



Master's thesis
Physics

Outgassing Studies of Some Accelerator Materials

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Tiivistelmä — Referat — Abstract This Master's thesis has been produced at CERN (European Organization for Nuclear Research) in the Vacuum, Surfaces and Coatings group during an interesting time period for accelerator physics. With the High Luminosity Large Hadron Collider (HL-LHC) upgrade in progress and future accelerators under study, we will soon have particle beams with unprecedented luminosity and energy. This provides new challenges to maintain the vacuum conditions at acceptable levels. One of the most critical factors to consider when choosing materials to accelerators and other vacuum systems are their outgassing rates. In this work, outgassing was studied with two systems. One was used to test the outgassing of baked samples with accumulation method at different temperatures. Another system was used to test unbaked samples with throughput method as a function of time and temperature. In addition, a smaller experiment was assembled for testing the effect of different venting gases and venting times to the pumpdown curve of a vacuum fired 316L stainless steel chamber and it is included in the appendix. These measurements are of importance as many of the tested materials or coatings are used or going to be used in the accelerators at CERN. The results can be used for vacuum simulations or in the design of a new component to predict its outgassing, that needs to comply with the strict vacuum acceptance criteria for the accelerator vacuum systems. As a conclusion, the unbaked samples presented high outgassing rates as expected. Water outgassing was prevalent with polymers, but was also significant with Macor and the two graphite samples. A high temperature heat treatment for graphite decreased the outgassing rate considerably and improved the residual gas spectrum. The baked samples were found to have low outgassing rates particularly at room temperature, where the background outgassing of the sample chamber was significant. Upper limits for the outgassing rates were evaluated for Macor and tungsten samples. However, alumina coated SS304L samples were distinct from the background and the outgassing rates were determined at five temperatures to assess the applicability of the coating for the vacuum tanks of the kicker magnets.			
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Geneva, 15.05.2018 Ari Riihimäki

List of abbreviations

ALICE	A Large Ion Collider Experiment
ATLAS	A Toroidal LHC ApparatuS
BAG	Bayard-Alpert Gauge
CERN	European Organization for Nuclear Research
CF	ConFlat flange
CMS	Compact Muon Solenoid
CCG	Cold Cathode Gauge
DN	Diameter Nominal
ELENA	Extra Low ENergy Anti-proton facility
ESD	Electron Stimulated Desorption
HL-LHC	High Luminosity Large Hadron Collider
HCG	Hot Cathode Gauge
ISR	Intersecting Storage Rings
LHC	Large Hadron Collider
LINAC2	LINEar ACcelerator 2
LSS	Long Straight Section
MID	Multiple Ion Detection
NEG	Non Evaporable Getter
PS	Proton Synchrotron
PSB	Proton Synchrotron Booster
QMS	Quadrupole Mass Analyzer
RGA	Residual Gas Analyzer
SPS	Super Proton Synchrotron
SEM	Secondary Electron Multiplier
TSP	Titanium Sublimation Pump
UHV	Ultra High Vacuum
VSC	Vacuum, Surfaces and Coatings
XHV	Extreme High Vacuum

Table of contents

Abstract

Acknowledgements	i
------------------	---

List of abbreviations	ii
-----------------------	----

Table of contents	iii
-------------------	-----

1 Brief introduction	1
-----------------------------	----------

1.1 European Organization for Nuclear Research	1
1.2 Vacuum at CERN	3
1.3 Introduction to vacuum technology	5

2 Theory of outgassing	11
-------------------------------	-----------

2.1 Desorption	12
2.2 Diffusion	13
2.3 Permeation	14
2.4 Mitigating outgassing	15

3 Vacuum instrumentation	16
---------------------------------	-----------

3.1 Vacuum pumps	16
3.2 Pressure gauges	19
3.3 Residual gas analyzer	21
3.4 Variable leak valve	23
3.5 Temperature control of the systems	23
3.6 Sample chambers	23

4 Experimental methods for outgassing studies	24
--	-----------

4.1 Accumulation system	24
4.2 Throughput system	31

5 Uncertainty considerations	35
-------------------------------------	-----------

5.1 Temperature errors	35
5.2 Epistemic uncertainties	35

6 Samples	39
------------------	-----------

6.1 Vespel SP-1	39
6.2 Polyetheretherketone (PEEK)	40
6.3 Macor	40
6.4 Plasma sprayed 100 % fine alumina coating on stainless steel 304L	41
6.5 Tungsten 99.95 %	43
6.6 Graphite R 8500	43

