***Quadrupole Mass Spectrometer** were invented 1958 at the University of Bonn by*

Paul, Steinwedel, von Zahn

1962 Start of development in Liechtenstein for industrial use

(based on a licence from Siemens)

First applications were residual gas analysis vacuum diagnostics

because these instruments are rather small and easy to be transported/installed compared to magnetic MS

Now these instruments are used as „intelligent sensor“ in various industrial and scientific applications

Now „Q-poles“ are used in various applications:

- Single units for vacuum-diagnostics
- Process Monitors
- Detector for SIMS
- Bench-Top Instruments
- GC-MS for trace analysis
- Plasma Diagnostics
- Endpoint Detection for Etching in the gas phase
- Breath gas analysis
- .
- .
- Integration into environmental analysis systems

Quadrupole Mass Spectrometer

as RGA’s

in UHV and XHV

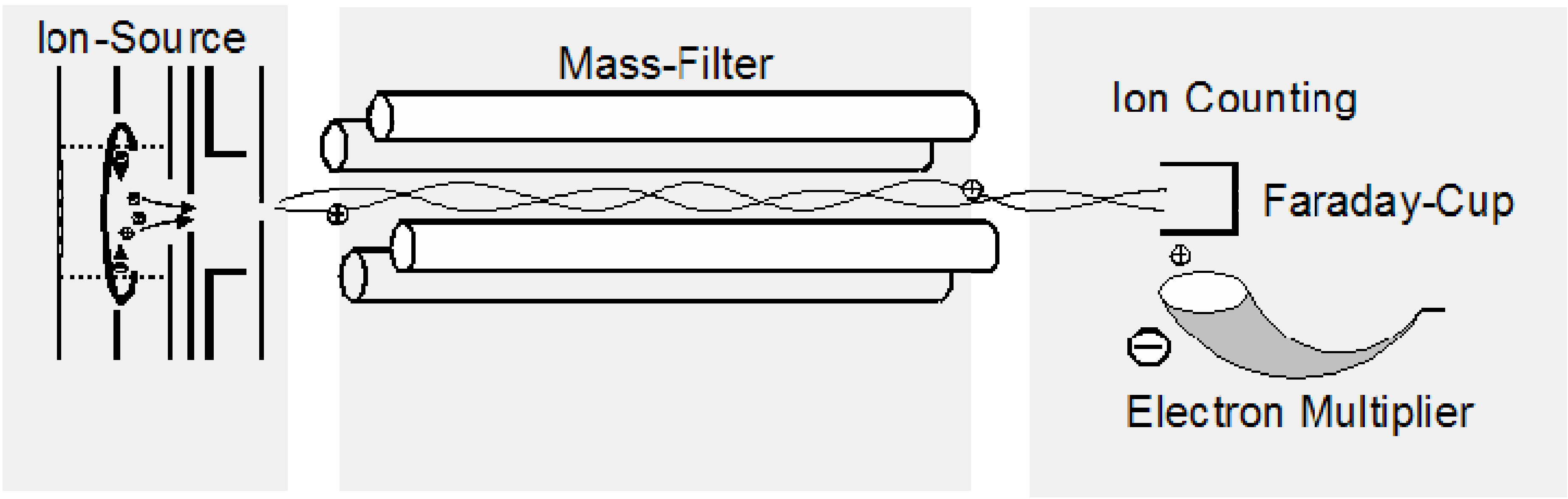
What is the difference compared to a partial pressure gauge for HV-Applications?

Scope of this lesson:

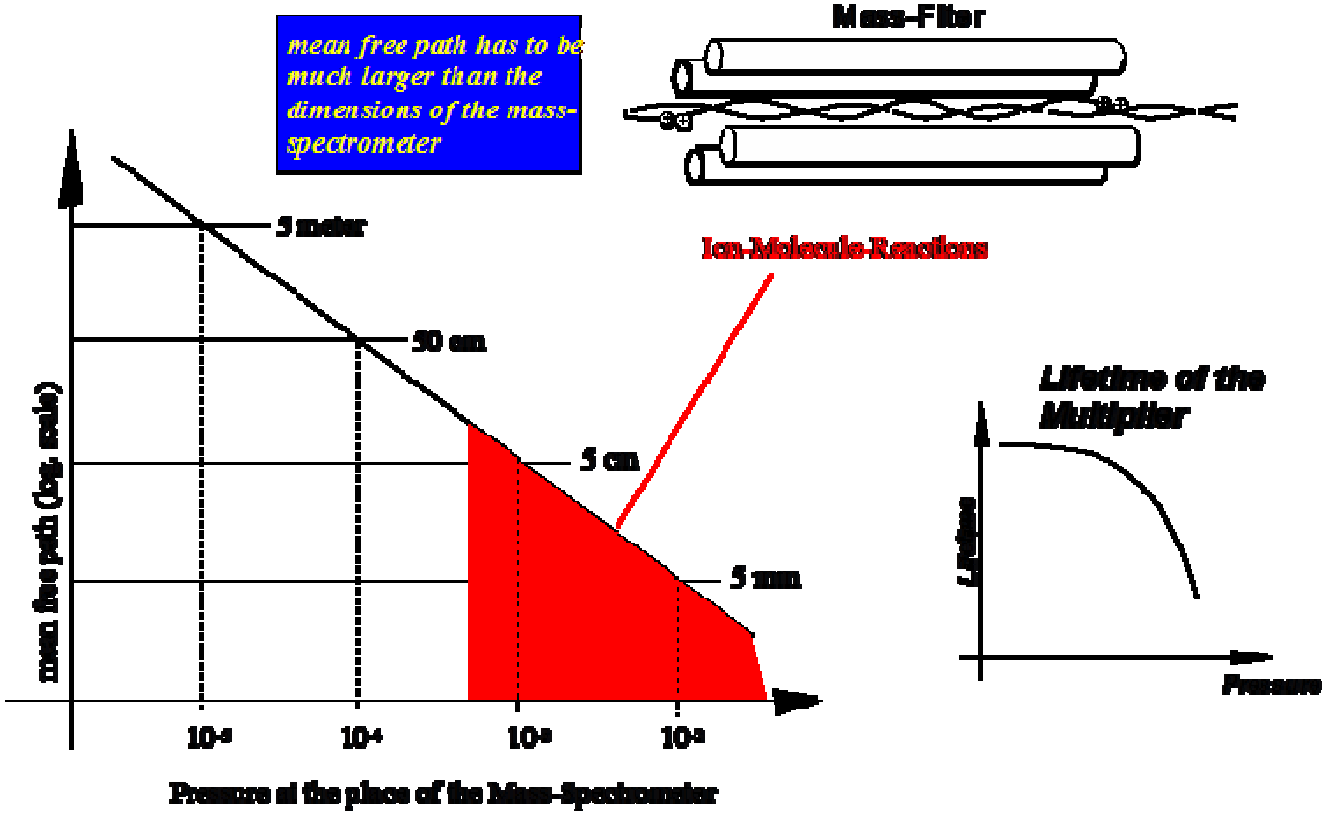
- Principle of Operation, functional units of an “RGA”
- Interpretation of Spectra
- Calibration, detectors, electron energy
- Key Features of quadrupole mass spectrometers
- → XHV/UHV
- Demands to a Partial Pressure Gauge in the UHV/XHV
- Technical Solution
- How to bake an RGA, cold spots
- Residual gas spectra in the UHV and artefacts (EID-Ions)

Partial Pressure Gauges

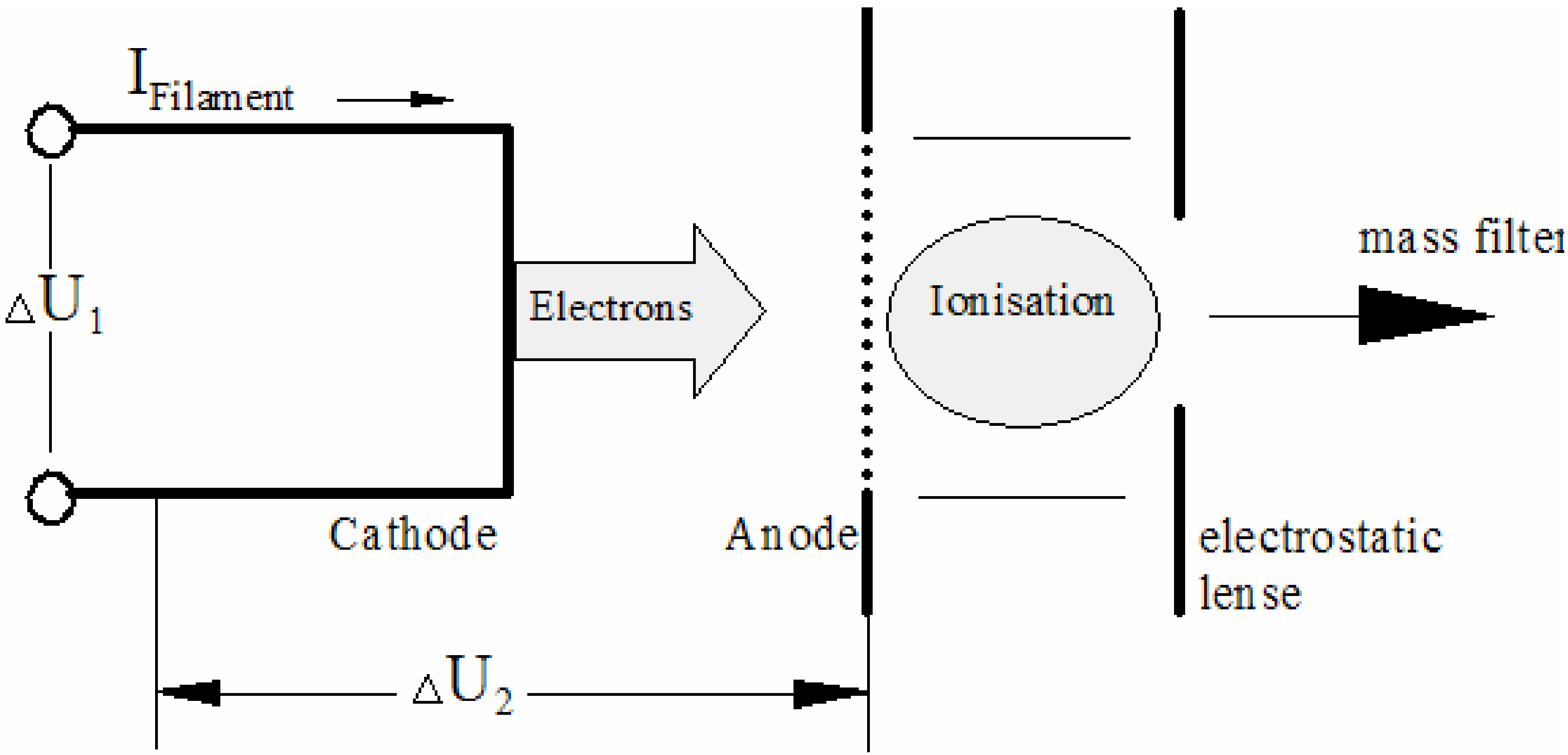
Functional units of a quadrupole mass spectrometer



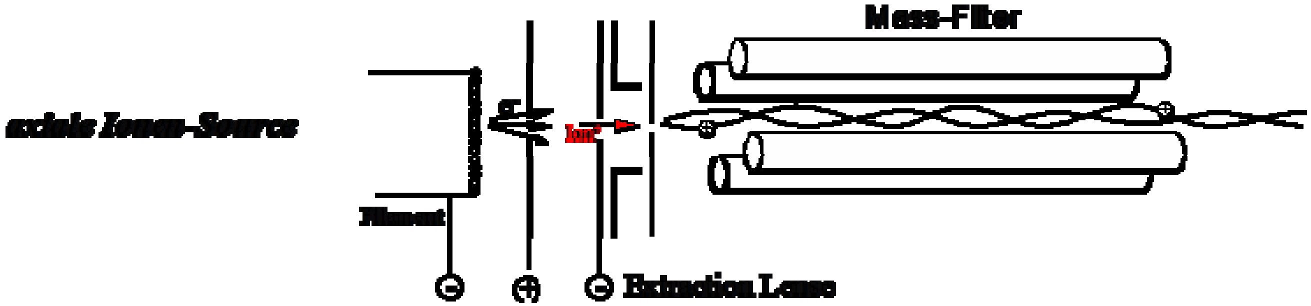
Requirements to operate a quadrupole mass spectrometer

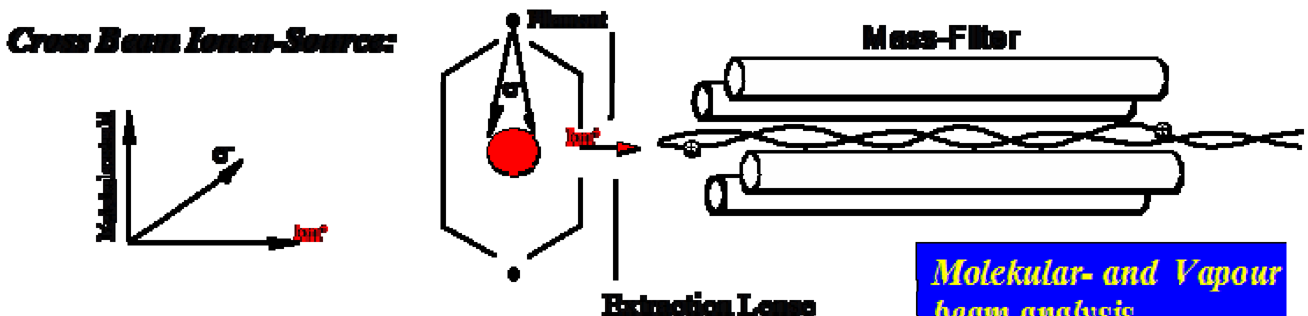


Ionisation, Ion Sources:



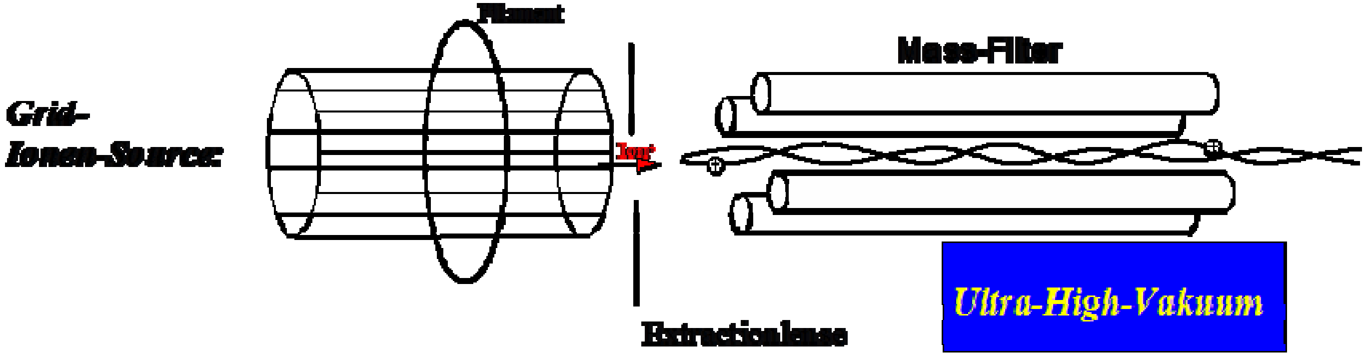
Ionisation, Ion Sources:

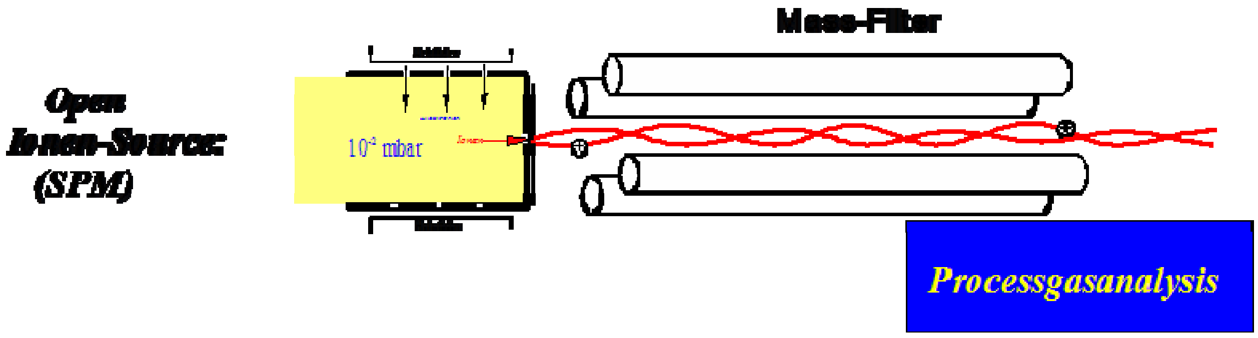




Molekular- and Vapour beam analysis

Ionisation, Ion Sources:





Ionisation, Ion Sources:

Surface is minimized,
therefore
minimum degassing
minimum artefacts from
electron impact desorption

only metal or Al_2O_3 used
gaps avoided
and
threads have additional holes
for easy degassing

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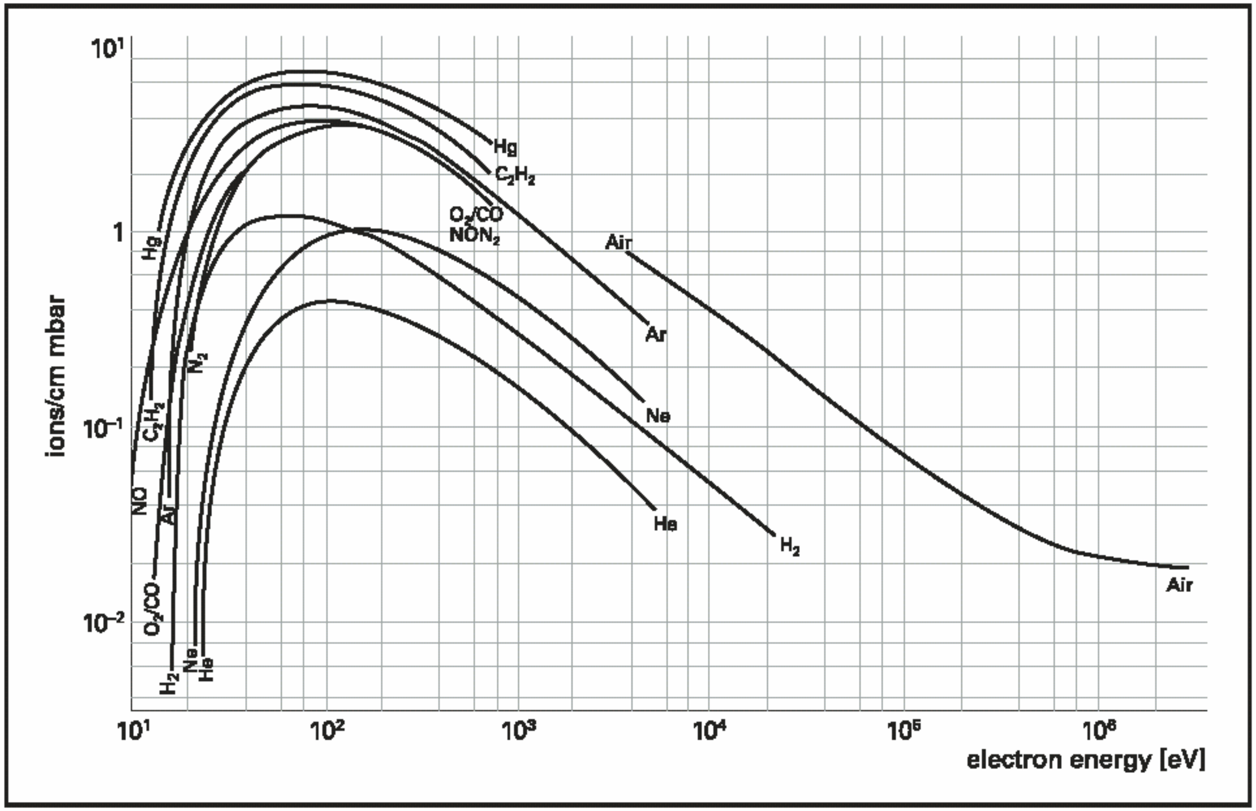
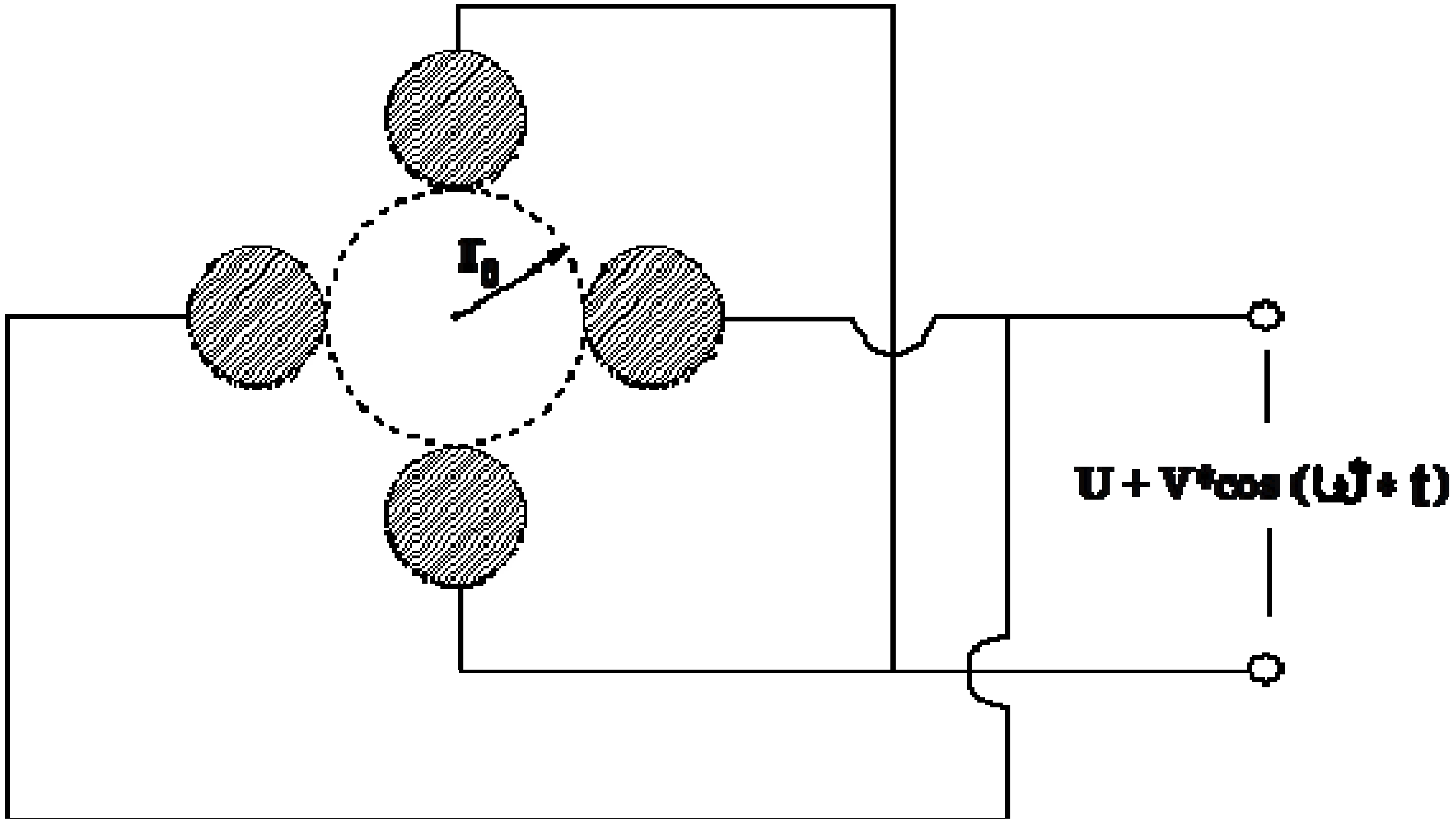
Ionisation, Ion Sources:

Because electron impact ionisation is applied, it's a gas specific gauge:



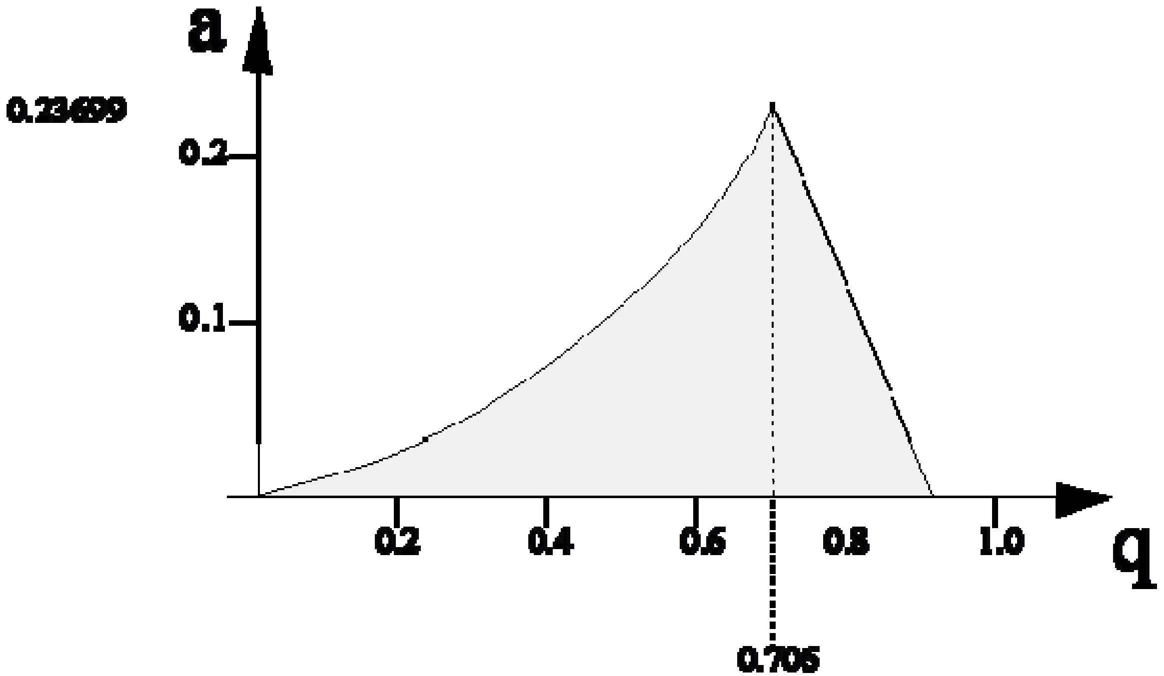
Mass separation in an electrical field:

Mass separation in an electrical field:



Mass separation in an electrical field:

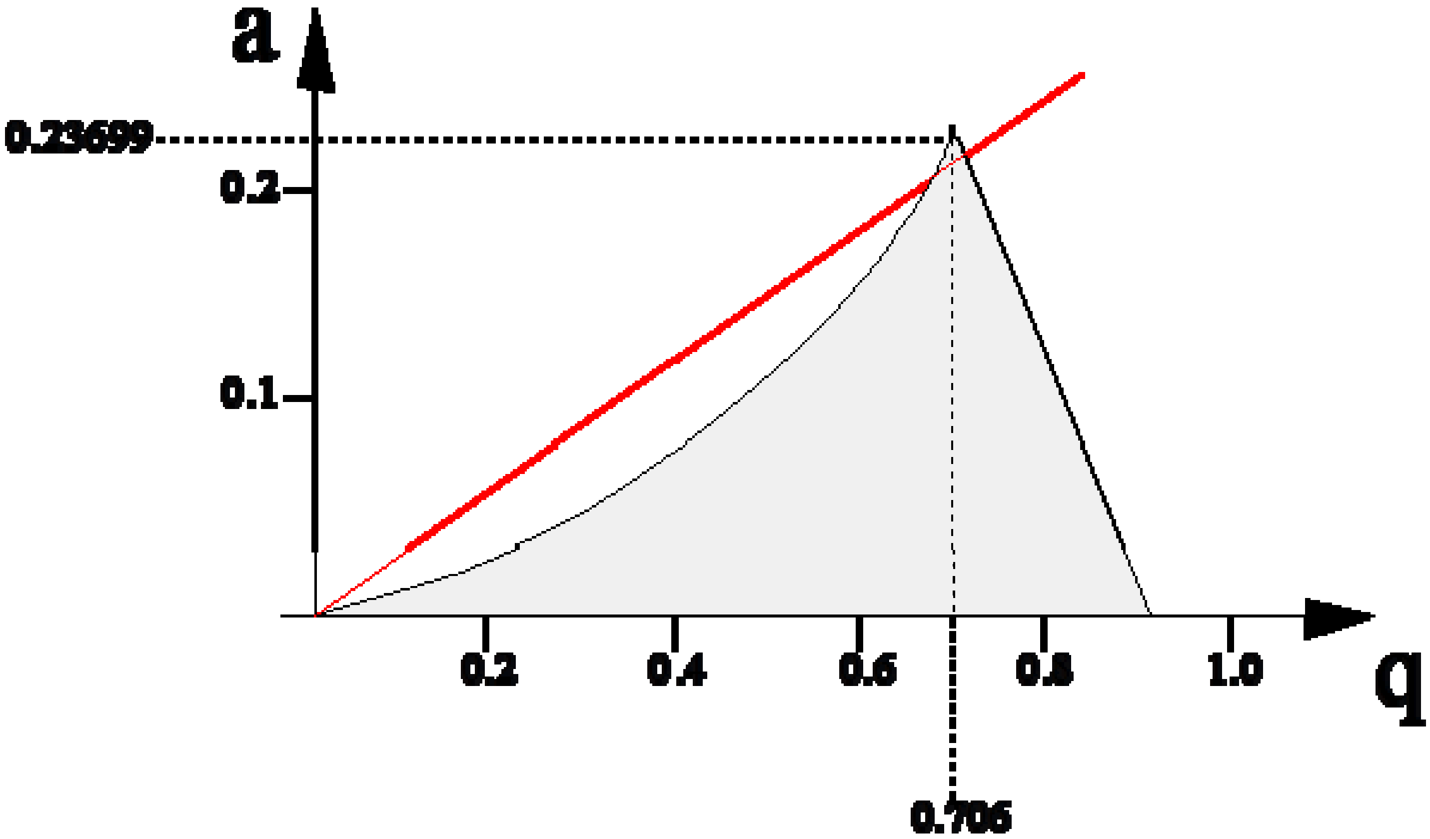
Only ions with a well defined m/e ratio can achieve stable trajectories in the Rf-field



$$a = \frac{8 * e * U}{m * r_0^2 * \omega^2}$$

$$q = \frac{4 * e * V}{m * r_0^2 * \omega^2}$$

Mass separation in an electrical field:



Mass separation in an electrical field:

The ratio U/V is kept constant; the absolute value
Is increased starting from zero:

First ions with m/e = 1 enter the stability diagram,
then ions with m/e = 2 enter the stability diagram
………………….

The value of U/V which results in a stable trajectory
is a linear function of the mass.

Increasing U/V from zero results in a linear mass scale

Mass separation in an electrical field:

For the user of a quadrupole mass spectrometer it is less important to be "able to solve the Mathieu's differential equations"

Important to keep in mind:

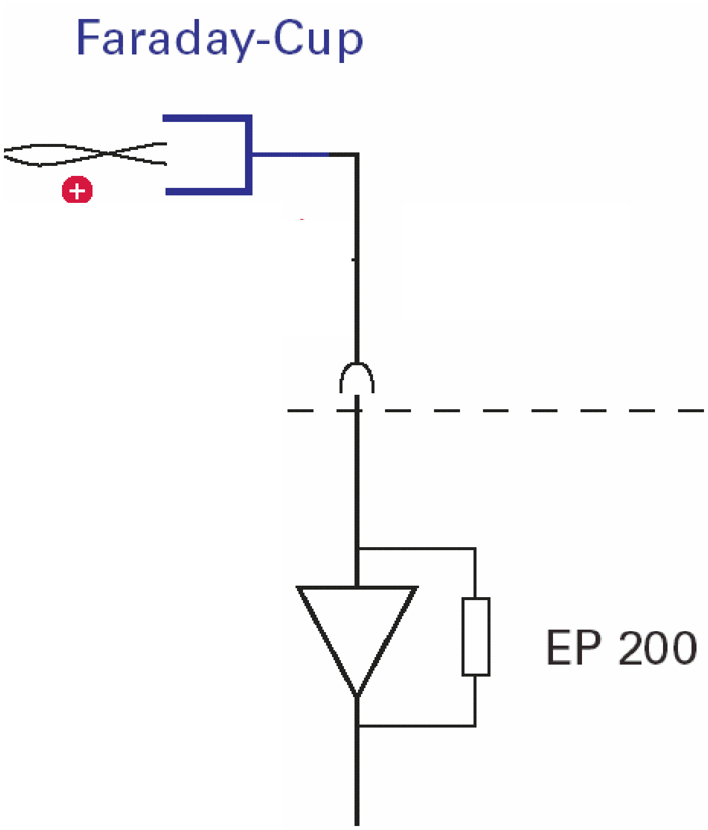
- The required mechanical precision of the filter is in the range of microns
- The stability and precision of the applied Rf-frequency determines the performance of the mass filter in addition
- The inner range of the filter has to be absolutely clean; small dielectric particles and or coatings may lead to a poor performance

Detectors

Ions leaving the quadrupole mass spectrometer fly into a *Faraday-Cup* and give off their charge

Charge is measured as a current by an electrometer amplifier

Measurable currents are from 1E-15 to 1E-8 A

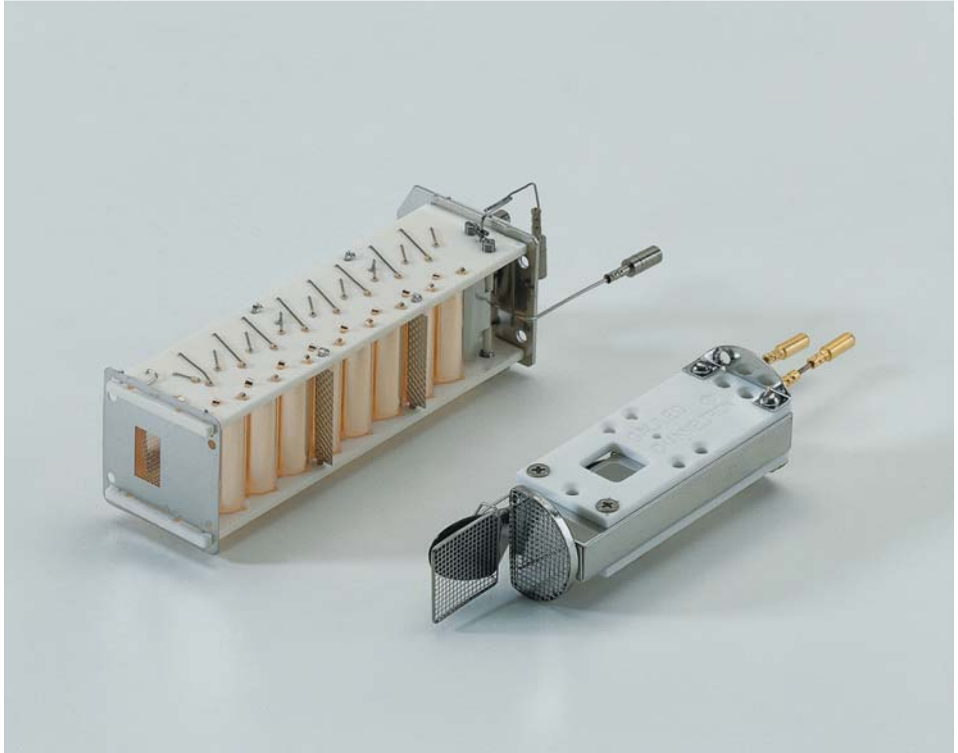


Detectors

Secondary Electron Multipliers

SEM 217,
17 discrete dynodes

Channeltron^{TM},
continuous dynode
(incl. Faraday Detector)



Detectors

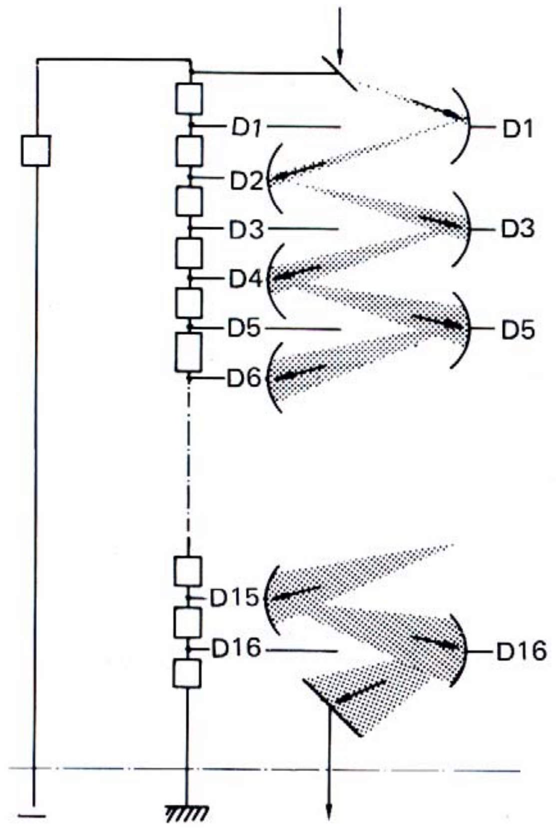
Particles (ions, neutrals, electrons, photons) hitting a surface with high energy release several „secondary electrons“

Use of several dynodes allows for an amplification of up to 10^8

Low ion currents can be detected easily

Measuring range 1E-15 to 1E-5A

„Counting“ of individual electron bursts allows for the detection of single ions (1E-19A)



