Gas chromatography

Gruppe 13:

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Abstract: The aim of the experiment was to familiarize ourselves with gas chromatography. In a first experiment different injection techniques (hot needle, solvent flush, flush sample and on-column) were compared. In the second experiment chromatograms of a mixture of C_{10}-C_{23} alkanes were measured at different temperatures and compared to each other. The third task was to find the retention index of decanol. The obtained value for 1-decanol was 1201, which lies below the found literature values (1250-1270) [3]. The fourth experiment was the optimization of the carrier gas flow, to optimize the chromatograms. Finally, chromatograms of two different whiskeys (Jim Beam and Jack Daniels) were measured.

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1. Theory [1],[2]

Gas chromatography is a method to separate volatile substances. A sample is injected through an injector onto the column, which is a thin, long glass tube (capillary). The walls of the tube are either covered with a thin layer of SiO_2 (or modified Silicates) or with a thin liquid layer.

There are two different types of sample injectors. One is the on-column-injector, where the sample is directly injected onto the column. The second one is the split injector. With this technique the sample is first injected in an evaporation area, before the sample is pushed onto the column with the carrier gas.

For the on-column-injector, there is only one method to bring the sample on the column, the direct one, where a certain volume is pressed on the column. With a split injector, there are three different ways to inject the sample onto the column. The first method is the filled needle technique. Only the needle is filled with the sample. The solution evaporates when the needle passes the septum. The second method is the hot needle technique. After the sample, some air is soaked up until the air can be seen. Then, the needle is put through the septum. After about five seconds, the sample in the barrel gets injected. The third and last technique is the solvent flush technique, where the syringe is first filled with the solvent, then air is soaked in until the needle is full. Then the needle is filled with the sample. The last layer is air again. The syringe is then entered like in the hot needle technique into the injector.

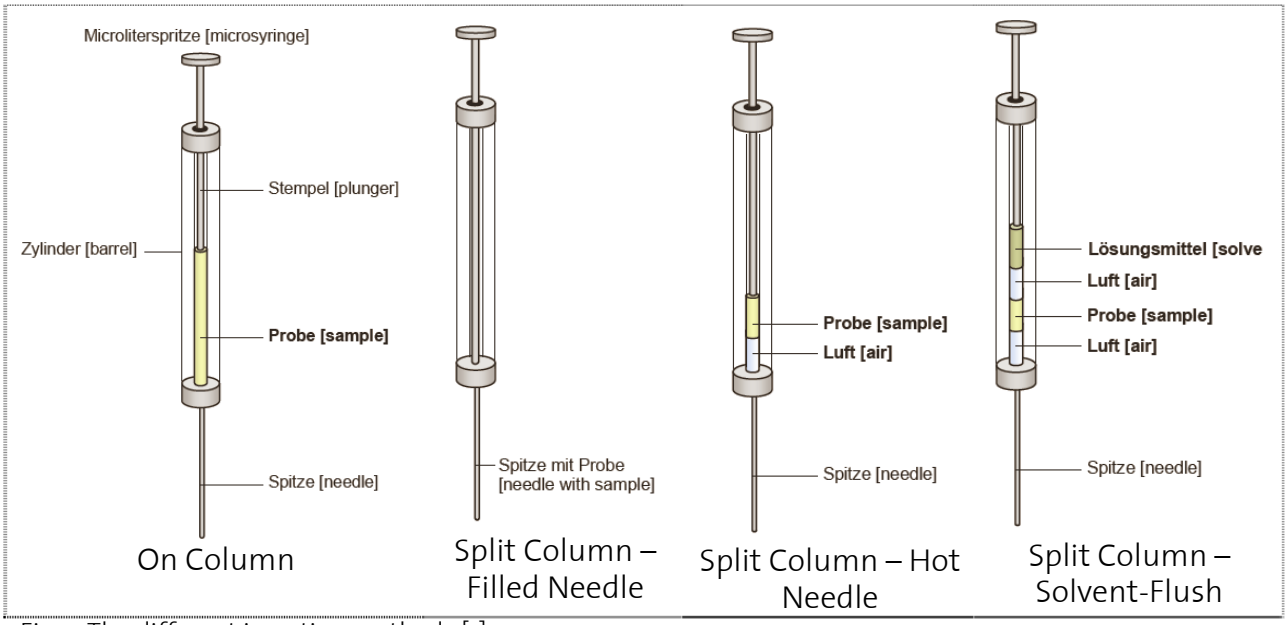

Fig. 1: The different insertion methods [1]

