

# Mass Spectrometry



## 0 Motivation

Today, a quadrupole mass spectrometer is the most important tool for analysing gas compositions. It is a very compact and reliable device.

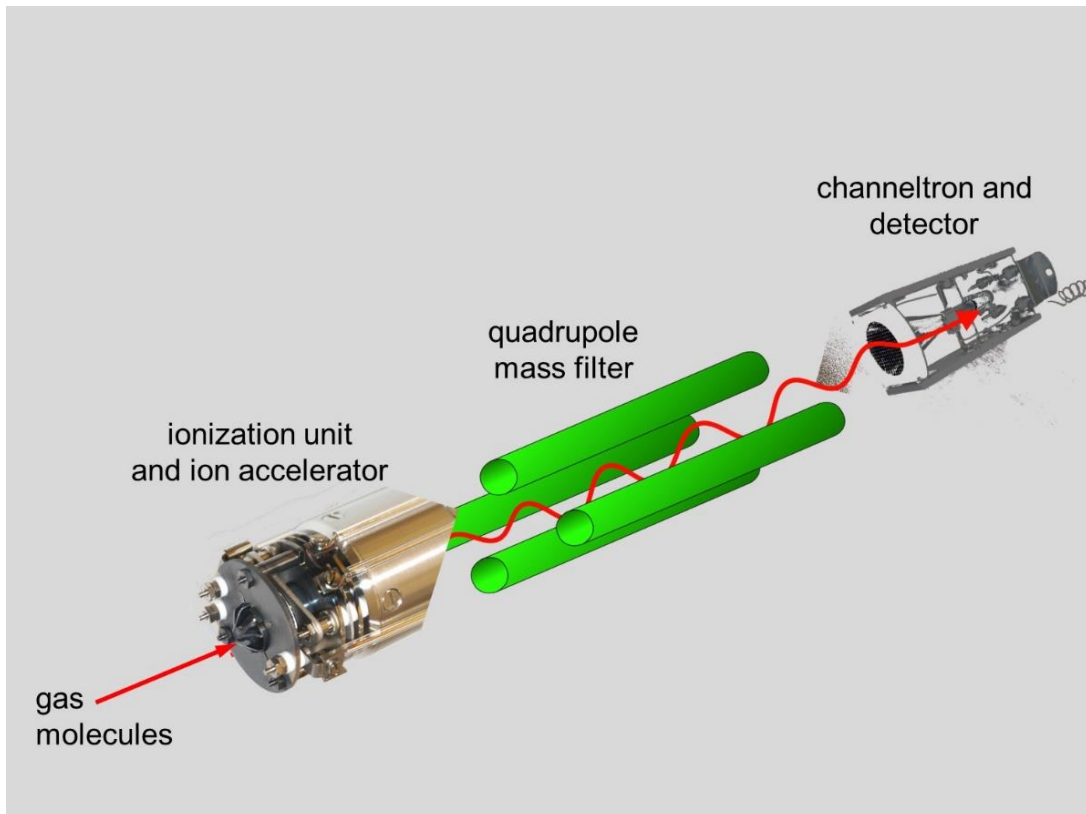
In ultra-high vacuum technology (UHV) the mass spectrometer is a very useful tool to analyse vacuum properties. So nearly every UHV system has a quadrupole mass spectrometer included. When the desired pressure is not reached, a mass spectrometer provides valuable evidence of an existing problem, e.g. the amount of water is too high or compounds of oil from the pumps can be found. Also very small leakages can be detected in the chamber by using helium as a test gas.

In addition, a mass spectrometer is used for chemical analysis of sample compositions. Thermo-sorption spectroscopy measures the gas components desorbing from a sample surface are measured with respect to the applied sample temperature.

This lab course experiment teaches the physics and handling of a quadrupole mass spectrometer and the interpretation of mass spectra. In addition the participant should get first-hand experience with ultra-high vacuum technology, which is very important in surface science research.

## 1 The Quadrupole Mass Spectrometer

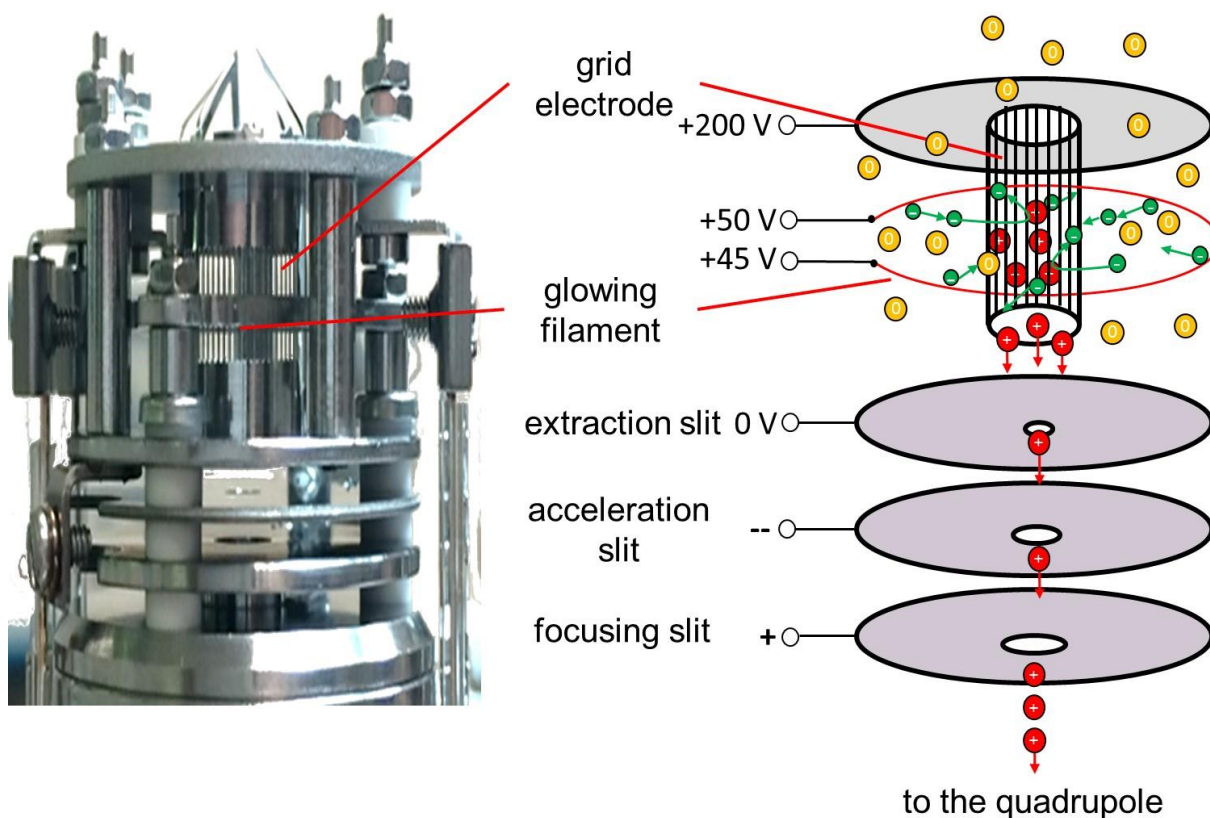
A quadrupole mass spectrometer (QMS) is a device used for mass spectroscopy of ions or charged molecules by their specific charge. The QMS was first theoretically suggested by W. Paul and H. Steinwedel 1953 and experimentally realised in 1954 by W. Paul and M. Raether. A quadrupole mass spectrometer consists of three main parts. First, an ionization unit in order to charge up the atoms/molecules. Second, the quadrupole mass filter, which can only be passed by the charged molecules with a specific mass. This mass can be controlled by the applied voltages to the quadrupole. And third, a detector to measure the ion current which passed the mass filter.



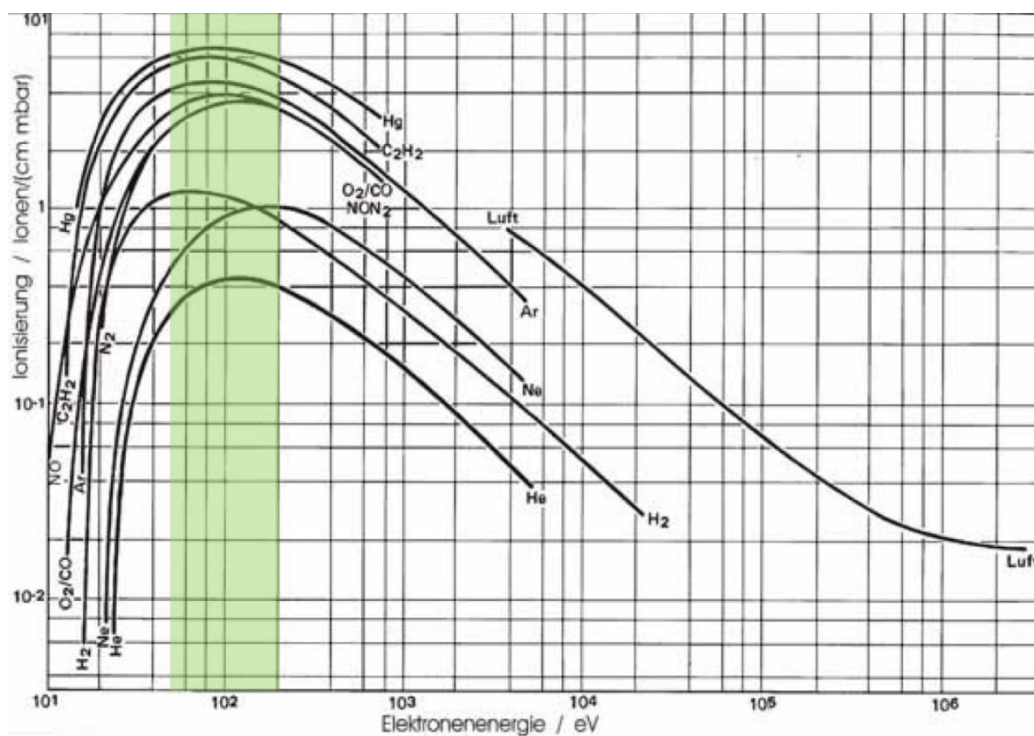
**Fig. 1:** The quadrupole mass spectrometer consists of three main parts: The ionization unit, the quadrupole mass filter and the ion detector unit.

