Thermal Treatment of Stainless Steel towards the Zero Outgassing Rate

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Hydrogen - metal interactions are intensively studied in the fundamental science with a close relation to numerous technical fields. Different physical and mathematical models were proposed in the past, which are experimentally verified at a high temperature and pressure. In the last years, the interest increased for metals with a high hydrogen solubility as they can be used as efficient storage devices.

Far apart seems to be the problem met in the UHV practice: obtaining the lowest residual outgassing after applying a feasible thermal treatment. The kinetics measurement methods in UHV are extremely sensitive and give reliable results. Anyhow, an overview of reports on outgassing rate values from stainless steel shows a noticeable discrepancy to physical models. These still lean on conventional solubility determination methods and on permeation measurements. A "regular diffusion" is still often assumed to be the limiting process also for the hydrogen outgassing rate during the heating. It was thus generally accepted that the initial hydrogen concentration before any thermal treatment is high and can be substantially reduced by a long-term vacuum heating. In the mean time, hydrogen concentration determination by nuclear methods, or by long term thermal extraction were performed, which gave a much higher hydrogen content in stainless steels than usually stated. The proposed explanation for this deviation may be in the deeply trapped hydrogen that restores the kinetic data of regular permeation and these new findings.

The role of these deep states, termed also as the "residual hydrogen", on the achievement of very low outgassing rates, will be clearly presented by a new interpretation of our previous experiments.

New results of extremely precise hydrogen permeation rate measurements through a stainless steel membrane will be also presented. A regular permeation at 200°C and 250°C could be repeated easily at an upstream hydrogen pressure of the order of 200 mbar with a good agreement with the literature data. Contrary, the kinetics of approaching a new equilibrium slows down substantially at a hydrogen pressure below $1x10^{-2}$ mbar. The membrane becomes highly impermeable, since the permeation rate is governed by a small number of protons occupying "regular" sites. Slow "de-trapping" is manifested in the very long transients even at 200°C and a membrane thickness of only 0.15 mm. This process thus explains the almost constant outgassing rate value in any realistic experimental time, usually observed in UHV chambers at room temperature. These new data will be compared to the existing theoretical models in order to help answering the question: "What is the optimal thermal treatment of stainless steels to approach the zero outgassing rate?"

Thermal treatment of stainless steel towards the zero outgassing rate

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The outline of the talk

- A brief outlook of models for hydrogen interaction with stainless steel - thermodynamics and kinetics
- Verifying of models by three experiments

Experiment 1: two identical thin walled chambers, d=0.6 mm ⇒ negligible fraction of hydrogen extracted, but q_{out} low

Experiment 2: thin walled cell d=0.15 mm ⇒ permeation rate 2.2×10^{-15} mbar l cm^{-2} s^{-1} at 55°C to the atmosphere at the upstream $p_{up} = 1.7 \times 10^{-4}$ mbar

Experiment 3: thin walled cell d=0.15 mm ⇒ permeation studied in a wide pressure and temperature range

Introduction

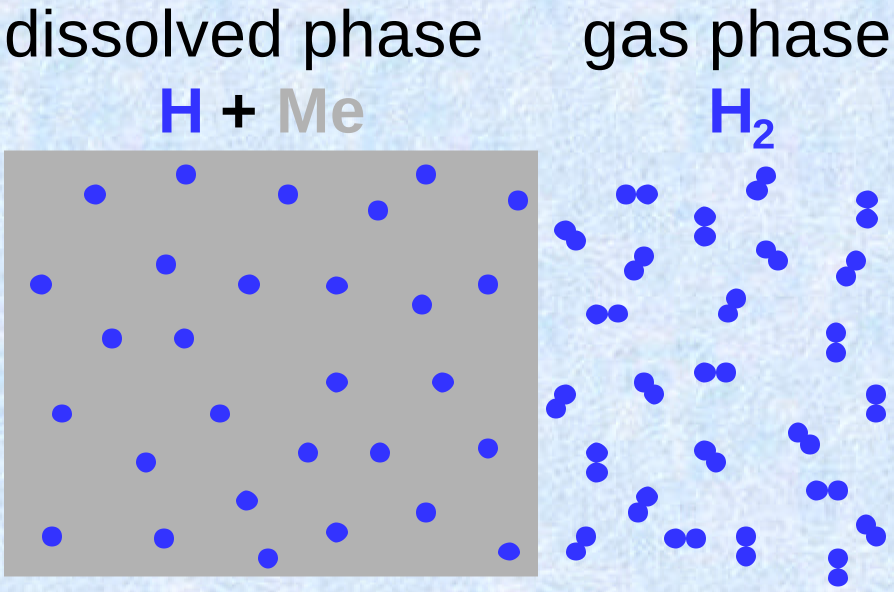
One of the main problems in UHV and EXV practice is to suppress the hydrogen outgassing rate q_{out}

the ultimate pressure
in UHV and EHV chambers

the lifetime
of sealed vacuum devices

lowest q_{out} Þ baking at very high T?
the majority of H really expelled?

The q_{out} is a consequence of a non-equilibrium state between in the dissolved and gas phase.



dissolved phase

$H + Me$

gas phase

H_2

Equilibrium:

formal condition:

$$m_{\text{diss.}} = \frac{1}{2} m_{\text{gas}}$$

experimental condition:

$$\frac{dp_{H_2}}{dt} = 0$$

The existing models

TD equilibrium:

Sieverts law:

$$C_{eq.} = K_{S_0} \exp\left(- E_S / k_B T\right) \sqrt{p_{H_2\ eq.}}$$

$\frac{1}{2}H_2 \rightarrow H + Me$ is an endothermal reaction ($E_S>0$).

Example 1: T=1000°C, p_{H_2}=1 bar Þ $C_{eq.}$= 1.2x10^{19} H at./cm^3

Example 2: T=25°C, p_{H_2}=5x10^{-4} mbar Þ $C_{eq.}$= 6.5x10^{14} H at./cm^3

The relation has never been experimentally verified at low hydrogen pressures, since the equilibrium state dp/dt=0 had not been established during the time of the experiment.

Models for kinetics of approaching the equilibrium

1) Diffusion limited model (DLM)

- q_{out} determined by diffusion of H atoms occupying identical interstitial sites
- random walk steps between sites described by diffusion equation

$$\frac{\partial C}{\partial t} = D(T)\,\nabla^2 C$$

Fourier characteristic time for a plate, thickness d:

$$Fo = d^2/4D(T)$$

The most relevant paper that probably influenced our physical picture:

R. Calder, G. Lewin: Reduction of stainless-steel outgassing in ultra-high vacuum, Britt. J. Appl. Phys., 18, 1459, (1967)

2) Recombination limited model (RLM)

- q_{out} determined by recombination of H atoms on the metal surface.
- surface sites more tightly bound than interstitial bulk sites
- diffusion equation solved by second order boundary conditions

giving: $$q_{out} = K_L(T)C^2_{surf.}$$

$K_L(T)$ values very scattered and almost useless for vacuum practice where the observed q_{out} values after thermal treatment are much higher than predicted by the RLM and seems to be pressure independent in the observation time.

Relevant papers related to Tokamak plasma reactors:

I.Ali-Khan, K.J.Dietz, F.G.Waelbroeck, J.Nucl.Mater., 76&77, 337 (1978)

M.A.Pick, K.Sonnenberg, J Nucl Mater, 131, 208 (1985)

3) Models which include bulk states at deep energy levels

- kinetics determined by recombination on the metal surface.
- several bulk sites exist where hydrogen is more tightly bound than at regular interstitial sites, their number could only be estimated by TD, unknown by present experimental techniques
- unfortunately, complex mathematical treatment can not be applied easily in the experimental work

Relevant papers:

P.K.Foster, Nature, 4748, 399 (1960).

A. McNabb, P.K.Foster, Trans.Metall. Soc. AIME 227, 618 (1963)

P.L.Andrew, A.A.Haasz, J.Appl.Phys, 72, 1749 (1992)

A.Turnbull, R.B.Hutchings, D.H.Ferriss, Mat.Sci.Eng., A238, 317 (1997)

The experimental facts

- most papers report q_{out} after some thermal procedure, indicating only that $\mu_{diss} > \mu_{gas}$
- little data on precise *in situ* q_{out} measurements at elevated T
- no data found about kinetics close to the equilibrium in the high vacuum range
- little data about hydrogen concentration in the wall after thermal treatment, since its value below the detection limit
- atmospheric side was often supposed to be the source, rather than a hydrogen sink, but no reliable data on H_2 partial pressure available

Experiment 1 - part 1

SS chamber, V= 12.5 l, A=4000 cm^2, d=0.6 mm, including flanges etc
walls AISI 304, thinned flanges AISI 316L, gaskets and stem, Cu

by heating (150°C, 2h) ⇒ **q_{out}(295K)@2x10^{-12} mbar l/(cm^2s)**

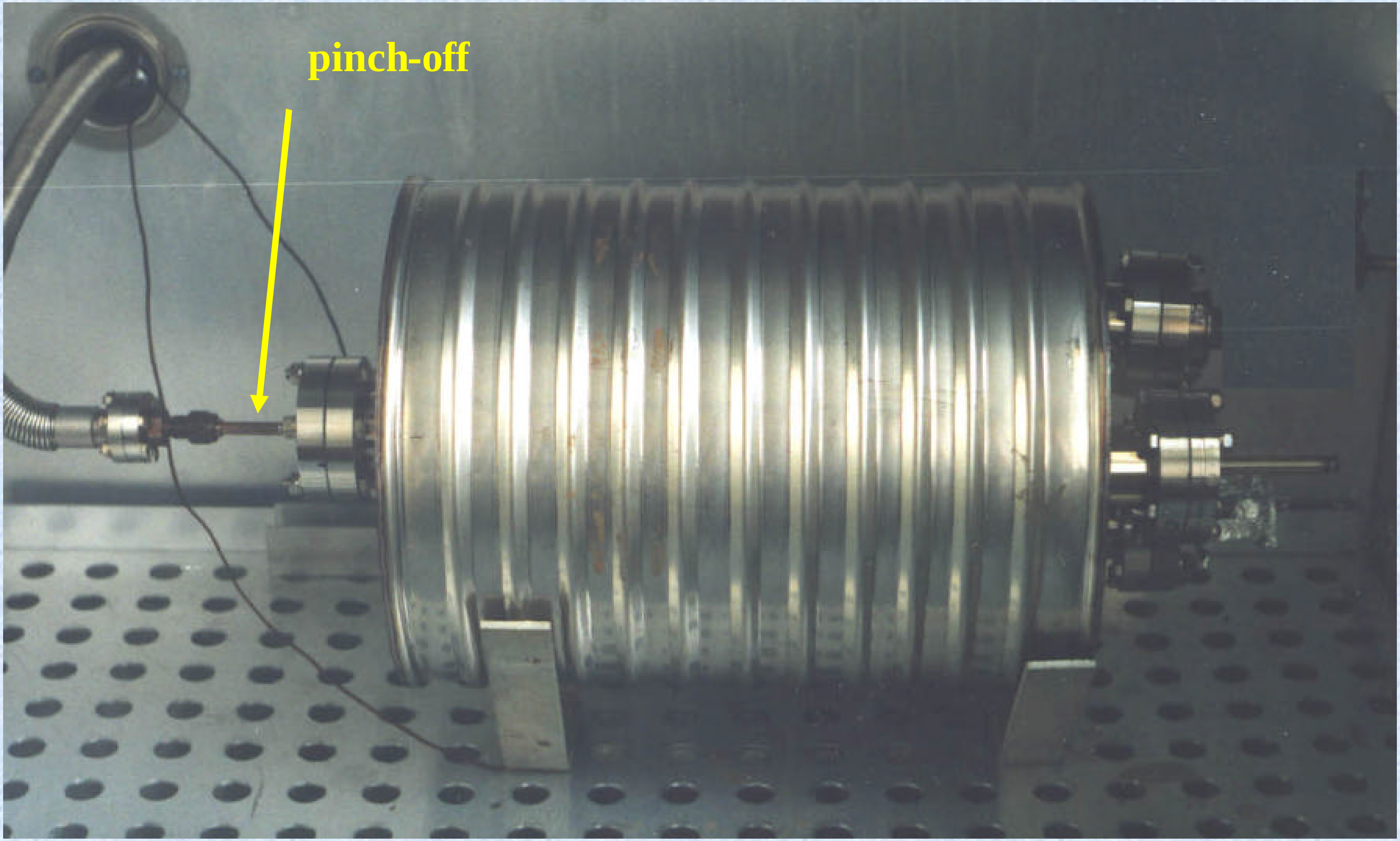
by heating (200°C, 72h, Fo=3 by the DLM) finished at

q_{out}(473K)@6x10^{-10} mbar l/(cm^2s), ($\Delta C \cong 7\times10^{17}$ atoms H/cm^3)

⇒ final **q_{out}(295K)** @ **1.0x10^{-13} mbar l/(cm^2s)**

V. Nemanic, J.Setina, JVST A18, 1789 (2000).

d=0.6 mm, including flanges etc, walls AISI 304, thinned flanges AISI 316L, gaskets and stem, Cu, pinched off for the SRG



Experiment 1 - Part 2

After Part 1, the same material was investigated further by a long-term thermal extraction. Three sample types prepared:

Type A: only cleaned. (By the "fusion" method LECO RH-402, the total amount: **C_0@1.5 x10^{19} atom H/cm^3**.)

Type B: cleaned and annealed for 20 min at 1050°C (Fo≅110) in dry hydrogen at 1 bar. Expected value: **C_0=1.2x10^{19} at. H/cm^3**

Type C: **reference sample,** cleaned and annealed in a high vacuum furnace (p<10^{-5}mbar) for 5.5 h at 950°C (Fo≅1200). Oxide free and expected to be **"hydrogen free".**

Sample pretreatment greatly influenced q_{out} at temperature below 400°C: the initial q_{out} from vacuum annealed Sample C1 was 1000 times lower than from the hydrogen annealed samples B1 or B2, but it had a little effect on the kinetics above 700°C:

	Fo	ΔC	ΣFo	$\Sigma\Delta$C
A2			3425	**4.9 x10^{19}**
B1	110	*	483	**8.9 x10^{19}**
B2	110	*	234	**9.6 x10^{19}**
C1	1200	*	257	**9.1 x10^{19}**

B. Zajec, V. Nemanic, Vacuum 61, 447 (2001).

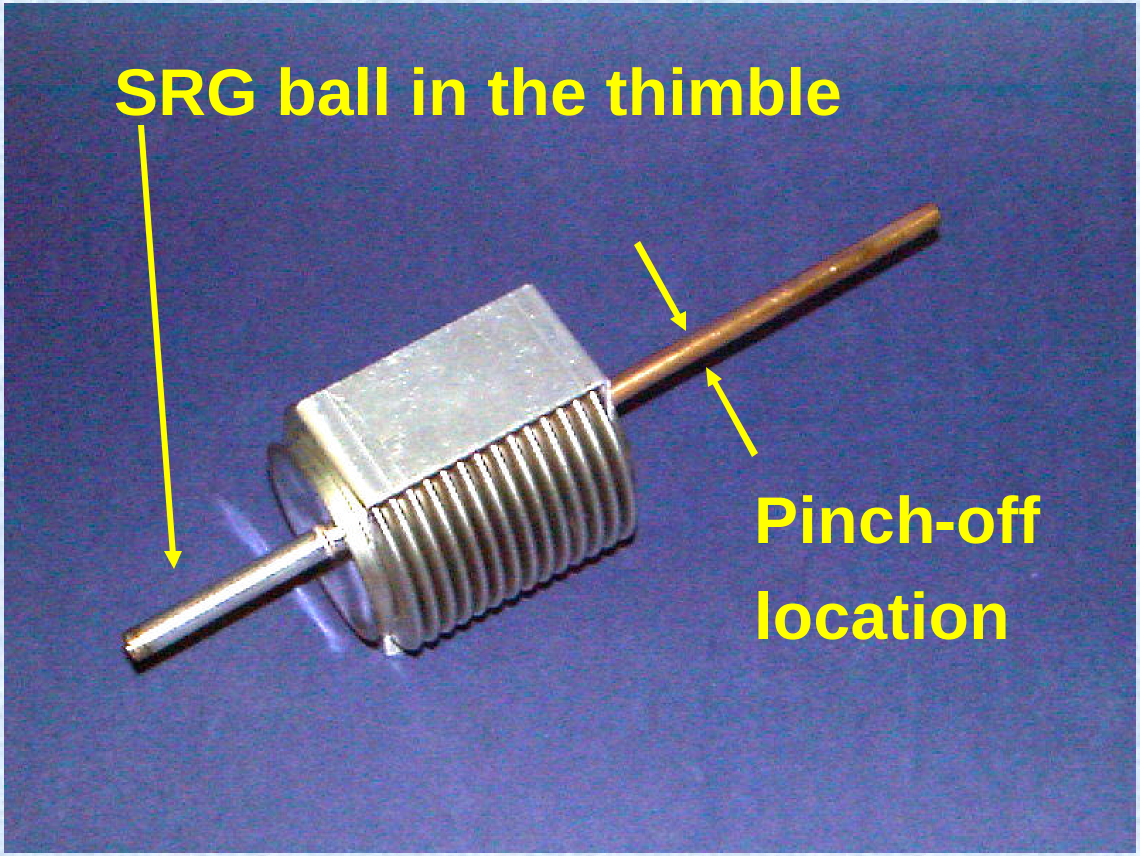
V. Nemanic, B. Zajec, J. Setina, JVST A19(1), 215 (2001)

Conclusions for Experiment 1

- after the preprocessing (72 h, 200°C, 3 Fo) 2 chambers **q_{out}(25°C)** @ **$1.0x10^{-13}$ mbar l/(cm^2s),** but the released H_2 was equiv. to $\Delta C \cong 7x10^{17}$ atoms H/cm^3 and thus represented less the 1 % of the total since $C_0 \sim 9\times10^{19}$ at.H/cm^3.....
but in 3 Fo, the wall should be "hydrogen free“ by the DLM.

The extraction of this tiny fraction of the total hydrogen content at 200°C had essential effect on the observed kinetics at room temperature.

Experiment 2



SS cell data:

- bellows AISI 316L

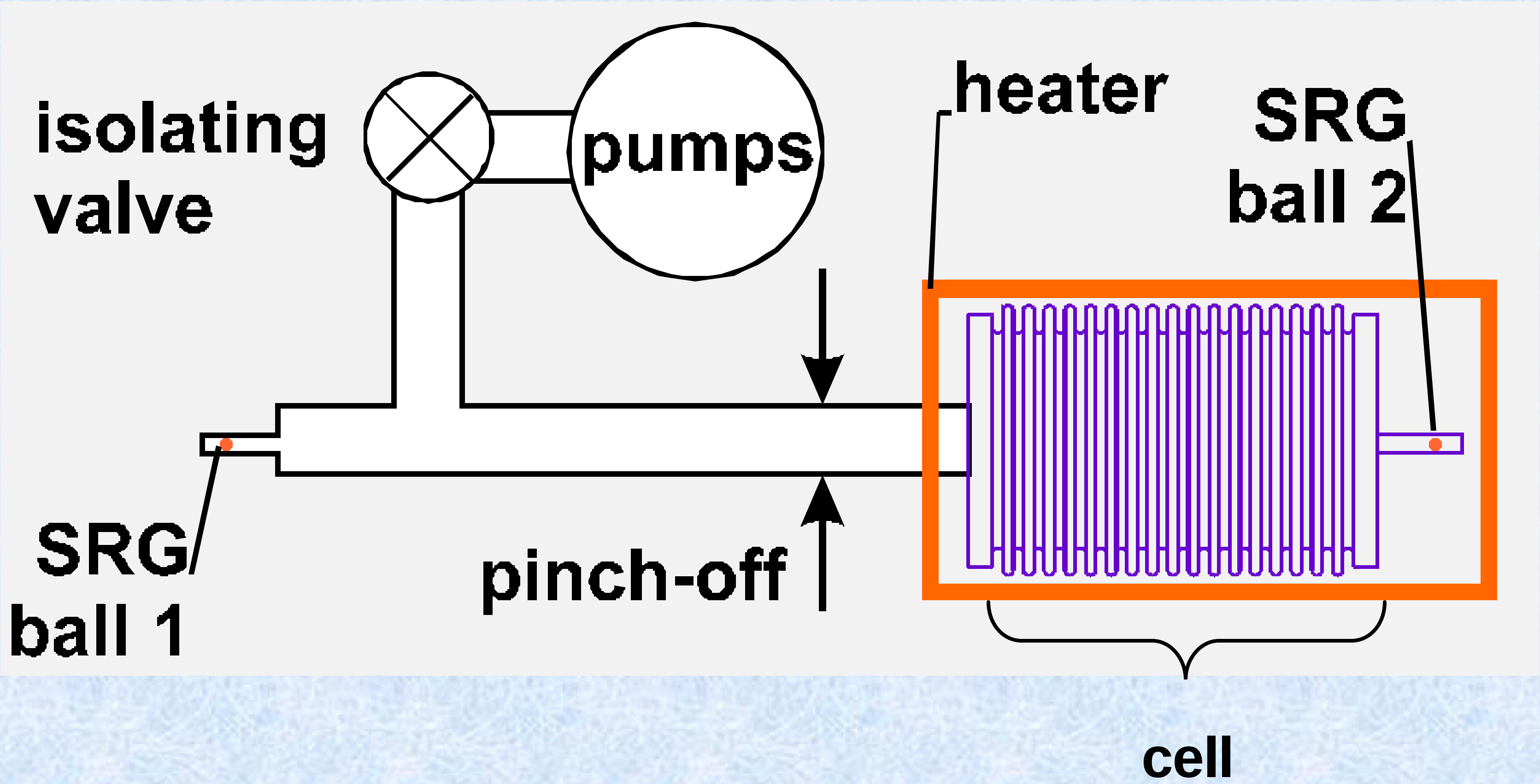
endplates AISI 304,

- d=0.015 cm
- A=460 cm^2
- V=125 cm^3

Cu tubing to allow pinch-off

Very low q_{out} achieved after simple thermal treatments

V.Nemanic, J.Šetina, JVST A17, 1040 (1999).


isolating
valve
pumps
heater
SRG
ball 2
SRG
ball 1
pinch-off
cell

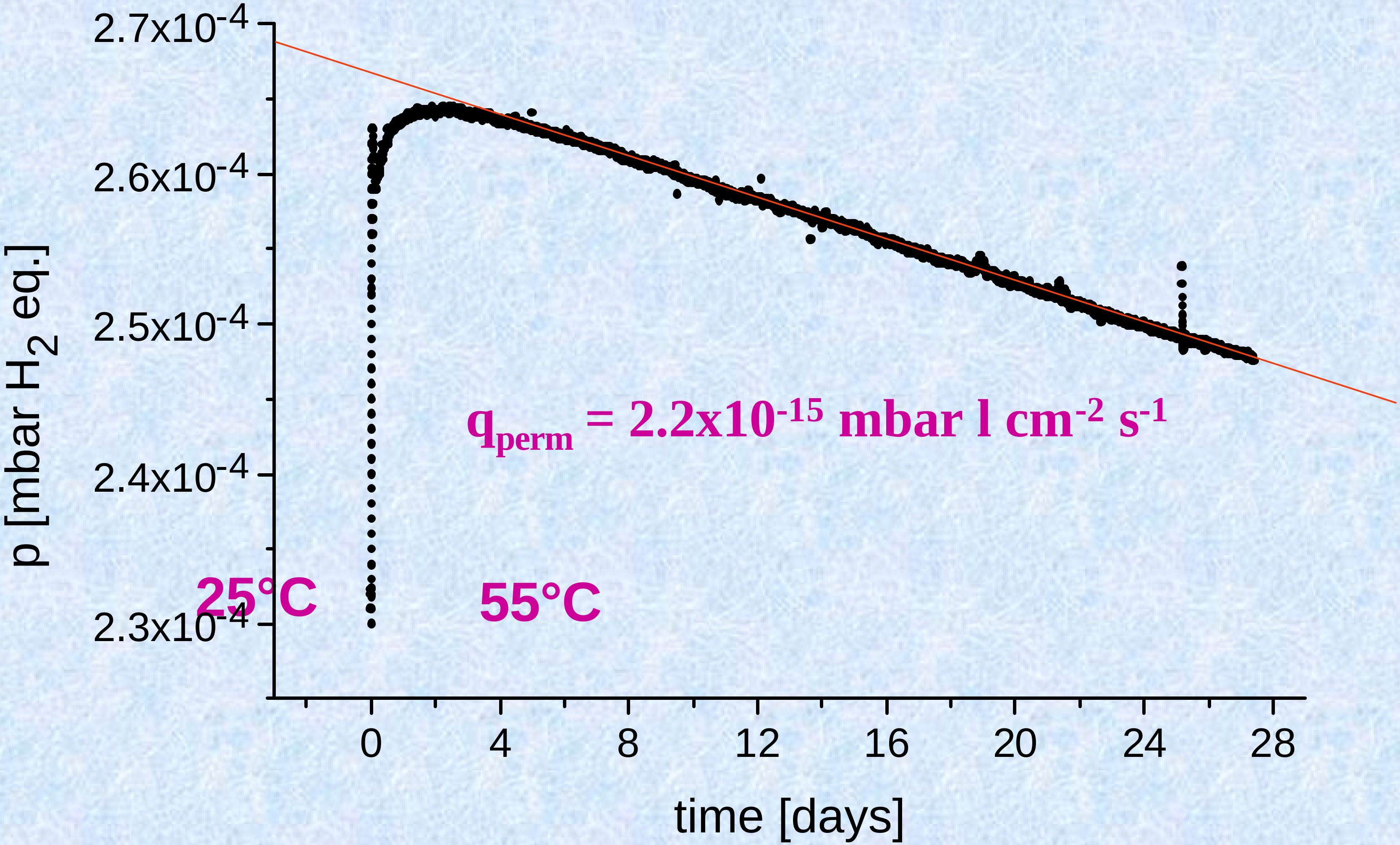
Preprocessing - thermal outgassing:

- 109 hours at T=200°C ⇒ equivalent to Fo=23
- q_{out} measured by the pressure rise method using the SRG 1
- final $q_{out}(200°C)=4.5\times10^{-12}$ mbar l $cm^{-2}s^{-1}$ - before cool-down
- average H concentration decrease $\Delta C=8.8\text{x}10^{16}$ at.H/cm^3

assuming that both surfaces outgassed equally

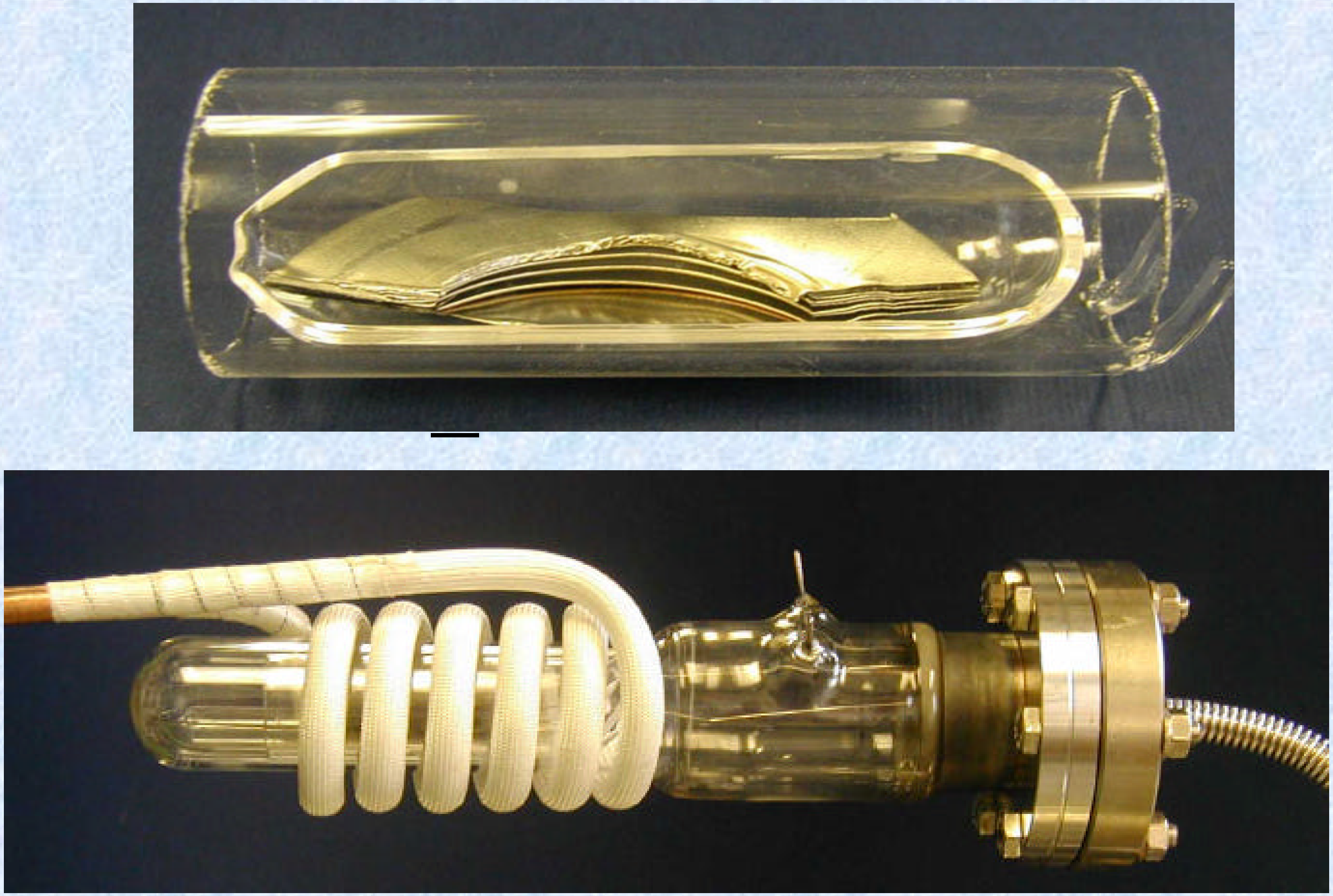
25°C ® 55° jump followed by 28 days at 55°C in a thermostat

After the pinch-off, $p(H_2)$ decreased, presumably by permeating to the atmospheric side, where estimated $p=5\times10^{-4}$ mbar ?!