As a detector a flame ionization detector (FID) was used during the experiments. In a FID the sample is burned with compressed hydrogen and air. The peak area is proportional to the number of carbon atoms burned by the FID.

The capillary is surrounded by an oven, which can either hold a constant temperature or heat up at a certain rate. The oven is needed because the retention time of a certain sample is dependant from the temperature, the used column and pressure. If the temperature is too high, the substances elute too fast and the resulting peaks aren't separated, if the temperature is too low, the analysis takes too much time.

The retention time depends on many factors. To compare different types of GC (e. g. different tube length, pressure) the retention index I_x was established:

Temperature gradient: $$I_x = \frac{100 \cdot (t_x - t_n)}{t_{n+1} - t_n} + 100 \cdot n \quad (1)$$

Isothermal: $$I_x = 100 \cdot \frac{Log(t_x) - Log(t_n)}{Log(t_{n+1}) - Log(t_n)} + 100 \cdot n \quad (2)$$

Where n is the number of Carbon atoms in the alkane whose peak precedes the one of the analyzed substance.

The retention volume can be expressed by the volume flow and the retention time using the following equation:

$$V_R{}^0 = t_R{}^0 \cdot F \quad (3)$$

Where

$$F = \frac{L_{Column} \cdot 2\pi \cdot r_{Column}}{t_R{}^0} \quad (4)$$

The ideal gas flow can be found by the following equation, with f =3.5 $\frac{s}{m}$ for Helium:

$$t^0 = f \cdot L_{Column} \quad (5)$$

2. Execution of the experiment

2.1. Set up

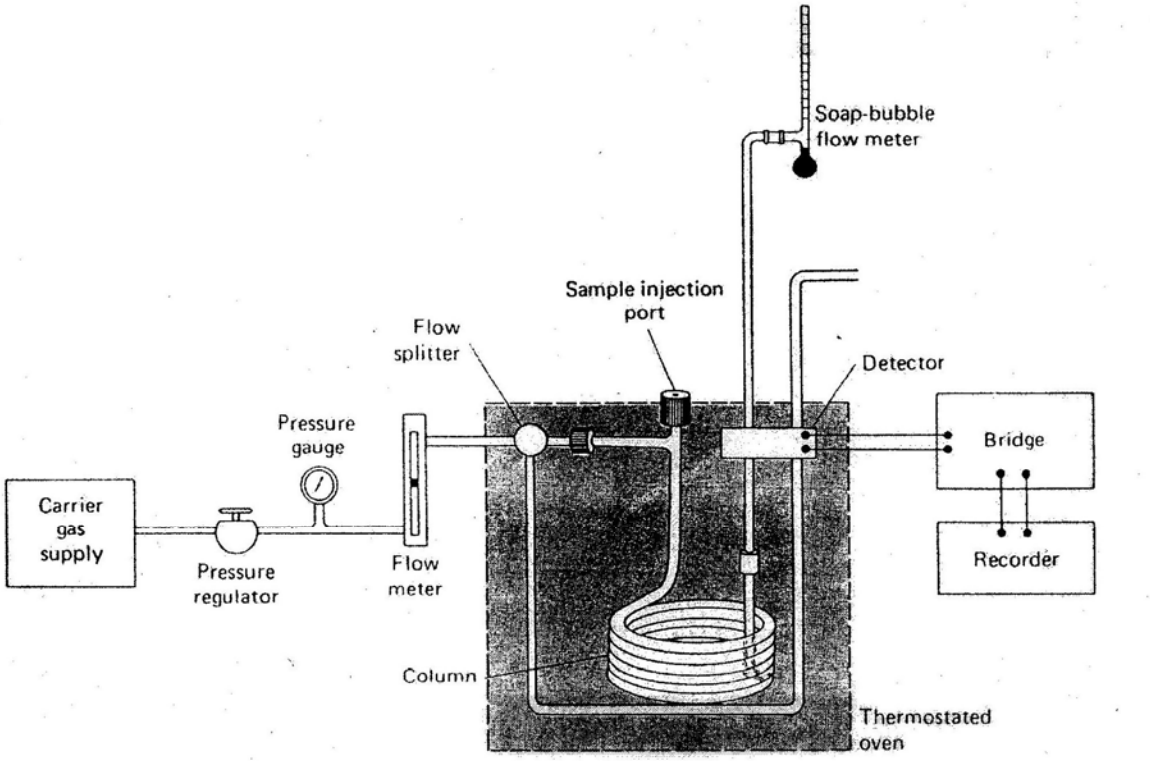

Fig. 2: The used setup for the experiment [2]

A gas chromatograph consists of four different parts. The first one is the injector, the second the oven, the third is the column and the last the detector. An On-Column-Injector and a Split Injector were used to bring the sample onto the column. The used column was a thin layer capillary column, type SE54 (DB 8) with a length of 30 m. As a detector a flame ionizations detector (FID) in which H_2 (100 kPa) and air (60 kPa) were burned at 290 °C.

2.2. Substances

All solutions used for the experiments were obtained from the assistant. In table 1 a list of all used solutions is shown. The substances were diluted 1:5000 in n-hexane. The concentration for the alkanes was chosen in a way that the concentration in g/l is the same for every alkane, so that the FID always provides the same height of the peaks.

Solution Number	Solution
1	C_{10}-C_{23}, n-alkanes
2	C_{10}-C_{15}, n-alkanes
3	C_{10}-C_{15}, n-alkanes and n-Decanol

Tab. 1: Solutions used in the experiments

2.3. Tasks

2.3.1 Variation of the insertion technique

Apparatus 1:

Start temperature	80 °C
End temperature	240 °C
Heating rate	20 °C/min
Resolution	Range: 0-100, Attenuation 2
Solution	1
Carrier gas pressure	65 kPa

Tab. 2: Settings for the experiment

In the first experiment, a variety of the insertion techniques were used: First the "filled needle technique" was used to insert solution 1. After the 15th component (fourteen from the probe and an extra one from the hexane) the plotter was stopped and the system was cooled down to proceed with the next part of the experiment. This time the insertion technique used was the hot needle technique. The third technique was the solvent flushed needle technique; therefore the resolution was changed from attenuation 2 to 1. As an addition, the technique of on-column was used on the second apparatus with the following data:

Apparatus 2:

Start temperature	120
End temperature	240
Heating rate	15 °C/min
Resolution	Range: 0-100, Attenuation 4
Solution	1
Carrier gas pressure	54 kPa
Insertion technique	0.3 µl On-Column-Technique

Tab. 3: Settings for the experiment

2.3.2 Isothermal gas chromatography

Resolution	Range: 0-100, Attenuation 4
Solution	2
Carrier gas pressure	54 kPa
Insertion technique	0.3 µl On-Column-Technique

Tab. 4: Settings for the experiment

In this experiment, the influence of the temperature on a chromatogram was examined. At four different temperatures (121-122 °C, 130-131 °C, 140-141 °C, 150 °C) the gas chromatogram was measured. After the 4th peak the temperature was increased up to 240 °C to save some time.