## 1.1 The Ionization Unit

Fig. 1.1.1 shows a photo and a schematic drawing of the ionization unit. It consists of a heated filament, which emits electrons. These electrons are accelerated to a cylindrical grid electrode (ion formation chamber). On their way to the grid electrode the electrons can hit other atoms, which emit more electrons. The developed electron avalanche increases the current (depending on the pressure). Some of these electrons hit the grid and are absorbed. Others pass the grid and hit a gas atom in the formation chamber. This atom is also ionized and emits a second electron. Later the remaining two electrons will again be absorbed by the grid electrode. The created positive ion is extracted from the formation chamber by the extraction slit, which is on ground potential. Two additional slits will further accelerate and focus the ion beam into the quadrupole. The needed energy for the ionization process depends on the type of gas. Typically used values are between 50eV and 150eV (see Fig. 1.2.2).



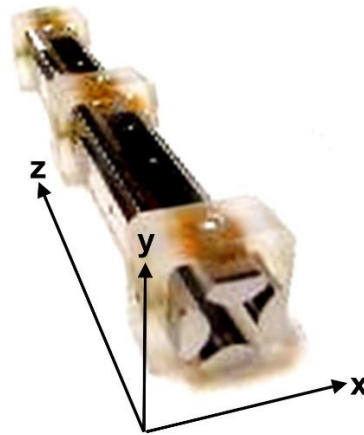
**Fig. 1.1.1: Photo and schematic drawing of the ionization and acceleration unit.**



**Fig. 1.1.2: Ionization energies of some selected gases [1]. In the green shaded area the highest ionization rates are expected**

## 1.2 The Quadrupole Mass Filter

A quadrupole mass filter is an arrangement of four metallic rods with a hyperbolic shape. An applied voltage to these electrodes generate an electromagnetic field (see Fig.1.2.1). If amplitude and frequency of the field are chosen correctly, ions or molecules with a specific mass to charge ratio are confined in the x/y-plane, while the movement in the z-direction is not restricted. Therefore these ions with an additional momentum along the z-axis can pass the quadrupole and will be detected. Let us have a closer look to the field properties which are needed to run a QMS.



**Fig. 1.2.1:** The quadrupole mass filter is an arrangement of four metallic rods, used as electrodes, which generate an alternating electromagnetic field.

We start with the underlying force, the Lorentz force:

$$\underline{F} = q(\underline{E} + \underline{v} \times \underline{B}).$$

In order to confine the ions in the x/y-plane we have to apply a repulsive force, i.e., a force which increases with the radial position of the ion:

$$\underline{F} \propto r^n \frac{\underline{r}}{|\underline{r}|}$$

For  $n=1$  the potential can be written as

$$\Phi(\underline{r}, t) = \Phi_0(\underline{r}, t) \cdot (\xi x^2 + \eta y^2 + \theta z^2),$$

which has to fulfill the Laplace equation

$$\nabla^2 \Phi(\underline{r}, t) = 0,$$

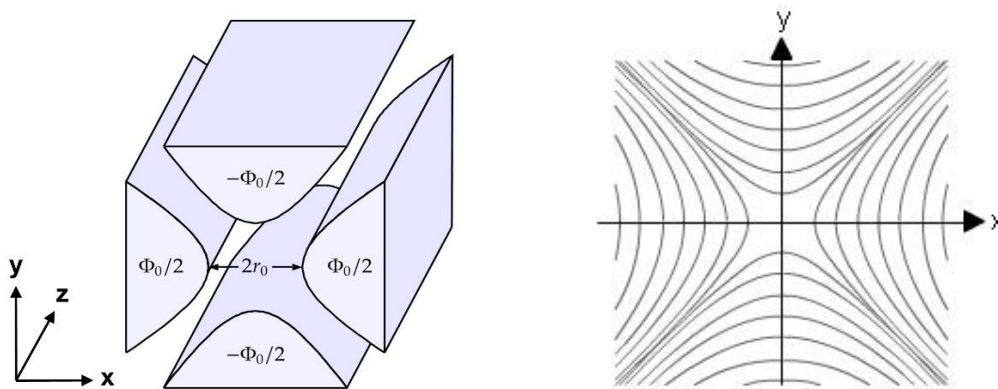
neglecting any volume charge between the electrodes. This requires

$$\xi + \eta + \theta = 0,$$

which can be realized, i.e., by  $\xi = \eta$  and  $\theta = -2\xi$ . This is the potential of a three dimensional “Paul Trap” (3D ion trap) and will not be discussed in detail. The potential of a linear ion trap or a quadrupole can be realized by  $\xi = -\eta$  and  $\theta = 0$ . The ideal quadrupole field is generated by hyperbolic electrodes as shown in Fig. 1.2.2 (left). Assuming that the electrodes are aligned along z-direction and that the distance between the (0,0,z)-axis and the vertices of the hyperbolic electrodes is  $r_0$ , the potential can be written as:

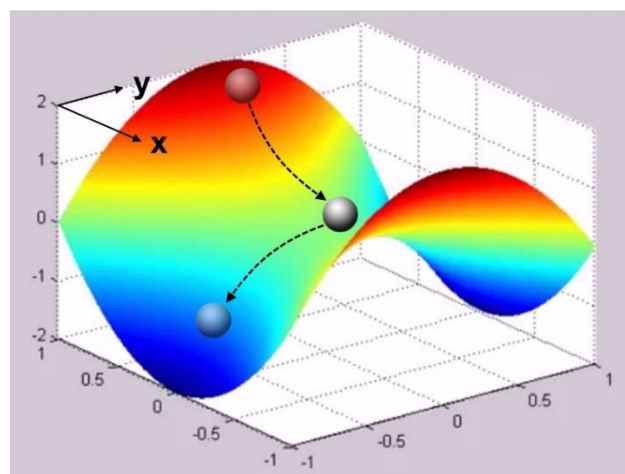
$$\Phi(x, y, z, t) = \Phi_0(t) \cdot \frac{x^2 - y^2}{r_0^2},$$

with a potential  $\pm \Phi_0(t)/2$  applied to adjacent electrodes.



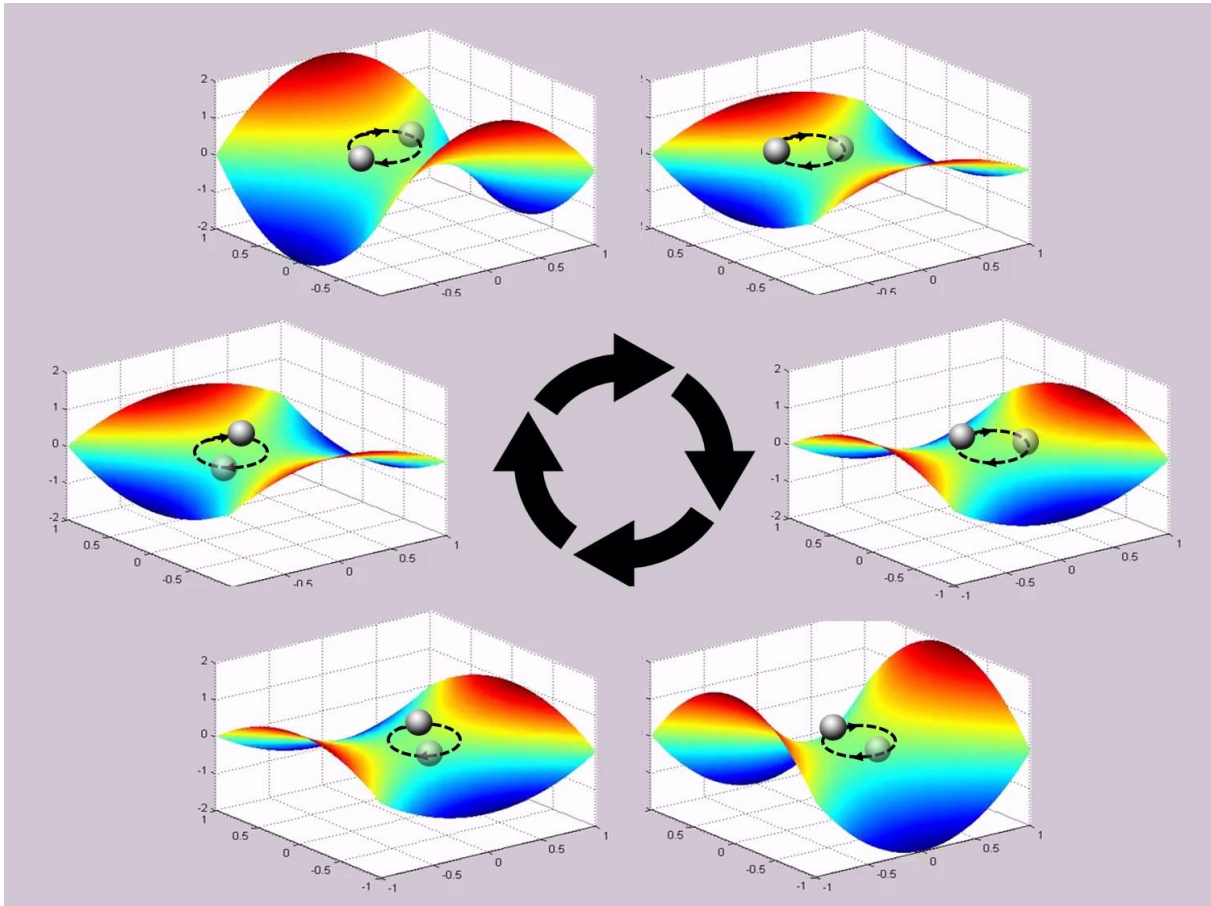
**Fig. 1.2.2: Left: Hyperbolic electrodes of an ideal quadrupole mass spectrometer. The distance between opposite vertices of the hyperbolas is  $2r_0$ . Right: Equipotential lines for a fixed voltage applied to the electrodes (right) [2].**

Thus, the potential has infinitesimal translation symmetry along the z-axis and no force is affecting ion movement along the z-direction. Fig. 1.2.2 (right) shows the equipotential lines for a fixed voltage applied to the electrodes. As can be seen in the 3D plot of this potential in Fig.1.2.3, the field focuses charged particles in one direction, e.g., the x-direction, while it defocuses in the y-direction, causing the ions hit the y-electrodes and disappear.



**Fig. 1.2.3: 3D plot of the fixed potential. A negatively charged ion (grey ball) is focused in x-direction and defocused in y-direction. This ion will hit the y-electrode [3].**

By only using electro static fields it is not possible to create a stable position for a charge in the  $x/y$ -plane. Therefore an alternating voltage  $U_{AC}$  is applied to the electrodes with a phase shift of  $180^\circ$  between the  $x$ - and  $y$ -direction. Additionally a constant voltage offset  $U_{DC}$  is applied. Adopting an appropriate angular frequency  $\omega$  of the alternating voltage (typically around  $f = \omega/2\pi = 1-2$  MHz), an alternating focussing and defocussing of the ions in  $x$ - and  $y$ -direction can be realised.



