Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin
Nationales Metrologieinstitut

17th CCM meeting May 16/17, 2019

Traceable desorption and outgassing rate measurements

Karl Jousten, PTB, Berlin, Germany

1. Short tutorial on related vacuum physics
2. Method of outgassing rate measurement
3. Written and measurement standards
4. Conclusions

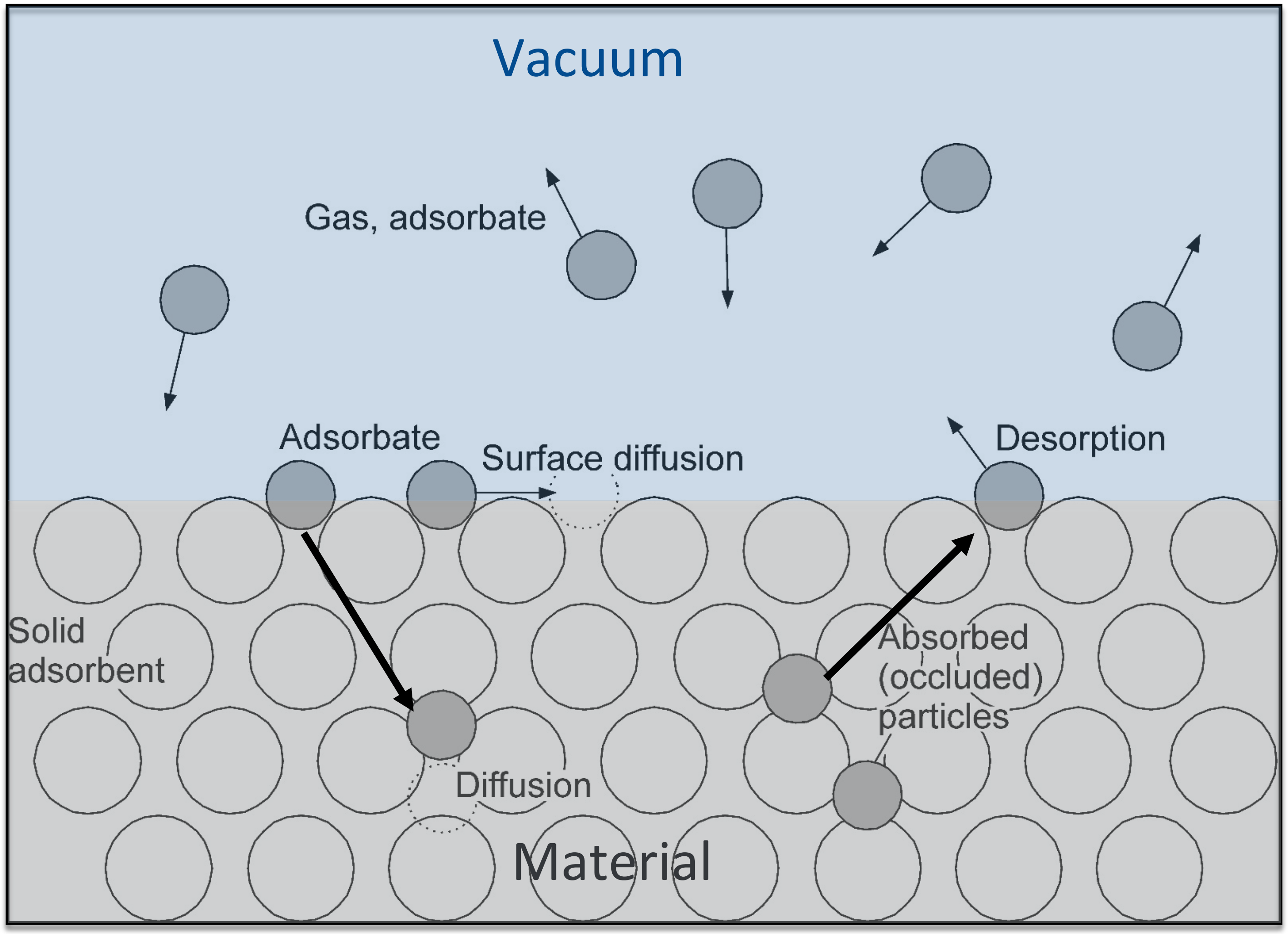
What is desorption, what is outgassing?

Desorption:
Release of molecules from a surface – Surface effect

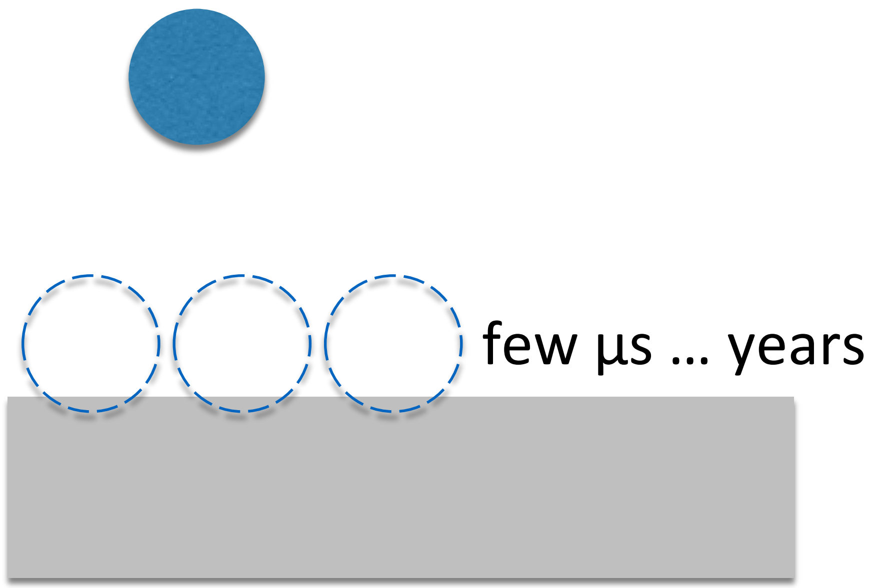
Will be „zero“ after cleaning or long times – rate depends on time