2.3.3 Retention Index

Apparatus 1:

Start temperature	140
End temperature	240
Heating rate	After the 4th-Peak the temperature was raised to the end temperature
Resolution	Range: 0-10, Attenuation 1
Solution	2
Carrier gas pressure	65 kPa
Insert technique	1 µl Hot-Needle-Technique

Tab. 5: The settings for the experiment

Apparatus 2:

Start temperature	120
End temperature	240
Heating rate	After the 4th-Peak the temperature was raised to the end temperature
Resolution	Range: 0-100, Attenuation 0
Solution	2
Carrier gas pressure	54 kPa
Insert technique	0.3 µl On-Column-Technique

Tab. 6: Settings for the experiment

In this experiment, the retention index of n-decanol was determined. First a blank chromatogram was measured (only C_{10} to C_{15} alkanes). The second measurement was then done with solution 3 (C_{10} to C_{15} alkanes and n-decanol).

2.3.4 Carrier gas optimization

In order to find the optimal gas flow for the column, a probe of methane (5 µl) was inserted into the column and the flow was optimized until 105 seconds were obtained as retention time. For the calculations equation (5) was used.

2.3.5 Real life sample: Whiskey

The sample was prepared by the assistant. The whiskey was extracted with hexane, so no water was inserted onto the column.
Two different Whiskeys, Jack Daniels and Jim Beam, were analyzed.

Apparatus 1:

Start Temperature	40 °C for 5 Minutes
End Temperature	240 °C
Heating rate	15 °C/min
Resolution	Range: 0-10, Attenuation 4
Solution	Whiskey in Hexane (1:5000)
Carrier gas pressure	56 kPa
Insert technique	1 µl Hot-Needle-Technique

Tab. 7: Settings for the experiment

Apparatus 2:

Start Temperature	40 °C for 5 Minutes
End Temperature	240 °C
Heating rate	15 °C/min
Resolution	Range: 0-100, Attenuation 4
Solution	Whiskey in Hexane (1:5000)
Carrier gas pressure	62 kPa
Insert technique	0.3 µl On-Column-Technique

Tab. 8: Settings for the experiment

3. Results

3.1 Variation of the insertion technique

In Figures 3 & 4 the results of the variation of the insertion technique are shown.

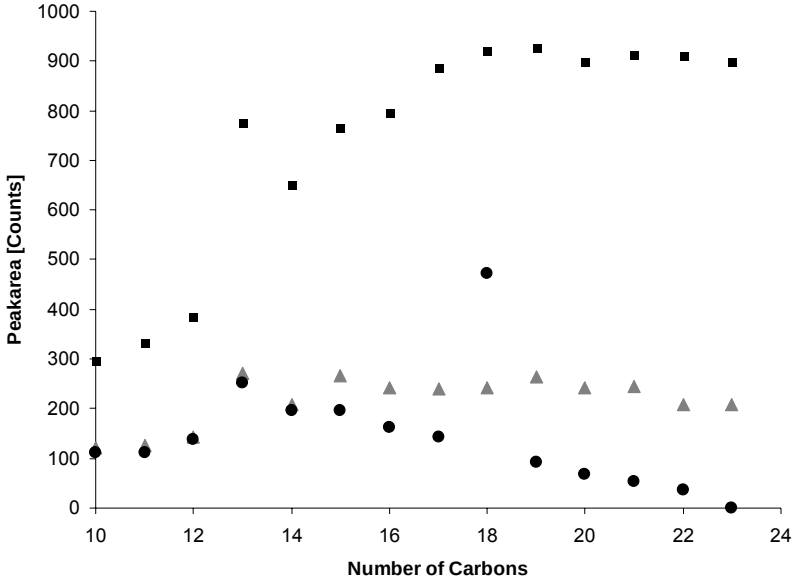

Fig 3. Peak area versus the number of carbon atoms measured on apparatus 1. Squares: solvent flush technique, circles: hot needle technique and triangles: filled needle technique.

