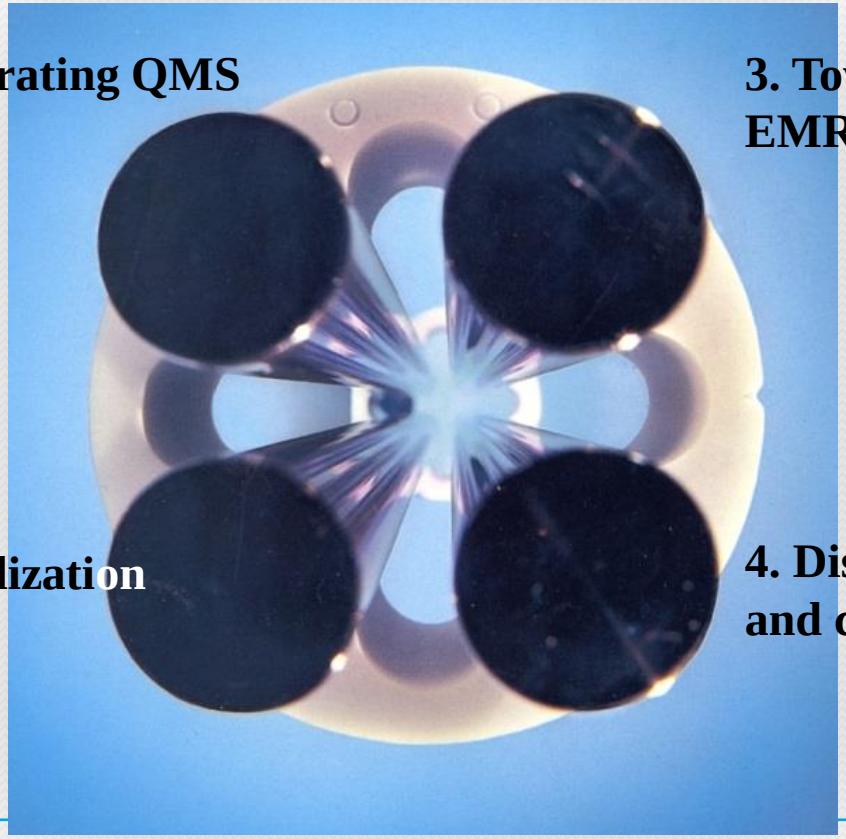
Recent steps toward traceability for partial pressure and outgassing measurements

Karl Jousten, PTB, Berlin

1. Problems of calibrating QMS



3. Toward traceability in EMRP IND12

2. Toward standardization in ISO TC 112

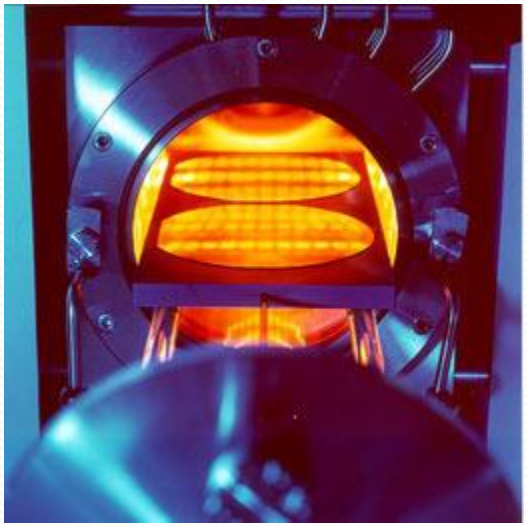
4. Discussion and conclusions

Introduction

For a long time until about 1990:
Magnetic sectors are used for leak detection and quadrupole mass spectrometers (QMS) for both leak detection and analysis of background residual gas level causing the name *Residual gas analyzers*.

Nowadays in addition QMS for:

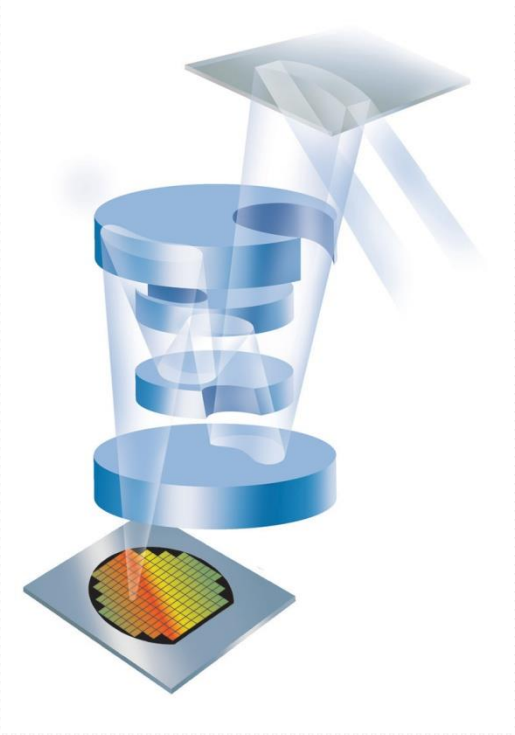
- Gas purity, in-situ analysis for reagent gases and low-level components in semiconductor Industry.
- Sputter process control
- CVD monitoring, gas abatement analysis
- MBE source control
- End point detection (etching)
- Gas chromatography
- Outgassing rate measurements



