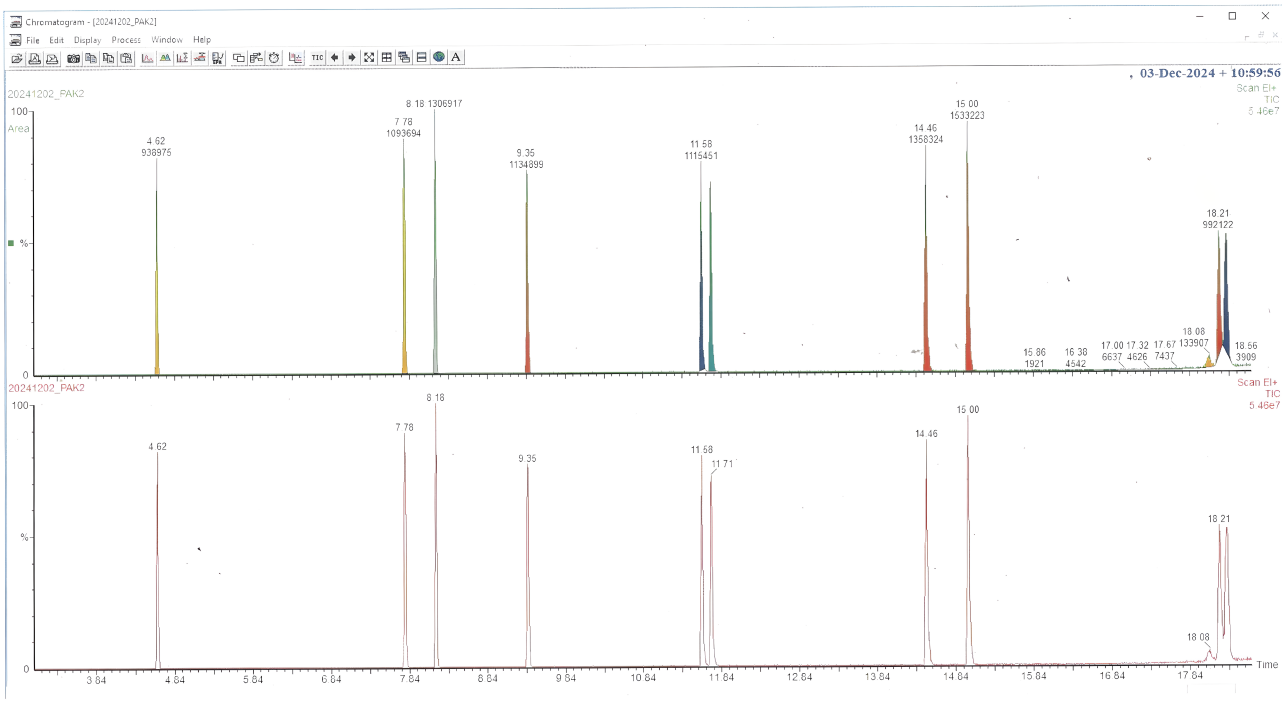

Figure 1: Chromatogram

The GC-MS chromatogram reveals the PAHs detected in the chromatography experiment. Each peak corresponds to a specific compound separated based on its retention time. The x-axis represents retention time (minutes), while the y-axis shows the relative abundance (intensity) of the detected compounds.

The graph displays several distinct peaks, where the height of each peak reflects the intensity of the signal generated by the detector, which is proportional to the compound's concentration. The retention time of each peak increases from left to right, indicating that compounds with higher boiling points and greater hydrophobicity elute later from the column.

3.1.1 Data analysis

Table 2: Compounds data

Nr.	Compound name	Concentration (ng/mL)	Retention time	Peak area	m/z fragments	RF
1	Naphthalene	1000	4.62	938975	128	939
2	Acenaphthylene	1000	7.78	1093694	152	1094
3	Acenaphthene	1000	8.18	1306917	154	1307
4	Fluorene	1000	9.35	1134899	166	1135
5	Anthracene	1000	11.58	1115451	178	1115
6	Phenanthrene	1000	11.71	N.D.	178	N.D.
7	Pyrene	1000	14.46	1358324	202	1358
8	Fluoranthene	1000	15.00	1533223	202	1533
9	Chrysene (1)	1000	18.08	133907	114	134
10	Chrysene (2)	1000	18.21	992122	228	992

The table summarizes the key results from the GC-MS analysis, listing the detected PAHs, their retention times, peak areas, and m/z fragments.