**Fig. 1.2.4:** 3D plot of an alternating potential in  $x$ - and  $y$ -direction with a phase shift of  $180^\circ$ . Depending on the frequency, amplitude and dimensions of the quadrupole an ion (grey ball) with a specific mass and charge circulates around the center and is therefore confined in the  $x/y$ -plane [3].

The resulting potential is given by

$$\Phi(x, y, z, t) = (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{x^2 - y^2}{r_0^2}.$$

The equation of motion of an ion with charge  $q$  and mass  $m$  can be derived easily

$$\begin{aligned}
m\ddot{\underline{r}} &= q\underline{E} = -q\underline{\nabla}\Phi(x, y, t) \\
\Leftrightarrow m \cdot \begin{pmatrix} \ddot{x} \\ \ddot{y} \\ \ddot{z} \end{pmatrix} &= -q \cdot \begin{pmatrix} (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{2x}{r_0^2} \\ (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{-2y}{r_0^2} \\ 0 \end{pmatrix} \\
\Leftrightarrow \begin{pmatrix} m\ddot{x} + (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{2qx}{r_0^2} \\ m\ddot{y} + (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{-2qy}{r_0^2} \\ m\ddot{z} \end{pmatrix} &= \underline{0}
\end{aligned}$$

The z component describes a linear movement of the ion along the z-axis because there is no force in that direction. The x and y components are homogeneous differential equations of second order, which cannot be solved analytically in this form. The movement in x- and y-direction can be written as Mathieu's differential equations:

$$\begin{aligned}
\frac{dx^2}{d\tau^2} + (a_x - 2b_x \cos(2\tau)) \cdot x &= 0 \\
\frac{dy^2}{d\tau^2} + (a_y - 2b_y \cos(2\tau)) \cdot y &= 0
\end{aligned}$$

This differential equations differ only in definition of their transformation parameters:

$$\begin{aligned}
a_x &= -a_y = \frac{8qU_{DC}}{mr_0^2\omega^2} \\
b_x &= -b_y = \frac{4qU_{AC}}{mr_0^2\omega^2} \\
\tau &= \frac{\omega t}{2}
\end{aligned}$$

Herein  $a_{x/y}/4$  gives the ratio of potential energy in the dc voltage field to the kinetic energy of the oscillation, whereas  $b_{x/y}/2$  denotes the ratio of potential energy in the ac field to the kinetic energy of the oscillation:

$$\begin{aligned}
\frac{a_x}{4} = -\frac{a_y}{4} &= \frac{2qU_{DC}}{mr_0^2\omega^2} = \frac{qU_{DC}}{\frac{1}{2}mv^2} = \frac{E_{pot}^{DC}}{E_{kin}^{AC}} \\
\frac{b_x}{2} = -\frac{b_y}{2} &= \frac{2qU_{AC}}{mr_0^2\omega^2} = \frac{qU_{AC}}{\frac{1}{2}mv^2} = \frac{E_{pot}^{AC}}{E_{kin}^{AC}}
\end{aligned}$$



The solution of Mathieu's differential equations is known already and can be written as a superposition of two linear independent parts, which consists of a sum of exponential functions:

$$x(\tau) = A e^{i\beta(a_x, b_x)\tau} \sum_{n=-\infty}^{\infty} C_n e^{2in\tau} + B e^{-i\beta(a_x, b_x)\tau} \sum_{n=-\infty}^{\infty} C_n e^{-2in\tau}$$

$$y(\tau) = A e^{i\beta(a_y, b_y)\tau} \sum_{n=-\infty}^{\infty} C_n e^{2in\tau} + B e^{-i\beta(a_y, b_y)\tau} \sum_{n=-\infty}^{\infty} C_n e^{-2in\tau}$$

while  $A$  and  $B$  can be determined by the initial conditions  $x(\tau = 0), \dot{x}(\tau = 0)$ , the characteristic exponent  $i\beta(a_{x/y}, b_{x/y})$  defines the properties of the solution and therefore the movement of the ions in the quadrupole.  $\beta$  depends on the transformation parameters  $a_{x/y}$  and  $b_{x/y}$  and is given by the continued fraction:

$$\beta(a_{x/y}, b_{x/y}) = a_{x/y} + \frac{b_{x/y}^2}{(2+\beta)^2 - a_{x/y} - \frac{b_{x/y}^2}{(4+\beta)^2 - a_{x/y} - \dots}} + \frac{b_{x/y}^2}{(2-\beta)^2 - a_{x/y} - \frac{b_{x/y}^2}{(4-\beta)^2 - a_{x/y} - \dots}}$$

If  $i\beta$  consists of a real part, the  $e^{\pm i\beta\tau}$  tends to infinity and therefore also  $x(t)$  (and  $y(t)$ ). The consequence is that the ion moves far away from the center, hits the electrodes and cannot pass the quadrupole. To get a periodic and stable solution  $i\beta$  must be purely imaginary. A more detailed mathematical analysis exhibits, that solutions with integer  $\beta$  are periodic, but unstable solutions, as the amplitude of the oscillation increases continuously.

If we rewrite the formula by using the Euler equation ( $e^{\pm ix} = \cos(x) \pm i \sin(x)$ ), addition theorems and  $\tau = \omega/2 \cdot t$ , we can learn something about the frequency of the ion movement in the quadrupole:

$$x(\tau) = D \sum_{n=-\infty}^{\infty} C_n \cos\left((2n+\beta)\frac{\omega}{2}t\right) + iE \sum_{n=-\infty}^{\infty} C_n \sin\left((2n+\beta)\frac{\omega}{2}t\right),$$

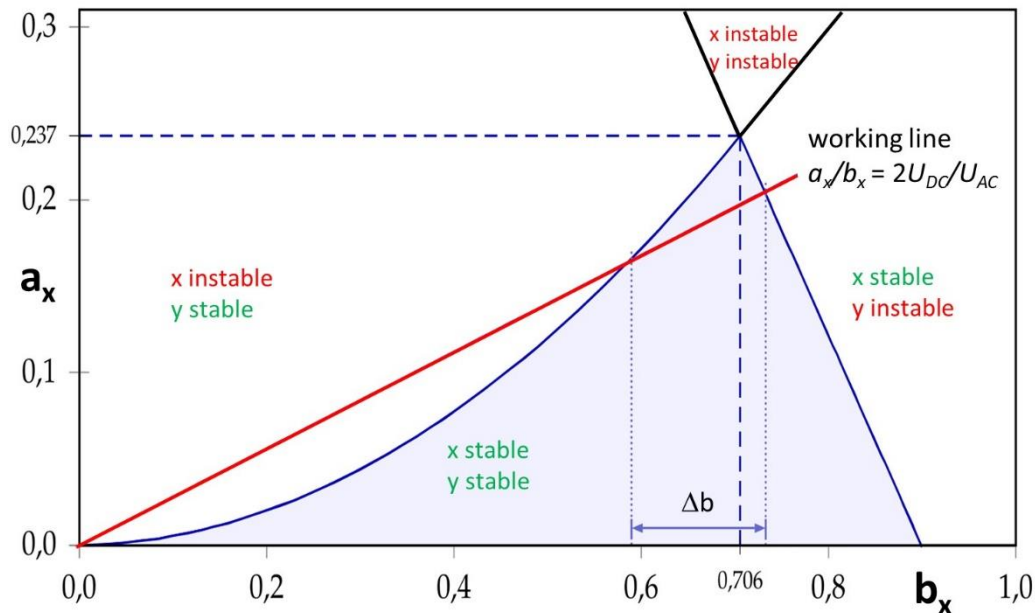
Where  $D$  and  $E$  are linear combinations of  $A$  and  $B$ . From this equation the oscillation amplitudes  $C_n$  and angular frequencies  $\omega_n$  ( $f_0 = \beta \frac{f}{2}$ ) of the ions in the quadrupole with respect to the frequency of the ac voltage  $\omega$  can be determined by:

$$\omega_n = (2n+\beta)\frac{\omega}{2}, f_n = (2n+\beta)\frac{f}{2}$$

The lowest possible frequency is given by  $n=0$ :  $f_0 = \beta \frac{f}{2}$

For a detailed analysis of the stable solution for the  $x$  movement, we plot the parameter  $a_x$  with respect to  $b_x$ . Notice that for the  $y$  movement the stable solutions have exactly the same shape, only with flipped axis due to  $a_y = -a_x$  and  $b_y = -b_x$ . Fig.1.2.5 shows the areas of stable solutions bounded by Mathieu's functions. A stable movement of the ions through the quadrupole is only possible for values given by the grey shaded triangular area, i.e., the area of stable movement in  $x$ - and  $y$ -direction. This means that

the red working line, given by  $a_x/b_x = 2U_{DC}/U_{AC}$ , must cut the grey shaded area.  $\Delta b$  can be adjusted by the slope of the working line.

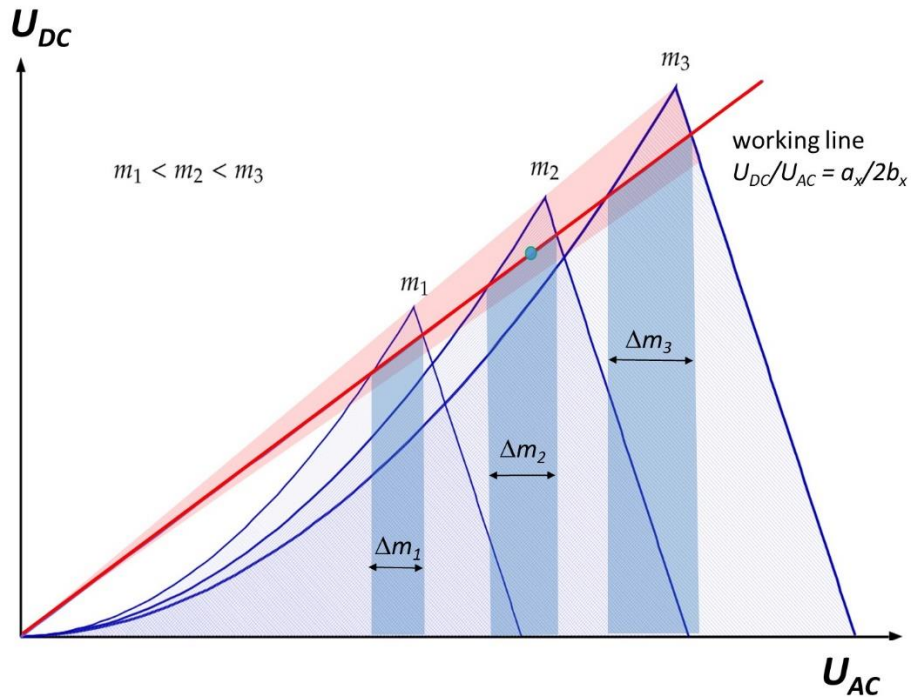


**Fig. 1.2.5: Parameter  $a$  plotted versus  $b$  of Mathieu's differential equation. Values of the grey shaded area give stable solutions for the ion movement in  $x$ - and  $y$ -direction. The working line (red) is set to a fixed ratio of  $a/b$  [7].**