7 Results	45
7.1 Throughput system results	45
7.2 Accumulation system results	60
8 Conclusions	68
Bibliography	69
Appendixes	74
A Calibration of the RGA	74
B Pumping speeds in the accumulation system	77
C Throughput system RGA calibration	79
D Polymer tests with the accumulation system	80
E Throughput system analog scans	84
F Accumulation system measurements	85
G Venting system measurements and results	90

1 Brief introduction

1.1 European Organization for Nuclear Research

CERN is a European research organization and the world's leading particle physics research center. Since its foundation in 1954 CERN has provided the means for high energy physics research. The accelerator complex shown in figure 1 is used to provide high energy particles for different experiments to make new discoveries and to test existing theories, such as the Standard Model of particle physics, which classifies all the known elementary particles and describes the electromagnetic, weak and strong interactions. Even though the Standard Model is very well established and the most precisely tested physics theory, it leaves many questions unanswered and many phenomena unexplained.^[1]

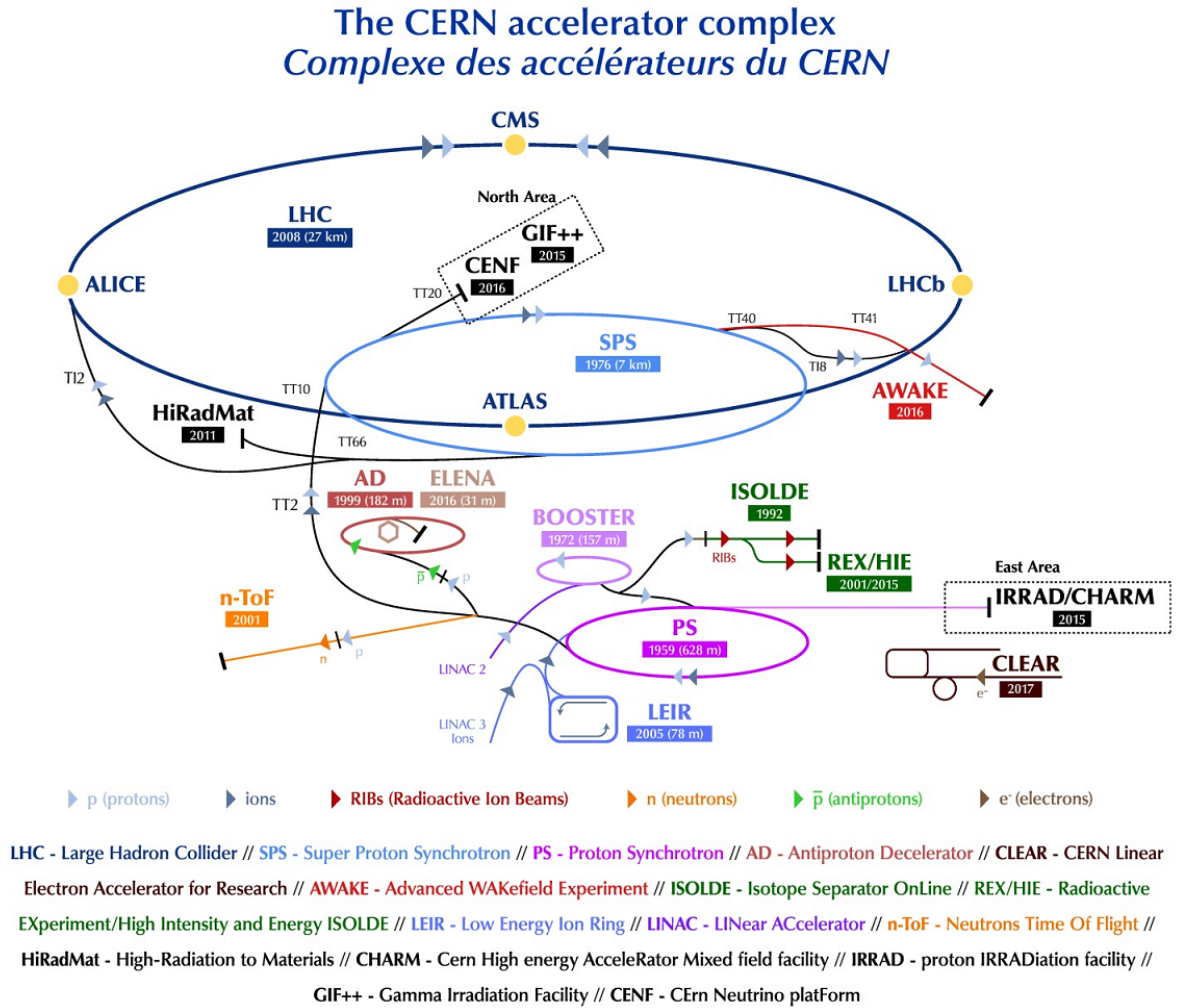


Figure 1: The accelerator complex at CERN. Courtesy of CERN.

The accelerator complex shown in figure 1 presents the steps of acceleration for all the different experiments at CERN. The complex is used to accelerate mainly protons and lead ions, but different particles such as xenon nuclei can also be accelerated^[2]. Protons are first accelerated with LINAC2 and injected in the proton synchrotron booster (PSB). They can be accelerated even closer to the speed of light with PS, SPS or they can be delivered to different experiments along the way.^[1]