Data interpretation
Retention time increases progressively from 4.62 min to 18.21 min in correlation with increasing molecular weight and complexity of the compounds.

Naphthalene elutes first due its lower molecular weight and boiling point, while Chrysene (2) elutes later, consistent with its higher boiling point and hydrophobicity.

Peak area
The peak area reflects the relative abundance of each compound in the sample.

Compounds like Fluoranthene and Pyrene show high peak areas, indicating higher concentrations. In contrast, Chrysene (1) has a significantly lower peak area, suggesting a lower relative abundance.

m/z fragments
The m/z values provide confirmation of the molecular identity of each compound.

Naphthalene shows m/z = 128, corresponding to its molecular ion, and Chrysene (2) shows m/z = 228, consistent with its larger structure and molecular weight.

Response factor (RF)
The RF values indicate the sensitivity of the detector to each compound. Higher RF values suggests stronger signal responses, while lower values may reflect weaker detection efficiency.

3.2 PAHs detected

3.2.1 LMW PAHs

Low Molecular Weight PAHs exhibited lower retention times due to their smaller molecular weights and lower boiling points.

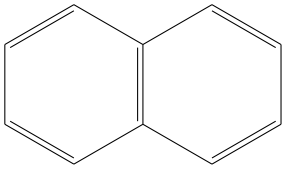

Figure 2: Naphthalene

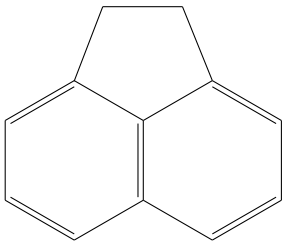

Figure 3: Acenaphthene

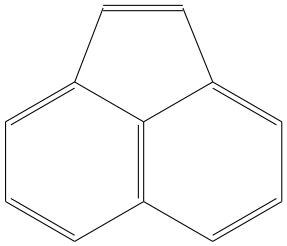

Figure 4: Acenaphthylene

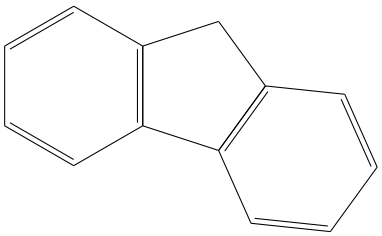

Figure 5: Fluorene

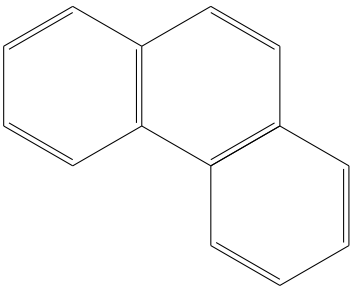

Figure 6: Phenanthrene

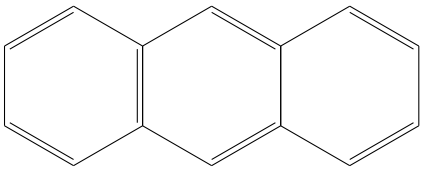

Figure 7: Anthracene

3.2.2 HMW PAHs

High Molecular Weight PAHs were identified at longer retention times. These compounds are characterized by their larger molecular structures and higher boiling points.

