Analysis of lighter fuel by gas chromatography

Aims of the experiment

- To understand the principle of gas chromatography
- To perform a simple separation of lighter fuel gases (hydrocarbons)
- To learn about methods for the identification of substances
- To recognise that every lighter has a different composition of gases

Principles

Gas chromatography is a method by means of which mixtures of gases can be separated into their individual components. For example, it is possible to both identify the individual components of a mixture (qualitative analysis) as well as determine the exact composition of the mixture (quantitative analysis).

As with all chromatographic methods, gas chromatography (in short GC) is based on the different chemical or physical properties of the substances (analytes) to be investigated. In the case of the analysis of hydrocarbons, as here in lighter fuel, the separation is based on the small differences in polarity of the substances. The substances are separated in a two-phase system consisting of a mobile phase and a stationary phase. These two phases have a different polarity. The mobile phase in this simple chromatograph consists of air that is drawn through the column containing the stationary phase using a pump. The stationary phase consists of a carrier material coated with silicone oil.

If a sample consisting of several gases is introduced into the air stream, they will dissolve more (non-polar substances, e.g. isobutane) or less (polar substances, e.g. ethane) in the stationary phase, the silicone oil, depending on their polarity. At every point in the column and at every point in time, an equilibrium will form between dissolved and undissolved substance. However, the undissolved substance is carried along by the air stream. This leads to the situation that small, polar hydrocarbons, such as ethane, are the first to migrate through the column, while larger, non-polar hydrocarbons, such as isobutane, have longer retention times on the column. For this reason, ethane leaves the column before isobutane.

The resolution of a chromatography column depends on many influencing factors. Substances with very small differences in properties can also be separated, depending on the carrier gas and the column material. Capillary columns provide the best resolution in such cases. They consist of a tube that is very narrow (less than 1 mm) and very long (several hundred meters) and coated on the inside with the stationary phase. A further improvement in resolution can be achieved by using a column with a temperature gradient.

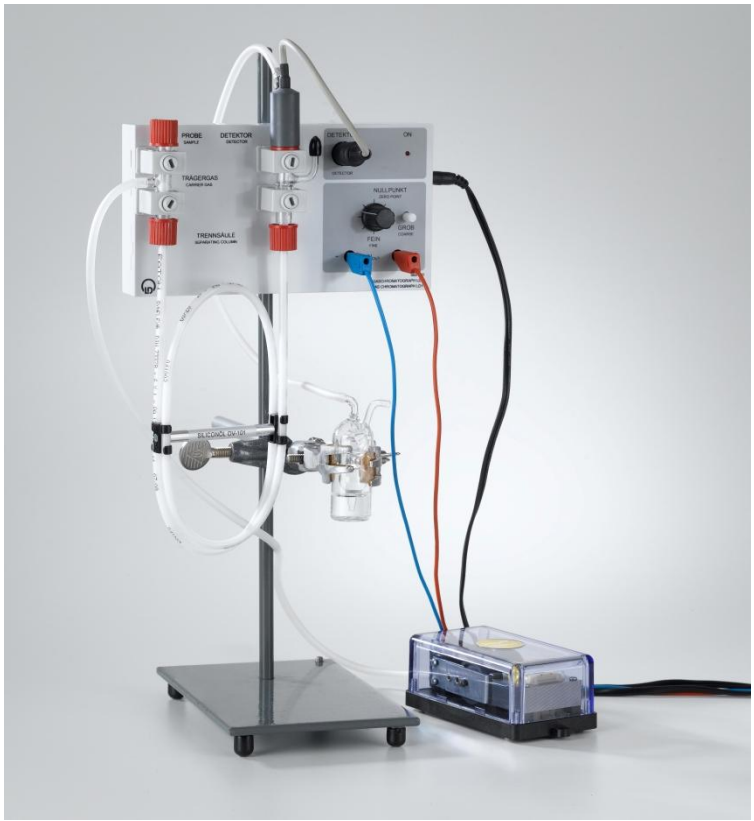

Fig. 1: Set-up of the experiment.

