Mass spectrometry and the usage @ PITZ

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Technisches Seminar 29.05.2007

Outline

1. introduction
2. generation of gas phase ions
3. overview of mass spectrometry systems
4. residual gas analysis (RGA)
5. RGA @ PITZ
6. summary and outlook

If not special cited, than the pictures are taken from: "**Mass Spectrometry of Inorganic, Coordination and Organometallic Compounds**" - W. Henderson and J.S. McIndoe

introduction

- Where can one use MS?
  - biology
  - chemistry
  - physics
    - in this talk Residual Gas Analysis (RGA)
  - environmental pollution
  - …

introduction

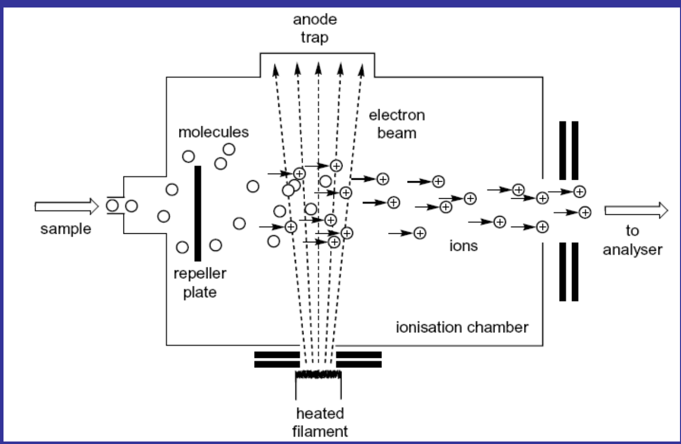
- What does a mass spectrometer (MS)?

1. generation of gas-phase ions
2. separation to the mass-to-charge ratio
3. counting

ionization	ion optics	m/z analysis	counting
1	1	2	3

1. introduction
2. generation of gas phase ions
3. overview of mass spectrometry systems
4. residual gas analysis (RGA)
5. RGA @ PITZ

Electron ionization



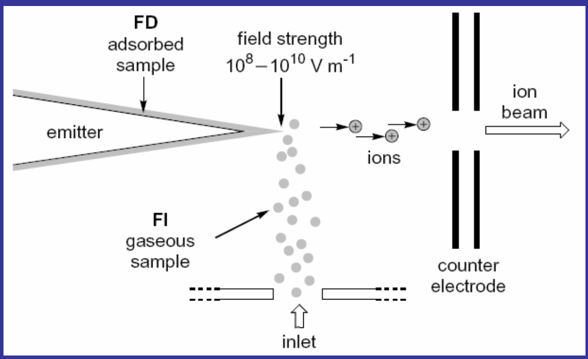
• typical electron energies below 100 eV
• used in most RGA's

2. generation of gas-phase ions

Electron ionization

- strengths
  - established and very good understood
  - reproducible mass spectra
  - fragmentation can provide structural information
- weaknesses
  - sample must in gas phase

Field ionization



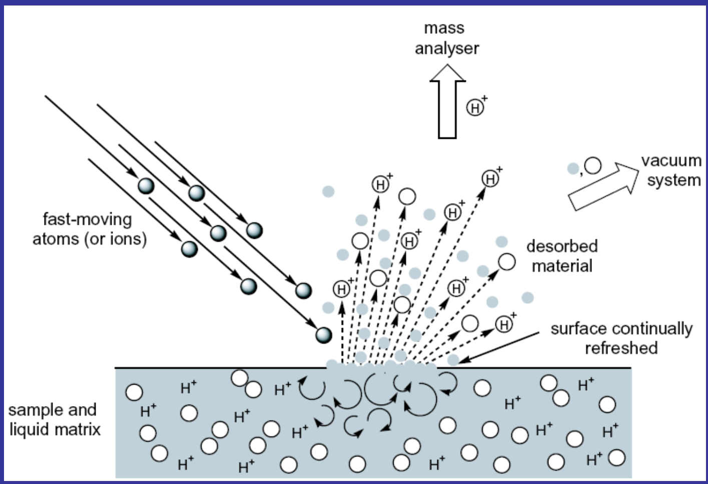
Field ionization

- strengths
  - very soft ionization
  - nearly no chemical background
- weaknesses
  - preparation of the emitter
  - high fields often require use of sector MS

2. generation of gas-phase ions

Fast ion/atom bombardment

used for solids ore liquids (matrix assisted)



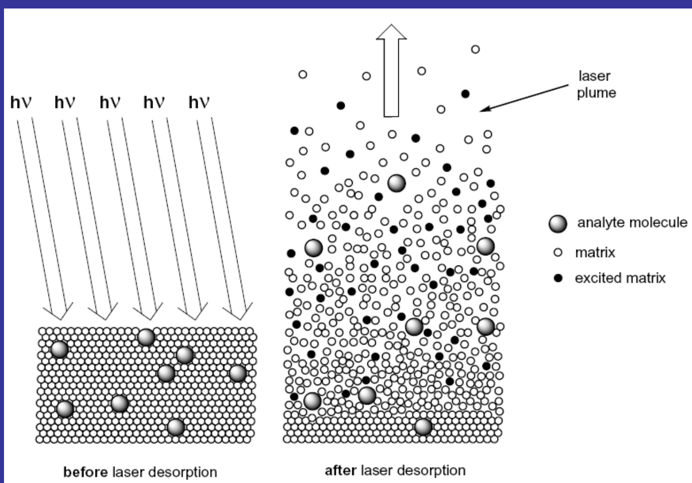
2. generation of gas-phase ions

Fast ion/atom bombardment

- strengths
  - simple
  - also cold samples can be studied
  - high ion currents => good resolution
- weaknesses
  - high background
  - lower m/z dominated by matrix