MOCVD reactor for ferroelectric coating

Introduction

VACOM Outgassing rate measurement

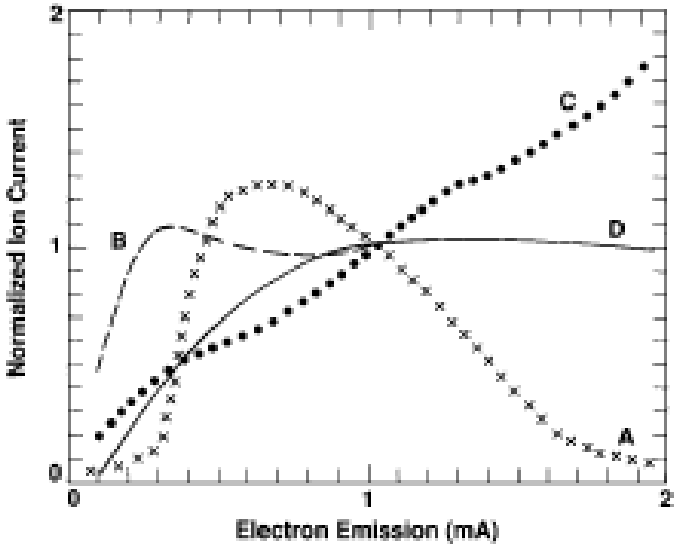


EUV-Lithography

Problems of QMS for calibration

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



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

$$I^+ = SI_e p$$

Problems of QMS for calibration

Sensitivity on gas species for different QMS. Huge differences and hardly related to ionization probability!

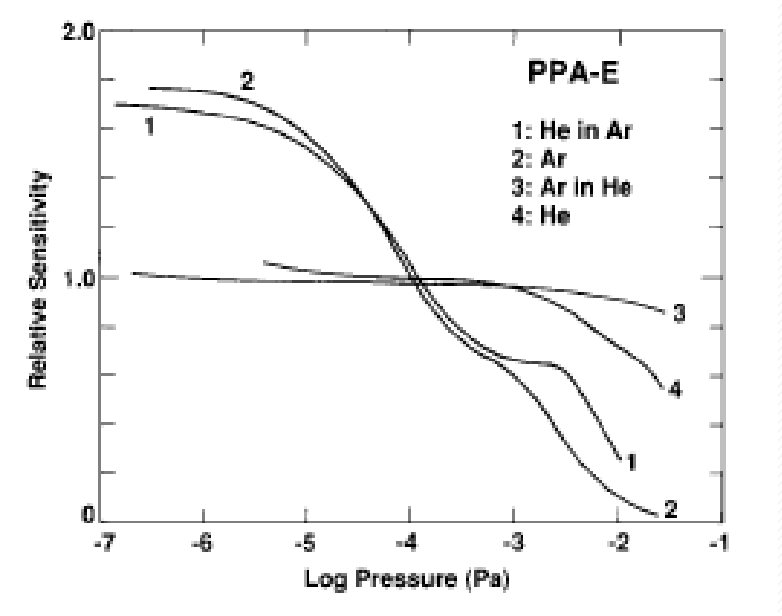
Relative sensitivity factors for different QMS A-E

Gas species	A	B	C	D	E
Ar	1,96	1,33	1,56	2,08	1,23
CH_4	1,18	0,96	1,23	0,77	0,86
CO_2	1,47	0,77	1,39	1,52	0,94
N_2O	1,27	0,47	0,91	0,90	0,63
CO	1,04	0,99	1,05	1,00	0,99
N_2	1,00	1,00	1,00	1,00	1,00
H_2	0,61	1,09	1,42	0,31	1,54
He	0,10	0,35	0,31	0,48	0,40

Problems of QMS for calibration

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, Filipelli, Tilford, JVST A 8 (1990), 3838…3854

QMS calibration

Calibration for gas combinations

About 20 relevant gas species (H_2, He, Ne, Ar, Kr, Xe, N_2, O_2, CH_4 + higher hydrocarbons, CO, CO_2, H_2O, NO_x, SiH4, SF6, ...) for total pressure gauges.

More relevant gases for QMS (even proteins etc.), 100?

For 100: $1.27 \cdot 10^{30}$ possibilities of combination of gas species!

For 30: $1.07 \cdot 10^{9}$ possibilities of combination of gas species!

For 10: 1023 possibilities of combination of gas species!

Impossible task!!!

Calibration for gas combinations and ratios

In addition of the possible combination of the gases the user wants to scale the different gases, e.g. ratio of gas 1 to gas 2 of 1:1, 2:1, 10:1, 30:1, 100:1, 1000:1, 1:2, 1:10, 1:30, 1:100, 1:1000 etc.

The number of possible test gas mixtures for calibration is quasi infinite!

The consequence:

Standardization, *but*

a standardized calibration can only give an exemplary test of an instrument and some hints for the user.