$q_{perm} = 2.2\times10^{-15}$ mbar l cm^{-2} s^{-1}

After several months of SRG measurements, the cell was cut ⇒ pieces put in a quartz crucible within a quartz tubing ⇒ melted by RF in vacuum ⇒ $V.\Delta p$ ⇒ QMS analysis



Two most interesting findings:

the calculated C at the final $p_{up}=1.7\times10^{-4}$ mbar should be $C=5\times10^{14}$ at. H/cm^3, but in 5 melting cycles, a lot of hydrogen was extracted: $\Delta C \cong 7.6\times10^{18}$ at H/cm^3

⇒1) The atmospheric side may be thought as the sink for hydrogen, not the source, as often estimated.

⇒2) A negligible fraction of hydrogen participated in the permeation process, which led in the past to the conclusion that the membrane is almost hydrogen free

Conclusions for Experiment 2

- during the preprocessing (109h, 200°C, 23Fo)

$\Delta C = 8.8 \times 10^{16}$ at.H/cm^3 << expected $C_0 \sim 10^{19}$ at.H/cm^3

The extraction of a tiny fraction of the total hydrogen content at 200°C had again essential effect on the observed kinetics close to the equilibrium.

- long-term pressure decrease indicated permeation from the cell to the atmosphere, where partial $p(H_2) < 1.7 \times 10^{-4}$ mbar, (probably <<) and thus not contribute a noticeable part to the q_{out} in UHV chamber even during the bake out.

Comparison to the DLM and RLM clearly shows an inadequacy of both models to describe the data

- measured $q_{perm} = 2.2\text{x}10^{-15}$ mbar l cm^{-2} s^{-1} at 55°C, is lower than $q_{perm} = 3.4\text{x}10^{-14}$ mbar l cm^{-2} s^{-1} (by the DLM)
- oxidised surfaces could reduce the q_{perm} by a factor of 15, (by the RLM), which is an acceptable agreement unless….

DISCREPANCY IN THE PHYSICAL PICTURE

- both models apply Sieverts law, when $C \approx 5\text{x}10^{14}$ at. H/cm^3
- the released H_2 during the melting $\Delta C = 7.6\text{x}10^{18}$ at H/cm^3

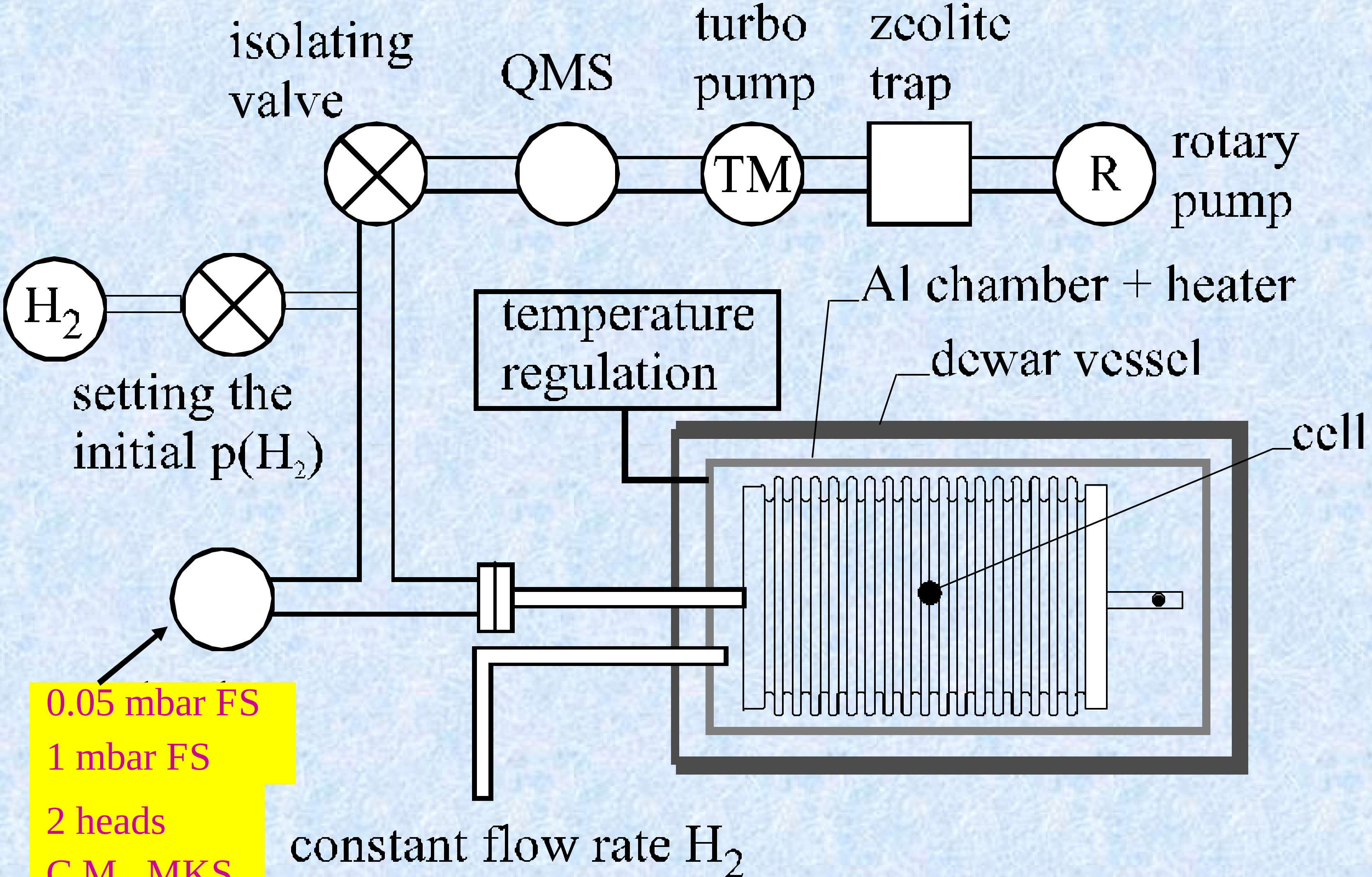
⇒ a great amount of H not taken into account ⇒for a thick wall chamber, such low q_{out} would be recorded for millennia

- What is the driving force for this low q_{out}?

Experiment 3

An equivalent cell from Experiment 2 used as a membrane for investigation the role of trapped hydrogen in permeation experiment at 200°C (up to 400°C), long term $\Delta T=0.1°C$. Both sides could be made as "downstream side":

- q_{perm} measured after setting the initial upstream pressure from $p_{up}=5x10^{-3}$ mbar up to 0.85 mbar
- downstream $p(H_2)$ measured while flushing the outer side by H_2/Ar mixture, at only one value $p_{up}(H_2)\cong 200$ mbar



0.05 mbar FS

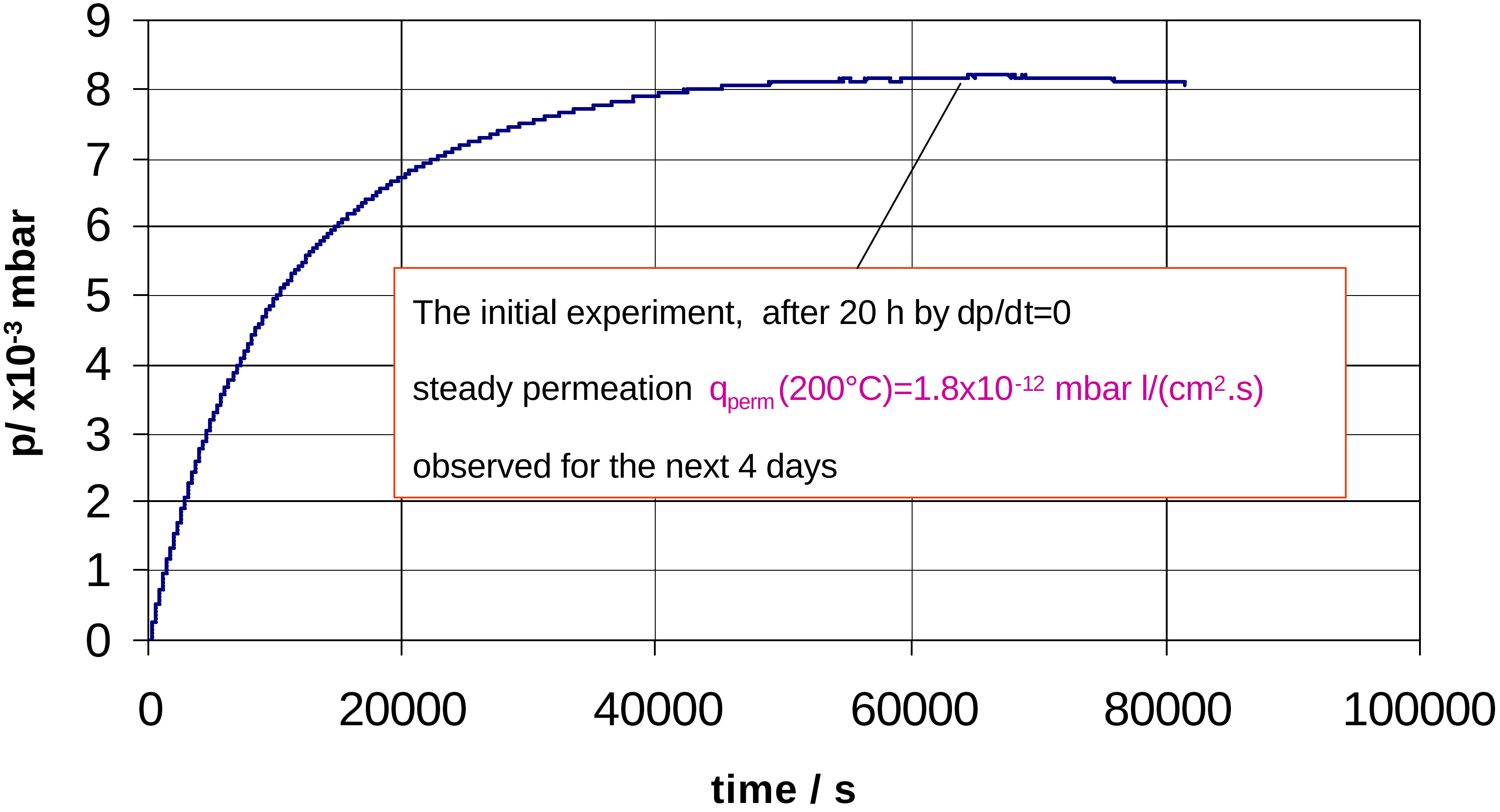
1 mbar FS

2 heads

C.M., MKS

Published data for diffusivity of stainless steel and calculated characteristic times for the cell at three temperatures, used in the experiment, D_0=0.012 cm^2/s, E_D=0.57 eV

		permeation d^2/D	outgassing (=Fo) $d^2/4D$
T	D / cm^2/s	t_0 / s	t_0 / s
200°C	1.1×10^{-8}	5300	1325
250°C	4.0×10^{-8}	1398	350
400°C	6.6×10^{-7}	84	21



The initial experiment, after 20 h by dp/dt=0

steady permeation $q_{perm}(200°C)=1.8\text{x}10^{-12}$ mbar l/(cm^{2}.s)

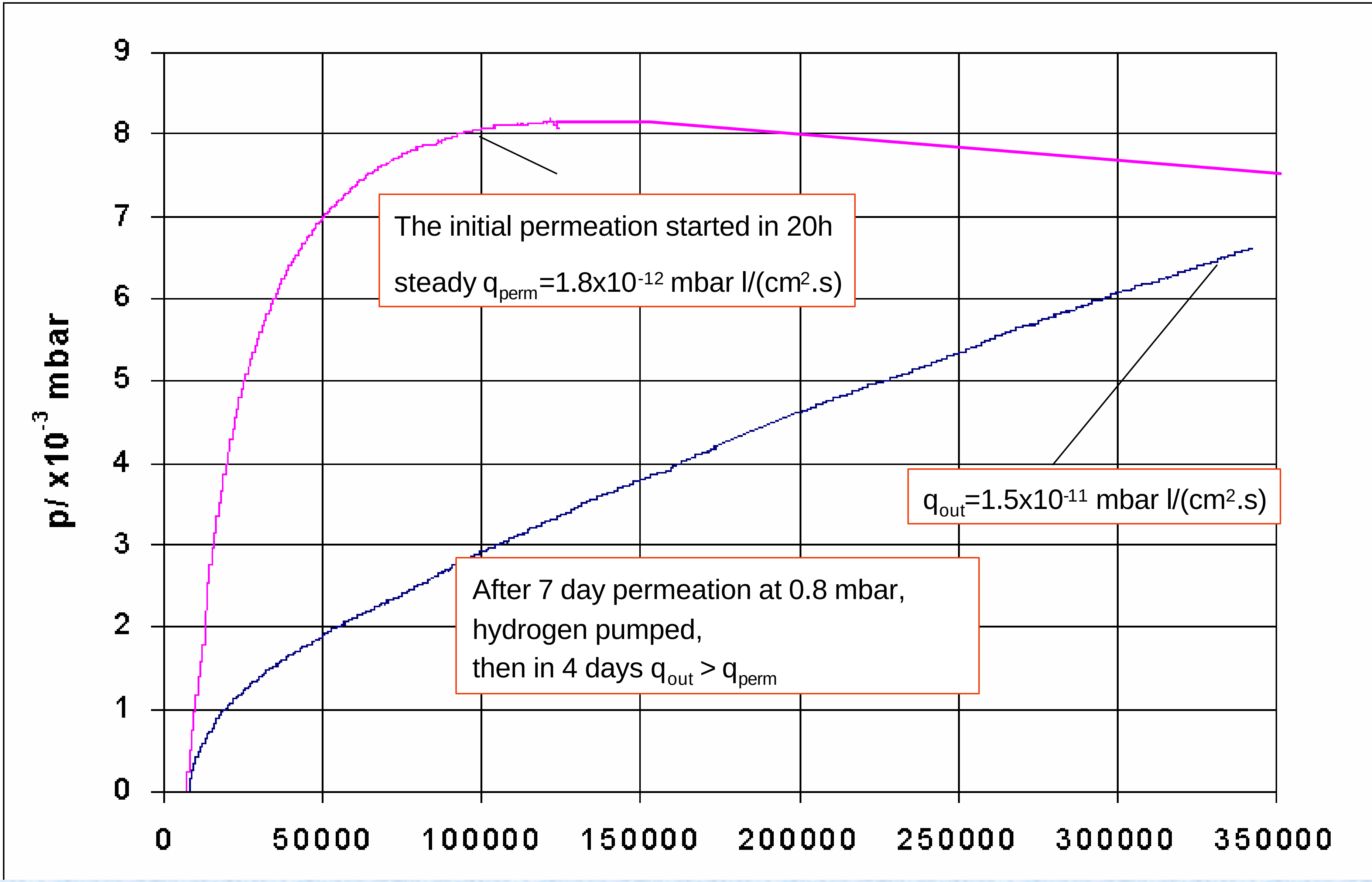
observed for the next 4 days

Permeation from p_{up}= 0.8 mbar to the atmospheric side

q_{perm} (200°C) $\cong$ 1.0x10^{-10}mbar.l/(cm^2.s), for $\cong$ 7 days q_{perm} was approx. 65 times higher than at p_{up}=0.008 mbar, both values indicate "surfaces limited permeation"; sticking coefficient of the order of s $\cong$ 1.5x10^{-11}.

After 7 days ⇒ hydrogen pumped ⇒ a transient was expected that should lead again to a new equilibrium ⇒ a new permeation rate expected to lie between the previous limits.

In what a period could it be observed?? In 20 hours?



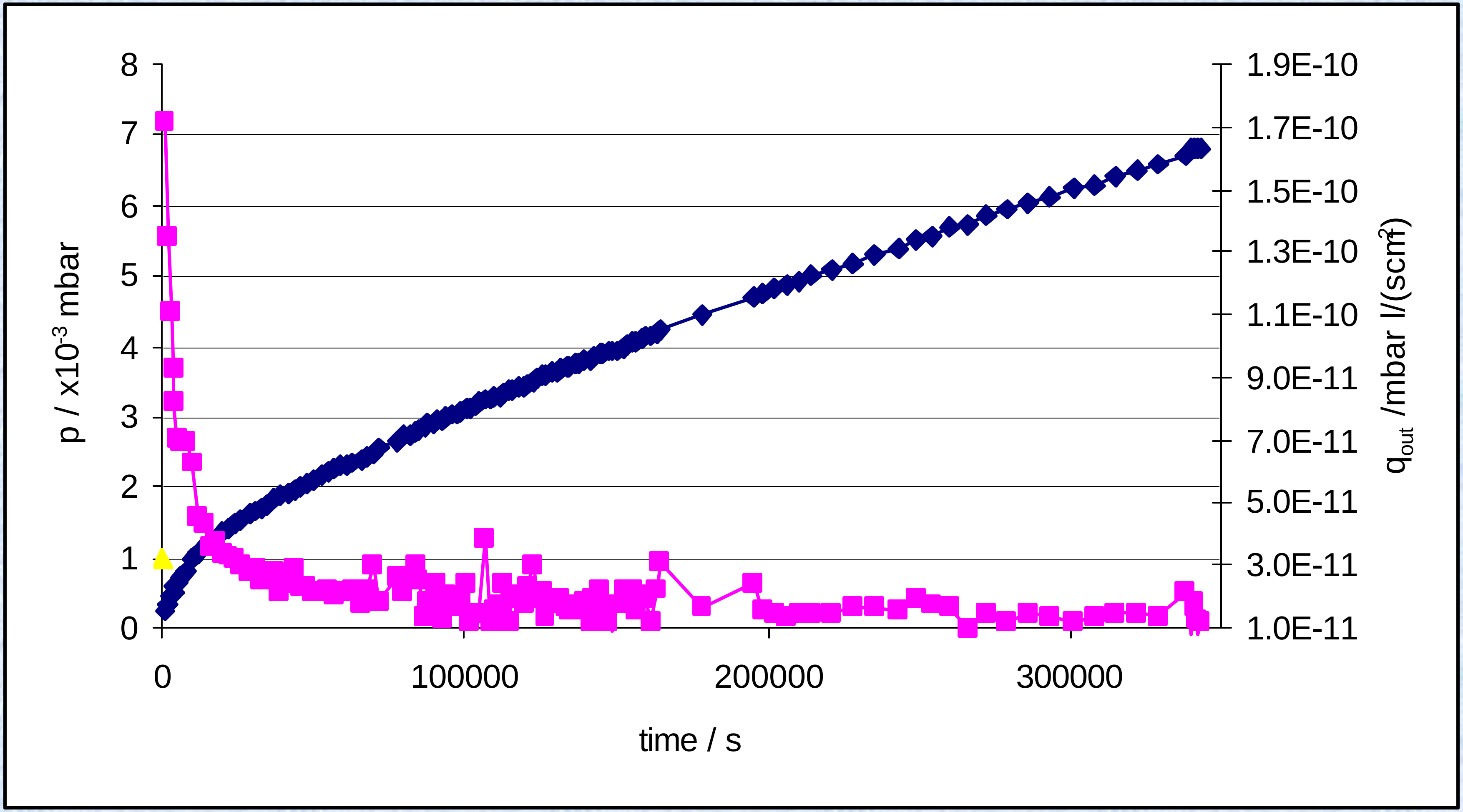
The initial permeation started in 20h

steady $q_{perm}=1.8\times10^{-12}$ mbar l/(cm^2.s)

$q_{out}=1.5\times10^{-11}$ mbar l/(cm^2.s)

After 7 day permeation at 0.8 mbar,
hydrogen pumped,
then in 4 days $q_{out} > q_{perm}$

Outgassing prevailed over the permeation for all 4 days with a slow tendency towards dp/dt=0, final value $q_{out}=1.5\times10^{-11}$ mbar l/(cm^2.s).



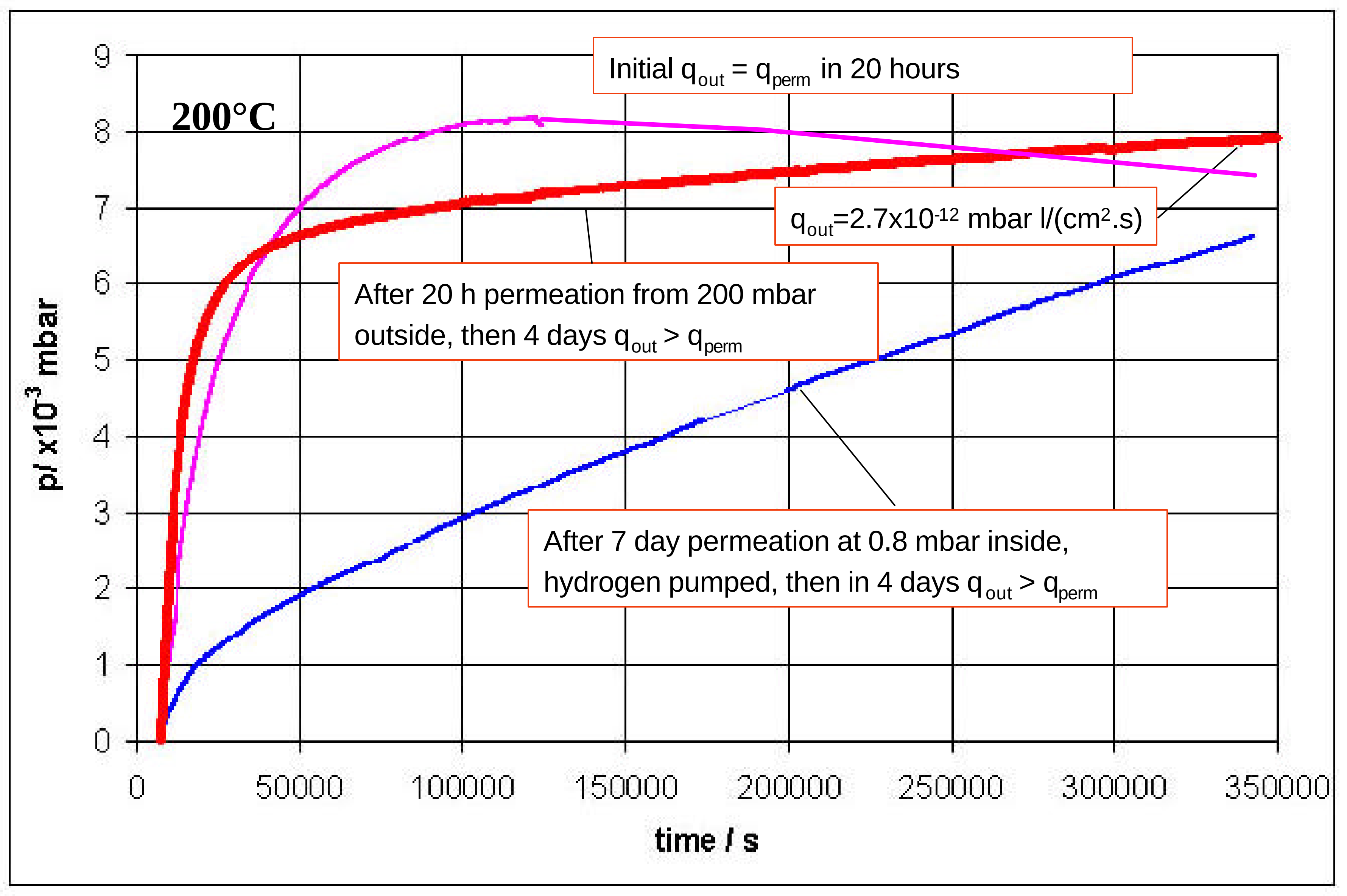
Permeation into the cell from the atmospheric side

At p_{up}= 200 mbar (set by constant flows of pure Ar and H_2), dp/dt change detected fast, while in the next 20 h, steady value approached slowly $q_{perm}(200°C) = 8.4\times10^{-10}$ mbar l/(cm^2.s)

After 20 h, H_2 flow stopped, accumulated H_2 pumped ⇒ a transient expected that should lead again to a new equilibrium ⇒ it was approached too slowly to reach it in 4 days.

Final q_{out}=1.5x10^{-11} mbar l/(cm^2.s) at p_{up}=8x10^{-3} mbar, while only ΔC = 6.3x10^{16} at H/cm^3 released from the wall.

Hydrogen fills and detraps deep states slowly



Initial $q_{out} = q_{perm}$ in 20 hours

q_{out}=2.7x10^{-12} mbar l/(cm^2.s)

After 20 h permeation from 200 mbar outside, then 4 days $q_{out} > q_{perm}$

After 7 day permeation at 0.8 mbar inside, hydrogen pumped, then in 4 days $q_{out} > q_{perm}$

Temperature dependence of the permeation rate

1) after the initial permeation at 0.008 mbar, H_2 pumped, cell cooled to RT for 16 h. When heated again in 2 h, the difference of q_{out}(RT) compared to q_{out}(200°C) after previous long term outgassing at 200°C was low and undistinguishable from the Q_{backg}

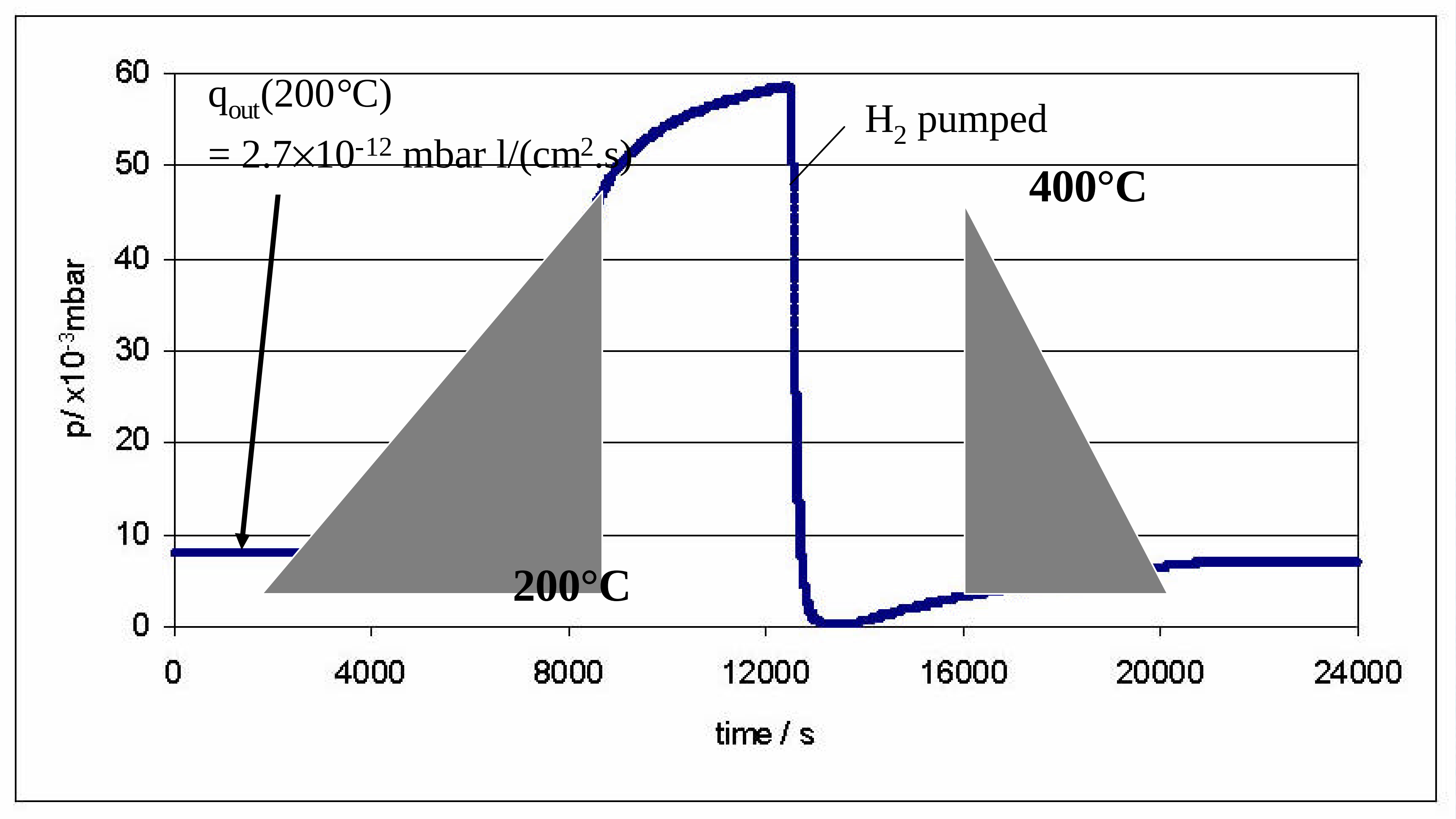
2) Contrarily, after the 4 day outgassing at 200°C, T changed to ⇒ 250°C, q_{out} changed substantially, $q_{out}(250°C) / q_{out}(200°C) = 19$!! (DLM 3.8) and decreased in three days to $1.8 \mathrm{x} 10^{-11}$ mbar l/(cm^2.s),

but even at the $p_{up}(250°C) \cong 2.2 \times 10^{-2}$ mbar H_2 $\mathbf{q_{out} > q_{perm}}$

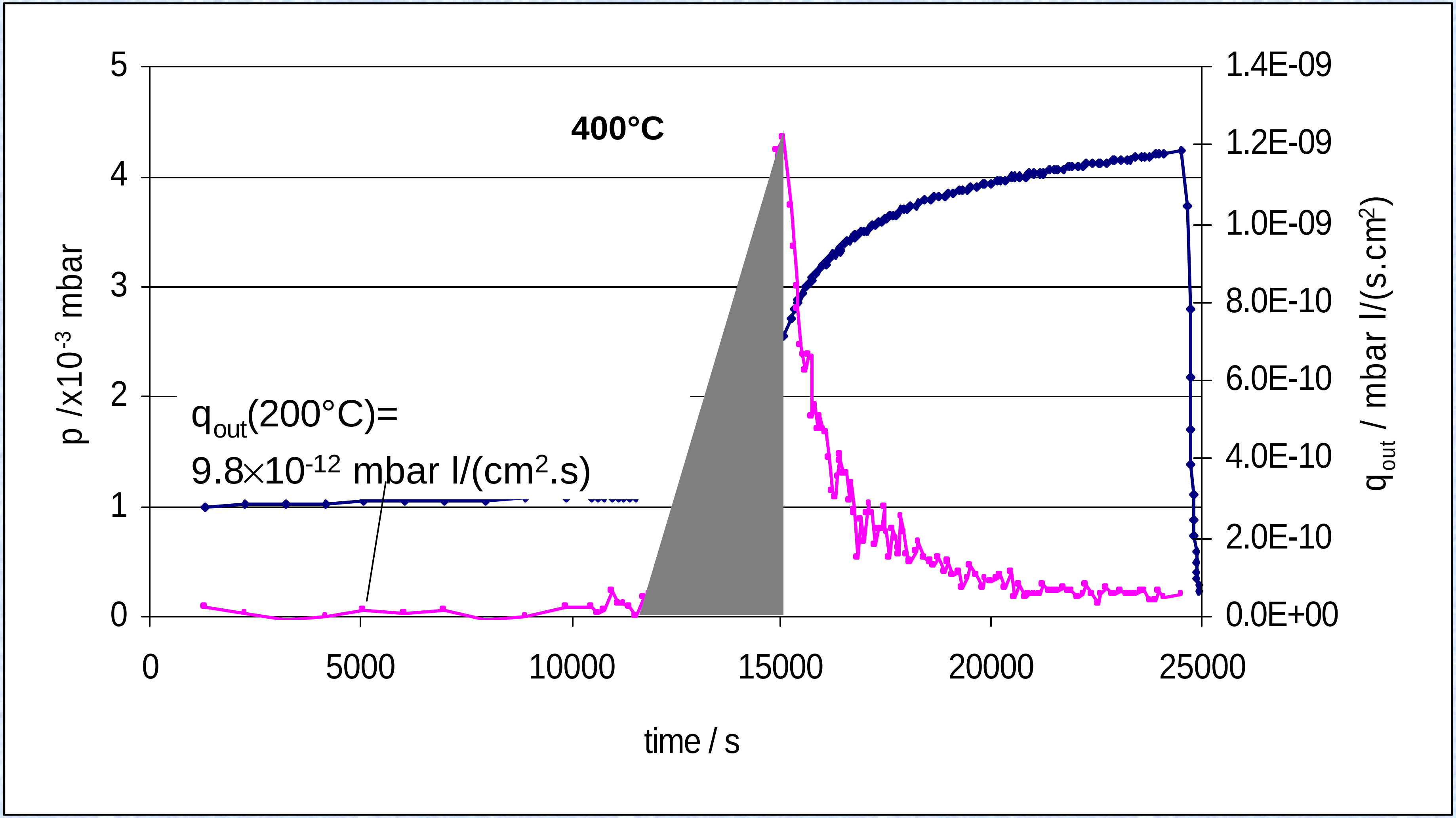
3) Much higher $q_{out}(400°C)/q_{out}(200°C) = 100$ registered !!