The last stage in the accelerator chain is the Large Hadron Collider (LHC), which constitutes the largest scientific and technical project ever built on Earth. It has two separate beam pipes where mainly protons and lead ions $^{208}\text{Pb}^{82+}$ circulate in the opposite directions providing proton-proton, Pb-Pb and Pb-proton collisions^[1]. The circumference of the ring is 26.7 km and it consists of eight long straight sections (LSS) and eight bending sections called arcs, where 1232 superconducting magnets guide the beams with a maximum magnetic field of about 8.3 tesla. The electric current necessary to maintain this field is approximately 11.8 kA which sets restrictions on geometry and heat loads and therefore the magnetic coils are made of superconducting cables of fine strands of Nb-Ti alloy embedded in a copper matrix. The coils are kept below the critical temperature of the Nb-Ti alloy with superfluid helium below 1.9 K.^[1,3]

The protons in the LHC can be accelerated to a center-of-mass energy of 7 TeV with radiofrequency (RF) cavities which contain an oscillating electromagnetic field. 16 RF cavities are encapsulated in four cryomodules shown in figure 2 that keep the cavities at superconducting temperatures. Each cavity can reach an accelerating voltage of 2 MV, producing 16 MV per beam. The cavities are structured with a particular shape and size so that the electromagnetic waves become resonant and switch the direction with a frequency of 400 MHz. Therefore the arrival timing of the particles to the cavity is critical. When the LHC has reached maximum energy, an ideally timed particle with the right energy will not be affected at all. Particles with different timing or energy will be accelerated or decelerated closer to the desired value. As a result, the oscillating field keeps the beam separated into discrete bunches. Each beam consists of 2835 bunches and each of them contains an average of 1.05×10^{11} protons.^[4,5]

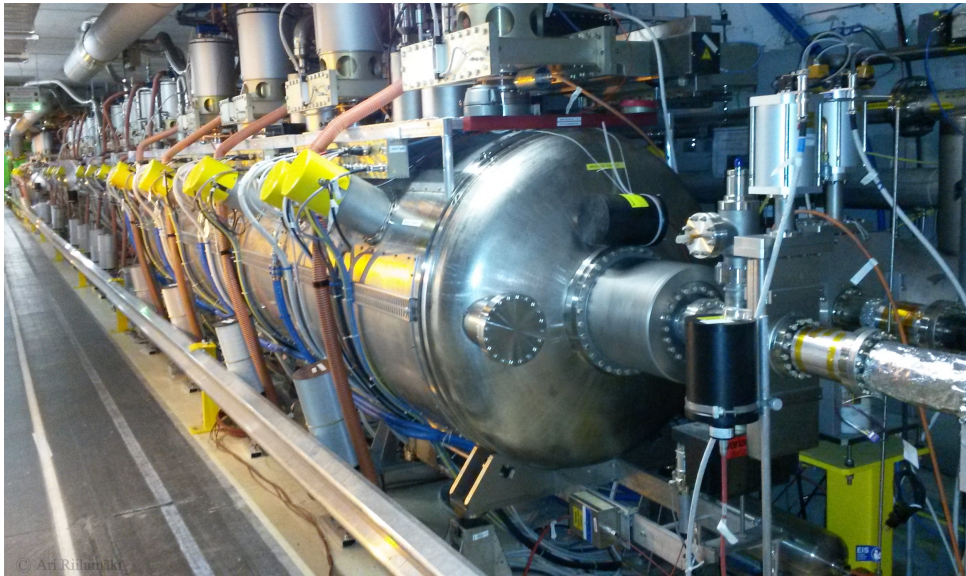


Figure 2: Cryomodules containing the RF cavities.

