



"In-situ" calibration of QMS for gas flow measurements

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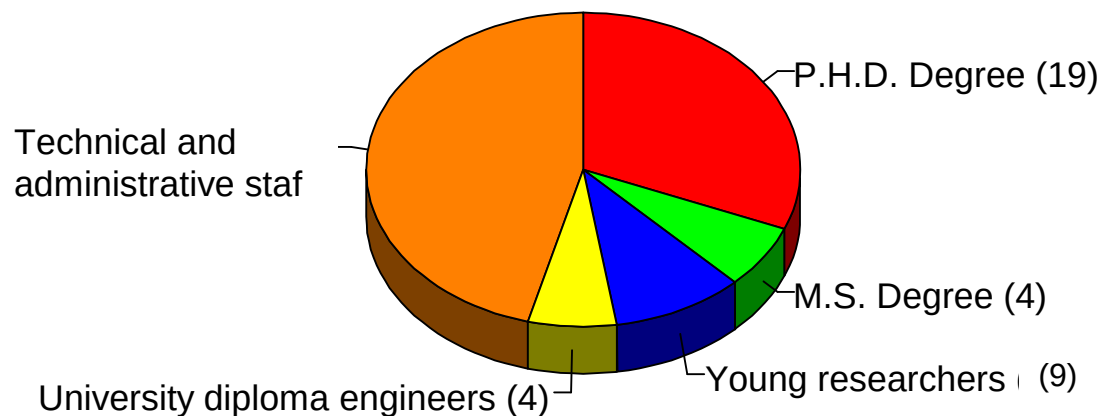




Institute of Metals and Technology (IMT)

(Public research institute)

- Founded in 1950 by Slovenian Government (**Institute of Metallurgy**)
- Renamed to **Institute of Metals and Technology (IMT)** in 1991
- In 1997 – new status: **public research institute**
- In 2009 the Institute had **68 employees**:





IMT Departments:

Metallic materials and process technology:

- Laboratory for Process Metallurgy
- Laboratory for Measurements in Heat Engineering
- Laboratory for Powder Metallurgy
- Non-Ferrous Metals and Alloys
- Metallic Materials with Special Properties
- Laboratory for Experimental Development of Metallic Materials

Applicability and lifetime of metallic materials and products:

- Laboratory for Mechanical Testing
- Laboratory for Creep
- National Centre for the Revitalization of Industrial Structures and Equipment
- Laboratory for Corrosion
- Laboratory for Analytical Chemistry

Surface engineering and applied surface science:

- Laboratory for the Surface Characterization of Materials
- Laboratory for Metalography
- Vacuum Heat Treatment and Surface Engineering Centre

Vacuum science and opto electronics:

- Laboratory for Vacuum Science and Optoelectronics

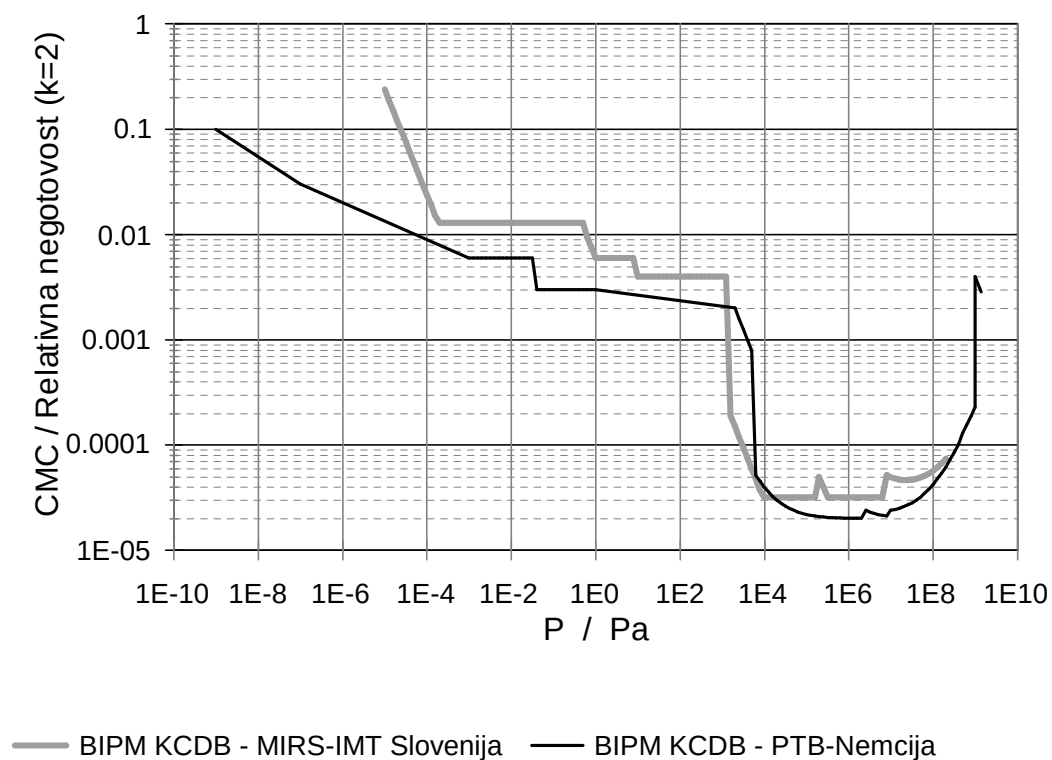
Laboratory of Pressure Metrology



Vacuum science and optoelectronics group

- 2 senior researchers
- 1 technician
- 1 young researcher (PHD student)

Accredited laboratory for calibration of pressure and vacuum gauges





HISTORY

I started working in Vacuum field in 1983 at IEVT
(Institute of Electronics and Vacuum Technique)

- development of second generation image intensifiers
(proximity focus and electrostatic image inverters)

We had to solve many vacuum problems:

- thermal outgassing
- ultimate tightness of:
 - ceramic to metal seals
 - glass frit seals of FO plates to metal flanges
 - low temperature In solder seal of photocathode plate to the housing
- electron impact outgassing of surfaces during operation of the tube
- field emission of electrons in high electric field & electrical breakdown





