Reconstruction of mass spectra
on the basis of partial pressures

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Why reconstructing ?

- Visual: Analyser ***resolution***, ***noise***, ***offset*** and ***artefacts*** can be included

- RGA are NOT ideal instruments:

High uncertainties in gas the specific sensitivities and fragmentation .

Reconstruction by assimilation to measured spectrum is an alternative to solving (by deconvolution) for partial pressures.

- Simulation allows training of personal on many cases without need for measurements.

- Check for suspected contaminants by adding fragmentation pattern of suspected component to library

- Convincing, if residual gas composition is well identified. Discussions on acceptance can be more specific.

Some definitions used here

Sensitivity ion gauge: $\beta_n = \frac{\Delta I_{c,n}}{I_e \ \Delta P_n}$

Proportionality factor of the measured chande in collector current $I_{c,n}$ *as a reaction to a change in the partial pressure of a gas species* **n** *divided by the electron emission current* I_e.

Sensitivity residual gas analyser RGA: $\alpha_n = \frac{\Delta I_{M,n}}{\Delta P_n}$

Proportionality factor of the measured detector current at mass **M** *as a reaction to a change in the partial pressure of a gas species* **n**. *If* **M** *is not indicated, it refers ot mass with maximum intensity in fragmentation pattern.*

Normalised or relative sensitivity: $\kappa_{n-N_2} = \frac{\beta_n}{\beta_{N_2}}$

Sensitivity of an **Ion gauge** to a gas species with respect to the sensitivity for nitrogen (here)

$\eta_{n-N_2} = \frac{\alpha_n}{\alpha_{N_2}}$

Sensitivity of an **RGA** to a gas species with respect to the sensitivity for nitrogen (here)

Reconstruction of mass spectra on the basis of partial pressures

Mass spectrum: Measurement of Ion detector current as functin of ***m/z***

Ion (detector) currents at mass ***m*** ***[A]***

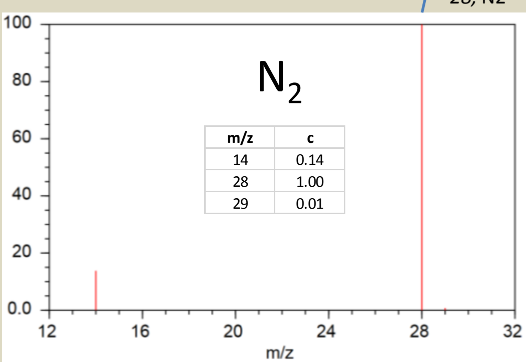
Contribution of component ***b*** to ion current signal at mass ***m***

Sensitivity of analyser to reference peak ***[A / mbar]***

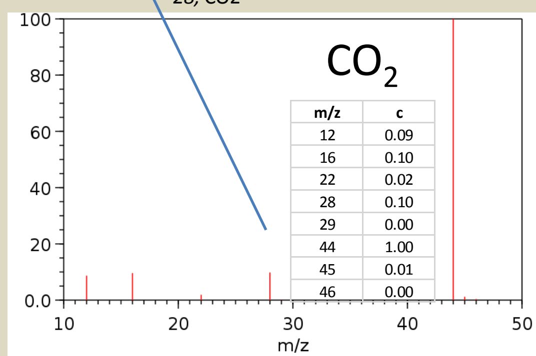
Partial pressure ***[mbar]***

$$I_m = c_{m,a}\alpha_a P_a + c_{m,b}\alpha_b P_b + c_{m,c}\alpha_c P_c + \dots + c_{m,N}\alpha_N P_N$$

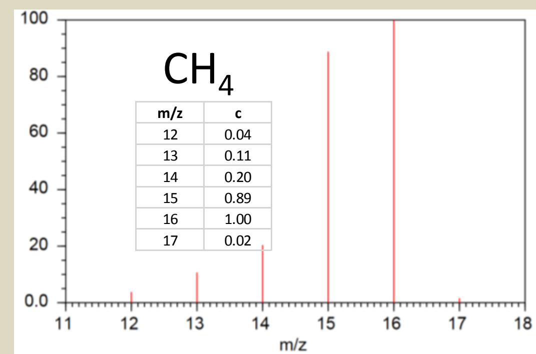
$C_{28,\,N2} = 1$ $\quad$ $C_{28,\,CO2} = 0.1$ $\quad$ $C_{28,\,CH4} = 0$