QMS standardization (ISO TC 112)

Secretary TC 112: DIN VDMA, Frankfurt

ISO Technical committee 112
Vacuum technology

Chair: GER, F. Justen

China, France, Germany, Italy, Japan, Korea, Russia, Spain, Switzerland, UK, USA plus 17 observers

WG 1
Vacuum pumps
Chair: UK, St. Omrod

WG 2
Vacuum instrumentation
Chair: GER, K. Jousten

WG 3
Vacuum hardware
Chair: J, M. Hirata

QMS standardization

What we do not intend with standards for QMS:

Pretend that a QMS can be calibrated in all its features
Make an attempt to qualify a QMS as secondary standard
Try to guidelining a user for interpreting complex spectra

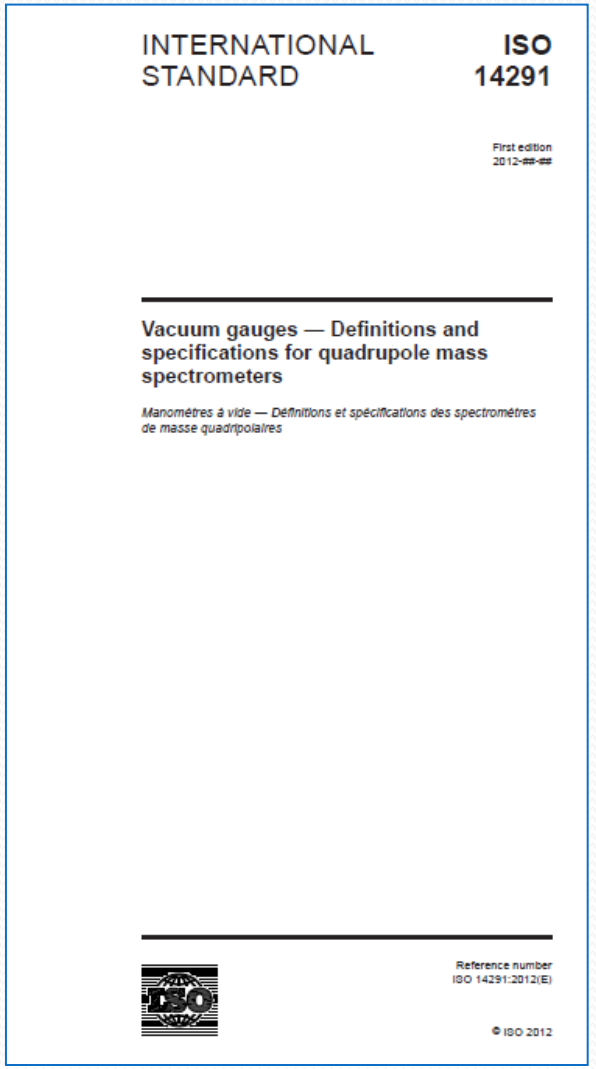
What we do intend with standards for QMS:

Make different QMS for a user comparable (when buying)
Establish a calibration procedure valuable for those users interested in accuracy and reproducibility
Give traceability to SI for selected, but relevant, application
Guideline for proper use of QMS and its limitations

QMS standardization (ISO TC 112)

Content:
Terms and Definitions
Principle of QMS
Specifications for QMS to be provided by manufacturers
Optional specifications for QMS to be provided by manufacturers

Scope: $m/z < 300$, electron impact ionization



INTERNATIONAL STANDARD

ISO 14291

First edition
2012-##-##

Vacuum gauges — Definitions and specifications for quadrupole mass spectrometers

Manomètres à vide — Définitions et spécifications des spectromètres de masse quadripolaires

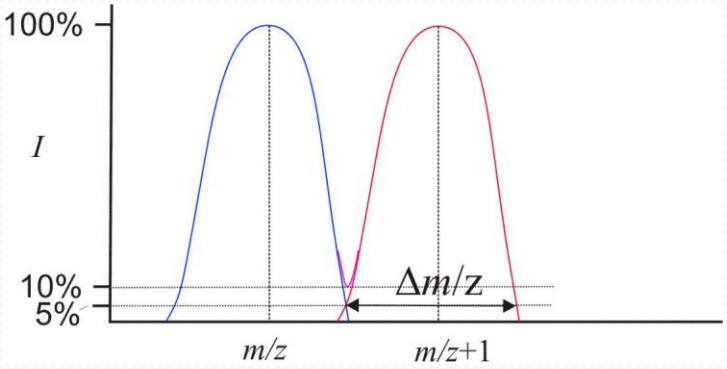
Reference number
ISO 14291:2012(E)

QMS standardization (ISO TC 112)

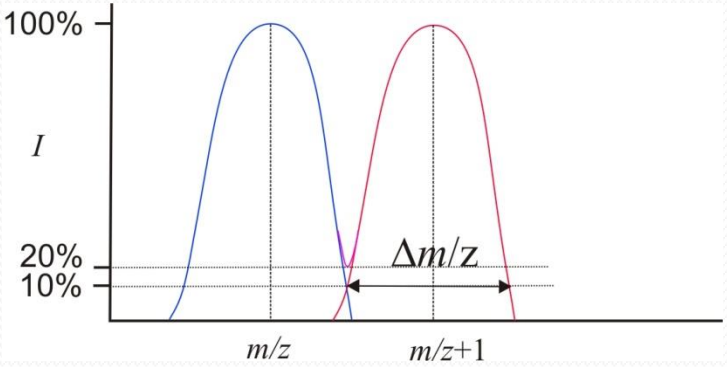
Mass resolution: Difference on *m/z* scale for x% valley between neighbored peaks of equal height (0.5x% height isolated peak).

Aim: the minimum mass difference between two peaks that can still be resolved.