We had to master different technologies:

- cleaning of vacuum materials
- vacuum and hydrogen firing
- glass to metal sealing
- ceramics metallization and brazing to metal
- construction and operation of UHV systems
- vacuum measurements and leak detection
- synthesis of high sensitivity (NEA) photocathodes $\text{Na}_2\text{KSb}(\text{Cs})$



SRG became commercially available in early 80's

We got our first SRG in 1983

Our first application:

- ultra-sensitive leak detection of brazed ceramic to metal seals





Setina J, Zavasnik R, Nemanic V, J Vac Sci Technol **A 5**, p. 2650-2652 (1987)
Vacuum tightness down to the 10^{-15} mbarl/s range, measured with a spinning rotor viscosity gauge

Method:

rate of pressure rise in a sealed system

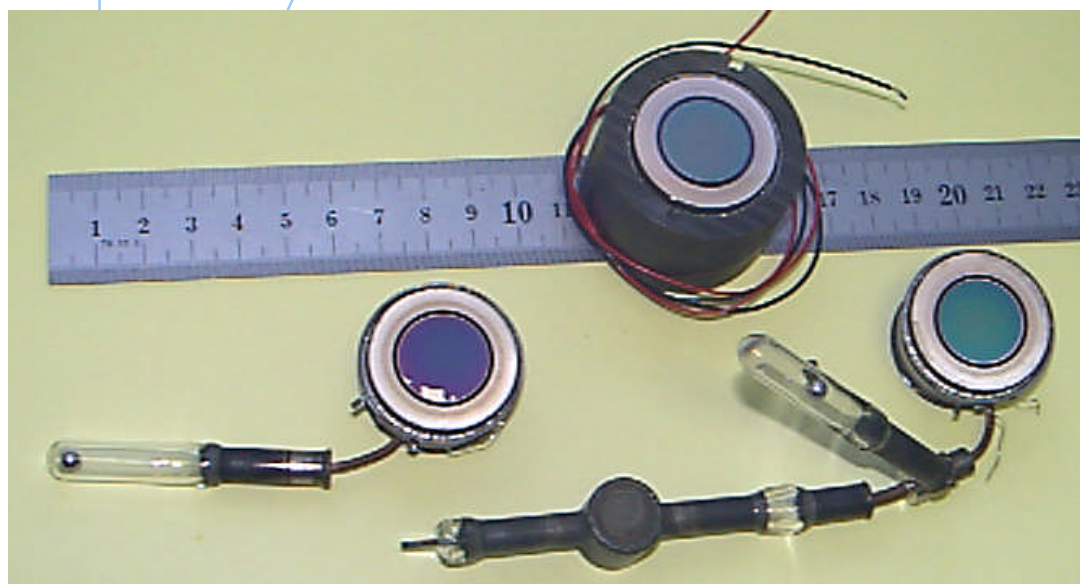
Resolution:

$$Q_{\min} \approx \frac{10^{-7} \text{ mbar} \times 5 \times 10^{-3} \text{ L}}{5 \times 10^5 \text{ s}} = 10^{-15} \text{ mbar} \cdot \text{L} / \text{s}$$

$$(5 \times 10^5 \text{ s} = 6 \text{ days})$$

Pressure measurements in photo-electron tubes

- Problems to study:
gas desorption, induced by electron bombardement of the micro-channel electron multiplier and phosphor screen







HISTORY – IMT group

Image intensifier "business" stopped in 1992 after split of Yugoslavia and in 2000 IEVT was closed

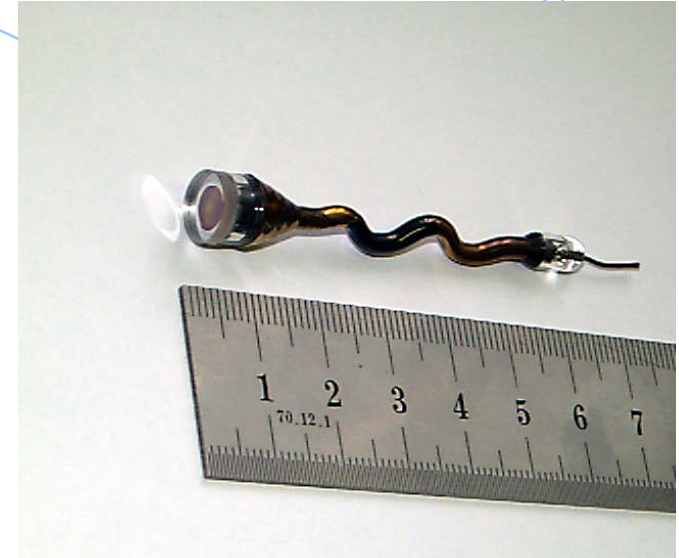
- in 1999 I have joined IMT
 - **Vacuum Science Group and Vacuum Metrology Lab have been established**
- in 2000 3 more people from IEVT joined and some equipment was transferred to IMT
- in 2002 we gained accreditation for calibration of vacuum and pressure gauges from 10^{-3} mbar to 70 bar
- in 2004 accreditation was extended from 10^{-7} mbar to 2000 bar
- in 2005 our Lab was recognized as a holder of Slovenian national standards for pressure and vacuum



Vacuum science and optoelectronics group

We continue research in "electron tube" business:

- collaboration with Perkin Elmer, Wiesbaden, Germany (formerly Heiman Optoelectronics)
 - **channel electron multipliers**
 - sealing techniques (glass frit, glass soldering with Indium)
 - synthesis of high efficiency $\text{Na}_2\text{KSb}(\text{Cs})$ photocathodes
 - development of vacuum transfer technique for photocathodes
 - study of vacuum problems
 - He permeation through glass
 - outgassing by electron bombardment
 - getter activation and sorption characteristics for various gasses





Other resaerch work

- Studies of Li, Ba and Cs intermetallic alloys as getter materials and alcali metal vapour source
(in cooperation with Constantin Technologies, Alvatec and Nanoshel from Austria)
- We have recently entered outgassing measurements of thermal insulation materials for aerospace applications
(for a company from Austria, in cooperation with Prof Dobrozemsky from Vienna)
- Studies of the use of getters in UHV metrology (static and dynamic primary calibration systems, primary methods for He leak calibrations)



I am working with Quadrupole Mass Spectrometers since 1985

In all this years I have gained "limited" experience with this type of instruments

We currently have 3 UHV research/measurement systems – all are equipped with QMS instruments

Most often we are using QMS just to look qualitatively into the "process":

- presence of leaks (re-assembly of vacuum system, bakeout...)
- contamination & "cleanliness" of the process
- ...