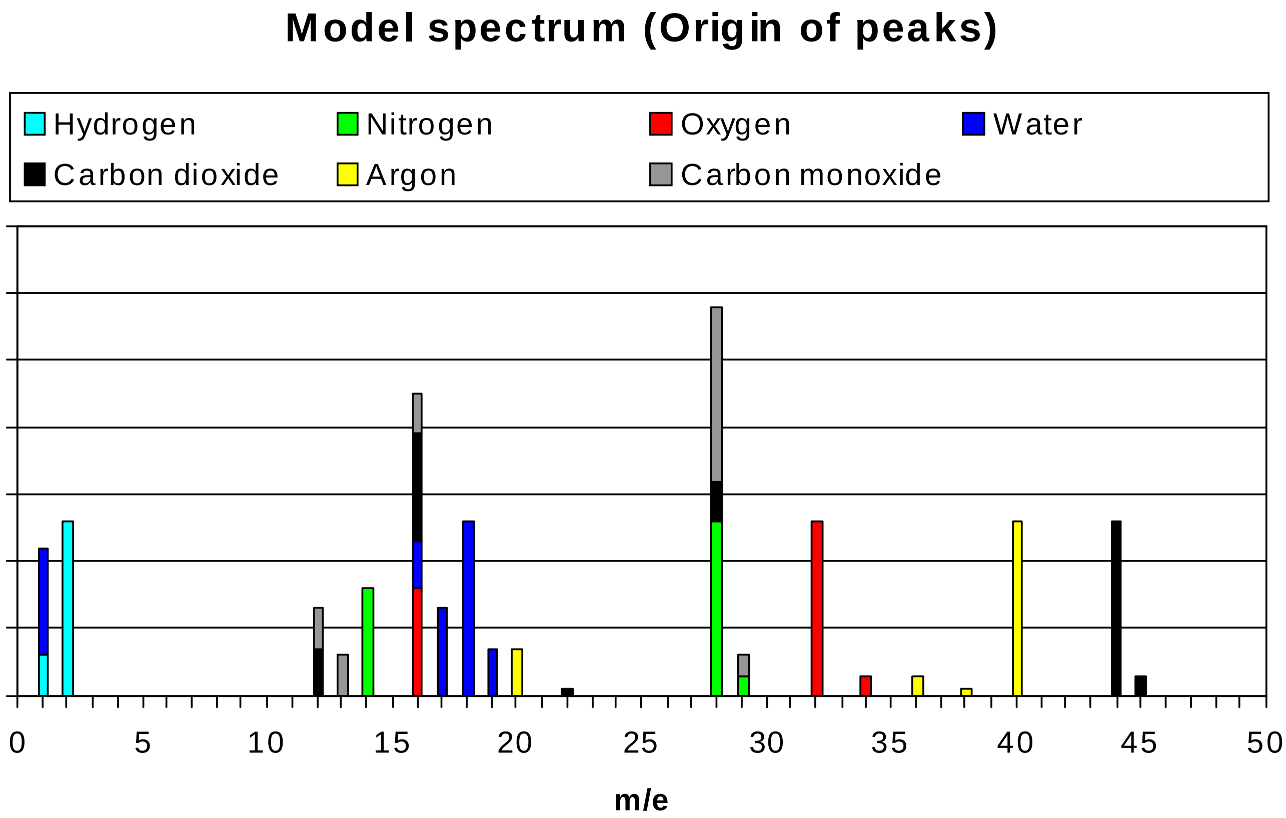
Interpretation of Residual Gas Spectra

Different molecules have the same mass, for example
N_2 and CO

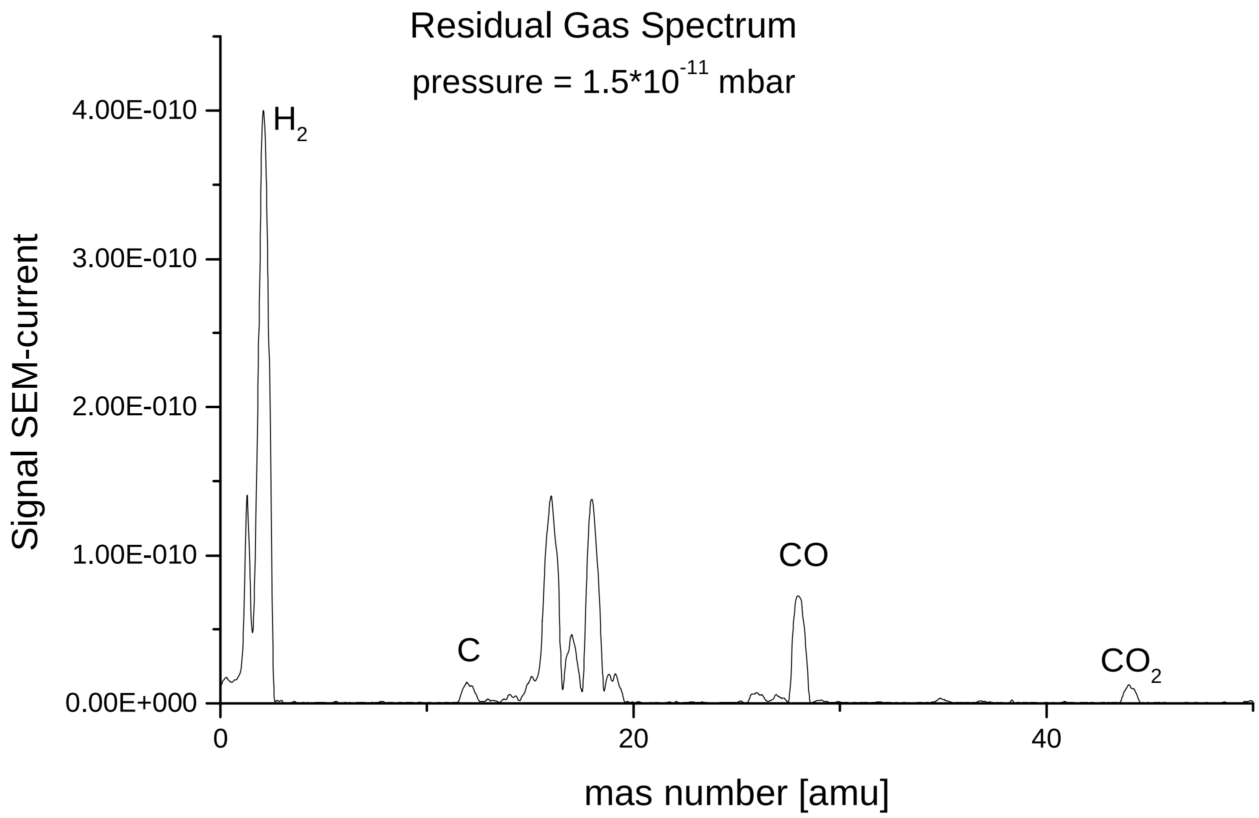
The gas molecules will be ionised and fractionised, for example water will give a signal at m/e = 1,2,16,17 and 18 corresponding to ions such as H^+, H_2^+, O^+, OH^+ and H_2O^+

This can result in rather complex spectra.

Interpretation of Residual Gas Spectra



Interpretation of Residual Gas Spectra in UHV/XHV



Interpretation of Residual Gas Spectra in UHV/XHV

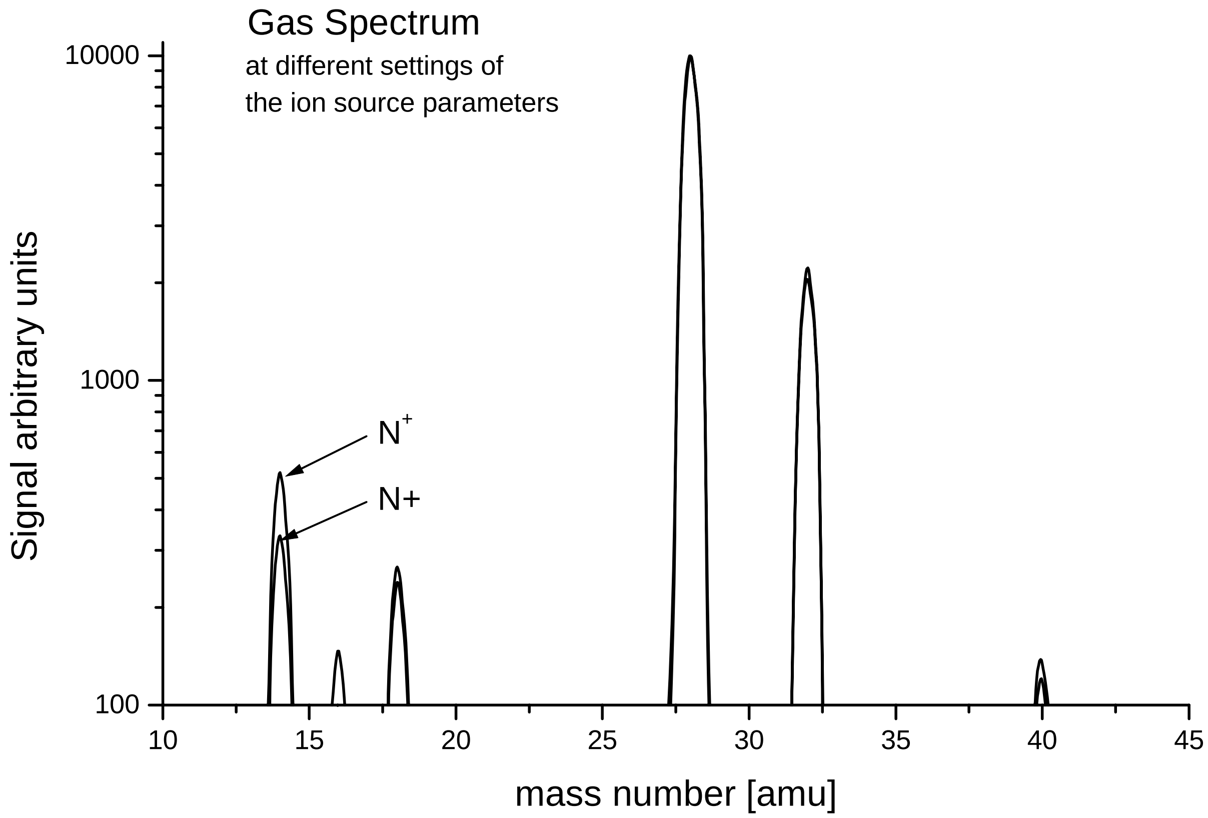
The main gases are hydrogen, carbon monoxide, carbon dioxide, sometimes there are very small quantities of water vapour even in the UHV.

All other gas components can be regarded as impurities, artefacts or will indicate a leak (N_2)

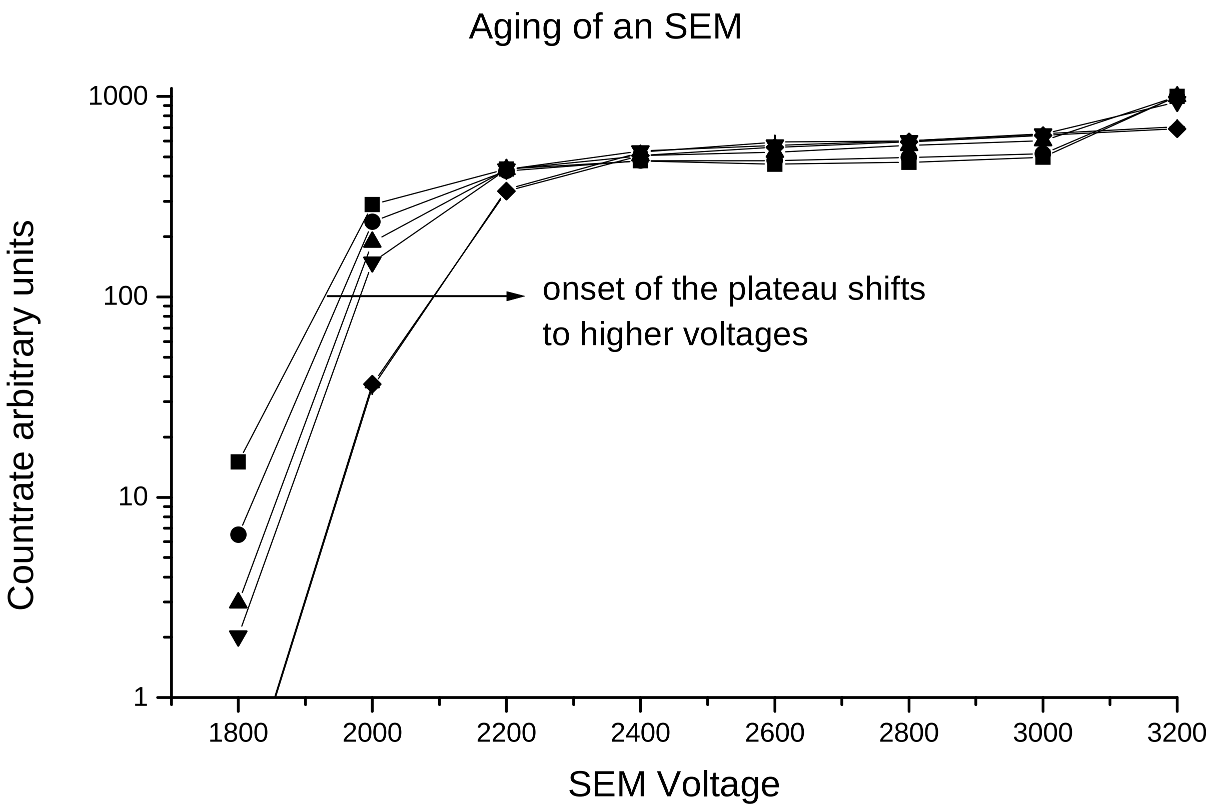
Sometimes UHV can be easier than HV!...

(It's not required to go into detail further with interferences and the like.)

Important to know: The Influence of the Electron Enegy



Important to know: The Aging of an SEM



Partial Pressure Gauges

- The quadrupole mass spectrometer is gas specific.
- The spectra obtained depend on the setting of the instrument – for example the electron energy has an influence on the spectra obtained.
- Obviously as with every spectrometer the resolution has an influence on the signal.
- An SEM is required for sensitivity reasons and every SEM undergoes aging.