Outgassing:
Release of molecules from a bulk – Bulk effect

Will „never“ end – time independent



Desorption rate with time



$\widetilde{n_0}(t)$ surface layer

Ideal vacuum/vacuum pump

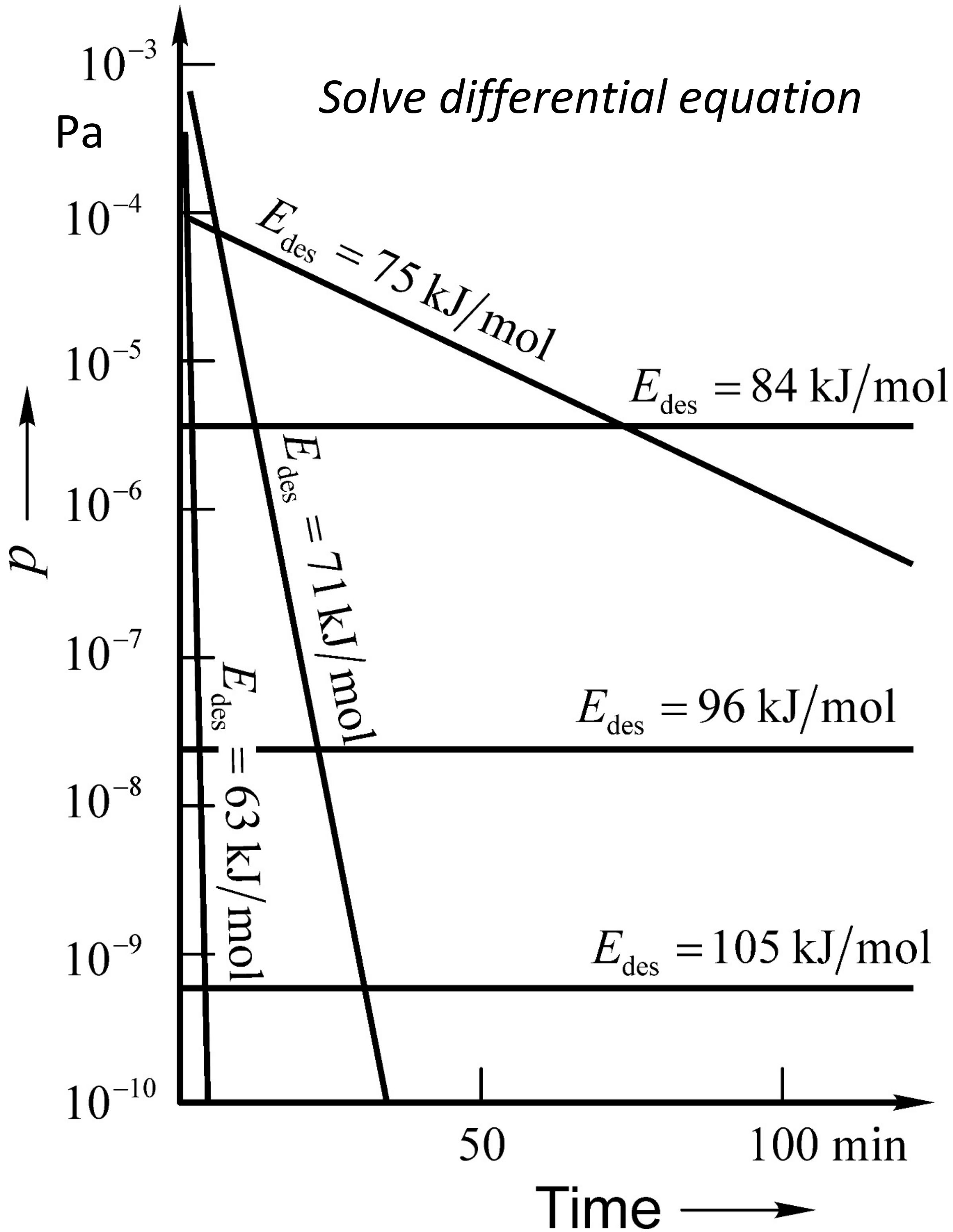
$$\tilde{n}(t) = \widetilde{n_0}(t)e^{-t/\tau}$$

$$\tau = \tau_0 e^{E_{\mathrm{des}}/RT}$$

Real case: readsorption

Reduction rate much lower than exponential

Desorption rate with time at real conditions



H_2O on stainless steel:

E_{des} 80 kJ/mol … 104 kJ/mol

Similar values for hydrocarbons

Our experience in vacuum technology

In any, not baked-out vacuum system water molecules dominate the residual gas (70 % to 95%).

Typically, any surface exposed to air is “coated” by a few monolayers of H_2O (typically a few up to 30).

All but the last monolayer of H_2O disappear quickly in a vacuum pump down process down to about 1 Pa.

Numbers: Mass per area

Mass/geometrical surface area = Number of sites per area * mass of individual molecule

One monolayer of H_2O molecules on a surface:

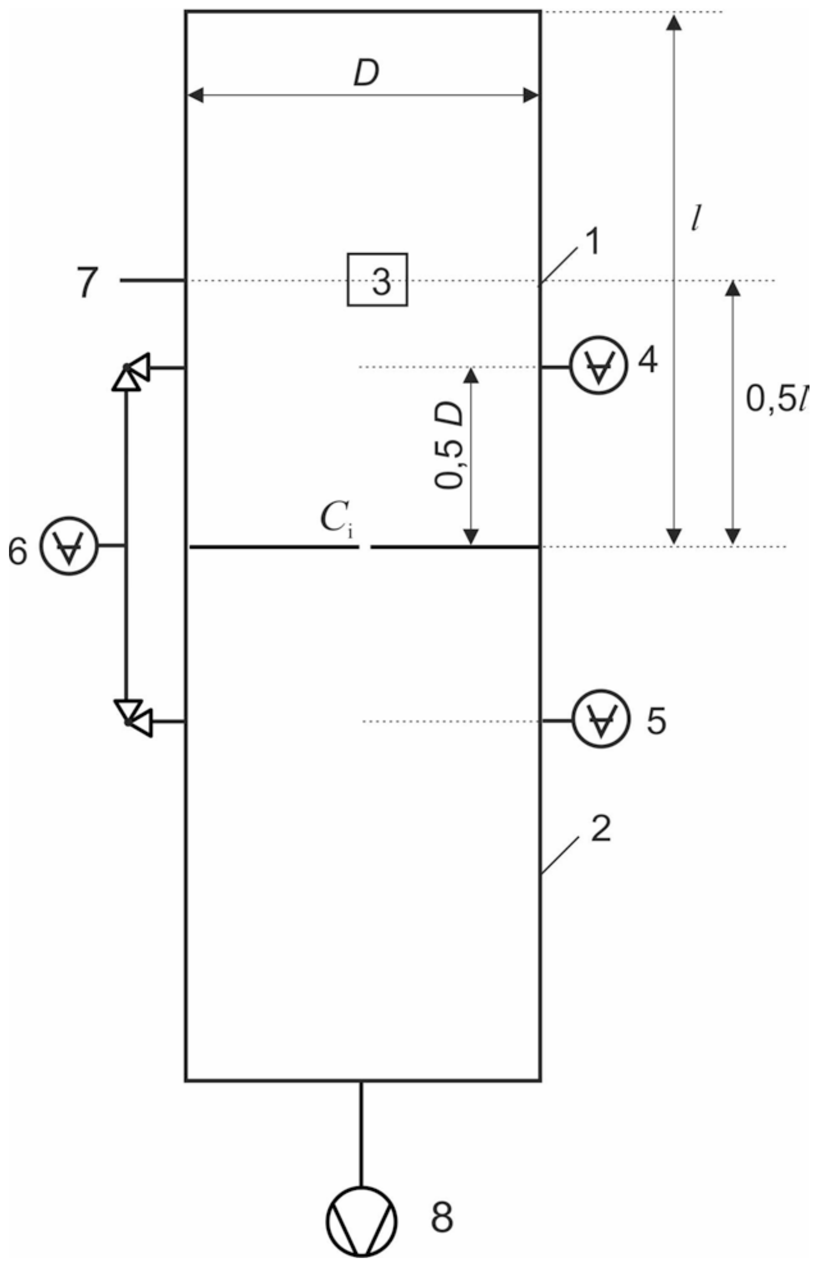
10^{15} cm^{-2}·18·1.66·10^{-27} kg = 3 ·10^{-11} kg cm^{-2} = 0.03 µg cm^{-2}

Metrologia 53 (2016), S. Davidson et al., Table 1: “Sorption value” below 1 Pa:

0.013 µg cm^{-2} … 0.16 µg cm^{-2}

10^{15} cm^{-2} = 4.1 ·10^{-3} Pa L cm^{-2} for 296 K (preferred and convenient units in vacuum metrology)

How to measure desorption/outgassing rates?

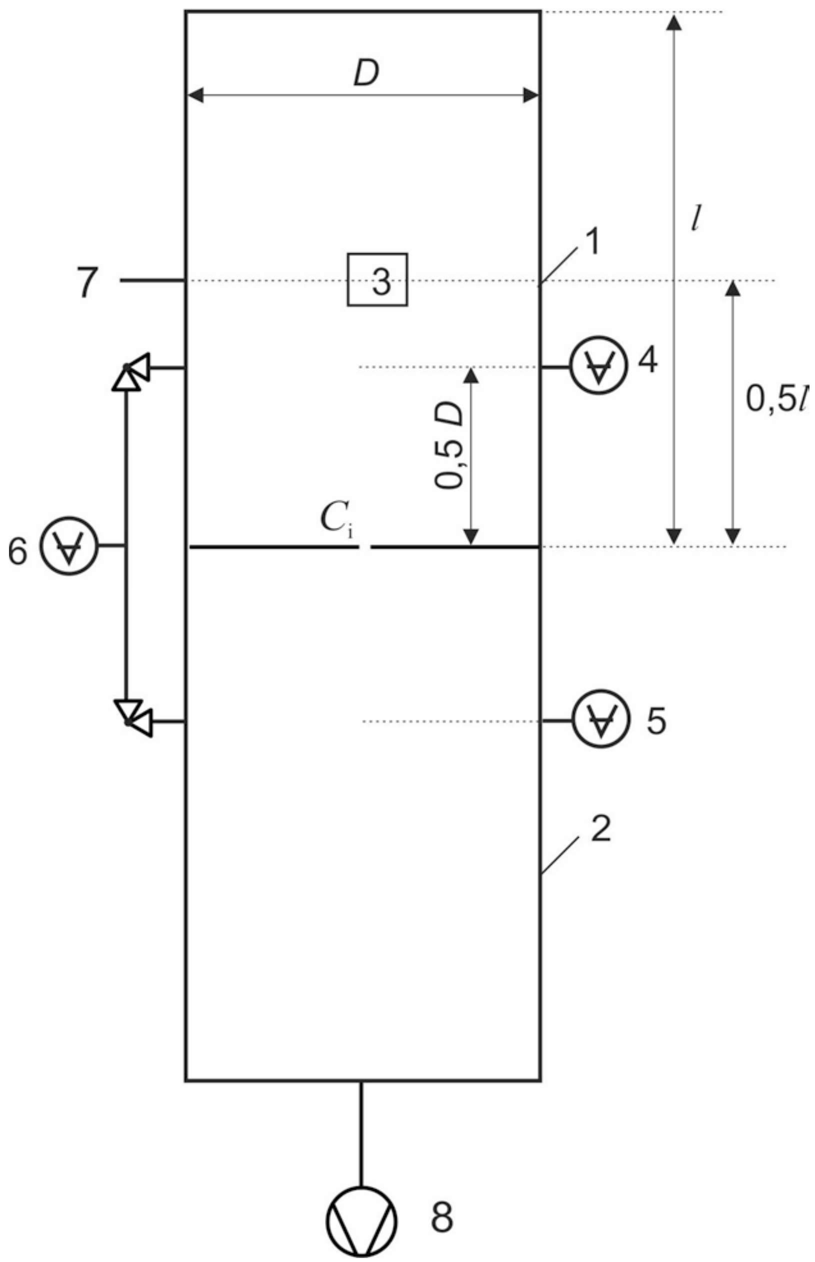


ISO TS 20177

$$q_{\mathrm{out},\,i} = C_i \left(p_{1,i} - p_{2,i} \right)$$

time dependent for desorption
time independent for outgassing

Why is it difficult?