The diagram in Fig 1.2.5 can also be transformed in a plot of  $U_{DC}$  with respect to  $U_{AC}$ , which gives a more practical information about the necessary adjustment of the applied voltages (see Fig. 1.2.6). The red working  $U_{DC}/U_{AC} = a_x/2b_x$  and the stable areas for different masses of ions are plotted (for constant  $\omega$  and  $r_0$ ). If the voltages are scanned with the constant ratio given by the working line, only ions with a mass  $m$  (and charge  $q$ ) inside the grey stability area can pass the quadrupole. Ions with a mass outside this area will hit the electrodes. The working line defines an interval  $\Delta U_{AC}$ , which can be directly assigned to a mass interval  $\Delta m$ . The mass resolution can be adjusted by changing the slope of the working line and can be calculated by:

$$\frac{m}{\Delta m} = \frac{0.126}{0.1678 - \frac{U_{DC}}{U_{AC}}}$$

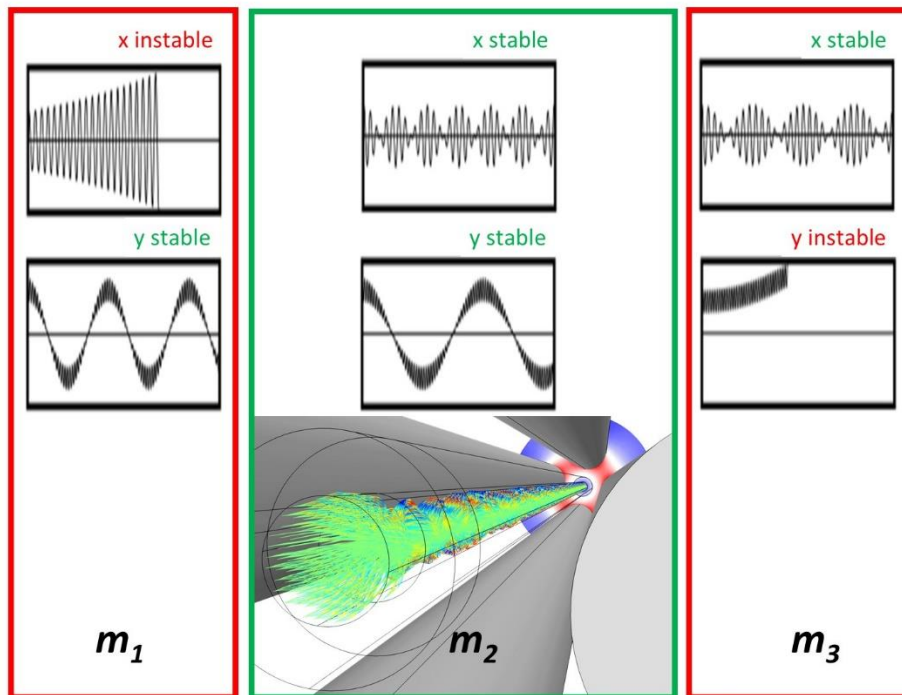
To increase the mass resolution (decrease  $\Delta m$ ) the working line must be set a bit below the maximum of the stable area. Reasonable values for the slope of the working line are found within the red area shown in Fig.1.2.6. The minimum of the slope is given by the overlapping of the stability areas for the masses, which shall be resolved. The maximum slope is given by the maximum of the stability areas.



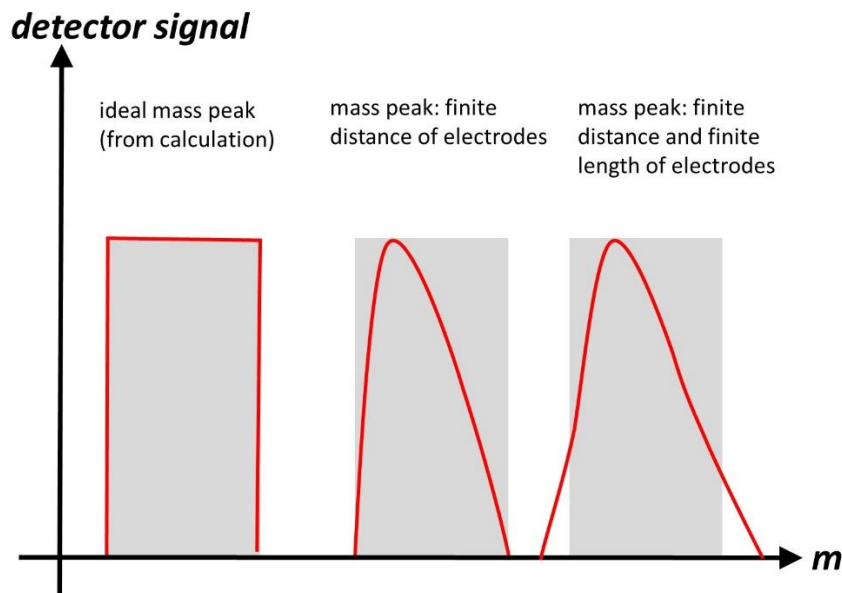
**Fig. 1.2.6: Solutions for different ion masses with respect to the applied ac and dc voltage. By scanning  $U_{AC}$  along the working line different masses  $m_1$ ,  $m_2$ ,  $m_3$ , which pass the quadrupole, can be selected. The mass resolution  $\Delta m$  depends on the slope of the working line (reasonable values for the slope are shown in the red shaded area) [7].**

Assuming a working point as indicated by the green dot in Fig.1.2.6, typical trajectories of the ions in x- and y-direction are shown in Fig 1.2.7. For ions with mass  $m_1$  the defocusing force in the x-direction is too strong and therefore the oscillation amplitude increases until the ions hit the electrodes. Ions with  $m_2$  show a stable movement in x- and y-direction and can pass the quadrupole. Ions with  $m_3$  are too heavy and not stable in y-direction. If  $U_{DC}=0V$  is chosen and only  $U_{AC}$  is varied the quadrupole works as a high pass filter. In this case all masses have stable solutions but with increasing  $U_{AC}$  small masses are cut off. The area under the observed spectrum is proportional to the total pressure in the system. If the total pressure is known, this information can be used to determine the partial pressure of certain gases.

Notice that the solutions for a real quadrupole differs a bit from the ideal one. Because of the finite length and distance of the electrodes the expected mass peaks are not rectangular any more. As a result of the finite distance of the electrodes some ions with the correct mass and certain initial conditions will also hit the electrodes. This effect is more distinct on the high mass side, causing an asymmetric rounded peak (see Fig. 1.2.8). Due to the finite length of the electrodes some ions with the wrong mass can pass the quadrupole anyhow, which leads to a broadening of the peaks (Fig. 1.2.8.). This happens if the increasing amplitude (for an instable solution) is not high enough at the end of the quadrupole to hit the electrode.



**Fig. 1.2.7:** Examples for ion movements in x- and y-direction depending on the area in the  $U_{DC}/U_{AC}$ -plane (Fig. 1.2.6). Only in the stable area (grey shaded in Fig. 1.2.6) the ions show periodic movements without an increasing amplitude, thus let them pass the quadrupole (see also 3D simulation in the middle of ion trajectories through the quadrupole of different initial values) [4].



**Fig. 1.2.8:** Ideal and real shape of the measured mass peaks [5]. For comparison the grey box indicates the ideal rectangular shape of the mass peak derived from the calculation.

### 1.3 The Detector Unit

The ion detection unit consists of a secondary electron multiplier (SEM) followed by a Faraday cup, i.e., an anode which collects the electrons. The measured current is proportional to the amount of incoming ions. The SEM is a channeltron which amplifies the ion current. It consists of a curved insulated tube, which is covered by a high ohmic layer (range of  $G\Omega$ ). A voltage of about 1000 V is applied between the two ends of the tube. Thus the potential increases constantly along the tube. In addition the inner surface of the tube is covered by a thin cesium layer. The Cs reduces the working function of the metal. If an incoming ion hits the wall of the tube, a few electrons leave the metallic surface. These electrons will again hit the inner wall of the tube and more electrons are released. The electron avalanche reaches the end of the tube and is detected at the anode (Faraday cup). The amplification factor strongly depends on the applied voltage.



Warning: The surface of the channeltron can be damaged if the channeltron is getting to hot  $T > 150^\circ\text{C}$  (Cs will evaporate) or the vacuum pressure is too high, i.e.  $p > 10^{-5}$  mbar (the Cs will be sputtered away by the high current).

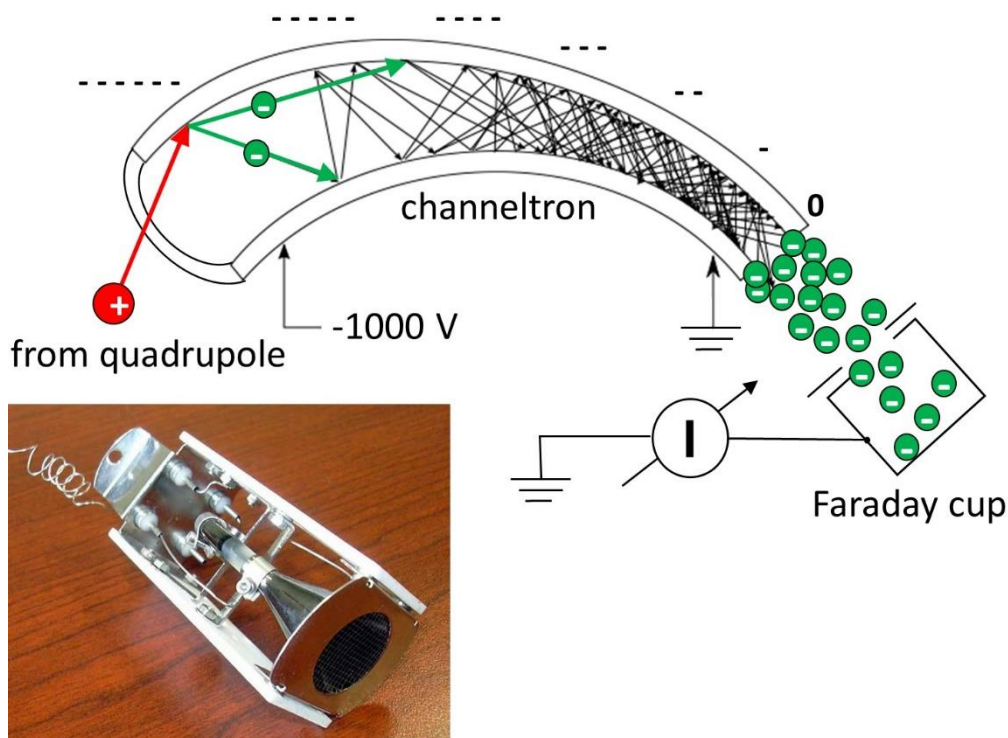


Fig. 1.3.1: Basic design of the ion detection unit. The channeltron (SEM) amplifies the ion current by using an electron avalanche effect. The Faraday cup selects the electrons and the current can be measured by a sensitive ampère meter (built in the QMS electronics) [6].