• 10% valley, 5% peak height
IUPAC gold book, ISO 14291 (M)



Alternatives:
• 20% valley, 10% peak height: easier to measure against noise (AVS recommendation)
• FWHM (50% peak height), IUPAC recommendation, ISO 14291 (O)



QMS standardization and calibration

ISO TC 112 WG 2 and EMRP IND 12

work together toward standardization for QMS

2011-2014

QMS calibration

EMRP IND12

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

EMRP IND12: Vacuum metrology for production environments

Budget: 2,8 Mio €
Duration: 2011-09-01 bis 2014-08-31
Coordination: Karl Jousten, PTB

NIMs (funded): CEM (Spain), CMI (CZ), IMT (Slovenia), INRIM (Italy)
LNE (F), UME (TK)
Industry (unfunded): Danfoss (DK), INFICON GmbH (Köln), INFICON AG (Liechtenstein), Lazzero (IT), VACOM (Jena)
REG: University of Genova, Karlsruhe Institute of Technology, University Thessaly (Greece)

plus 10 collaborators: Visteon, Cinquepascal, miCos, Philips, Reuter, Vaklab, NMIJ, KRISS, Russian Academy, KIT

QMS calibration

ISO TC 112 WG 2 and EMRP IND 12 (WP 3)
Road map towards standardization for QMS and outgassing rate measurements

Step 1 (2012), ISO: Definitions and specifications for quadrupole mass spectrometers ISO 14291

Step 2, IND12 (2011-14): Develop a primary standard for calibration and investigation of QMS.

Step 3, IND12 (2012-14): Investigate QMS long-term stability, influence of operational parameters for a single gas, gas mixtures, metrological charcteristics.

QMS calibration

ISO TC 112 WG 2 and EMRP IND 12
Road map towards standardization for QMS and outgassing rate measurements

EMRP IND12 Step 4, IND12 (2013): Are there typical reference conditions for QMS at use? (Workshop and questionaire)

EMRP IND12 Step 5, IND 12 (2013-14): Define reference conditions and explore calibration procedures

EMRP IND12 Step 6, IND12: Explore methods of outgassing rate measurements by comparing them with outgassing reference samples

QMS calibration

ISO TC 112 WG 2 and EMRP IND 12
Road map towards standardization for QMS and outgassing rate measurements

EMRP IND12

ISO

Step 7, IND12 and ISO (2014): Draft technical specifications for calibration of QMS and for outgassing rate measurements

ISO

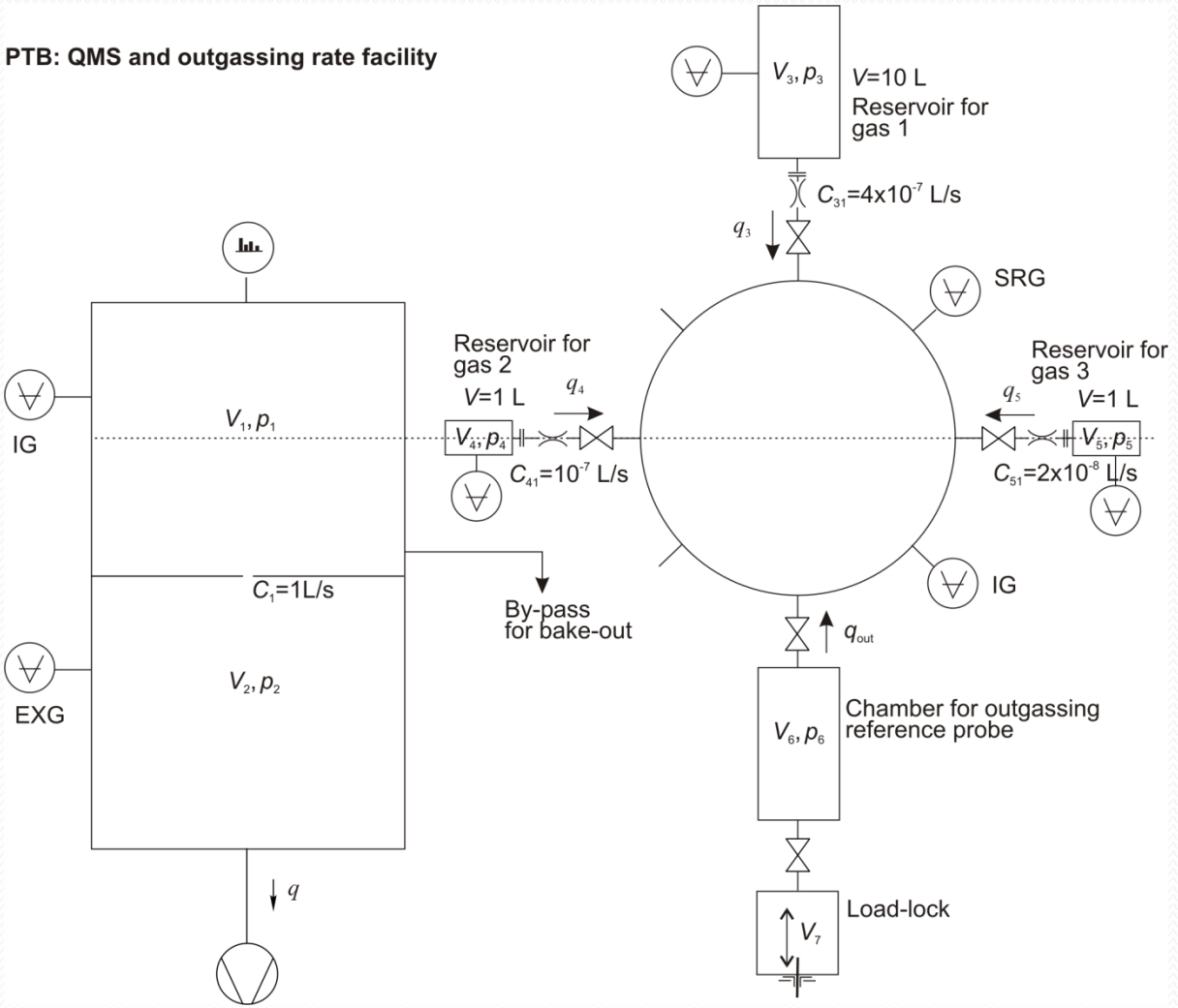
Step 8, ISO (2014-2016): Develop and publish technical specifications