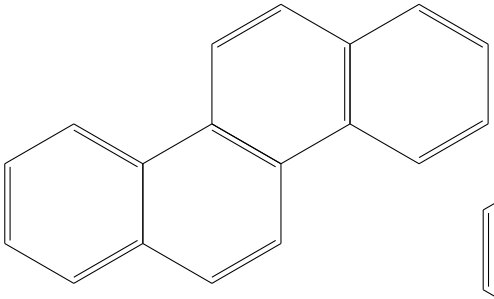

Figure 8: Chrysene

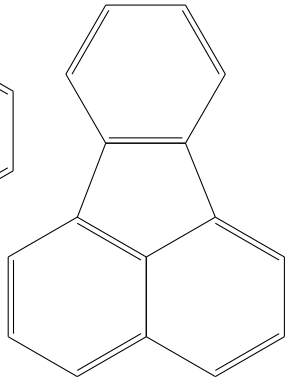

Figure 9: Fluoranthene

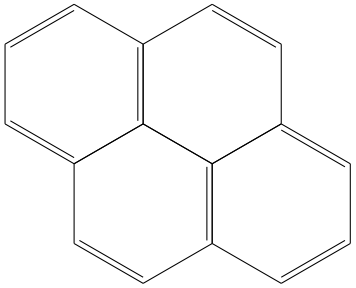

Figure 10: Pyrene

4 Discussion

4.1 Questions

4.1.1 Question 1

1. According to the chemical structures, hydrophobicity and boilind points, which compound will appear first in the GC chromatogram?

   R: Naphthalene elutes first.

2. Which compound will appear last?

   R: Benzo(g,h,i)perylene elutes last.

3. Explain why in a few sentences.

   R:
   Compounds separate and elute based on their physical and chemical properties, primarily their boiling points and hydrophobicity. Hydrophobicity refers to a compound's tendency to repel water and interact with non-polar environments, increasing with the number of aromatic rings due to enhanced molecular stability and larger surface areas. Similarly, boiling point rises with more aromatic rings because of stronger intermolecular forces.

   These properties allow them to travel through the GC column more quickly, resulting in shorter retention times and earlier elution in the chromatogram. (Restek [5]).

4. Consider the chemical structure of naphthalene. Which fragments will be visible in the MS spectrum?

   R: In the mass spectrum of naphthalene, the following fragments are commonly observed[1]:

   - Molecular ion (M^+), which corresponds to the intact naphthalene molecule with a single positive charge (m/z = 128);
   - Fragment ions, which are ionization results in the loss of hydrogen atoms (m/z = 127 for the loss of one hydrogen atom);
   - Smaller hydrocarbon fragments, which include common fragmet from cleavage of the aromatic ring (like m/z = 63).

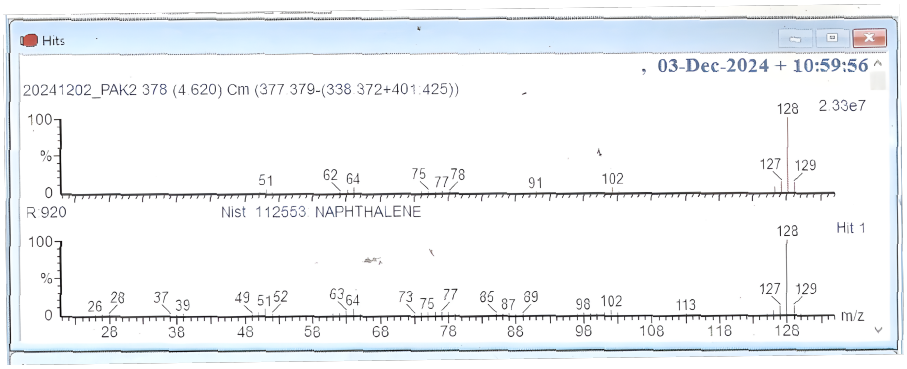

Figure 11: Naphthalene m/z fragments

5. Can you predict the order of appearance in the GC chromatogram for all PAHs?

Table 3: PAHs order of appearance

Order of appearance	**Compound name**	**Rings nr.**	**Boiling point[2] (°C)**
1	Naphthalene	2	218
2	Acenaphthene	3	278
3	Acenaphthylene	3	280
4	Fluorene	3	294
5	Phenanthrene	3	338
6	Anthracene	3	342
7	Fluoranthene	4	384
8	Pyrene	4	404
9	Benzanthracene	4	438
10	Chrysene	4	448
11	Benzo(k)fluoranthene	5	480
12	Benzo(b)fluoranthene	5	481
13	Benzo(a)pyrene	5	496
14	Dibenzo(a,h)anthracene	5	524
16	Indeno(c,d)pyrene	6	536
16	Benzo(g,h,i)perylene	6	550