The calibration factors  $C_1$  and  $C_2$  of the channeltron depend exponentially on the applied voltage and can be described as:

$$I = I_0 \cdot 10^{C_1 \cdot U_{SEM} + C_2 \cdot U_{SEM}^2},$$

where  $I$  is the measured ion current at the Faraday cup,  $I_0$  is a pre-factor depending on the peak amplitude and  $U_{SEM}$  represents the applied voltage to the channeltron.

## 1.4 Measuring Residual Gas Components

In this lab course experiment the residual gas components are measured in an ultra-high vacuum chamber made from stainless steel.

The remaining residual gas components of a good stainless steel UHV chamber usually are hydrogen and carbon monoxide. Notice, that the hot filaments in the ionization unit of the mass spectrometer and the Bayard-Alpert gauge can crack the gas molecules and new compounds can be formed. Therefore the remaining mass peaks in an UHV chamber are:

mass 1 (H)

mass 2 (H<sub>2</sub>)

mass 12 (C)

mass 16 (O)

mass 28 (CO)

mass 44 (CO<sub>2</sub>)

Hydrogen is stored within the steel and can only be reduced by baking the chamber for a long time at 400°C. The CO desorption gives the pressure limit of a stainless steel chamber, which is in the range of  $10^{-11}$  mbar to  $10^{-10}$  mbar. To reach such a good pressure the adsorbed water (mass 18/17) must be removed from the chamber surface by baking it at about 150°C. Sometimes compounds of oil from the mechanical pumps can be found in the mass spectrum (groups of mass peaks, which repeat with a distance of 14 mass units = always one CH<sub>2</sub> group more). This can only be removed by cleaning the whole chamber with soap and other solvents. A good indication for a leakage are the following mass peaks in the spectrum:

N<sub>2</sub> (mass 28/14)

O<sub>2</sub> (mass 32/16)

Ar (mass 40/20)

## 2 Ultra-High Vacuum

The classification of vacuum depending on the achievable pressure is shown in the table:

Classification	pressure
rough vacuum	1000 mbar - 1 mbar
medium vacuum	1 mbar - $10^{-3}$ mbar
high vacuum, HV	$10^{-3}$ mbar - $10^{-7}$ mbar
ultra-high vacuum, UHV	$10^{-7}$ mbar - $10^{-10}$ mbar
extreme high vacuum, XHV	$< 10^{-10}$ mbar

Tab. 2.0: Classification of vacuum pressure ranges.

Fig. 2.0 gives an overview over vacuum classification, generation, measurement and technical relevance.

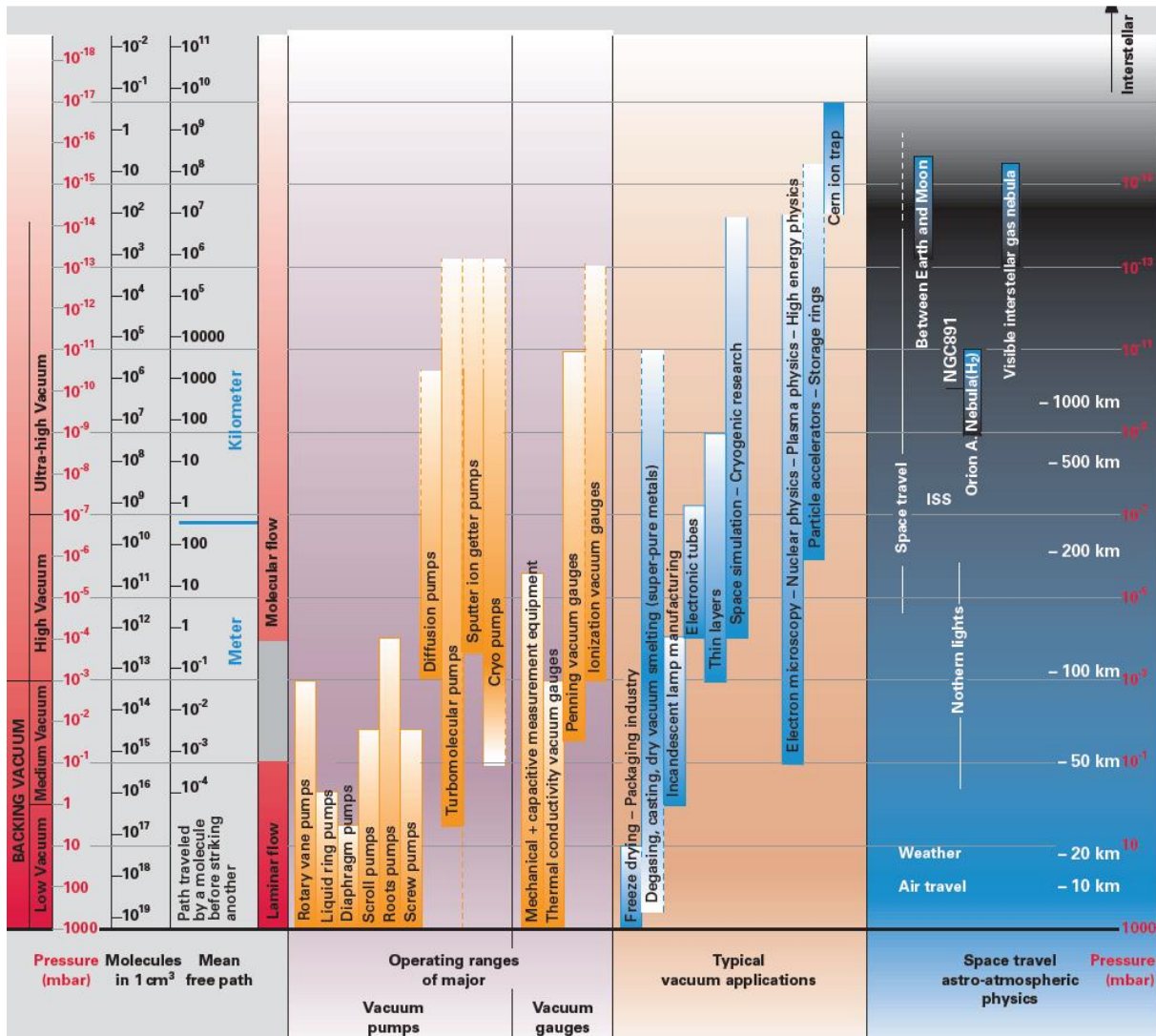


Fig. 2.0: Vacuum at a glance (image taken from the Vacuum Technology Book of Pfeiffer Vacuum GmbH [9]).

In this experiment we use an ultra-high vacuum chamber made from stainless steel. All flanges are sealed with copper gaskets (CF standard). The used UHV valves have also a metal sealing. The pressure is in the range of  $10^{-10} - 10^{-9}$  mbar. Notice that the mean free path of the gas molecules is about 100km.

## 2.1 Generation of Ultra-High Vacuum

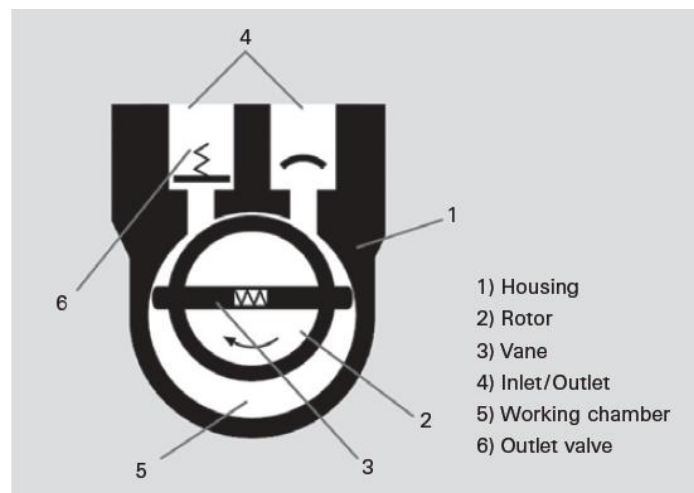
To reach ultra-high vacuum pressures in a chamber special types of vacuum pumps are needed. Typical UHV pumps are:

ion getter pumps,  
turbomolecular pumps,  
sublimation pumps,  
oil diffusion pumps  
cryogenic pumps.

All of these pumps cannot be used directly at ambient pressure to pump the recipient. Therefore additional rough vacuum pumps are needed to create a medium or high vacuum first, before switching on the ultra-high vacuum pumps. A rough vacuum can be created by rotary pumps, membrane or scroll pumps. In this experiment the external pumping station is equipped with a rotary pump which can reach a pressure of about  $10^{-3}$  mbar.

### The Rotary Pump

Fig. 2.1.1 shows the operating principle of the pump. The pumping system consists of a housing (1), an eccentrically installed rotor (2), vanes (3) that move radially under centrifugal and resilient forces and the inlet and outlet (4). The inlet valve is designed as a vacuum safety valve that is always open during operation. The working chamber (5) is located inside the housing and is restricted by the stator, rotor and the vanes. The eccentrically installed rotor and vanes divide the working chamber into two separate compartments with variable volumes. As the rotor turns, gas flows into the enlarging suction chamber until it is sealed off by the second vane. The enclosed gas is then compressed until the outlet valve opens against the atmospheric pressure. The sealing is provided by oil [9].



**Fig. 2.1.1: Sketch of a rotary pump [9].**



## The Turbomolecular Pump

Usually a turbomolecular pump is used as the second pumping stage. The turbomolecular pump was developed and patented at Pfeiffer Vacuum in 1958 by Dr. W. Becker. Turbomolecular pumps belong to the category of kinetic vacuum pumps. Their design is similar to that of a turbine. A multi-stage, turbine-like rotor with bladed disks rotates in a housing. Interposed mirror-invertedly between the rotor disks are bladed stator disks having similar geometries [9]. Typical rotation speeds are 1000-1500Hz depending on the size of the pump. Pumping speeds of 60-300l/s are quite usual. To reach a pressure of  $<10^{-9}$  mbar the chamber has to be heated up to 100-200°C in order to get rid of the adsorbed water at the stainless steel surfaces, thus reducing the outgassing rate.