- → Calibration is a MUST

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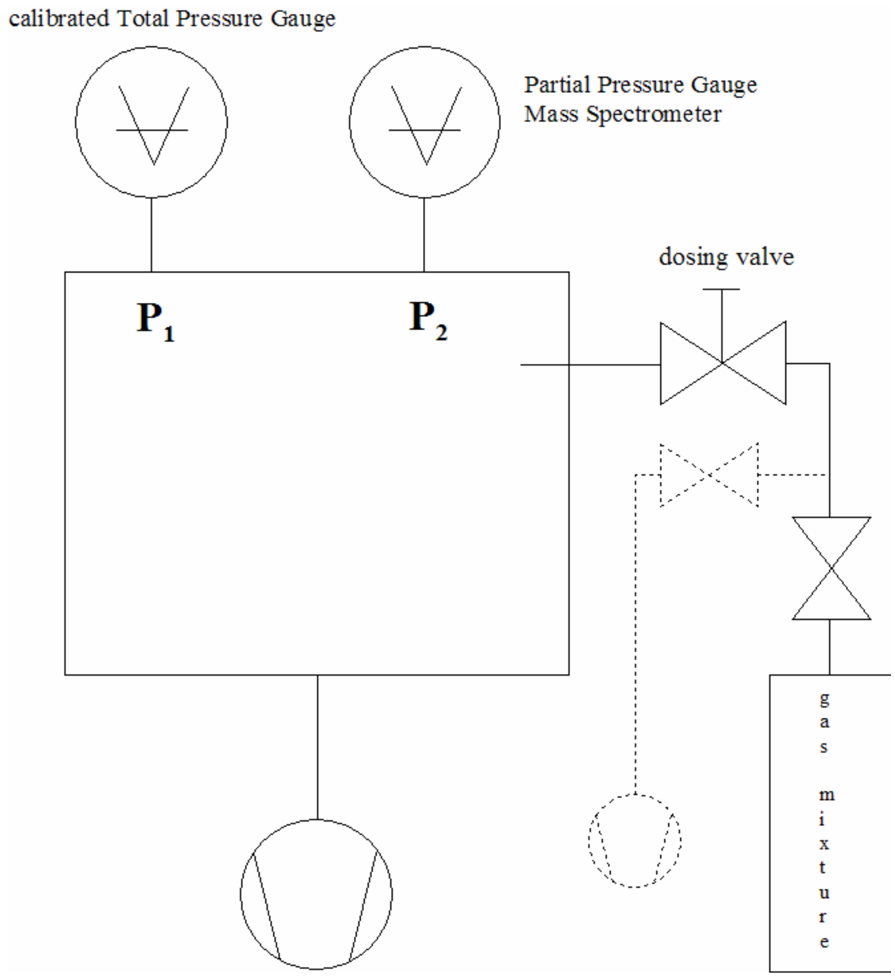
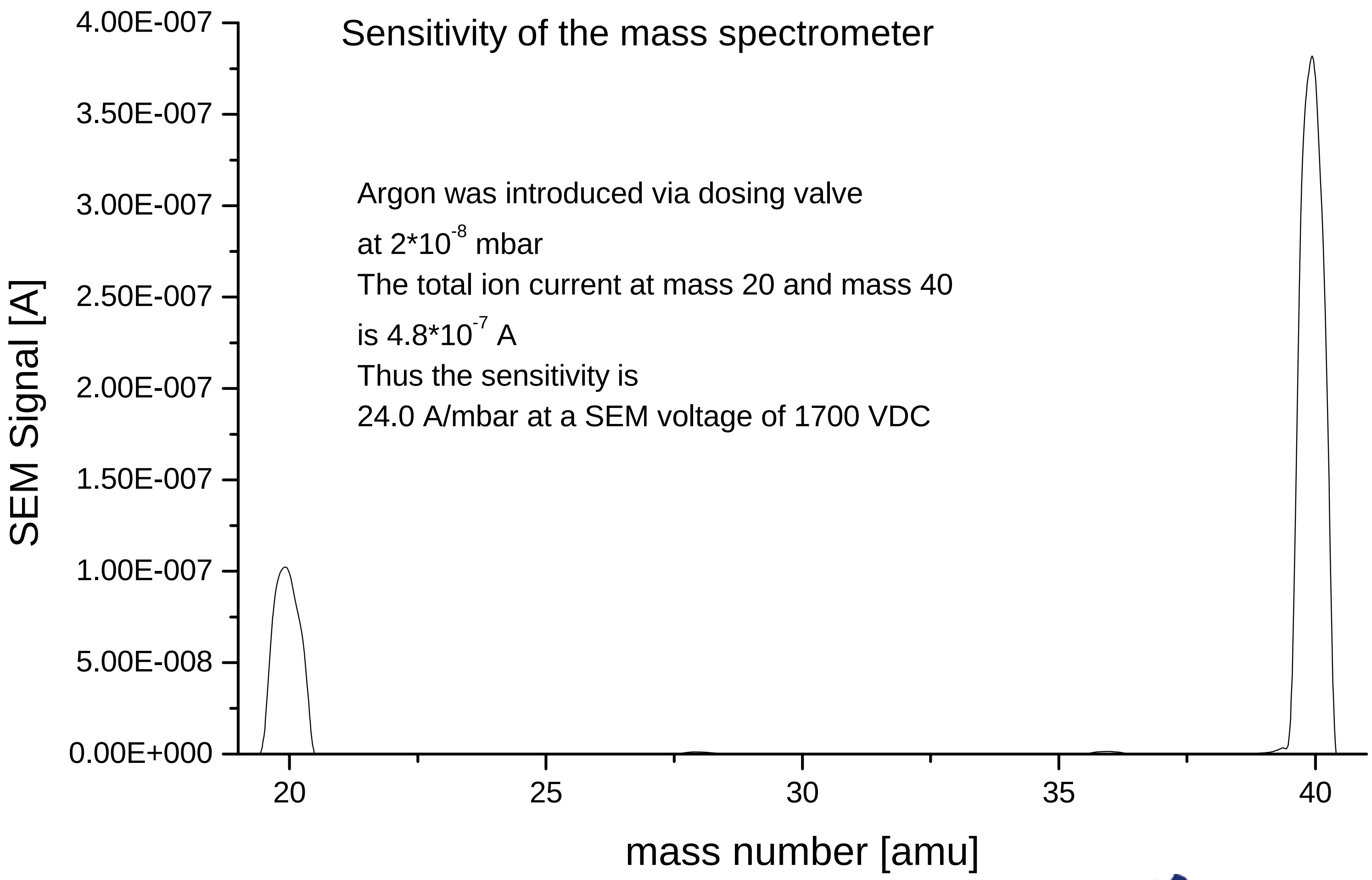
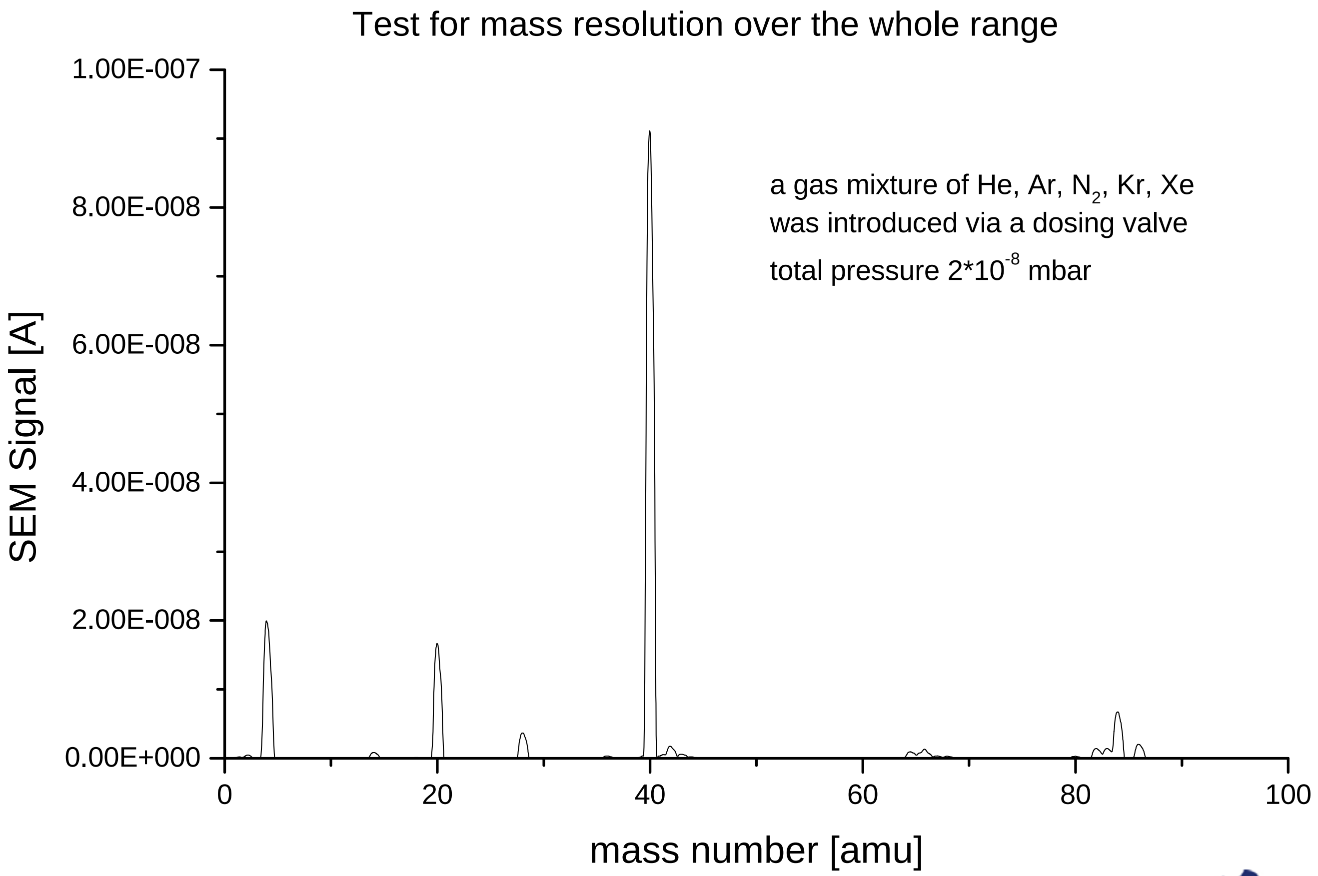
Calibration of Mass Spectrometers



Calibration of Mass Spectrometers



Calibration of Mass Spectrometers



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Large Hadron Collider

Test Protocol demanded by CERN

Test Report Residual Gas Analyzers **System No.5**

Name:	Articlenumber:	Serialnumber:
QMA 125	PTM10777-1	44197127
QME 125 -1	PTM36376	44197979
QMS 422	PTM26580	44198861
EP 422	BG444570-T	735
Cable length QME analyzer:		0.17m

IS-Voltage QME 125	
Ion. Ref	100V
Field axis	12V
Deflection	270V
Emission	2.00mA

Measurements after a bakeout at 300° C at an UHV-chamber

	Filename:
1. **Leak-Test** with Helium after bakeout at 300° C	rga nr.5 leaktest sem.bmp
2. **Spectrum** at base pressure with Faraday Cup, 10s/amu, 0-50amu	rga nr.5 restgasspektrum fc.sac
3. **Spectrum** at base pressure with SEM, (1600 VDC) 2s/amu, 0-100amu	rga nr.5 restgasspektrum sem.sac
4. **Spectrum** with Testgas (He, N2, Ar, Kr) Faraday to demonstrate the mass resolution	rga nr.5 gasspektrum fc.sac
5. **Spectrum** with Testgas (He, N2, Ar, Kr) SEM 1600 VDC to demonstrate the mass resolution	rga nr.5 gasspektrum sem.sac
6. **Sensitivity** for Argon Detector: Faraday $2x10^{-8}$ mbar argon 2s/amu Sensitivity: **1.68E-04** A/mbar	rga nr.5 empfindlichkeit fc.sac
7. **Sensitivity** for Argon, SEM at 1600 VDC $2x10^{-8}$ mbar argon 2s/amu Sensitivity: **8.71** A/mbar	rga nr.5 empfindlichkeit sem.sac

Test Protocol demanded by CERN

Detection Limit:
A signal two times the noise band of the detector determines the detection limit. For measurements with a SEM the noise band and the sensitivity are a function of the applied voltage. Therefore the sensitivity and the noise band have to be determined at various voltages to find the optimum SEM-Voltage. The noise band is determined by a measurement at mass 5.5 with a sampling time of 60 seconds for ten minutes.

8.	**Detection** Limit Faraday	Noise band:	**7.58E-15** A	rga nr.5 rauschen fc.mdc
		detection limit with Faraday Cup:	**4.50E-11** mbar	

Detection Limit with SEM at various SEM-Voltages $2x10^{-8}$ mbar argon, gauge calibrated for N2

SEM-Voltage:

1600 VDC:	Noise band:	**7.58E-14** A	Filename:	rga nr.5 rauschen 1600v.mdc
	Sensitivity:	**8.71** A/mbar	Filename:	rga nr.5 empfindlichkeit 1600v.sac
	Detection Limit:	**8.70E-15** mbar		
1700 VDC:	Noise band:	**1.26E-13** A	Filename:	rga nr.5 rauschen 1700v.mdc
	Sensitivity:	**24.49** A/mbar	Filename:	rga nr.5 empfindlichkeit 1700v.sac
	Detection Limit:	**5.14E-15** mbar		
1750 VDC:	Noise band:	**1.05E-13** A	Filename:	rga nr.5 rauschen 1750v.mdc
	Sensitivity:	**38.66** A/mbar	Filename:	rga nr.5 empfindlichkeit 1750v.sac
	Detection Limit:	**2.72E-15** mbar		

Question(s):

Which features describe such an instrument in a basic way?

Which features given in documents result from basic features or just contribute to them.

Are there data related to the whole system not only the RGA?

When data are reported, how can they be checked.

"Definitions to be complete if possible"

• Sensitivity	is gas-specific
• Mass-Resolution	depends on mass range,..
• Measurement Speed	depends on detection limit
• Detection Limit	speed, vacuum system,..
• Accuracy	standard to compare with
• Stability and Reproducibility	standard to compare with

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The key features of a mass spectrometer are:

* **Detection limit** (depends on the setting of the instrument and in some cases on the vacuum system too)
* **Dynamic Range** of the analysis
* **Mass Resolution**, the contribution to the neighbouring mass is an appropriate definition
* The measurement **speed**.

All these can not be discussed as single parameter, they mutual influence each others. For example the specified detection limit may never be achieved at the maximum measurement speed. A sensitivity can never be specified without the resolution of the instrument…..

Partial Pressure Gauges

Partial Pressure Gauges

So far all statements are valid for every quadrupole mass spectrometer.

Which restrictions to these instruments appear because of UHV/XHV environment?

