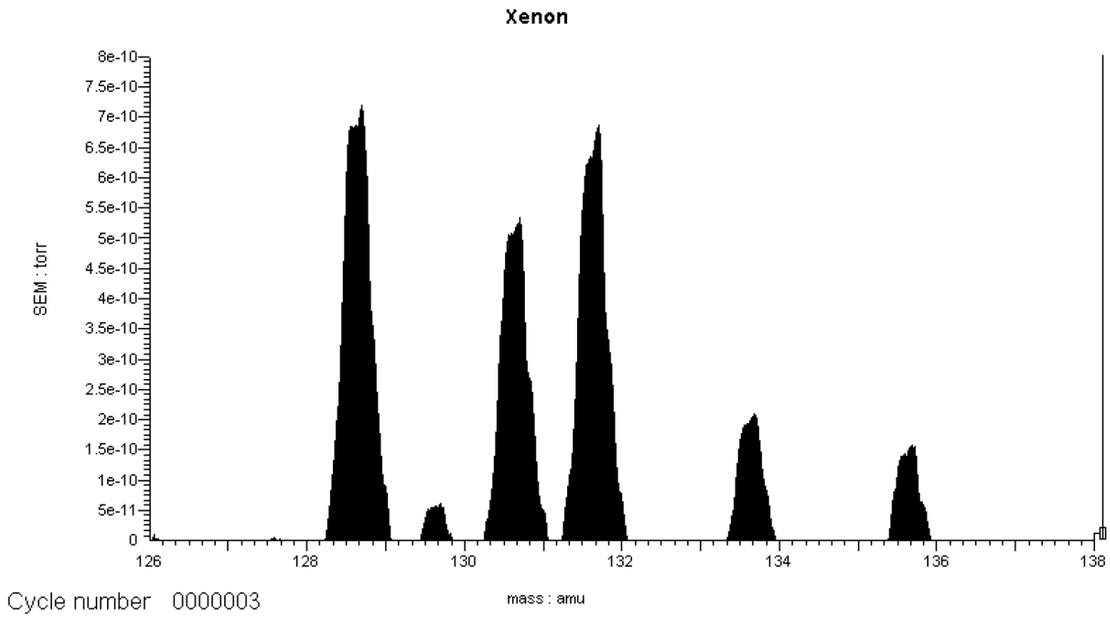
Physics Institute of the University of Bern

Mass spectrometry



Revision History

Revision	Date	Author(s)	Description
1.0	2000	Marcel Merz and Martin Wiesmann	created
1.1	2022	Nicole Schanche	translation and updates
1.2	2022	Nora Hänni	updates and corrections

Contents

1 Introduction

A mass spectrometer is an instrument that allows the components of a gas to be determined, with the separation taking place according to the ratio of mass / charge. The basic structure is the same for all types of instruments. A distinction is made between the ion source, analyzer and detector. There are different types of mass spectrometers:

- Ion trap mass spectrometer
- Time-of-flight mass spectrometer
- Magnetic sector felt mass spectrometer
- Omegatoron
- Quadrupole mass spectrometer

We will focus on the latter as it will be used in this lab.

2 Quadrupole mass spectrometer

2.1 Analyzer

The mass separation takes place through an electrodynamic quadrupole field. Depending on the voltage applied, only particles with certain mass / charge ratios can pass through the quadrupole field and reach the detector. Recording a spectrum therefore requires scanning the corresponding mass range.

2.1.1 Theory of quadrupole fields

A quadrupole field can be described in Cartesian coordinates as follows:

$$\vec{E} = \vec{E}(x, y, z) = E_0 \begin{pmatrix} ax \\ by \\ cz \end{pmatrix} \tag{1}$$

The three spatial directions are not coupled
1. Maxwell's equation:

$$\vec{\nabla}\vec{E} = \frac{\rho_e}{\epsilon_0}$$

Neglecting the space charge ($\rho_e = 0$) follows:

$$\vec{\nabla}\vec{E} = 0 \tag{2}$$

from (1) and (2)

$$E_0(a + b + c) = 0 \longrightarrow a + b + c = 0 \tag{3}$$

Equation (3) can be fulfilled by:

$$\begin{aligned} a &= -b \\ c &= 0 \end{aligned} \tag{4}$$

The $\vec{E}$-field can be described with a scalar potential Φ and a vector potential $\vec{A}$:

$$\vec{E} = -\vec{\nabla}\Phi - \frac{\partial \vec{A}}{\partial t}$$

The time independence of the E-field gives the following:

$$\vec{E} = -\vec{\nabla}\Phi$$

whereby

$$\Phi = -\frac{1}{2}E_0(ax^2 + by^2 + cz^2) \tag{5}$$

from (4) and (5)

$$\Phi = -\frac{1}{2}E_0 a(x^2 - y^2) \tag{6}$$

we get the equipotential lines:

$$\Phi = -\frac{1}{2}E_0 a(x^2 - y^2) = c = constant$$

This equation describes a hyperbola. The associated potential can be generated by a set of hyperbolic cylinders, whereby adjacent electrodes have potentials with opposite signs.