(DLM 63) q_{out} depression observed, but not yet the permeation

Cell heated in 2 h to 400°C, H_2 pumped out, $q_{out} \neq q_{out}(p)$, T back to 200°C linearly in 1.5 h, $q_{out}(200°C) = 8.2\times10^{-12}$ mbar l/(cm^2.s) …..3x higher than before the heating to 400°C!



similarly "well outgassed cell", T increase from 200°C to 400°C caused a noticeable increase of q_{out}(400°C) and **$q_{out} > q_{perm}$**



The q_{out} change during the increase from 200°C to 400°C and the amount of released H_2 depended thus on the previous "history"

the initial $q_{perm}(200°C) = 2.7\times10^{-12}$ mbar l/(cm^2.s) (after proceeding the permeation at 200 mbar from the atmosphere) was lower than in the second run when initial $q_{out}(200°C)= 9.8\times10^{-12}$ mbar l/(cm^2.s), but the amount of released hydrogen was 10 times lower than in the first case.

$q_{out}(200°C)$ is thus not an indicator of the total hydrogen content C

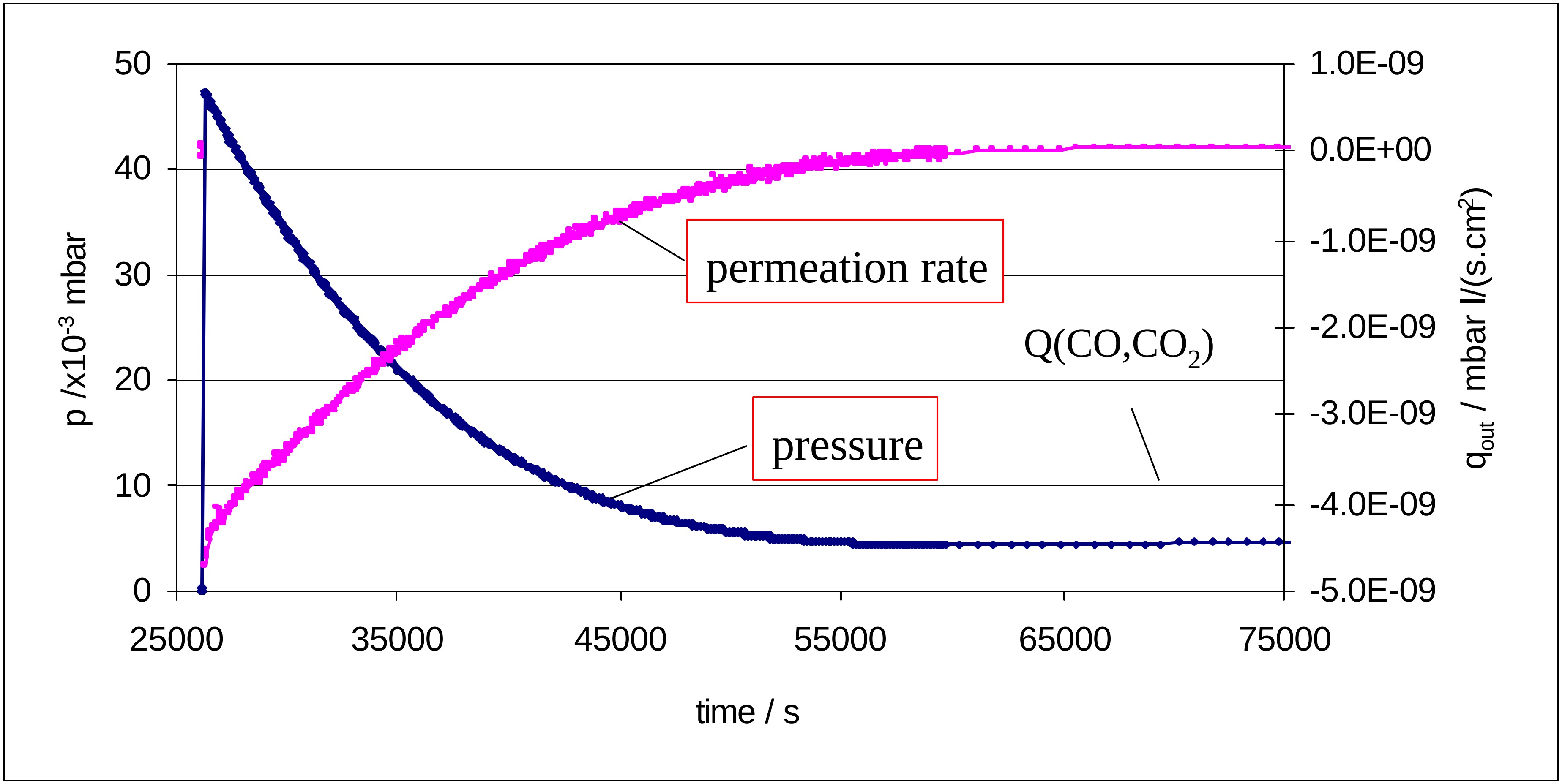
Permeation to the atmospheric side at 400°C

Pressure increased to $p_{up}(400°C) = 4.7x10^{-2}$ mbar ⇒

- permeation established immediately and observed for 12 h
- dp/dt and p correlated by the linear dependence
- low pressure limit set by the outgassing of CO, CO_2, not observed

at 200°C.

Permeation to the atmosphere



General conclusions

Kinetics of hydrogen evolution from stainless steel is governed

- by diffusion over the ordinary sites (fast process) and recombination at the surface (relatively fast process), described by diffusivity D, that is measured easily at high ***p*** and ***T***
- by release of H from deep states (slow process), observed in long term experiments. The complete mechanism is not known.

There is also a lack of data of the total C and the energy distribution of the sites. Concentration may greatly exceed the value expressed by the solubility.

- M.W.Ruckman, et al, JVSTA 13(4), 1994 (1995)
- V. Nemanic, B. Zajec, J. Setina, JVST A19(1), 215 (2001)

The possible application of these findings in processing for the lowest q_{out} at room temperature

1) the initial prolonged heating below 200°C is probably the best way

2) higher the bake out temperature, lower the q_{out} at room temperature not necessarily true, observed also by K. Jousten, Vacuum, **49,** 359 (1998). ⇒ exciting hydrogen from deep sites into regular sites.

3) atmospheric side may by always treated as the hydrogen sink ⇒ a vacuum furnace is a questionable investment

4) the prediction of q_{out} by changing the wall thickness is uncertain, but smaller the thickness, lower the q_{out} (*t* and *T* the same).

Not verified arguments. B. C. Moore, JVST A 19, 228 (2001)

Cleaning Strategies for UHV

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The selection of a particular cleaning process for vacuum systems for UHV service (i.e. below 10^{-9} mbar or so) requires some thought. It may be that the use to which the system is to be put will place particular constraints on what may or may not be permissible. In this presentation, I will concentrate on cleaning strategies for stainless steel, although much will be applicable to other materials. The relative merits in producing low outgasssing surfaces of processes such as simple detergent cleaning, solvent degreasing, electropolishing, etc., with and without baking will be discussed as will the applicability of each type of process.

Cleaning Strategies for UHV

Ron Reid
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Warrington WA4 4AD, UK

Why Do We Need To Clean For Vacuum?

- We may not always need to!
  - It depends on what we need vacuum for
    - Vacuum regime required (Base pressure)
    - Cleanliness
  - So we need to make a proper assessment of the real requirements of the application
  - But for UHV and XHV it is highly likely that some form of cleaning will be needed

Some Reasons for Cleaning

- Irrespective of the application – a manufacturer desires an attractive appearance!
- Characteristics of a surface (surface properties) may be altered by ‘contamination’ at the surface.
- Process may be poisoned by ‘contaminants’
- Quality of an in-vacuum process severely affected by presence of ‘contaminant’ gas phase molecules
- ‘Contaminant’ - a contaminant in one application may be an essential constituent of another!

Why Clean Accelerator Vacuum Systems?

- To ensure maximum transmission of particles and electromagnetic radiation
    - reduce beam-gas scattering
    - radiation absorption
- To reduce scattered radiation for health & safety (bremsstralüng)
- To maintain clean in-vacuum surfaces
    - preventing target poisoning
    - maintaining efficient optical properties for em radiation transmission
- To provide a controlled atmosphere

Vacuum System Design Issues

- The Vacuum Engineer should consider the following at the design stage:
  - How all parts can be cleaned (initially and in service)
    - Component level clean
    - Full assembly clean
    - Sub-assembly clean
- Cleaning Plant
  - Size
  - Robustness
  - Handling/Risks

Trapped Areas
Solvent Trapping

Vacuum System Design Issues

- Material choice
  - Porosity
  - Effect of cleaning on tolerances
  - Multiple materials
    - Varying effects of cleaning process
    - Risk of electro-chemical action (galvanic cell)
- Assessment of cleaning effectiveness

Requirements for UHV/XHV

- Minimise desorption
  - Remove ‘contaminants’ (i.e. components with high outgassing/vapour pressure)
  - Deplete reservoirs
    - Bulk gases
    - Surface overlayers (e.g. adventitious graphite)
  - Provide barriers
    - Bulk diffusion

How do we know if a surface is clean?

- Phenomenologically
  - Measure outgassing (thermal desorption)
  - Measure stimulated desorption (according to requirements of system)
  - In each case total and partial pressure measurements useful
- Characterise surfaces
  - Surface analysis

A Distinction

- Differentiate between
  - Cleaning
    - Removal of unwanted components
  - Passivation
    - Formation of barriers
    - Low sticking probabilities

Some examples of cleaning processes

- Solution
  - Water based
  - Solvent based
    - Alcohols
    - Chlorinated hydrocarbons
    - Freons
- Detergents
- Etchants
  - Acids
  - Alkalis
- Vacuum Baking/Firing

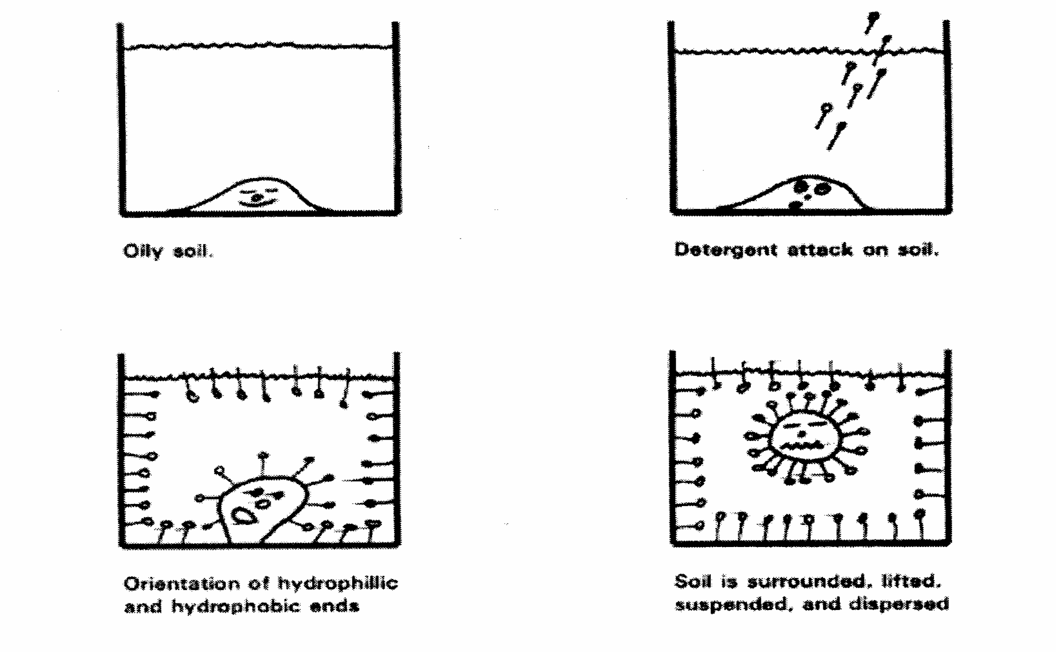
Some examples of passivation

- Air Baking
- Electropolishing
- Glow Discharge

- But note that **all** of these have some cleaning effect!

Science of Cleaning

- **Solvent** - A **solvent** is a substance that dissolves another substance or substances to form a *solution* (a homogeneous *mixture*). The solvent is the component in the solution that is present in the largest amount or is the one that determines the *state of matter* (i.e. solid, liquid, gas) of the solution.
- **Surfactants** - surface active agent

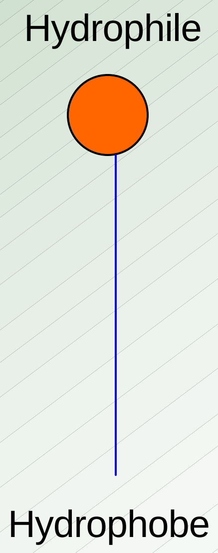


Oily soil.

Detergent attack on soil.

Orientation of hydrophillic and hydrophobic ends

Soil is surrounded, lifted, suspended, and dispersed



Science of Cleaning

- **Penetrating and Wetting agents**

  Surfactants which change the chemical composition of the hydrophobic and hydrophilic ends of the molecule, this opens up the possibility of

  Detergency
  Foaming
  Emulsifying
  Solubilising
  Dispersing

- **Chelators -** remove the hardness in water
- **Saponifiers -** convert animals fats into natural soaps

Typical Cleaning Agents

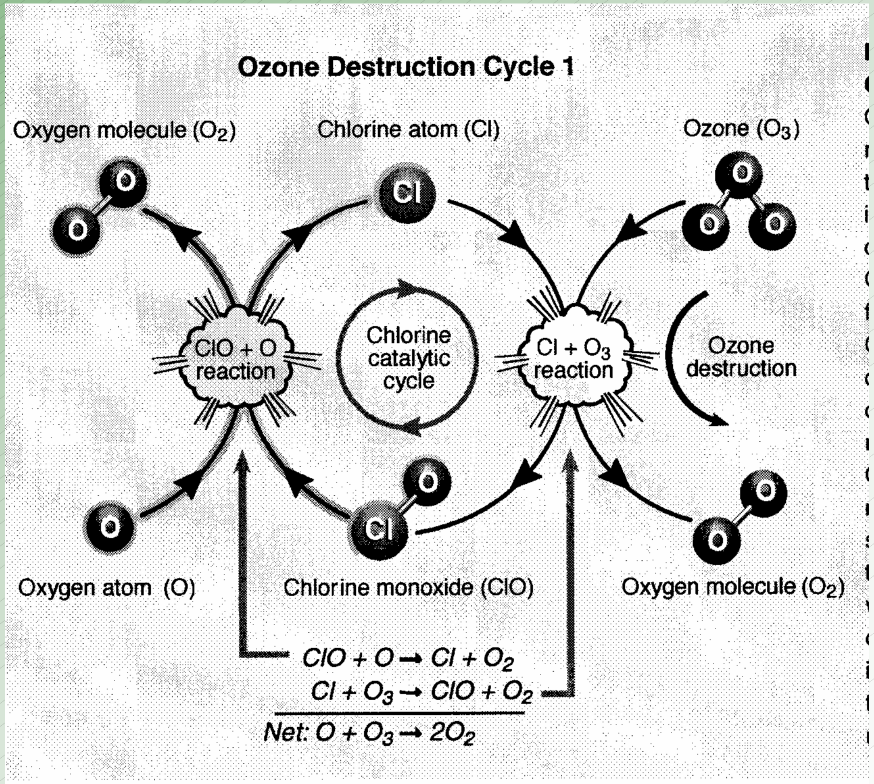
Agent	Examples	Advantages	Disadvantages	Disposal
Water		Cheap, readily available	Need de-min for cleanliness. Not a strong solvent	To foul drain
Alcohols	Ethanol, methanol, iso-propanol	Relatively cheap and readily available. Quite good solvents	Need control – affect workers; some poisonous; some flammable; stringent safety precautions.	Evaporate or controlled disposal.
Organic Solvents	Acetone, ether, benzene	Good solvents, evaporate easily with low residue.	Either highly flammable or carcinogenic	Usually evaporate
CFC's	Freon^{TM} (CFC-113)	Excellent solvents; evaporate easily with low residue	Banned	Strictly controlled, must not be allowed to evaporate
Chlorinated hydrocarbons	Trichloroethylene (Trike^{TM})	Excellent solvents. Non-toxic. Low boiling point. Low residue	Trike may be banned. Toxic, require stringent safety precautions.	Strictly controlled
Detergents		Aqueous solutions, non toxic. Cheap and readily available. Moderate solvents.	Require careful washing and drying of components. Can leave residues.	To foul drain and dilution
Alkaline degreasers	Almeco^{TM}, sodium hydroxide	Aqueous solutions, non- toxic. Moderate solvents	Can leave residues and may throw particulate precipitates	Requires neutralisation, then dilution to foul drain.

Some actual cleaning processes

SRS	**ANKA**	**BESSY II**
Hot water jet with detergent	Coarse cleaning with Chesterton (KPC820)	Wipe off surface dirt
Surface stripping with alumina beads	Rinse in hot de-min water	Ultrasonic with trichloroethane
Ultrasonic wash in hot Triklone	Ultrasonic wash in hot P3-Almeco 18	Treatment with hot perchloroethylene (120°C)
Vapour Wash in hot Triklone	Rinse in de-min water	Ultrasonic cleaning in hot P3-Almeco 18 for 10 minutes.
Rinse with de-min water	Dry in warm dust free air, bag and seal.	Rinse for 15 minutes with tap water.
Immerse in hot alkaline bath of P3-Almeco 36 at 60°C		Wash in hot de-min water for 90 minutes.
Rinse in de-min water		Open air drying and cooling of components.
Dry in warm, dust free air, bag and seal.		

Current legislative situation

- **Vienna Convention - 1985**
- **Montreal Protocol - 1987**
  - Amendments - most recent 2000
  - Protection of the Ozone Layer
  - CFC's
  - HCFC's
  - Carbon Tetrachloride
  - Methyl Chloroform
  - Other halogenated hydrocarbons
- **Why Change?**
  - **Reclassification of 1,1,2-Trichloroethylene (Trike^{TM})**
  - Improved Health and Safety regulations



$ClO + O \rightarrow Cl + O_2$

$Cl + O_3 \rightarrow ClO + O_2$

Net: $O + O_3 \rightarrow 2O_2$

Future possibilities

- Other solvents

  Further n-propyl bromides

  Non flammable ethers

  …….
- Aqueous systems

  e.g. Micro 90

What strategy should be adopted?

- The least that is proved to be effective for the task in hand
- But understand what is required and the limitations of each process
- Pay enormous attention to detail
- Pay enormous attention to health and safety!

Acknowledgments

- Joe Herbert
- Keith Middleman

Road Map to Extreme High Vacuum*

Ganapati Rao Myneni

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Ultimate pressure of a well-designed vacuum system very much depends on pretreatments, processing and the procedures [1,2]. Until now much attention has been paid in minimizing hydrogen outgassing from the chamber material. However, procedures and processing deserves further scrutiny than hitherto given so far. For reducing the gas load, high sensitivity helium leak detection techniques with sensitivities better than 1×10^{-12} Torr l/sec need to used. Vacuum measurement instrumentation induced effects need to be improved in order to obtain accurate pressure measurements. In this presentation clean assembly procedures, metal sponges for cryosorption pumping of hydrogen to extreme high vacuum, low cost surface diffusion barriers for reducing the hydrogen gas load, cascade pumping, sensitive helium leak detection techniques and the use of modified extractor and residual gas analyzers will be discussed.

1. Bills, D.G., "Ultimate Pressure Limitations", J. *Vac. Sci.* Technol. **6**, 166 (1969).
2. Várdi, P. F., "Effect of Pretreatment on the Degassing of Materials", Trans. 8th AVS Vac. Symp. (Pergamon Press, New York, 1962) pp 73-77.

*This work was supported by U.S. Department of Energy Contract No. DE-AC05-84ER40150

X – VAT Workshop

Karlsruhe

April 23-25, 2003

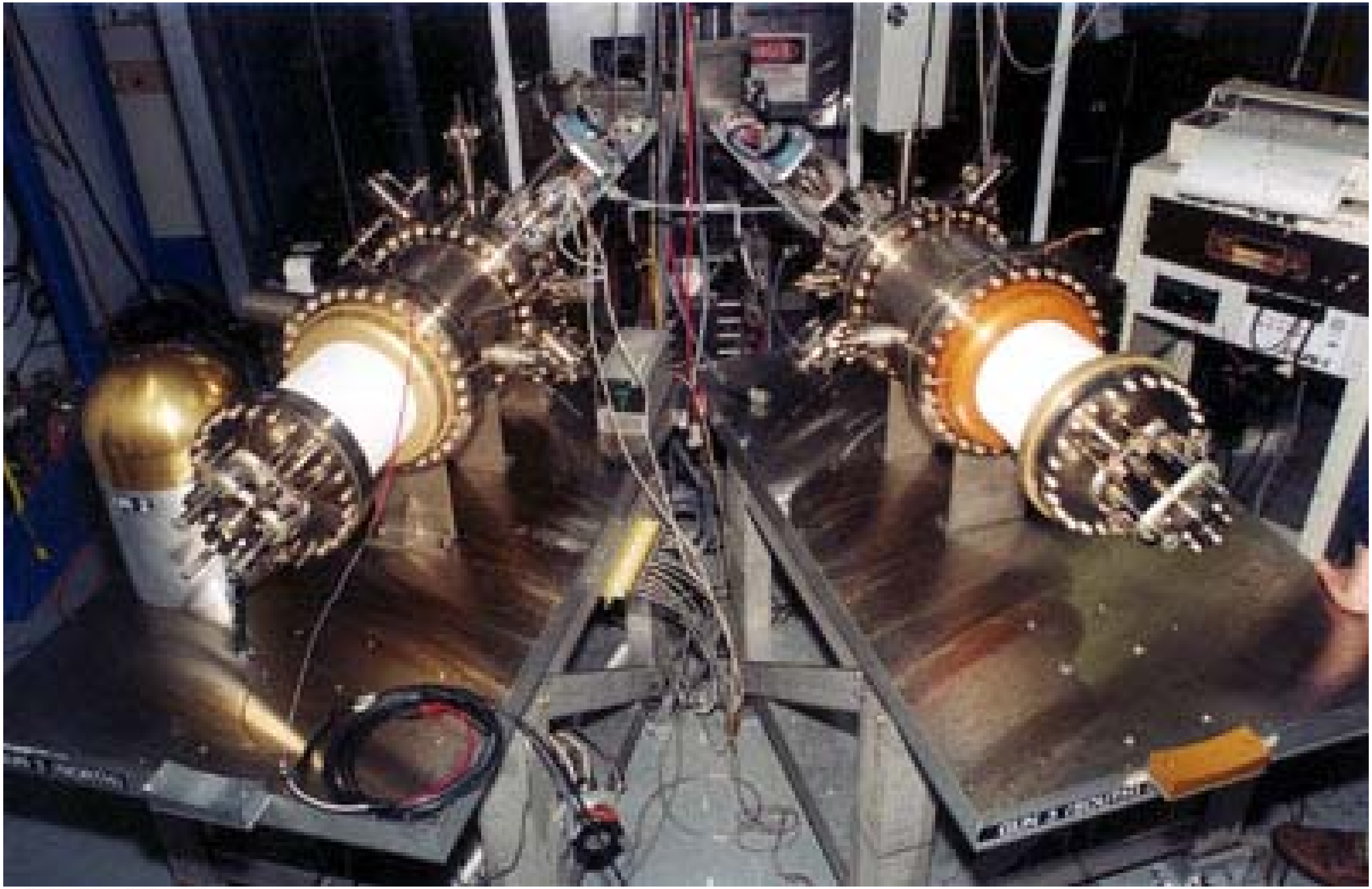
Ganapati Rao Myneni

Extreme High Vacuum

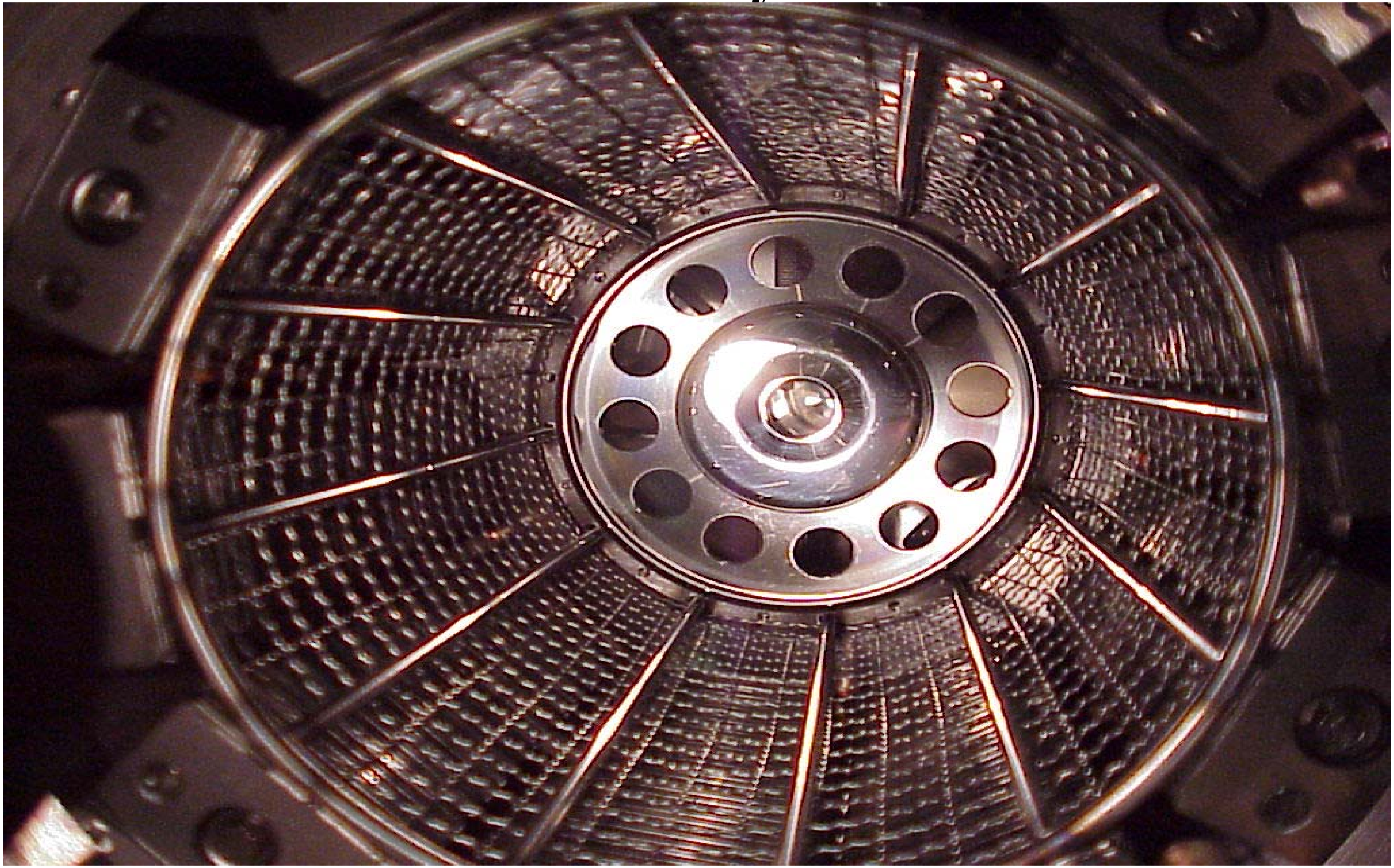
INTRODUCTION

- **AVS defines XHV as pressure below 7.5 X 10^{-13} Torr**
- **Hydrogen is the most dominant (~90 %) residual gas in the UHV/XHV systems**
- **Oxides of Carbon and CxHx are the next predominant species**
- **Surface Diffusion Barriers (pretreatments), processing and procedures are likely to help to minimize these residual gas species**
- **High sensitivity helium leak detection techniques (better than 1.0 X 10^{-12} Torr liter/sec) are essential to minimize external leaks**
- **Cryosorption metal sponges, cascade pumping and modified extractor and RGA's are reviewed**

