

# Determination of Optimized Parameters for the Separation of PAHs using GC CHEM 4303 Analytical Separations

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October 16, 2018

Date Performed: September 11, 2018  
Date Completed: October 2, 2018  
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## Abstract

PAHs are contaminants due to their toxicity, and so there is a need to separate a mixture of them, efficiently, in order to accurately identify them in a chromatogram. This experiment involves attempting to design an optimized set of parameters for a GC-FID method so that the peaks of the PAH in the chromatogram are well spaced, and was analyzed in under an hour. Two methods were run on the PAH mixture; in the first method

The computational part of this experiment involves running simulations to get the best possible chromatogram. This is done with the help of a software called GC-SOS<sup>®</sup> by altering the temperature conditions of the column. The retention times, peak amplitudes and peak widths are monitored until a satisfying chromatogram is simulated, (in which the time and resolution between the peaks had to be compromised).

The number of theoretical plates for peak 7 (fluoranthene) was calculated to be 193 025 plates, and its plate height was 1 m. And the resolution of peaks 5 and 6 (phenanthrene and anthracene, respectively) was calculated to be 1.

# 1 Introduction

Polynuclear aromatic hydrocarbons (PAHs) are a class of contaminants in which its structure consists of one or more carbonylic oxygen(s) bonded to an aromatic ring structure [1]. There is an importance of tracking, separating and identifying these PAHs in the environment as they have the reputation of being mutagenic and toxic [1], as well as carcinogenic, including its derivatives [2]. In particular, the most carcinogenic of the PAH is considered to be the benzo[ $\alpha$ ]pyrene (BaP) [3], and is one of 16 PAHs [2] that are especially kept track of, and these 16 PAHs are often known as "priority PAHs" [1].

A flame ionization detector (FID) is the most common detector for a GC [4], and it is used for detecting organic compounds [5]. This is because it responds well to compounds that have carbon-hydrogen bond [4]. The main reason for this response is that as the solutes pass through a flame in the FID, they burn and consequently produce ions and electrons, which eventually causes a current to flow [4]. This current is processed in order to form a chromatogram [5]. And the ions that are created are, for the most part, formed by the breaking of C–H bonds [5]. This is why FID are excellent as organic detectors. In addition, this type of detector works best when the carrier gas is N<sub>2</sub> as it greatly decreases its detection limit, compared to He [6].

Furthermore, cold trapping can be used to concentrate the solutes so that it will be able to give out sharp bands; note that this is only required with the splitless injection method as it the solutes enter column at a slow rate [6].

## 2 Objectives

### First Objective

Optimize and assess vital GC parameters for the separation of PAHs with the help of high resolution gas chromatography.

### Second Objective

Finding out the plate height as well as the number of theoretical plates for peak 7 (fluoranthene) in the chromatogram of PAH mixture.

### Third Objective

Determining the resolution of peaks 5 (phenanthrene) and 6 (anthracene) in the chromatogram of PAH mixture

## 3 Methods and Instrumentation

### 3.1 Chemicals

Toluene (HPLC grade chemical, LOT: 591103-A6, CAS: 108-88-3), naphthalene (Fisher Scientific, LOT: 895861, CAS: 91-20-3), and a mixture of PAH (PAH mix 1, LOT w00382; PAH mix 2, CD-1661; Ultra EPA 2138N-1, EOA 2139N-1, ACN) were used in this experiment.

The safety information for the aforementioned chemicals:

**Toluene** flammable, potential acute and chronic health effects.

**Naphthalene** flammable, toxic and carcinogenic.

**PAH mixture** flammable, can cause death, health hazard, can cause damage to the aquatic environment.

### 3.2 Instrumentation

The analysis of the PAH mixture was performed on an Agilent 6890N Network GC System (by Agilent Technologies), equipped with an FID detector. Before each analysis, the apparatus was left on standby so that the flame was able to reach the desired temperature for that particular analysis. The separation was performed on an Agilent 122-5032 J&W DB-5 capillary column, 30 m length  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m thickness, 7 inch cage. Its stationary phase was 5% Phenyl/95% methylpolysiloxane (DB-5). In addition, each analysis was conducted with the injection mode at splitless and the carrier gas in the GC-FID was He, with a flow rate of 1  $\frac{\text{mL}}{\text{min}}$ . The injector port temperature was set to 260 °C and for the analyses of toluene and naphthalene, the detector temperature was set to 280 °C, and it was increased to 300 °C for the analyses of the PAH mixture.