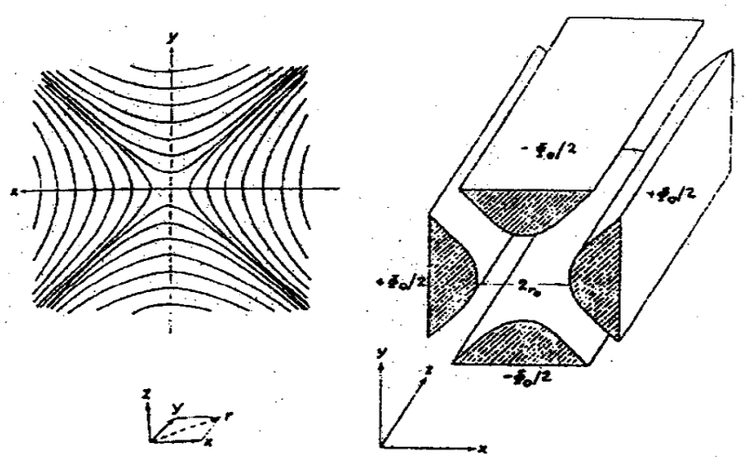


Figure 1: left: equipotential lines of the potential in Eq (6) right: electrode arrangement to generate the potential in Eq (6)

In practice, however, the hyperbolic rods are approximated by round rods, since these can be produced more easily with sufficient mechanical accuracy. In general:

$$U = \int \vec{d}r\vec{E}$$

with the X-component:

$$\int_0^{r_0} dx \frac{2E_0}{r_0} x = -\frac{\Phi_0}{2} \longrightarrow E_0 = -\frac{\Phi_0}{2} \tag{7}$$

From (7) in (6) with the choice of $a = \frac{2}{r_0}$, one obtains for the potential:

$$\Phi = \Phi_0 \frac{x^2 - y^2}{2r_0} \tag{8}$$

The equations of motion for ions with mass m and charge q reads:

$$m\ddot{\vec{r}} = q\vec{E} = -q\vec{\nabla}\Phi \tag{9}$$

From (8) and (9) there are three components

$$\ddot{x} + \left(\frac{q}{mr_0^2}\right)\Phi_0 x = 0 \tag{10}$$

$$\ddot{y} - \left(\frac{q}{mr_0^2}\right)\Phi_0 y = 0 \tag{11}$$

$$\ddot{z} = 0 \tag{12}$$

It can be seen from (12) that the ions move uniformly in the Z direction (towards the detector). The solution for (10) is a sinusoidal oscillation in the XZ plane. The ions will never run through the field exactly on the axis of symmetry and experience a focusing force in the XZ plane, they describe a sinusoidal path. The solution to (11) is an exponential function, the ions experience a defocusing force in the YZ plane and are lost on the walls. At static potentials, only very heavy ions can reach the detector due to the defocusing in the YZ plane.

In order to make stable orbits possible for all masses, an alternating voltage is superimposed on the static potential. The resulting potential now consists of two components. Heavy ions, due to their inertia, are unable to follow the alternating component (alternating voltage). If this is greater than the static potential, the light ions, which can follow the alternating component, tend to have unstable orbits in the XZ plane with increasing deflections. The X-axis thus corresponds to a high-pass mass filter. The opposite is true in the YZ plane. The orbits of light ions can be stabilized by the alternating component at a suitable frequency and order of magnitude. The Y-axis therefore corresponds to a low-pass mass filter.

The two components together result in a mass filter with a certain transmission characteristic. The ion paths (trajectories) are only stable for a small range of the mass / charge ratio, depending on the applied potential.

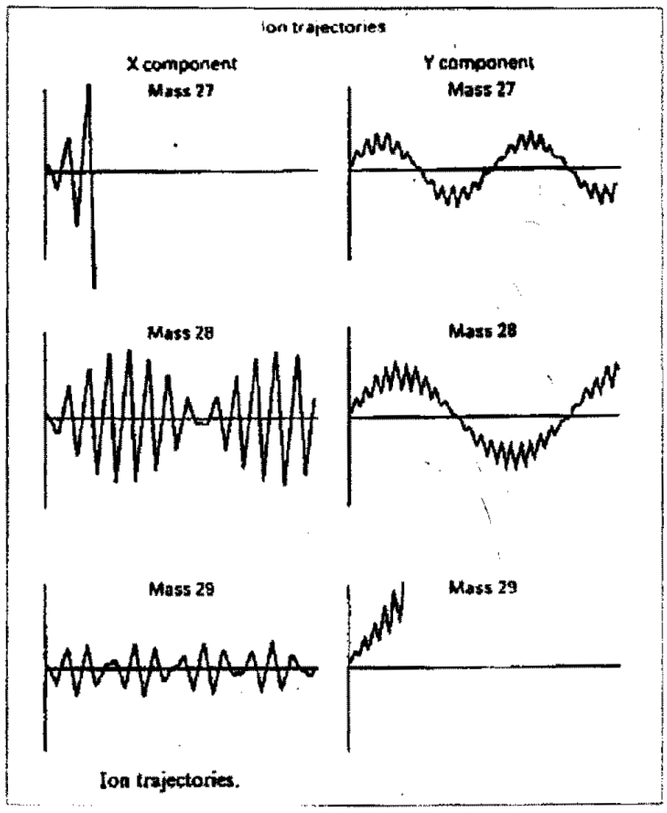


Figure 2: Trajectories of ions of different mass. Top: Light ions follow the alternating voltage and are deflected in the X direction. Middle: Only mass 28 reaches the detector in this example. Bottom: Heavy ions are deflected in the Y direction because they are too slow to be able to follow the alternating voltage.

Specifically, the following potential, consisting of a static and an alternating component, is applied to the electrodes:

$$\Phi_0 = U - V\cos(\omega t)$$

The equations of motion now have the following form:

$$\ddot{x} + \left(\frac{q}{mr_0^2}\right)(U - V\cos(\omega t))x = 0 \tag{13}$$

$$\ddot{y} - \left(\frac{q}{mr_0^2}\right)(U - V\cos(\omega t))y = 0 \tag{14}$$

$$\ddot{z} = 0$$

Equations 13 and 14 are special cases of Matthieu's differential equations. A further discussion can be found in [1] from page 114.

