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# Mass Spectrometric Analysis of Gases using the Quadrupole Mass Filter



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## 1 Introduction

Mass spectrometry is one of the primary and most frequently used techniques in analytical chemistry and also finds many important applications in material sciences as well as fundamental research in physics, chemistry, geo-science and climatology, biology and medicine. There are several ways to perform mass selection of charged species, i.e. ions of atoms, molecules or clusters. Common are sector field magnets to separate charged particles of different masses after electrostatic acceleration according to their mass-to-charge ratio. In a homogeneous magnetic field they follow a circular track with a radius  $r$  simply given by the equivalence of the Lorentz force as

$$e \cdot v \cdot B = m \cdot \frac{v^2}{r} \quad (1)$$

With  $e$  the elementary charge,  $B$  the magnetic field strength,  $v$  the velocity, and  $m$  the mass of the particle. Particles of similar charge but different mass have different trajectories and corresponding deflection angles in the sector field magnet and as the result can be separated. Standard acceleration potentials for the entering ion beam are between 5 and 60 keV.

Another option for mass separation is a quadrupole mass filter (QMF) that operates usually with much lower accelerating voltages in the range of 50 to 100 V. The two-dimensional QMF structure was developed by W. Paul in 1953 and proposed as a mass spectrometer, for which he

was awarded the Nobel Prize in 1989. He also considered and studied the three-dimensional quadrupole structure, which serves as ion trap with multiple applications including aside of analytics e.g. atomic clocks or quantum computers. For mass selection finally the flight time of charged particles in so called time-of-flight (TOF) mass spectrometers can be analyzed.

The goal of the experiment at the QMF is to understand the operation principle of this very typical instrument with wide range application. Analytically we shall study the elemental and molecular composition of different gases, investigate the precision on the mass scale as well as the peak height and learn about the characteristic fragmentation, which serves of calibration. The operating conditions and all parameters of the quadrupole mass filter (QMF) are to be adjusted, the QMF is to be calibrated and finally unknown substances will be identified.

## 2 Operation Principle of a Quadrupole Mass Filter

The particular property of a two-dimensional quadrupole field, as applied in a QMF, is the confinement of charged particles of a specific charge to mass ratio  $\frac{q}{m}$  in the radial direction, while other particles are deflected out of the beam axis. As in the sector field magnet the underlying effect is the Lorentz force but this time involving alternating (AC) fields in the GHz frequency range. We restrict ourselves here to particle charge of  $q = 1$  without limitation of general validity.

The QMF structure and geometry is given in Fig. 1 with particles move along the z-axis. The distance between opposite surfaces of the hyperbolic electrodes is twice the free field radius, i.e.  $2r_0$ .

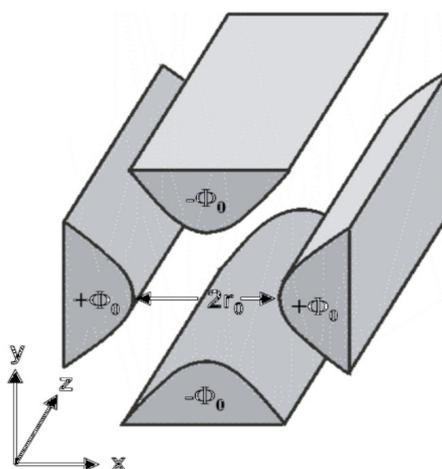


Fig.1: Spatial arrangement of the QMF electrodes

To keep the track of the desired particles along the central QMF axis, a repulsive force  $F$  is needed. For the quadrupole field this is linearly increasing with  $r$  according to  $\vec{F} \propto -|r| \cdot \vec{e}_r$ , which facilitates setting up the equations of movement.

The ideal quadrupole field is generated by hyperbolic electrodes, while in real systems also spherical structures are used with correction electrodes to simplify construction. Assuming that the electrodes are aligned along the  $z$ -direction and that the distance between the  $(0,0,z)$ -axis and the hyperbolic electrodes is  $2r_0$ , the potential can be written as:

$$\Phi(x, y, t) = \Phi_0(t) \frac{x^2 - y^2}{r_0^2}, \quad (2)$$

with a potential of  $\pm\Phi_0(t)$  applied to adjacent electrodes. Thus, no force is affecting the ion movement along the  $z$ -direction. The radial potential is shown in 2d and 3d representation in Fig. 2.

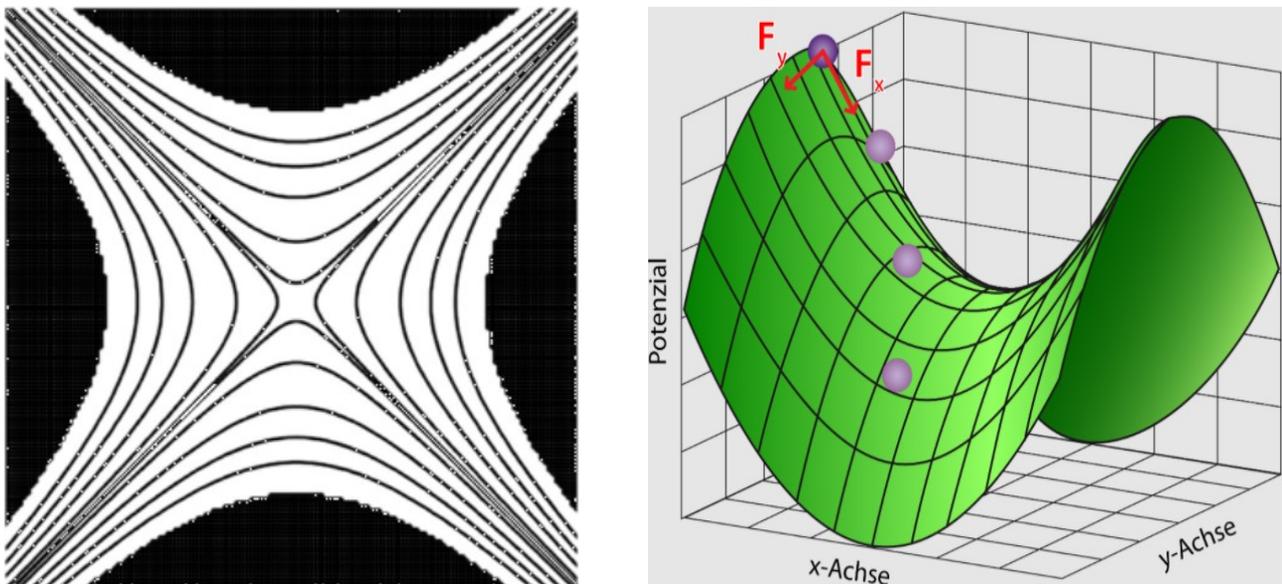


Fig. 2: a) Equipotential lines in the  $x,y$ -plane for a constant voltage applied to the electrodes. b) 3d representation of the potential for a constant voltage applied to the electrodes. While focusing in  $x$ -direction, it is defocusing in  $y$ -direction, the corresponding movement of a charged particle is indicated.