QMS calibration system

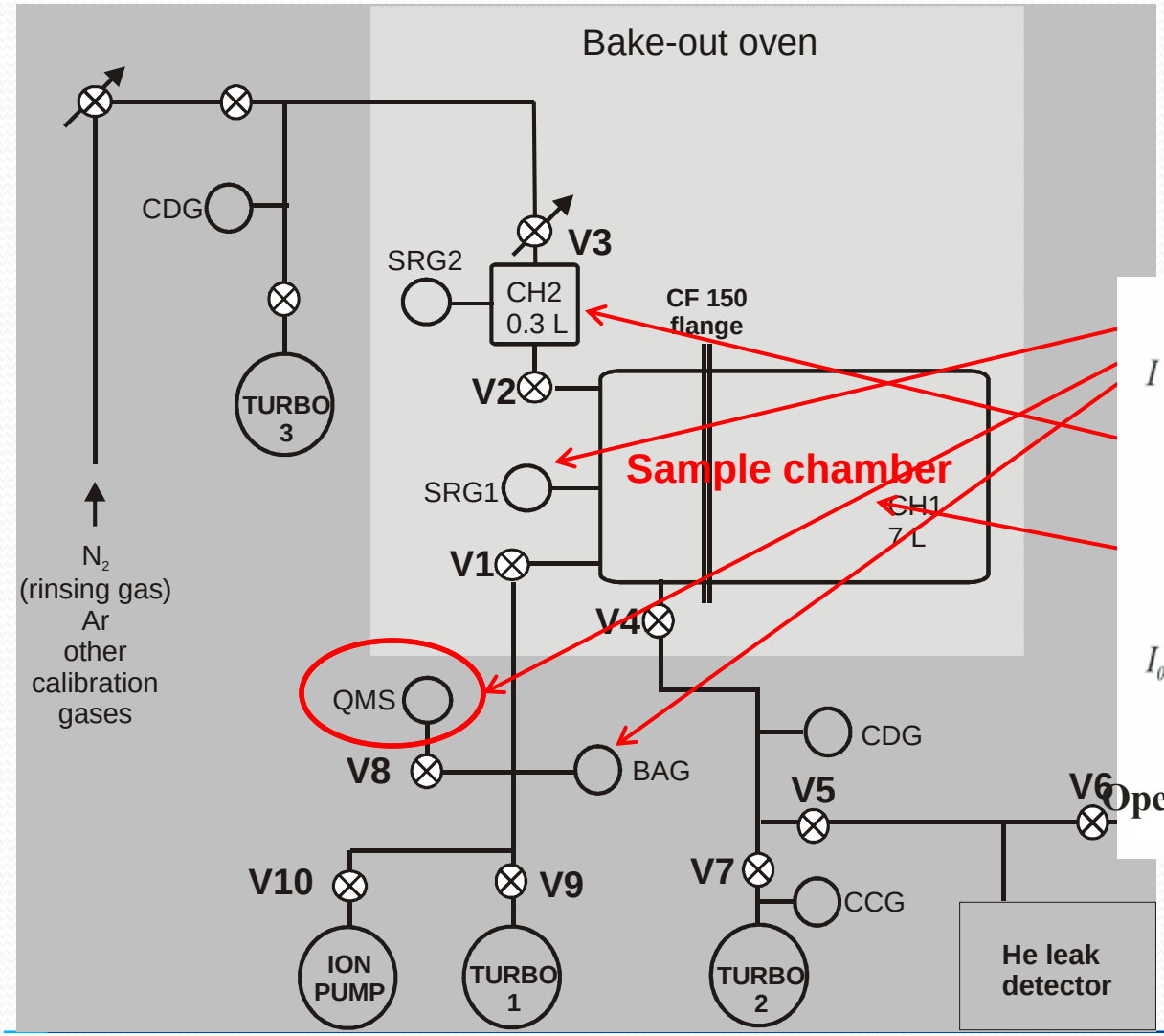
(Step 2 of road map)

New PTB system for QMS calibration and outgassing rate measurement

$$p_{1,i} = \frac{p_i \cdot C_i}{C_{1,\mathrm{eff}}} \qquad i = 3,4,5$$

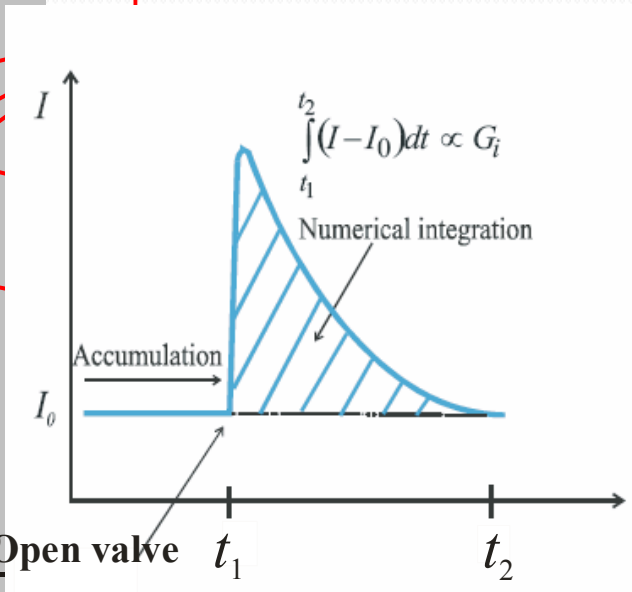


(Step 2 of road map)