In this experiment, the Gas Chromatograph LD 1 with a silicone oil column is used to separate gaseous hydrocarbons. These occur in lighter fuels, for example. The substances are detected using a hydrocarbon sensor. This contains a layer of metal oxide, e.g. stannic oxide (SnO_2). Exposed to air, oxygen attaches to the surface of the tin oxide granules. Because of the then negatively charged particles, current is no longer free to flow from one grain to the next. In the presence of reducing gases, e.g. hydrocarbons, oxygen is removed from the surface and replaced by hydrocarbon molecules, hence the conductivity increases. This is registered and recorded in CASSY Lab.

Substances are separated by gas chromatography. The concurrent identification of the substance is made only indirectly. In a stable system, a substance will generally leave the column (it eluates) always after the same time period. This time is called the retention time. By comparison with control runs using known substances, an unknown substance can be identified. This will be carried out in this experiment.

Risk assessment

Combustible gases are used in very small amounts in this experiment. The expected risk is therefore only small. If possible, work in a ventilated room.

Ethane (Minican pressurised gas can)	
  **Signal word: Hazard**	**Hazard statements** H220: Extremely flammable gas. H280: Contains gas under pressure; may explode if heated. **Precautionary statements** P210: Keep away from heat/sparks/ open flames/hot surfaces. No smoking. P377: Leaking gas fire: Do not extinguish unless leak can be stopped safely. P381: Eliminate all ignition sources if safe to do so. P403: Store in a well ventilated place.
Isobutane (Minican pressurised gas can)	
  **Signal word: Hazard**	**Hazard statements** H220: Extremely flammable gas. H280: Contains gas under pressure; may explode if heated. **Precautionary statements** P210: Keep away from heat/sparks/ open flames/hot surfaces. No smoking. P377: Leaking gas fire: Do not extinguish unless leak can be stopped safely. P381: Eliminate all ignition sources if safe to do so. P403: Store in a well ventilated place.

Equipment and chemicals

For setting up with stand materials:
1 Base plate for Bunsen stand, 13 x 21 cm 666 503
1 Stand rod 450 mm, 12 mm diam., M10 thread666 523
1 Universal clamp 0...80 mm 666 555
1 Bosshead S 301 09

For setting up in CPS
1 Panel frame C50, two-level, for CPS 666 425
1 Base panel for gas chromatograph LD1 ..... 665 588
1 Pedestal, CPS 666 441
1 Blank panel 200 mm, CPS 666 467
1 Blank panel 300 mm, CPS 666 468

For both versions
1 Gas chromatograph LD 1 ..... 665 580
1 Hydrocarbon sensor 665 582
1 Separation column with silicone oil OV101 ... 665 5831
1 Pocket-CASSY 2 Bluetooth 524 018
1 CASSY Lab 2 ..... 524 220
1 UIP Sensor S 524 0621
1 Aquarium pump, 100 l/h 662 2861
1 Bubble counter with flash-back protection 664 814
1 Disposable syringe 1 mL 665 957
1 Disposable syringe 5 mL 665 955
1 Cannula 0.45 mm diam., set of 10 ..... 665 960
1 Connecting leads 19 A, 50 cm, pair 501 45
1 Septa, set of 10 ..... 665 589
1 Silicone tube 4 mm diam., 1 m 667 197
1 Fine regulating valve for Minican cans 660 980
1 Minican pressurised gas can, ethane 660 988
1 Minican pressurised gas can, i-butane 661 0011
Also required:
Lighter fuel refill pack
Computer with Windows XP/Vista/7/8
Also necessary for wireless measurement:
1 Battery for Pocket-CASSY 2 Bluetooth 524 019
1 Bluetooth dongle 524 0031

Set-up and preparation of the experiment

Set-up of the gas chromatograph LD 1

Set-up with stand materials

Firmly screw the gas chromatograph LD 1 to the Bunsen stand (see Fig. 1) and connect to the power. Attach the bubble counter beneath the gas chromatograph with a universal clamp.

Set-up in CPS

Mount the base panel for the gas chromatograph LD1 in the upper section of the panel frame and fix the gas chromatograph on the panel. Lock the bubble counter in place in the position provided on the base panel. Also, insert the smaller blank panel. Place the pedestal and the larger blank panel into the lower section. The aquarium pump and the Pocket CASSY can be placed onto the pedestal.

Set-up for both versions

Fill the bubble counter with water so that the inner glass tube is just immersed.

Fit the hydrocarbon sensor to the gas chromatograph as shown in Fig. 1. Supply current to the gas chromatograph.