2.1.2 Stability diagram

In order for an ion to reach the detector, there must be a stable path in both the X and Y directions. The stability diagram shows those areas in which there is stability in both directions. We define the following quantities:

$$a = \frac{4eU}{m\omega^2 r_0^2} \quad q = \frac{2eV}{m\omega^2 r_0^2} \tag{15}$$

The quotient $v = \frac{a}{q} = \frac{2U}{V}$ is independent of the mass / charge ratio and corresponds to the slope of the so-called working line. Of the various options for recording a mass spectrum with the mass filter, the one in which the frequency ω and the voltage behavior v are fixed while the voltages U and $V = \frac{2U}{v}$ are varied is usually chosen. Figure 3 shows that the ratio $v = 0.2$ provides all parameter values q in the area $q_1 ... q_2$, i.e. after Equation 15 in the area $m_1 ... m_2$, stable trajectories. By approximating v to $v = 0.336$, one reduces the mass range that is allowed to pass through.

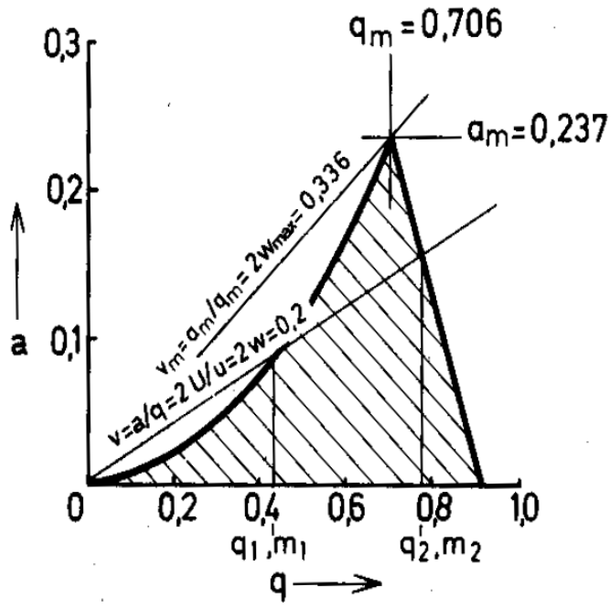


Figure 3: Stability diagram with two different working lines and a hatched stable area

2.1.3 Resolution

The resolution describes the ability of the spectrometer to separate different mass / charge ratios. A common definition for mass spectrometers: Resolution r (resolution): $r_{10} = \frac{m}{\Delta m}$ (where Δm is measured at 10% of the signal peak)

This means that neighboring signals of the same height are well resolved, but the definition leaves open the problem of detecting small signals next to a large signal. Depending on the transmission characteristics of the quadrupole, the peaks of the individual masses can no longer be distinguished from one another. By adapting the working line, however, the resolution can be improved at the expense of the signal intensity:

low resolution $\Longleftrightarrow$ high intensity
high resolution $\Longleftrightarrow$ low intensity

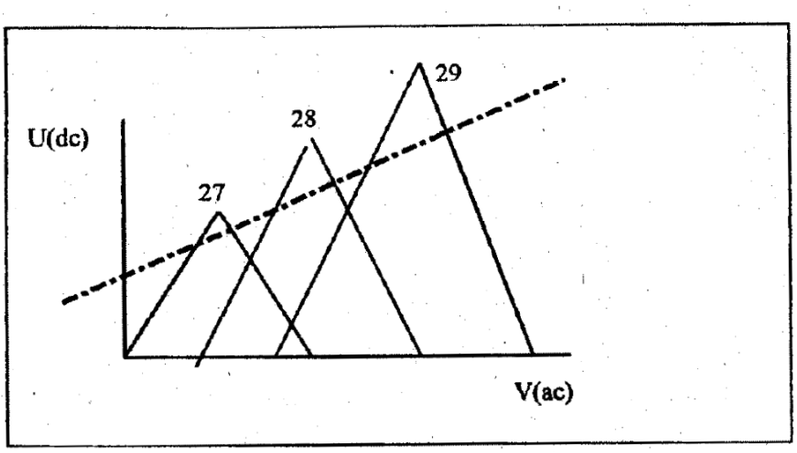


Figure 4: Working line that guarantees a good resolution. The stable areas of the masses 27, 28, 29 do not overlap in the area of the straight lines, but their peaks are correspondingly smaller.

The operating software contains the two parameters *resolution* and *delta-m* to influence the resolution:

resolution: Incline of the working line (greater influence with high masses)
delta-m: Y-axis intercept of the working line (greater influence with low masses)

2.2 Ion Source

So that a mass separation can be carried out in the analyzer, the gas particles in the sample must first be ionized in the ion source. In the ion source of the practical experiment, this is done by electron impact ionization. Electrons emerge from a glowing filament, which are then accelerated in an electric field (between 1 and 2 in Figure 5 with a standard acceleration voltage of 70V). In the sample chamber, the electrons flow

together with the uncharged gas atoms or molecules, causing them to be ionized (requirement: ionization energy $\leq$ electron energy). Essentially, positively charged ions are simply generated. The ionized atoms or molecules are accelerated towards the analyzer and detector.

Various factors influence the ionization yield:

- The stronger the electric current is chosen through the filament, the more electrons are emitted (however, there is no more linear relationship).
- With increasing acceleration voltage, the electron energy and thus the ionization capacity grows (the ionization cross-section is a maximum of about 70 eV).
- Ionization cross-section of the sample gas.
- Mean free path of the electrons in the ionization volume (= pressure).