MALDI

Matrix Assisted Laser Desorption Ionisation



MALDI

- strengths
  - soft ionization poor fragmentation
  - rapid molecular weight determination
- weaknesses
  - MS/MS different
  - pulsed ionisation
  - spectra can depend on matrix

2. generation of gas-phase ions

1. introduction
2. generation of gas phase ions
3. <u>overview of mass spectrometry systems</u>
4. residual gas analysis (RGA)
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2. generation of gas-phase ions

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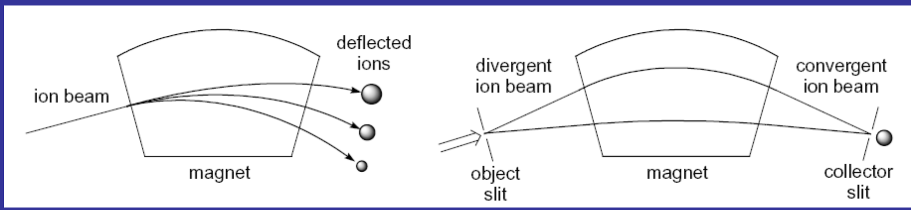
Sector MS



directional focusing

ion source →

$$E_{kin} = zV = \frac{mv^2}{2}$$

centrifugal and Lorentz force →

$$\frac{mv^2}{r} = B \cdot z \cdot v$$

$$\Rightarrow \frac{m}{z} = \frac{B^2 r^2}{2V}$$

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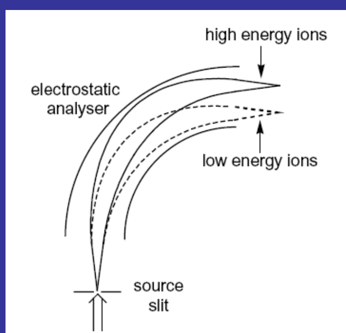
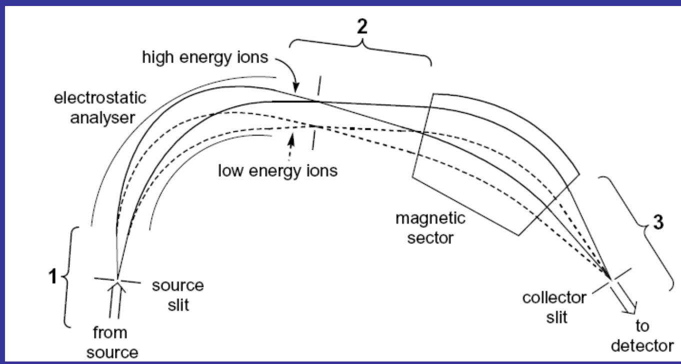
Sector MS

A magnetic sector will focus ions with same m/z but different kinetic energy to different points. Therefore an electrostatic analyser is used before the magnetic sector.



3. overview of mass spectrometry systems

Sector MS



strengths:

- high resolution, sensitivity ,and dynamic range

weaknesses:

- very large, expensive

TOF-MS

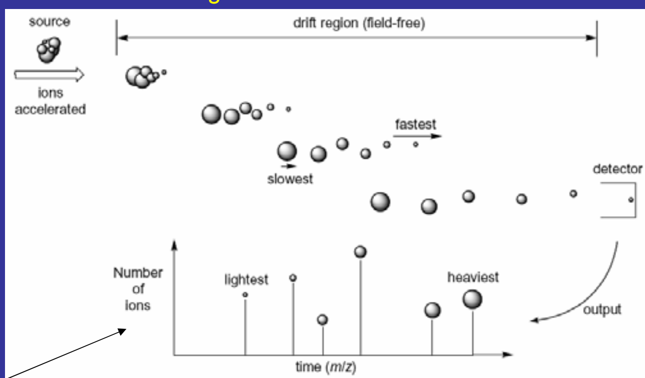
Time Of Flight MS: ions are accelerated by an electric field to the same kinetic energy
→ ions with different mass but same E_{kin} have different velocity v
→ heavier ions reach the detector after lighter ones

$$E_{kin} = U \cdot e \cdot z = \frac{m}{2} v^2$$

$$U \cdot e \cdot z = \frac{m}{2}\left(\frac{dx}{dt}\right)^2$$

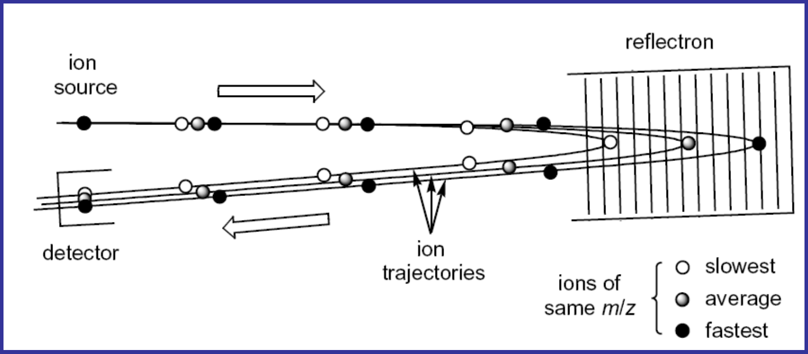
$$\Rightarrow \frac{m}{z} = \frac{2 \cdot e \cdot U \cdot dt^2}{dx^2}$$

$$\Rightarrow \frac{m}{z} = const. \cdot dt^2$$



TOF-MS

reflection TOF-MS

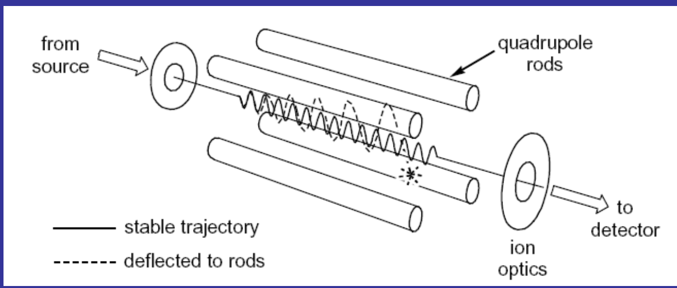


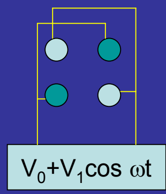
In a TOF-MS nearly all ions have same kin. energy. To ensure that really all ions with the same m/z ratio arrive at the same time at the detector an electronic ion mirror is used. The different kinetic energies are compensated by the different penetration depths. This provides an increase in resolution of the TOF-MS