m/z	c
14	0.14
28	1.00
29	0.01



m/z	c
12	0.09
16	0.10
22	0.02
28	0.10
29	0.00
44	1.00
45	0.01
46	0.00



m/z	c
12	0.04
13	0.11
14	0.20
15	0.89
16	1.00
17	0.02

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Equations for all masses

Mass spectrum

Fragmentation pattern
Relative height to reference peak

Sensitivity
to reference peak

Partial pressure

Composition of ***N*** gases

$$
\begin{aligned}
I_1 &= c_{1,a}\alpha_a P_a + c_{1,b}\alpha_b P_b + c_{1,c}\alpha_c P_c + \ldots + c_{1,N}\alpha_N P_N \\
I_2 &= c_{2,a}\alpha_a P_a + c_{2,b}\alpha_b P_b + c_{2,c}\alpha_c P_c + \ldots + c_{2,N}\alpha_N P_N \\
I_3 &= c_{3,a}\alpha_a P_a + c_{3,b}\alpha_b P_b + c_{3,c}\alpha_c P_c + \ldots + c_{3,N}\alpha_N P_N \\
&\vdots \\
I_z &= c_{z,a}\alpha_a P_a + c_{z,b}\alpha_b P_b + c_{z,c}\alpha_c P_c + \ldots + c_{z,N}\alpha_N P_N
\end{aligned}
$$

$$
\begin{bmatrix} I_1 \\ I_2 \\ \vdots \\ I_z \end{bmatrix} = \begin{bmatrix} c_{1,a} \\ c_{2,a} \\ \vdots \\ c_{z,a} \end{bmatrix}\alpha_a P_a + \begin{bmatrix} c_{1,b} \\ c_{2,b} \\ \vdots \\ c_{z,b} \end{bmatrix}\alpha_b P_b + \begin{bmatrix} c_{1,c} \\ c_{2,c} \\ \vdots \\ c_{z,c} \end{bmatrix}\alpha_c P_c + \ldots + \begin{bmatrix} c_{1,N} \\ c_{2,N} \\ \vdots \\ c_{z,N} \end{bmatrix}\alpha_N P_N
$$

Reconstruction of mass spectra on the basis of partial pressures

$$\begin{bmatrix} I_1 \\ I_2 \\ \vdots \\ I_z \end{bmatrix} = \begin{bmatrix} c_{1,a} & c_{1,b} & \cdots & c_{1,N} \\ c_{2,a} & c_{2,b} & \cdots & c_{2,N} \\ \vdots & \vdots & \cdots & \vdots \\ c_{z,a} & c_{z,b} & \cdots & c_{z,N} \end{bmatrix} \begin{bmatrix} \alpha_a P_a \\ \alpha_b P_b \\ \vdots \\ \alpha_N P_N \end{bmatrix}$$

$$\underbrace{\begin{bmatrix} I_1 \\ I_2 \\ \vdots \\ I_z \end{bmatrix}}_{\vec{I}} = \underbrace{\begin{bmatrix} c_{1,a} & c_{1,b} & \cdots & c_{1,N} \\ c_{2,a} & c_{2,b} & \cdots & c_{2,N} \\ \vdots & \vdots & \cdots & \vdots \\ c_{z,a} & c_{z,b} & \cdots & c_{z,N} \end{bmatrix}}_{\underline{C}} \underbrace{\begin{bmatrix} \alpha_a & 0 & \cdots & 0 \\ 0 & \alpha_b & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \alpha_N \end{bmatrix}}_{\underline{\alpha}} \underbrace{\begin{bmatrix} P_a \\ P_b \\ \vdots \\ P_N \end{bmatrix}}_{\vec{P}}$$

Ion current vector $\vec{I}$

Fragmentation pattern matrix $\underline{C}$

Sensitivity matrix $\underline{\alpha}$

Partial pressur vector $\vec{P}$

$$\vec{I} = \underline{C} \bullet \underline{\alpha} \bullet \vec{P}$$

Whole spectrum expressed in simple mathematical form using matrices and vectors.

Equation for spectra simulation with $\underline{C}$ as <u>fragmentation pattern library</u> and partial pressures in vacuum system.