Connect the pump to the inlet of the chromatograph with a piece of tubing. Use the other tubing to connect the outlet of the chromatograph to the bubble counter.

Screw the column into the chromatograph using the GL fittings so that the marking on the column faces forwards. If

necessary, push the inlet of the column in the chromatograph upwards so that it is about 5 mm below the septum.

Connect the voltage output socket of the chromatograph to the voltage input socket of the UIP sensor of the Pocket CASSY using the connecting leads. Connect the Pocket CASSY to the computer.

Performing the experiment

Blank run

First perform a blank run. In this case, no substances are to be separated on the column.

1. Connect the pump to the power. It then runs automatically. Bubbles should now rise in the bubble counter so quickly that they are difficult to count.
2. Load CASSY Lab settings
3. Initially set the voltage U_{B1} on the GC to approximately 0 with the coarse control. Re-adjust with the fine control.
4. Start the measurement by clicking on the symbol .

Note: CASSY Lab automatically subtracts the measured voltage at the start of the measurements from all further measured values. This ensures that all measurements start at 0.

5. Stop the blank run after around 10 to 15 minutes. The voltage U should then have settled to a constant value.

Note: The blank run is needed so that the column is ready to use and constant values can be expected.

Analysis of lighter fuel gas

1. Remove lighter fuel gas from a refill can. To do this, connect a piece of tubing (approx. 2 cm) to the large syringe (5 mL) and attach it to the appropriate adapter. The syringe quickly fills with gas when the valve is pressed. Flush the syringe twice with gas (fill and empty again).
2. Fill the syringe with a sample (5 mL) of lighter fuel gas.
3. Place a thin cannula onto the syringe.
4. Insert the cannula into the septum on the GC.
5. Start the measurement in CASSY Lab. After 5 seconds (visible in the field "measuring time"), press the entire contents of the syringe quickly into the GC.
6. The measuring time is 15 minutes.
7. Other lighter fuel gases can be investigated in the same way.

Chromatograms of the reference substances

In order to identify the individual substances in lighter fuel gas, pure gases will be injected. Ethane and isobutane are available as examples. Inject about 0.2 mL of ethane or 5 mL of isobutane in order to see comparable signals in the chromatogram.

Co-injection with reference substances

For positive identification of the signals, a co-injection is necessary. In this case, sample (lighter fuel gas) and reference substance (ethane) are mixed beforehand in a syringe and injected together. For this, draw 5 mL of lighter fuel gas into the large syringe and 0.2 mL of ethane into the small syringe. Connect the two syringes together using a piece of tubing and mix the gases by moving them back and forth between the syringes. Draw the gases completely into the large syringe and separate them on the gas chromatograph.

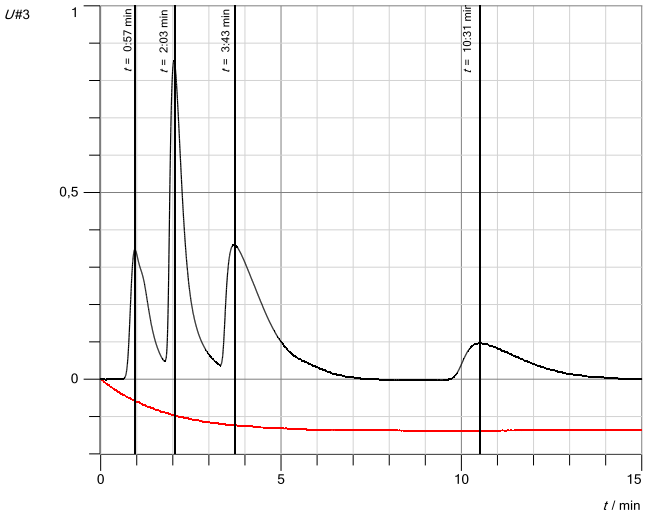

Fig. 2: Chromatograms of lighter fuel gas (black) and blank run (red).

Observation

In the chromatogram of the blank run, only the baseline can be seen (see Fig. 2). This initially shows a strong drift, but then remains at a constant value.

Depending on the lighter fuel, up to five signals can be seen in the chromatogram of the lighter fuel gas, which overlap to a certain extent (see Fig. 2). The gases ethane and isobutane show only one signal in each case. The ethane signal is very sharp, whereas the signal from isobutane is broader.