### 3.3 Methods

Initially, analyses were performed on toluene once and then on naphthalene twice because the GC had to be set up and checked if the precision was up to standards before proceeding with the analyses of a mixture of PAH. The name of the

method used for these analyses was “RJWEEK1.M”. Hereafter, all the remaining separations were performed on this mixture.

For the first method, which was named “RJ1WEEK2.M”, the oven temperature was initially set at 110°C for 0.5 min, and it was increased by  $7.5 \frac{^{\circ}\text{C}}{\text{min}}$  all the way to 300 °C; and it was held at this temperature for 40 minutes. The total runtime for this method was 65.83 min.

In the second method, named “RJ2WEEK2.M”, the oven temperature was set at 75°C for 2 min, it was increased by  $5 \frac{^{\circ}\text{C}}{\text{min}}$  all the way to 300 °C; it was held at this temperature for 40 minutes. And the total runtime for the second method was 87 min.

Just before setting the parameters for the final method, the GC-SOS<sup>®</sup> software was used to simulate a separation of the PAH via gas chromatography, using parameters that was retrieved from the previous runs, including the two methods that were used on the PAH mixture (“RJ1WEEK2.M” and “RJ2WEEK2.M”). Through trial and error, it was realized that the optimum temperature conditions for the separation of the PAH mixture, comprising between resolution and time taken, are as follows: the initial temperature was set to 75 °C; it was held at this temperature for 1 min; it was then increased at a rate of  $10 \frac{^{\circ}\text{C}}{\text{min}}$  all the way to 130 °C, and it was held at this temperature for 25 min; finally, the temperature was again increased at a rate of  $12 \frac{^{\circ}\text{C}}{\text{min}}$  until it peaked at 250 °C, and it was held at this temperature for 21 min. The simulated chromatogram, its temperature parameters, the column conditions and the retention data are all shown in Figure 7. These very same temperature conditions/parameters were set up into the method called “OPTRJ.M”, and a final analysis was initiated on the PAH mixture.

## 4 Results and Discussion

### 4.1 Results

The GC-FID chromatograms for the analyses of naphthalene and toluene are given in Figures 1, 2 (both are for naphthalene) and 3 (toluene), respectively. The integration results for the chromatogram of the analysis of the PAH mixture using the method “RJ1WEEK2.M” is shown in Table 1, while the chromatogram is shown in Figure 4. Also, the chromatogram for the second analysis of PAH using the method “RJ2WEEK2.M” is shown in Figure 5, and its integration results are

shown in Table 2. Finally, the chromatogram for the optimized analysis of PAH (method name was “OPTRJ.M”) is shown in Figure 6, and its integration results are shown in Table 3. Note that in each table, there are numbers that are encircled next to the peak number; this is to show which peak represents which hydrocarbon. Refer to Table 1 of [1] under the PAHs section of the table to locate which peak number represents which hydrocarbon. The peaks that are not next to the numbers are considered noise and, thus, should be ignored.

## 4.2 Discussion

As it can be seen in Figure 4, when the initial temperature of the column was set to 110 °C, the majority of the first 7 peaks are quite compact. This goes double for peaks 3 and 4, and peaks 6 and 7. Their retention times for these two pairs of peaks are quite close to each other (8.463 min and 8.976 min for peaks 3 and 4, and 13.232 min and 13.370 min for peaks 6 and 7). However, in Figure 5 (the second GC-FID analysis of the PAH mixture), peaks 3 and 4 are resonable far apart; their retention times are 17.872 min and 18.736 min, respectively.