Reconstruction of mass spectra on the basis of partial pressures

Bar graph spectrum

$$\vec{I} = \underline{C} \bullet \underline{\alpha} \bullet \vec{P}$$

Ion current

Partial pressures

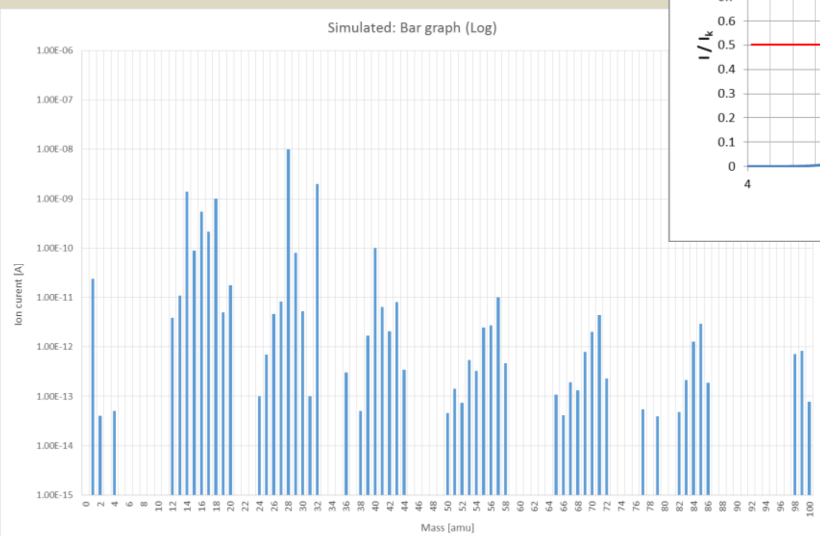
Gas specific sensitivities

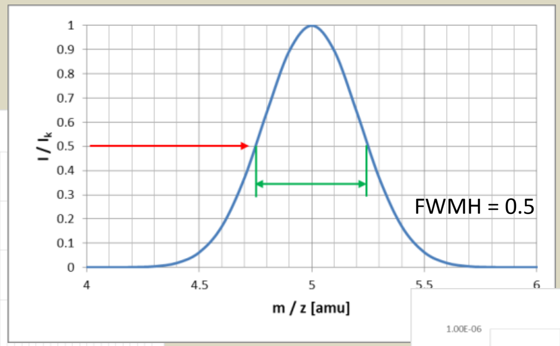
Reference spectra library (fragmentation patterns)

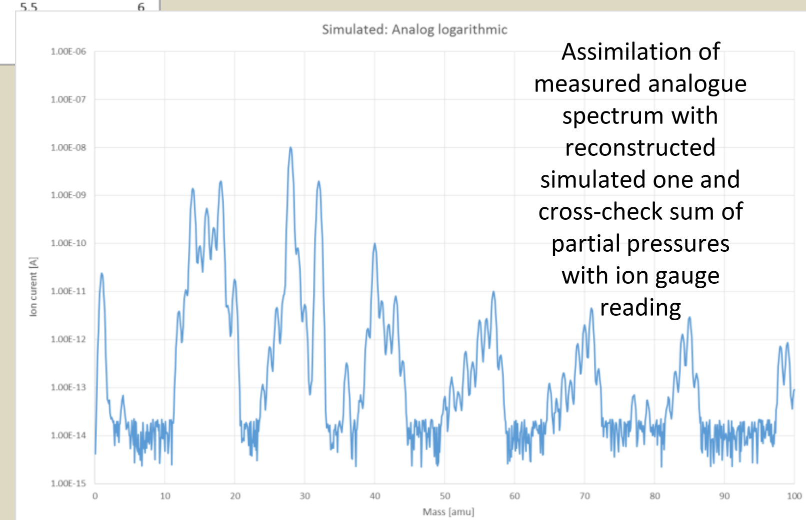
Analogue spectrum

$$I(m) = \sum_{k=0}^{z} I_k e^{\frac{-(m-m_k)^2}{2c^2}} + I_{offs} + I_{noise}$$

$$\mathrm{FWHM} = 2\sqrt{2\ln 2}\, c \approx 2.35482c.$$







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Cross-check: Comparison with ionization gauge

$$P_{tot} = \sum_{n=1\ldots N} P_n$$

P_n Partial pressure of species **n**

Collector current is sum of the contribution of all partial pressures multiplied by their respective sensitivity