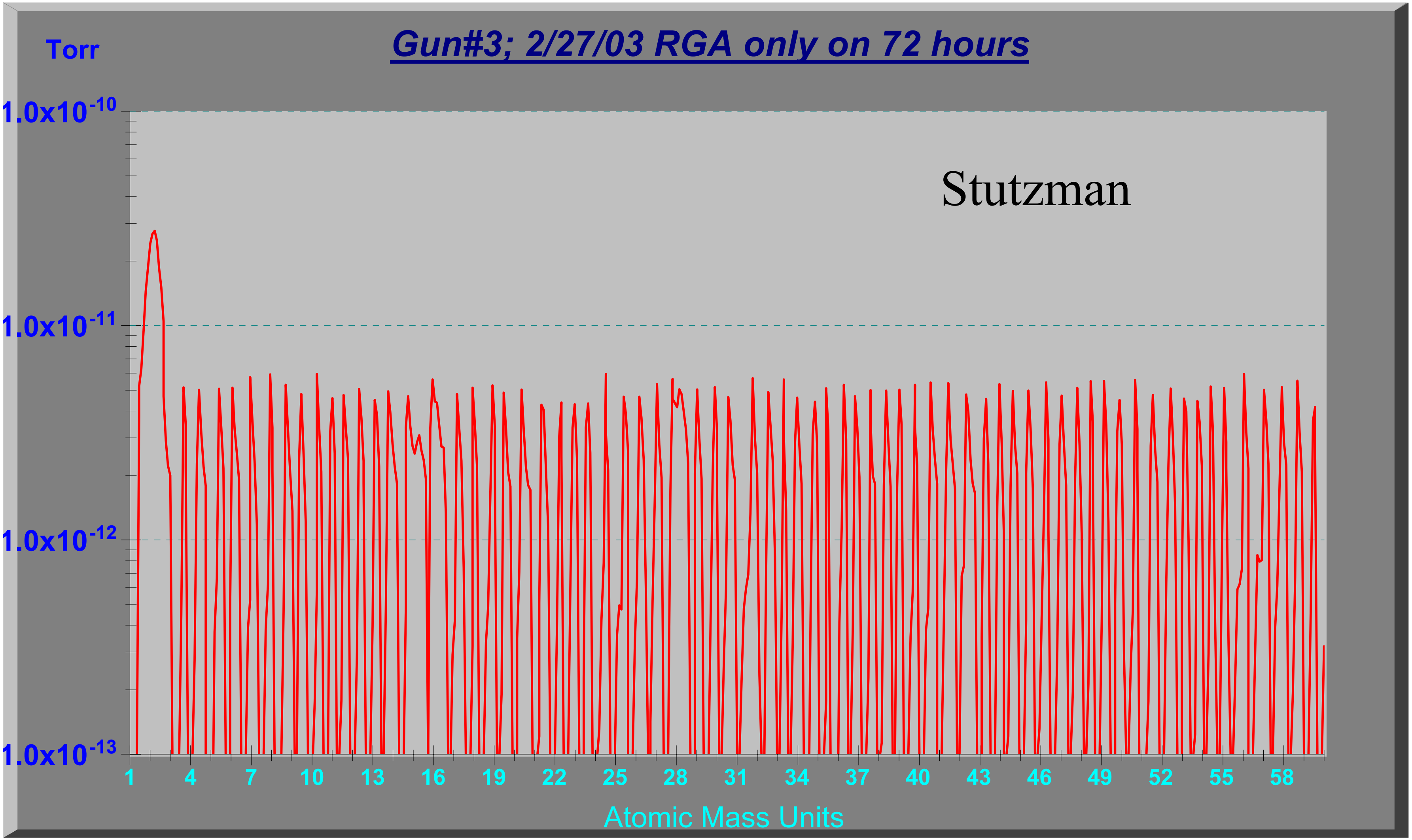
CEBAF Polarized Electron Guns



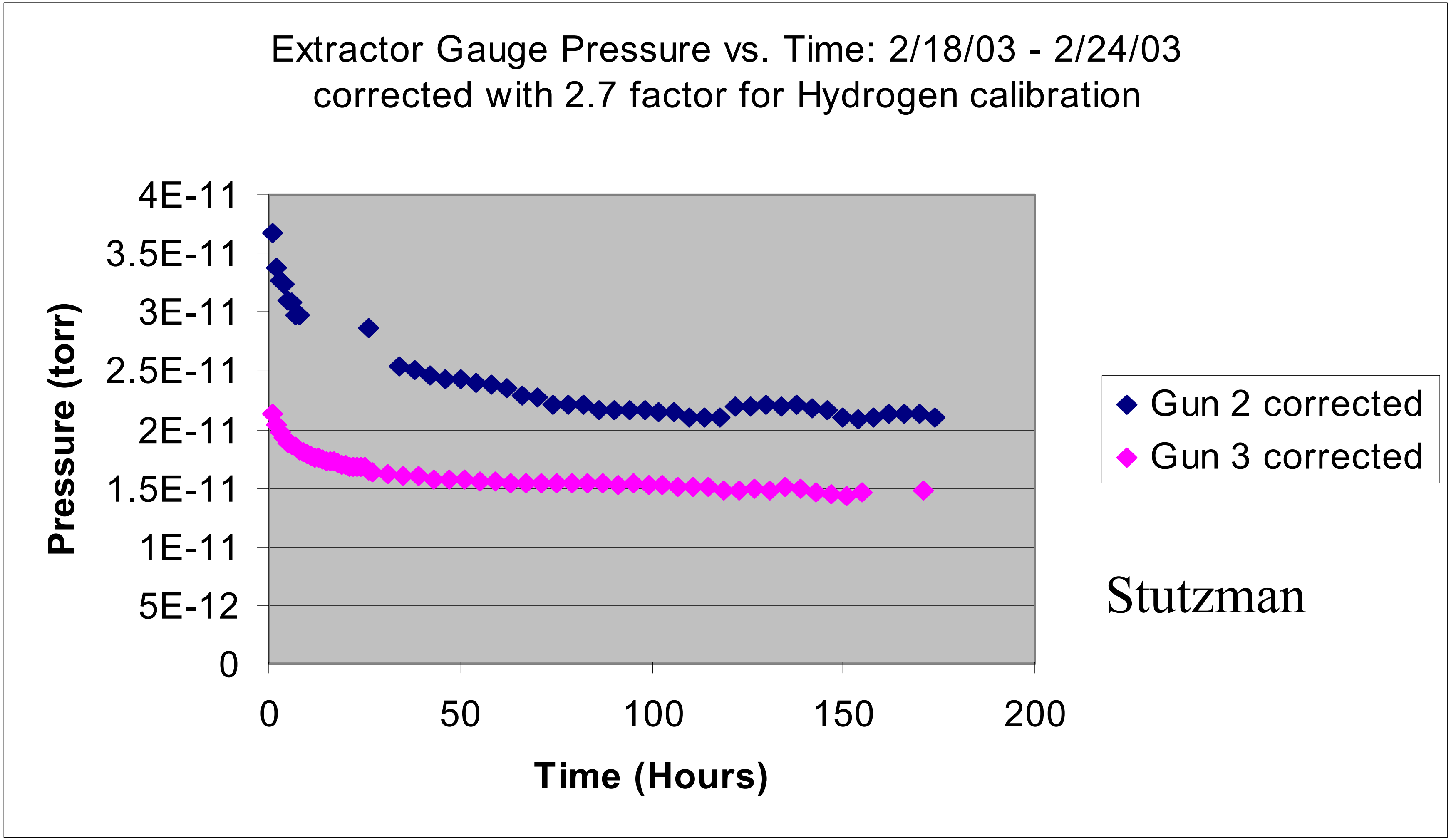
Polarized Gun NEG Array



RGA Spectra of Gun#3

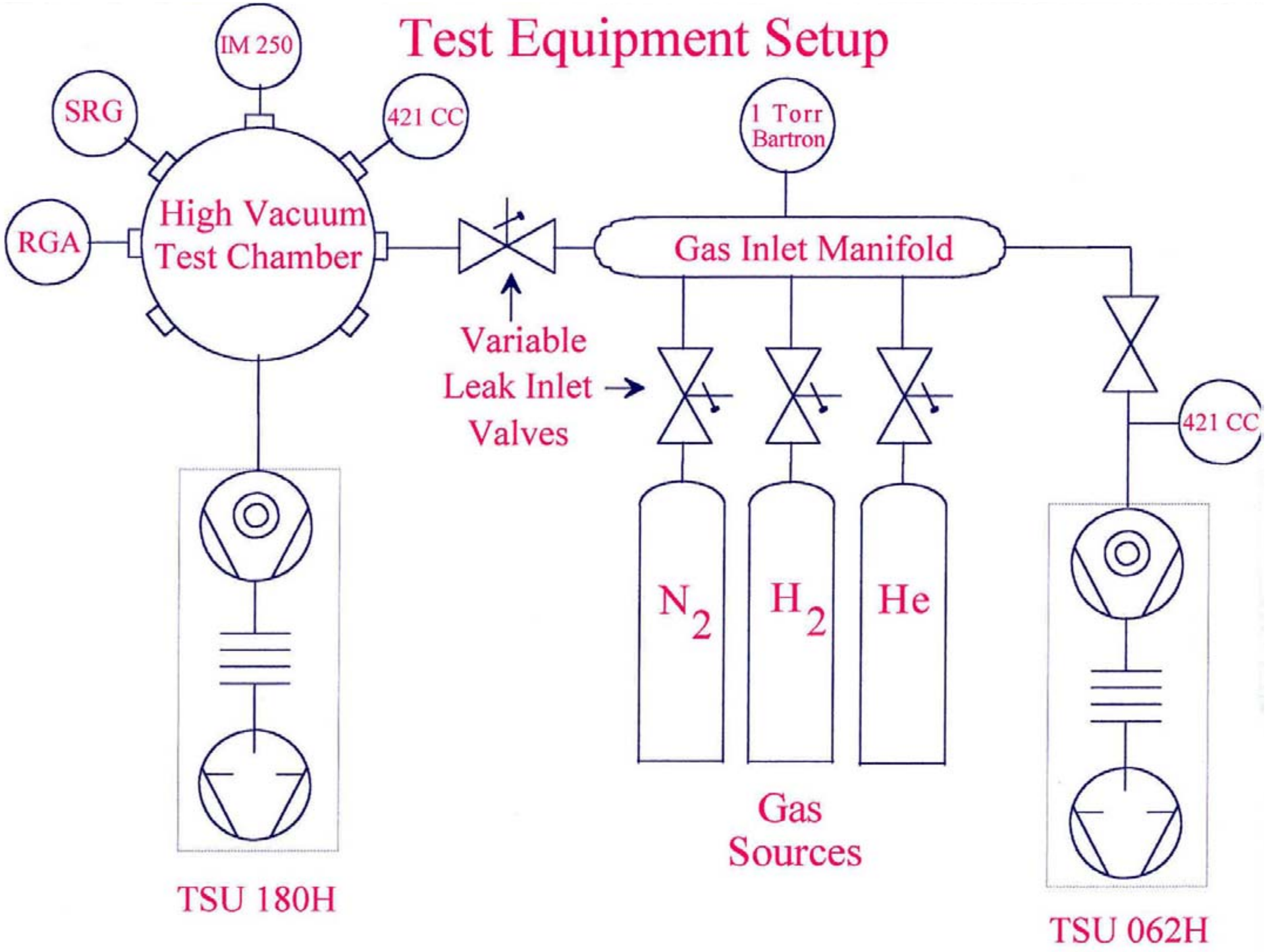


Polarized Gun Pressure



Stutzman

UHV Gauge Calibration System Schematic



Thomas Jefferson National Accelerator Facility
Institute for SRF Science and Technology

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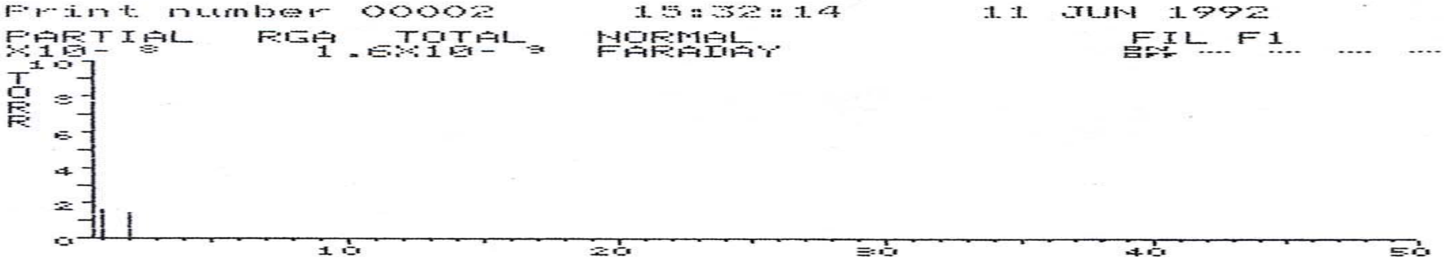
UHV Gauge Calibration System

Unbaked System RGA Spectra



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X10- 8      1.6X10- 9     FARADAY                   BN ----  ----  ----  ----
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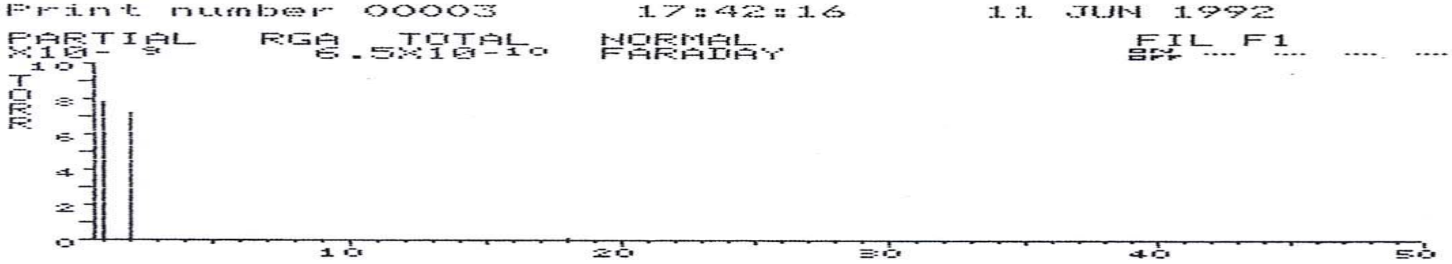

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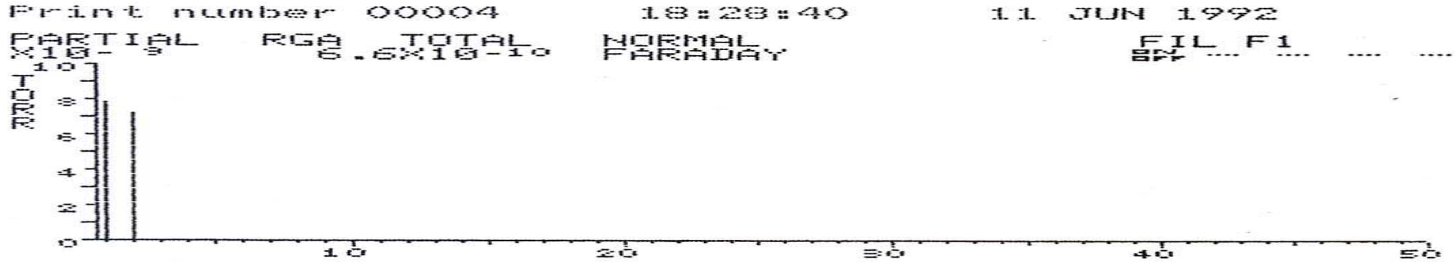

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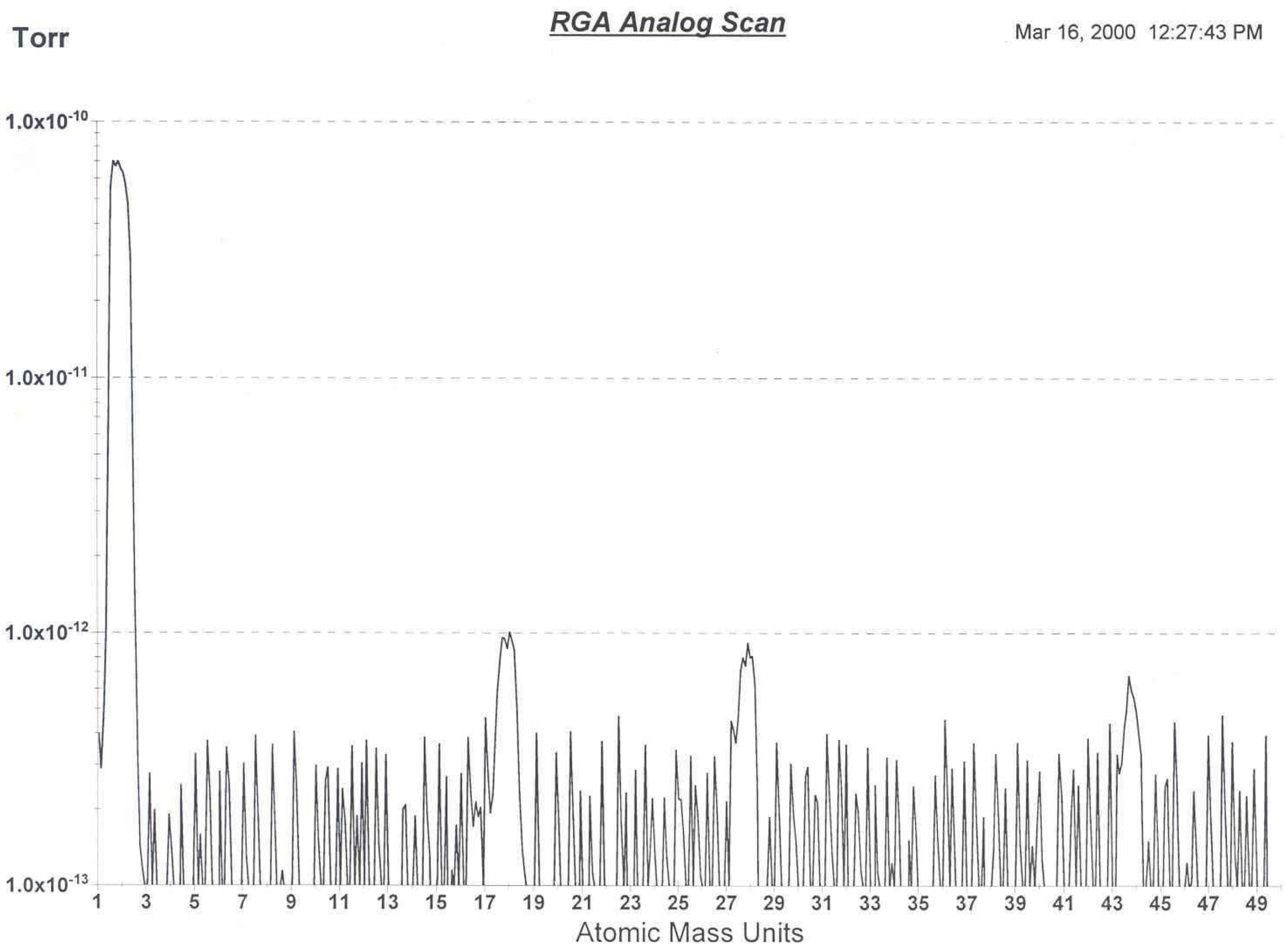
Baked System RGA Spectra



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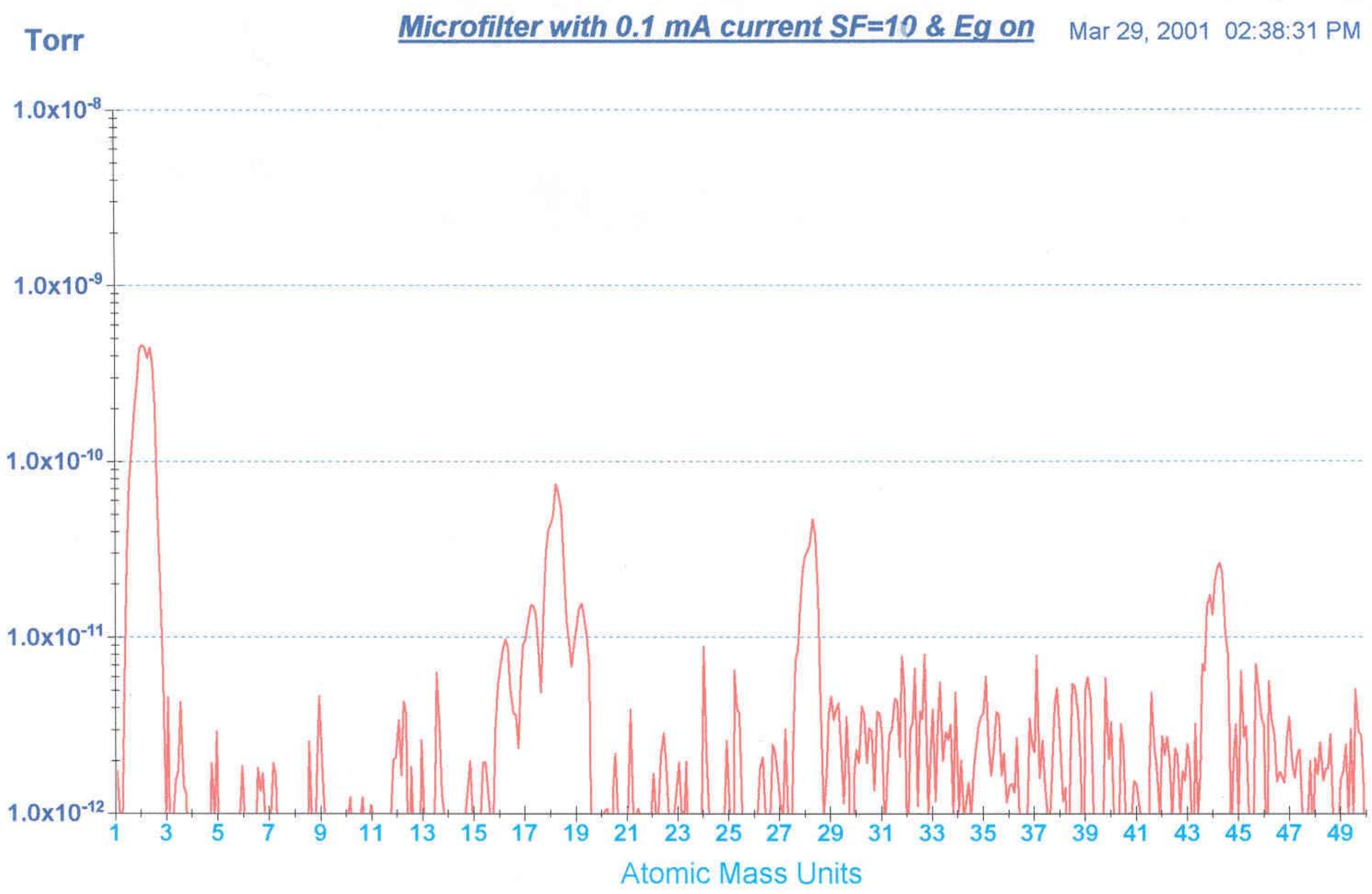
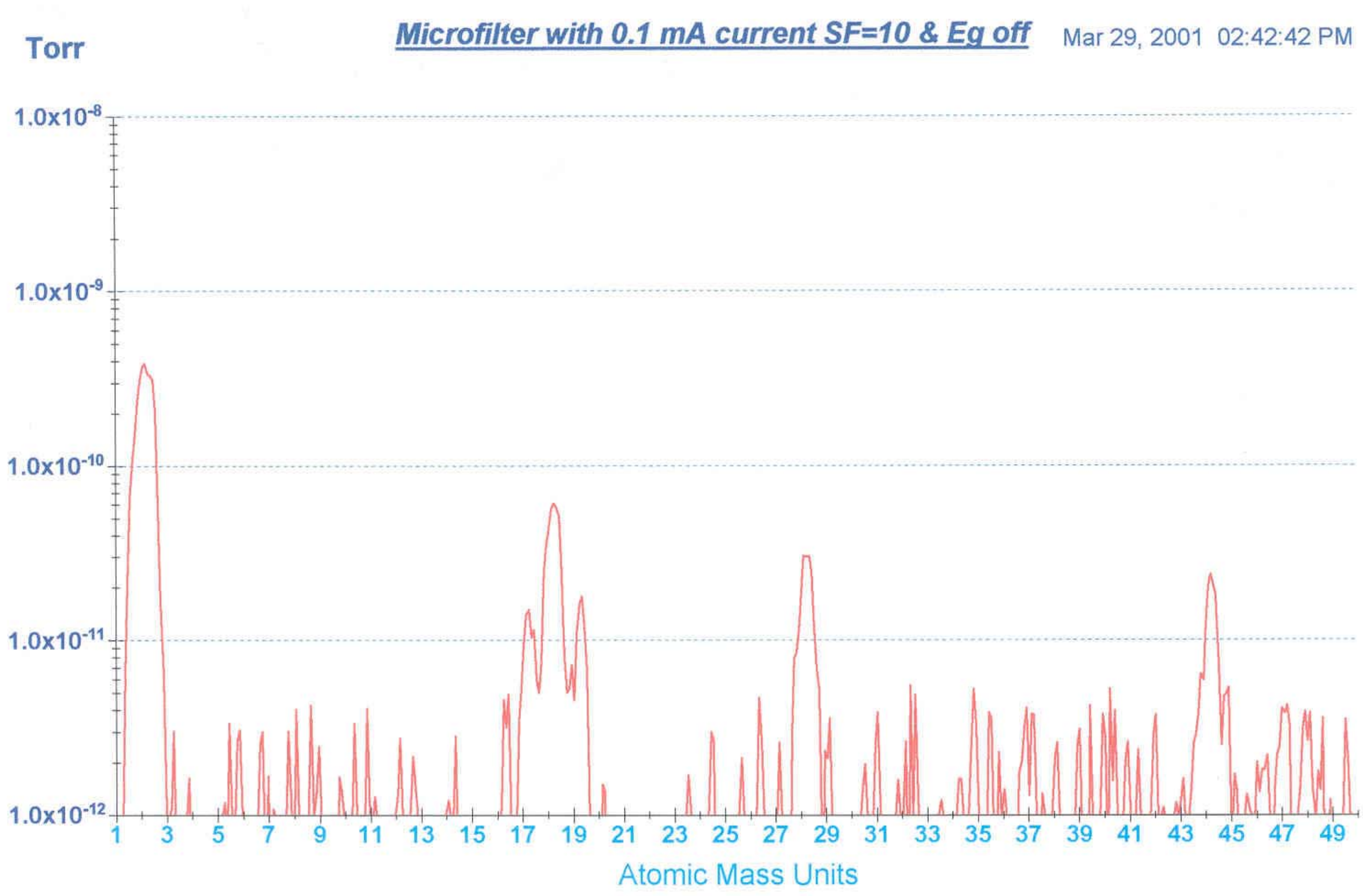
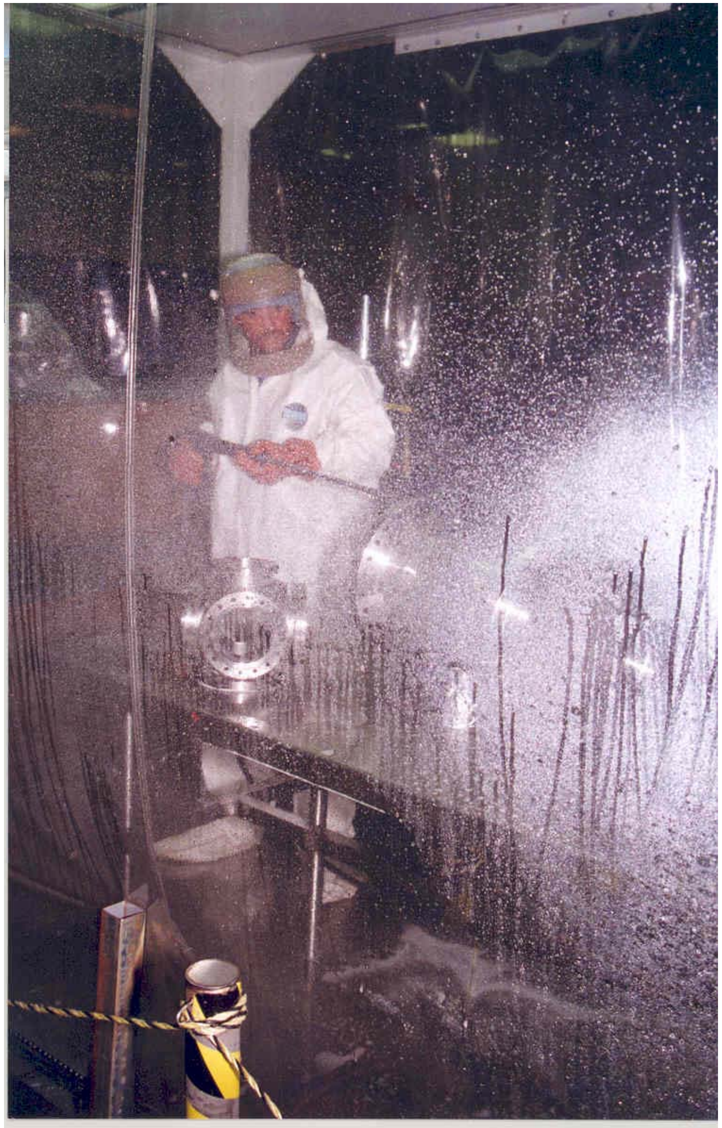
RGA Spectra with Extractor On