However,
to quantify cleanliness of vacuum materials i.e. outgassing,
(effectiveness of cleaning and other treatments)

we need to measure gas flow:

- from measuring chamber (background): Q_{bg}
- from chamber filled with sample material: Q

Result:

outgassing rate of a sample $Q_s = Q - Q_{bg}$
(in **mbar×L/s** with associated **uncertainties!**)

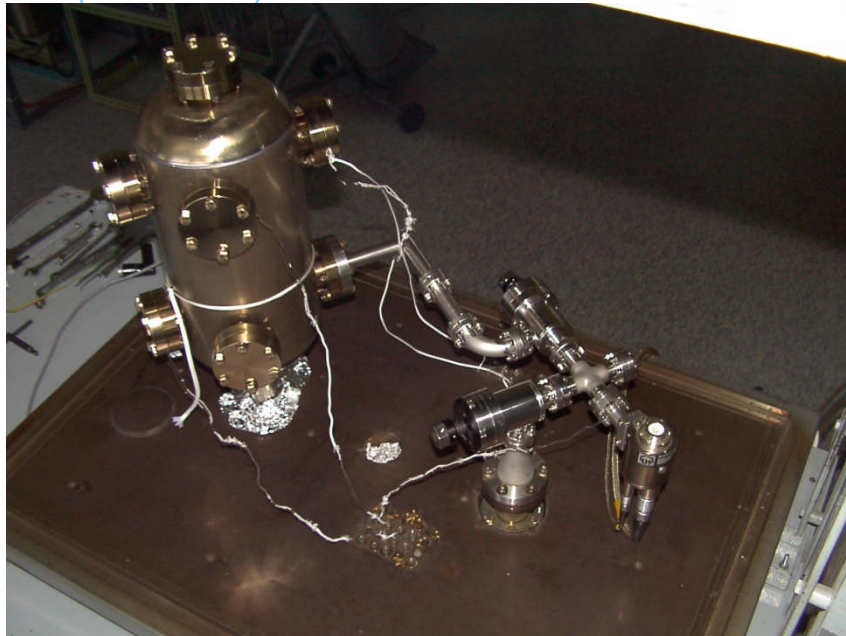
To measure low outgassing materials it is important to reduce background!



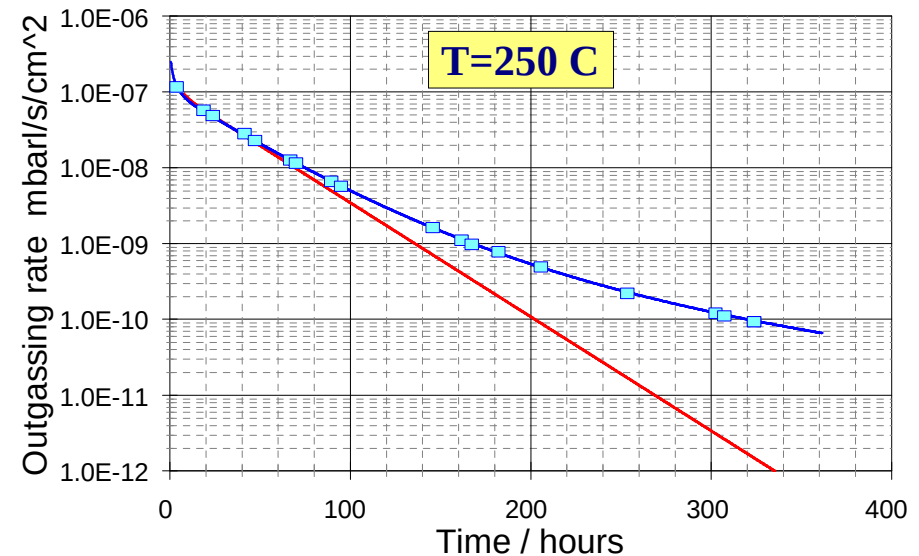
Result of our study of bakeout of stainless steel chamber

- Material: Stainless steel (type 304), wall thickness 2.5 mm
- Volume 5.7 dm³, Area 2600 cm²
- Inner surfaces were mechanically polished before welding
- Final cleaning: hot water + detergent, rinsed in deionized water

Blank flanges were vacuum fired at 900 C for 5 h



HYDROGEN OUTGASSING RATE AT 250°C VERSUS TIME OF BAKE



— Diffusion model

— Recombination model

Room temperature outgassing after treatment (320 h at 250°C):

$3 \times 10^{-14} \text{ mbar} \times L / (\text{s} \times \text{cm}^2)$
(Hydrogen equivalent!)



Quantitative measurements with QMS

RGI
residual
gas
indicator



CALIBRATION

RGA
residual
gas
analyser



Gas flow measurements (outgassing, permeation, diffusion...)