It should also be noted that in the case of molecules, in addition to ionization through electron impacts, fragments of the molecules are also generated (fragmentation). As the electron energy increases, the likelihood of multiple ionization and fragmentation increases. The probability of a single ionization is about an order of magnitude higher than that of multiple ionization.

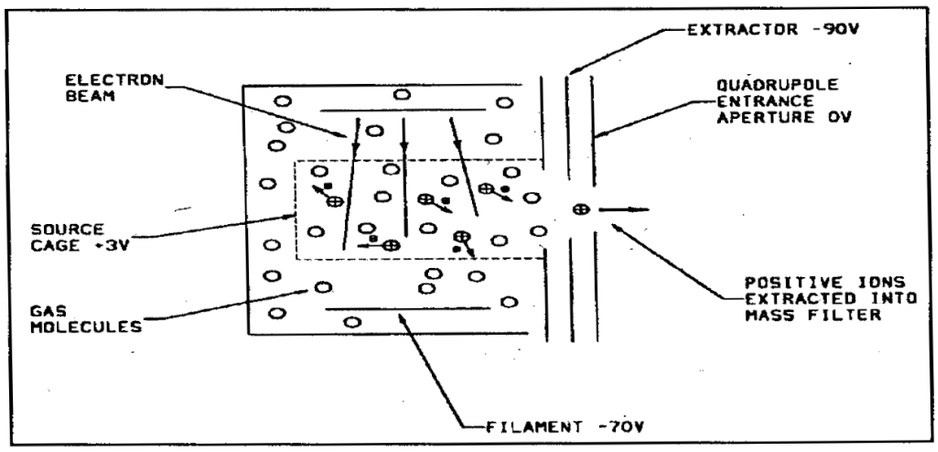


Figure 5: Schematic representation of the ion source.

2.3 Detectors

The ion current is measured in the detector. The spectrometer in the lab offers two detectors to choose from: the Faraday cup detector and the secondary electron multiplier.

2.3.1 Faraday cup

The Faraday cup (FC) detector consists of a passive conductive surface (collector) on which the ions impinge. The resulting electron current is measured with a sensitive electrometer using an amplifier. Secondary electrons, generated by the impacting ions, are suppressed by a suppressor electrode in order to prevent the measurement from being falsified. The detection limit is at a partial pressure of approx 10^{-11} Torr, which corresponds to an ion stream of approx 10^{-15} amperes.

2.3.2 Secondary electron multiplier

The secondary electron multiplier (SEM), also called Channeltron, has a surface that can emit secondary electrons. A single ion or electron hitting the surface of the detector generates two to three additional electrons, which are accelerated in the electrical field of the SEM. Each of these electrons carries out further collisions on the surface, so that ultimately an electron avalanche occurs. The power for generating this electron avalanche is provided by a high voltage (800-3000 Volts) applied to the SEM. The gain that can be achieved with an SEM is in the range of 10^2 to 10^8. The effective improvement of the detection sensitivity is limited by the noise of the ion statistics (Poisson distribution). A partial pressure of 10^{-14} Torr results in an ion current of 6 ions / second. Because of the ion statistics alone, the noise is therefore $\frac{\sqrt{6}}{6} = 40\%$. The minimum detectable partial pressure is therefore in the range of 10^{-14} Torr.

Due to the constant bombardment of the surface layer, it is subject to an aging process. With a correspondingly higher voltage, the aging can be compensated within certain limits. Another problem can occur at high voltage (3000V) and a bad vacuum, the so-called ionic feedback: the electron avalanche collides with one or more positive ions against the output of the Channeltron, which are accelerated back to the entrance by the electric field, where they trigger another electron avalanche trigger and thus generate multiple pulses. In order to suppress this feedback, the Channeltrons have a curved geometry.

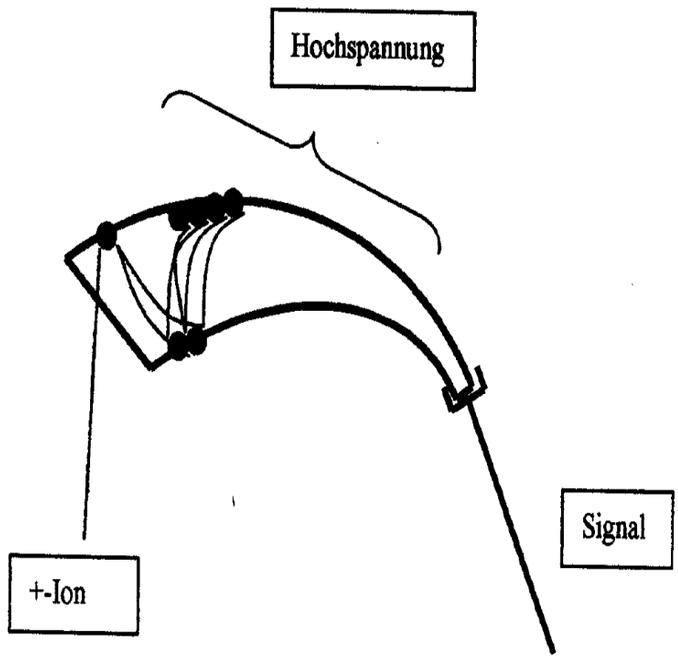


Figure 6: Schematic representation of a Channeltron (Hochspannung=High Voltage).