ISO TS 20177

$$q_{\text{out},i} = C_i\left(p_{1,i} - p_{2,i}\right)$$

1) Pressure gradients in vacuum systems:

- Positioning of sample
- Positioning of conductance
- Positioning of detector
- Non-infinite pumping speed

2) Outgassing/desorption from vacuum chamber: „zero“=residual pressure, its Stability

3) Time dependence: When is *t* =0 ?

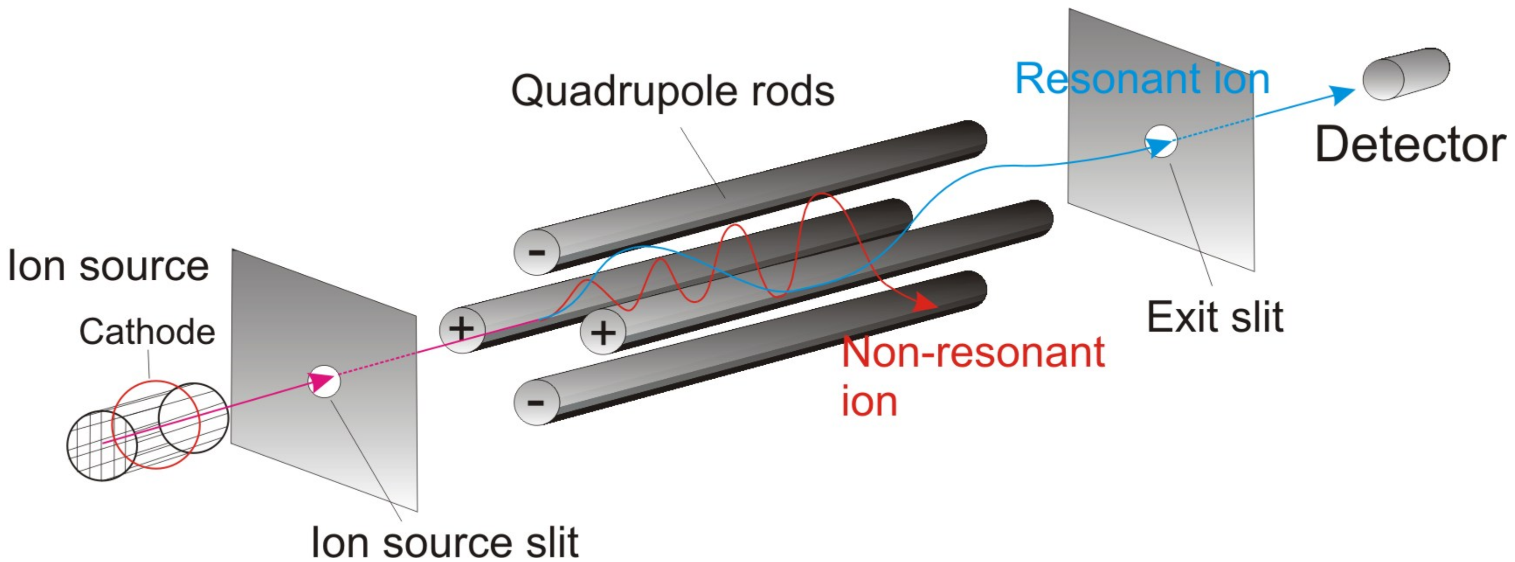
4) Mixture of outgassing species: Sensitivity of total pressure vacuum gauge unknown

and the worst:

5) Partial pressure measurement: Quadrupole mass spectrometers cannot be calibrated

Quadrupole mass spectrometers

How they work



What we know

•Settings of QMS play an important role: emission current, electron energy, ion energy, field axis potential, m/e resolution, scan speed, multiplier gain

•Settings of each type of QMS have different consequences in their metrological characteristics

