Laboratory Courses in Physical Chemistry
for students the study courses chemical engineering
Technische Universität München SS 2003

Elaboration of the experiment 8.1

Gas Chromatography

Group 3
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1 Problem

First for six pure substances solutions and one mixture the gas chromatograms have to be measured and analysed. Furthermore the identification of the three components of the mixtures has to be done on the basis of the calculated data from the pure substances.

2 Theory

In this experiment the basic principles of gas chromatography are demonstrated.
Gas chromatography is one of the most important chromatographical methods, applied in analytical chemistry. Its positive aspects are on the one hand a very short time of analysis, and on the other hand the rather small amount of sample which is needed for separation and detection of each component. This furthermore leads to the a proportionally high sensitivity of this method.

It can be applied to different sorts of samples, which should have a boiling point under 400°C. Gas chromatography can also be used in a preparative way.

There are fundamental differences between all chromatographical methods, concerning their features of separation quality of a sample mixture, and the curves of detection, which are the final output of most automated procedures. Chromatographical methods are primarily classified by te type of stationary phase used:

1. A solid which is able to adsorb the components of the mixture, which leads to adsorption chromatography
2. A liquid which is usually applied to a solid carrier to enlarge the accessible surface, which leads to partition chromatography.

The mobile phase can either be liquid or gaseous which leads to liquid chromatography or gas chromatography.

The separation of the components hence is a function of the distribution of the different components between the two used phases. This distribution can be described with the partition coefficient which is the quotient of the specific concentration in the stationary phase and the specific concentration in the mobile phase; its value depends on the chromatographical method and column used.

Gas chromatography is a non-ideal, linear chromatographical method. This means, that the isothermal lines of the partition are linear, but the circumstances of mass transfer are not ideal. This results in a broadening of the peak bases. The peaks get the shape of a gaussian curve, because of diffusion processes, which are happening inside the column. The broadening of the peaks increases with increasing time of retention, as the underlying processes inside the column can last longer.

In this experiment the most commonly used technique of elution is deployed. The sample is applied to a column which is filled with the stationary phase via the carrier gas, which is hydrogen. The molecules of the sample-gas distribute between the two phases and the components split up.

Because of their different partition coefficients the single components are held back in the column for a different length of time and washed out of the column one after the other.
The components are detected by a so-called FID (Flame Ionisation Detector), where the carrier gas is burned. This leads to an ionisation of the flane, which can be measured.

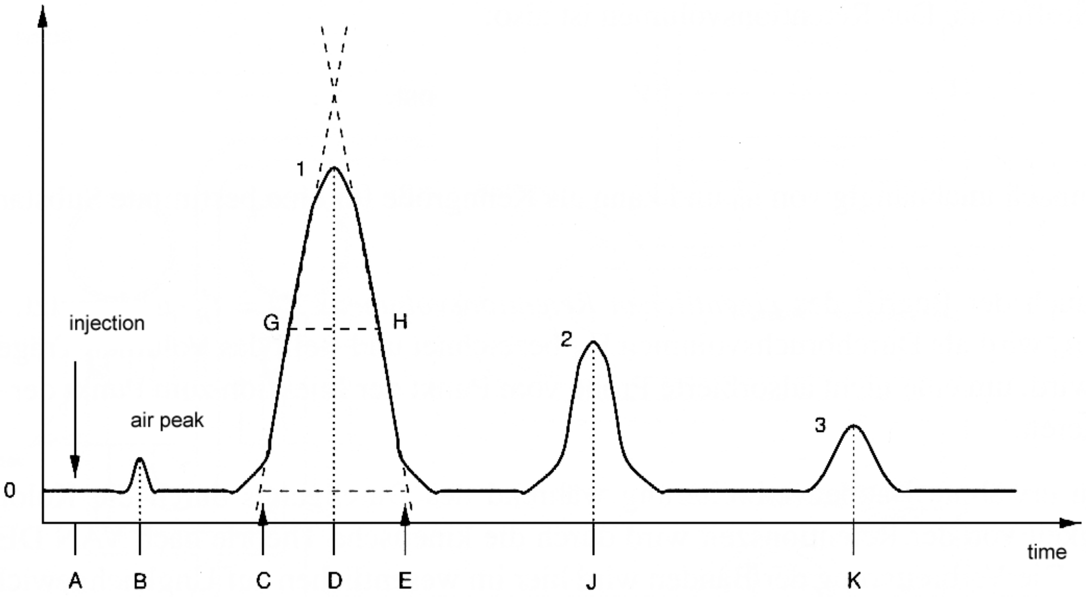


Figure 1: Chematic example of a chromatogram

The total time of retention passes from the point of injection of the sample until the point of detection and is abbreviated by t_R, which is constant and usable for the identifcation of single com-ponents (Fig. 1).

$$t_R = \overline{AD} \tag{1}$$

The amount of the single substances commensurates to the area F of the correspondent peak. It can be measured in approximation as shown in Picture 1.

$$F = \overline{DI} \cdot \overline{GH} \tag{2}$$

If the separation of the components is not complete, a different chromatogram output occurs. Two peaks melt together and the area in which they diverge from gaussian curves still a mixture of both components exists, which can just be separated by another chromatography of the fraction through a short column or a new chromatography of the sample through a longer column.