As given in Fig. 2b, the field focuses in one direction ( $x$ -direction), while it defocuses in the other ( $y$ -direction), making an ion hit the quadrupole rods there. To prevent this an alternating (AC) voltage  $V$  is applied in addition to the constant direct (DC) voltage  $U$ , which must be properly chosen in amplitude and frequency. In this way an alternating focusing and defocusing in  $x$ - and  $y$ -direction can be realized. The resulting potential can be written as:

$$\Phi(x, y, t) = (U + V \cos(\omega t)) \cdot \frac{x^2 - y^2}{r_0^2} \quad (3)$$

The equation of motion of an ion with charge  $e$  and mass  $m$  can be derived a:

$$m \frac{d^2}{dt^2} \vec{r} = e \vec{E} = -e \vec{\nabla} \Phi(x, y, t) \quad (4)$$

For the individual spatial directions, they are given by:

$$m \frac{d^2 x}{dt^2} + \frac{2e}{r_0^2} (U + V \cos(\omega t)) x = 0 \quad (5)$$

$$m \frac{d^2 y}{dt^2} - \frac{2e}{r_0^2} (U + V \cos(\omega t)) y = 0, \quad (6)$$

$$m \frac{d^2 z}{dt^2} = 0 \quad (7)$$

While the third equation describes a uniform movement along z-direction as mentioned above, the first and second are homogeneous differential equations of second order, which cannot be solved analytically in this form. To solve this problem, we can use the transformations:

$$2\tau = \omega t, \quad (8)$$

$$a_x = -a_y = \frac{8eU}{m\omega^2 r_0^2} \quad (9)$$

$$q_x = -q_y = \frac{4eV}{m\omega^2 r_0^2} \quad (10)$$

Then, the equations for x- and y-movement can be rewritten as Mathieu's differential equations, which are identical except for one minus sign:

$$\frac{d^2 x}{d\tau^2} + (a_x + 2q_x \cos(2\tau)) x = 0 \quad (11)$$

$$\frac{d^2 y}{d\tau^2} - (a_y + 2q_y \cos(2\tau)) y = 0 \quad (12)$$

General solutions can be calculated as expansions of exponential functions. These can be related to the parameters  $a_{x,y}$  and  $q_{x,y}$ , respectively, leading to parameter areas in a two dimensional  $a, q$  spaces for both dimensions. They either show instable or stable trajectories, the latter areas being called stability ranges. These are indicated in Fig. 3 for the y-movement.

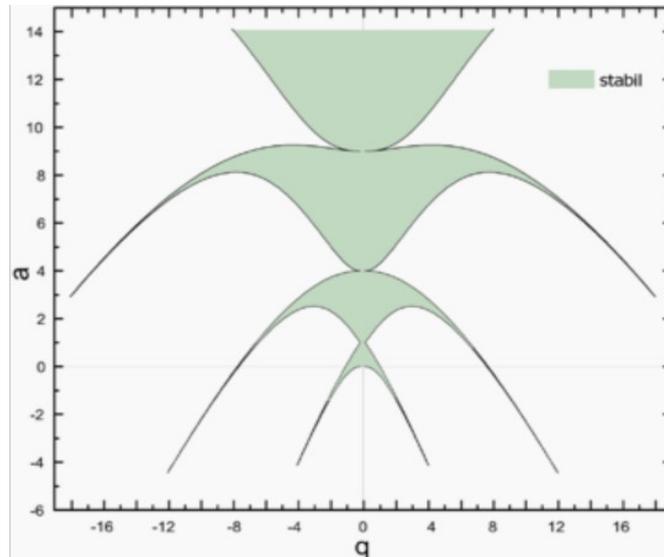


Fig. 3: Diagram of stable solutions for y-movement (green areas), the corresponding pattern for the x-movement is obtained by an inversion of the pattern at the  $a = 0$  and the  $q = 0$  axes.

As only ions with stable trajectories in both, x- and y-direction can successfully transmit the mass filter, areas of stable solutions for both directions must be selected. Overlapping the stability areas for x- and y-direction leads to the overall stable solutions, as displayed in Fig. 4.

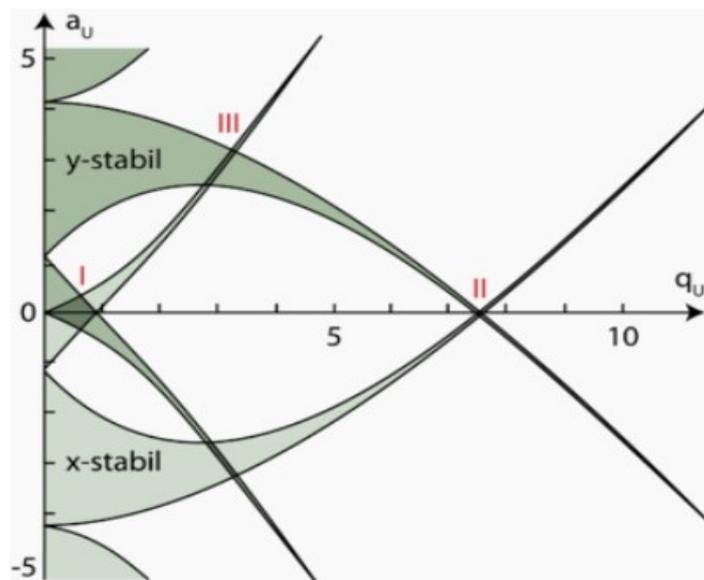


Fig. 4.: Diagram of stable solutions for x- and y-movement. The overlapping areas of stable solutions in both directions are numbered with I to III.

For a given polarity of the dc potential  $U$  and for limited voltage we are restricted to the non-negative  $a$  and  $q$  part of stable area I, resulting in the common stability triangle of a QMF. A closer look on it is presented in Fig. 5. Outside the triangle the ions show unstable movement, will hit the electrode and will be lost.