RGA Spectra with Extractor Off

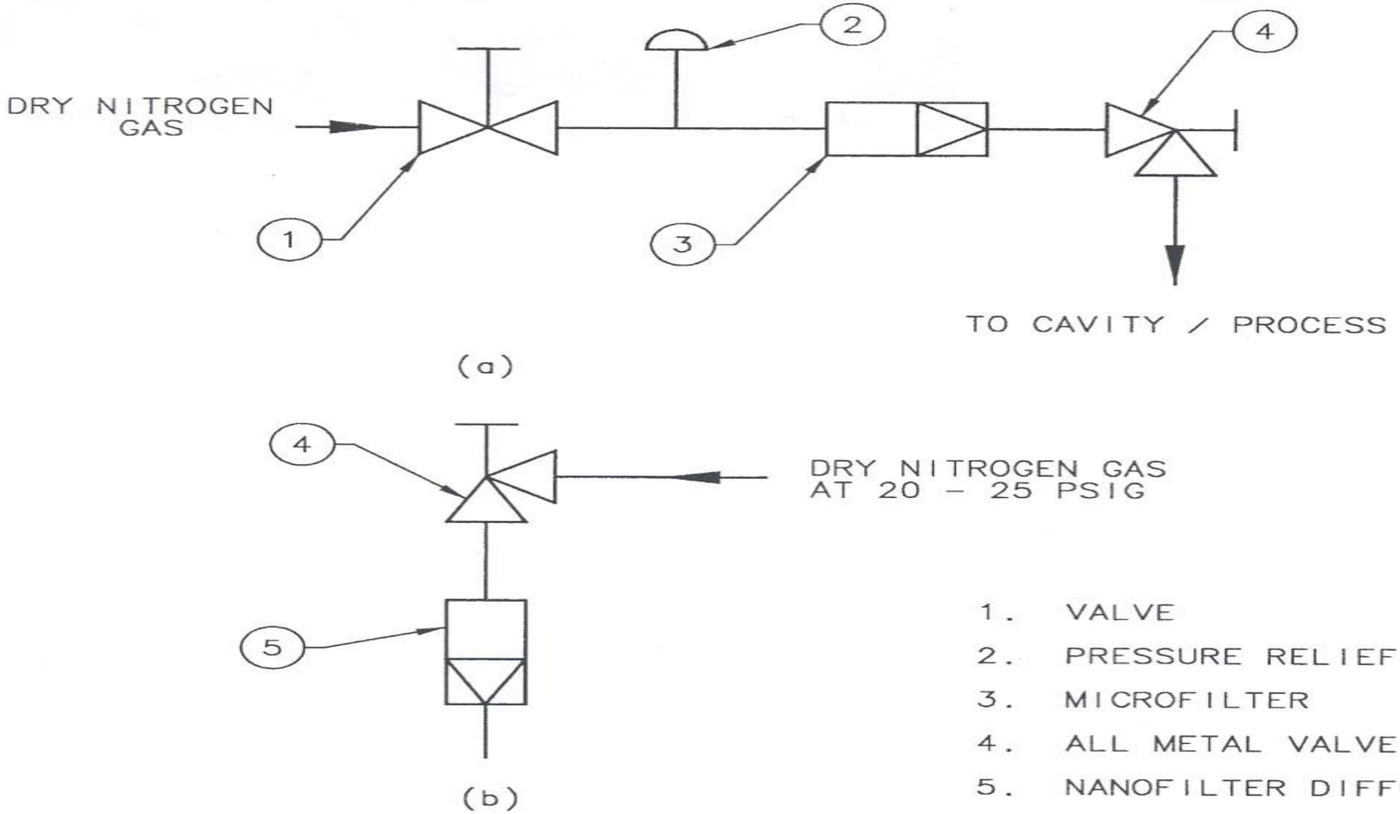


High Pressure DI Hot Water or Steam Cleaning



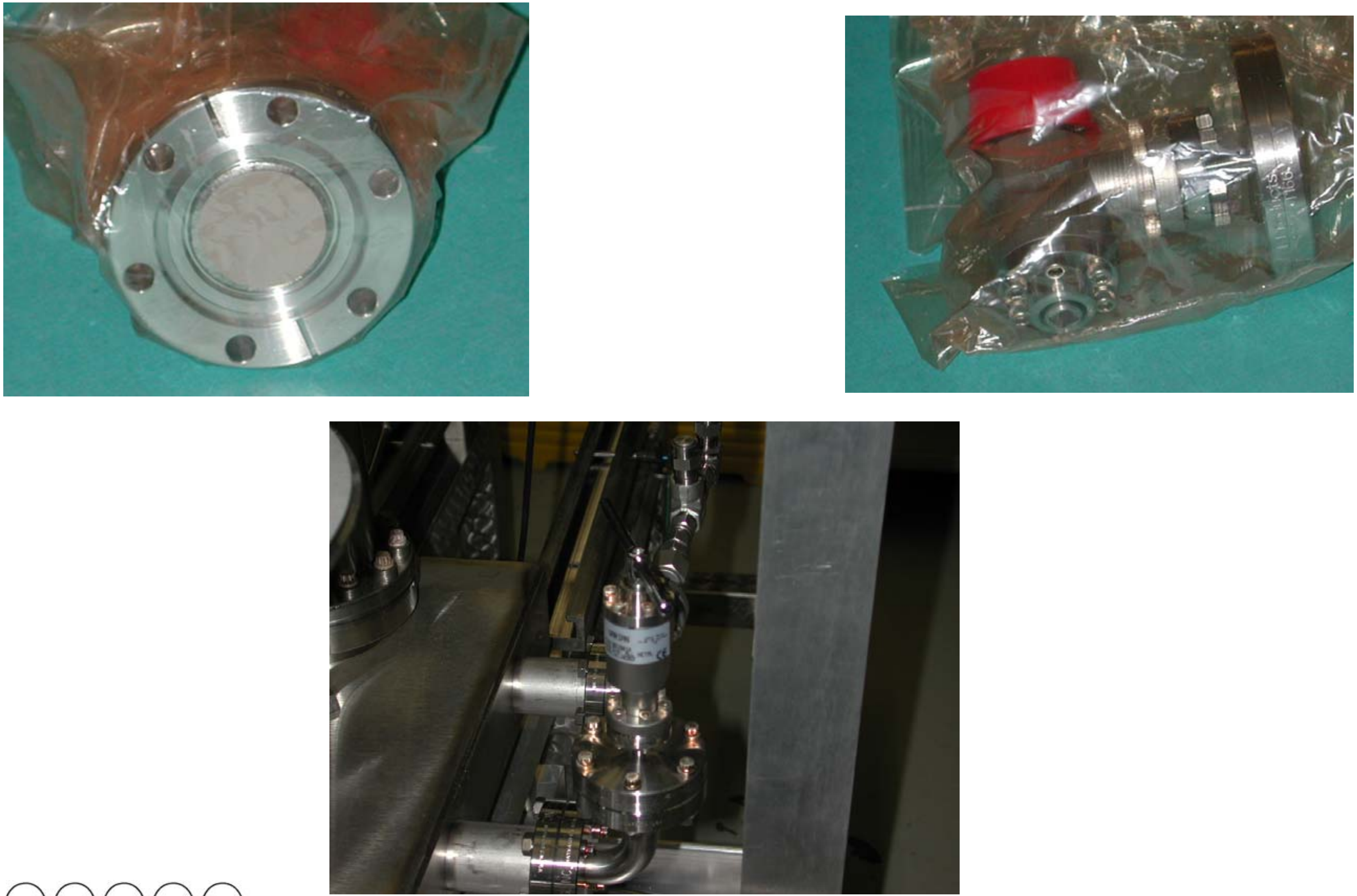
UHV Particulate Counter

Nanofilter Installation Scheme

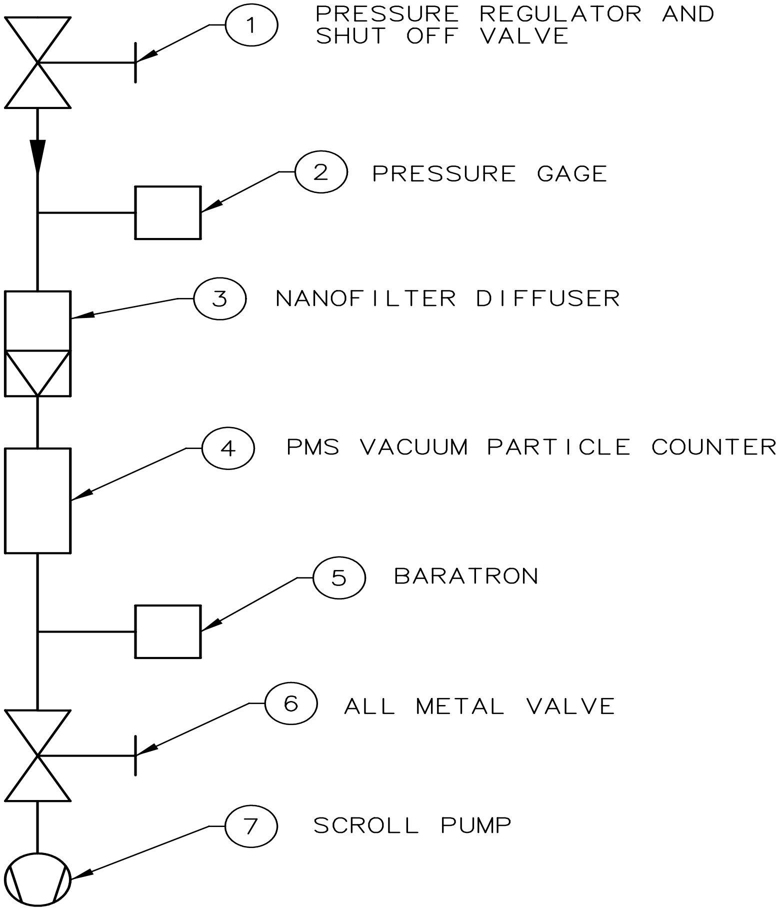


1. VALVE
2. PRESSURE RELIEF PLATE
3. MICROFILTER
4. ALL METAL VALVE
5. NANOFILTER DIFFUSER

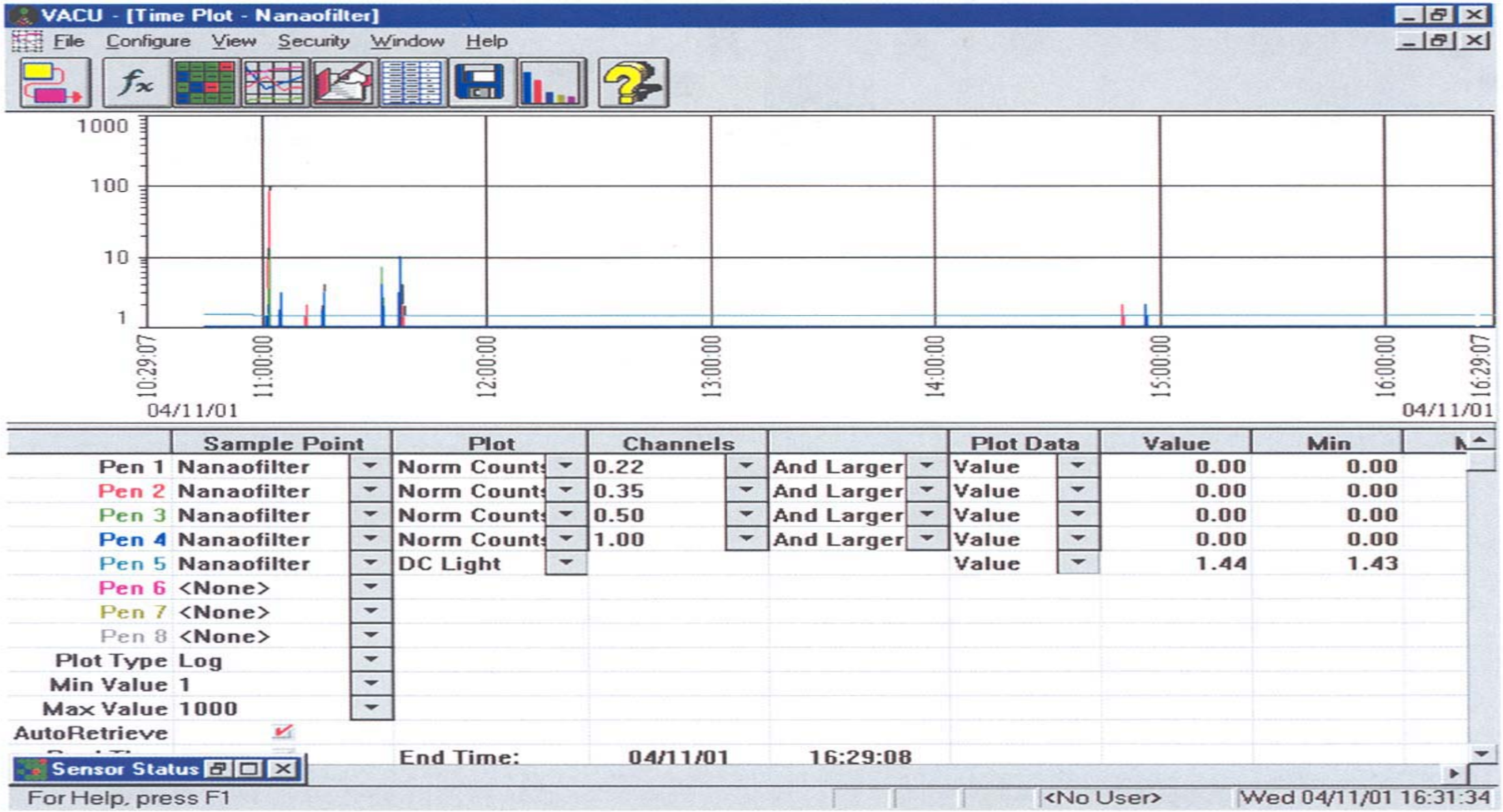
Nanofilter



Nanofilter Evaluation Set up



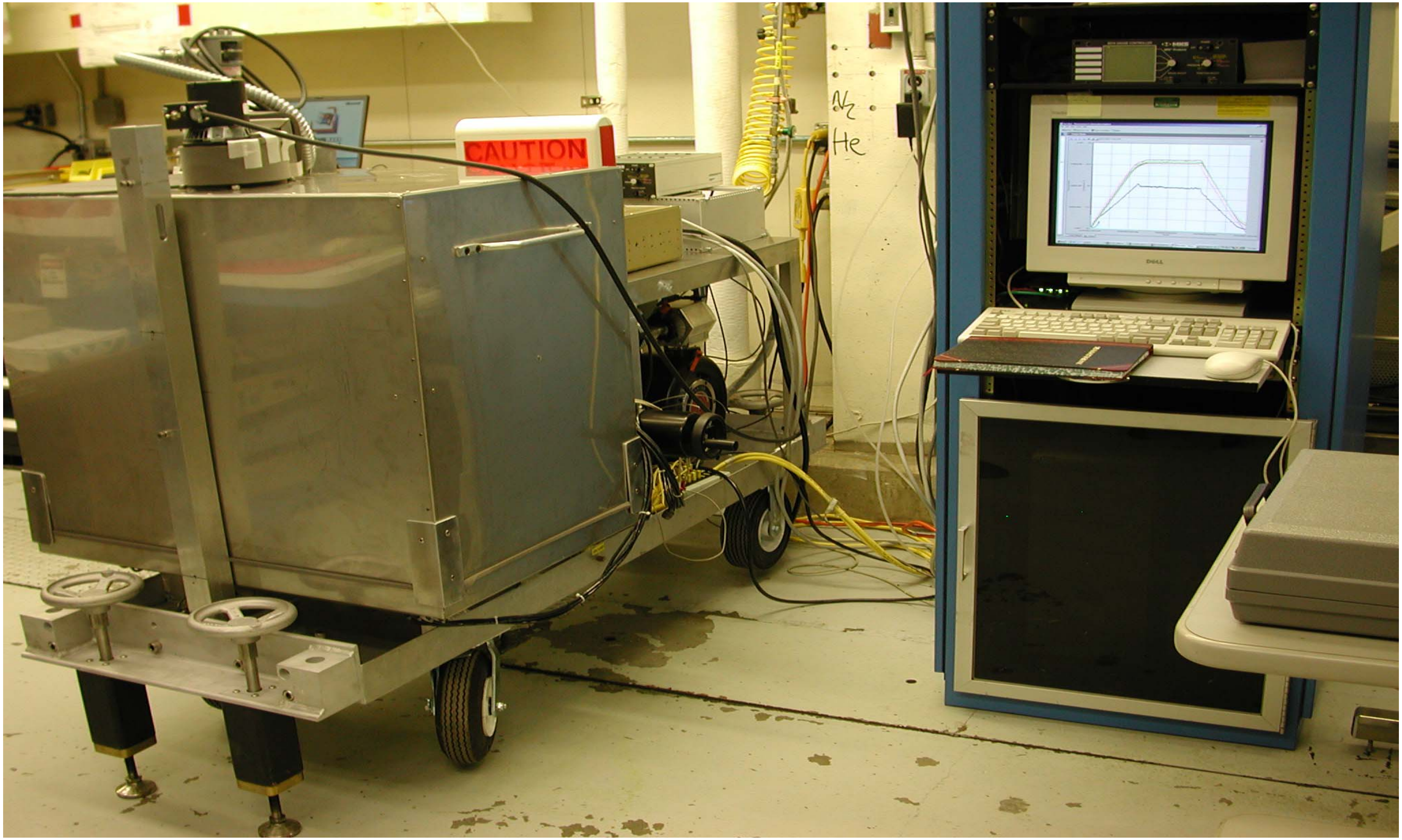
Nanofilter Particulate Retention



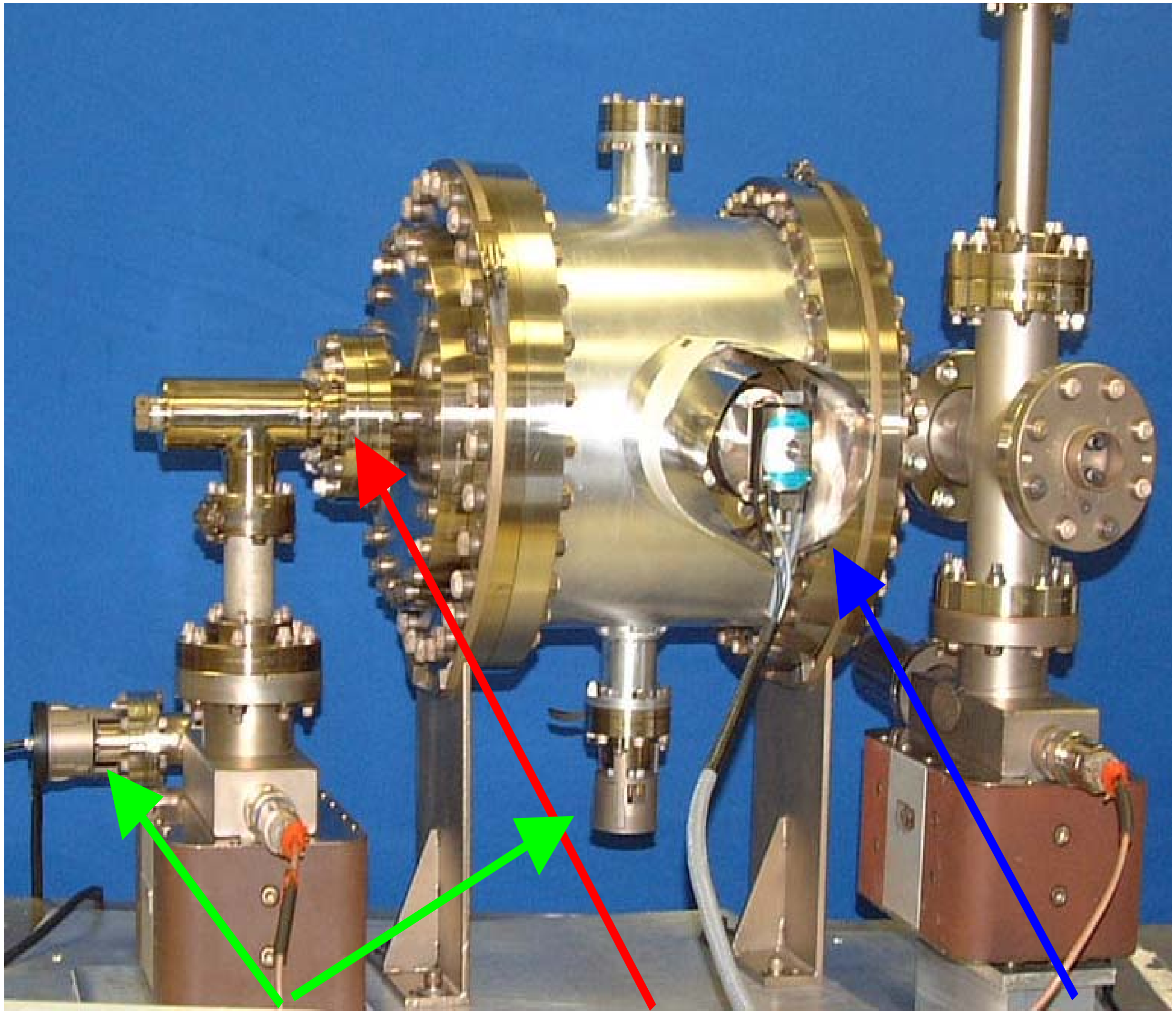
	Sample Point	Plot	Channels		Plot Data	Value	Min
Pen 1	Nanaofilter	Norm Counts	0.22	And Larger	Value	0.00	0.00
Pen 2	Nanaofilter	Norm Counts	0.35	And Larger	Value	0.00	0.00
Pen 3	Nanaofilter	Norm Counts	0.50	And Larger	Value	0.00	0.00
Pen 4	Nanaofilter	Norm Counts	1.00	And Larger	Value	0.00	0.00
Pen 5	Nanaofilter	DC Light			Value	1.44	1.43
Pen 6	<None>						
Pen 7	<None>						
Pen 8	<None>						
Plot Type	Log						
Min Value	1						
Max Value	1000						
AutoRetrieve	☑						
		End Time:	04/11/01	16:29:08			

Figure 3. Nanofilter particulate retention during pressure transients

High Power RF Couplers Baking Box



Outgassing Measurements



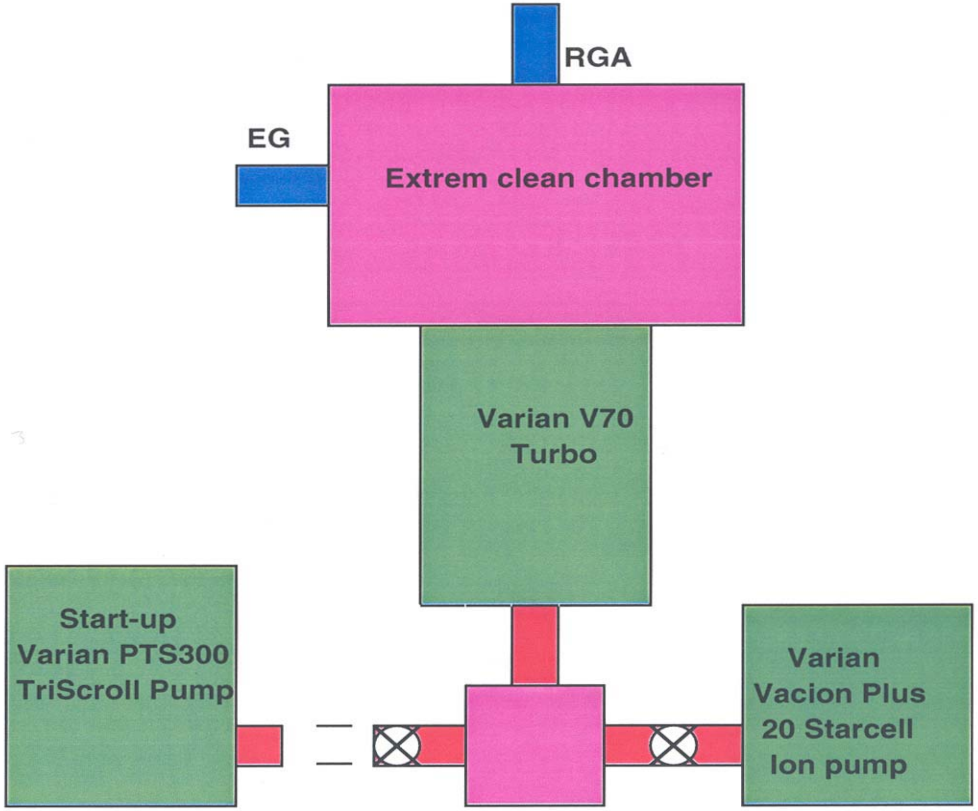
Outgassing Rates for Three Chambers

TABLE 2. Measured Outgassing Rates

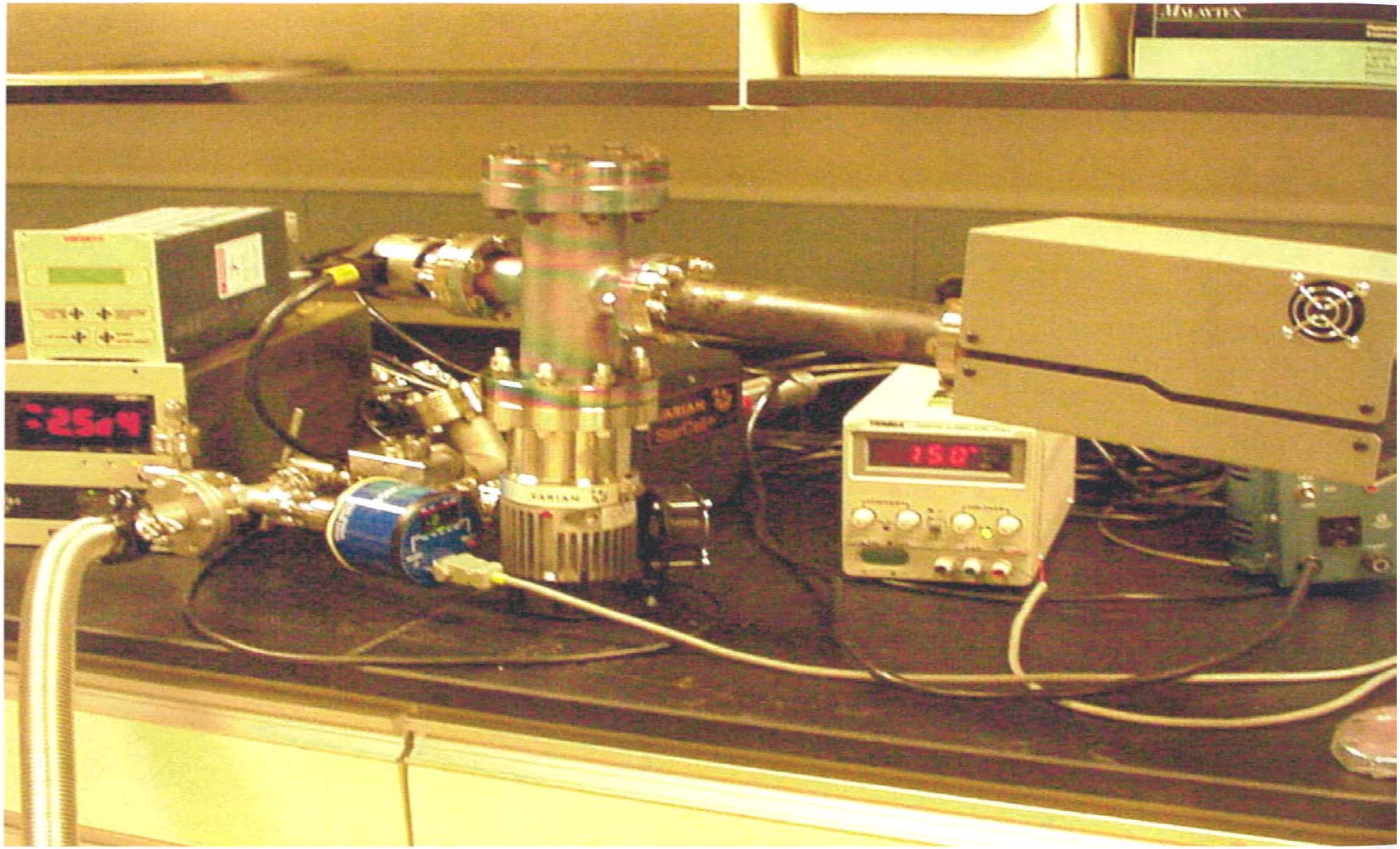
Chamber Material	**Orifice Method (Torr·l/s·cm^2)**	**Rate of Rise Method (Torr·l/s·cm^2)**
304 Stainless Steel	0.97×10^{-12}	1.1×10^{-12} (70 hours)
316L Stainless Steel	1.3×10^{-12}	1.2×10^{-12} (70 hours)
6061-T6 Aluminum	1.1×10^{-12}	1.1×10^{-12} (70 hours)