I_c BA-gauge collector current

$$I_c = I_e \sum_{n=1\ldots N} \beta_n P_n$$

I_e BA-gauge emission current

β_n Sensitivity of BA gauge to species ***n*** *[mbar^-1]*

$$\frac{I_c}{I_e \beta_{N_2}} = \sum_{n=1\ldots N} \frac{\beta_n}{\beta_{N_2}} P_n$$

κ_{n-N_2} Relative sensitivity of BA gauge to with respect to N_2

$$P_{N_2-eq.} = \sum_{n=1\ldots N} \kappa_{n-N_2} P_n$$

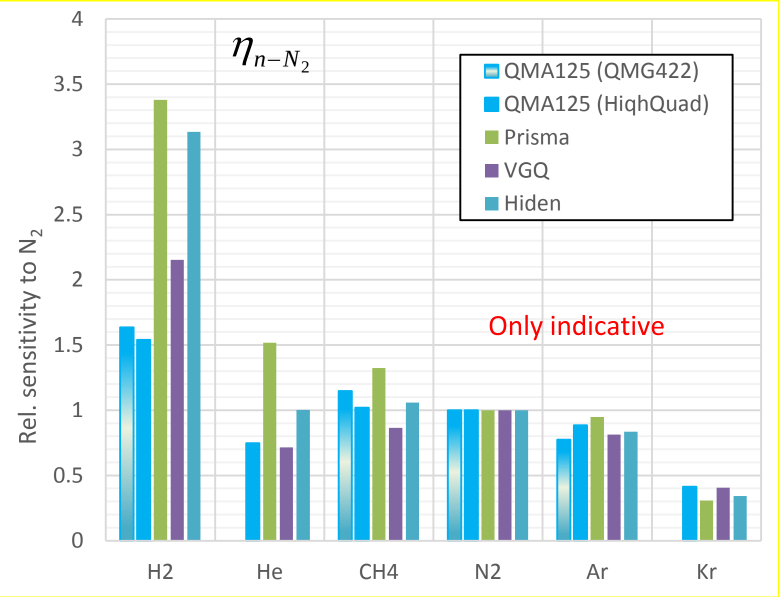
N_2-equivalent pressure indication

P_{n_RGA}

Cross-check RGA

Comparing relative sensitivities

QMS for UHV applications



Normalised sensitivity for different quadrupole mass spectrometers (QMS) at **factory settings**

-> High dispersion at low masses

η_{n-N_2} ↘ with mass ↗

Opposite to ion gauges

Ionisation cross-section + extraction + transmission probability

! **RGA:** Sensitivity to **reference peaks** of fragmentation patterns

*Ion gauges collects **all** fragments*

When comparing with ion gauges **sum up all fragments** of a residual gas component