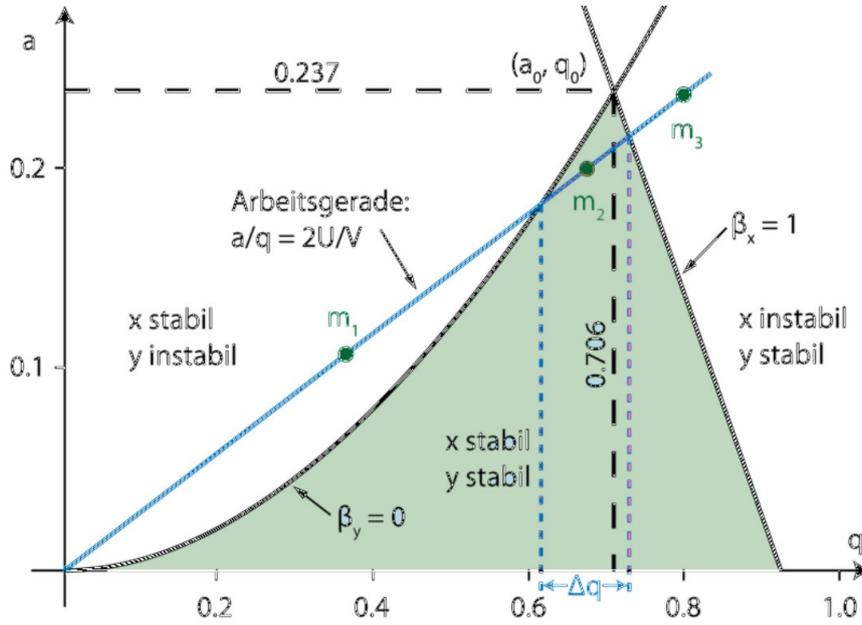


Fig. 5: According to its triangular shape, the stability area (I) is called stability triangle. The working line (solid blue) is given by the chosen value of the ratio  $a/q$ , which defines the resolution.

Fig. 5 also shows the so-called working line, which is given by a well-defined ratio  $\frac{a}{q} = 2\frac{U}{V}$ . According to the definition of  $a$  and  $q$  in equations 9 and 10, particles with a given mass  $m$  lie on a well-defined point on this line. For a reasonable ratio of  $a/q$ , the slope is low enough to have the working line intersect the stability triangle. In this case a variation of both potentials  $U$  and  $V$  along this line defines an interval  $\Delta q$  of stable movements, which can be assigned directly to a mass interval  $\Delta m$ . Only ions with a mass inside this interval have stable trajectories and can pass the QMF. By changing the ratio  $a/q$  the mass resolution can be adjusted via the slope of the working line as given by:

$$\frac{m}{\Delta m} = \frac{0.126}{0.1678 - \frac{U}{V}} \quad (13)$$

As can be verified by converting the q-a graph into a V-U graph via equation 9 and 10, the stability triangle splits into identically shaped triangles to individual masses, which scale with the mass  $m_1 < m_2 < m_3$  as shown in Fig. 6. In this representation important aspects become visible:

- while in sector field mass spectrometers the mass spectrum follows a square root function, for an QMF it is perfectly linear.
- the relation between resolution and the slope of the working line is perfectly obvious.

In the experiment the mass scan is carried out by moving along the working line and crossing the tips of the individual stability triangles consecutively leading to a mass spectrum. The resolution here is adjusted by tuning a function  $U = c \cdot V + d$ , where d denotes an additional DC offset voltage and c defines the resolution. For  $d = 0$  a constant mass resolution is realized, for positive d the resolution is reduced for higher masses, which counteracts imperfections of the real QMF.

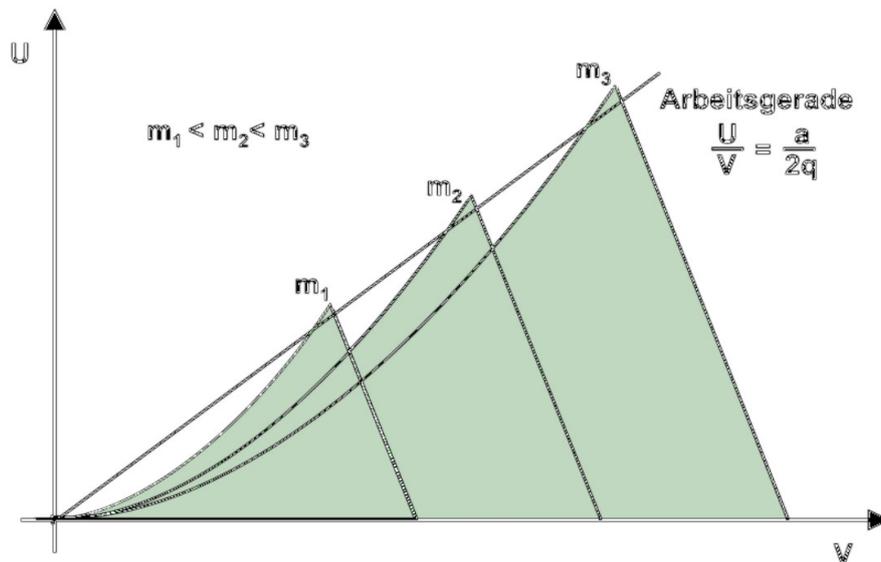


Fig. 6: The stable areas in U/V-space have the exact same shape as in a/q-space, but are scaled by the mass. Every mass has its own triangle, but only if the working point (on the working line, defined by the value of U/V) is inside the triangle the corresponding mass is transmitted by the quadrupole.

### 3 Experimental setup

The basic experimental setup is displayed in Fig. 7. The inlet area is filled with the gas, which is to be analysed. The gas flux from the inlet area to the vacuued area is

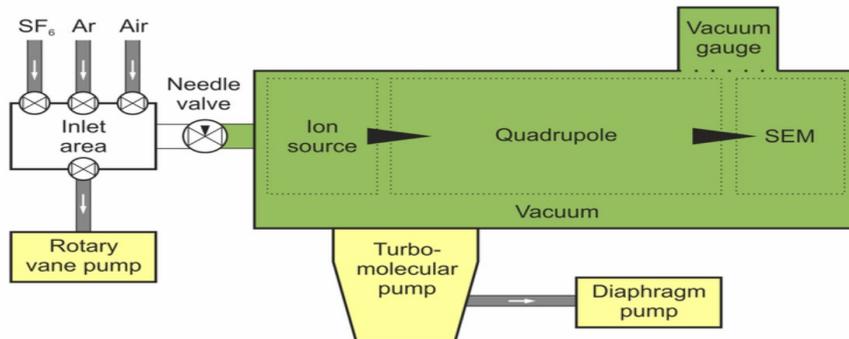


Fig.7:Schematic experimental setup. The inlet area is filled with gas. Gas molecules are ionised and registered by the detecting secondary electron multiplier (SEM), if they pass the quadrupole.

dosed with the needle valve so that the pressure inside the vacuum chamber is less than  $10^{-4}$  mbar. Gas molecules diffuse to the ionisation area and are ionised by electrons there. These ions then pass the quadrupole (or don't) and are detected by a secondary electron multiplier, that is connected to an electrometer, the signal of which is conducted to a computer. The vacuum itself is generated by a set of pumps, consisting of a turbo-molecular pump and a rotary vane pump, both of which should be turned on some time prior to the first analysis is performed. Together they generate a vacuum of about  $10^{-7}$  mbar.