TOF-MS

- strengths
  - unlimited mass
  - simplicity
  - no scanning necessary (detects all at once)
  - high transmission
- weaknesses
  - requires pulsed ionization or beam switching
  - high vacuum conditions required

Quadrupole MS



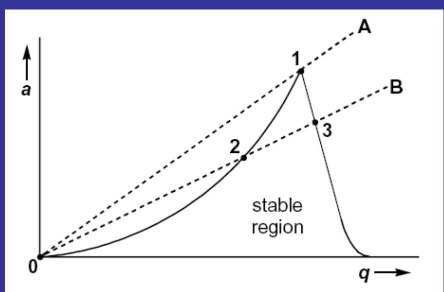


$$\frac{m}{z} = \text{const.}\frac{V_1}{\omega^2}$$

For constant ω (typically some MHz) a mass scan is performed by changing V_1. The precision depends on the ratio V_0/V_1 so that V_0 is changed together with V_1.

Quadrupole MS

stability diagram (a ~ V_0, q~V_1)



Quadrupole MS

- strengths
  - compact
  - simplicity
  - fast scanning
  - mass spectra good reproducible
- weaknesses
  - resolution
  - not suited for pulsed ionization methods

Comparison

MS	Price	Size	Resolution	Mass range
Sector	+	+	++	++
Quadrupole	+++	+++	+	+
TOF	++	++	++	+++

1. introduction
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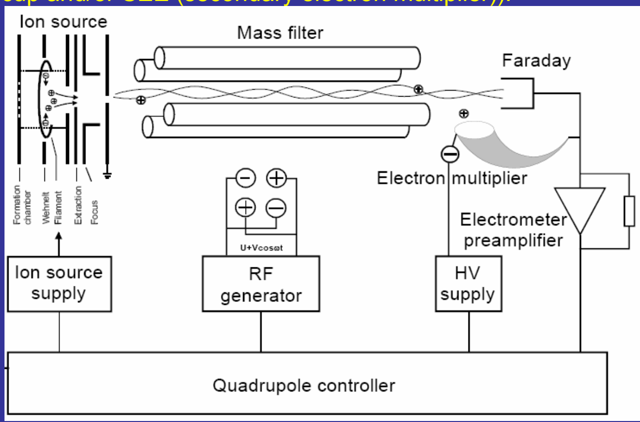
3. overview of mass spectrometry systems
4. residual gas analysis (RGA)
5. RGA @ PITZ

residual gas analysis (RGA)

- RGA's can provide information on:
  - residual gasses
  - air leaks in vacuum systems
  - Helium leaks especially in Helium leak tests
  - compositions of processes
  - impurities in process gasses

residual gas analysis (RGA)

A residual gas analyser measures the partial pressures of individual masses in a gas mixture (vacuum). The sum of all partial pressures is the total pressure, which one can also measure with an vacuum gauge or an ion getter pump. Common systems consists of an ion source, a Quadrupole analyser, and an counter (Faraday cup and/or SEE (secondary electron multiplier)).



MS Basics M. Mueller **4. residual gas analysis (RGA)**

residual gas analysis (RGA)

Calculating the partial pressures P_A from measured currents I_{AB}:

$$P_A = \frac{FF_{N28}}{FF_{AB} XF_{AB} TF_B DF_{AB} G \cdot S} I_{AB}$$

from INFICON LEYBOLD

Analyser factors:
G: gain of the SEE or 1 for FC
S: sensitivity for pure Nitrogen
DF_{AB}: detection factor, 1 for FC and for SEE dependent on ion mass and the chemical nature, measured relative to the reference gas (usual Nitrogen)
TF_B: transmission factor, fractions of ions passing through the quadrupole relative to nitrogen $TF_B = 28/M$
Material factors
FF: fragmentation factors, FFN28 is the FF
XF: ionization probability

So the calculation of the partial pressure crucially depends on the chemical element itself and how the analyser can handle this element

4. residual gas analysis (RGA)

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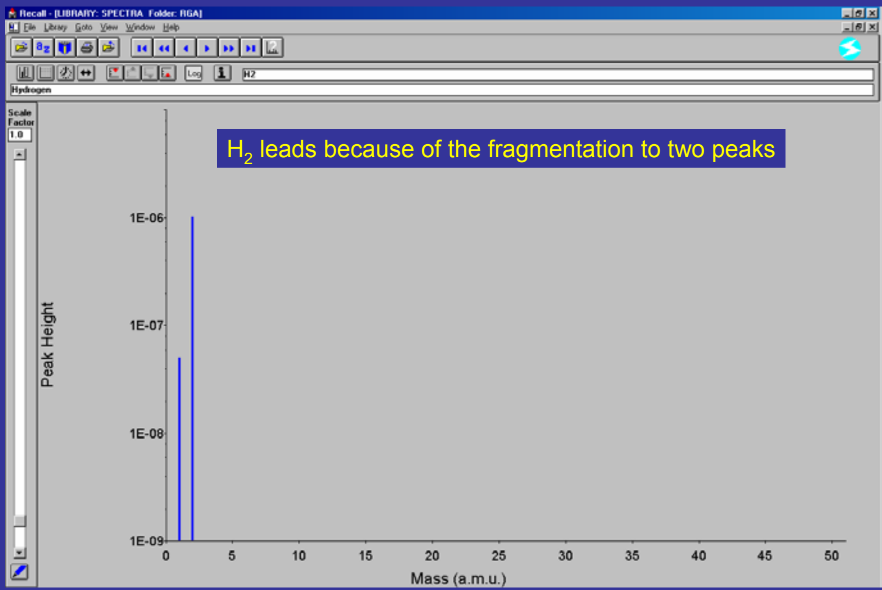
residual gas analysis (RGA)