Ion gauges

κ_{n-N_2}

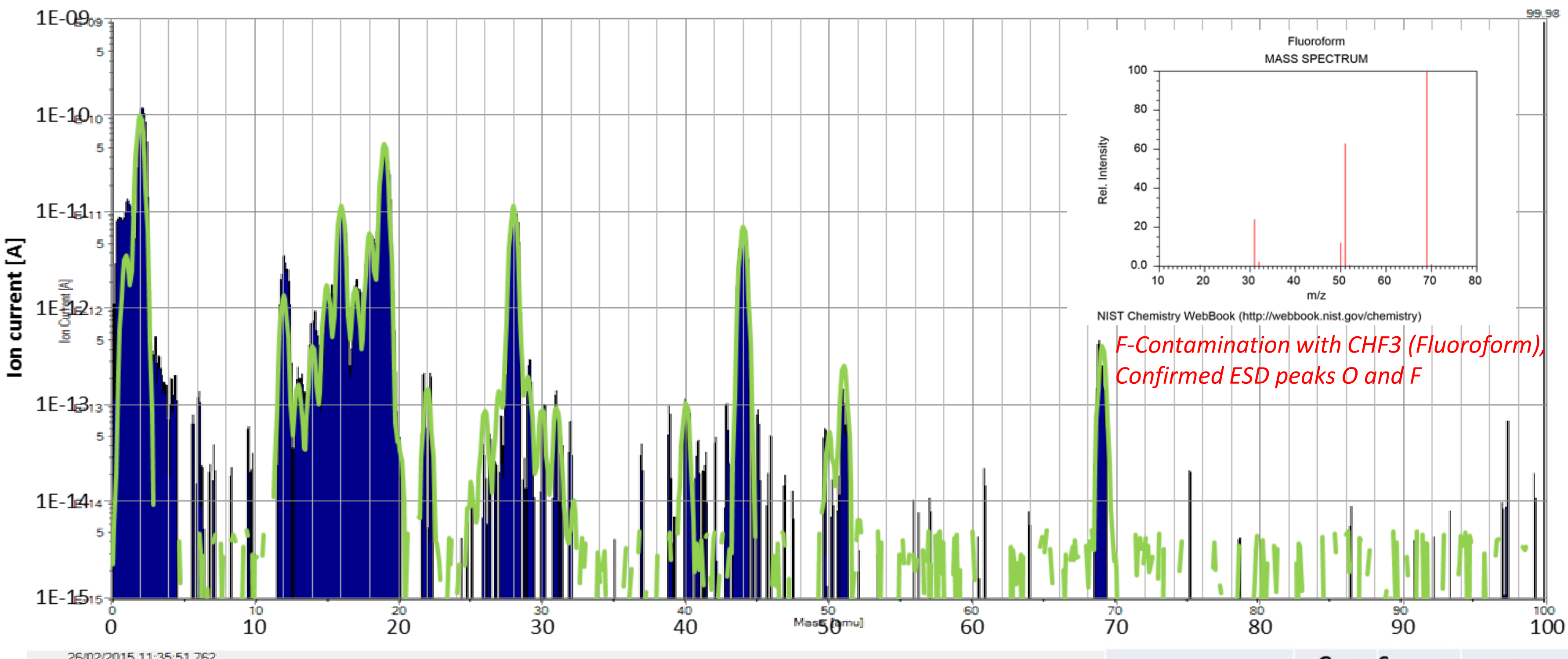
Gas	f_c
He	0.18
Ne	0.3
Ar	1.29
Kr	1.94
Xe	2.87
H_2	0.46
N_2	**1**
O_2	1.01
Air	1
CO	1.05
H_2O	1.12
CO_2	1.42
CH_4	1.4
C_2H_6	2.6
C_3H_8	4.2

Uncertainty < 20 %

Ratio mainly determined by ionisation cross-section

Example of reconstruction of measured with simulated spectrum

Simulated spectrum (analog logaritmic)