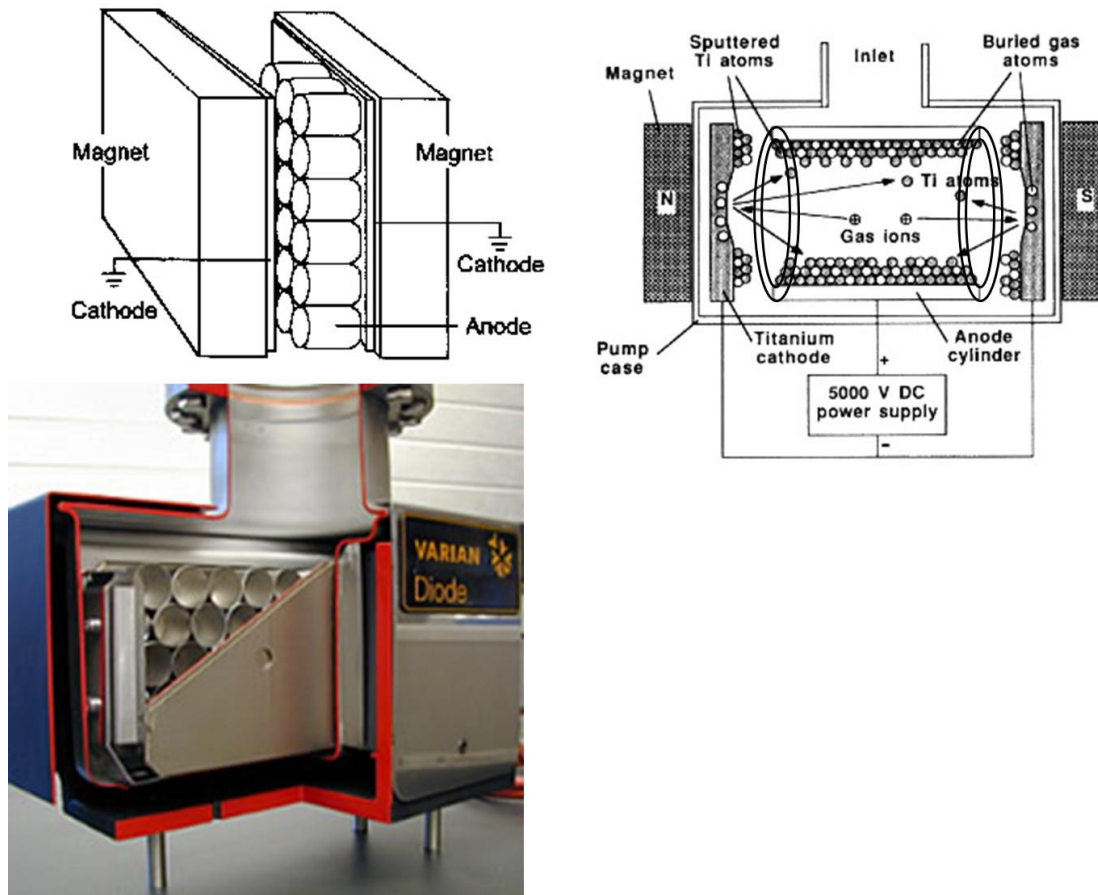
*Fig. 2.1.2: View inside a turbomolecular pump [10].*

## The Ion Getter Pump

In our experiment we use an ion pump to keep the ultra-high vacuum. This type of pump is an electrostatic pump without any moving parts. A high voltage of 3000-7000V is applied to two parallel titanium plates (cathodes) and cylindrical titanium anodes in between (see Fig. 2.1.3). If the gas molecules hit the titanium cylinders they are adsorbed by the surface. After some time the whole surface will be covered and the pumping speed will decrease. Therefore the residual gas molecules are ionized and accelerated to the titanium plates. If they hit the titanium plate with a high energy, the titanium will be sputtered onto the cylindrical anodes, thus, creating a fresh titanium surface again, keeping the pump effect running.

There are two processes, which contribute to the pumping effect. First the adsorption of the residual gas molecules by the titanium surfaces (Ti is a good getter material). Second the implantation of gas ions or charged molecules into the titanium plates. The two processes depend on the gas pressure and the applied high voltage. The rule of thumb is the lower the pressure the lower the applied voltage. To increase the ionization process at low pressures a strong magnetic field is needed to decrease the mean free path of the electrons (spiral path) between the collisions with the gas atoms. The main advantages of ion pumps are:

- no vibrations,
- low power consumption,
- high pumping speed
- little maintenance



**Fig.. 2.1.3: Construction of an ion getter pump (diode pump). A strong magnetic field is needed to decrease the mean free path of the ions keeping the glow discharge running at low pressures [8].**

## 2.2 Determination of the Pumping Speed

If a vacuum chamber is continuously pumped at a volume flow rate  $S=dV/dt$  (pumping speed), an equilibrium pressure  $p_{eq}$  will be reached if the throughput is equal to the total outgassing/leakage rate [9]:

$$Q = S \cdot p_{eq}$$

To determine the actual pumping speed, the outgassing rate of the chamber has to be determined. Therefore the pump is switched off and the increase of pressure is measured for a time  $\Delta t$ . The outgassing rate is given by:

$$Q = \frac{\Delta p}{\Delta t} \cdot V .$$

Knowing the chamber volume  $V$ , the pumping speed can be calculated by:

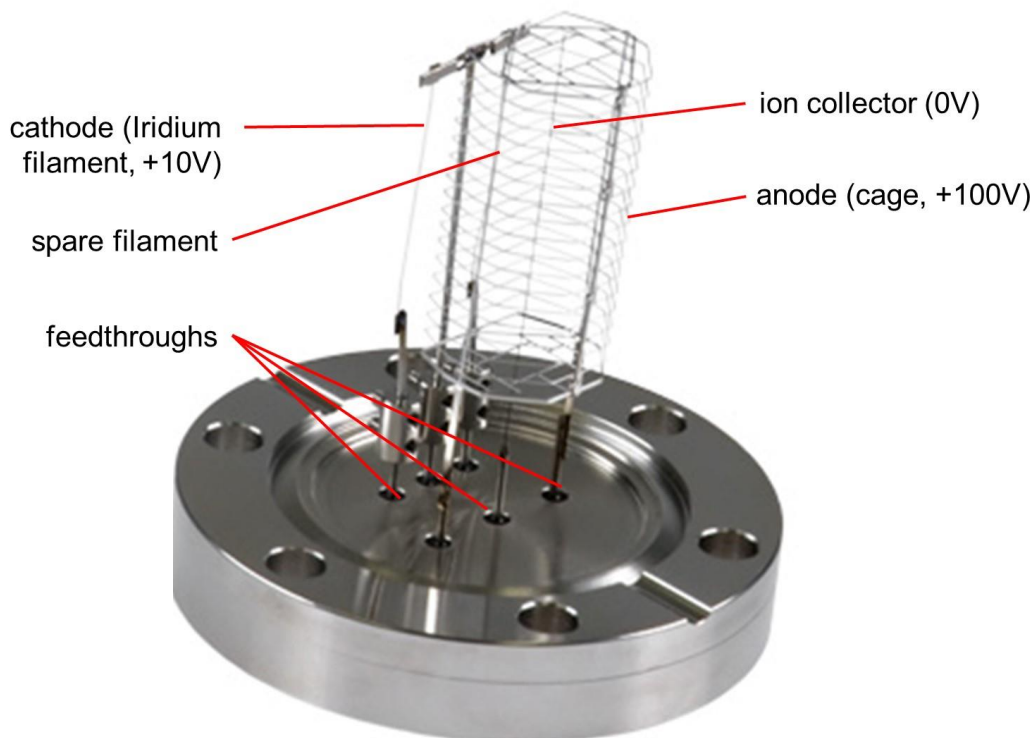
$$S = \frac{Q}{p_{eq}} = \frac{\Delta p \cdot V}{\Delta t \cdot p_{eq}}$$

The common units for the leakage rate and pumping speed are mbar/l/s and l/s.

## 2.3 Measuring Ultra Low Pressures

There are only a few devices which can measure UHV pressures in the range of  $10^{-10}$  mbar. Ionization vacuum meters and spinning rotor vacuum meters. Spinning rotor gauges are very rare and expensive. They consist of a magnetic ball in the vacuum chamber, which is levitated by an electromagnetic field. The ball rotates with a frequency of about 44Hz. The applied power of keeping the ball rotating at the fixed frequency is measured and depends on the pressure due to the friction of the gas molecules with the ball. This type of vacuum gauge is often used to calibrate other types of UHV gauges.

The most common device for measuring UHV is the hot cathode ionization vacuum meter (Bayard-Alpert gauge). In this case electrons are generated with the aid of a heated cathode. Fig. 2.3.1 shows a photo of a Bayard-Alpert gauge. A thin wire is arranged in the middle of the cylindrical, lattice shaped anode. This wire serves as the ion collector. A voltage of approximately 100 V is applied between anode and cathode. The electron emission current is kept constant. A part of the emitted electrons hit the lattice of the anode and are absorbed. The other part permeates the grid anode. Inside the cage the electron can hit a residual gas atom and ionize it. The positively charged molecules are attracted by the neutral ion collector in the middle of the cage. Using a nano-ampere meter the ion current is measured, which is proportional to the residual gas pressure. Since the electron emission current is also proportional to the ion current, it can be used to set the sensitivity of the gauge, i.e., the lower the pressure the higher the emission current. Typical values are 0.1mA up to 10mA [9].



**Fig. 2.3.1: Photo of the used Bayard-Alpert gauge. Two emitting filaments, the grid (anode) and the inner ion collector can be seen. An example of useful voltages are shown.**

Pressures can be accurately measured down to  $1 \cdot 10^{-10}$  mbar with Bayard-Alpert vacuum gauges. Measuring errors result from the pumping effect of the sensor, as well as from the following two limiting effects:

- **X-ray bremsstrahlung:** Electrons that strike the anode cage cause x-rays to be emitted. Some of the x-rays strike the ion collector. This effect causes the collector to emit photo electrons that flow off towards the anode. The resulting photoelectron current increases and falsifies the pressure-dependent collector current. Consequently the collector wire should be selected as thin as possible so that it collects only very little x-ray radiation. The lower measurement limit is therefore also known as the x-ray limit.
- **ESD ions:** ESD (electron stimulated desorption) means that gas molecules deposited on the anode cage are desorbed and ionized by electrons. These ions also increase the pressure-proportional ion current. A hot cathode vacuum gauge also gives a gas type dependent pressure signal. However the measurement results are significantly more accurate (typically  $\pm 10\%$ ) than those obtained with a cold cathode ionization vacuum gauge (typically  $\pm 25\%$ ).