4. residual gas analysis (RGA)

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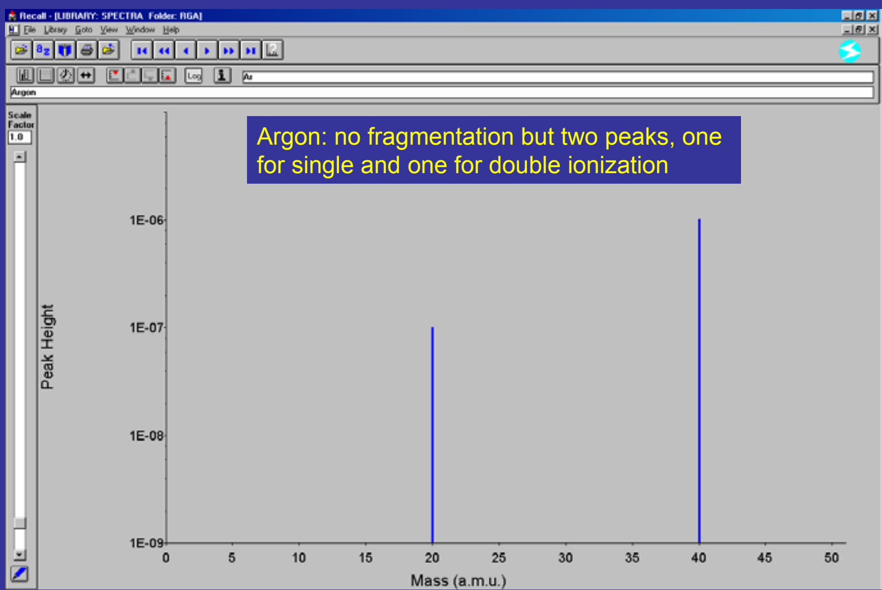
residual gas analysis (RGA)



4. residual gas analysis (RGA)

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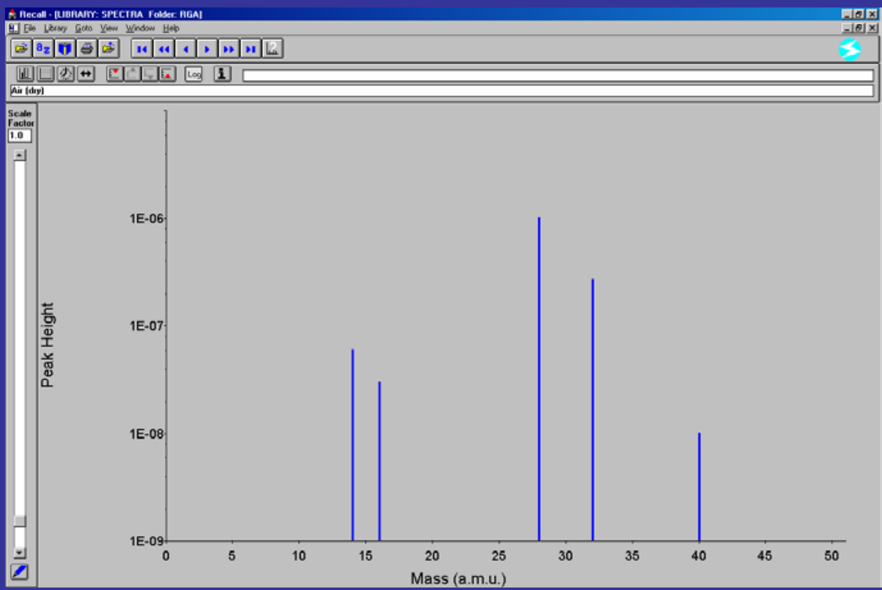
residual gas analysis (RGA)



2. generation of gas-phase ions

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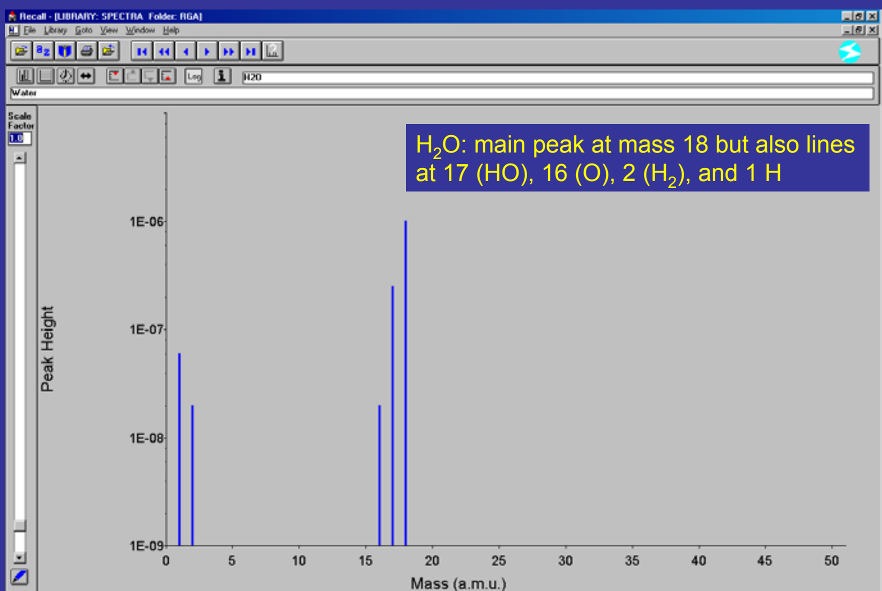
residual gas analysis (RGA)