A value called the retention volume V_R is also commonly used for the detection and descripion of detected substances. It is constant and does not depend on the velocity of the streaming gas. It can be calculated with the velocity of the gas stream u_0:

$$V_R = t_R \cdot u_0 \tag{3}$$

The peak-broadening, which has already been described before can be explained by the VAN DEEMETER Equation:

$$\mathrm{HETP} = \mathrm{A} + \frac{\mathrm{B}}{u} + \mathrm{C} \cdot u \tag{4}$$

In this equation several parameters are taken into account. u is the velocity of the gas stream, A a constant, which stands for turbulence diffusion and therefore is dependent on the column and its packing, B is dependent on the axial diffusion and C is a constant, which reflects the inequities concerning the mass diffusion between the phases.
HETP is a equivalent to the height of a theoretic platform and would be the height in which (in a vertical column) the equilibrium of the molecular partition would take place.
As a value for the effectiveness of a certain column the number n of theoretic platforms, is significant.

$$n = 16 \cdot \left(\frac{t_R}{\overline{CE}} \right)^2 \tag{5}$$

So the HETP-Value is:

$$\mathrm{HETP} = \frac{L}{n} \tag{6}$$

with the total length L of the column.

3 Experiment

3.1 Execution of the Experiment

The apparatus was activated as suggested by the given description. The settings which had to be done were also taken from the description. A chromatography with 0,6 μl of the pure substance solutions No. 1 to 6 and the mixture sample P were performed three times each. The chromatograms were saved on hard-disk first, and at the end of the experiment, saved to floppy-disk. The total length L of the column was 1,83 m.

3.2 Discussion of the Experiment

3.2.1 Measurements of the pure substance solutions

Substance	t_R/s	$\overline{t_R}$	CE	$\overline{\text{CE}}$	n	HEPT	F	$\overline{\text{F}}$	$\overline{\text{F}} \cdot \text{E}$
2-Butanol	82,2	81,47	25,50	23,67	189,586	0,0097	8,22	8,95	1145,33
	81,6		23,00				6,48		
	80,6		22,50				12,15		
Acetone	65,6	68,00	9,50	11,83	528,352	0,0035	2,24	4,20	537,45
	67,1		14,00				4,94		
	71,3		12,00				5,41		
Dioxan	99,2	99,23	13,00	17,67	504,808	0,0036	7,30	7,80	998,60
	98,7		24,00				8,49		
	99,8		16,00				7,62		
Ethanol	61,9	66,43	20,00	29,50	81,142	0,0226	7,01	6,96	891,42
	69,1		35,50				6,79		
	68,3		33,00				7,10		
Ethylacetat	80,1	80,73	12,50	13,67	558,342	0,0033	7,65	6,76	865,17
	81,7		12,50				5,21		
	80,4		16,00				7,42		
Isopropanol	69,6	69,53	18,00	19,00	214,289	0,0085	6,89	6,87	879,62
	67,0		20,00				7,42		
	72,0		19,00				6,30		

Table 1: Pure substance solutions

3.2.2 Measurements and calculations of the mixture solution

Peak	t_R/s	$\overline{t_R}$	Substance	F	$\overline{\text{F}}$	$\overline{\text{F}} \cdot \text{E}$	Content	Error
1	68,5		Acetone	5,77			129,08	14,53
	69,8	69,57	Ethanol	5,33	5,42	693,96	77,83	8,76
	70,4		Isopropanol	5,16			78,87	8,88
2	80,7		2-Butanol	5,77			60,57	6,82
	81,7	81,53	or	5,33	5,42	693,96		
	82,2		Ethylacetat	5,16			80,19	9,02
3	98,9			2,77				
	97,5	98,57	Dioxan	2,53	2,58	330,63	33,07	4,10
	99,3			2,45				

Table 2: Mixture solution of three substances

All the data were plotted and analysed in Origin and multiplied with corresponding factors to get back to the units used in the graphs (Fig. 2).
Sensitivity E was $2^7 = 128$. The same apparatus was used for all chromatographies.

The content was calculated with:

$$\text{Content } [\%] = \frac{\overline{\text{F}} \text{ mixture}}{\overline{\text{F}} \text{ pure}} \cdot 100 \tag{7}$$

The error with:

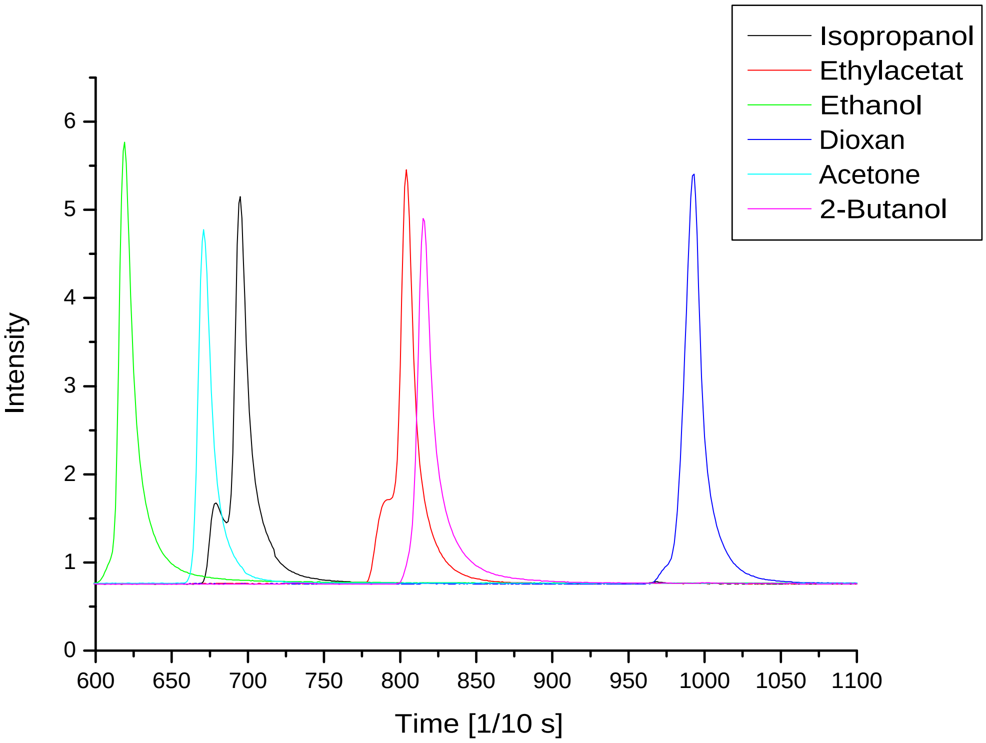
$$\text{Error} = \frac{\Delta_{max}(\overline{F}, F) \text{ Mixture}}{\overline{\text{F}} \text{ pure}} \cdot 100 \tag{8}$$

4 Discussion

Only the third peak of the mixture was significant, the other two were hard to identify. Regarding the fact that the three components of the mixture have to result in 100 percent, the best two identifications are: Ethanol, 2-Butanol and Dioxan or Isopropanol, 2-Butanol and Dioxan.
The most important error had been produced by the time difference between the injection and the activation of measurement.

The Plate CE calculated by Origin is sometimes quite long, longer than the hand-crafted would be. This results in a small number of theoretical platforms n.

5 Appendix



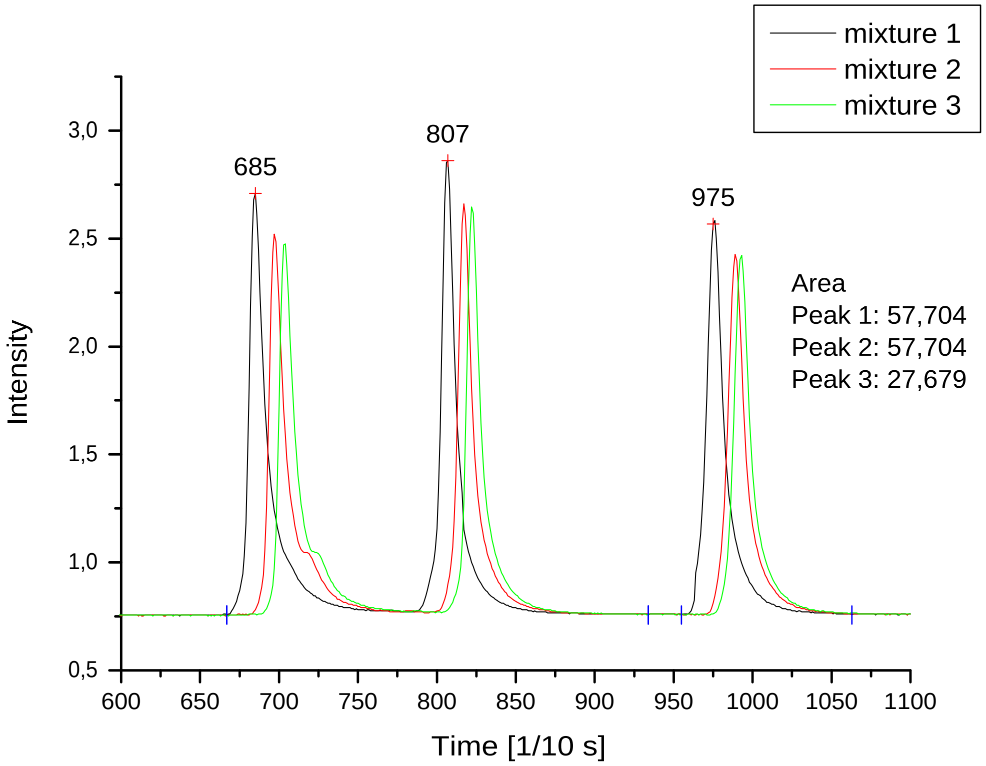


Figure 2: Pure substances and mixtures