## 3 Experimental Setup

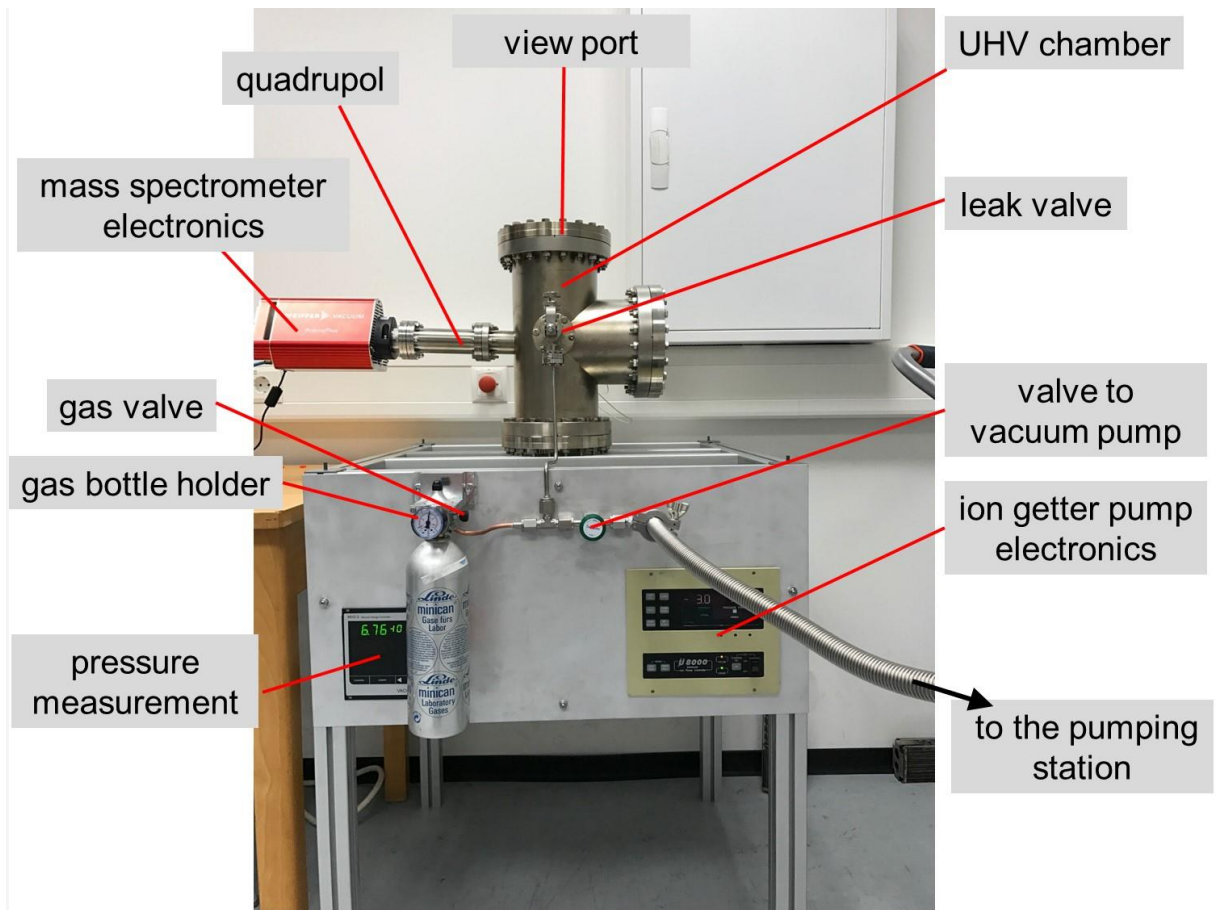
### 3.1 The UHV System

The experimental setup consists of a stainless steel ultra-high vacuum chamber with a quadrupole mass spectrometer, an ion pump with a pumping speed of 40 l/s, a Bayard-Alpert gauge and a gas inlet system. The “MiniCan” gas bottles can be exchanged and screwed to the gas bottle holder. A manometer shows the actual pressure of the used bottle (max. 12 bar). Two valves are used to close either the gas bottle or the connection to the pumping station. A leak valve is mounted on a flange of the vacuum chamber. With the leak valve a defined amount of gas can be applied to the vacuum chamber.



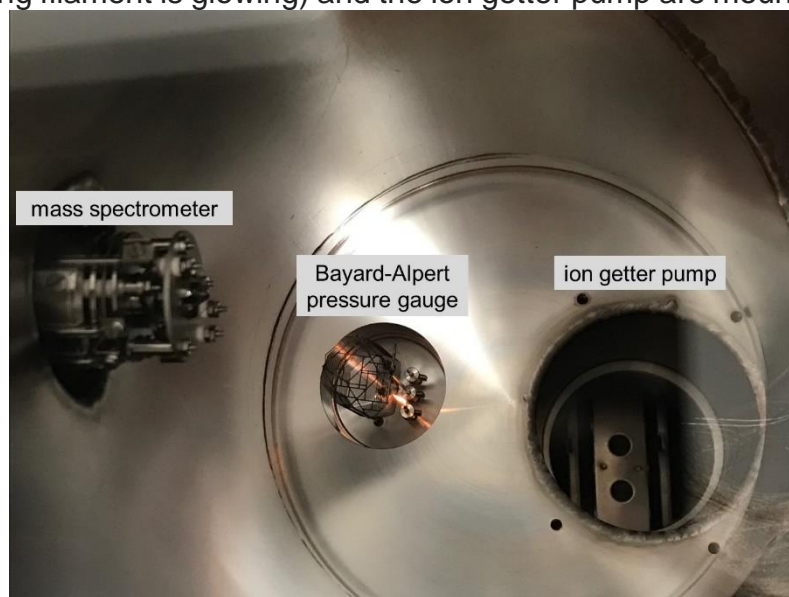
**Attention:** Open the leak valve very carefully by turning the double screw counterclockwise. Notice that at the beginning the pressure increases only slightly, but after one turn it increases very quickly. Always **stay below  $10^{-8}$  mbar** in the chamber!

Fig. 3.1.1 shows a photo of the experimental setup. The ion pump is mounted below the chamber and cannot be seen. The controllers of the ion pump and the Bayard-Alpert gauge are mounted at the front panel of the setup.



**Fig. 3.1.1: Setup of the experiment with the UHV chamber and gas inlet system.**

In Fig. 3.1.2 a view inside the chamber is presented. A part of the mass spectrometer with the ionization unit can be seen on the left side. The Bayard-Alpert gauge (the electron emitting filament is glowing) and the ion getter pump are mounted from below.



**Fig. 3.1.2: View inside the UHV chamber.**

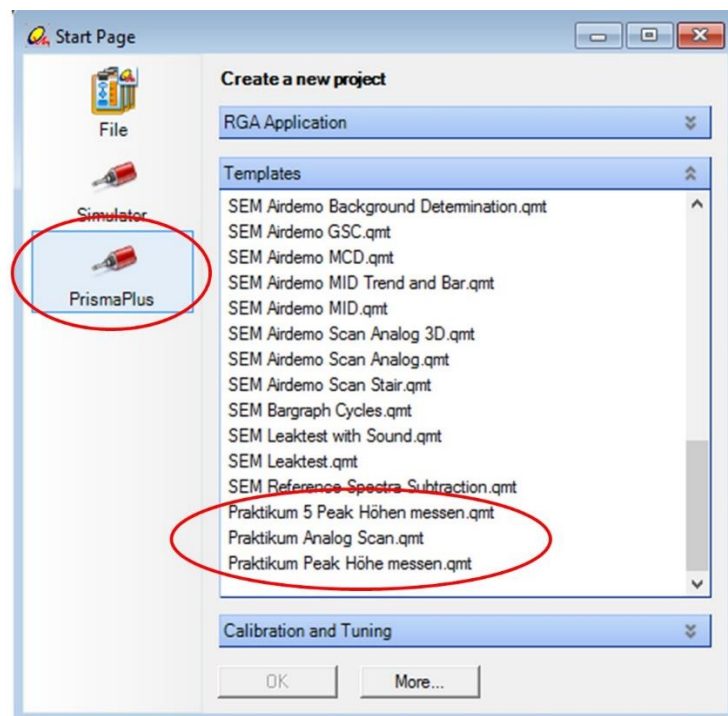
## 3.2 The Mass Spectrometer Software

Before starting the “QUADERA” mass spectrometer software, the spectrometer electronic must run for at least 6 minutes to establish all connections. At the start screen the section “PrismaPlus” has to be chosen. For the lab course experiment three scanning templates are available:

“Praktikum Analog Scan”: measures the whole mass spectrum

“Praktikum Peak Höhe messen”: measures the peak height of a specific peak with respect to time

“Praktikum 5 Peak Höhen messen”: measures 5 different peak heights vs. time



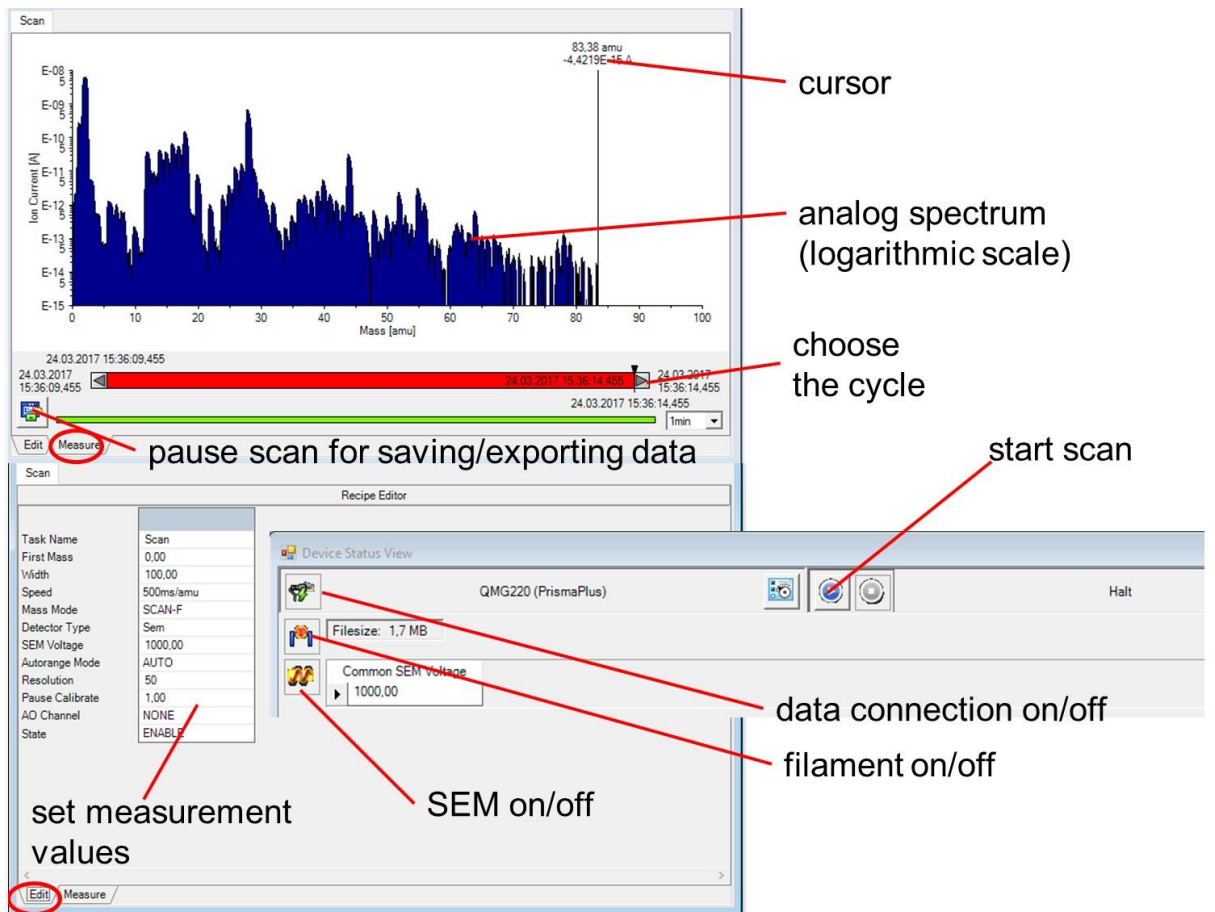
**Fig. 3.2.1: QUADERA software: choosing the scanning template**