The experimental setup of our laboratory is shown below:



Photo 1: The workplace. On the left one might see the power supplies and measuring equipment. In the middle the experimental system is shown: the inlet area, vacuum chamber with ion source, quadrupole and SEM. On the right the computer connected with the system by which one can control the variables.

A better look on the power supplies is in the photo 2:

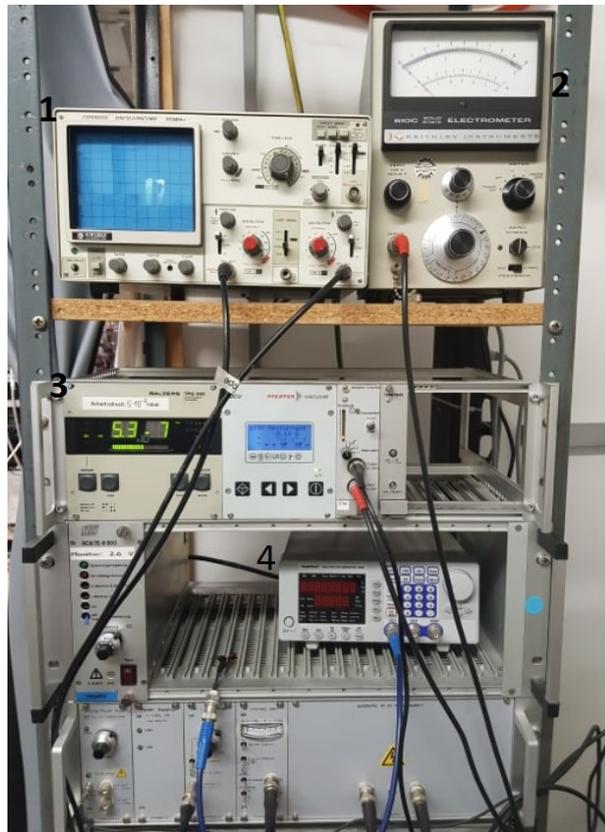


Photo 2: Power supplies.

With help of the oscilloscope (1) one might see the alternating voltage. The signal of the SEM is measured by a very sensitive electrometer (2). With (3) one can control the pressure inside the system and with (4) the frequency (1.78 MHz) and amplitude (5 Hz) of the alternating voltage can be set.

The voltages of each part of the system can be read out on the power supply unit of the ionisation area (photo 3):



Photo 3: Power supply unit of the ionization area.

The values of voltages are listed in the table 1:

Table 1: Values of the voltages of different elements of the setup.

Element	Value [V]
Wire 1	10.8
Wehnelt 1	5.8
Elektron lens 1	194.5
Ionization box 1	187.5
Repeller	180.6
Ion lens1	163.3
Ion lens 2	9.9
Ion lens 3	94.3
Total voltage	194.7

#### 4 Gas inlet

The gas inlet (photo 4) allows the insertion of the samples into the ionization region. Different inlet valves for  $SF_6$ , argon and a hose for different samples as well as ambient are available. The flow into the vacuum chamber can be precisely controlled by the means of a needle valve. To clean the gas inlet region, a rotary vane pump is used.

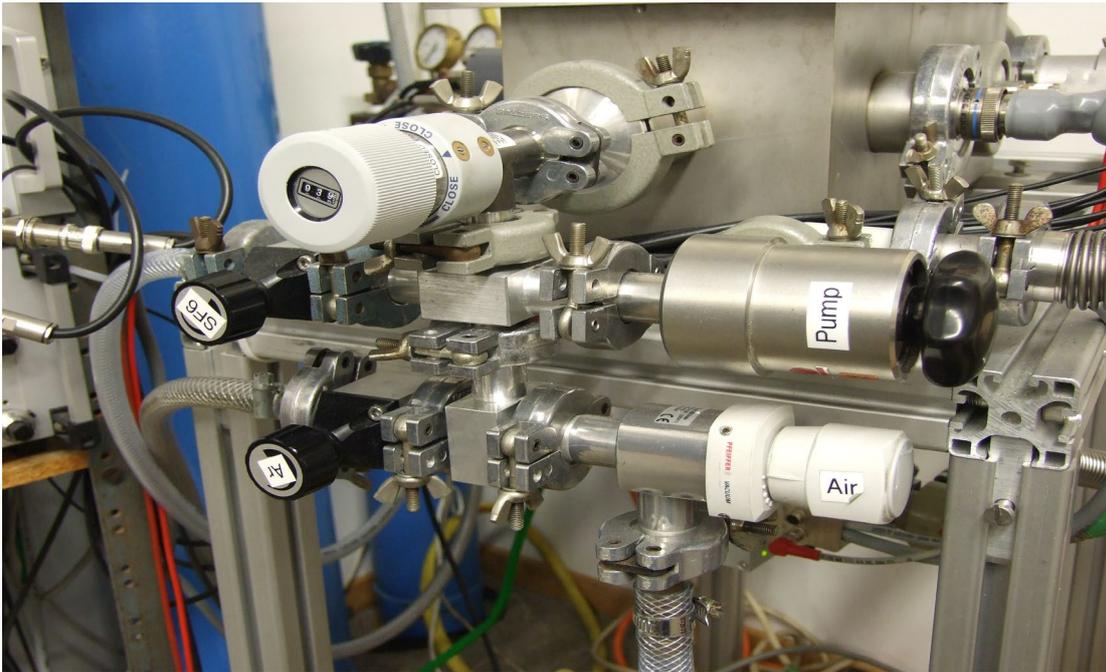
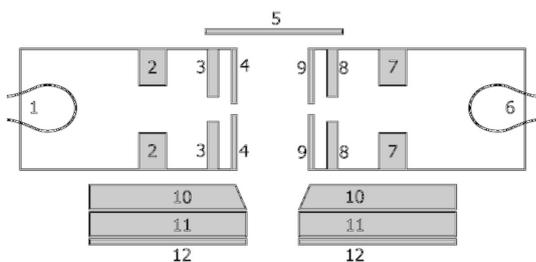


Photo 4: The inlet area with the vacuum pump,  $SF_6$ , Ar and air valves.