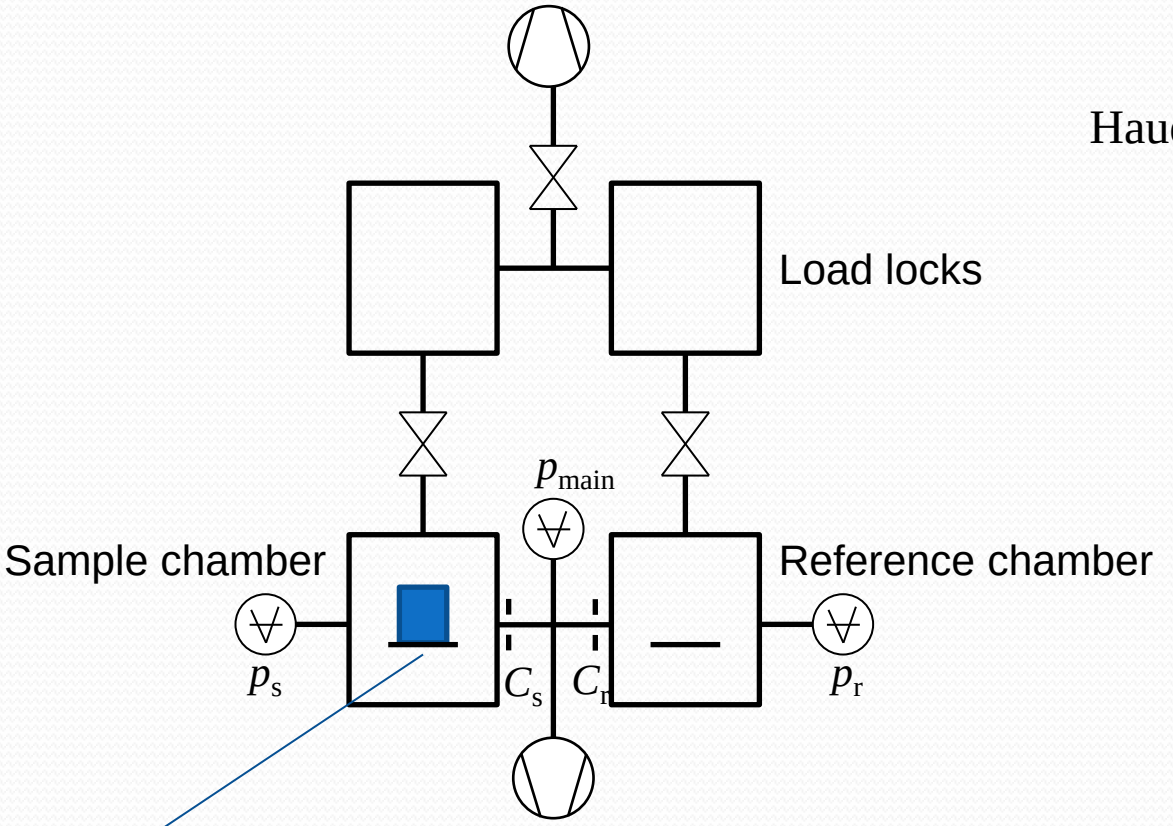
IMT system for QMS calibration and outgassing rate measurement

pressure rise and



KIT Outgassing Measurement Apparatus (OMA)

Hauer and Battes, KIT



$$Q_{out} = C_S\left(p_S - p_{main}\right) - RC_R\left(p_R - p_{main}\right)$$

Conditions for QMS calibration

Step 4 of road map

Workshop on measurement characteristics and use of quadrupole mass spectrometers for vacuum applications

in Bled, Slovenia, April 10-13, 2012

Main Results:

- The performance of QMS is still poor in many aspects
- Simulation of ion trajectories may improve QMS in the future
- Reasonable calibration (usually on-site or two steps NMI+ on site) is necessary for some applications
- There was doubt that applications in *industry* exist which can be covered by a „key“ application procedure
- Applications of QMA as RGA and outgassing measurement tool appear more promising as subject for calibration than as process tool
- List of QMS manufacturers

Conditions for QMS calibration

Step 4 of road map

Questionnaire for manufacturers and users of QMS

- Contains 9 questions. Purpose: Find out, which application (gas species, gas mixture, total pressure range) needs accuracy or at least reproducability. Find out, which parameters of a QMS are important for users.
- 32 copies distributed, 7 answered.