Ion Pump Backed Turbo Pump

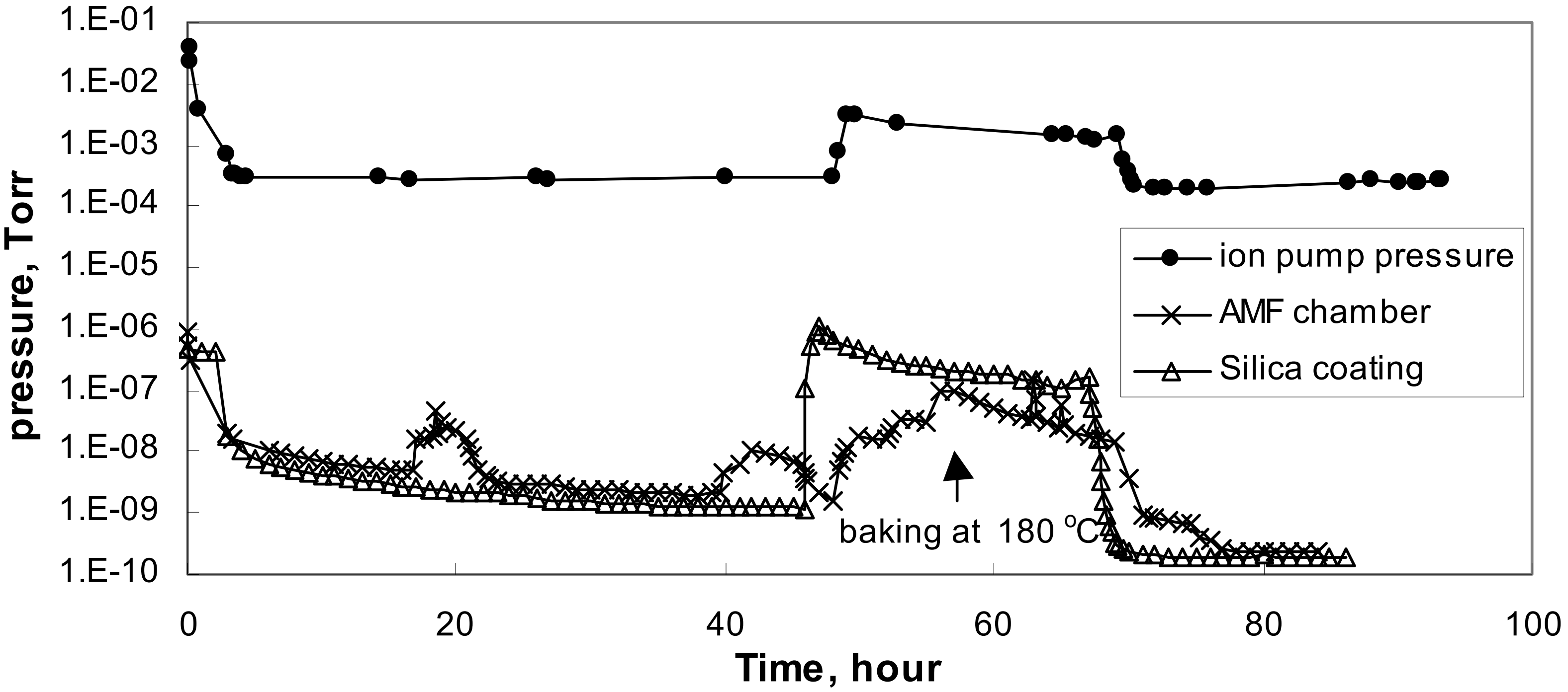
Block Diagram of an Ion Pump Backed Turbo Pump System



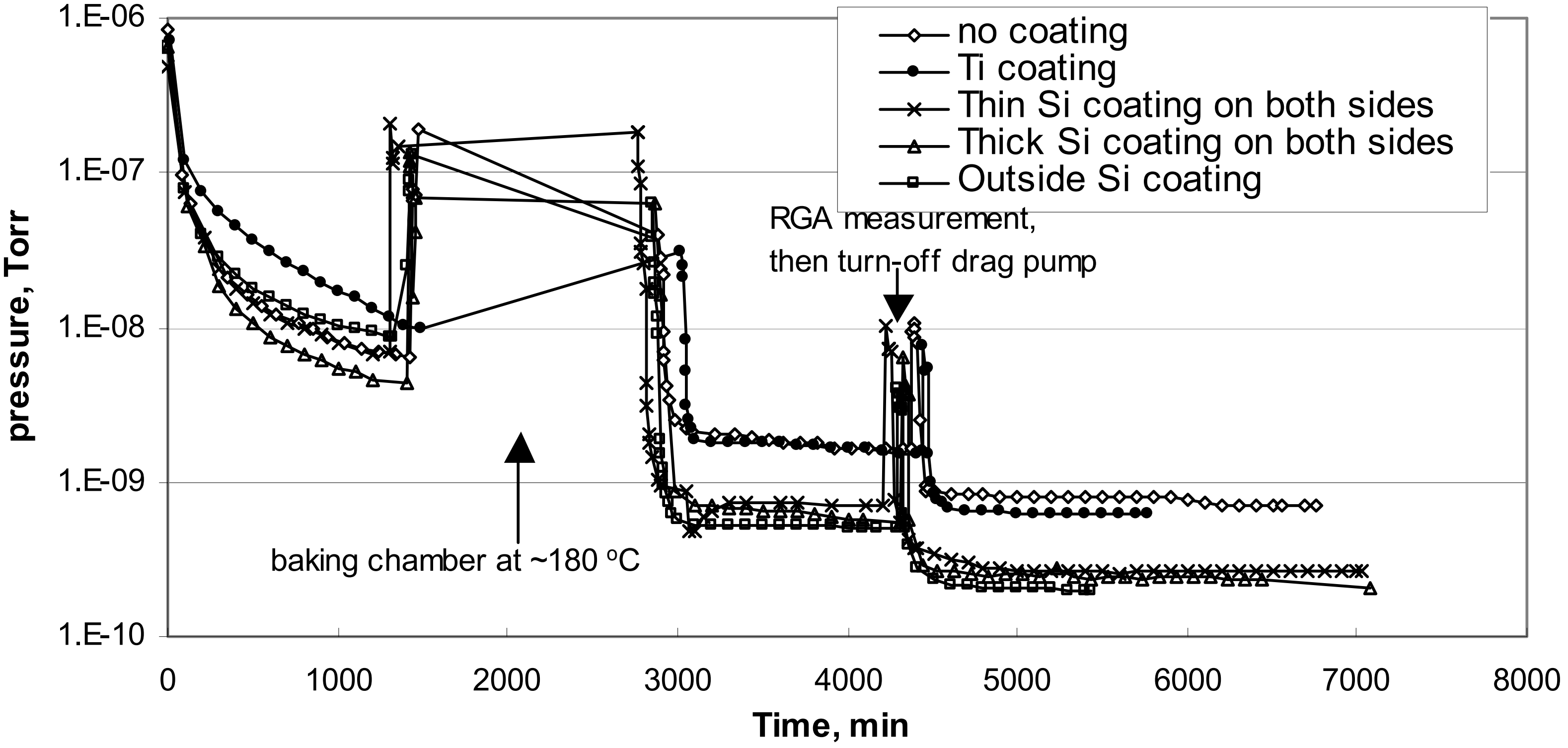
Ion Pump Backed Turbo



BeCu & Silica Coated Chambers



Pump down with Coatings



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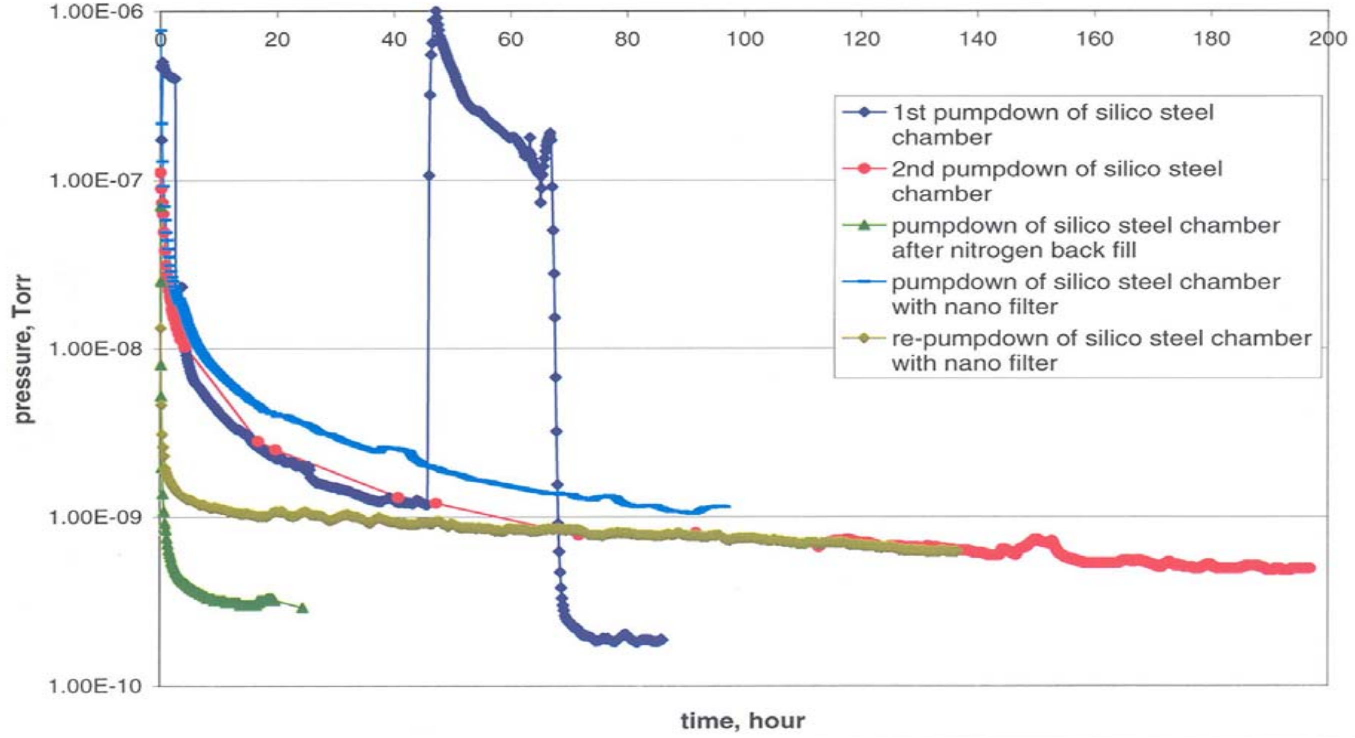
Silica coating & nanofilter

Fig. 4. Pumpdown comparison of silico steel chamber with nano filter



High Sensitivity He Leak Detector

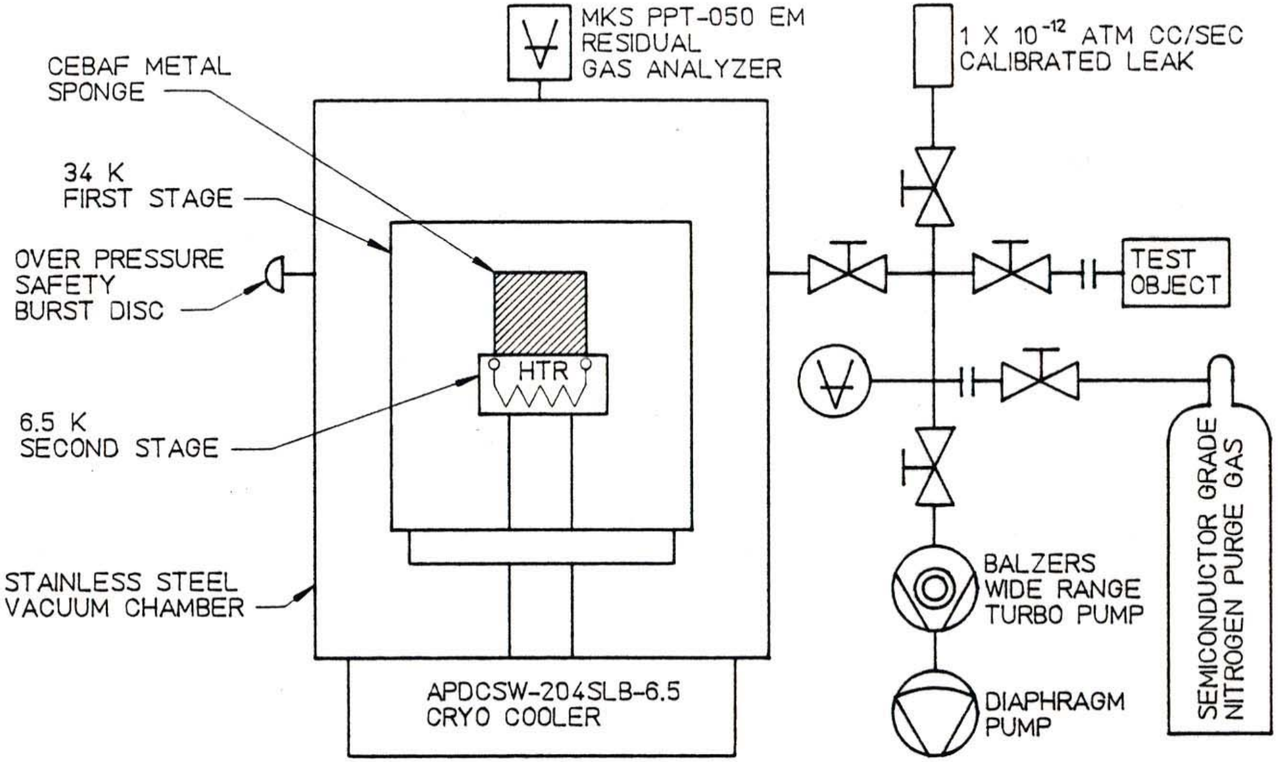
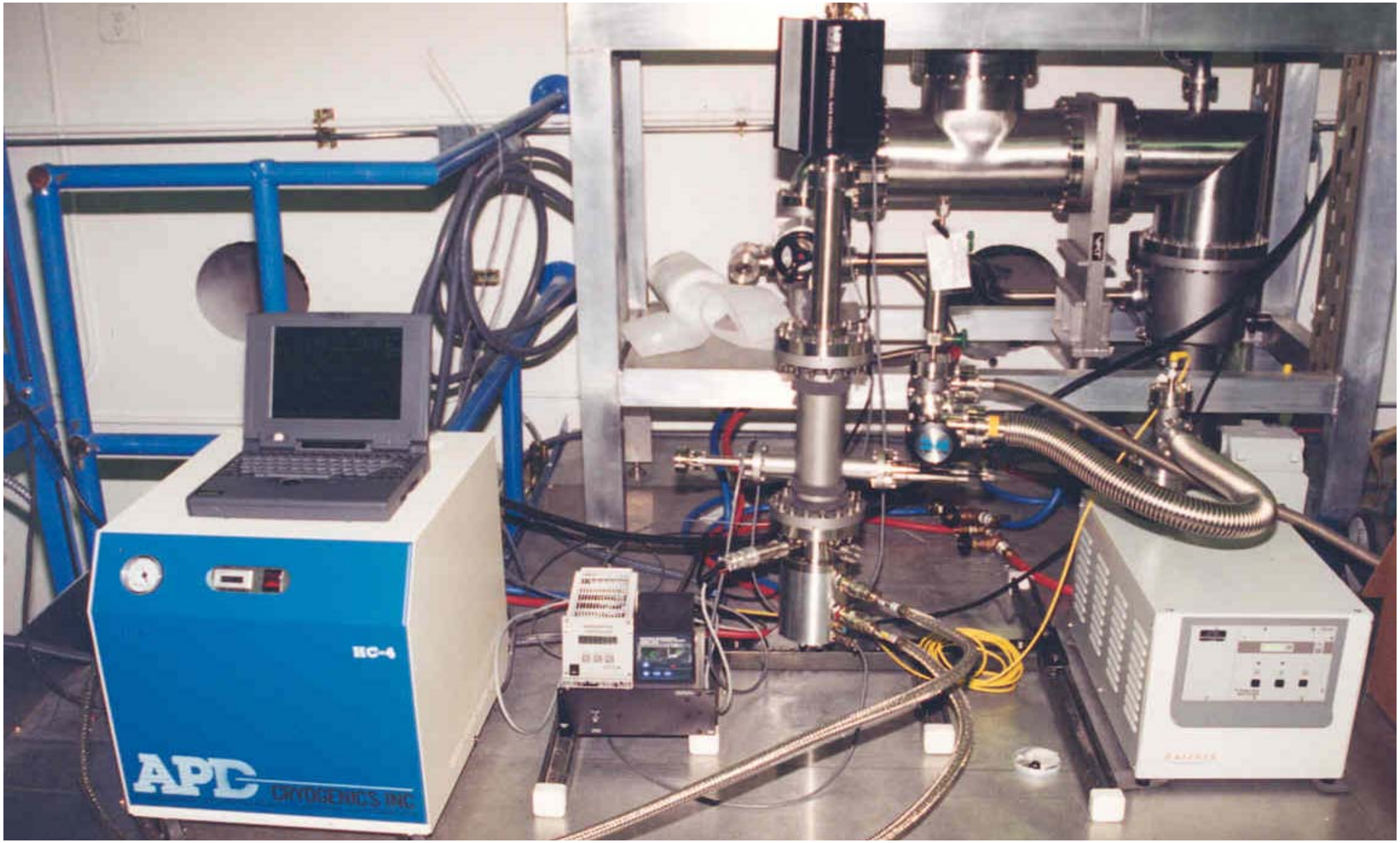
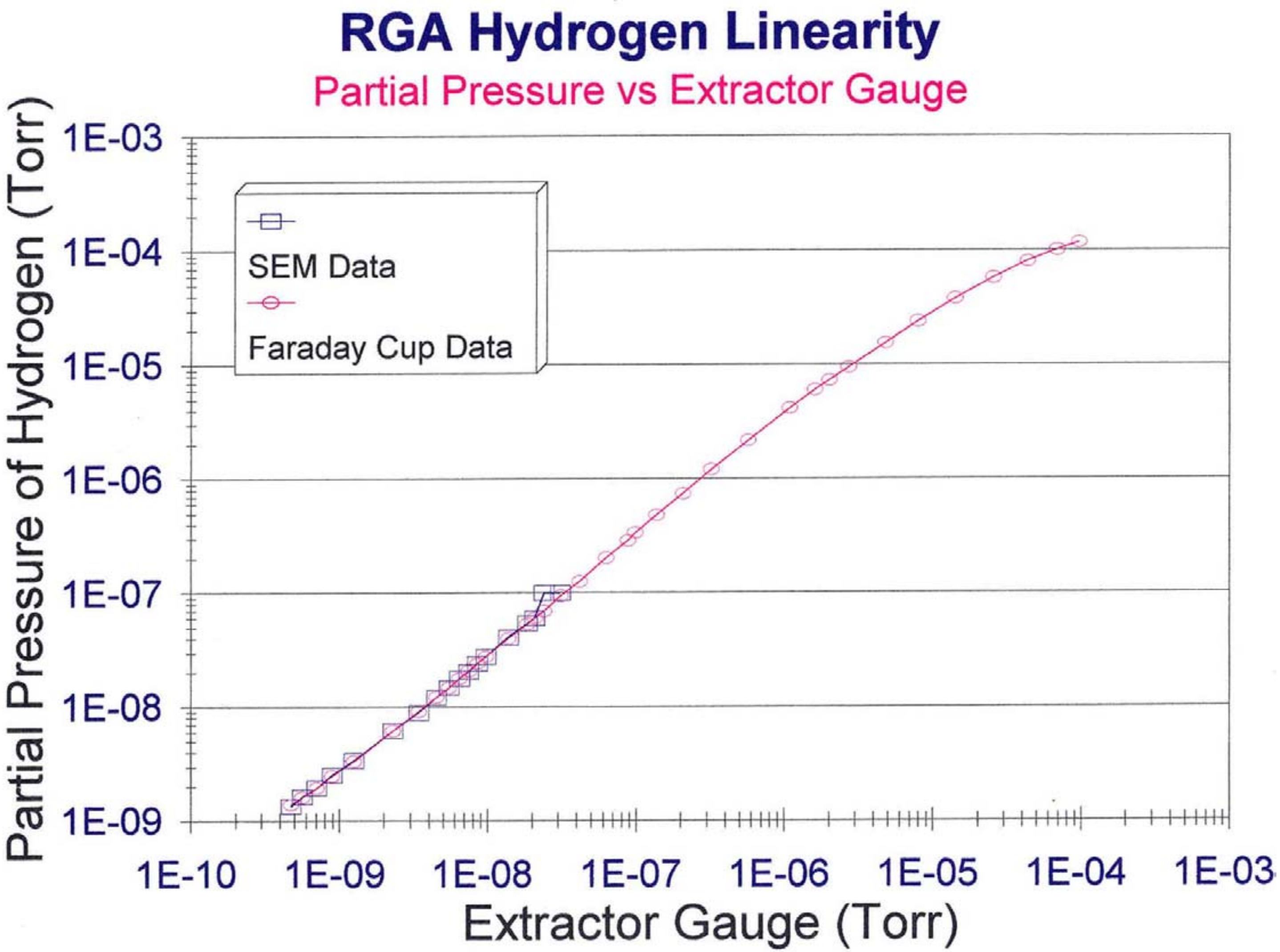


FIG. 1 SCHEMATIC OF THE EXTREME SENSITIVITY
He LEAK DETECTOR

Extreme Sensitivity Leak Detector



Special RGA for H_2 Linearity



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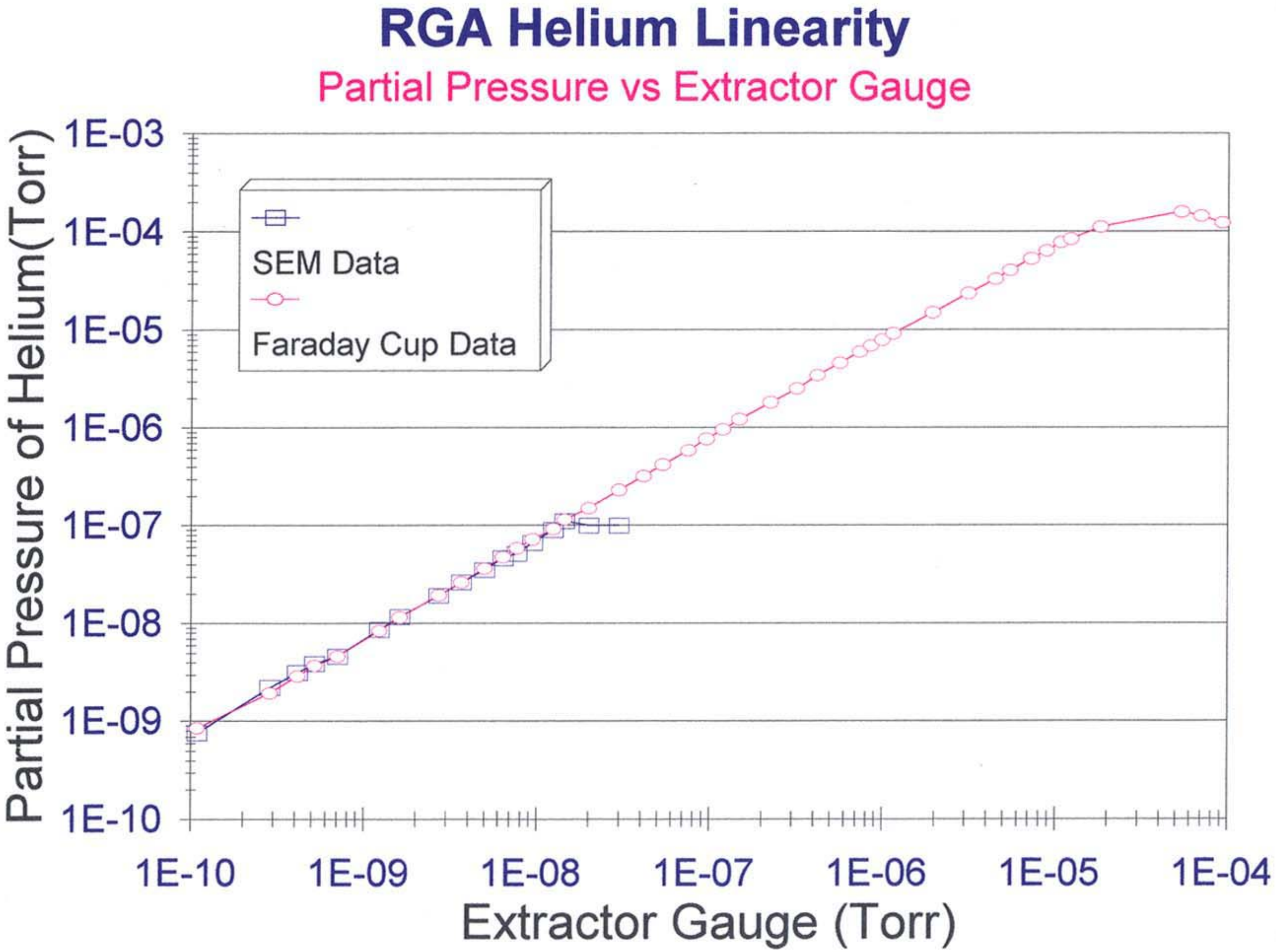
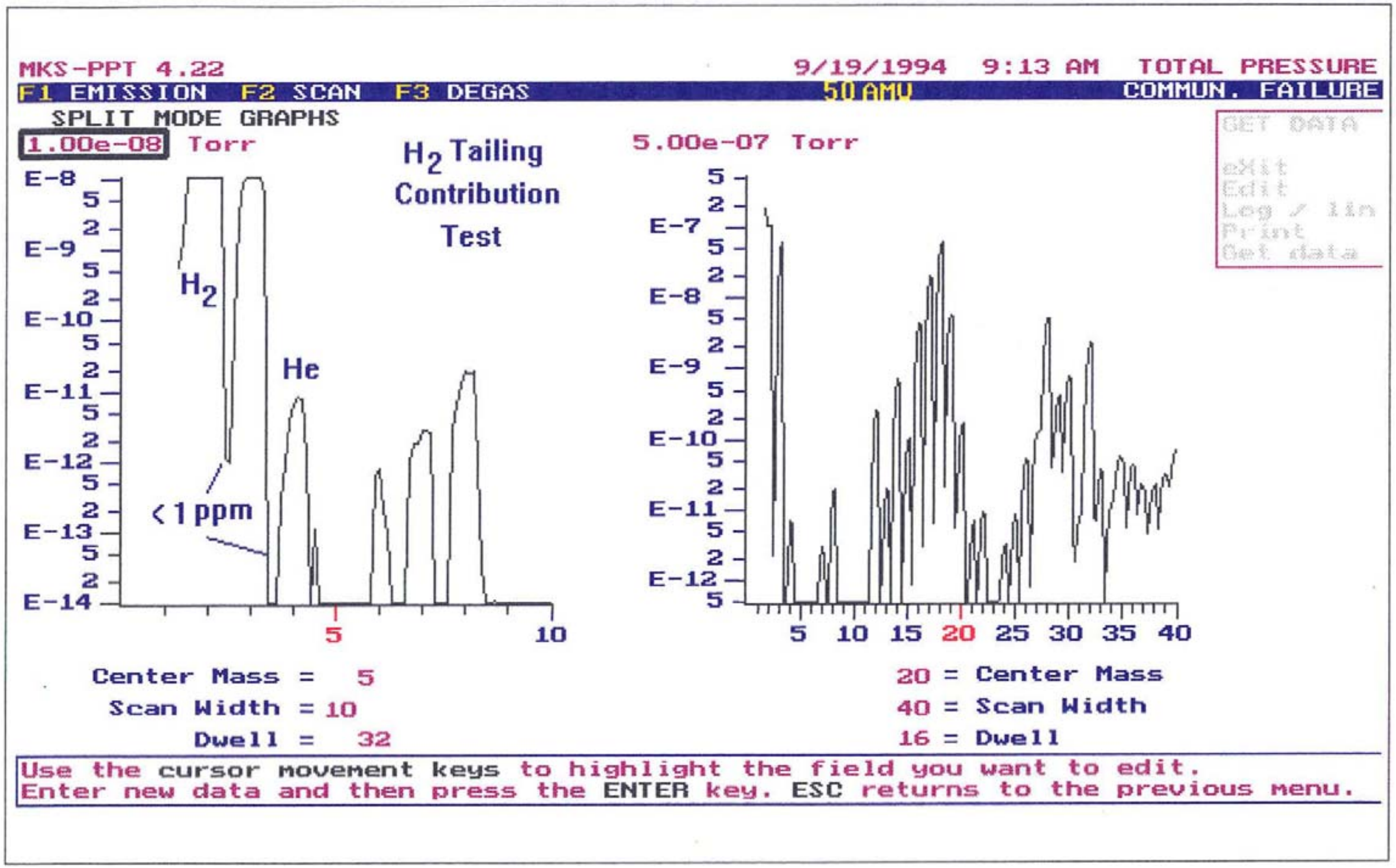
Special RGA He Linearity