Requirements to a Partial Pressure Gauge used in UHV/XHV

•**Detection Limit 5* 10^{-15} mbar ,**impurities in the residual gas have to be detected, 5*10^{-14} mbar is already a compromise for other reasons

•**Gauge has to "survive" the baking of the vacuum system**

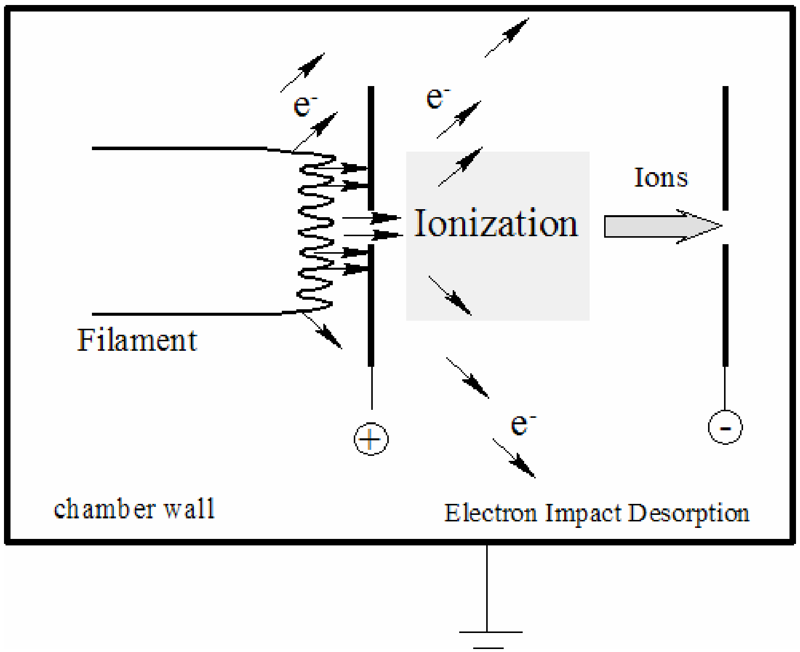
•**No influence of the gauge to the vacuum**

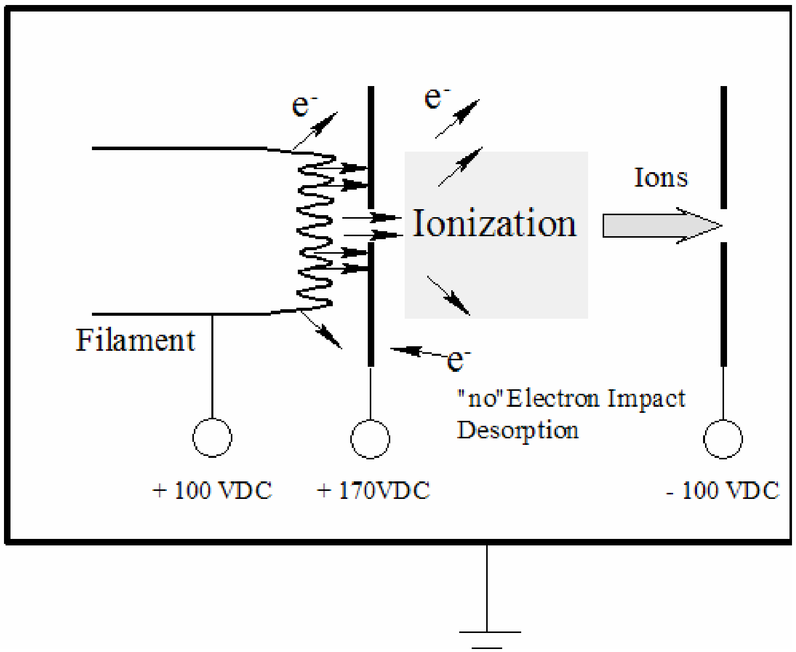
•**Gauge has to "survive radiation"**

Detection Limit: Reduce Background

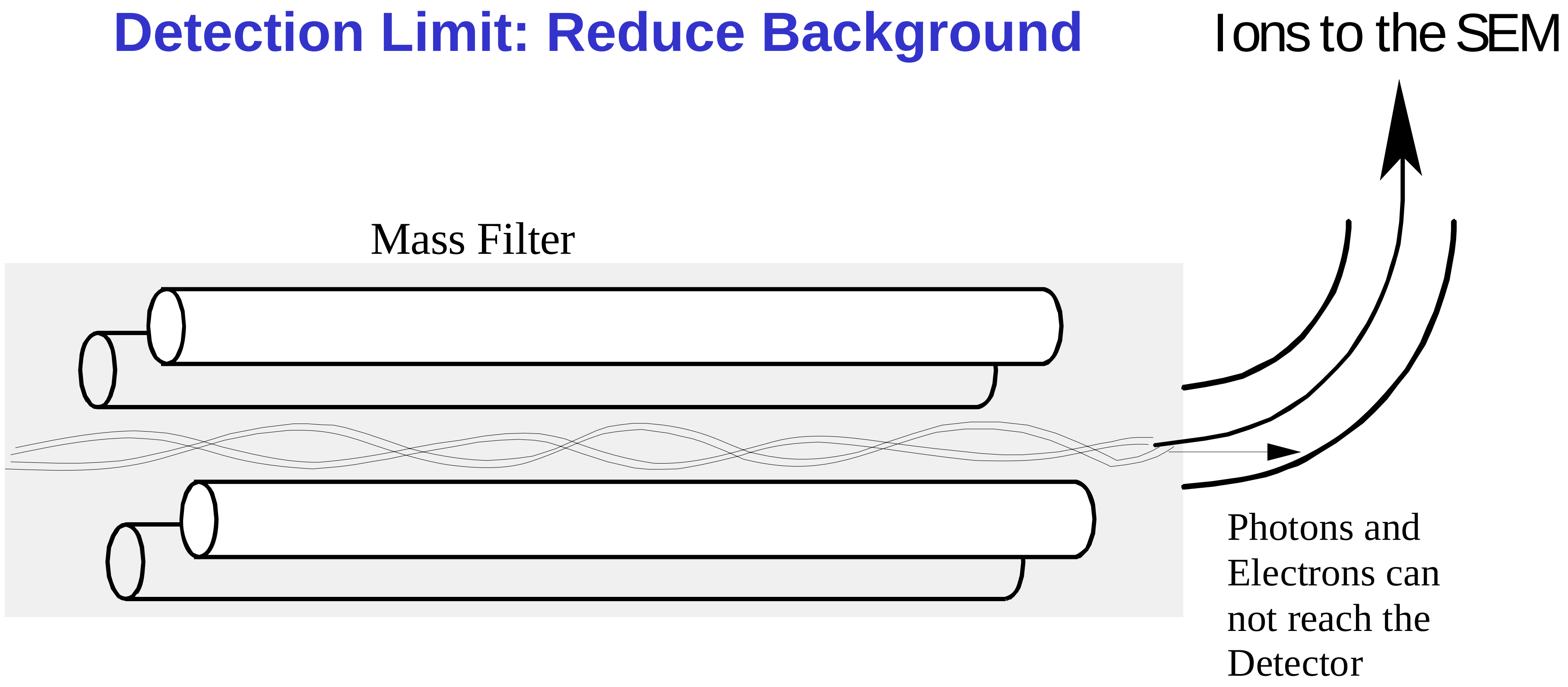
most used technique: no electrical bias

biased system: cathode is most positive electrode



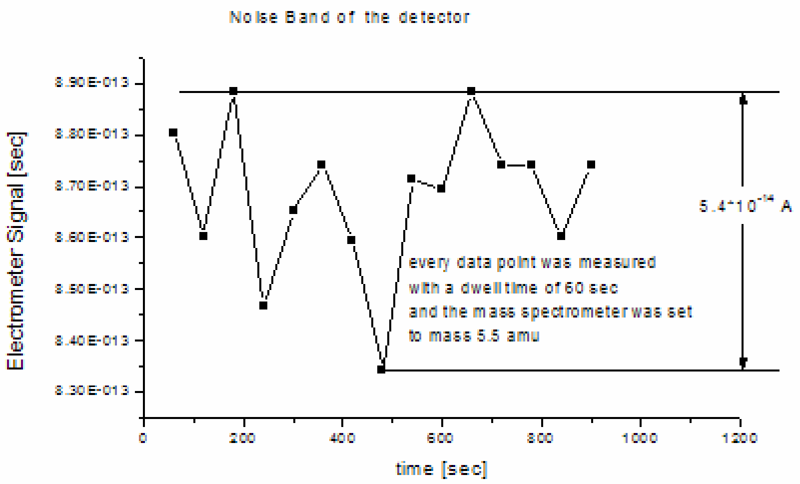


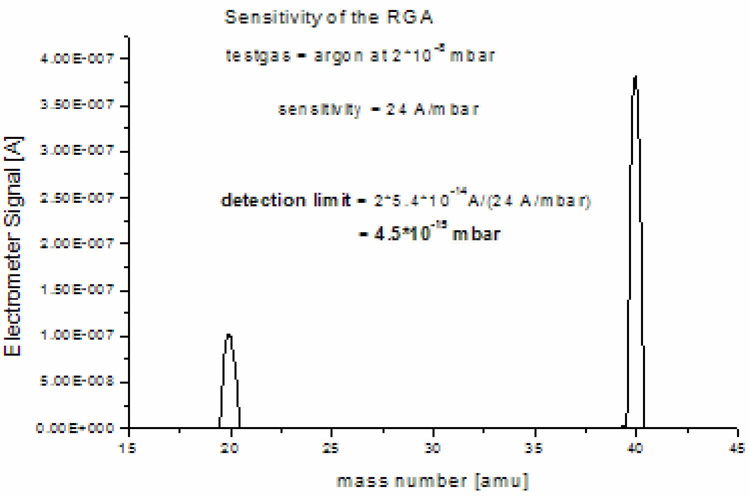
Detection Limit: Reduce Background



Detection Limit

Noise Band and Sensitivity determine the detection limit





Noise band and the sensitivity increase with increasing SEM-Voltage
→ search for an optimum:

1600 VDC	Sensitivity:	9.35 A/mbar
	Noise band	$9.12*10^{-14}$ A
	Detection Limit	$9.75*10^{-15}$ mbar
1700 VDC	Sensitivity:	24.20 A/mbar
	Noise band	$1.08*10^{-13}$ A
	Detection Limit	$4.47*10^{-15}$ mbar
1750 VDC	Sensitivity:	37.90 A/mbar
	Noise band	$1.56*10^{-13}$ A
	Detection Limit	***$4.13*10^{-15}$ mbar***

Requirements to a Partial Pressure Gauge used in UHV/XHV

- **Detection Limit 5* 10^{-15} mbar ,**impurities in the residual gas have to be detected, 5*10^{-14} mbar is already a compromise for other reasons

- **Gauge has to "survive" the baking of the vacuum system**

- **No influence of the gauge to the vacuum**

- **Gauge has to "survive radiation"**

Choice of the material:

- Metal
- Ceramics
- Thermal expansion coefficients of the partners

→ Metal and Al_2O_3 electrical feed-through

Requirements to a Partial Pressure Gauge used in UHV/XHV

- **Detection Limit 5* 10^{-15} mbar ,** impurities in the residual gas have to be detected, 5*10^{-14} mbar is already a compromise for other reasons

- **Gauge has to "survive" the baking of the vacuum system**

- **No influence of the gauge to the vacuum**

- **Gauge has to "survive radiation"**

Choice of the Filament- Material

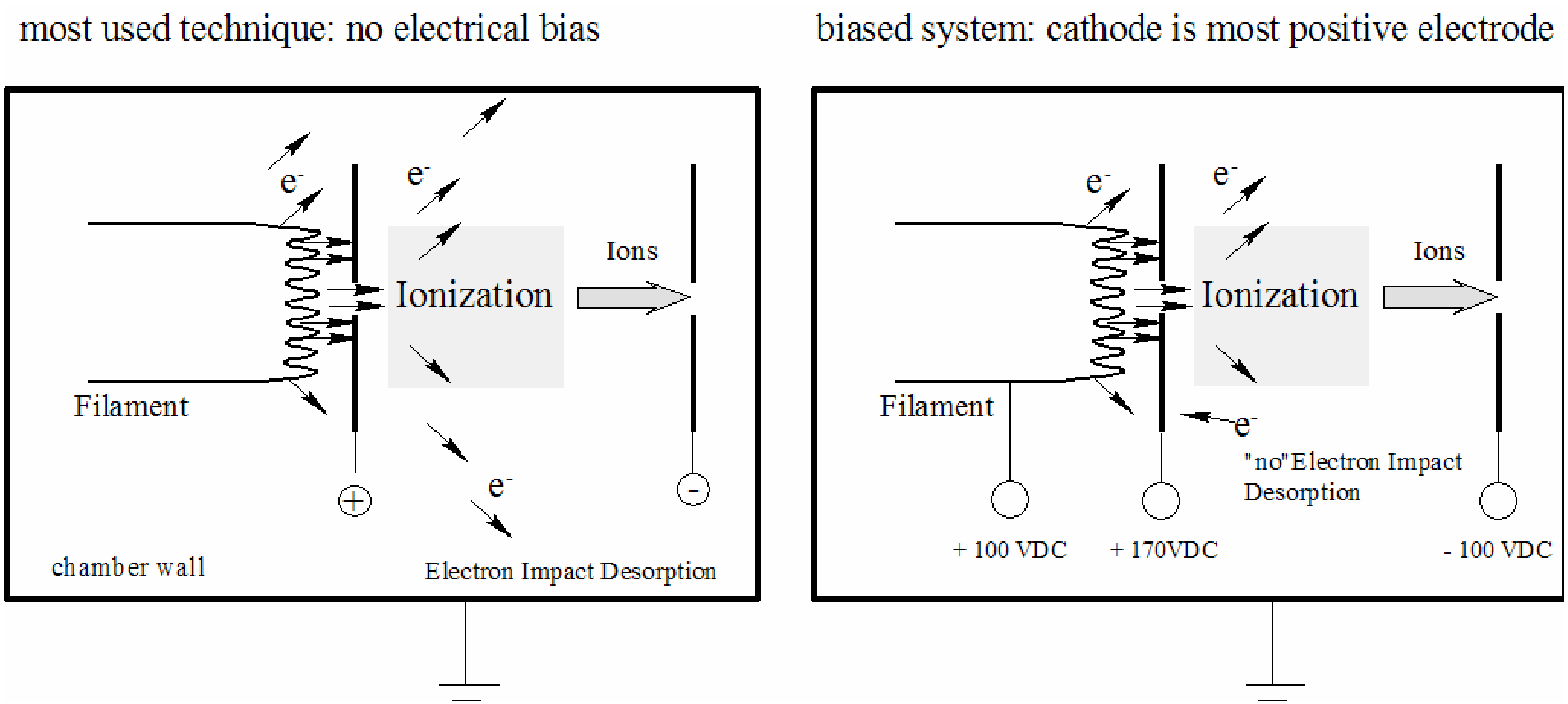
Rhenium: rather high vapuor pressure

used manily in High Vacuum

Tungsten: used in the UHV, has a longer lifetime than Rhenium and a lower vapour pressure

Yt-Oxide on Iridium rather resistant against air, temperature is much lower compared to pure metall

Avoid Electron Induced Desorption



Avoid degassing of the gauge:

- By design no gaps, if threads are necessary they have to have additional holes for degassing,..
- By the choice of material again metal and “real Al_2O_3”
- By pre-treatment of the components → vacuum firing at 900^0C prior to assembly
- The SEM also has to be consequent UHV-designed

- → then < 10^{-10} mbar l*s^{-1} degassing is achieved

What about the filament?:

The filament of a gauge is at > 1000^0C

Therefore the filament has to be switched on during the baking of the vacuum system, otherwise,……

Requirements to a Partial Pressure Gauge used in UHV/XHV

- **Detection Limit 5* 10^{-15} mbar ,** impurities in the residual gas have to be detected, 5*10^{-14} mbar is already a compromise for other reasons

- **Gauge has to “survive” the baking of the vacuum system**

- **No influence of the gauge to the vacuum**

- **Gauge has to “survive radiation”**

Separate analyzer and electronics to be able to shield the electronics

Sometimes longer distances than shown here are required.
This has an effect on the sensitivity!