3 Hardware: experimental setup

3.1 System description

In the sample reservoir, between the gas and capillary valve, a rotary vane vacuum pump is used to create a fore-vacuum. The pressure is measured with a Kistler cell. The gas sample is admitted from the sample reservoir via the inlet system (valves B & E) into the measuring unit of the mass spectrometer. There is a high vacuum of approx. 10^{-8} mbar in the measuring unit. It is produced by two pumps connected in series. The membrane pump works against air pressure and creates a fore vacuum of 10^{-3} mbar. The downstream turbo-molecular pump requires this fore-vacuum because it cannot pump against atmospheric pressure. It creates a high vacuum of 10^{-7} to 10^{-8} mbar.

3.2 Operation instructions

1. Pump out the sample reservoir: Open the vacuum valve (V). Close capillary valve (K) & gas valve (G). Switch on the pressure measuring device (gray box with red display). The pressure should be 0 mbar.

2. Admit the gas sample: close the vacuum valve and open the gas valve. The measuring device shows the pressure increase in the sample reservoir. Then close the gas valve again.

3. The inlet system: Open the bypass valve (B) a little. Open inlet valve (E) only a few degrees. Monitor the pressure on the green display of the pump system. It must not rise above $2 * 10^{-6}$ mbar. The capillary valve (K) can now be opened. The flow of the gas sample can be recognized by the falling pressure in the sample reservoir.

4. Ending the gas inlet: Close capillary valve & inlet valve. The bypass valve can remain open. In this way, the remaining gas components in the mass spectrometer are extracted more quickly.

3.3 Cooling system

The system has air cooling (built-in fan) and water cooling. The water cooling must be permanently in operation while working with the mass spectrometer. To do this, flip the switch on the unit on the floor and watch the flow meter.

3.4 Heating system

Water vapor enters the system with the ambient air. This then precipitates as condensate on the walls of the mass spectrometer. By heating the capillary, the inlet system and the quadrupole, the adhesive forces between the molecules and the inner walls are overcome. The steam is then sucked off by the turbo molecular pump with the residual gas. The heating does not have to be switched on for measurements with noble gases. When measuring breathing gas, water vapor enters the system. The capillary heating and heating A (overview) must be put into operation approx. 5 minutes before the measurement: Turn on the orange switch on the front of the spectrometer. The temperature in the capillary and inlet system rises above 100° C. This prevents condensation of the water vapor present in the breathing air.