•Often settings of individual QMS of the same type have different consequences

•Relative sensitivity for single gas species (to nitrogen) cannot be predicted

Problem of sensitivity ->

Quadrupole mass spectrometers

What we know

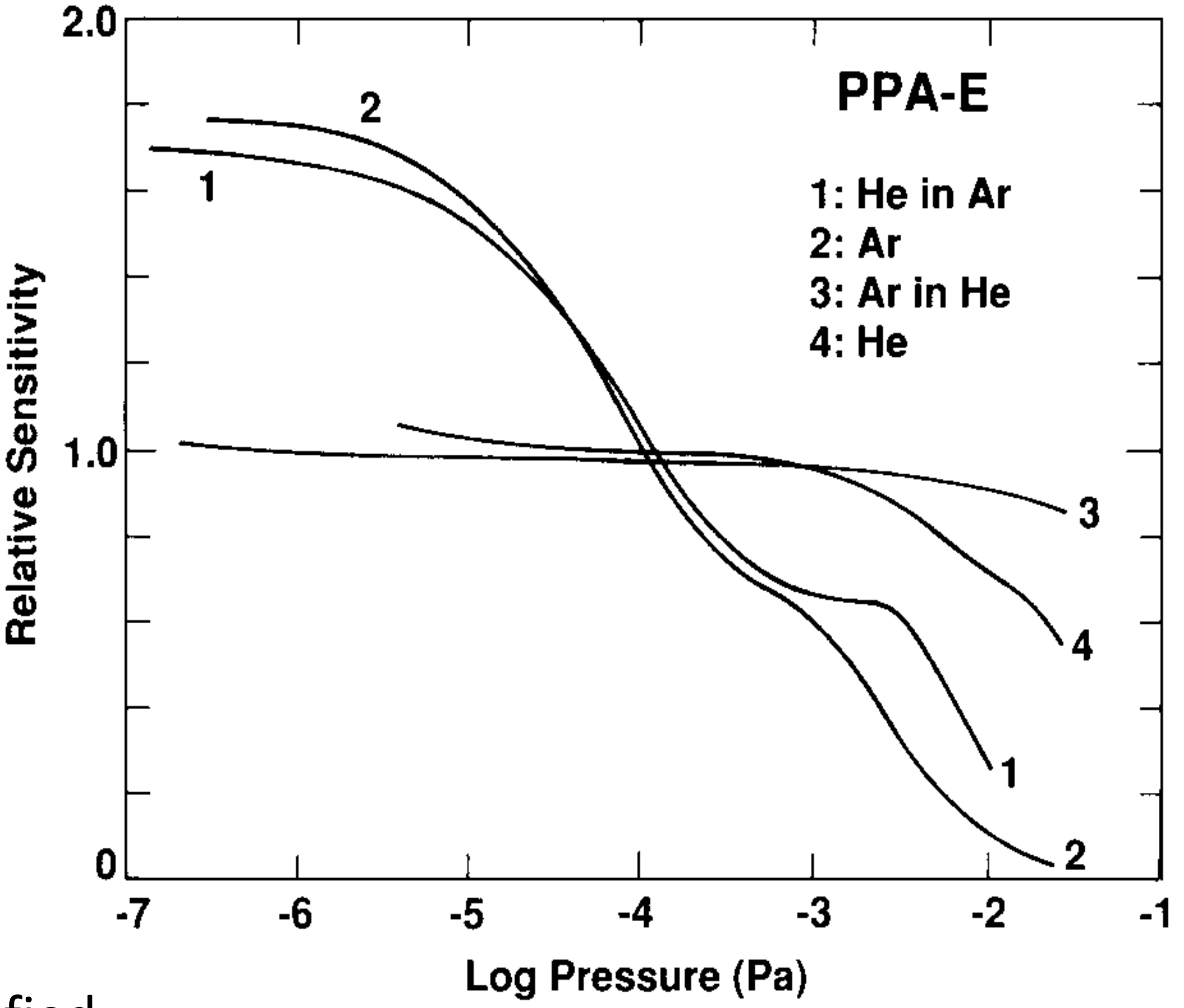
•Sensitivity depends on total pressure

•Sensitivity depends on gas mixture →

•Ion source fragmentates molecules

•Ion source generates multiple charged atoms and molecules

•QMS produces and measures own mass peaks (CO, CO_2, H_2O, m/e=19)



Lieszkovsky, Filippelli, Tilford, JVST A 8 (1990), 3838…3854

Conclusions:

- No general calibration possible
  30 gas species: 1E9 possibilities to mix!
- Conditions and gases must be carefully specified
- Performance depends on application
- In-situ calibration with ion gauge helps

Standardization and traceability

Instruments difficult to use
QMS is not a “switch on - read value” instrument.

Too many measurement possibilities which give different results:
Clear description of conditions

Lack of guidance
No standards how to measure parameters of QMS.
No standards how to measure outgassing rates.

Standardization

ISO

Traceability to SI
Measured quantity – true quantity

Measurement standards
on NMI level

Measurement standards on NMI level

What is needed ?

- "Fundamental" method (no simple comparison) to realize partial pressure
- Total pressure should vary between 10^{-8} Pa (ideally) to 10^{-2} Pa
- Partial pressure for at least 2 gas species, the more the better
- Partial pressure for special gas like helium <10^{-10} Pa
- Known partial pressures in varying mixture (ideally 1:1 down to 10^{-6}:1)

NMIs that provide measurement standard for partial pressures (not officially as calibration service):

PTB, Germany

- 3 gases at the same time
- incl. H_2O and dodecane
- Total pressure 10^{-6} Pa to 10^{-2} Pa
- 1:1 down to 10^{-6}:1
- Est. 2014

IMT, Slovenia

- 3 gases at the same time
- incl. H_2O and dodecane
- 10^{-6} Pa to 10^{-2} Pa
- 1:1 down to 10^{-6}:1
- Est. 2014

NMIJ, Japan

- 2 gases at the same time
- 10^{-4} Pa to 10^{-2} Pa
- Est. 2008

NIST, USA

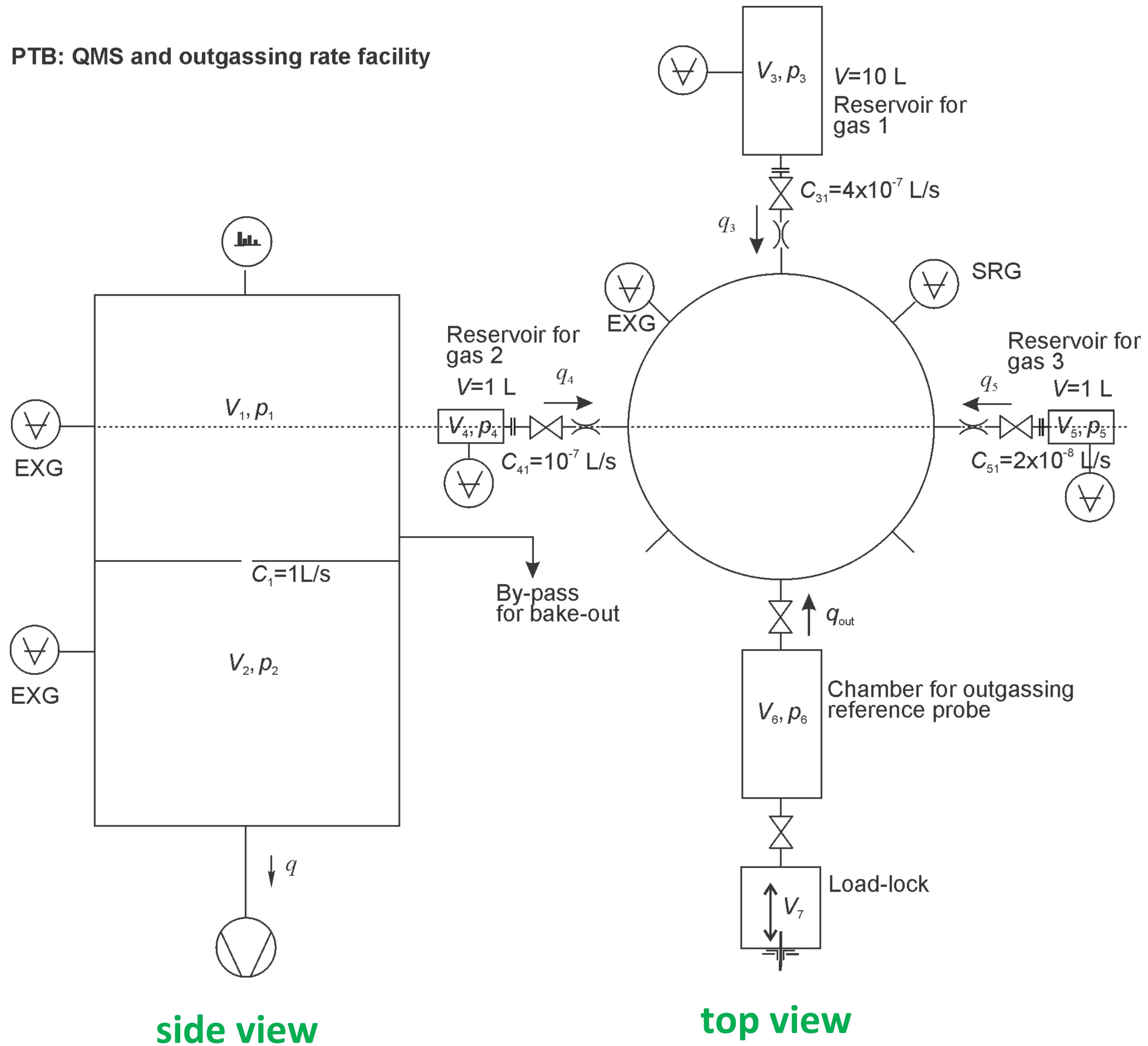
- 2 gases at the same time
- 10^{-6} Pa to 10^{-2} Pa
- Est. 1989 ("sleeping" status)