After about 15 minutes of acceleration in the LHC, the protons are brought to a collision course in four interaction points for seven different experiments. The largest experiments are ATLAS, CMS, ALICE and LHCb. In 2012 ATLAS and CMS announced they had observed a new particle consistent with the properties of Higgs boson that validates the Standard Model mechanism of mass generation. Even still, more precise measurements are needed to determine its properties and interactions with other particles. This requires the increase of luminosity, which in accelerator physics is a measure of the performance of the accelerator and describes how many events N are occurring in a certain time t to interaction cross section σ as^[1]

$$L = \frac{1}{\sigma} \frac{dN}{dt}. \quad (1)$$

Luminosity has units of events per time per area and it is dependent on several beam parameters such as beam width, particle flow rate etc. Increasing the luminosity allows more data to be collected from the experiments for analysis. The LHC design luminosity is $10^{34} \frac{1}{\text{scm}^2}$, which gives an estimate of roughly 600 million collisions per second in the LHC^[1]. The integrated luminosity expresses the cumulative luminosity over a given time period and it gives a measure of the total amount of events.^[1]

The High-Luminosity Large Hadron Collider (HL-LHC) project aims to increase the integrated luminosity by a factor of 10 over the LHC's design value^[1]. This will allow more precise measurements for the Higgs boson and enable to observe more rare processes and possibly discover other new particles. The design study for the HL-LHC has been finished and the objective is to have the HL-LHC operational after 2025. Preparations are underway and currently the LHC Injectors Upgrade (LIU) project is ongoing so that the injector chain can reach the new requirements of intensity and reliability for delivering the beams to the HL-LHC. The project includes the replacement from LINAC2 to LINAC4 and significant improvements to PSB, PS and SPS.^[6,7]

1.2 Vacuum at CERN

Although CERN is mainly dedicated to particle physics, its premises are also used for a variety of other fields of engineering and physics as well. These fields work in harmony to provide better designs for magnets, detectors, vacuum systems etc. Vacuum technology has been developed by CERN since its beginning. The Intersecting Storage Rings (ISR) brought many breakthroughs in the field due to its strict vacuum requirements in the interaction areas. Nowadays, the Vacuum, Surfaces and Coatings (VSC) group in the Technology Department is responsible for the design, construction, maintenance and operation of vacuum systems in the accelerators and detectors in CERN.^[8]

The vacuum environment serves an indispensable role in particle accelerators. Ultra high vacuum conditions are necessary to minimize gas-beam interactions, which are responsible for several harmful effects in particle accelerators that can reduce the beam lifetime and increase the background in the experiments^[9]. The elastic scattering with a residual gas molecule changes the trajectory of the particle and inelastic scattering decreases the speed of the particle. In both cases the particle could be lost if the change in trajectory or speed is too large to be corrected. Because both scattering processes also depend on the interacting gas species, residual gas composition in the beam pipes is also important. Reducing the number of gas-beam interaction events also lowers the radiation hazards related to stray particles.^[5,9]

Different vacuum criteria apply for different accelerators and experiments. The most demanding conditions are required for example in ELENA (Extra Low ENergy Anti-proton facility) and in LHC. In 2008 the LHC became one of the biggest operational vacuum systems in the world with over 104 kilometers of piping under vacuum. LHC has three major vacuum systems, one for the beam pipes, and two vacuum systems for insulating the helium distribution lines and the cryogenic magnets. The most advanced vacuum technology is needed for the beam pipes, where the pressure is in the order of 10^{-11} to 10^{-10} hPa. In the arcs these pressures are maintained by cryogenic pumping. The beam pipes are kept at cryogenic temperatures so that most of the gases are physisorbed on the walls. In the room temperature sections, mostly in the eight long straight sections (LSS),

the UHV is maintained usually with ion pumps and non evaporable getter (NEG) coatings which transform the beam pipe from a gas source into a gas sink by adsorbing the gas molecules on the surface.^[1,8]