H_2O: main peak at mass 18 but also lines at 17 (HO), 16 (O), 2 (H_2), and 1 H

2. generation of gas-phase ions

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residual gas analysis (RGA)

AMU	ION(S)	SOURCE(S)
1	H	Hydrogen, Water, Acids, HY
2	H_2	Hydrogen
	D	Deuterium
3	HD	Hydrogen – Deuterium
	He	^{3}Helium
4	He	Helium
6	C	DI Carbon
7	N	DI Nitrogen
8	O	DI Oxygen
10	Ne	DI Neon
11	Ne	DI ^{22}Neon
12	C	Carbon dioxide or monoxide, HY, HL
13	CH	Methane, HY
14	CH_2	Methane, HY
	N	Nitrogen, Ammonia
15	CH_3	Methane, HY
	NH	Ammonia
16	CH_4	Methane, HY
	NH_2	Ammonia
	O	Oxygen, Carbon dioxide or monoxide, Water, Alcohol
17	NH_3	Ammonia
	OH	Water, Alcohol
18	H_2O	Water
	Ar	DI ^{36}Argon

AMU	ION(S)	SOURCE(S)
19	F	Fluorine, Hydrofluoric acid, HL, Silicon tetrafluoride, PFK, PFTBA
20	HF	Hydrofluoric acid
	Ar	DI Argon
	Ne	Neon
22	Ne	^{22}Neon
	CO_2	DI Carbon dioxide
24	C_2	HL, HY
25	C_2H	HY
	CF_2	HL, DI CF_2
26	C_2H_2	HY
	CN	Hydrogen cyanide
27	C_2H_3	HY
	HCN	Hydrogen cyanide
28	C_2H_4	HY
	CO	Carbon dioxide or monoxide
	N_2	Nitrogen, Air
	Si	Silicon, Silicon tetrafluoride
29	C_2H_2	HY
	COH	Alcohol
	N_2	^{15}Nitrogen + ^{14}Nitrogen
30	C_2H_6	HY
	COH_2	Alcohol
	N_2	^{15}Nitrogen$_2$
	NO	Nitrogen oxides

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eration of gas-phase ions

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residual gas analysis (RGA)

AMU	ION(S)	SOURCE(S)
31	CH_3O	Alcohol
	CF	HL, PFK, PFTBA
	P	Phosphorus
32	CH_3OH	Alcohol
	CHF	HL
	O_2	Oxygen
	S	Sulfur
33	SH	Hydrogen sulfide
	S	^{33}Sulfur
	CH_2F	HL
34	H_2S	Hydrogen sulfide
	SH	Hydrogen^{33} sulfide
	S	^{34}Sulfur
	CH_3F	HL
35	H_2S	Hydrogen^{33} sulfide
	C1	Chlorine, Hydrochloric acid, HL, Chlorobenzene, Carbon, tetrachloride
	OF	HL
36	H_2S	Hydrogen^{34} sulfide
	HC1	Hydrochloric acid
	C_3	HY
	Ar	^{36}Argon
37	C1	^{37}Chlorine, HL, Hydrochloric acid Chlorobenzene, Carbon tetrachloride
	C_3H	HY
38	HC1	Hydrogen^{37} chloride
	C_3H_2	HY
	F_2	HL, Fluorine

AMU	ION(S)	SOURCE(S)
39	C_3H_3	HY
40	C_3H_4	HY
	Ar	Argon
41	C_3H_5	HY
	C_2HO	Alcohol
42	C_3H_6	HY
	C_2H_2O	Alcohol
43	C_3H_7	HY
	C_2H_3O	Alcohol, Acetone, Methyl Ethyl Ketone
44	C_3H_8	HY
	CO_2	Carbon dioxide
	N_2O	Nitrous oxide
	CS	Carbon disulfide
45	C_2H_5O	Alcohol
46	C_2H_5OH	Alcohol
	NO_2	Nitrogen dioxide
47	CC1	Carbon tetrachloride, HL
	SiF	Silicon tetrafluoride
48	CHC1	HL
	SO	Sulfur dioxide
49	CH_2C1	HL, Chlorobenzene
	CC1	Carbon tetrachloride, HL
50	CHC1	HL, Chlorobenzene
	CF_2	HL, PFK, PFTBA
	C_4H_2	HY
	SO_2	Sulfur dioxide

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2. generation of gas-phase ions