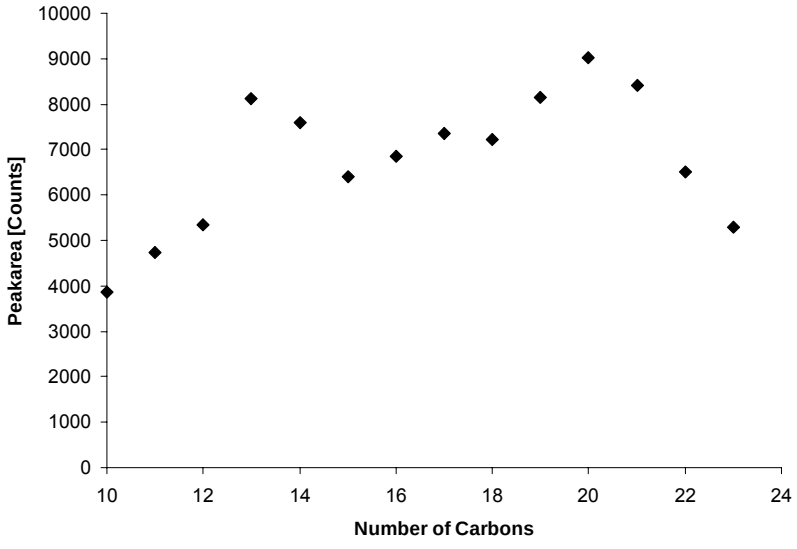

Fig 4. Peak area versus the number of carbon atoms obtained using the on column injection.

3.2 Isothermal gas chromatography

Figure 5 shows the result of the isothermal gas chromatography. Only the first 5 alkanes (C_{10} – C_{14}) were measured, then the GC was heated up to accelerate the speed of elution.

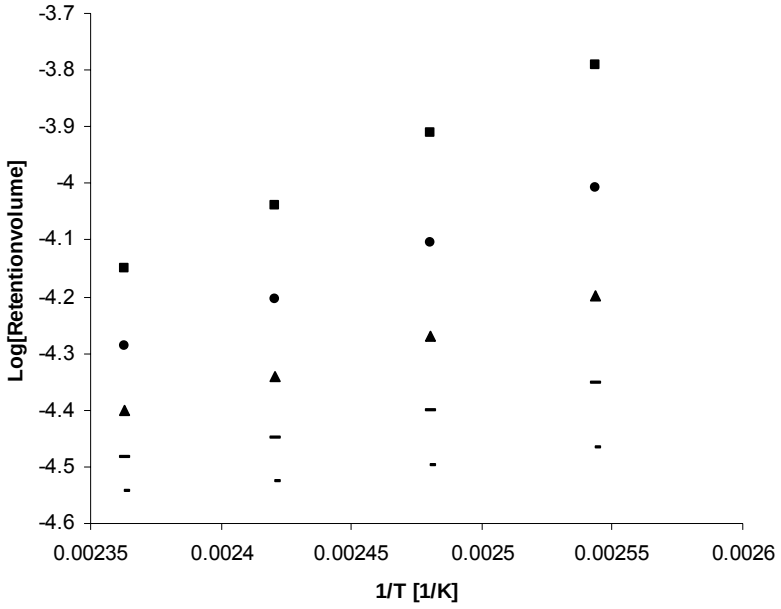

Fig 5. Logarithms of the Retention Volume versus the reciprocal temperature in Kelvin. The first column corresponds to the C_{10} alkane, the second to the C_{11} and so on.

3.3 Retention Index

Table 9 shows the result of the determination of the retention index for decanol.

Apparatus 1	Apparatus 2
1201	1201

Tab. 9: The obtained values of the retention index for decanol.

3.4 Carrier gas optimization

In Figure 6 the results of the gas optimization are shown. The optimum f-value for helium is 3.5 $\frac{s}{m}$.