Measurement standard of PTB

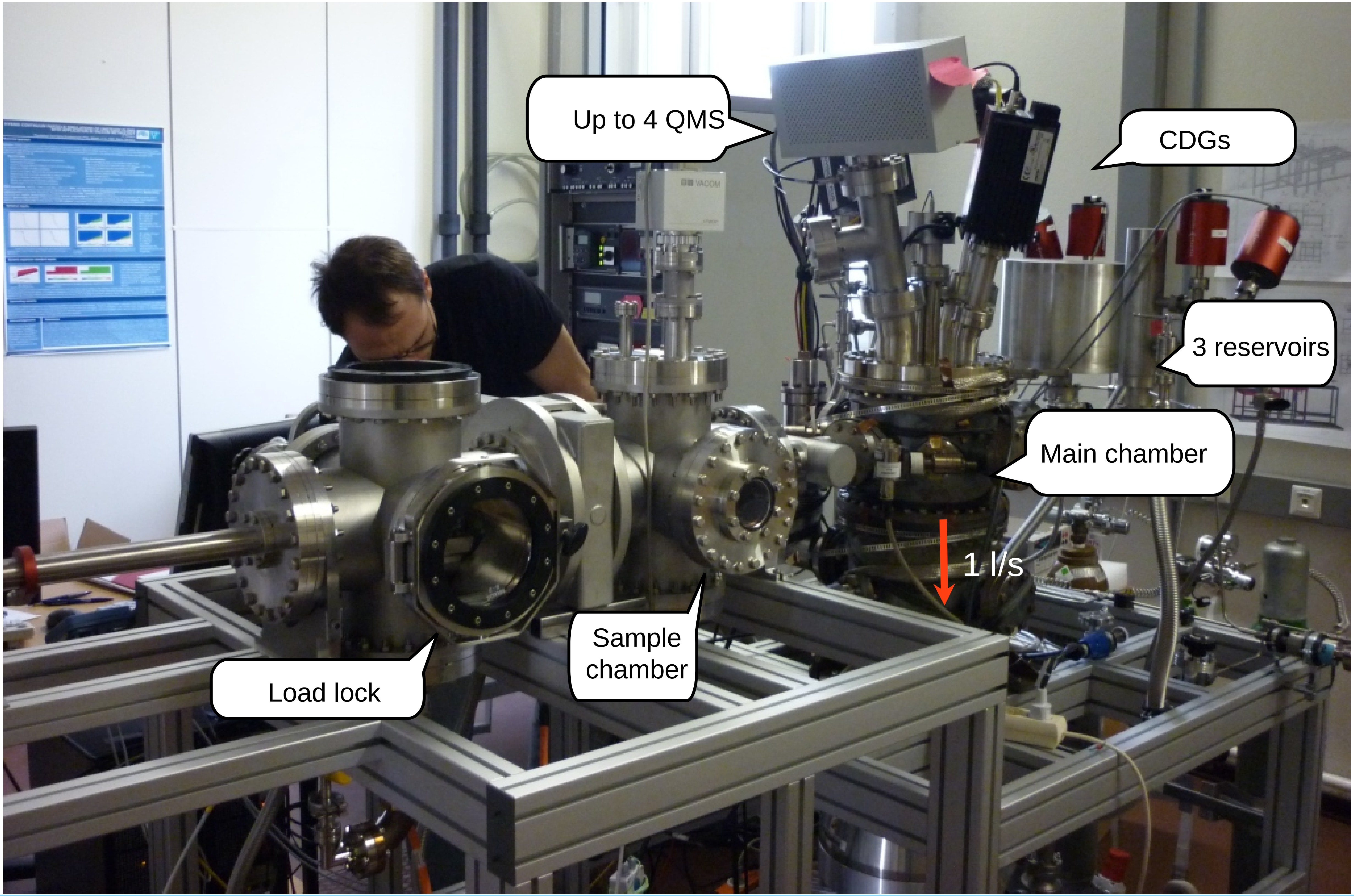
3 gases each with known partial pressure can be established in chamber V_1 at the same time