1. introduction
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3. overview of mass spectrometry systems
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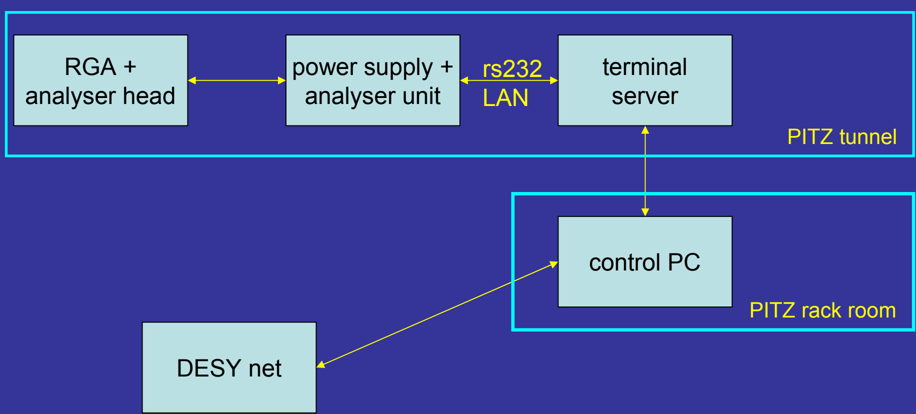
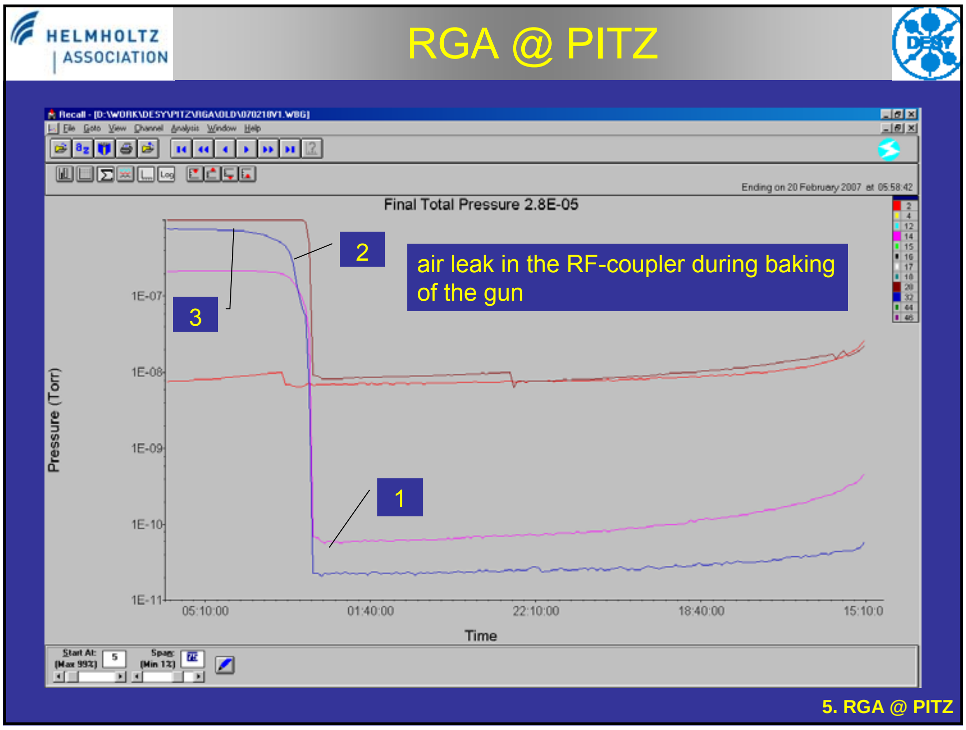
5. RGA @ PITZ

RGA @ PITZ

As RGA a Spectra Satellite LM61 (100 amu) is used.
The RGA is located near the PITZ RF-gun. The system needs 5 min. for measuring one spectrum from mass 1 to 50 (gun and coupler: Cu 64 amu).