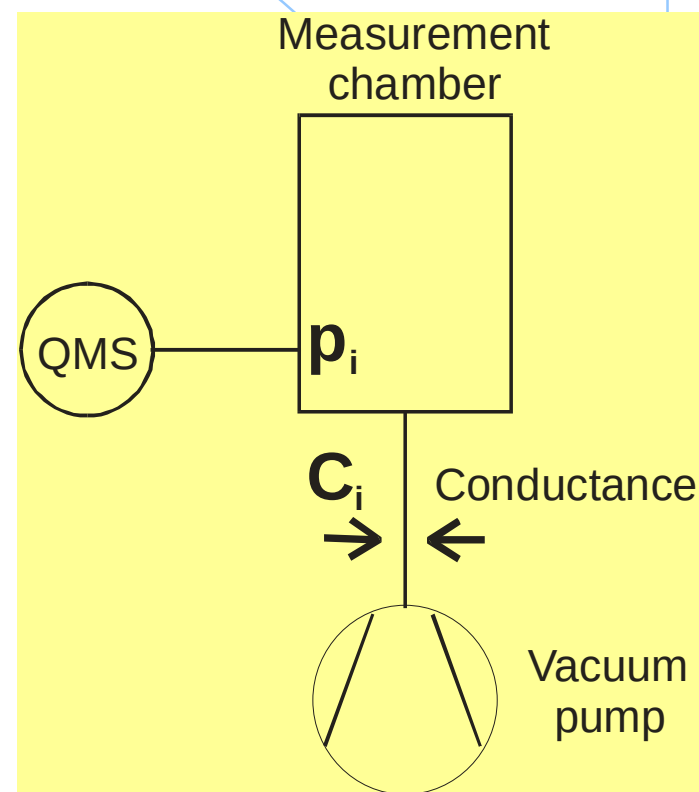
A. Dynamic (throughput) procedure:

- accurate (traceable) measurement of partial pressures p_i
- calculated or calibrated conductance for different gases (C_i)

$$Q_i = \Delta p_i \times C_i$$

Additional sources of uncertainty:

- gas flux distribution (deviation from Maxwellian distribution)
- reaction on hot filament



Gas flow measurements (outgassing, permeation, diffusion...)

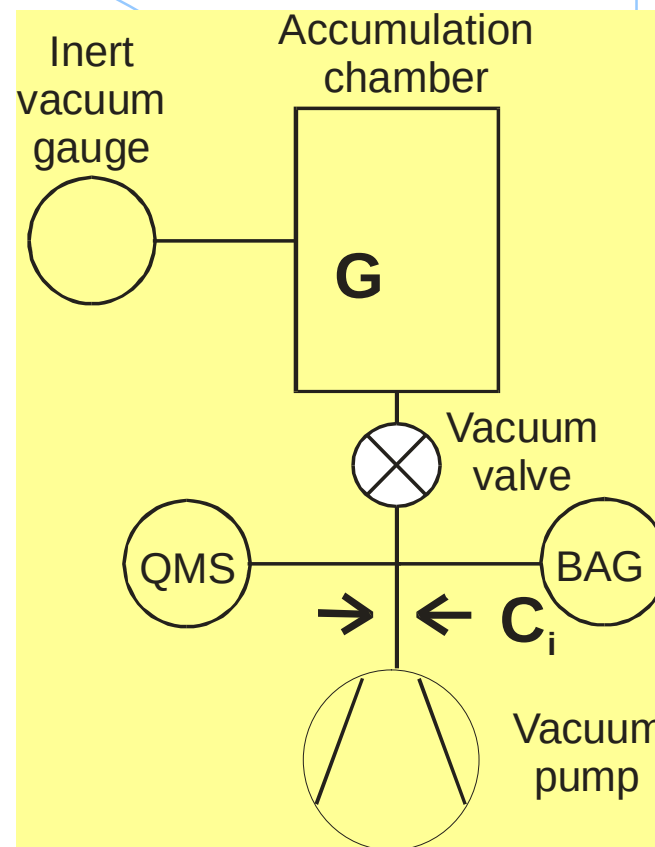
B. Static (pressure rise) method:

- Accumulation of gas for certain time t_a
- measurement of accumulated **gas quantity** G

Mean gas flow is:

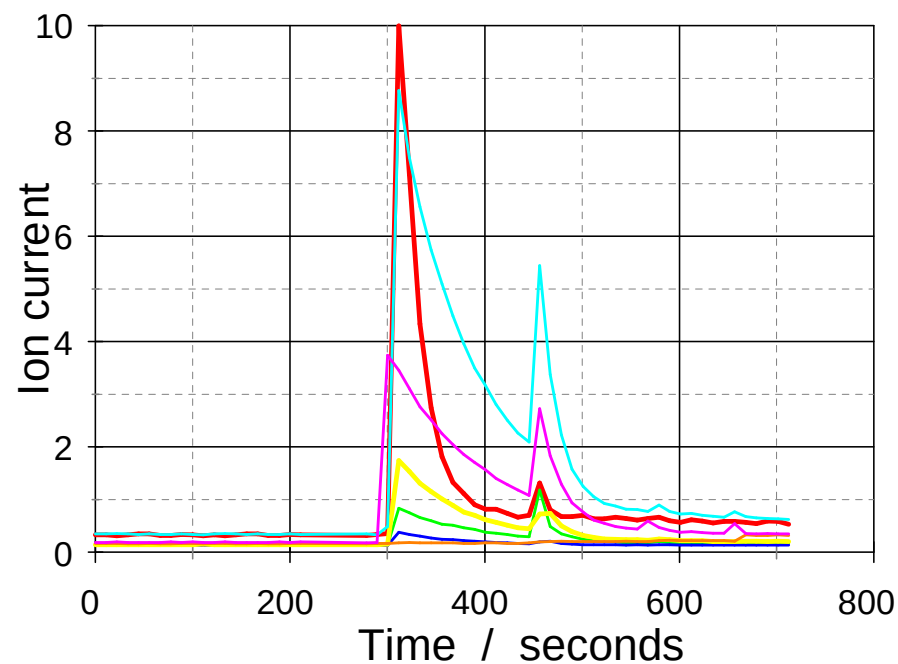
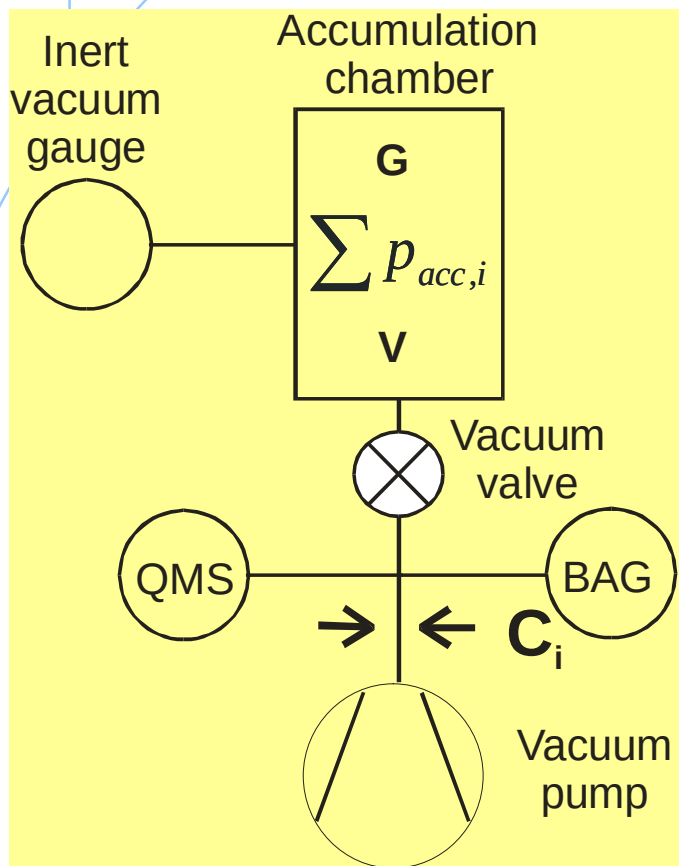
$$\bar{Q} = \frac{G}{t_a}$$