$$q_{res\ j,i} = p_{res\ j} C_{res\ j}^{molec}$$

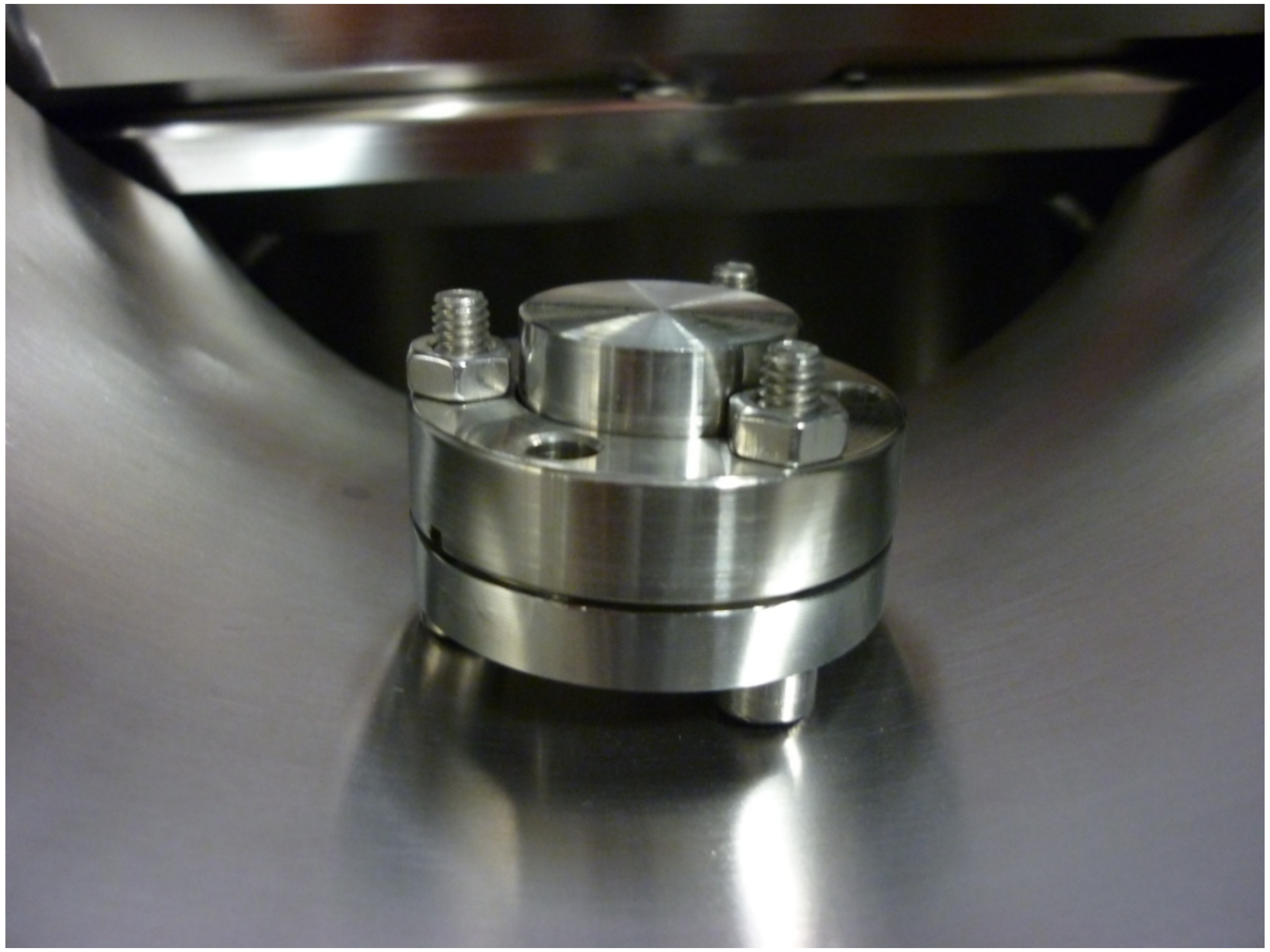
$$q_{out,i} = \frac{I_{out,i}}{I_{res\ j,i}} q_{res\ j,i}$$



Measurement standard of PTB



Reference outgassing samples for comparisons of different outgassing rate measurement systems



Patent pending DE102014200907 A1 published 2015-07-23: Reference outgassing sample Setina/Jousten

TECHNICAL SPECIFICATION

ISO/TS 20175

First edition 2018-04

Vacuum technology — Vacuum gauges — Characterization of quadrupole mass spectrometers for partial pressure measurement

Technique du vide — Manomètres à vide — Description des spectromètres de masse quadripolaires pour mesurage de la pression partielle

https://www.iso.org/standard/67207.html

TECHNICAL SPECIFICATION

ISO/TS 20177

First edition 2018-06

Vacuum technology — Vacuum gauges — Procedures to measure and report outgassing rates

Technique du vide — Manomètres à vide — Méthodes de mesurage et de rapport du taux de dégagement de gaz

https://www.iso.org/standard/67208.html

Written standard vs Technical Specification

Written standard	Technical Specification
Ripe field	Emerging field
Well known parameters	Parameters partly not (yet) reliable
Long term	Field test
Minimum flexibility	Maximum flexibility

ISO Technical Specification 20177 to measure and report outgassing rates

Measurement systems

- **Several options** for measuring systems
- Some kind of **traceability** is ensured for all systems
- Concept of **nitrogen equivalent**

Nitrogen equivalent outgassing rate: outgassing rate when all gases released from the sample are assumed to be nitrogen molecules

Sensitivity of gauge for nitrogen

Conductances and pumping speed for nitrogen

Why? Same gauge reading p_{N2} could lead to different outgassing rates, e.g. $p_{N2}\,C_{H2}$ and $p_{N2}\,C_{CO2}$.

ISO Technical Specification 20177 to measure and report outgassing rates

Options for Measurement systems

- **Continuous expansion system as flow comparator**

$$q_{\text{out},i} = q_{pV,i}\frac{\left(I'_i - I_{i,0}\right)}{\left(I_i - I_{i,0}\right)}$$

- **Throughput system**
  - **Calculated conductance; One-path**

$$q_{\text{out},i} = C_i\left(p_{1,i} - p_{2,i}\right)$$

  - **Calculated conductance; Two-path**

$$q_{\text{out},i} = C_i\left(p_{1\text{A},i} - p_{1\text{B},i}\right)$$

  - **Measured effective pumping speed**

$$q_{\text{out,N2}} = C_{\text{eff}}\left(p_{\text{N2}} - p_0\right)$$

  - **Modulated conductance**

$$q_{\text{out},i} = \frac{p_{1,i} - p_{2,i}}{C_{1,i}^{-1} - C^{-1}}$$

- **Accumulation system**
  - **basic**

$$q_{\text{out,N2}} = \left(\frac{\Delta p_{\text{N2}}}{\Delta t} - \frac{\Delta p'_{\text{N2}}}{\Delta t'}\right)V$$