[1]Source: LibreTexts [2], National Institute of Standars and Technology [3]
[2]Source: PubChem [4]

4.1.2 Question 2

Chrysene, a 4-ring PAH, is detected in an environmental water sample using GC-MS. The concentration of Chrysene in the sample must be calculated! Calculate the concentration with two method:

1. The calibration curve method
A set of samples with known concentration of Chrysene were measured and gave the following result in the chromatogram:

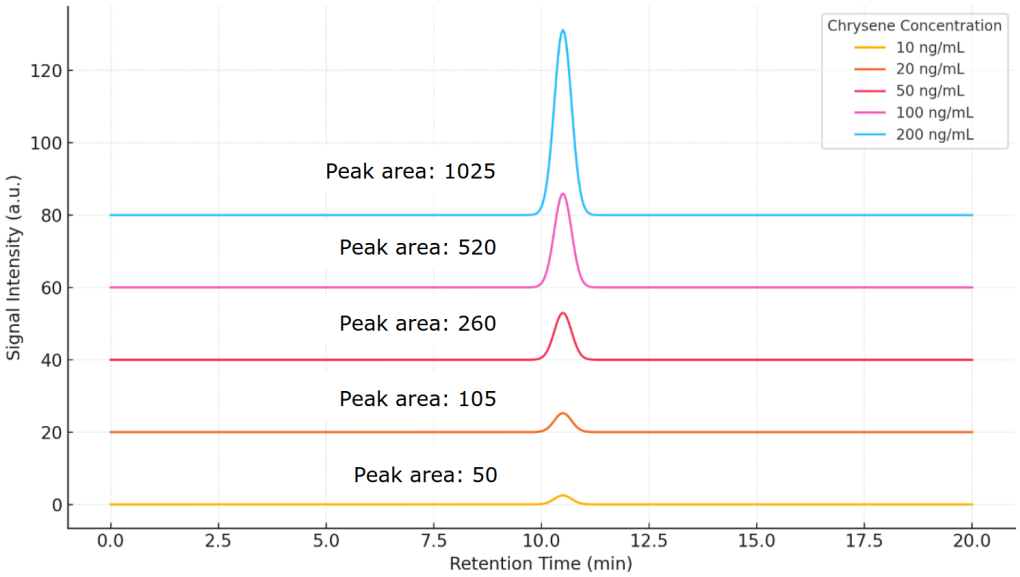

Figure 12: Chrysene samples CG-measurements

Formulas:

- Calibration curve with linear regression:

$$A = mx + b$$

Equation 3: Calibration curve

where:
A = peak area
m = slope of the line
x = concentration
b = y-intercept

- Concentration measurement (x):

$$x = \frac{A - b}{m}$$

Equation 4: Concentration of the unknown sample

The unknown sample of Chrysene gave the following result: Peak Area = 300 a.u.;

Calculate the concentration of the unknown sample:

R:

The slope has been calculated with a Python script (6.1) using the following formula:

$$m = \frac{\sum x \cdot y}{\sum x^2}$$

Equation 5: Calibration curve slope

With this script, which forces the function to pass by the point (0,0), a slope of $m = 5.14$ is obtained.