- QMS (or other hot filament gauge) should not be used in accumulation chamber
- residual gas analysis is possible only after accumulation





Analysis of accumulated gas



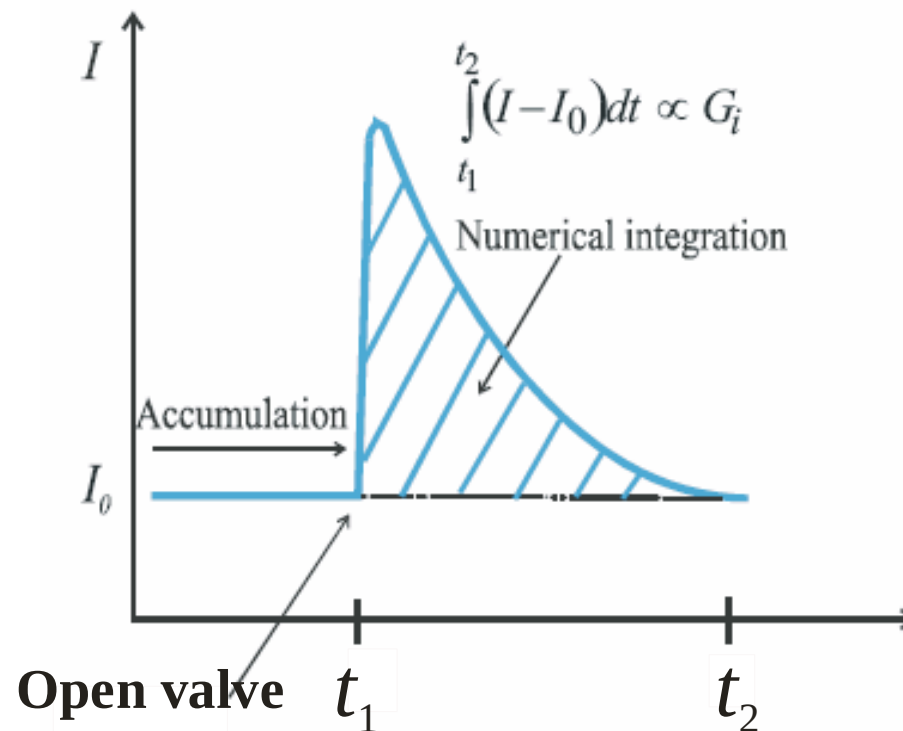
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- Area of pressure burst proportional to gas quantity:

$$\int_{t_1}^{t_2} (I_i - I_{i,0}) dt \propto G_i$$

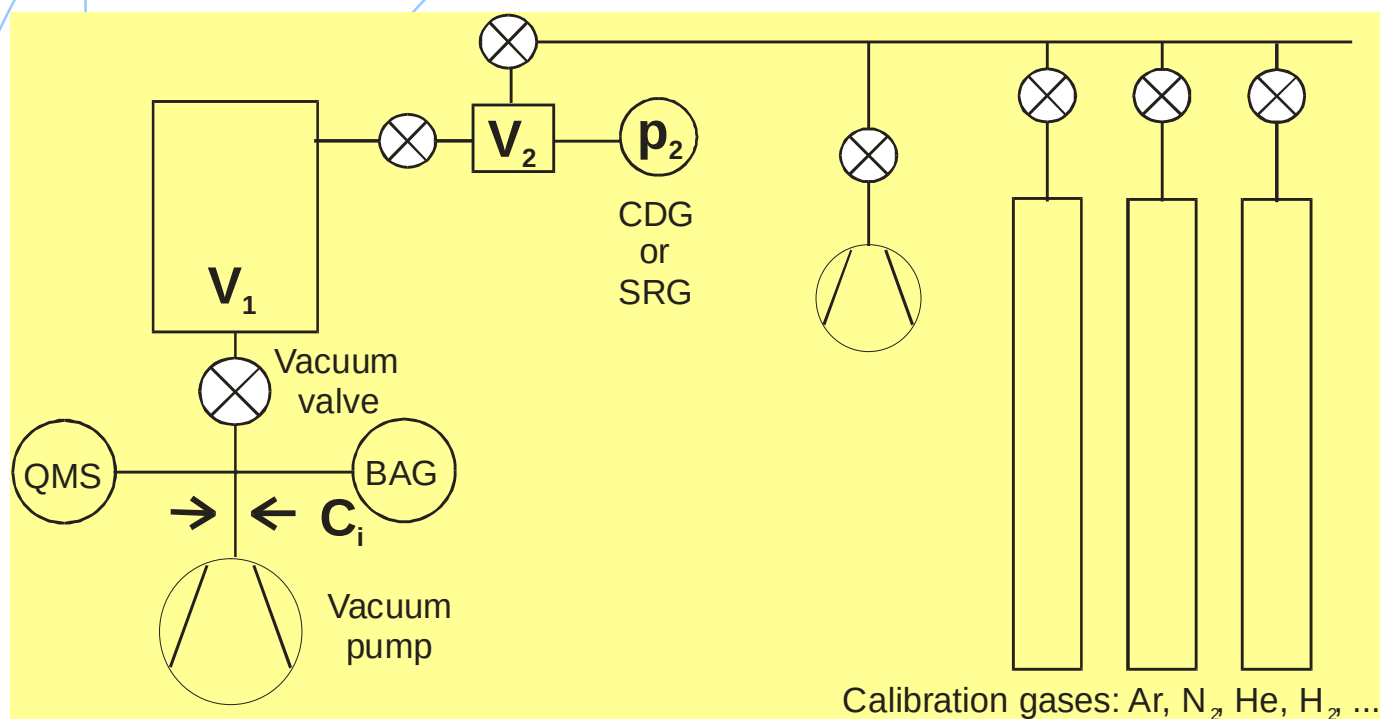
- Gas quantity:

$$G_i = V \times p_{\text{acc},i}$$





We can use the same principle for "in-situ" calibration
R.Dobrozemsky, Vacuum, 41 (1990), p. 2109



"Calibration" gas quantity:

$$G = p_2 \times V_2$$

uncertainty

$$U \approx 1\% \text{ to } 5\%$$

reproducibility

$$< 1\%$$



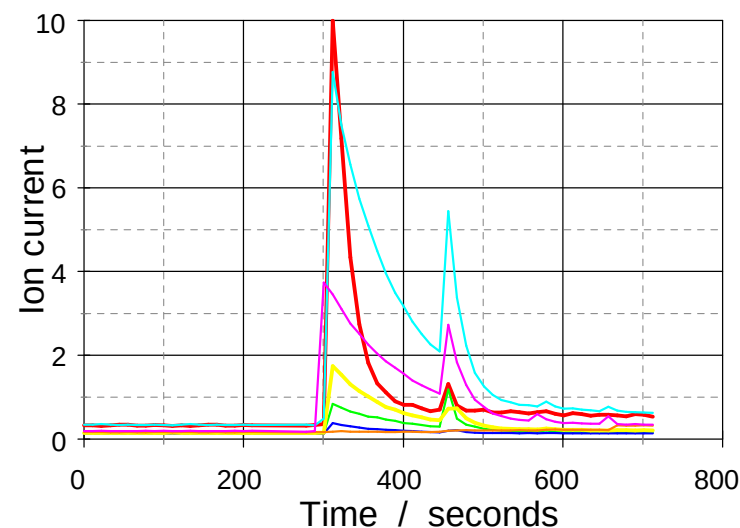
Gas quantity conversion factor Ψ

We define ratio of gas quantity to the area of pressure burst as "Gas quantity conversion factor" Ψ

$$\Psi_i = \frac{p_{2,i} \times V_2}{\int_{t_1}^{t_2} (I_i - I_{i,0}) dt} \quad \text{units: } \frac{\text{mbar} \times \text{L}}{\text{A} \times \text{s}}$$

After we have "calibrated" a set of Ψ_i for different gases, we can quantify unknown composition of accumulated gas quantity:

$$G = \sum_i G_i, \text{ where } G_i = \Psi_i \times \int_{t_1}^{t_2} (I_i - I_{i,0}) dt$$



— 2 — 12 — 14 — 16 — 18 — 28 — 44



What is contained in Ψ

Gas flow into measurement chamber is evacuated by a given "effective pumping" speed C_i (combined effect of orifice & tube conductance & pumping speed):

$$Q_i = p_i \times C_i$$

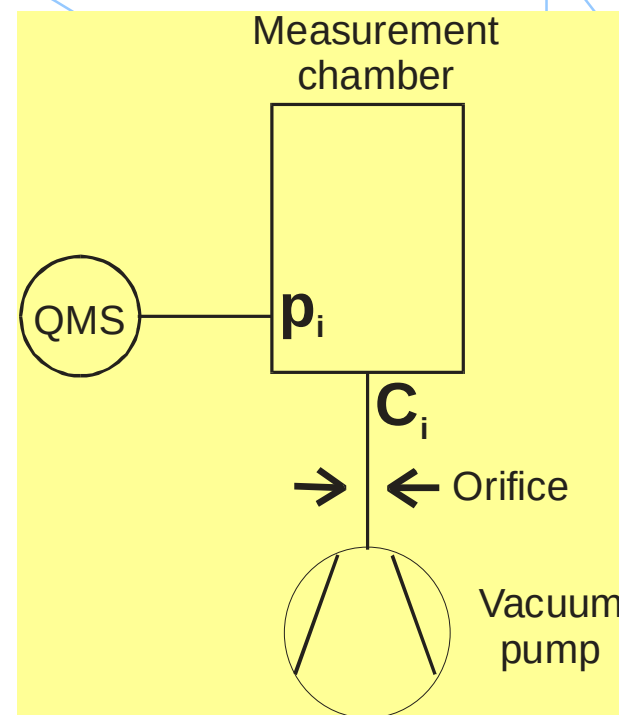
Partial pressure measured by QMS:

$$p_i = \frac{I_i^+}{I_e^- \times \varepsilon_i \times EXTR_i \times TR_i \times MULT_i} = \frac{I_i^+}{S_i}$$

S_i is "absolute sensitivity".