Partial Pressure Gauge which can be used in UHV/XHV

- Detection Limit 5* 10^{-15} mbar , or even below
- All metal-ceramic design, according to UHV-design rules
- Material is pre-cleaned, vacuum fired for lowest degassing
- Gauge and electronics are separated because of radiation

Partial Pressure Gauges

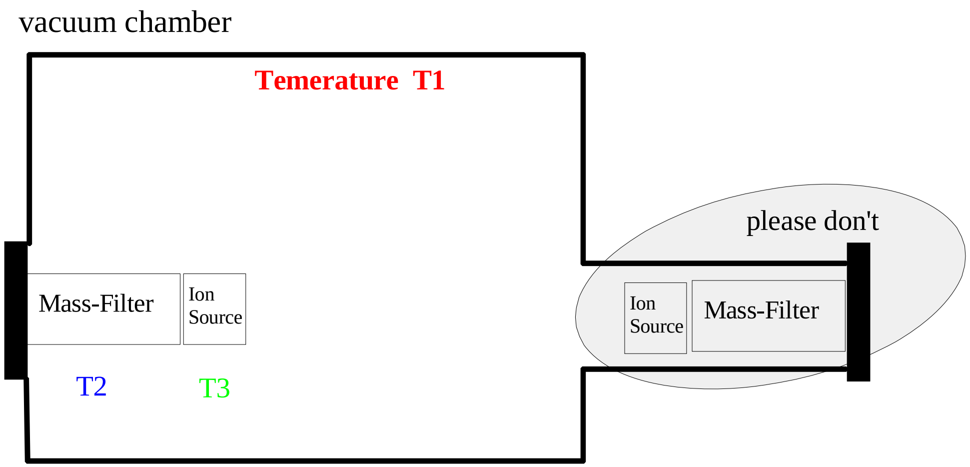
How to operate a partial pressure gauge in the UHV

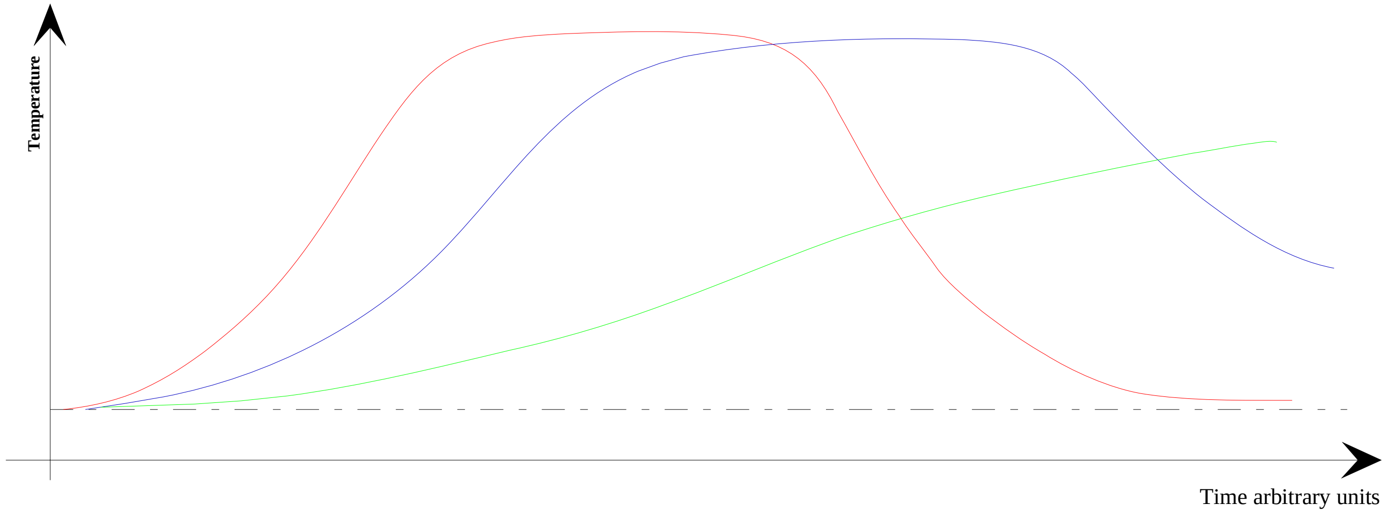
few remarks to the

state of the art practise

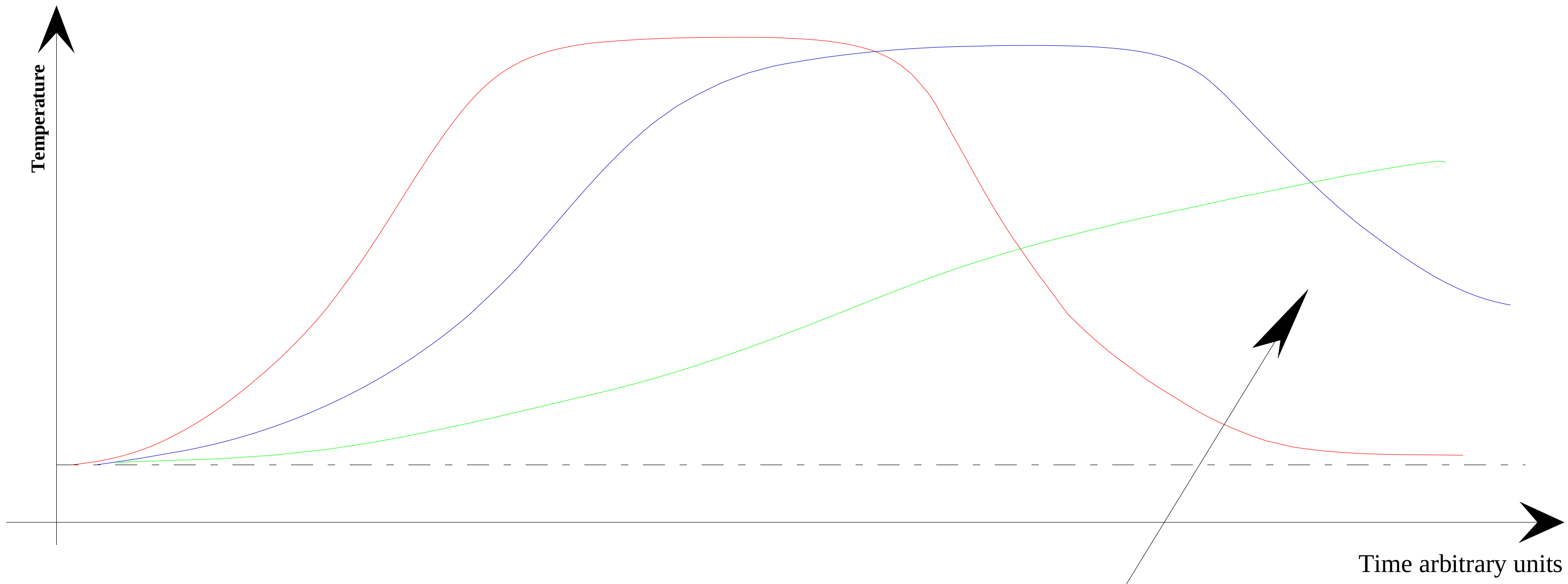
Günter J. Peter

How to bake an RGA:





How to bake an RGA:



Desorption from the walls starts

partly condensation onto the mass filter and here esspecially

condensation onto the Ion Source

How to bake an RGA:

If possible the instrument has to be installed inside the chamber not inside a tube.

Avoid „cold spots“ at the instrument and inside the chamber wherever possible.

Otherwise there might be condensation onto this surfaces.

Make sure that the whole system is at equal temperature for a sufficient time.

If ever possible switch on the filament of the RGA during baking.

Thus the Ion Source stays at high temperature and no condensation may occur there.

Results obtained with partial pressure gauges in the UHV

after integral baking at 300^0 over night

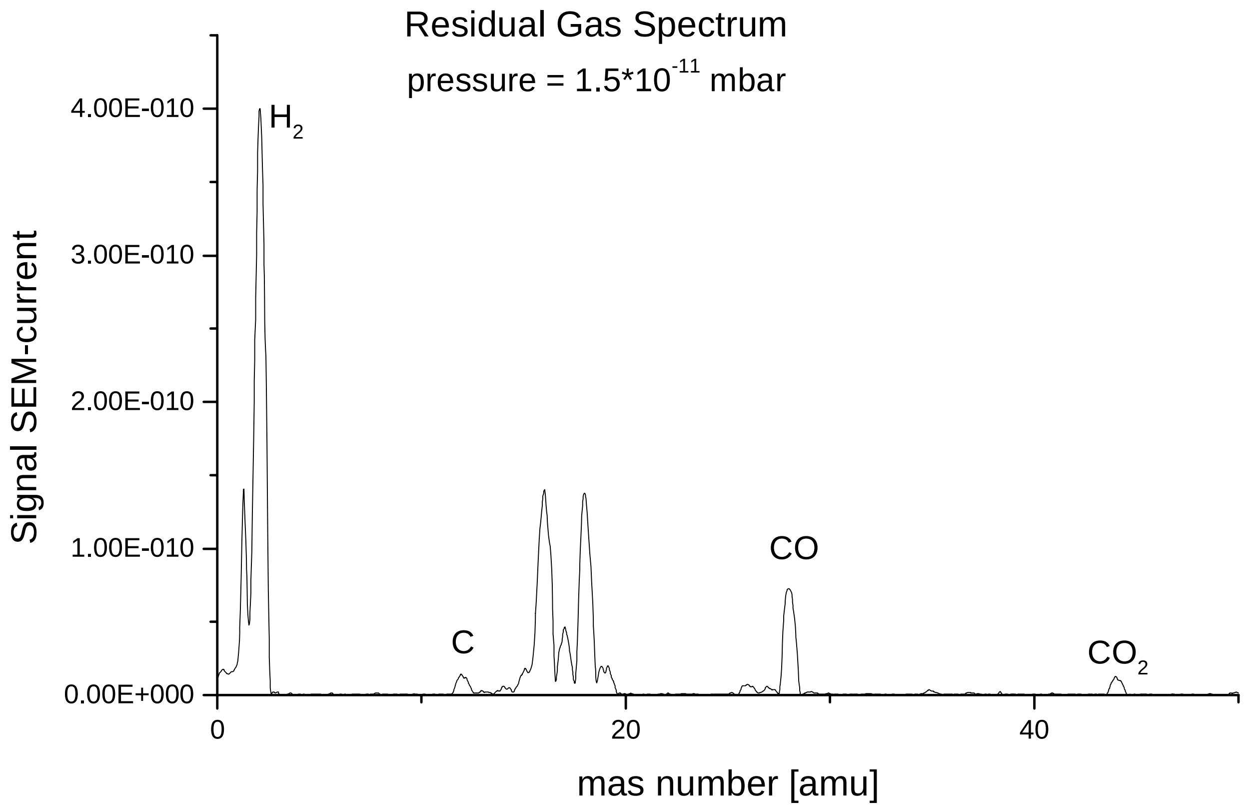
filament switched on during the cool down procedure
after degas at 150^0C