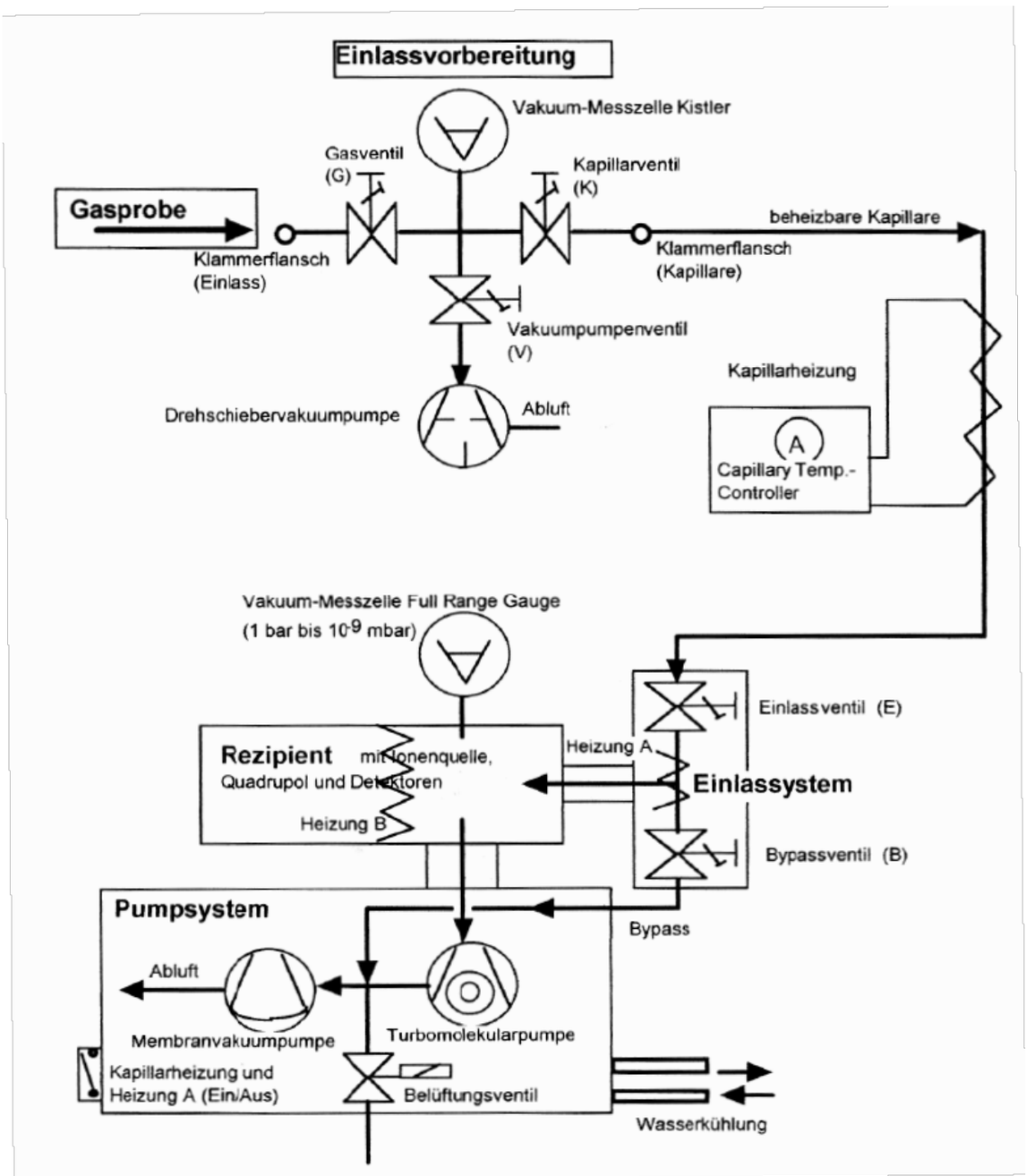


Figure 7: Schematic overview of the vacuum and inlet system

3.5 Additional information

If the pressure in the measuring unit rises above 10^{-5} mbar, the ion source and detector are automatically switched off. This prevents damage from electrical discharges and filament burns. The keypad on the front of the pump system may only be operated by the assistant. From time to time the recipient and the inlet system should be baked out in order to maintain the quality of the vacuum and to pump off the condensates on the inner walls. In addition to the capillary heating and heating A (see above), heating B must be switched on. Heater B consists of a heating tape wrapped around the flanges of the quadrupole. It is connected to a Variac (adjustable transformer) under the table with a red and blue cable (setting: 90V). To put the heater into operation, all you have to do is plug in the power plug of the Variac. It should be heated for at least 30 minutes, ideally at least 2 hours. ONLY RESUME MEASUREMENTS WHEN COOLED AGAIN.

4 Software and data evaluation

The Hiden Analytical program is used to control the mass spectrometer and monitor the data acquisition. The program runs under Windows 3.11. First enter *win* after the computer has started up. Then select the MASoft program in the Hiden Applications window.

4.1 Measurement Modes

Before you can start recording a spectrum, you must define the measurement mode. Click 'Gallery' on the command line. Four different measurement modes are available:

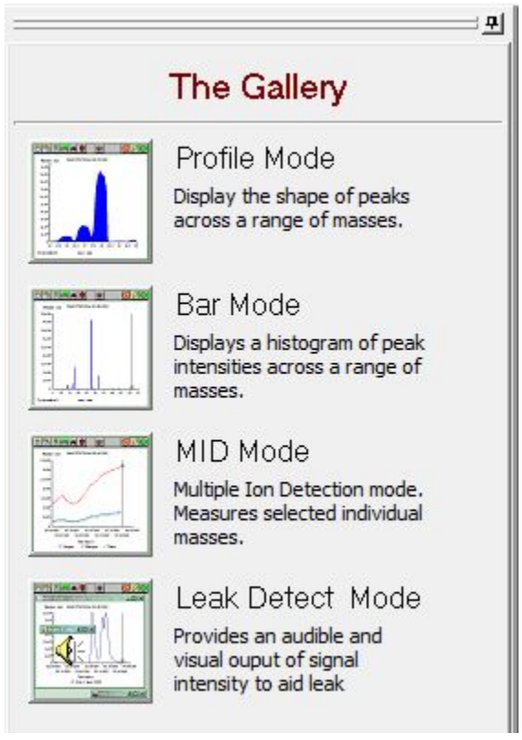


Figure 8: Gallery.

Only the first three modes are required for the lab. Continuous mass spectra can be recorded with bar and profile modes.

4.2 Setting the Parameters

4.2.1 Profile and Bar Modes

Enter the desired measuring range with Start / Stop mass. Then select the detector and the number of measuring points. The spectrum title can be entered under View title. Select values between -10 and -5 for the detection sensitivity (acquisition range). Lin / Log for displaying the Y-axis.

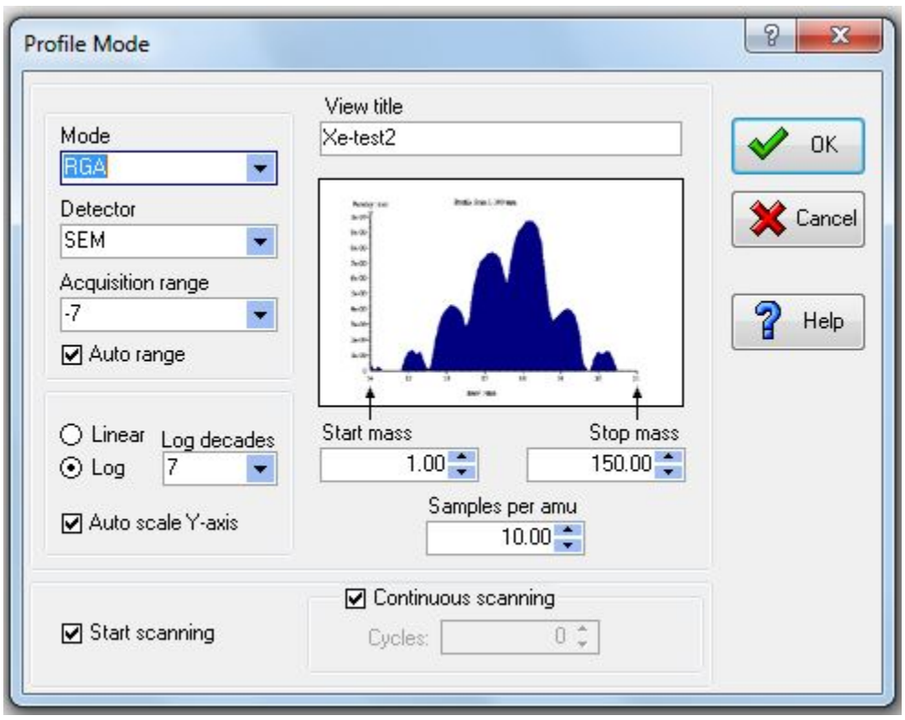


Figure 9: Profile mode.