The analog scan template can be used to take a whole mass spectrum with a width up to mass 100. In the “Device Status View” window the filament of the ionization unit and the SEM can be switched on and off. The scan is started by pressing the “Play” button. After one complete spectrum the scan starts again with the next cycle until the “Stop” button is pressed. The scan parameter can be set in the “edit”-sheet.

All the spectra can be stored at the end of the measurement.

**Attention:** The standard data format can only be viewed by the QUADERA software. It is important to store the spectrum in asci-format. Therefore pause the scan by the button in the left corner below the scan (see Fig. 3.2.2). Then choose “data export” in the menu and select the correct cycle you want to save.





**Fig. 3.2.2: QUADERA software: Analog scan and device status view window.**

The template for measuring 5 peak heights is shown in Fig.3.2.3. Here the peak height of the chosen masses (in the “edit”-sheet) are plotted vs. time. If the 5 masses are measured one cycle is over. Exporting the data is similar to the analog scan.

**Attention:** Be sure that you stored all cycles of the measurement to save the full time dependent measurement.

Further questions concerning the software can be answered by the help section or your supervisor.





**Fig. 3.2.3: QUADERA software: Template “Praktikum 5 Peak Höhen messen” and parameter edit window.**



## 4. Experimental Procedure and Tasks

The experiments should be done in the following order. Parts marked in green can be done at home during the preparation of the protocol:

### 4.1 Calibration of the Current Amplification Factors of the SEM



The SEM can be damaged if the vacuum pressure or the applied voltage is too high. Always switch off the high voltage during changing its value and never exceed 1500V!!!

1. In this part the properties of the SEM are analyzed. Therefore the dependence of the voltage with respect to the ion current has to be determined.
2. Check the UHV pressure. It should be  $<10^{-9}$ mbar. Switch on the filament and the SEM of the mass spectrometer.
3. Start measuring an analog mass spectrum with an SEM voltage of 1000V (template "Praktikum Analog Scan"). Get familiar with the software and try to change the SEM voltage (switch off the high voltage during changing the value!). What is the minimum SEM voltage to see the highest mass peak at this pressure?
4. Which residual gas components are dominant in the UHV chamber? Why? Plot the taken spectrum and discuss it.
5. Choose the highest peak in the mass spectrum and determine the peak height with respect to the channeltron (SEM) voltage. Start at the lowest voltage you determined before and go up to 1500V in steps of 50V. Measure the peak height at least 20 times for every voltage (use the "Praktikum Peak Höhe messen" template) to get a good statistics. Don't forget to switch off the SEM voltage during changing it.
6. Show the peak height vs. the SEM voltage. Plot the current in a logarithmic way. Notice that the intrinsic error of the quadrupole peak height is about  $\pm 0.5\%$ . In addition, the statistical error of the 20 measurements have to be considered.
7. Determine the calibration factors  $C_1$  and  $C_2$  of the SEM. Discuss the errors!

### 4.2 Measuring the Residual Gas Composition



In this part the residual gas of the vacuum chamber and the gas inlet system has to be investigated. Ask the supervisor to explain how to operate of the external pumping station. Don't use it by yourself!

1. Cleaning of the gas inlet system: Start pumping the gas inlet system by the external pumping station only by the rotary pump until a pressure of  $10^{-1}$  mbar is reached. Be sure that the gas valve is closed (!) and the valve to the pumping station is open. Close the valve to the pumping station and flood the gas inlet system by shortly opening the gas valve. After that open the valve to the n

pumping station again. Do this twice in order to get the gas compounds out of the pipes. Start the turbo pump and wait until a pressure of  $10^{-5}$  mbar is reached.

2. Take an analog mass spectrum at 1000V SEM voltage (template “Praktikum Analog Scan”).
3. Open the leak valve carefully and increase the pressure by a **factor of 2** in the UHV chamber. Always write down the pressure (before and after opening the leak valve).
4. Again take an analog mass spectrum at 1000V SEM voltage. Compare the two spectra in order to get the residual gas composition in the gas inlet system.
5. Plot the difference spectrum of the two measurements.
6. Close the leak valve again and wait until the pressure in the chamber reaches the base pressure again.
7. Calculate the partial pressure of the dominating peaks and its error. To do so use the total pressure measured by the Bayard-Alpert gauge (error +/-20%), which corresponds to the integrated spectrum. The error of the measured peak height is +/-0.5%.

### 4.3 Analyzing Unknown Gases

In this part of the experiment two unknown gases have to be analyzed and determined. Ask the supervisor of the lab course experiment to give you two “Mini Can” gas bottles.

1. Choose a gas bottle and screw it to the holder. The manometer should show the pressure of the bottle (max. 12 bar).
2. Cleaning of the gas inlet system as described before: Close the valve to the pumping station. Then shortly open the gas valve to flood the gas inlet system. Be sure that only the rotary pump is working and turbo pump velocity is 0Hz. Do the flooding and pumping process twice again. Then pump the gas inlet system again with the turbo pump until the pressure reaches  $10^{-5}$  mbar. Then close the valve to the pumping station and shortly open the gas valve.
3. Take an analog mass spectrum at 1000 V (SEM) as a reference for the background.
4. Ask the supervisor how to handle the leak valve correctly. **Carefully** open the leak valve and increase the pressure by a **factor of 2** in the ultra-high vacuum chamber.
5. Take an analog mass spectrum at 1000 V (SEM) again.
6. Plot the difference spectrum and discuss it. Which gas components stem from the unknown gas? Which from fractions of the gas molecules? Which from the changing background pressure?



7. What kind of gas could it be (argumentation needed)? Notice, that the gas molecules might be cracked by the hot filament within the mass spectrometer and lighter gas compounds can also be build.

#### 4.4 Determination of the Pumping Speed

Ask the supervisor how to handle the power supply of the ion getter pump before!

1. **Switch off filament and SEM voltage** of the mass spectrometer and wait until the pressure reaches a constant value in the UHV chamber.
2. Determine the pumping speed of the ion getter pump: Switch off the ion pump and measure the pressure until it reaches a value of  $2 \cdot 10^{-7}$  mbar. Don't increase the pressure too much because it will take some time to pump down the system again. The LabView software can be used to store the time and pressure development.
3. Switch on the HV of the getter pump again.
4. Calculate the pumping speed averaged for a pressure range between  $10^{-9}$  and  $10^{-7}$  mbar in l/s. Also discuss the errors.
5. How many gas molecules are pumped per second by the ion getter pump?

#### 4.5 Outgassing of Stainless Steel

In the last part of the experiment the outgassing of the stainless steel UHV chamber should be analyzed.

1. Put aluminum foil around the chamber in order to get a good heat insulation and a uniform heat distribution over the stainless steel surface. Wear gloves to avoid contact with the scratchy glass fibers within the heating wires.
2. Measure an analog spectrum (SEM=1000V) at room temperature ( $T=?$ ,  $p=?$ )
3. Make a time dependent measurement of 5 dominant mass peaks during heating up the chamber to  $100^{\circ}\text{C}$  with the "Praktikum 5 Peak Höhen messen" template (time per point =2s  $\rightarrow$  10s per cycle; SEM=1000V). Start the LabView software in order to save the chamber temperature, pressure and time (time per point =10s).
4. Measure another analog spectrum at a chamber temperature of about  $100^{\circ}\text{C}$  ( $p=?$ ).
5. Plot a difference spectrum for the two temperatures.
6. Plot the chamber pressure vs. temperature. Estimate the temperature error.

7. Plot the peak height with respect to the temperature of the 5 chosen masses and discuss the result.
8. Calculate the outgassing rate per  $m^2$  of the stainless steel at room temperature and  $T=100^\circ\text{C}$  in  $\text{mbar}\cdot\text{l}/(\text{m}^2\text{s})$ . Use the previously determined pumping speed  $S$ , a chamber volume of  $V=14$  liters (chamber surface  $A\approx 0.3\text{m}^2$ ).
9. Calculate the outgassing rate of the 5 chosen gas components at room temperature and  $T=100^\circ\text{C}$ .

## 5. General Safety Instructions



- Don't open the gas bottles or try to inhale the gases (they might be unhealthy).
- Don't heat up the gas bottles or treat them with fire (danger of explosion).
- Never increase the pressure in the UHV chamber above  $10^{-6}\text{mbar}$  by the leak valve. This could damage the ion pump.
- Wear gloves during installing the heating wires and aluminum foil (glass fibers).
- The allowed temperature gradient of the view ports is about  $2\text{K}/\text{min}$ . Don't install the heating band directly at the view port.
- The ion getter pump is working with voltages up to  $7500\text{V}$  and currents up to  $500\text{mA}$ . There is the risk of a lethal electric shock while damaging the high voltage cable or putting some metal parts (screw driver etc.) in the high voltage connector.
- Never vent the pumping station until the turbo pump is working.
- Never move or kick the pumping station until the turbo pump is working. This will damage the bearings of the pump.

## 6. Literature

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