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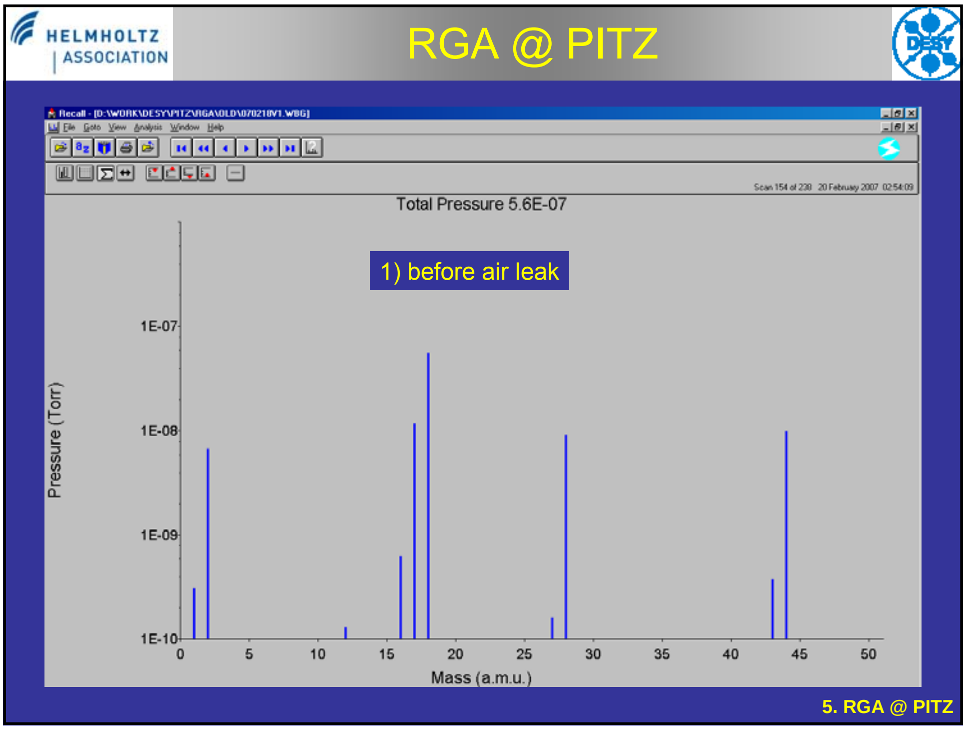
RGA @ PITZ
Ending on 20 February 2007 at 05:58:42
Final Total Pressure 2.8E-05
2
air leak in the RF-coupler during baking of the gun
3
1
Pressure (Torr)
1E-07
1E-08
1E-09
1E-10
1E-11
05:10:00
01:40:00
22:10:00
18:40:00
15:10:0
Time
5. RGA @ PITZ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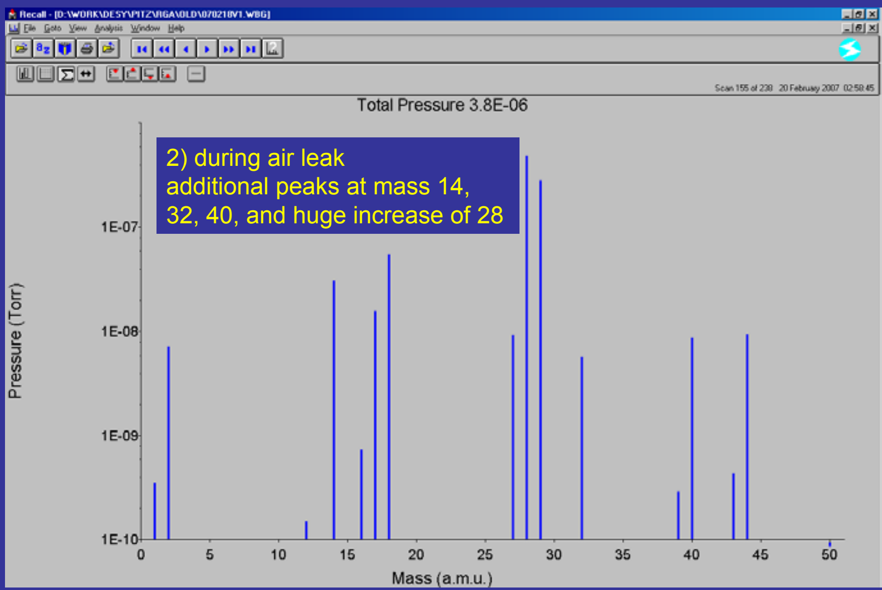
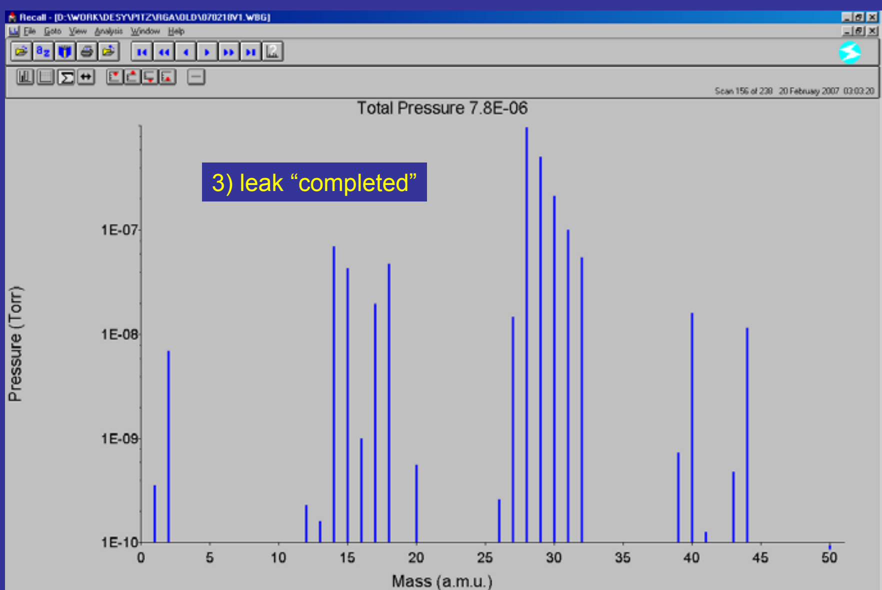
RGA @ PITZ
Total Pressure 5.6E-07
1) before air leak
Pressure (Torr)
1E-07
1E-08
1E-09
1E-10
0
5
10
15
20
25
30
35
40
45
50
Mass (a.m.u.)
5. RGA @ PITZ