4.2.2 MID Mode

The elements or molecules to be detected are to be entered under Details. Select the name, mass and color of the graph and add it to the list with Add. List elements can be deleted again with Delete. The racing car must be completely visible in the keypad (speed of the data acquisition).

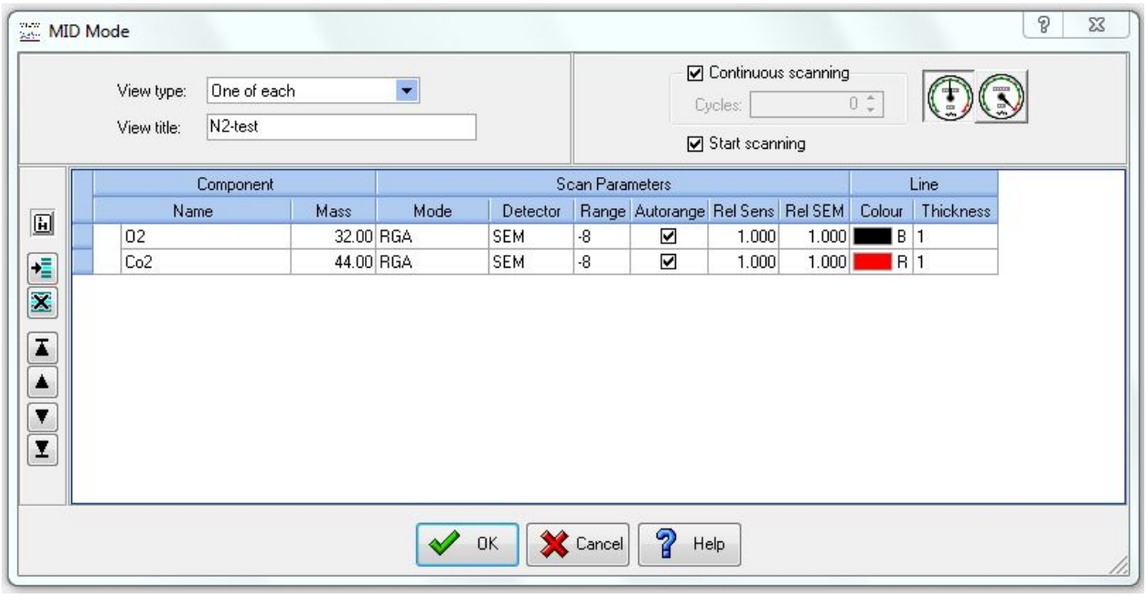


Figure 10: MID mode.

4.3 Traffic light symbols

Figure 11: Menu options.

4.4 Graphics window

After the data acquisition has started, a graphic window and a first window appear. The section and the scaling can be set by double-clicking on the axes. The spectrum title can be set under 'Views', 'Graphical'.

4.5 Block diagram

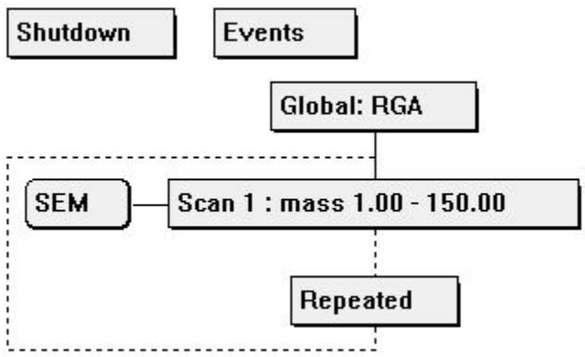


Figure 12: Block diagram.

Global RGA: Among other things, the following parameters can be set in the Environment Editor window (typical values in brackets):

- resolution (0)
- delta-m (50)
- electron-energy (70 eV)

Scan mass: mass range and number of measuring points.
SEM / Faraday: detector.
Repeated: number of cycles or continuous scanning.

4.6 Subtraction of measured blank spectra

It makes sense to record a residual gas spectrum immediately before admitting the gas sample. This can then be subtracted from the spectrum. Both measurements must be opened with the graphics window. Enter the command Tile vertical under Window. Now activate the RG spectrum and choose under Views, Source view. Then activate the second graphic and select the Background subtract command again under View.

4.7 Saving and loading spectra

Since you will record and save different spectra, it is recommended that you set up your own folder on the hard drive so that you have all your data together and can find them again quickly. To save a recorded spectrum, select under 'File' 'Save' or 'Save as'. You need 'Save as' when you save a spectrum for the first time, as you can determine the name and location of the file there.
To call up saved data select under 'File' 'Open'.
If you not only want to view the last scan pass (cycle), but also all other passes, then you can do this under 'Views': 'Graphical': 'Mode': 'Historical Data'.
When opening saved measurements, only the block diagram appears. To open the associated graphic window, click once on Scan mass, then click on the binoculars icon in the command line.

4.8 Data processing with Origin

The measurement data can be further processed with the Origin program. In particular, the areas under the measured mass profile can be calculated.

Export data to Origin: Open the file with the graphics window. Select the Export command under 'File'. In the Save as window, select AsciFiles and the name of the file (*.csv). Enter the number of scan cycles in the Cycles section window.

Now start the Origin program.

Select the Import command under 'File' and open the desired file in the 'File open' window.

Edit data: Activate the measurement data and display it with a plot (line). Click on the axes and set zero so that it can be integrated. Select under Analytical Integration and set the integration limits with the opposite arrows. Note: Data can be evaluated with any other program of personal preference.