## 5 Ionisation area

Picture below (Fig.8) illustrates the setup for the ionisation of the gas molecules. A tungsten wire (1) is used to generate electrons by thermionic emission, which are accelerated mainly by Wehnelt cylinder (2), focussed and collimated by electrostatic lens (3) in combination with (2) and (4) to hit and ionise molecules of the gas to be examined (between 4 and 9). Absorbing the electrons, the reflector (5) repels the positive ionised gas molecules, accelerating them towards the quadrupole. A set of electrostatic lenses (10 - 12) are used to focalise the ions to the entry of



the quadrupole. Electron emission components (1 - 4) exist twice for redundancy.

During the ionisation process not only single and multiple-charged molecules are generated, but also fragments of the original ones. Moreover, residual gas molecules need to be considered. The number and type

of generated ions depend on the energy of the electrons hitting the molecules, to separate shell electrons. Above a minimum energy, which is typical for every kind of gas, the yield of ions increases rapidly with the kinetic energy of the ions, reaching a maximum at the order of 50 to 100 eV. For higher energies the rate decreases slowly.

The voltages of every single abovementioned part can be set and read out on the power supply unit of the ionisation chamber.

The distance between the rods of the quadrupole is:  $2r_0 = 5,2mm$ .

## 6 Detection

The molecule ions, that pass the quadrupole, need to be detected. Therefore a secondary electron multiplier (SEM) is used. The principle is very similar to a photomultiplier tube except, that the conversion dynode does not use photoelectric effect. When an ion hits the first electrode (conversion dynode) an electron is emitted and accelerated towards another electrode. This secondary electron striking the dynode produces several electrons, that are then accelerated to the next dynode. Each dynode has a more positive electrical potential than its predecessor, thus accelerating the electrons to a high kinetic energy. Hence, an arrangement like this is able to amplify the tiny current of the ions passing the quadrupole, typically by a factor of one million.

In the Fig.9 you can see a schematic picture of how a secondary electron multiplier works.

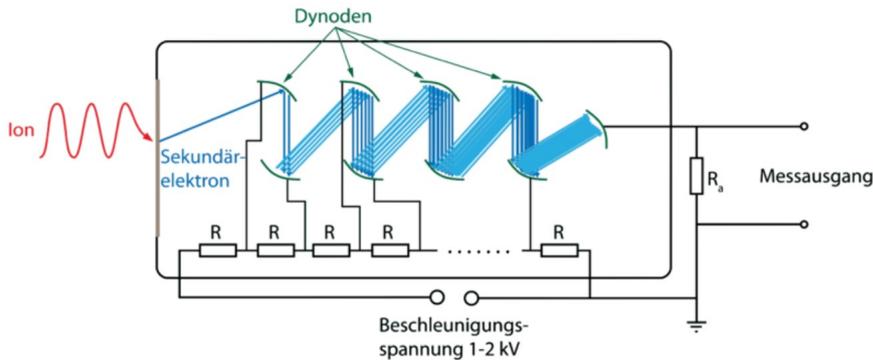


Fig.9: Schematic of a secondary electron multiplier [3].

The signal of the SEM is measured by a very sensitive electrometer which is connected to the computer. There a designated program records the data and drives the measurement. With the parameters "Steigung U/V" the slopes of the working line can be set. "Offset DC - Steuerspannung U(V)" sets the possible DC voltage offset of the working line. With "Start V" and "Stop V" the interval for the alternating voltage and "Schritte" the number of data points in this range is set, respectively.

## 7 Energy of electrons and ions

The electrons gain the kinetic energy in the space between the wire and ionization box. Then, the energy can be calculated with the following equation:

$$E_{e^-} = e \cdot (V_{\text{Ionisierungskathode}} - V_{\text{Faden}}), \quad (14)$$

which gives:

$$E_{e^-} = (283.07 \pm 0.16) \cdot 10^{-19} \text{ J}. \quad (15)$$

The energy of ions is dependent on their charge and can be written as:

$$E_{\text{ion}} = q \cdot (V_{\text{Repeller}} - V_{\text{Ionenlens 3}}) = q \cdot (180.6 - 94.3) \text{ V} = (n \cdot e)(86.3 \text{ V}) = n \cdot 86.3 \text{ eV}, \quad (16)$$

which brings:

$$E_{\text{ion}} = (138.25 \pm 0.1602) \cdot n \cdot 10^{-19} \text{ J}. \quad (17)$$

## 8 Experimental tasks

In our experiment, you will use the following program:

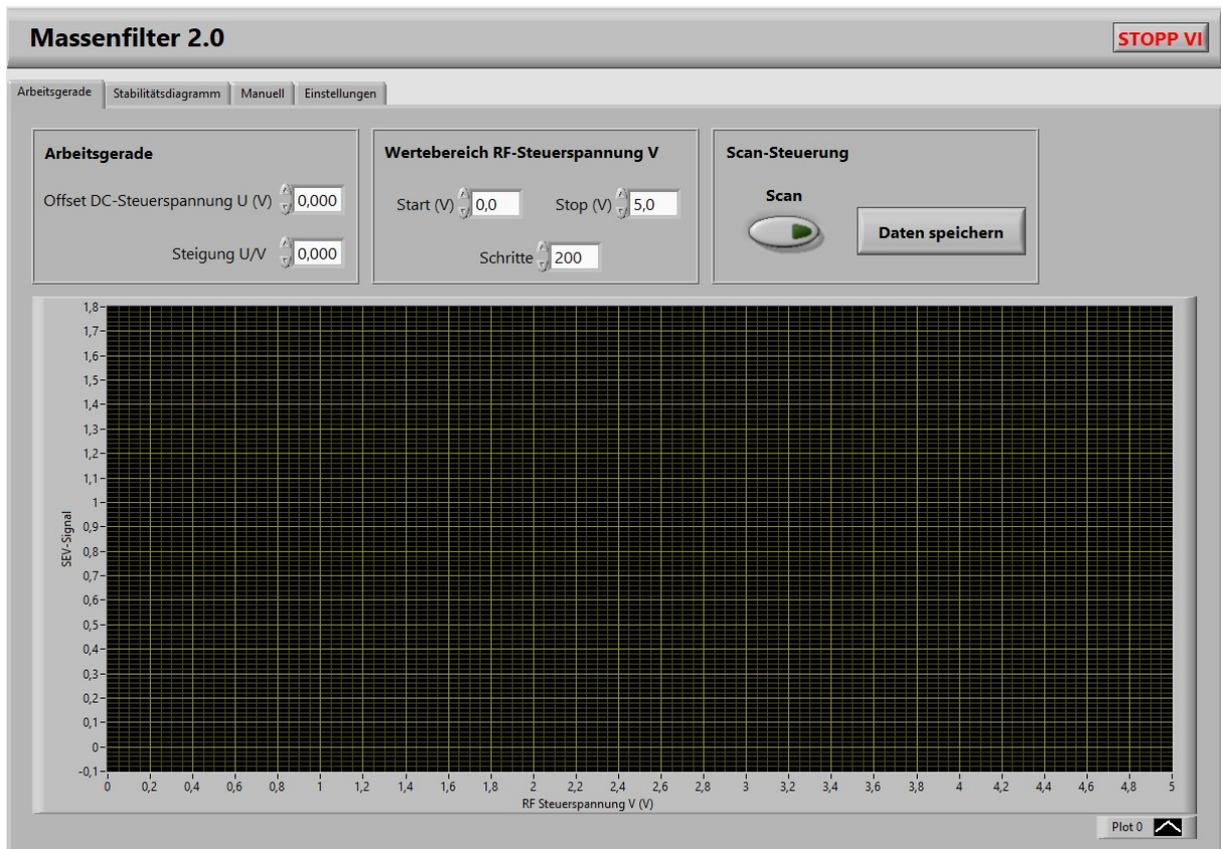


Fig.10: The program used for setting the working line and the peak's visualisation.

## 8.1 For every measurement

For every following spectrum these steps are to be taken:

1. Open up the needle valve carefully until the pressure in the vacuum area is at approx.  $5 \cdot 10^{-5}$  mbar. It may not be higher than  $10^{-4}$  mbar, as the tungsten wire may blow and the SEM might be severely damaged.
2. Start the measurement with the computer program. Depending on the duration of measurement and the fugacity of the gas the pressure in the vacuum chamber may decrease drastically. For compensation the needle valve can be opened wider during the measurement process.
3. Make sure to save the data as you are asked by the program directly after every measurement. Saving data later is not possible and you will have to perform the measurement again. For your convenience, the spectra shown in the computer program can be saved as bitmap by rightclicking.
4. Close the needle valve.

## 8.2 Setting the working line

To set proper conditions for the experiment the gas  $SF_6$  is used. The first task is to take a rough spectrum of the  $SF_6$  gas with the predefined values. Take some more rough spectra for different

values of U/V and the DC voltage offset. Now you should see a rough spectrum of  $SF_6$  with several mass peaks of  $SF_5^+$ ,  $SF_4^+$ , etc. As the stability triangles for different masses are not perfectly scaled by factor m, for a good spectrum a nonzero DC offset is necessary. Find parameters which produce spectra with narrow mass peaks but also high enough intensity to have a good signal to noise ratio.

The obtained  $SF_6$  spectrum should be similar to the one in the Fig.11:

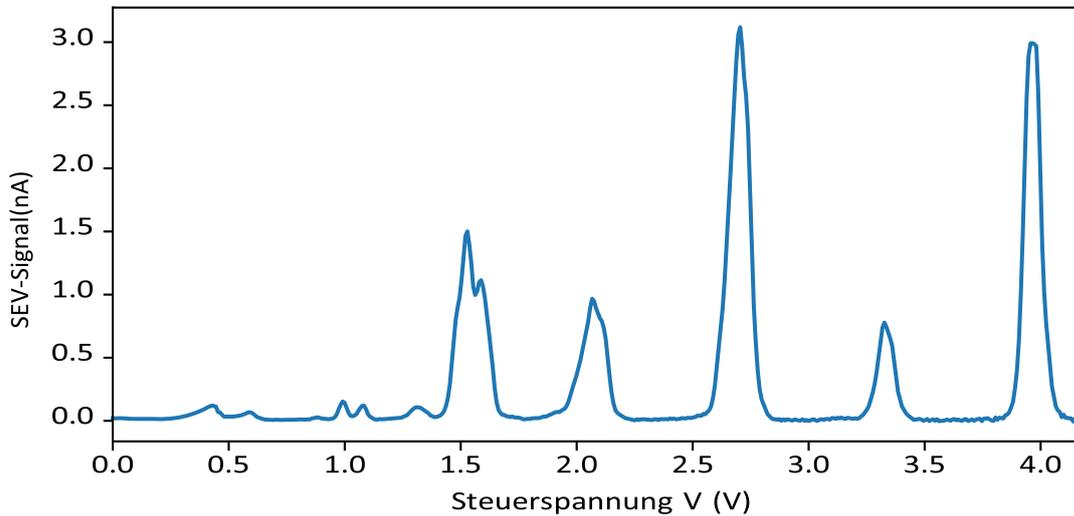


Fig.11: Spectrum of  $SF_6$  with several mass peaks.

### 8.3 Mass calibration

The spectra taken by the computer program have a voltage scale on the axis of abscissas. To analyse unknown gases, which is to be done later, a conversion to a m/q scale is necessary. Therefore, take a spectrum of  $SF_6$  (or/and argon, oxygen) with the working line defined before. Assign the peaks in the spectra to molecule ions i.e. values of m/q, determine the voltage of each peak and make a calibration line.

In the Table 1 you can see the mass spectrum of  $SF_6$  for 3 different ionizing voltages:

Table 2:  $SF_6$  mass spectrum for 50, 70 and 100-volt electrons [4].