However, in both of the aforementioned chromatograms, the pairs of peaks 6 and 7, peaks 10 and 11, and peaks 14 and 15 are all close to each other and are overlapping with each other. The optimized method “OPTRJ.M” was designed to get a good resolution out of these peaks while not sacrificing the time it would take for the GC-FID analysis to be completed. In the end, it was decided that an initial low temperature had to be set (75 °C) for cold trapping of the solutes to take place. Afterwards, after a minute, once it was decided that all of the rapid increase of temperature is

In conclusion, it can be seen that decreasing the temperature of the taking advantage of the cold trapping technique gives a much better chromatogram. Most of the peaks are away from each other

## 5 References

### References

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## 6 Appendix

### 6.1 Calculations

**Mass required to make 10 mL of 1  $\frac{\text{mg}}{\text{mL}}$  (1000 ppm) naphthalene in toluene**

$$1 \text{ ppm} = 1 \frac{\mu}{\text{mL}} = 1 \frac{\text{mg}}{\text{L}} \text{ and}$$

$$1 \text{ ppb} = 1 \frac{\text{ng}}{\text{mL}} = 1 \frac{\mu}{\text{L}}$$

$$M_{r_{\text{naphthalene}}} = 128.17 \text{ g mol}^{-1}$$

$$1 \frac{\text{mg}}{\text{mL}} = 1 \text{ g L}^{-1} = 0.001 \text{ g mL}^{-1}$$

$$\text{molarity} = \frac{0.001 \text{ g mL}^{-1}}{128.17 \text{ g mol}^{-1}}$$

$$= 7.8021 \times 10^{-6} \frac{\text{mol}}{\text{mL}}$$

$$\text{moles} = \text{volume} \times \text{concentration}$$

$$= 10 \text{ mL} \times 7.8021 \times 10^{-6} \frac{\text{mol}}{\text{mL}}$$

$$= 7.8021 \times 10^{-5} \text{ mol}$$

Mass of naphthalene required

$$= 7.8021 \times 10^{-6} \text{ mol} \times 128.17 \text{ g mol}^{-1}$$

0.01 g of naphthalene is required

**Determining the number of theoretical plates for peak 7**

Peak 7 was identified as fluoranthene.

$$N = 5.545 \left( \frac{t_r}{w_{\frac{1}{2}}} \right)^2 = 16 \left( \frac{t_r}{w_b} \right)^2 \quad (1)$$

In equation 1,  $N$  represents the number of theoretical plates;  $w_{\frac{1}{2}}$  and  $w_b$  are the widths of the peak at half-height and at the base, respectively.

$$\begin{aligned} N &= 5.545 \left( \frac{t_r}{w_{\frac{1}{2}}} \right)^2 \\ N &= 5.545 \times \left( \frac{25.393 \text{ min}}{0.1361 \text{ min}} \right)^2 \\ N &= 193\,024.8952 \text{ plates} \approx 193\,025 \text{ plates} \end{aligned}$$

**Determining the plate height for peak 7**

Peak 7 was identified as fluoranthene.

$$H = \frac{L}{N} \quad (2)$$

In equation 2,  $H$  represents plate height,  $L$  represents the length of the column, and  $N$  is the number of theoretical plates [6].

$$\begin{aligned} H &= \frac{30 \text{ m}}{193024.8952} \\ H &= 1.5542 \times 10^{-4} \text{ m} \approx 1.55 \times 10^{-4} \text{ m} \end{aligned}$$

**Determining the resolution for peaks 5 and 6**

Peaks 5 and 6 were identified as phenanthrene and anthracene.

$$R = \frac{2 \times (t_{r,B} - t_{r,A})}{w_A + w_B} \quad (3)$$

Equation 3 was referenced from [5].

$$\begin{aligned} R &= \frac{2 \times (17.981 - 15.989)}{0.364 + 0.303} \\ R &= \frac{3.984}{0.667} \\ R &= 5.973 \approx 6 \end{aligned}$$

## 6.2 Chromatograms

There are 10 pages of printouts that were collected during this experiment, 6 of which are GC-FID chromatograms.