External pumping with turbomolecular pumps and primary pumps in the LHC is only needed for the initial pumpdown from atmospheric pressures if the system has been vented for maintenance or safety reasons. The pressures that can be achieved during the pumpdown process depend on several factors including the selected venting gas, materials and pumpdown time. If the system has been exposed to air, in situ heating process known as bakeout is usually required. Heating the system over 120°C for several hours effectively removes the gas molecules, especially water, adsorbed on the vacuum chamber walls. Pressure profiles in the LHC without the presence of beam generally depend on outgassing of different materials, distribution of pumps and their pumping capacity for different gases and the local geometries. For example a higher conductance allows molecules to move freely, which allows non-getterable gases like methane to reach the ion pumps in the NEG coated sections.^[1,10]

Dynamic vacuum

In particle accelerators, especially in the LHC, dynamic vacuum effects needs to be considered explicitly. This non-thermal outgassing is mostly due to beam induced energetic particles hitting the surface, where they release all or part of their energies. As a consequence, molecules adsorbed on the surface are desorbed if the released energy is enough to break the bond between the surface and the molecule.^[11]

The beam induces a variety of other effects as well. For example, synchrotron radiation exposes the vacuum chamber walls to significant heat loads. In the LHC for example, the superconducting magnets need to be protected from the heat loads with a specially designed racetrack shaped beam screen which is positioned inside the beam pipe. It has two cooling tubes on its sides where pressurized helium keeps the temperature of the beam screen around 5 K and 20 K. The inside of the beam screen has a thin layer of oxygen free high conductivity copper to transfer the beam induced image currents without producing resistive heat loads for the magnets.^[11,12]



Figure 3: Beam screen sample of the LHC.

For the vacuum point of view, photon stimulated desorption (PSD) presents a much more detrimental effect than heat loads. When synchrotron radiation photons hit the surface of the beam screen, they can release molecules adsorbed on the surface. The number of desorbed molecules N_d is directly proportional to photon flux N_γ as $N_d = \eta_\gamma N_\gamma$, where η_γ is the molecular desorption yield usually expressed in units of desorbed molecules per photon. It depends on several factors including the surface material, adsorbed gas, temperature and previous exposure to synchrotron radiation also known as the beam scrubbing effect. In the superconducting magnets the vacuum is maintained by cryogenic pumping, so that the desorbed molecules are pumped by the cold surfaces. This presents a problem as the pumped molecules can re-desorb by photons with a much higher yield. This recycling of the residual gas molecules can be reduced by pumping slots that are visible on figure 3 on the flat parts of the beam screen. A fraction of the desorbed molecules can travel through the slots to the cold beam pipe wall where they are removed from recycling as photons can not reach the beam pipe walls.^[11,13]

Ion stimulated desorption is a similar phenomena as PSD that also induces pressure rises in the machines. The beam particles ionize residual gas molecules which are repelled by the positively charged beam and hit the surface with energies in the range of 100 eV up to some keV^[11]. The molecular desorption yield η_i is also proportional to the number of impinging particles, but is expressed in units of molecules per ions. It also depends on same factors as PSD, but is also a factor of the type of ion interacting. As molecules are desorbed from the surface, the pressure rises accordingly, which leads to more molecules being ionized by the beam, which in turn increases ion stimulated desorption. This self-amplifying process can result in an uncontrolled pressure runaway that leads to the loss of the beam.^[11,12]

Another self-amplifying effect that can occur with electrons is known as beam induced electron multipacting. Free electrons in the accelerators can be produced by synchrotron radiation, ionization of the residual gas molecules, field emission etc. The bunched beam provides a changing electric field that accelerates the electrons, which upon impact with the chamber walls release secondary electrons. If the secondary electron yield (SEY) exceeds unity and the electrons can oscillate in synchronism with the changing electric field, the number of electrons increases exponentially. For example the nominal SEY threshold in the LHC is 1.3^[14]. This formation of the so called electron cloud has many harmful effects, one of which is the electron stimulated desorption (ESD) that can produce high pressure spikes.^[14,15]

1.3 Introduction to vacuum technology

The concept of vacuum is normally understood as a space void of matter. The term absolute vacuum was introduced for small volumes completely devoid of any molecules that could exist for example in intergalactic space. However, modern physics points that even absolute vacuum is not truly empty, at least in terms of energy^[16]. A vacuum energy of unknown nature permits particles to be spontaneously generated for very short time intervals by fluctuating quantum fields^[16]. Often a more practical usage of the term vacuum is needed and for the purpose of this thesis, the term vacuum is used for a confined space containing fewer particles than the surrounding environment. Using this common definition, vacuum comprises pressure regimes that range over fifteen orders of magnitude. These regimes are referred with labels given in table 1.