<i>m/e</i>	Ion	Relative intensities		
		50 volts	70 volts	100 volts
16	S <sup>++</sup>	0.03	0.06	0.09
19	F <sup>+</sup>	3.37	5.63	9.11
25.5	SF <sup>++</sup>	-----	0.76	1.97
32	S <sup>+</sup>	5.60	9.96	13.5
33	S <sup>+</sup>	0.06	0.09	0.11
34	S <sup>+</sup>	.27	.47	.60
35	SF <sub>2</sub> <sup>++</sup>	1.36	6.80	13.3
35.5	SF <sub>2</sub> <sup>++</sup>	-----	0.10	0.10
36	SF <sub>2</sub> <sup>++</sup>	0.07	.33	.62
44.5	SF <sub>3</sub> <sup>++</sup>	0.38	1.26	2.17
45.5	SF <sub>3</sub> <sup>++</sup>	-----	0.07	0.11
51	SF <sup>+</sup>	8.66	11.0	11.6
52	SF <sup>+</sup>	0.07	0.09	0.11
53	SF <sup>+</sup>	.40	.51	.64
54	SF <sub>4</sub> <sup>++</sup>	4.05	11.0	17.6
54.5	SF <sub>4</sub> <sup>++</sup>	-----	0.09	0.11
55	SF <sub>4</sub> <sup>++</sup>	0.23	.54	.78
70	SF <sub>2</sub> <sup>+</sup>	5.74	6.39	6.46
71	SF <sub>2</sub> <sup>+</sup>	0.04	0.07	0.09
72	SF <sub>2</sub> <sup>+</sup>	.27	.30	.27
89	SF <sub>3</sub> <sup>+</sup>	27.6	33.5	35.7
90	SF <sub>3</sub> <sup>+</sup>	0.20	0.26	0.24
91	SF <sub>3</sub> <sup>+</sup>	1.22	1.48	1.56
91.8	SF <sub>3</sub> <sup>+</sup> →SF <sub>4</sub> <sup>+</sup> +F	0.21	0.26	0.24
108	SF <sub>4</sub> <sup>+</sup>	8.98	10.8	11.5
109	SF <sub>4</sub> <sup>+</sup>	0.07	0.11	0.10
110	SF <sub>4</sub> <sup>+</sup>	.41	.47	.51
127	SF <sub>5</sub> <sup>+</sup>	100.	113	117
128	SF <sub>5</sub> <sup>+</sup>	0.92	1.14	1.15
129	SF <sub>5</sub> <sup>+</sup>	4.30	4.89	4.87
131	SF <sub>5</sub> <sup>+</sup>	0.04	0.04	0.04

## 8.4 Air

In this part the differences between fresh air and human breath shall be determined.

First take a mass spectrum of fresh air. Close all valves to the inlet area, including the needle valve. Turn on the rotary vane pump to evacuate the inlet area. If the pump is jamming, just wait for a few moments, the pump should start up after some time. Open the valve to the rotary vane pump and (with some care) the valve labeled with "Air" to full extent. This will flush the inlet area with fresh air and removes residual gases that might interfere with later measurements. Perform

flushing for approximately one minute, then close the valve for the rotary vane pump and the "Air" valve in this order. Now air at ambient pressure is inside the inlet area. Open the needle valve for the measurement.

To perform the measurement with breathed air take a breath sample and inflate a balloon. By exhaling the same air several times into the balloon the effects on the mass spectrum can be amplified (which effects do you expect?). Close all valves to the inlet area, turn on the rotary vane pump and evacuate the inlet area by opening the valve to the pump. To flush residual fresh air from the inlet area and the hose, tightly stick the ballon on the inlet glass joint and open the "Air" labeled valve carefully. The sample is now pumped through the inlet. Close the valve to the rotary vane pump in time, so that the balloon does not get stuck in the inlet hose. Now the air sample is in the inlet area. Close the "Air" valve, open the needle valve and begin the measurements.

During measurement the pressure in the vacuum chamber might drop due to depletion of the sample. Readjust the needle valve to keep the pressure on a constant level, if necessary repeat sample taking procedure.

## 8.5 Mystery samples

The task is to analyse and identify two similar substances. You can choose two out of the set of pentane, hexane, heptane, octane or acetone. Take one mass spectrum for each substance and compare the results. Set the slope and offset of the working line to the values that were determined before.

The insertion of the sample is performed similar to the procedure described for breathed air: First, close all valves and turn on the rotary vane pump. Open the valve to the pump and evacuate the inlet area. Connect a bottle of a substance to the glass joint of the inlet and open the "Air" labeled valve to full extent. Due to the low pressure, the substance will be evaporated (some of the substances might even boil). Wait about two minutes to let the sample flush the inlet area. Then close the valve to the pump and the "Air" valve in this order. Carefully (!) remove the glass bottle from the joint, by gently twisting and with patience (if you pull to hard, the sudden pressure drop will spill the liquid into the inlet hose and you have to flush for a long, long time to get it out of there). Then open the needle valve and start the measurements. Repeat this procedure if necessary.

Below you can find the spectra of octane, acetone, pentane, hexane and heptane, respectively:

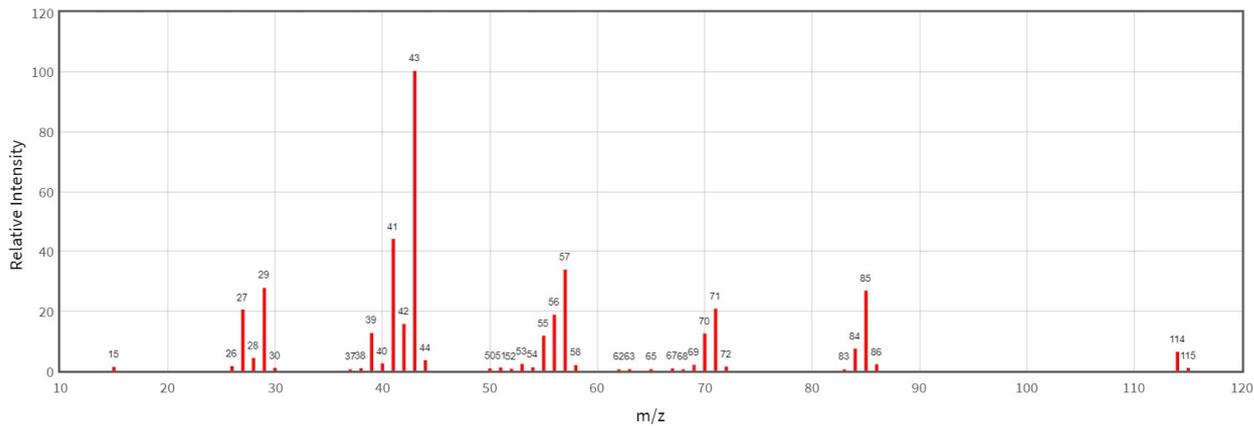


Fig.12: Octane's mass spectrum [5].