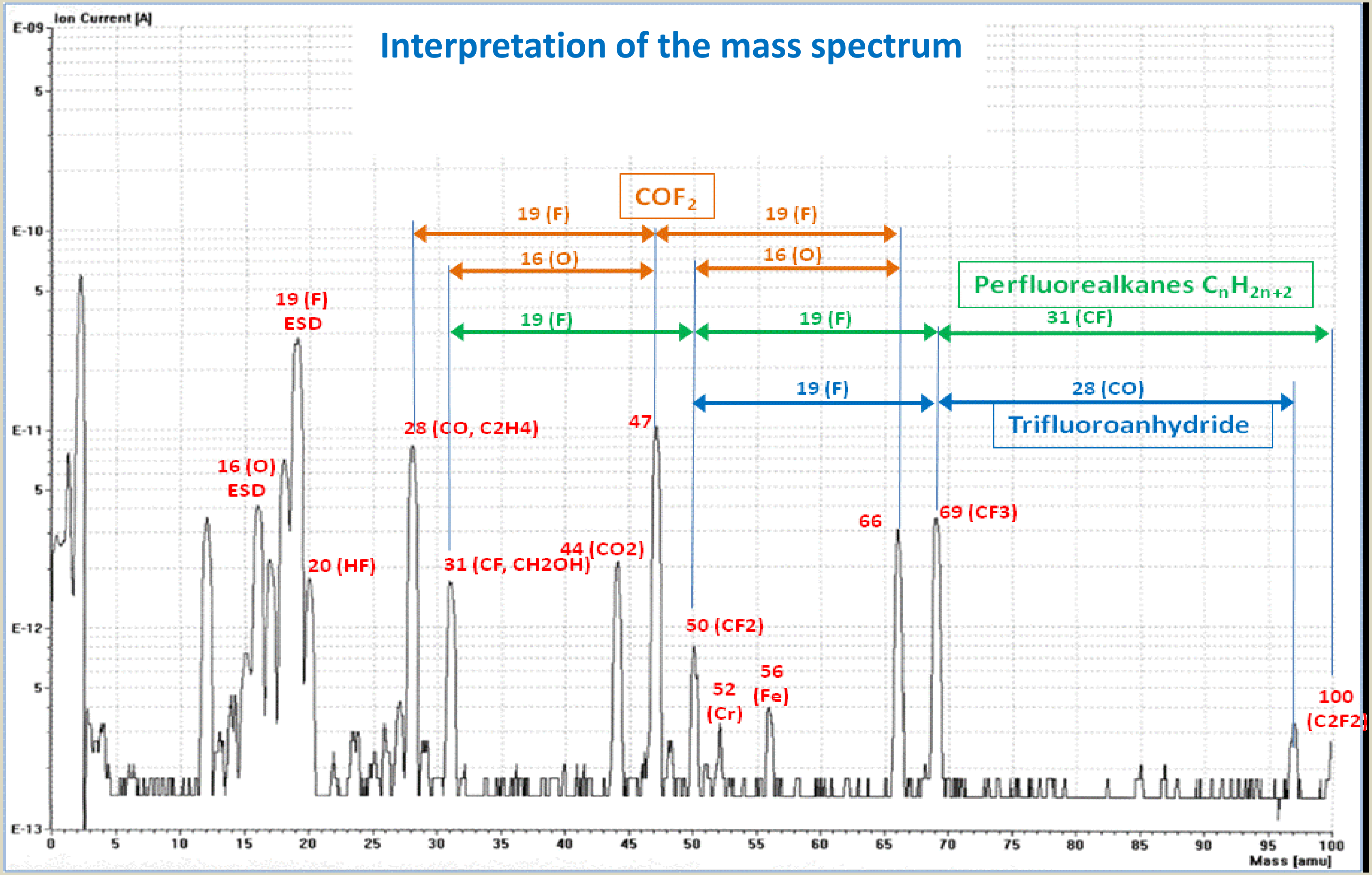


SEM_Multipl.	10000
Sensitivity Ar (FAR) [A/mbar]	1.00E-04
FWHM	0.5

Background dist	1.00E-14
Background offs	-5.00E-15

	Gas	S [A/mbar]	[mbar]
Hydrogen	H2	1.00E+00	1.00E-10
Methane	CH4	1.00E+00	2.00E-12
Water	H2O	1.00E+00	6.00E-12
Carbonmonoxide	CO	1.00E+00	1.00E-11
Ethane	C2H6	1.00E+00	4.00E-13
Argon	Ar	1.00E+00	1.00E-13
Carbondioxide	CO2	1.00E+00	7.00E-12
Oxygen (atomic)	**O**	**1.00E+00**	**8.00E-12**
Fluorine(atomic)	**F**	**1.00E+00**	**5.00E-11**
Freon 23	**CHF3**	**1.00E+00**	**4.00E-13**
		P_tot =	**1.84E-10**