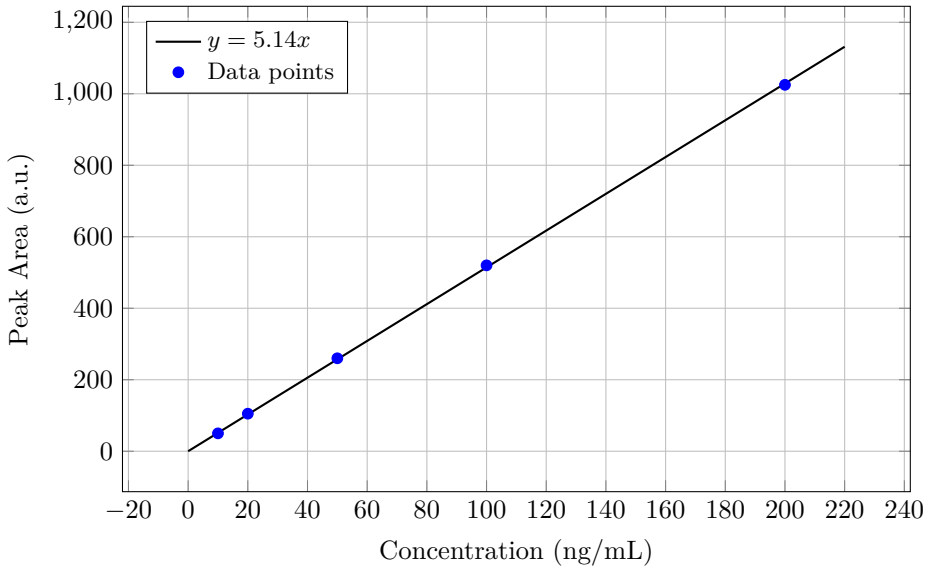

Figure 13: Chrysene calibration curve

Calculation:

Calculating the concentration of chrysene with $A = 300$ a.u., according to the Equation 4, we obtain:

$$\boxed{x = \frac{300 \text{ a.u.} - 0}{5.14} = 58.33 \text{ ng/mL}}$$

2. The internal standard method

An internal standard, Fluoranthene, was injected in the unknown Chrysene sample with concentration 50 ng/mL. The following chromatogram was obtained:

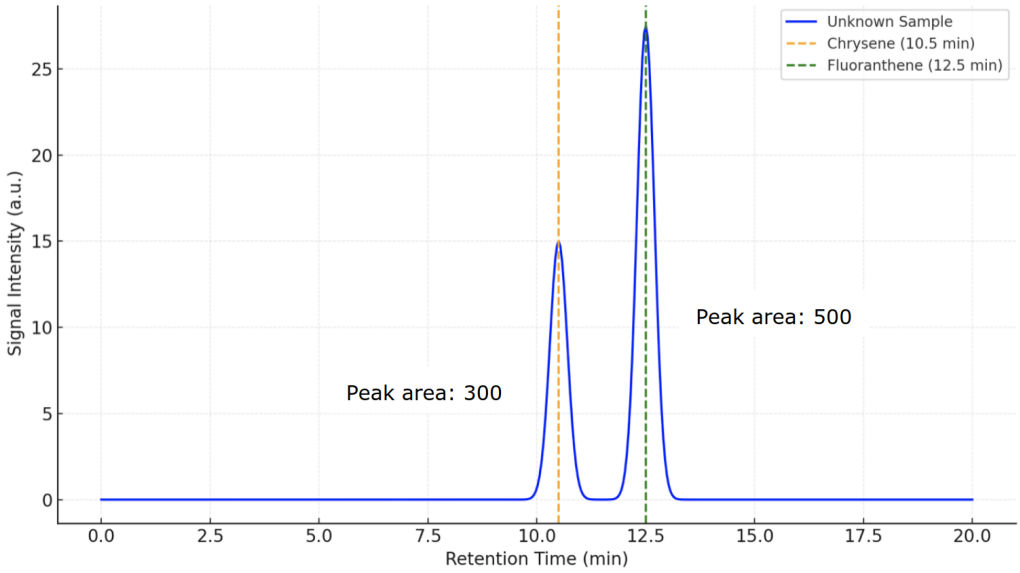

Figure 14: Unknown sample and Chrysene chromatogram

Formulas:

- Response factor of the sample **RF**:

$$RF = \frac{\text{Peak area}}{\text{Concentration}}$$

Equation 6: Response factor

- Relative response factor of the sample $\mathbf{RF_{rel}}$:

$$RF_{\mathbf{rel}} = \frac{\text{RF analyte}}{\text{RF internal standard}} = \frac{\frac{\text{Peak area of analyte}}{\text{unknown concentration of analyte}}}{\frac{\text{Peak area of internal standard}}{\text{concentration of internal standard}}}$$

Equation 7: Relative response factor

- Concentration of the unknown sample (x):

$$x = \frac{\text{peak of analyte} \cdot \text{concentration of internal standard}}{\text{peak area of internal standard} \cdot \text{relative RF}}$$

Equation 8: Unknown concentration of analyte

Based on the data provided, calculate the concentration of Chrysene in the sample:

R:

Assuming that $\underline{RF_{\text{rel}} = 1}$, then:

$$\boxed{x = \frac{300 \text{ a.u.} \cdot 50 \text{ ng/mL}}{500 \text{ a.u.} \cdot 1} = 30 \text{ ng/mL}}$$

5 Conclusion

5.1 Summary of the experiment

This experiment successfully demonstrated the application of Gas Chromatography-Mass Spectrometry (GC-MS) for the analysis and quantification of polycyclic aromatic hydrocarbons (PAHs) in plastic samples. The chromatographic separation provided clear identification of individual PAHs based on retention times, which increased with the molecular weight and complexity of the compounds. The mass spectrometry data, including characteristic m/z fragments, validated the molecular identity of the detected compounds, such as naphthalene and chrysene, aligning with theoretical expectations.

5.2 Calibration curve and quantification

The calibration curve approach showed high linearity. Using this method, the unknown concentration of chrysene in the sample was accurately determined as 58.33 ng/mL. Additionally, the internal standard method, incorporating fluoranthene, provided a secondary verification with a calculated chrysene concentration of 30 ng/mL, emphasizing the utility of complementary techniques to enhance data robustness.

5.3 PAHs separation

The results revealed the clear separation between low molecular weight (LMW) and high molecular weight (HMW) PAHs. Compounds with fewer aromatic rings eluted earlier due to lower boiling points and hydrophobicity, while larger PAHs required longer retention times. This trend was consistent with the expected behavior of PAHs during chromatographic separation.

5.4 PAHs mitigation

Mitigating the presence of polycyclic aromatic hydrocarbons (PAHs) in the environment is crucial due to their carcinogenic and toxic effects. Effective strategies include reducing emissions from industrial processes, vehicles, and other combustion sources by adopting cleaner technologies and fuels. Additionally, remediation techniques such as bioremediation, which employs microorganisms to degrade PAHs, have shown promising results in contaminated soils and waters.

Regulatory measures also play a vital role in mitigation. Enforcing stricter emission standards and monitoring programs can help limit PAH release into the environment. Recycling and proper disposal of materials containing PAHs, like plastics, further contribute to minimizing environmental contamination. Public awareness campaigns and industrial compliance with environmental regulations are essential for the long-term reduction of PAHs, ensuring both environmental and human health protection Haritash and Kaushik [1].

List of Figures

List of Tables

List of Equations

References

[1] Haritash, A., & Kaushik, C. (2009). Biodegradation aspects of polycyclic aromatic hydrocarbons (pahs): A review. *Journal of Hazardous Materials*, **169**(1), 1–15. https://doi.org/https://doi.org/10.1016/j.jhazmat.2009.03.137

[2] LibreTexts, C. (n.d.). Fragmentation patterns in mass spectrometry. **11.8**. https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map%3A_Organic_Chemistry_(Wade)_Complete_and_Semesters_I_and_II/Map%3A_Organic_Chemistry_(Wade)/11%3A_Infrared_Spectroscopy_and_Mass_Spectrometry/11.08%3A_Fragmentation_Patterns_in_Mass_Spectrometry

[3] National Institute of Standars and Technology. (n.d.). Naphthalene. https://webbook.nist.gov/cgi/cbook.cgi?Name=naphthalene&Units=SI&cMS=on

[4] National Library of Medicine. (n.d.). PubChem. https://pubchem.ncbi.nlm.nih.gov/

[5] Restek. (n.d.). Optimized polycyclic aromatic hydrocarbon (PAH) analysis by GC-MS. https://www.restek.com/global/en/articles/optimized-polycyclic-aromatic-hydrocarbon-pah-analysis-by-gc-ms

6 Attachments

6.1 Question 2.1

Python script for the linear regression:

Listing 1: Calibration curve

```
    import numpy as np

    x = np.array([10, 20, 50, 100, 200])
    y = np.array([50, 105, 260, 520, 1025])

    slope = np.sum(x * y) / np.sum(x**2)

    print("slope:", slope)
    print("300/slope:", 300/slope)
```

Output:

```
    slope: 5.143396226415095
    300/slope: 58.32721936903888
```