Preliminary results

- From three manufacturers: About 20 customers/year require accuracy
- Major applications needing accuracy: leak testing, outgassing rate measurement
- Most important parameters: Sensitivity and its stability, minimum detectable pressure, minimum detectable concentration, linearity, cracking pattern, mass resolution
- Gas species of greatest interest: H_2O, N_2, O_2, CO_2, H_2, hydrocarbons

Step 5 of road map

Our present ideas for QMS calibration procedure

With calibration we only understand determination of sensitivity *S*, not *m*/*z* scale!

$$S_{\text{gas}} = S\left(I_e, U_e, U_{\text{ion}}, \Delta m, p_{\text{tot}}, p_{\text{gas}}, G_{\text{comp}}, \ldots\right)$$

- Well defined settings of the QMS (from step 3: which are most important)
- Known calibration gas mixture (as defined by a standard and/or by the user/application) both by gas species and species ratios
- A calibration standard reasonably standardized (ordinary calibration lab) or establishing absolute partial pressures (NMIs)
- Stability of calibrated values (from step 3: approximate long term stability values) checked by in-situ calibration

QMS calibration procedure

Several periods of attempts for standardization and recommendations for QMS

In Germany:

In the 1960s resulted in the DIN 28410 (1968)

Internationally:

In the 1970s: ISO 3529 and 3530

In the 1990s: ISO 5298, Part 1-2, 4-6. (CD)

In the US:

In the 1970s: Tentative standard, 1972

In the early1990s: Recommended practice, 1993

2007: Recommended practice on process sampling

QMS calibration procedure

Step 5 of road map

As a consequence of the workshop and the questionnaire we will draft a calibration procedure for the use of QMS for leak rate measurement, residual gas analysis and outgassing rate measurement.

Exploring for **leak rate measurement**:

• Sensitivity for helium as pure gas and helium in nitrogen and normal (!) air in dependence of helium flow rate.

• Find out which by-gases are most disturbant and how to handle this (possibly also in situ)

In detail: 1) Determine helium sensitivity over full range for pure gas 2) Determine helium sensitivity for selected helium partial pressures for
helium 50%/nitrogen50%,
helium 50%/nitrogen40%/oxygen10%,
helium 50%/nitrogen39%/oxygen10%, argon1%,
helium 50%/nitrogen38%/oxygen10%, water 2%.
3) „Play“ with volumetric content according to results.

QMS calibration procedure

Step 5 of road map

Exploring for **residual gas analysis and outgassing rate measurement**:

- In a first step both application together
- Humid air (available anywhere) useful for calibration?

In detail: 1) Determine sensitivity over full range for pure gases for N_2, Ar, CO_2, Ne, He, CH_4, Kr, H_2O others?

2) Determine sensitivity for constituents of mixtures

N_2, Ar

N_2, CO_2

N_2, CH_4 and triple mixtures, later

H_2O + others like N_2, Ar, CH_4, dry air

3) How is H_2 affected by other species?

Dry air composition

S. Y. Park et al., Metrologia 41 (2004) 387...395.

Species	Relative part	Absolute
		Pa
N_2	0,78083	
O_2	0,20945	
H_2O		200...4000 (100% at 23°C: 2811)
Ar	9,33E-03	
CO_2	3,69E-04	
Ne	1,80E-05	
He	5,20E-06	
CH_4	1,50E-06	
Kr	1,10E-06	
H_2	5,00E-07	
N_2O	1,00E-07	
Xe	1,00E-07	

Outgassing rate measurement

Step 6 of road map

To compare different methods and validate a measurement system it is necessary to have a **reference outgassing sample**.

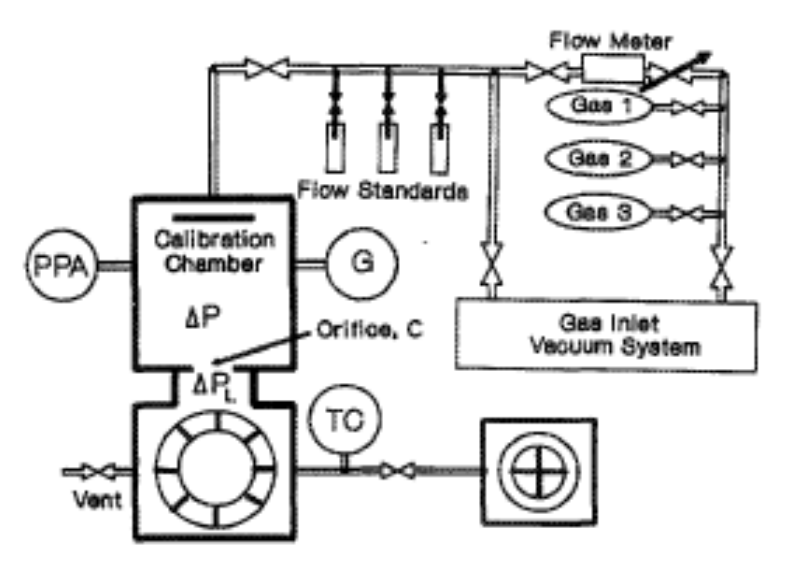
We will test 3 possibilities:

1. Elastomers loaded with gas
2. Nanotechnology designed device
3. Conventionally designed device

Discussion in-situ calibration

In-situ calibration will be necessary, either to calibrate QMS for special application or to check stability of already calibrated quantity