Evaluation

Analysis of lighter fuel gas

The signals in the chromatograms from the lighter fuel gas can now be defined. For this purpose, a retention time t_R is determined for each substance.

1. Mark with a vertical line the maximum of each signal.
2. Using drag-and-drop, drag the retention time t_R from the status bar into the diagram next to the vertical line.
3. Proceed in this way with all signals.

The chromatogram of lighter fuel gas and the retention times are shown in Fig. 2.

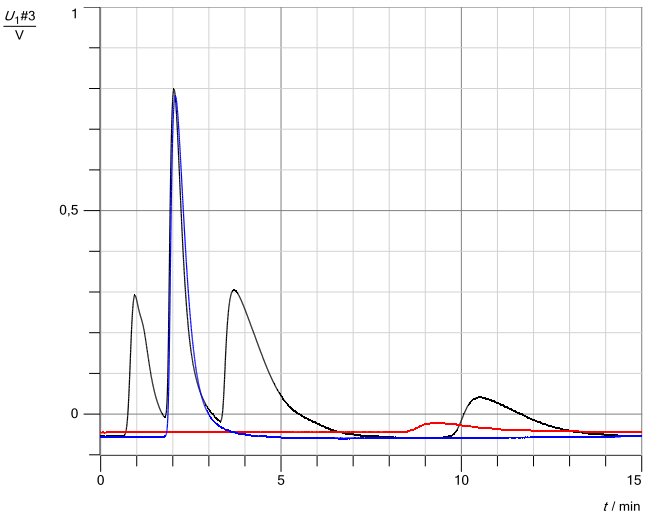

Fig. 3: Chromatograms of lighter fuel gas (black) and the reference substances ethane (blue) and isobutane (red).

Chromatograms of the reference substances

Compare the chromatograms of ethane and isobutane with that of lighter fuel gas (see Fig. 3). The blue peak of ethane corresponds with the second signal from the lighter fuel gas. This signal can therefore be identified as that of ethane. The signal from isobutane does not correspond with any of the signals. It is not contained in the sample.

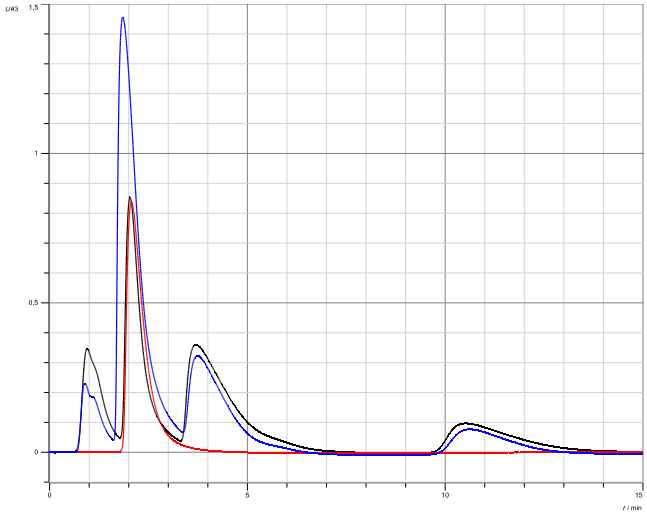

Fig. 4: Co-injection with ethane. Black: lighter fuel gas, red: ethane, blue: co-injection.

Co-injection with reference substances

Co-injection provides a more positive identification than the simple comparison of retention times. Co-injection is carried out with ethane (see Fig. 4). The ethane signal is twice the height. This has a somewhat shorter retention time which is attributable to the excessive sample quantity. Ethane can be identified without doubt as a component of lighter fuel.

Results

Ethane is present in the lighter fuel investigated, but isobutane is not. The other signals could be identified in a similar way.

If lighter fuels from different sources are used, the differences in the gases contained can be made visible by gas chromatography.

Cleaning and trouble-shooting

To ensure that no gases remain in the column, flush the column with air for a while after the final run. To do this, leave the aquarium pump running.

To store the column, it is best to unscrew it from the gas chromatograph and close it off again using the black plastic caps. Prepared in this way, store the column in a dark, dry place.

If the column ceases to provide satisfactory results, it could have become too damp. Heat it overnight at not more than 70 °C in a drying cabinet, let it cool for one day and then test it again.