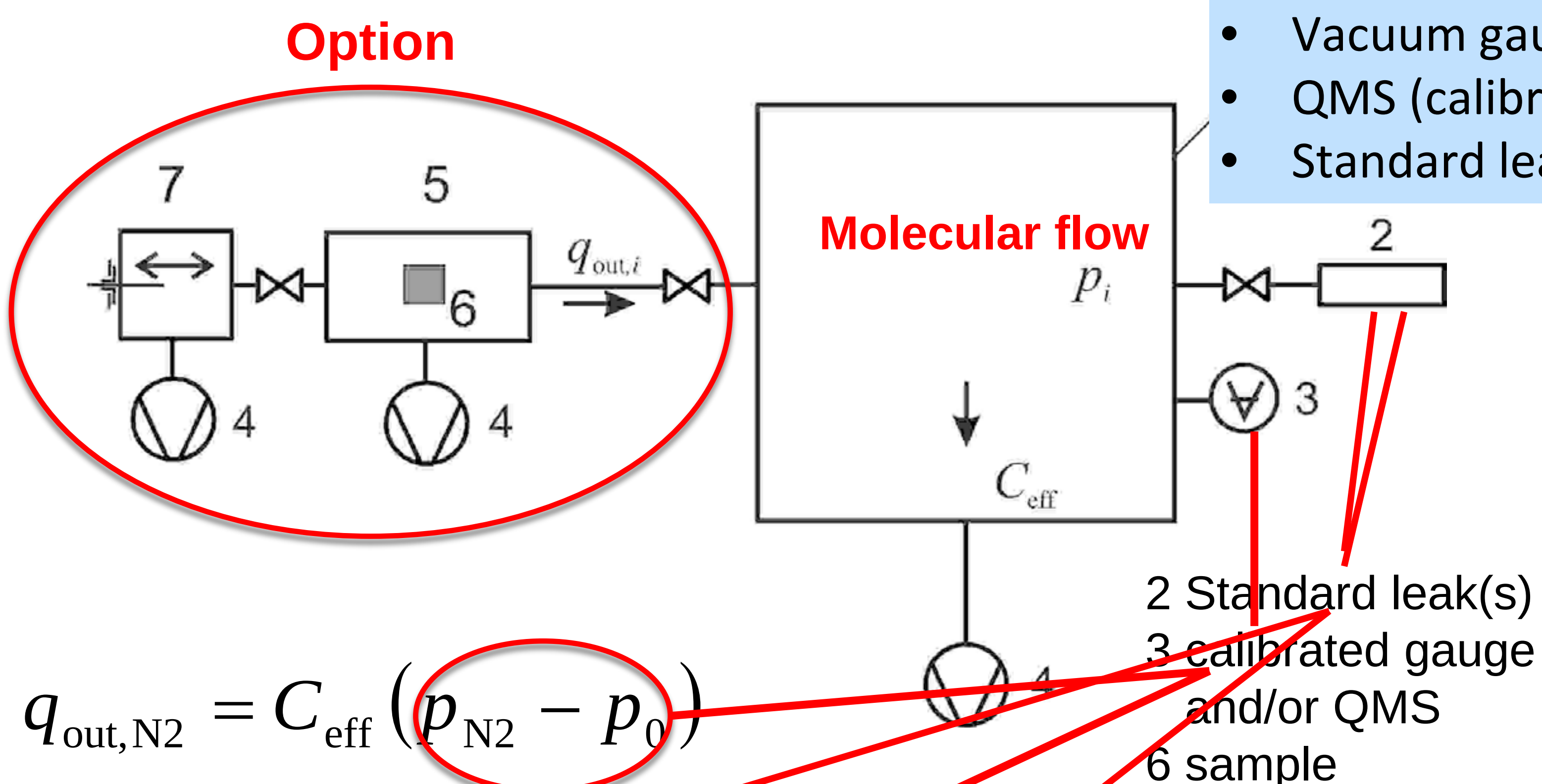
  - **With gas analysis**

$$q_{\text{out},i} = \frac{p_i V}{\Delta t}$$

ISO TS 20177
Throughput system with measured effective pumping speed: Explaining idea of traceability of outgassing rate

Traceability by:

- Vacuum gauge (nitrogen calibration)
- QMS (calibrated in-situ)
- Standard leak (nitrogen and others)



$$q_{out,N2} = C_{eff}\left(p_{N2} - p_0\right)$$

$$C_{eff} = q_{pV} / \left(p - p_0\right)$$

$$q_{out,i} = \frac{I_i - I_{0,i}}{S_i} \cdot C_{eff,i}$$

$$q_{out,i} = \frac{p_i - p_{0,i}}{p'_i - p'_{0,i}} \cdot q_{pV,i}$$

- **Pressure independent pumping speed**
- **Linearity of QMS (over decades)**
- **If no leak for *i* is available, uncertainty of relative gas sensitivity factor and different C_{eff}**
- **+ uncertainty of background**

What you find in ISO TS 20177

- Which measurement system is suitable for you
- How to prepare the measurement system
- What to calibrate before
- How to prepare the sample
- How to measure
- How to report
- Measurement uncertainties

Coming up: Improve in-situ traceability of QMS

QMS have to be calibrated in-situ, not only for nitrogen

↓

Calibrated ionization gauges are needed for many gases:
Big effort, relative gas sensitivity factors of text books inaccurate

↓

Relative gas sensitivity factors depend on type of gauge, manufacturer, and individual gauge

↓

Economical solution: Standardized ion gauge with no variation in relative gas sensitivity factors

European project 16NRM05
June 2017- May 2020
5 NMIs + VACOM and INFICON+ CERN+ University Lisboa

Research for standardized ion gauge

A look-up table of relative gas sensitivity factors can be produced by NMIs et al.

EMPIR EURAMET
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Support through the EMPIR 16NRM05 project is gratefully acknowledged. The EMPIR is jointly funded by the EMPIR participating countries within EURAMET and the European Union.

Conclusions

- Measurement standards for traceable desorption/ outgassing rate measurements are established
- Primary systems at NMIs exist
- Time dependent measurements can be performed
- Vacuum metrology can measure 10^{-14} kg/s
- Traceable outgassing measurements are not yet routine
- Comparison with mass loss measurements are very interesting for vacuum community

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Support through the EMPIR SIP01 project is gratefully acknowledged. The EMPIR is jointly funded by the EMPIR participating countries within EURAMET and the European Union.