Possibility 1: Continuous expansion method

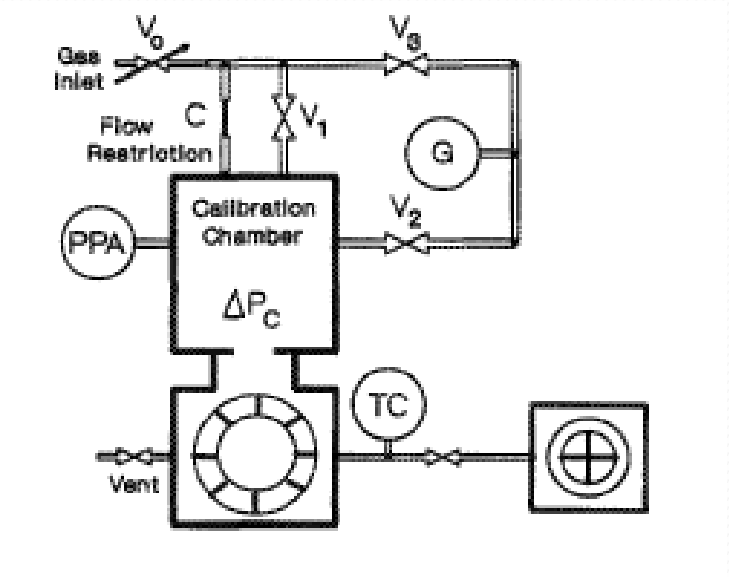


AVS recommended practice JVST A 11 (1993), A22…A40

Discussion in-situ calibration

Possibility 2: Pressure divider method

Pressure divider by C measured by G



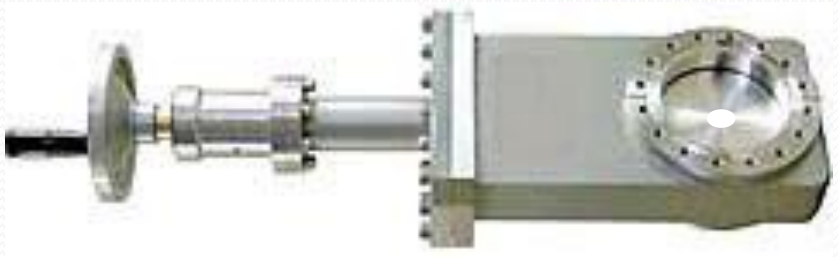
AVS recommended practice JVST A 11 (1993), A22…A40

Discussion in-situ calibration

Possibility 3 (Yoshida, NMIJ): Use of known conductance (SCE) and Conductance modulation method

Standard conductance element (Yoshida)

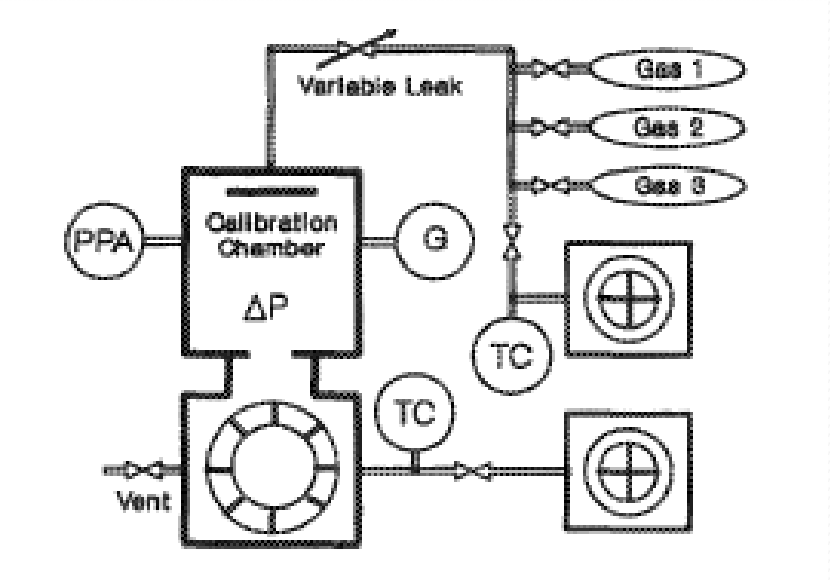
Known gas flow (molecular flow up to 100 mbar): Calibrated ionization gauge necessary.



With conductance modulation method, S_{eff} can be determined with some effort. Linear ionization gauge necessary only.

Discussion in-situ calibration

Possibility 4: Comparison method



Calibrated ionization gauge necessary for all gas species in use!

AVS recommended practice JVST A 11 (1993), A22…A40

Discussion in-situ calibration

Relative sensitivities for different gas species very uncertain (depend on type/manufacturer and individual gauge)!

Similar to relative sensitivities of QMS, but not as bad.

Proposal: **ISO standard ionization gauge**. Well defined geometry and materials.
Could be characterized by several NMIs. Users can use reliable tables for relative sensitivities without individual calibration for each gas.

Next or additonal step: **ISO standard QMS?**

AVS recommended practice JVST A 11 (1993), A22…A40

Conclusions

- QMS are very sensitive, versatile, and relative cheap
- QMS are good for qualitative measurements, but very difficult for quantitative measurements
- QMS cannot be calibrated in a general sense as partial pressure gauge – too many possibilities of gas combinations and settings
- Standardization is the only option to cover this problem
- Investigations and discussions are on the way

Thanks for your attention and contribution to discussion

QMS calibration

A few questions for discussion

- Key users that need accuracy or reproducibility?
- Which simplifications can you recommend? (M/z < 51 calibrate, M/z > 50 “hydrocarbons”?)
- Which in-situ calibration do you use ?
- Do you play around with parameter settings of QMS?
- How accurate you need the components of a gas mixture?