Special RGA Tailing Contribution

Tailing Contribution Measurement

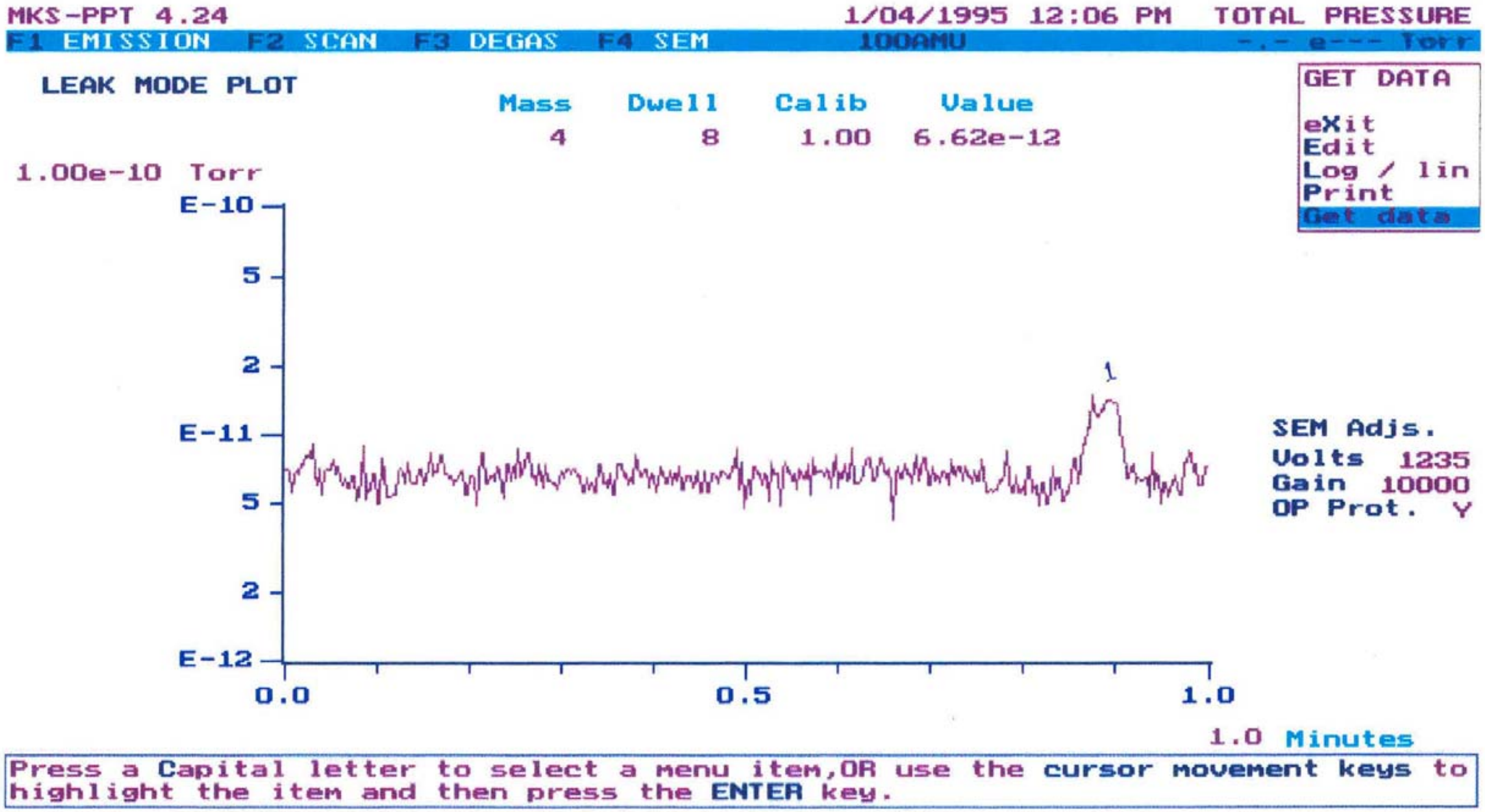
H_2 Pressure @ 1.0×10^{-6} Torr



```
MKS-PPT 4.22                                9/19/1994   9:13 AM   TOTAL PRESSURE
F1 EMISSION   F2 SCAN   F3 DEGAS            50 AMU               COMMUN. FAILURE
  SPLIT MODE GRAPHS
1.00e-08 Torr                        5.00e-07 Torr

   Center Mass  =  5                               20 = Center Mass
    Scan Width  = 10                               40 = Scan Width
         Dwell  =  32                              16 = Dwell
Use the cursor movement keys to highlight the field you want to edit.
Enter new data and then press the ENTER key. ESC returns to the previous menu.
```

Back streaming of Helium through turbo pump

Leak Detector Connected to the Turbopump

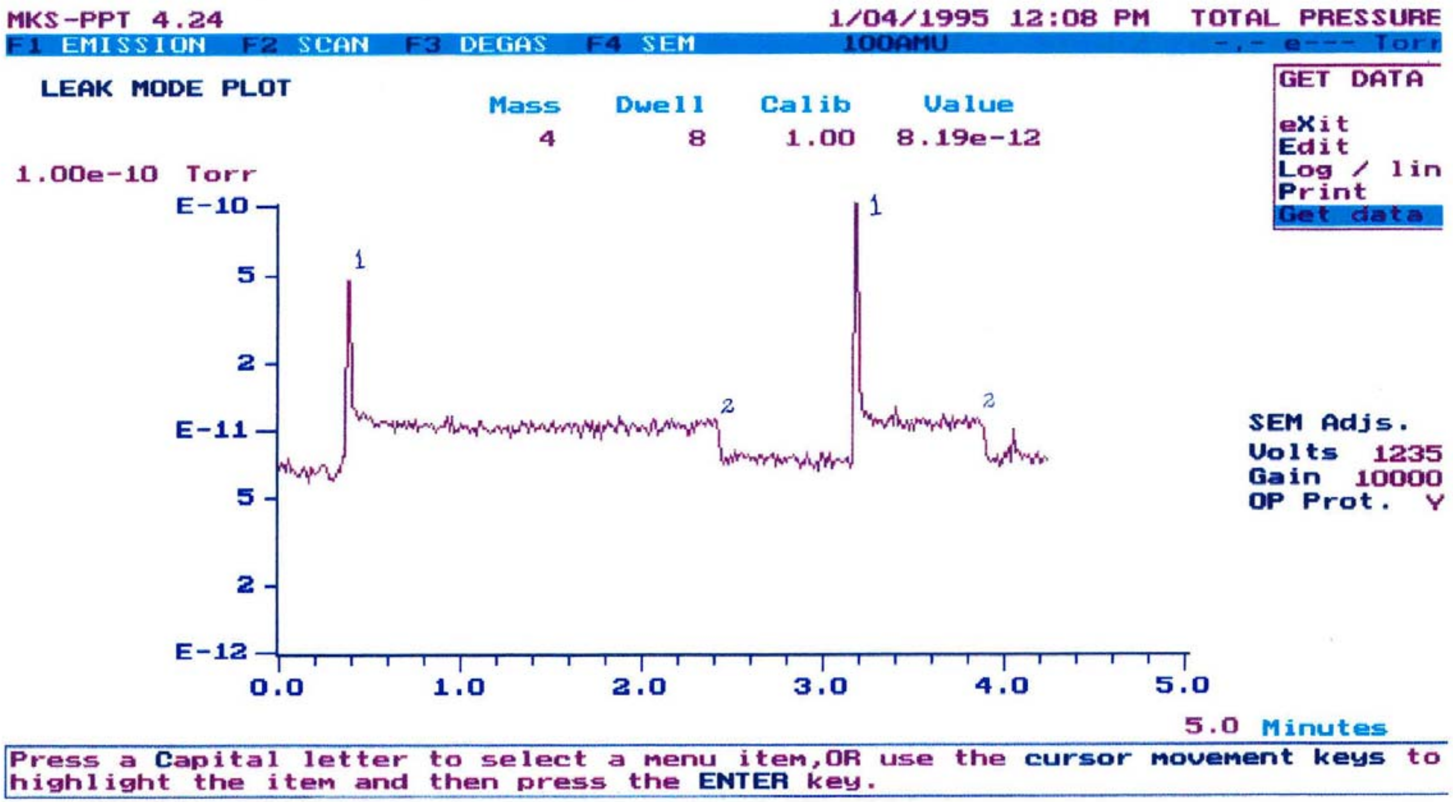


```
MKS-PPT 4.24                                   1/04/1995 12:06 PM   TOTAL PRESSURE
F1 EMISSION   F2 SCAN   F3 DEGAS   F4 SEM          100AMU               -.- e--- Torr
  LEAK MODE PLOT                                                      GET DATA
                    Mass     Dwell     Calib     Value
                      4         8       1.00    6.62e-12             eXit
                                                                      Edit
1.00e-10  Torr                                                        Log / lin
                                                                      Print
                                                                      Get data

                                                                   SEM Adjs.
                                                                   Volts   1235
                                                                   Gain   10000
                                                                   OP Prot.   Y

                                                         1.0 Minutes
Press a Capital letter to select a menu item,OR use the cursor movement keys to
highlight the item and then press the ENTER key.
```

1 Backstreaming of atmospheric helium through the turbopump

Calibrated leak

A 1×10^{-12} atm cc s^{-1} Calibrated Leak Opened and Closed to the Leak Detector

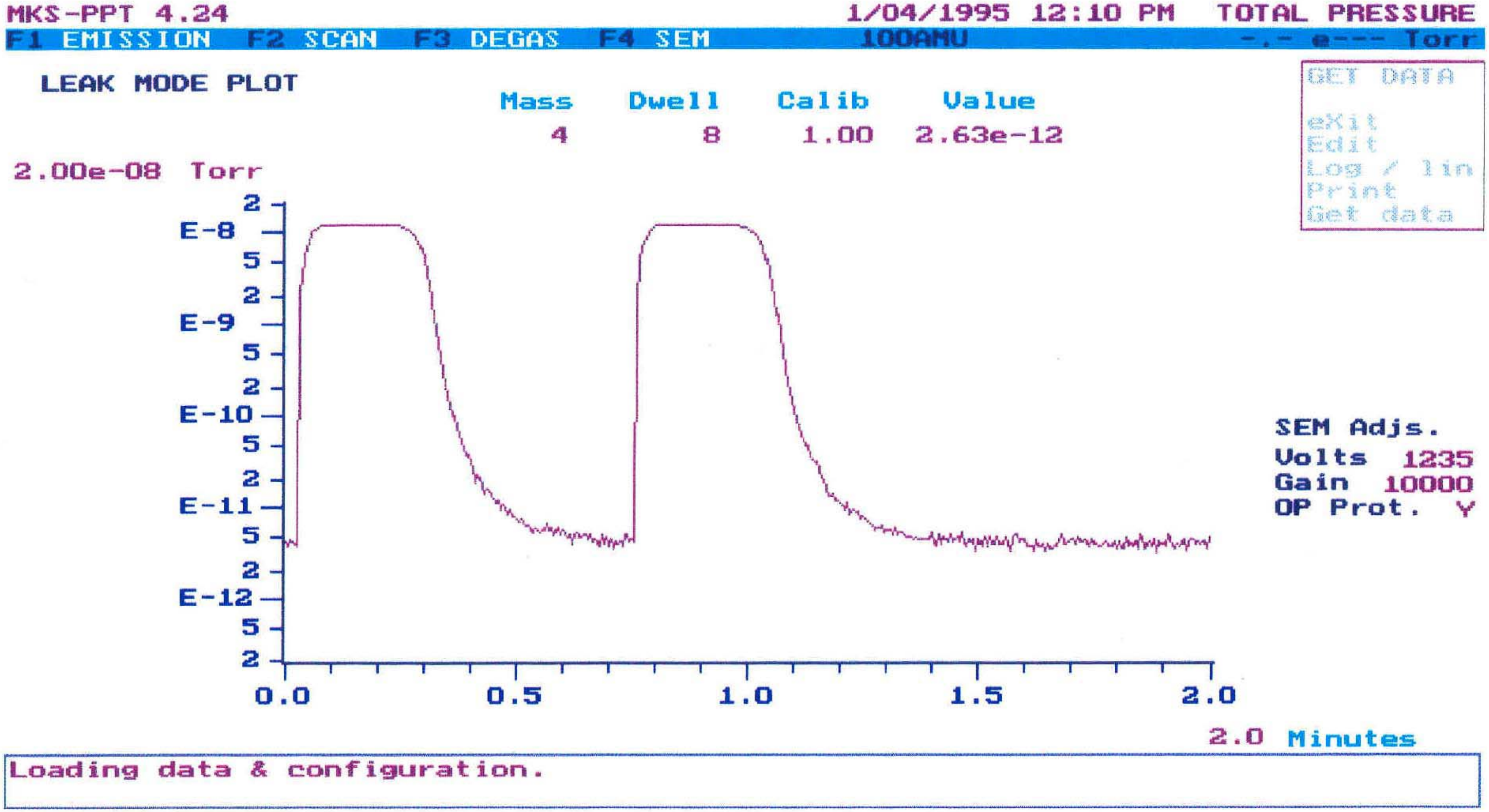


```
MKS-PPT 4.24                     1/04/1995 12:08 PM   TOTAL PRESSURE
F1 EMISSION  F2 SCAN  F3 DEGAS  F4 SEM    100AMU        -.- e--- Torr
 LEAK MODE PLOT
                    Mass    Dwell    Calib    Value
                     4        8       1.00   8.19e-12

                                                      SEM Adjs.
                                                      Volts   1235
                                                      Gain   10000
                                                      OP Prot.   Y

Press a Capital letter to select a menu item,OR use the cursor movement keys to
highlight the item and then press the ENTER key.
```

1. Calibrated leak opened to the leak detector

2. Calibrated lead isolated from the leak detector

Helium Accumulation Technique



MKS-PPT 4.24

1/04/1995 12:10 PM TOTAL PRESSURE

LEAK MODE PLOT

Mass	Dwell	Calib	Value
4	8	1.00	2.63e-12

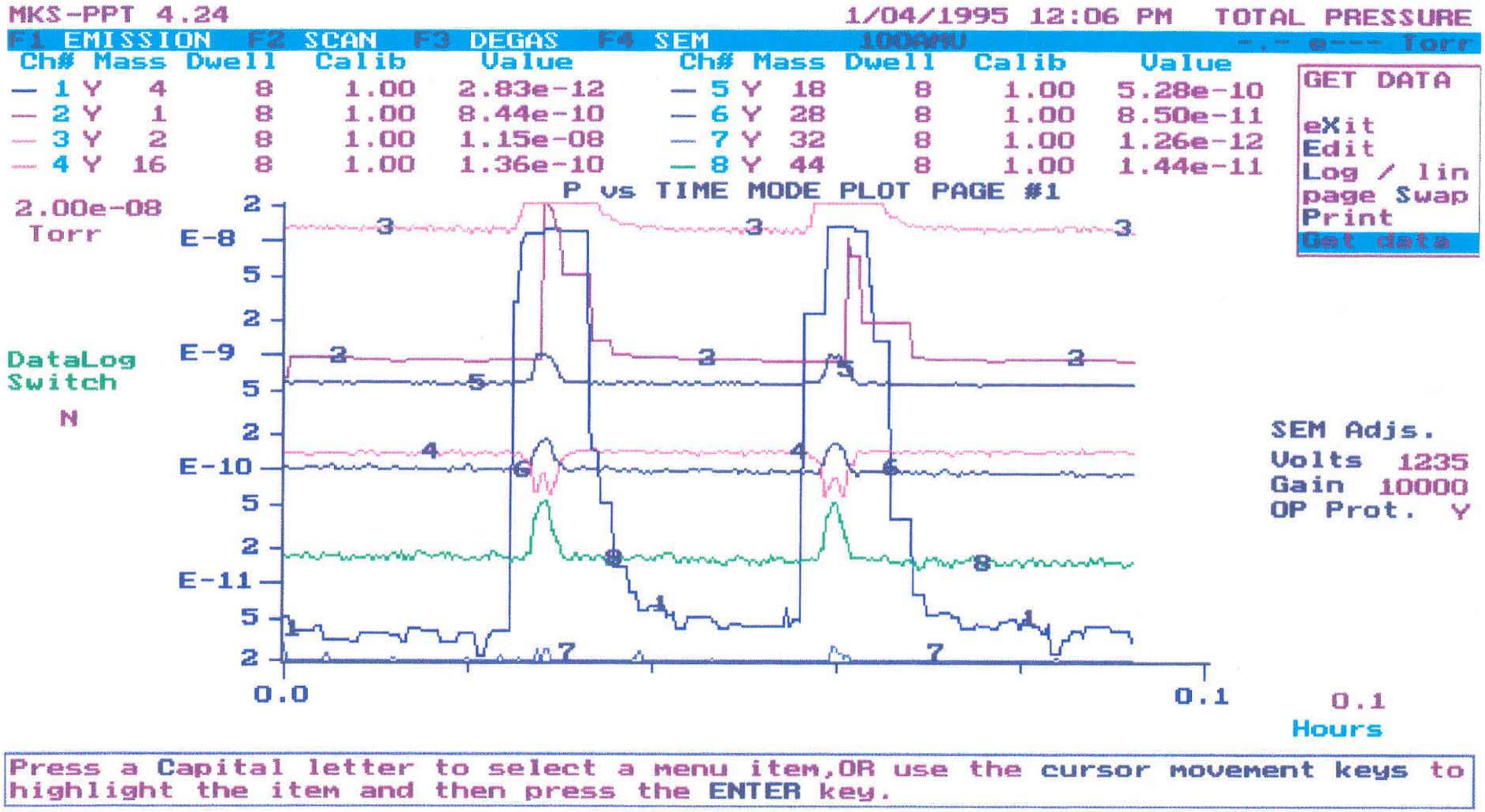
2.00e-08 Torr

SEM Adjs.
Volts 1235
Gain 10000
OP Prot. Y

2.0 Minutes

Loading data & configuration.

Adsorption – Desorption Cycle



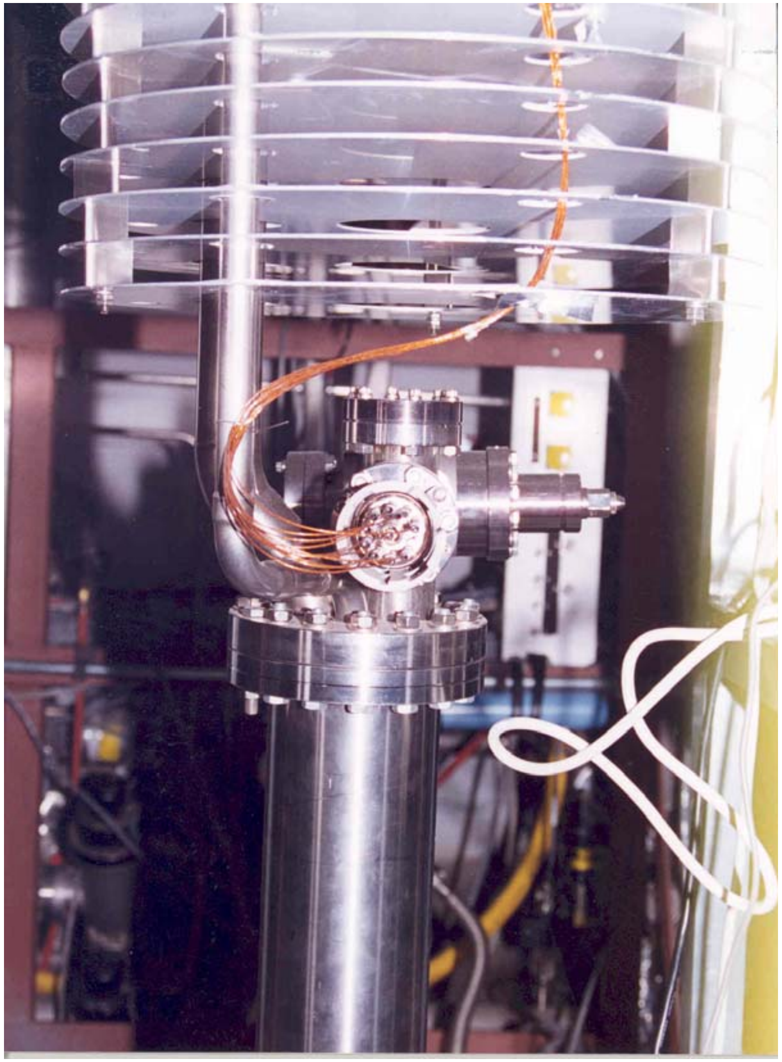
MKS-PPT 4.24 1/04/1995 12:06 PM TOTAL PRESSURE

Ch#	Mass	Dwell	Calib	Value	Ch#	Mass	Dwell	Calib	Value
1 Y	4	8	1.00	2.83e-12	5 Y	18	8	1.00	5.28e-10
2 Y	1	8	1.00	8.44e-10	6 Y	28	8	1.00	8.50e-11
3 Y	2	8	1.00	1.15e-08	7 Y	32	8	1.00	1.26e-12
4 Y	16	8	1.00	1.36e-10	8 Y	44	8	1.00	1.44e-11

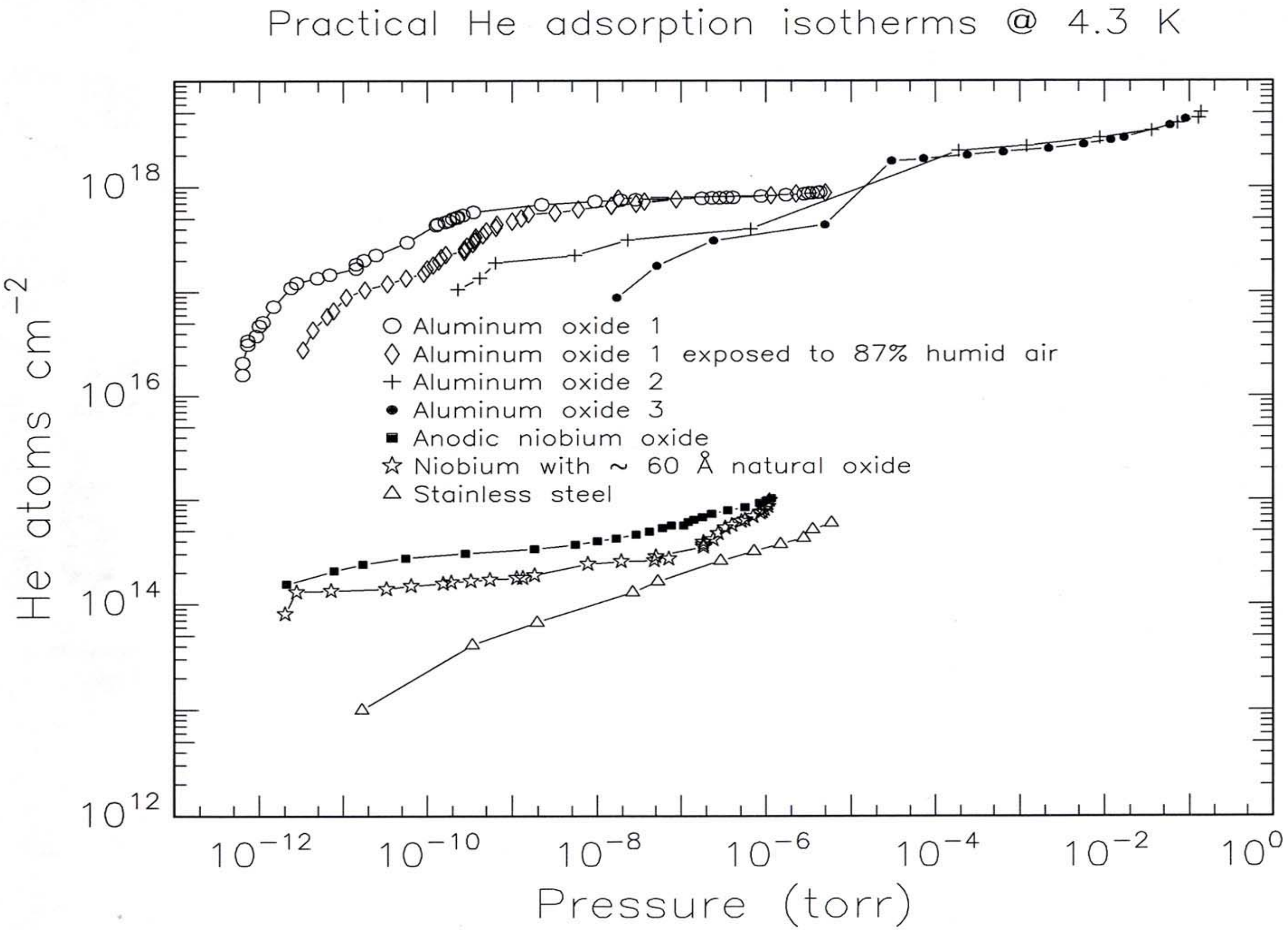
SEM Adjs.
Volts 1235
Gain 10000
OP Prot. Y

Press a Capital letter to select a menu item,OR use the cursor movement keys to highlight the item and then press the ENTER key.