So, for dynamic (throughput method):

$$Q_i = I_i^+ \times \frac{C_i}{S_i}$$





It can be easily shown, that

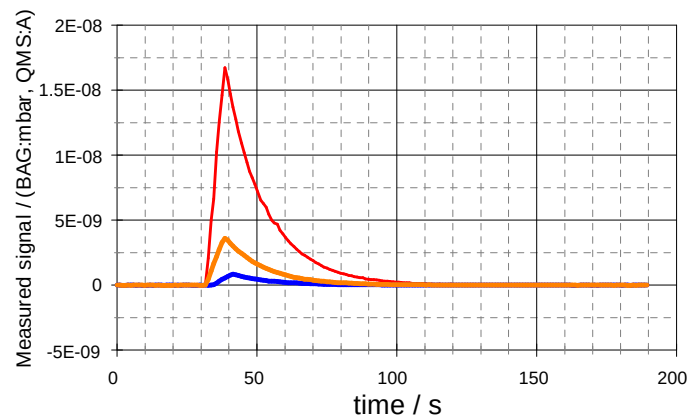
$$\frac{C_i}{S_i} = \psi_i \quad \text{units: } \frac{\text{mbar} \times \text{L}}{\text{A} \times \text{s}}$$

so the same conversion coefficient is applied for dynamic measurement also:

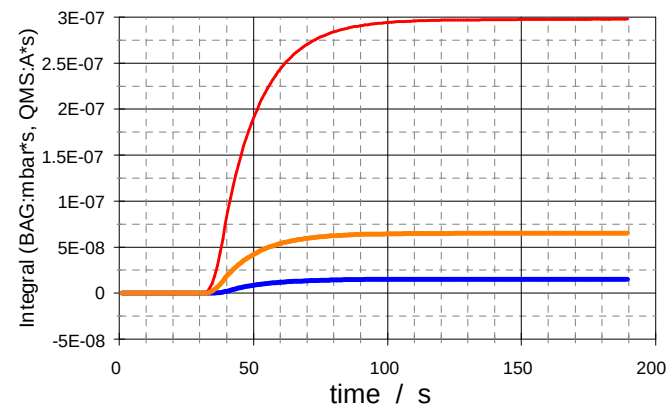
$$Q_i = \Psi_i \times I_i^+$$



Example of Argon calibration



— BAT — 20 — 40



— BAT — 20 — 40

$$V_1 = 0.294 \text{ L}$$
$$P_1 = 6.73 \times 10^{-6} \text{ mbar (SRG)}$$

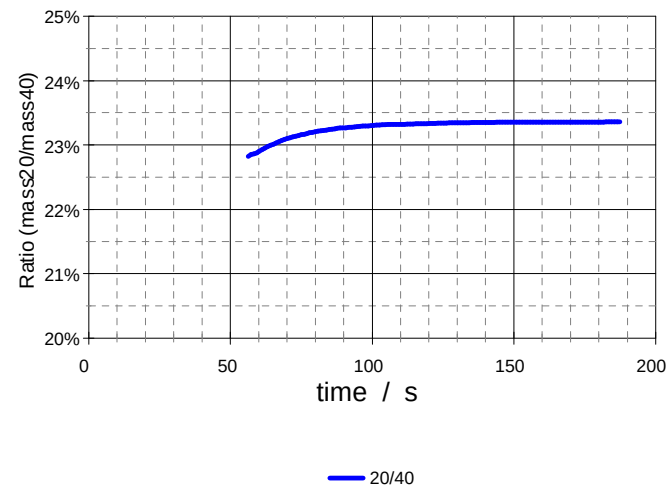




Table of results:

$G=P_1 \times V_1$ [mbar×L]	m/e	Integral $A \times s$	Ψ mbar×L/($A \times s$)	
1.857×10^{-6}	40	6.52×10^{-8}	28.48	$\Psi_{Ar,40}$
1.857×10^{-6}	20	1.52×10^{-8}	121,9	$\Psi_{Ar,40}$
1.857×10^{-6}	total 20+40	8.04×10^{-8}	23.09	$\Psi_{Ar,total}$
		mbar×s	mbar×L/(mbar×s)	
1.857×10^{-6}	BAG	2.98×10^{-7}	7.88	$\Psi_{Ar,BAG}$

from 5 repeated measurements:

Mean value: $\Psi_{Ar,40} = 28.40$ Rel. standard deviation = 0.88%



Use of Farady detector or SEM

SEM gain not stable with time

Experience from MCP used in image intensifiers:

- electron gain drops with "accumulated charge"

Reason:

- migration of Alkali metal ions in Pb glas under electron bombardment
- consequently SEY decrease