Reconstruction of mass spectra on the basis of partial pressures



Reconstruction of mass spectra on the basis of partial pressures

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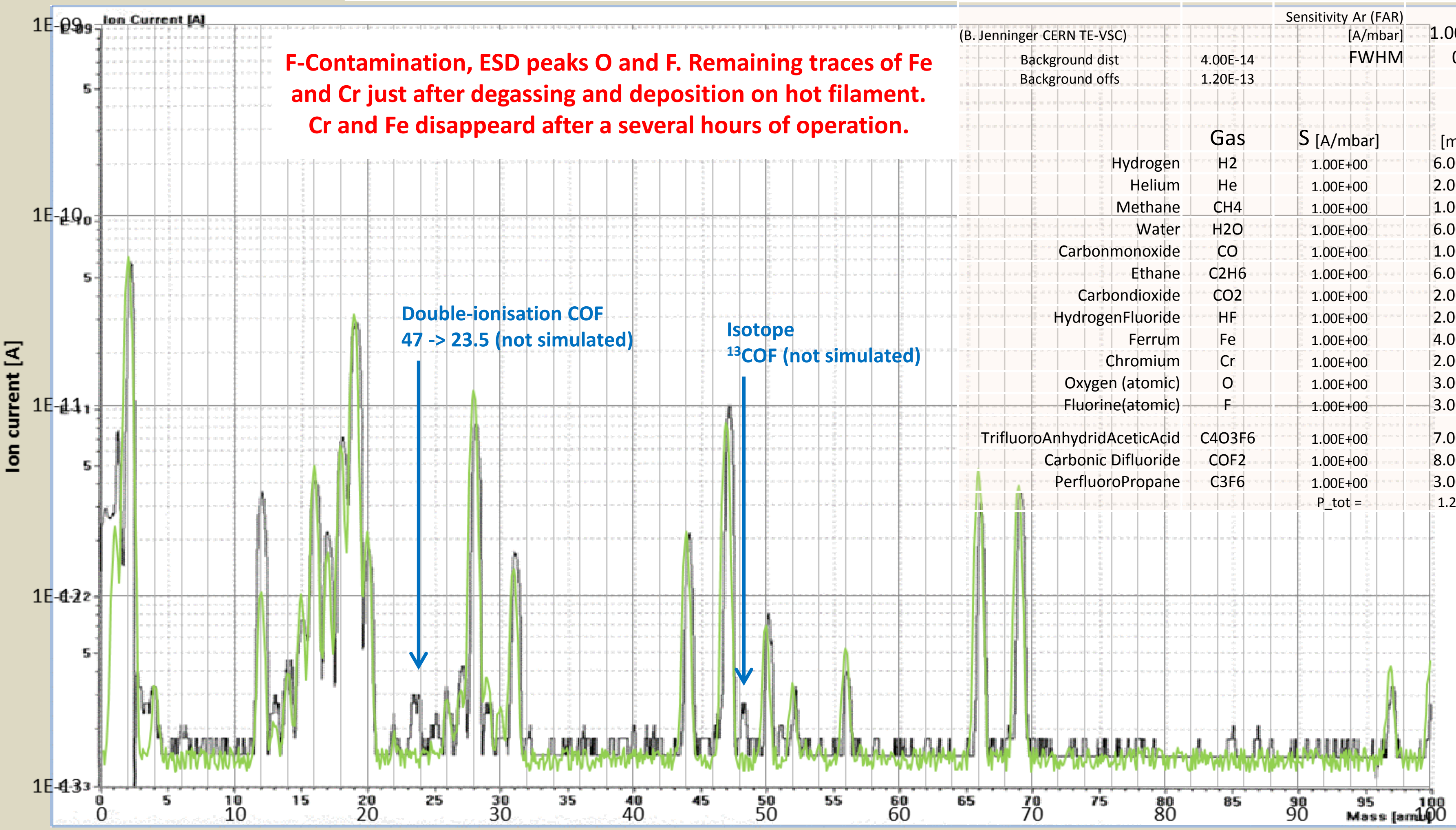
Measured / reconstructed mass spectrum



		SEM_Multipl.	10000
		Sensitivity Ar (FAR) [A/mbar]	1.00E-04
(B. Jenninger CERN TE-VSC)		FWHM	0.5
Background dist	4.00E-14		
Background offs	1.20E-13		
			Pi
	Gas	S [A/mbar]	[mbar]
Hydrogen	H2	1.00E+00	6.00E-11
Helium	He	1.00E+00	2.00E-13
Methane	CH4	1.00E+00	1.00E-12
Water	H2O	1.00E+00	6.00E-12
Carbonmonoxide	CO	1.00E+00	1.00E-11
Ethane	C2H6	1.00E+00	6.00E-13
Carbondioxide	CO2	1.00E+00	2.00E-12
HydrogenFluoride	HF	1.00E+00	2.00E-12
Ferrum	Fe	1.00E+00	4.00E-13
Chromium	Cr	1.00E+00	2.00E-13
Oxygen (atomic)	O	1.00E+00	3.00E-12
Fluorine(atomic)	F	1.00E+00	3.00E-11
TrifluoroAnhydridAceticAcid	C4O3F6	1.00E+00	7.00E-13
Carbonic Difluoride	COF2	1.00E+00	8.00E-12
PerfluoroPropane	C3F6	1.00E+00	3.00E-12
		P_tot =	1.27E-10

Spectrum can be fully explained with presence of Fluorine + known composition in hot ion source (C, O, H, Fe, Cr)

ISO 14291: Vacuum gauges — Definitions and specifications for quadrupole mass spectrometers

ISO/NP TS 20175 (in preparation): Vacuum technology -- Vacuum gauges - Calibration of quadrupole mass spectrometers for partial pressure measurement

ISO/NP TS 20177 (in preparation): Vacuum technology - Vacuum gauges -- Procedures to measure and report outgassing rates.

NOW

Exercise: Reconstructing a measured mass spectrum