RGA @ PITZ

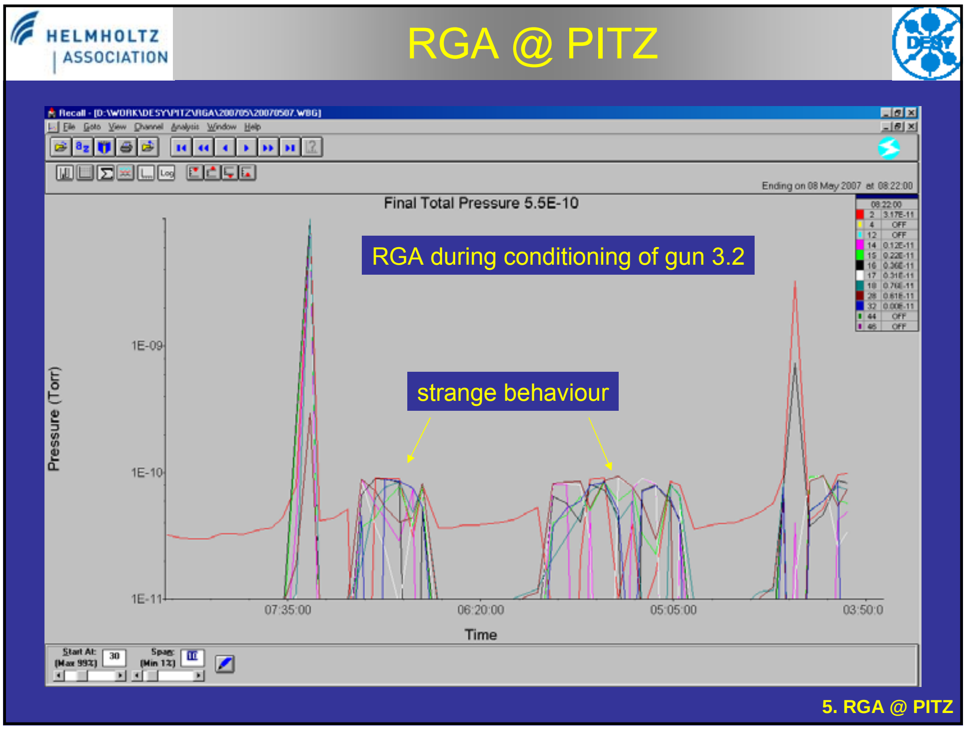


5. RGA @ PITZ

RGA @ PITZ



5. RGA @ PITZ



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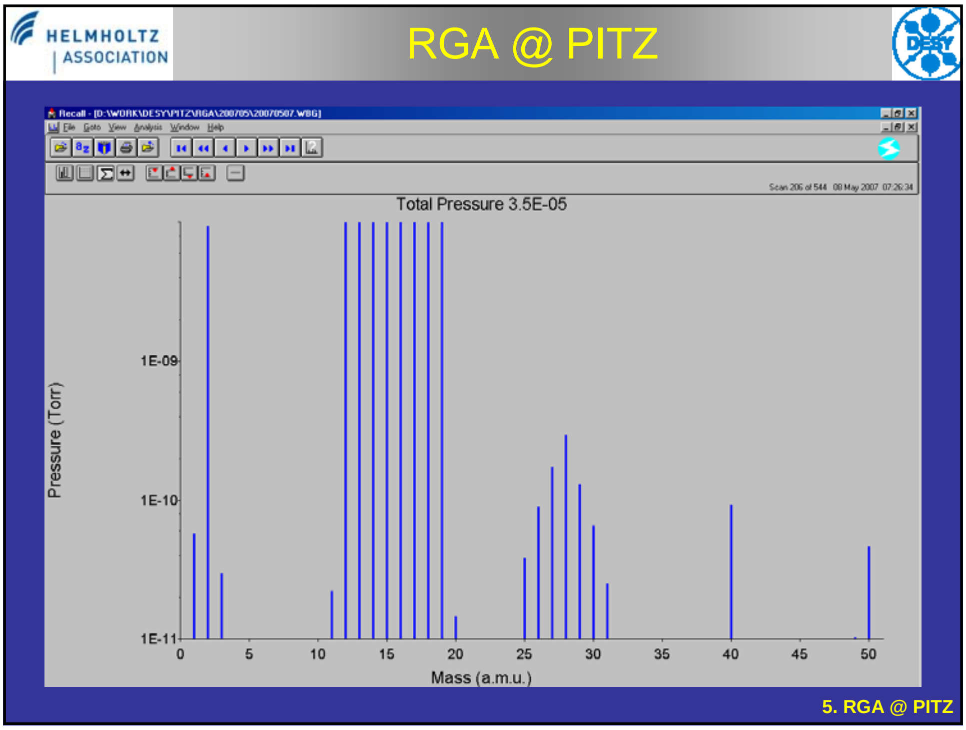
RGA @ PITZ
Final Total Pressure 5.5E-10
RGA during conditioning of gun 3.2
strange behaviour
Pressure (Torr)
1E-09
1E-10
1E-11
07:35:00
06:20:00
05:05:00
03:50:0
Time
5. RGA @ PITZ



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RGA @ PITZ
Total Pressure 3.5E-05
Pressure (Torr)
1E-09
1E-10
1E-11
0
5
10
15
20
25
30
35
40
45
50
Mass (a.m.u.)
5. RGA @ PITZ

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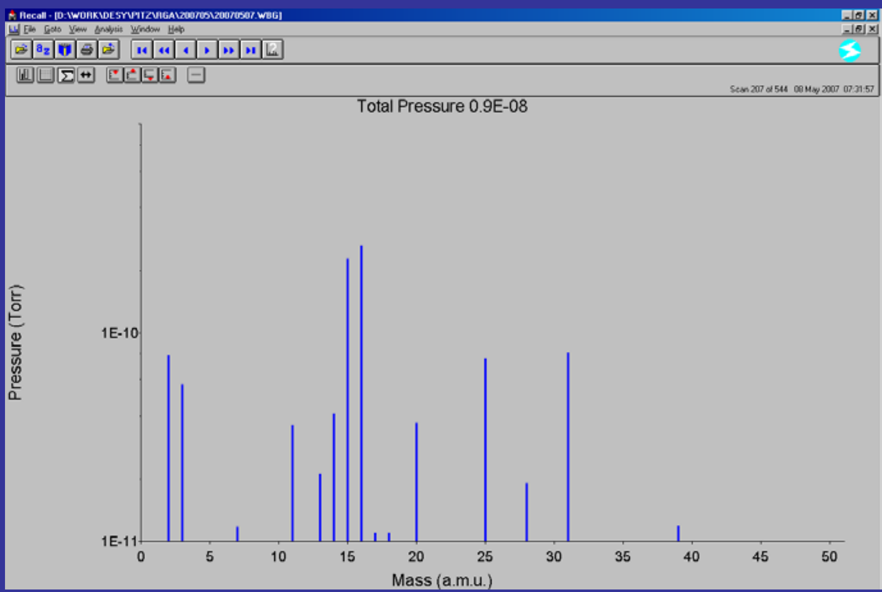
RGA @ PITZ



5. RGA @ PITZ

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summary and outlook

- summary
  - MS systems and ionisation techniques were presented
  - description of special MS-topic RGA
  - introduction to the usage of RGA @ PITZ
- outlook
  - understanding of the some times strange behaviour of the RGA @ PITZ
  - evaluation of the data taken during conditioning
  - new system
    - probably Pfeiffer QMS: consistency to system in vacuum lab, no complicate way of communication because of fibre connection

2. generation of gas-phase ions