Residual gas spectra

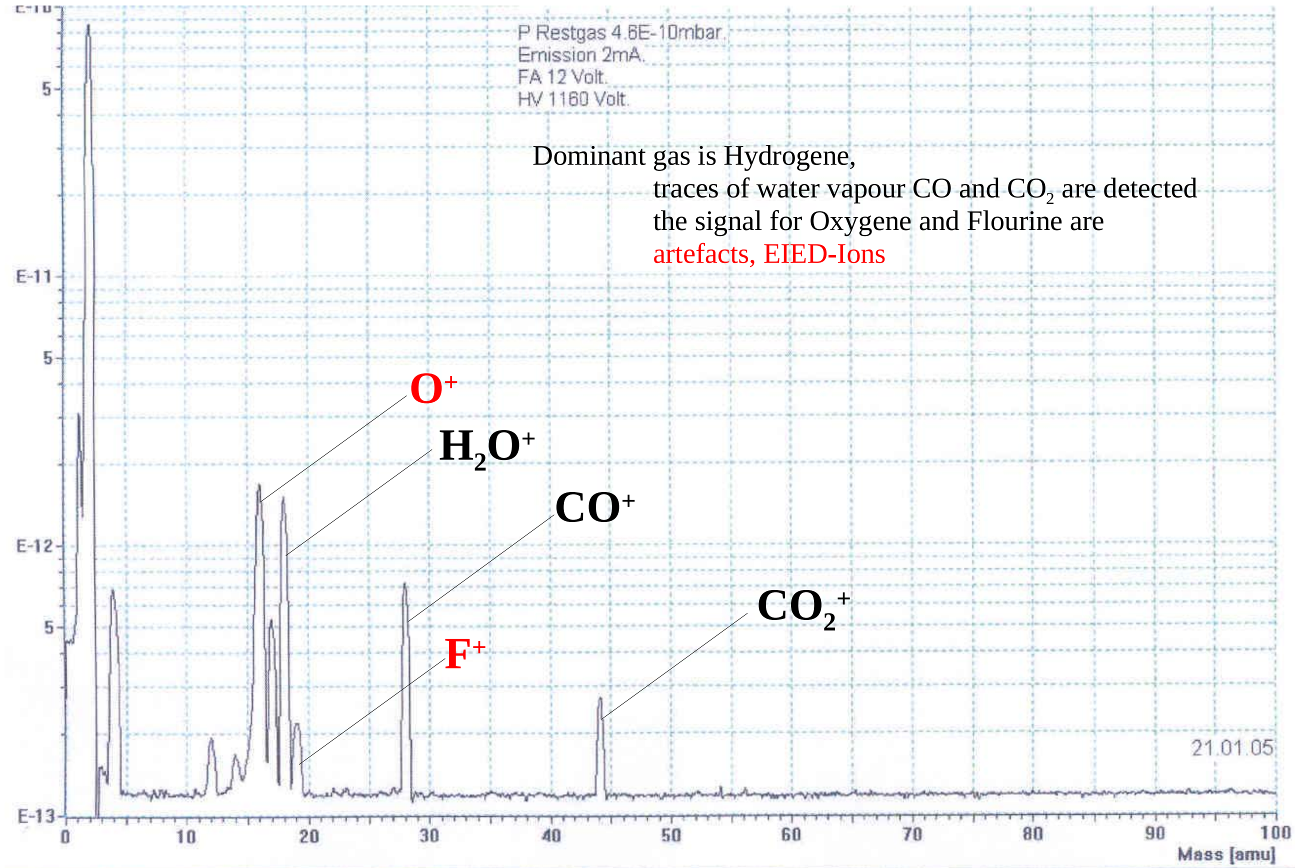
EID-Ions

Leak

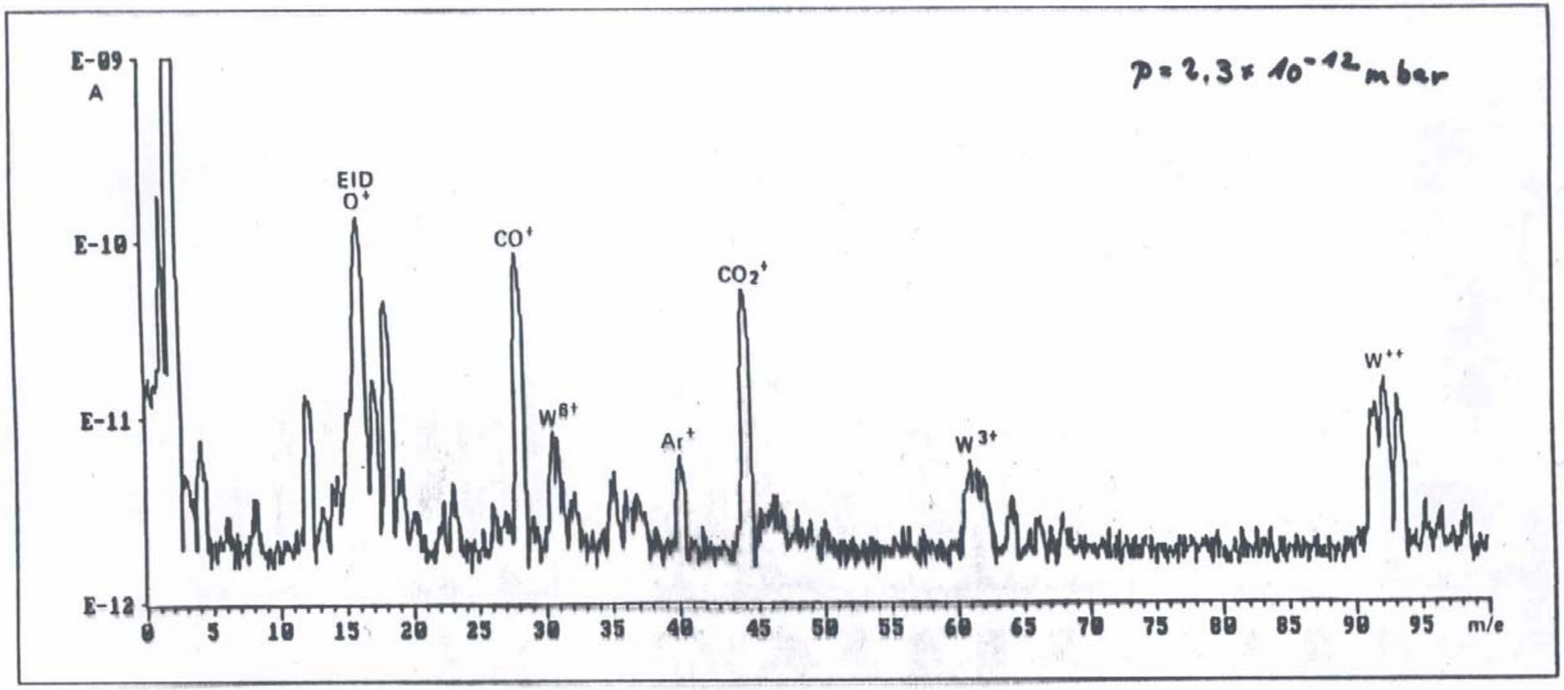
Results achieved



Results achieved : EID-Ions



Results achieved : EID-Ions



W.K. Huber et al., Vacuum 41, 2103 (1990)

„Physics doesn‘t change“

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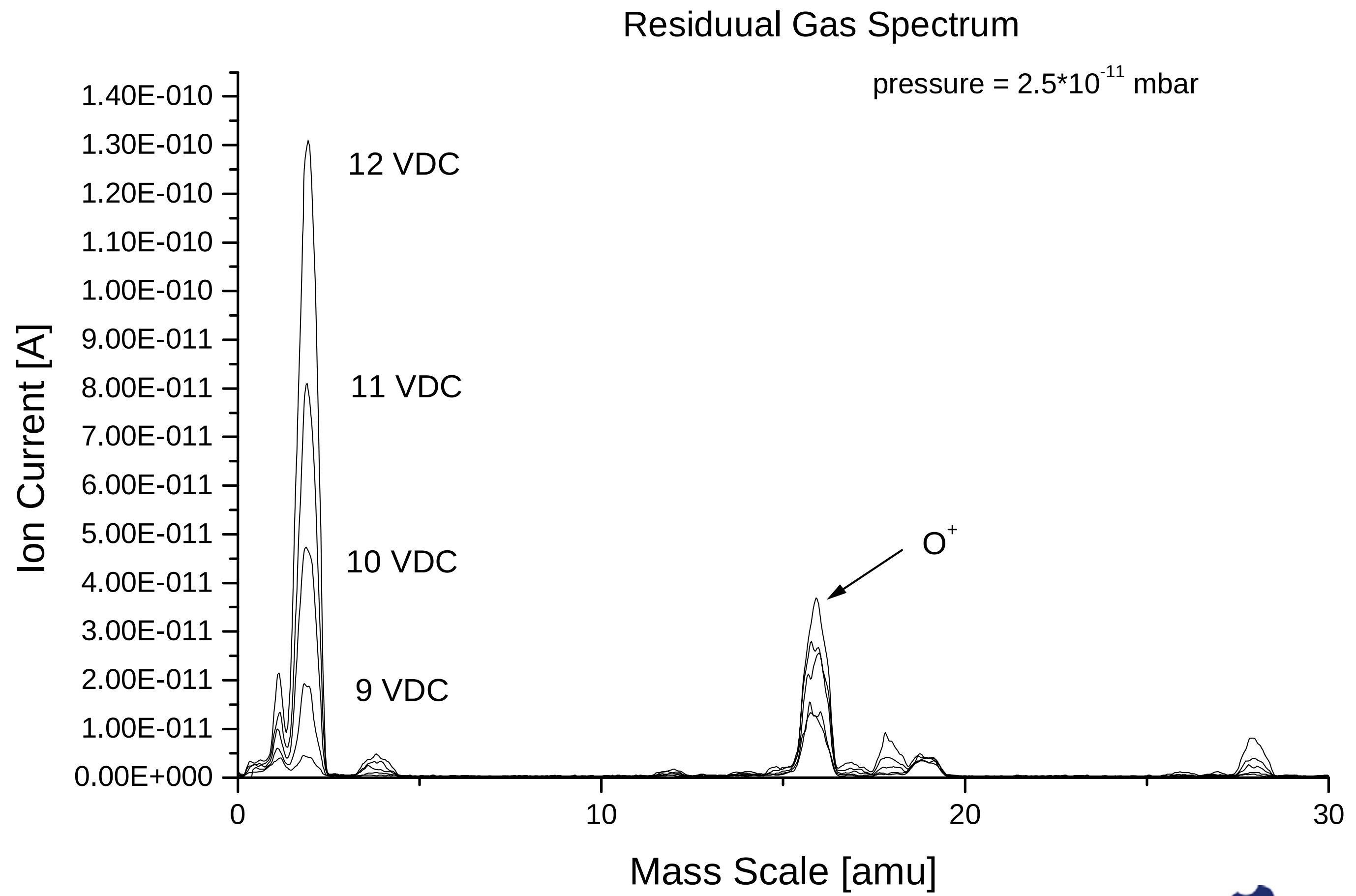
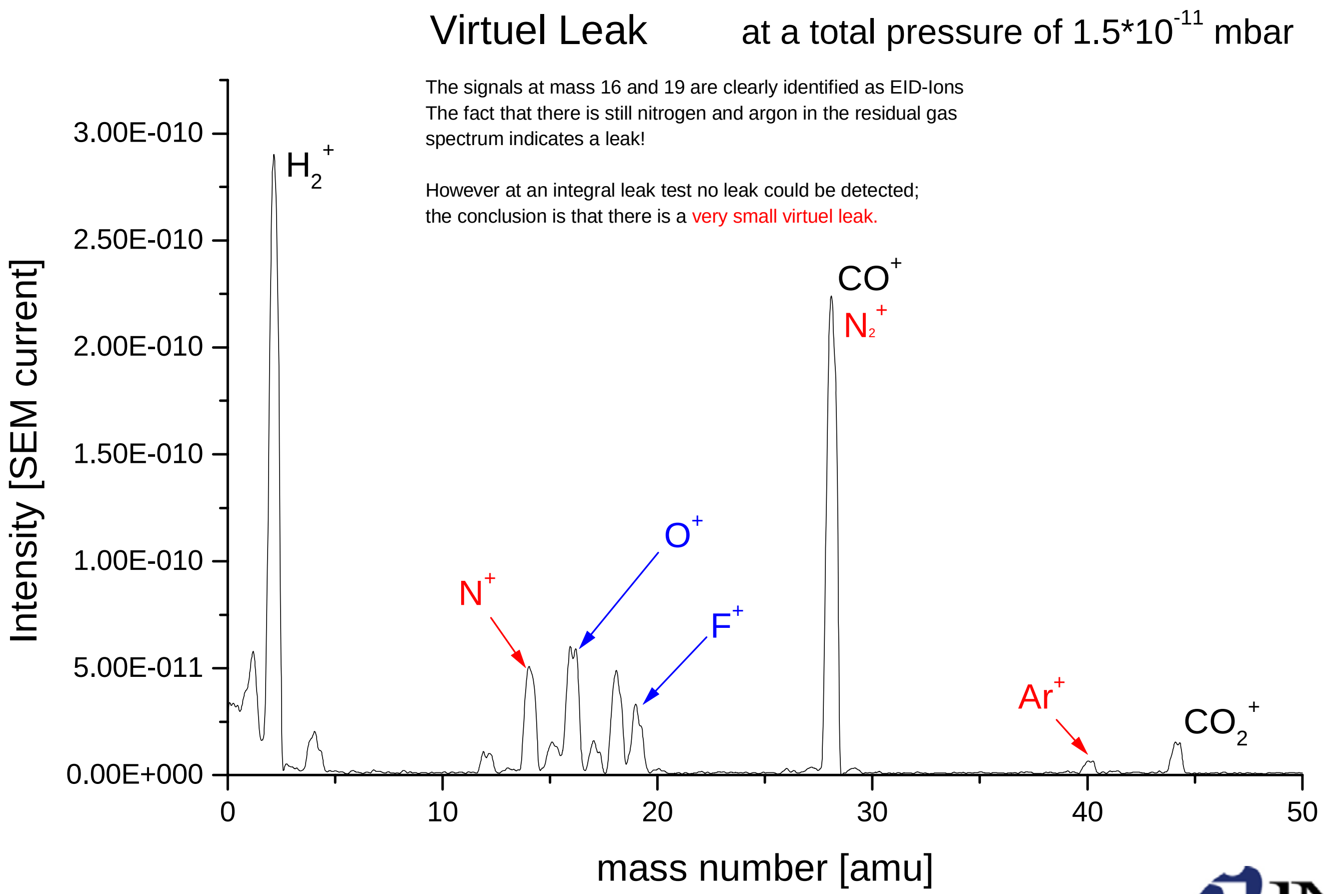
How to identify EID-Ions



Results achieved : Leak!



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Results achieved : Leak!

•Normally in HV-Systems the “presence of air” in the residual gas, means nitrogen, oxygen and argon, is an indication for a leak.

•Oxygen is a reactive gas which is gettered at the inner surface of an UHV-system. Therefore nitrogen and argon are an indication for a leak in this pressure range; oxygen is not observed.

•In the present case no leak form the outside could be detected during an integral leak test.

•Hypothesis was that there was some gas-bubble inside the vacuum. Later an inclusion at a gasket could be identified.

•After a new gasket was used and after an additional baking the leak “vanished”.

Summary Conclusions:

- **Gauges to be used in UHV/XHV require special electrical and mechanical design and pre-cleaned components.**
- **Because of the very high sensitivity achieved artefacts such as EID-Ions are found in the spectra.**
- **These instruments are used for trace analysis** and in addition
- **Can and should be used for leak-detection because of their high sensitivity.**

I would like to thank Hans Zogg, who did the most part of the practical work.

Thank you for your attention!