5 Important information before you start

- Keep the door open when you are inside the lab. NEVER WORK ALONE.
- Starting up the computer needs a USER (praktikum) and a PASSWORD (ms-versuch)
- Familiarize yourself with the system and the operation of the software before you start to experiment. Ask the assistant for help if you are unsure what to do.

- If you want to measure, switch on the control unit of the spectrometer BEFORE you start the MASoft program.
- You can only measure when the pressure is low enough (sp1 is ON on the display of the measuring unit), otherwise you will get an error signal (red light and beeping sound).
- Always do the pumping of volumes carefully and as described in the script. The turbo pump is very sensitive!
- Always operate just one filament, never both! At the moment, one of the filaments is broken. The filament block will be replaced when also the remaining one does not work anymore.
- Make sure to put the system into standby mode (shutdown environment) if you are not recording spectra.
- The heating system has a separate switch. To be sure no voltages/currents are applied, switch it off if you are not heating. NEVER touch the experiment when the heating is on and make sure the warning sign is visible to others.
- The Variac can be operated at max. voltages of 60 V - not more. Make sure to increase the voltage STEPWISE!
- Always let the system cool down to RT after heating before you measure.
- For security, the computer can not be connected to the internet. To get the data for analysis on your own machine, transfer it using a USB memory device. All memory devices MUST BE SCANNED for malware before use.
- Small programs written for data evaluation, such as Python scripts, should be included in the APPENDIX of your report!
- Master students MUST write their report in English, Bachelor students are strongly encouraged to do so too.
- Use the MS database from the National Institute of Standards and Technology (NIST) and the Nuclide Table for isotopic distributions as a basis to interpret your data.

6 Tasks

Learning objectives are formulated for each experimental task. The goals serve as a guide to the level of learning growth that you should achieve. You can also use the goals to structure your report.

6.1 Residual gas spectrum

Objectives: Record and evaluate/discuss a residual gas spectrum.

6.2 Test operating parameters

Objectives: Based on a residual gas analysis, investigate/discuss the influence of the operating parameters 'resolution', 'delta-m' and electron energy (70 eV +- 20 eV) and explore/discuss the differences between the SEM and FC detectors also in terms of advantages and disadvantages.

6.3 Noble gas isotopes

Objectives: Determine the isotope proportions of two different noble gases (choices are argon, krypton or xenon). Compare the experimental isotope distribution with expected (terrestrial) values and discuss possible deviations. Can you see multiply charged cations?
Procedure: Use the inlet for gaseous samples.

6.4 Unknown gas mixture

Objectives: Identify the composition of an unknown gas mixture and quantify the different components.
Procedure: Use the inlet for gaseous samples.

6.5 Breath analysis

Objectives: Measure the change over time in the proportions of oxygen and carbon dioxide between inhaled and exhaled air.
Procedure: Take an online measurement of a sequence of 'breath samples' using balloons for inhaling/exhaling the same air multiple times.

6.6 Alcohol measurement

Objectives: Measure technical ethanol and vodka and compare/contrast the two samples regarding purity, etc.
Procedure: Use the inlet system for liquid samples.
Optional: Examine the air you breathe after consuming an alcoholic beverage, trying to detect the alcohol.
Note: You must provide your own alcohol, the vodka in the lab is not suitable for use. Only one group member can consume the alcohol for safety reasons.

6.7 Additional measurement

Objectives: Design an additional experiment with a specific sample that you want to analyze (suitable inlet system etc.). Note: Only perform the experiment upon consultation with the lab assistant. Use the spectrum to determine the components of your sample.
Some ideas:

- Determine the composition of the gas-filling of an energy-saving lamp.
- Determine the composition of a deodorant spray.

7 Theoretical exercises

Before carrying out the experiment, the following tasks must be completed and discussed with the assistant.

7.1 Exercise 1

A gas mixture consists of the components methane, nitrogen and propane. The following peak heights are measured:

1.0012 V on Mass 16
0.896 V on Mass 28
0.753 V on Mass 29

The sensitivity of the mass spectrometer was determined as follows:

10 volts/Torr for methane on Mass 16
15 volts/Torr for nitrogen on Mass 28
5 volts/Torr for propane on Mass 29

In addition, the following peak height ratios were measured in the individual pure gases:

Methane 28/16 = 0; 29/16 = 0
Nitrogen 29/28 = 0.00769; 16/28 = 0
Propane 28/29 = 0.595; 16/29 = 0.0016

Determine the partial pressures of the individual components in the reservoir.

7.2 Exercise 2

Argon was extracted from 7 mg of a lunar soil sample from the Apollo 17 mission and the following peak heights were determined:

40/36 = 0.9800
40/38 = 5.191

Then $1.415*10^{-5}$ cc (STP) normal argon (from air) was added and the peak height ratios (sample & comparison amount) were determined:

40/36 = 7.747
40/38 = 40.86

The blank of the apparatus is 10^{-8} cc (STP) (isotopic composition like air argon) and the discrimination D(36/40) = 0.998.

Calculate the ^{40}Ar content (in cc / g) of the moon sample and the true ^{40}Ar/^{36}Ar and ^{40}Ar/^{38}Ar ratios (corrected with the blank.

Consider the basic advantages of such an isotope dilution method.

8 Bibliography

[1] Script mass spectrometry and ion optics, Prof. P. Eberhardt, Uni Bern.

MASsoft User Manual, Hiden Analytical.

Vacuum manuals, Hiden Analytical.

Introduction HAL LC, Hiden Analytical.

Vacuum technology Handbook, Wutz, Adam, Walcher, Vieweg, 6th edition (ISBN 3-528-44884-9 25450).