SEM gain in QMS depends on molecular species

- ion-electron conversion efficiency – different for different ions



Mass dependence of SEM gain

N.R.Reagan & all, JVST A5 (1987), 238

GAIN proportional to $m^{-1/2}$

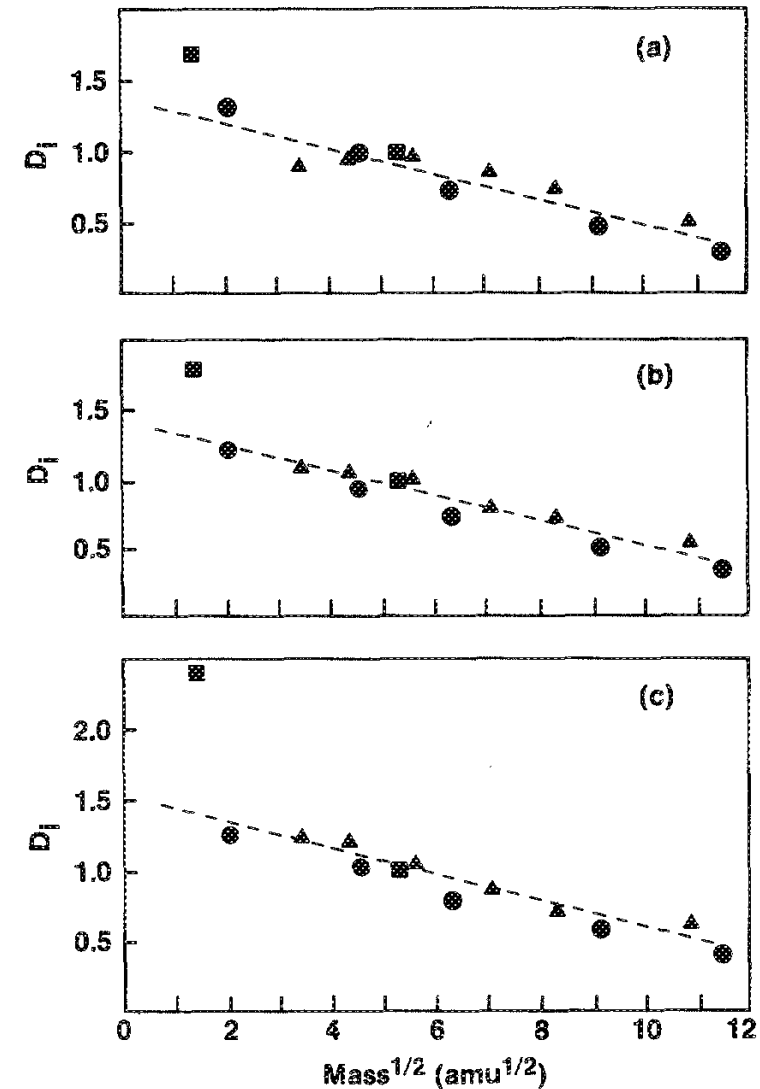


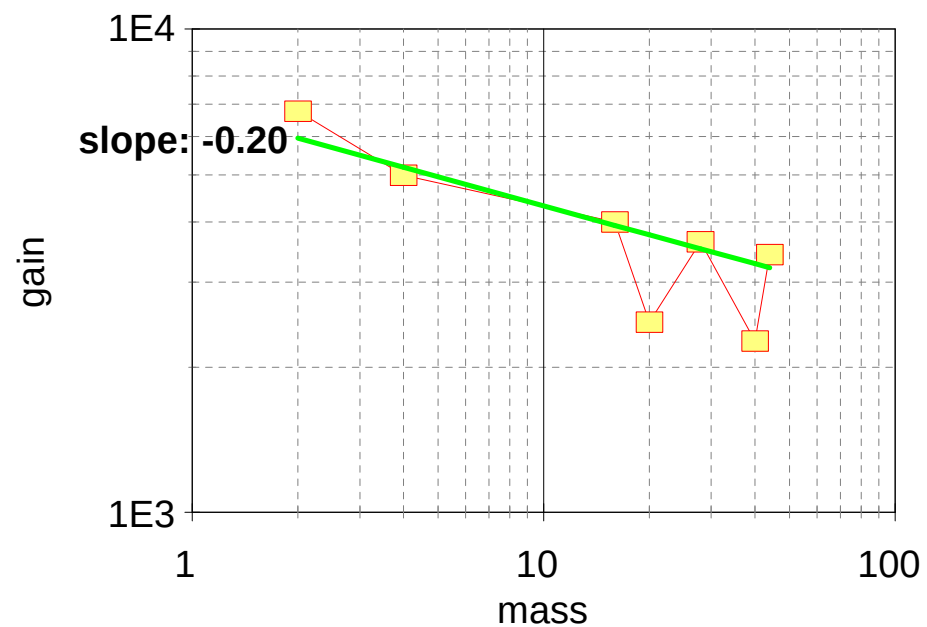
FIG. 3. D_i vs mass^{1/2} at multiplier voltages of (a) 1.3, (b) 1.5, and (c) 1.7 kV. Key to symbols: ● ions from inert gases, ■ ions from homonuclear diatomic gases, and ▲ ions from C_2F_6 .



Mass dependence of SEM gain

$$GAIN = \frac{I_{SEM} - I_{SEM,0}}{I_F - I_{F,0}}$$

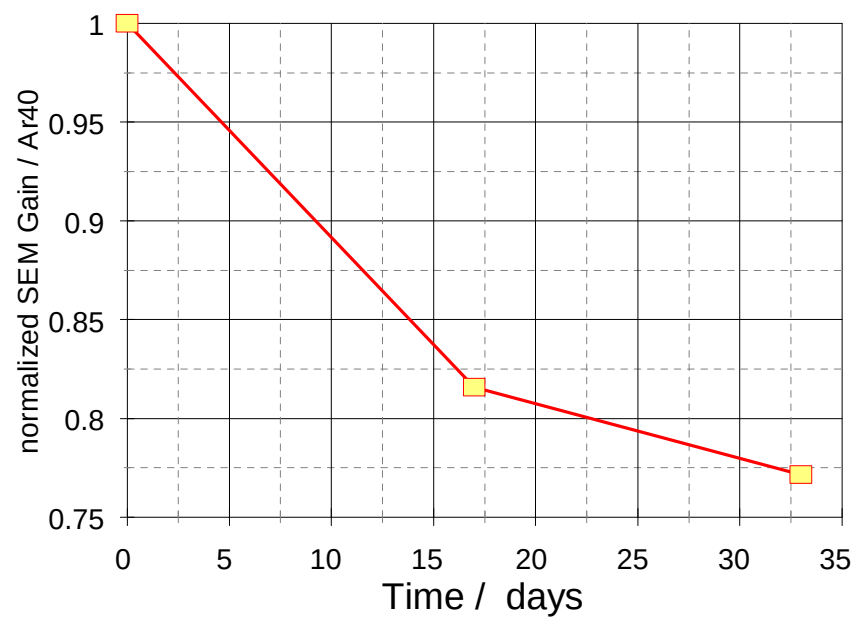
Mass dependence: GAIN proportional to $m^{-1/5}$





Time dependence of SEM Gain (Ar_{40})

Initial value at $t=0$: $G=3840$





Conclusions

Presented method for calibration of QMS is

- intrinsically very repeatable (long term stability of CDG or SRG)
 - suitable for studies of time stability
- traceability is straightforward
 - calibrated CDG or SRG
 - volume V_2 can be determined gravimetrically or from dimensional measurements
- reference pressure gauge (CDG) is virtually independent on gas species,
- or the dependence is well known (SRG proportional to $M^{-1/2}$, data from literature show $0.96 < \sigma_{\text{gas}} / \sigma_{\text{N}_2} < 1.04$)
- is performed "in-situ" – most corrections due to non Maxwellian gas distribution are canceled out
- effective conductance is automatically taken into "conversion factor" Ψ