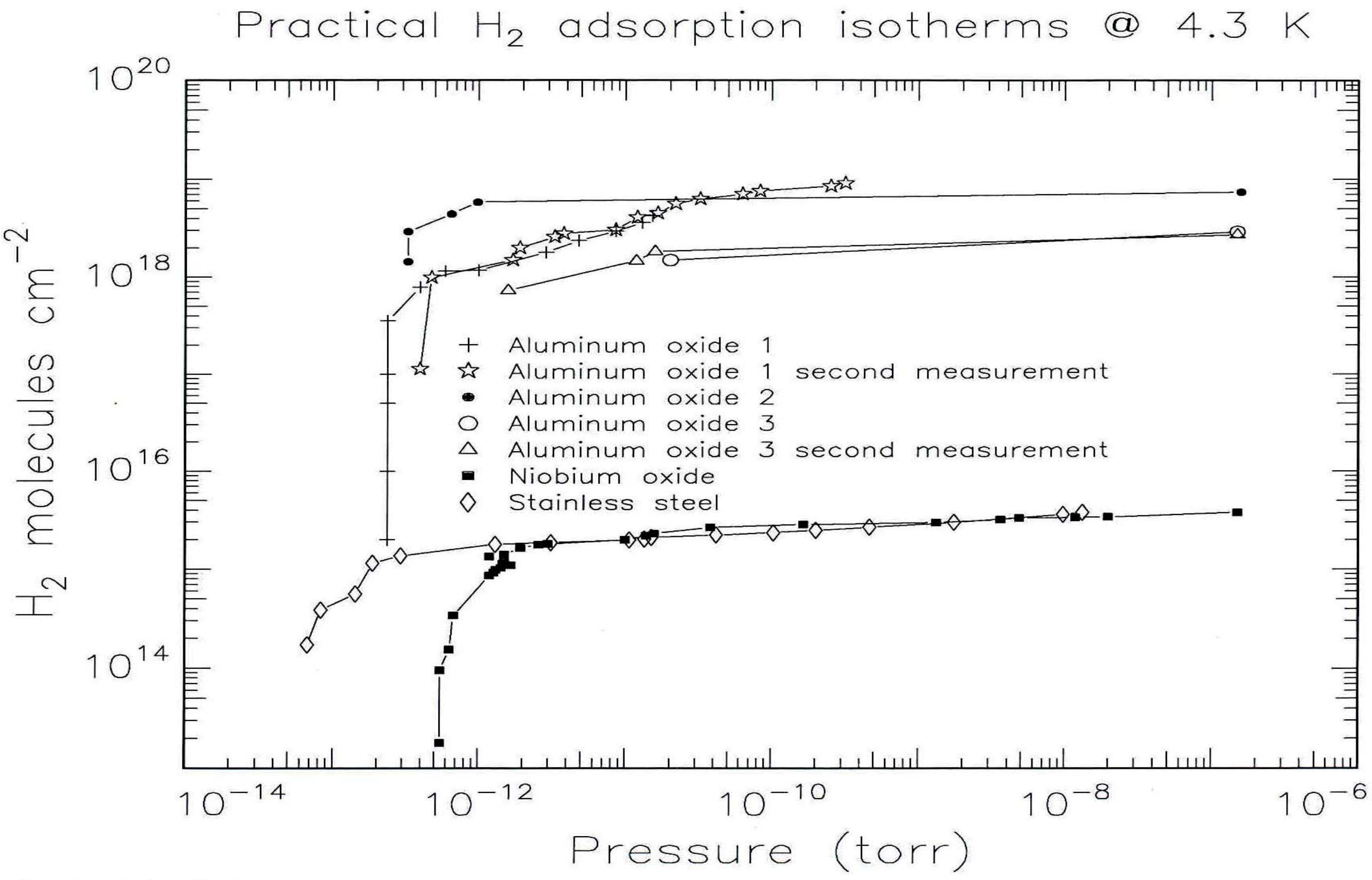
Unique Cryosorption Setup



Helium Isotherms



Hydrogen Isotherms



Calculated H_2 Isotherms for stainless steel

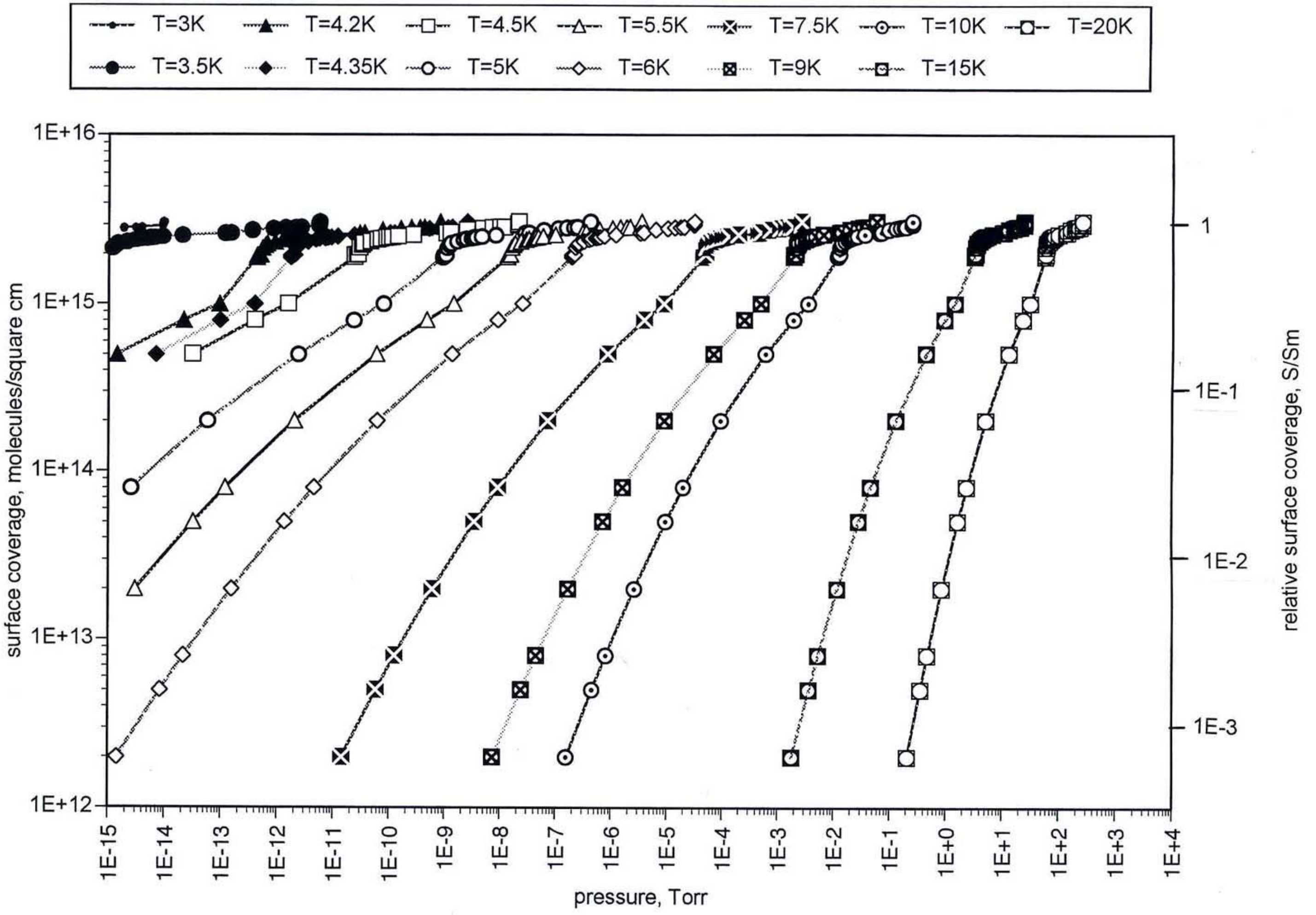


Fig.1 Calculation hydrogen adsorption isotherms on stainless steel

Calculated H_2 Isotherms for Metal Sponge

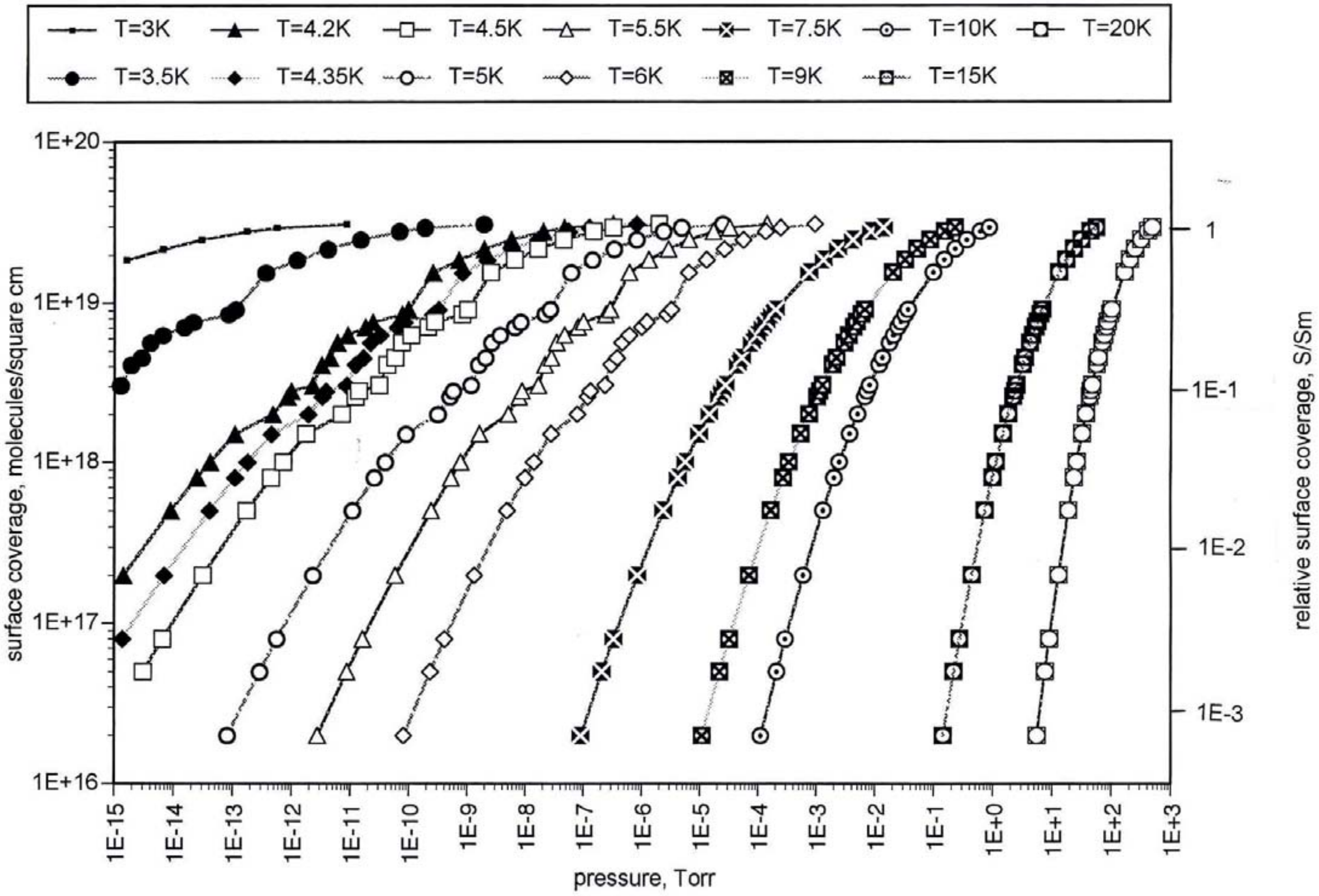
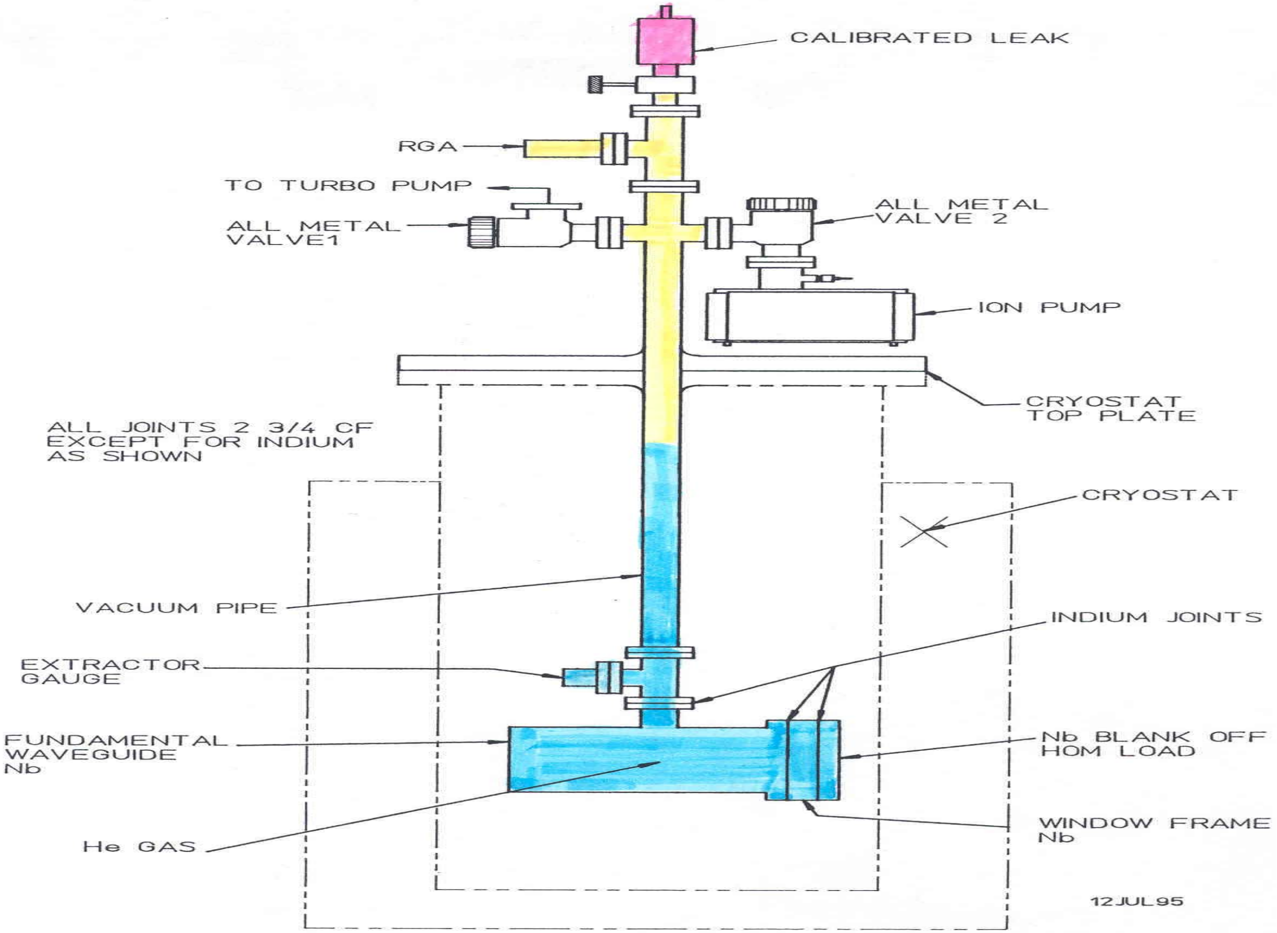


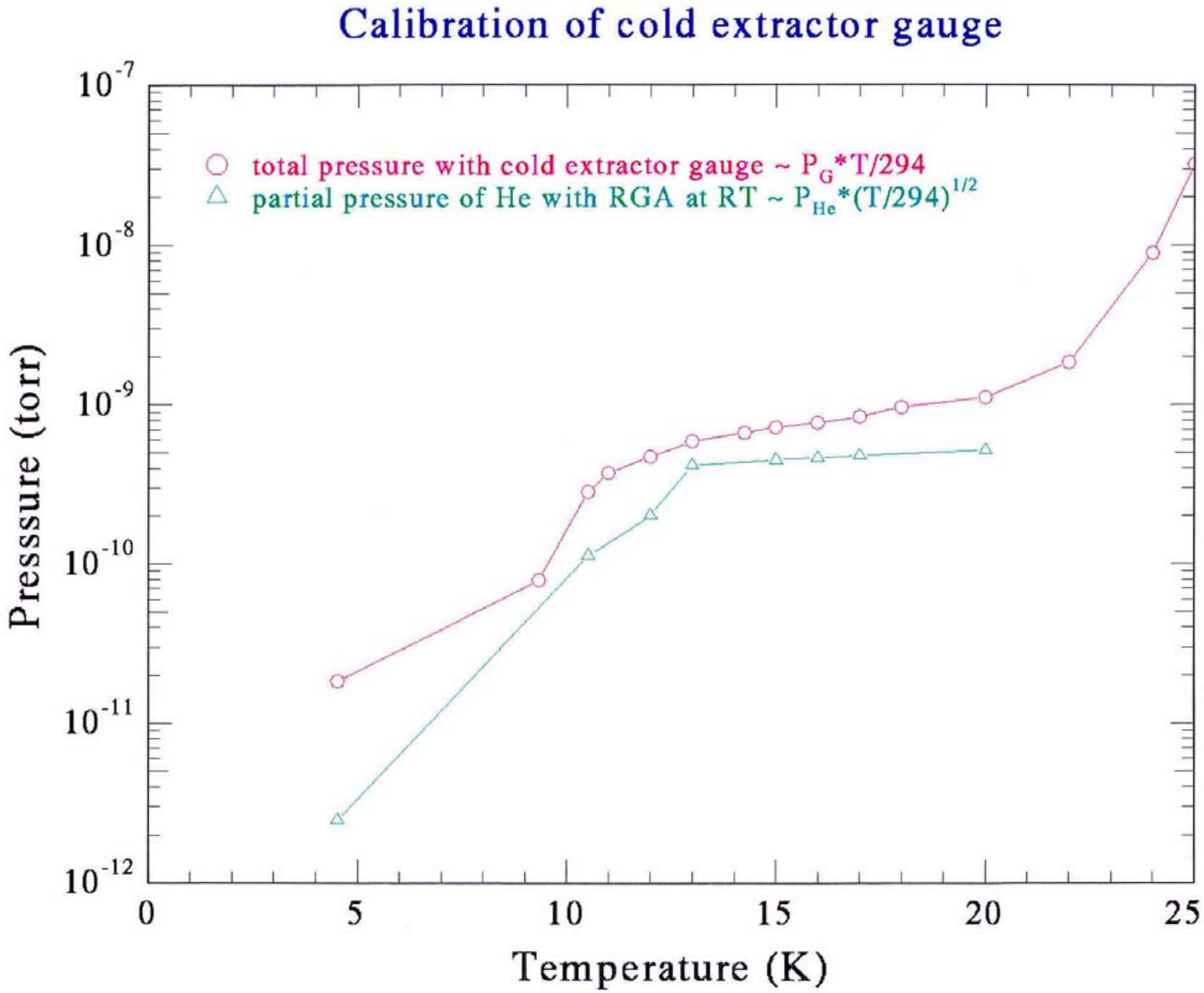
Fig. 2 Calculation hydrogen adsorption isotherms on anodized aluminum

Extractor Gauge Calibration with He

FIGURE 1 COLD EXTRACTOR GAUGE CALIBRATION SETUP



Helium Calibration 1



Helium calibration 2

CALIBRATION OF THE EXTRACTOR GAUGE

The quantity of He introduced in to the system during the experiment

= 3.76×10^{-6} atm cc

The amount of He estimated from the extractor gauge and RGA readings

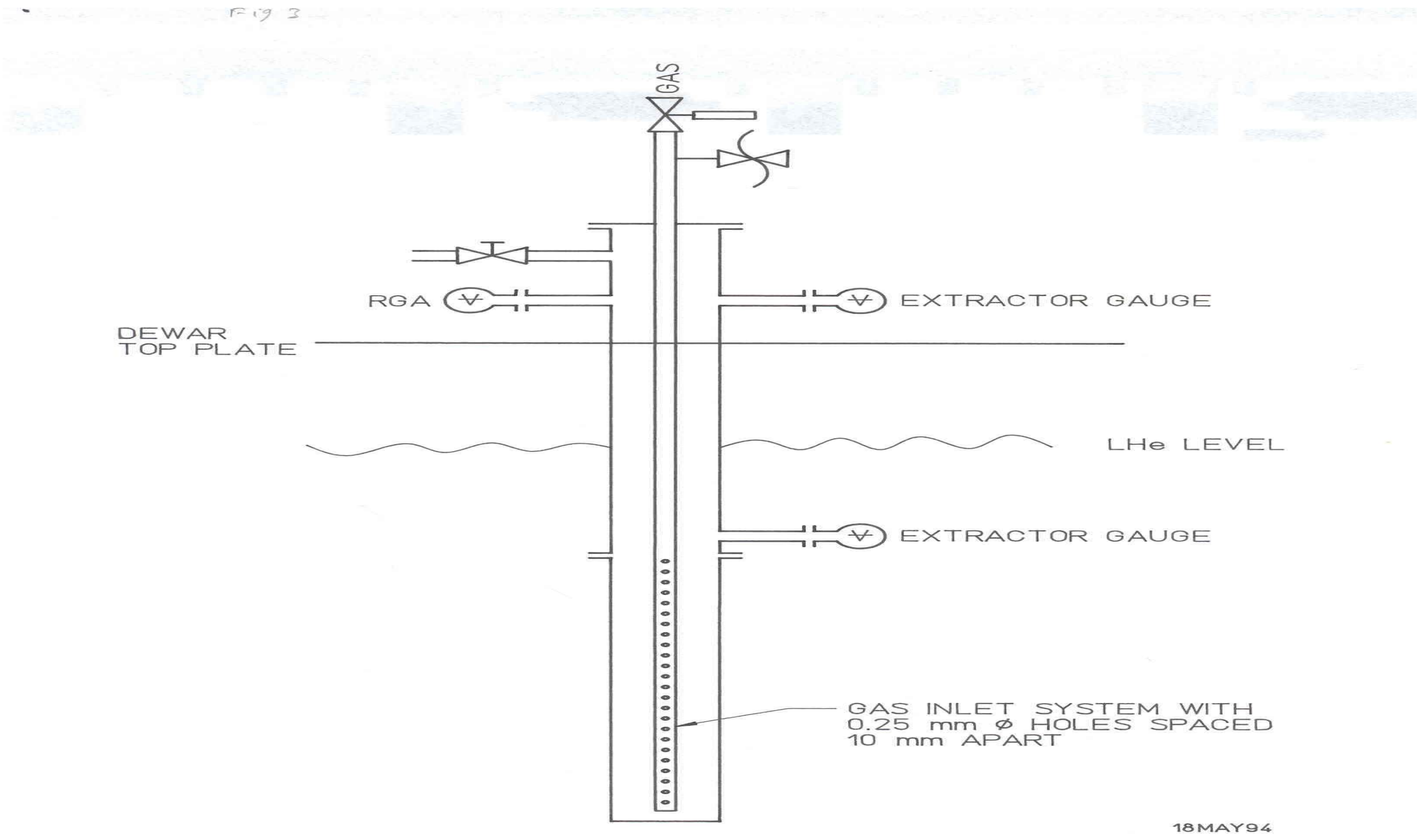
= 3.53×10^{-6} atm cc

With thermal transpiration correction the RGA He partial pressure value at room temperature translates to 1.05×10^{-8} torr at 11 K

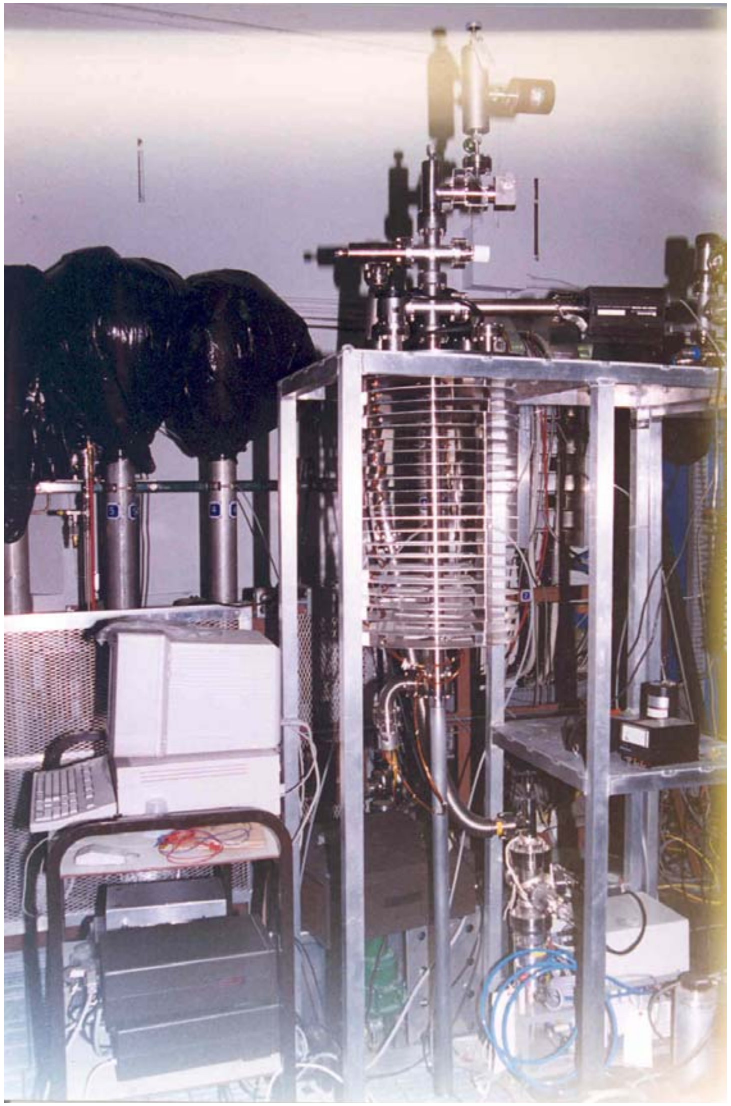
This value is in good agreement with the cold extractor gauge reading

{corrected for the temperature correction ~ (T/294) ~ (11/294) } = 1.0×10^{-8} torr

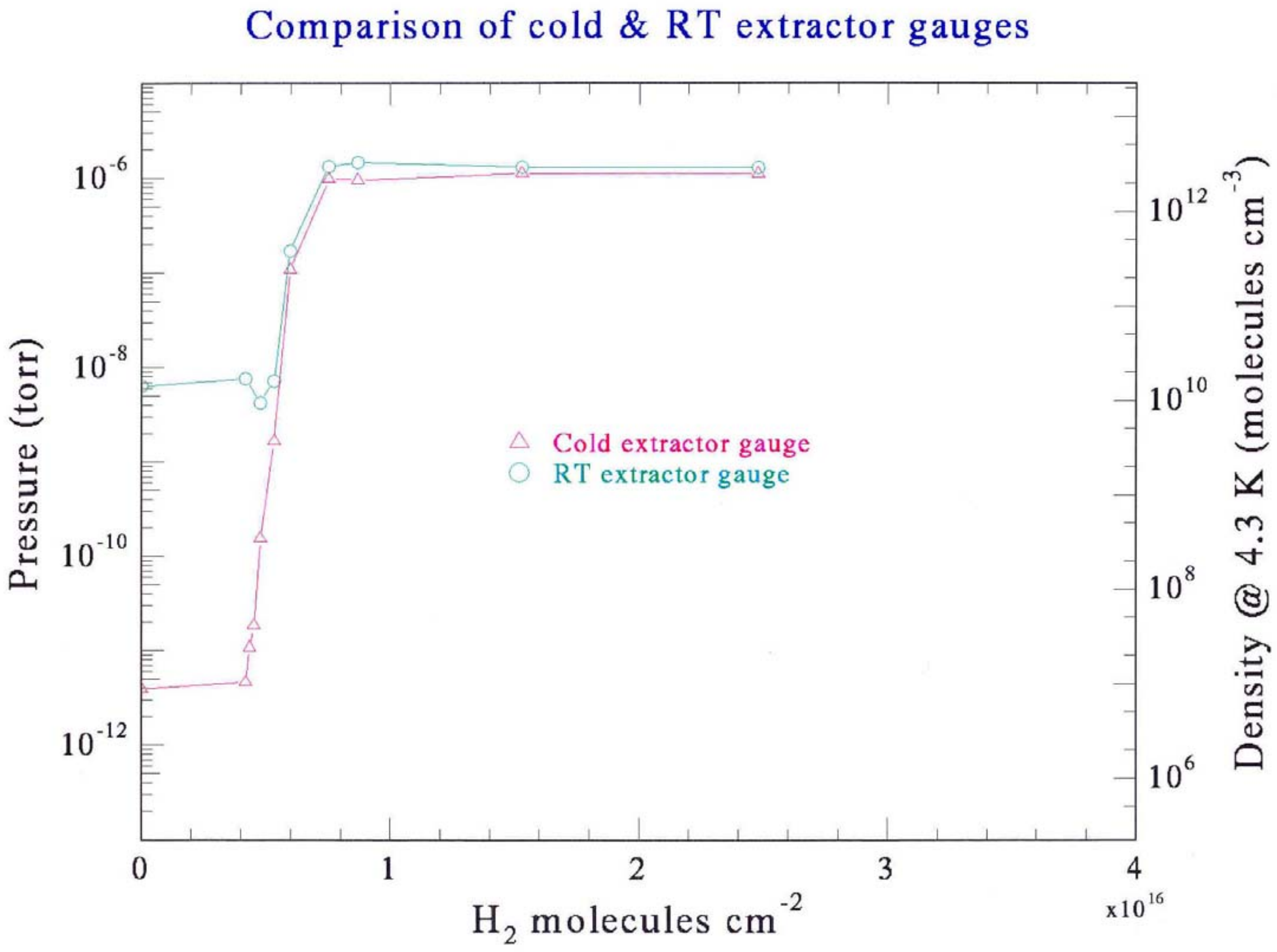
Extractor Gauge Calibration with H_2



Extractor Gauge Calibration Setup



Cold and RT Extractor Gauges



Extractor Gauge Calibration with Hydrogen

HYDROGEN VAPOUR PRESSURE MEASUREMENT WITH COLD AND RT EXTRACTOR GAUGES

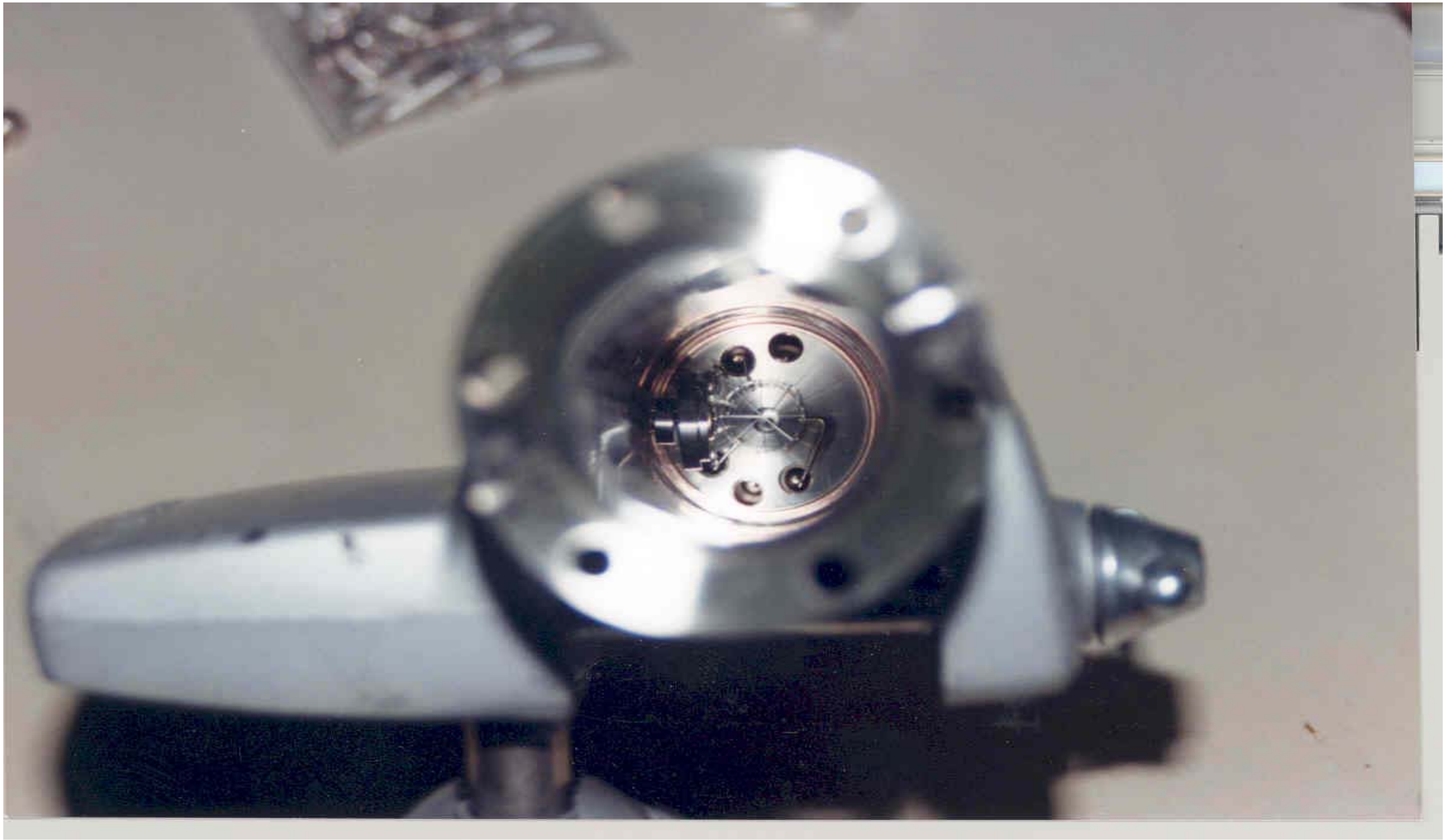
He bath pressure ~ 812 torr and the corresponding Temperature ~ 4.25 K

$P_{CALCULATED} = 1.39 \text{ X } 10^{-6}$ torr

$P_{COLDGAUGE} = 1.48 \text{ X } 10^{-6}$ torr

$P_{RTGAUGE} = 1.32 \text{ X } 10^{-6}$ torr

Modified Extractor Gauge with Spindt Field Emitter



G. Myneni April 18, 2003

Conclusions

- Pretreatments, Processing and Procedures are Critical for Achieving XHV
- High Sensitivity He Leak Detection is Crucial for Minimizing External Leaks
- Virtual Leaks Could be a Major Headache & Deserves Careful Attention
- Cryosorption Pumping will Undoubtedly Produce XHV
- Cascade Pumping Should be Explored
- XHV Instrumentation Development is Paramount for Success
- We are Open for Collaborations

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