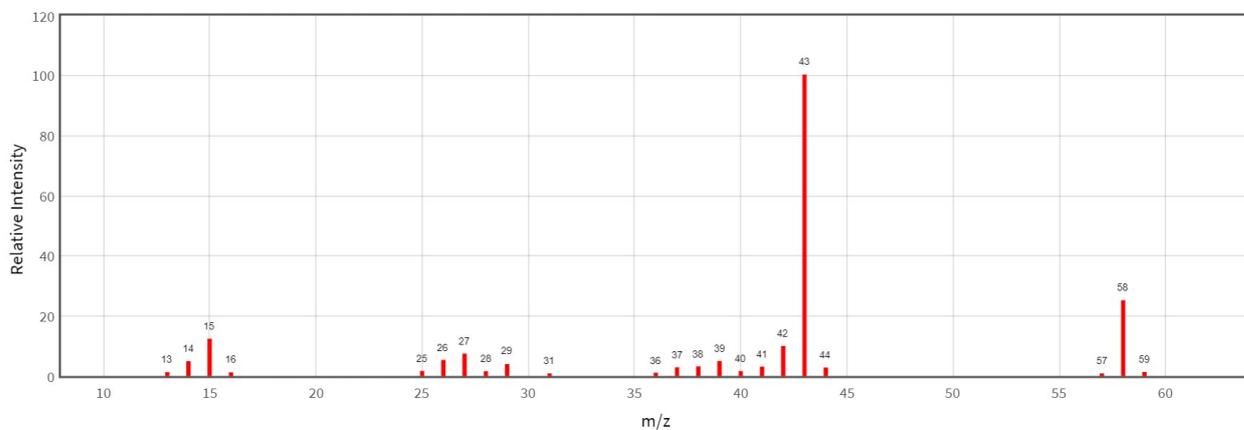


Fig.13: Acetone's mass spectrum [5].

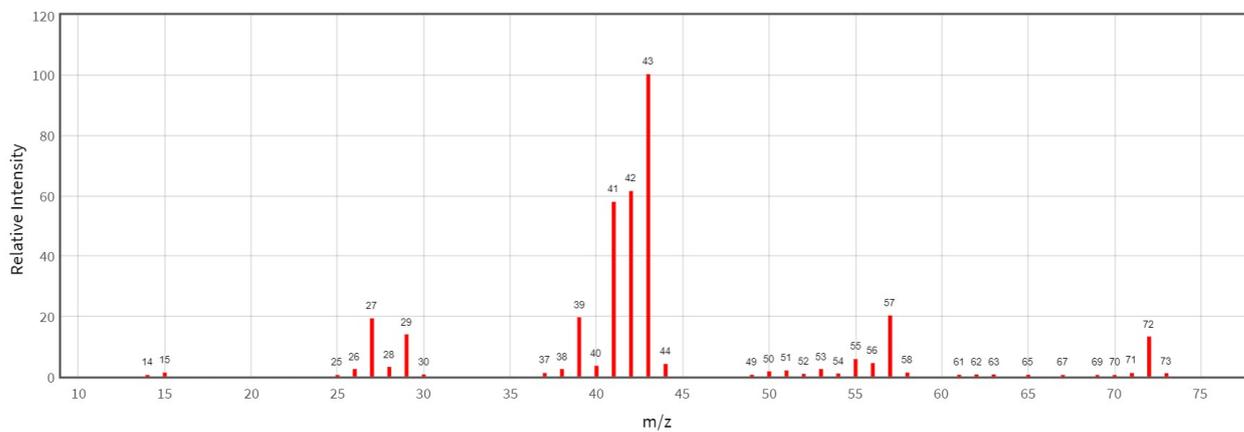


Fig.14: Pentane's mass spectrum [5].

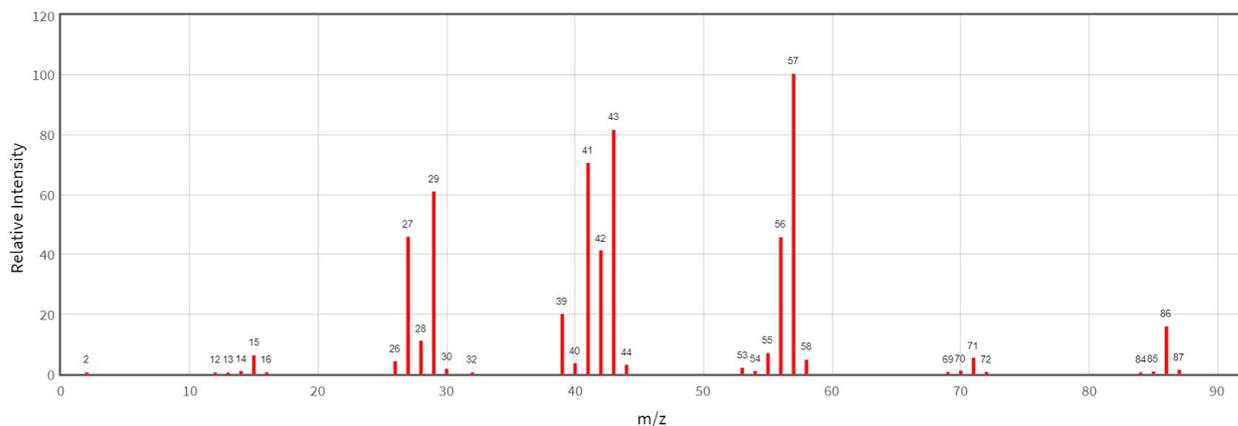


Fig.15: Hexane's mass spectrum [5].

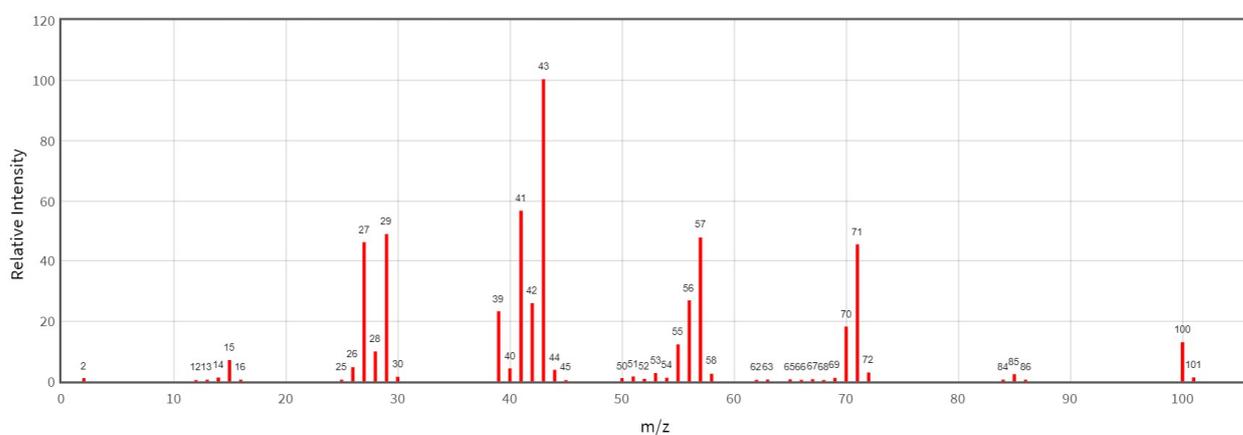


Fig.16: Heptane's mass spectrum [5].

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