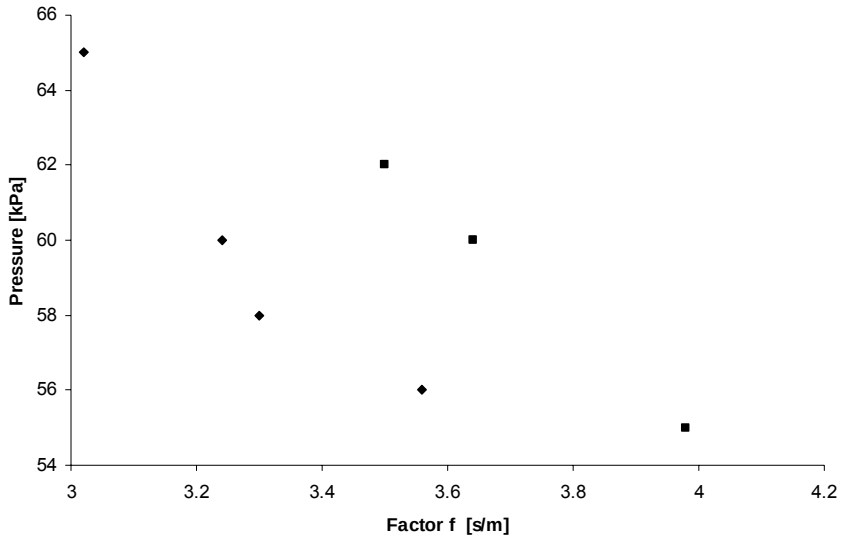

Fig 6: The Pressure versus factor f. Diamonds: Apparatus 1, Squares: Apparatus 2.

3.5 Real life sample: Whiskey

Both Whiskeys contained a polar and a nonpolar fraction. The obtained chromatograms can be found in the appendix.

4. Discussion

4.1 Variation of the insertion technique

As shown in figure 3 and 4, for every method a different amount of sample was detected. This occurs because the amount of substance which is inserted in to the column differs. For the method of filled-needle and ho-needle-technique, the difference can be easily explained; some sample remained in the syringe. The biggest amount of sample could be brought on to the column by using the solvent flush technique, because the syringe is washed by the solvent.
The difference of the direct-on-column-technique and the split-injector-technique is based on the different amount of substance which was brought onto the column.

One sees that some trends occur, at first there is an increase in the peak area, which is based on the faster evaporization of smaller alkanes, so there are less in the sample.

Injection Technique	Advantage	Disadvantage
Filled-Needle-Technique	Easy application	Small amount of sample on the column
Hot-Needle-Technique	Easy application	The waiting time always has to be the same
Solvent-Flush-Technique	The whole sample get into the injector.	Large solvent peak
Direct-on-column	Easy application	Overloading the column can easily happen

Tab 10: Advantages and Disadvantages of different injection techniques.

4.2 Isothermal gas chromatography

The effects described in the theory part of the report were observed. At low temperatures the elution took much longer than at higher temperatures. If a gas chromatogram would be taken at 50 °C the time spent waiting would most likely exceed the time limits of this experiment.

The peaks at higher retention times were flat and broad and therefore the quality of the chromatogram has to be considered worse compared to chromatograms measured using a temperature program.

The isothermal gas chromatography is advantageous if the sample contains compounds which have similar retention times. Time can be gained by using a temperature program when separating compounds, which have different volatilities. A combination of both methods, isothermal and programmed run is useful, if the sample consists of chromatographically similar substances. On the isothermal phases the substances separate well and this advantage is combined with a gain of time.

4.3 Retention Index

The obtained retention index (1201) for decanol is smaller than the one found on the webbook [3] (around 1250-1270, the exact column could not be found).
The reason for this could be that the carrier gas flow was not yet fully optimized.

4.4 Carrier gas optimization

The carrier gas pressure was optimized until a retention time of 105 seconds was obtained. The value 105 seconds was calculated using the equation (5).

4.5 Real life sample: Whiskey

One sees that whiskey contains a polar and nonpolar fraction. On Apparatus 2 the resolution which was chosen wasn't optimal.
Because no reference chromatogram was found, an interpretation of the results was not possible.

5. References

[1] Praktikum Analytische Chemie (4. Semester), *Gaschromatographie*, März 2007.
[2] Vorlesungsskript: Analytische Chemie II, Prof. R. Zenobi, SS 07, ETH Zürich.
[3] http://webbook.nist.gov/chemistry/, 13.06.2007.