Regime	Pressure range (hPa)
Low (rough) vacuum	1 – 1000
Medium vacuum	$10^{-3} - 1$
High vacuum	$10^{-8} - 10^{-3}$
Ultra high vacuum (UHV)	$10^{-12} - 10^{-8}$
Extreme high vacuum (XHV)	$< 10^{-12}$

Table 1: Vacuum pressure regimes.^[15]

The standard (SI) unit of pressure is pascal (Pa) which is defined as one newton per square meter. However, this concept of force per unit area is rarely useful for vacuum systems and more relevant concepts are mean free path or molecular density which are explained later. Moreover, the units of torr and mbar are still used for historical and practical reasons as it is easier to compare results. Because $0.76 \text{ Torr} \approx 100 \text{ Pa}$ and $1 \text{ mbar} = 1 \text{ hPa}$ ^[17], the pressure is expressed in this work in hPa as it is equivalent to mbar, which is the preferred unit in the VSC group in CERN.

Kinetic theory of gases

The behaviour of gases at low pressures can be understood with the kinetic theory of gases. The theory is based only on a few fundamental assumptions. Gas is thought of as a very large number of freely moving particles that hit the walls of the chamber and each other but other interactions are not considered. Collisions are presumed elastic and the particles are expected to be very small compared to the distance of the particles. The microscopic motion of individual particles is inherently related to the macroscopic properties such as pressure and temperature.^[18]

Ideal gas law

The most well-known equation of state in the kinetic theory of gases is the ideal gas law. It was first stated as a combination of empirical observations, although it can be derived from the kinetic theory as well as^[18]

$$pV = Nk_{\text{B}}T, \quad (2)$$

where p is pressure, V is the volume of the gas, N is the number of particles, T is the absolute temperature and k_{B} is the Boltzmann constant. In vacuum technology the product pV is called the quantity of gas, which at given temperature yields the energy of the gas or the number of particles when divided by $k_{\text{B}}T$. Unless stated otherwise, the quantity of gas is given at standard room temperature $T = 296 \pm 3 \text{ K}$.^[17]

Particle collisions

Due to the constant occurrence of collisions the particles have a nonuniform distribution of velocities. This is called the Maxwell-Boltzmann velocity distribution, from which the mean velocity $\langle v \rangle$ of the particles can be calculated as^[16]

$$\langle v \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi m}}, \quad (3)$$

where m is the mass of the particle. The mean velocity can be used to obtain the flux of particles hitting the surface, which is called the impingement rate^[18,19]

$$I = \frac{N}{4V} \langle v \rangle = \frac{p}{\sqrt{2\pi m k_B T}}. \quad (4)$$

The impingement rate I can be further used to estimate the monolayer formation time t_θ , which is another useful concept in vacuum technology. It gives an estimate of the time until the surface is covered completely by one layer of the impinging particles as^[19]

$$t_\theta = \frac{N_{\text{mono}}}{I}, \quad (5)$$

where N_{mono} is the number of molecules in a monolayer. It depends on the surface and the gas species, but is generally in the order of 10^{15} molecules/cm²^[18]. The formation time is calculated with the assumption that all of the impinging particles stick to the surface. This is rarely the case as the probability of the particle sticking to the surface, also known as sticking factor s , is between 0 and 1. However, in many cases the sticking factor is indeed close to unity, so considerations of surface saturation or cleanliness is often done with the monolayer formation time.^[16,19]

Another informative concept is the mean free path λ of the particles, which is the mean distance a particle travels before it collides with another particle. Table 2 shows the relations between the concepts.

Pressure (hPa)	Mean free path	Molecular density (cm ⁻³)	Monolayer formation time
1000	70 nm	3×10^{19}	3 ns
1	50 μ m	4×10^{16}	2 μ s
10^{-3}	5 cm	4×10^{13}	2 ms
10^{-6}	50 m	4×10^{10}	2 s
10^{-9}	50 km	4×10^7	1 hour
$< 10^{-12}$	$> 5 \times 10^4$ km	$< 4 \times 10^3$	> 100 hours

Table 2: Mean free paths, molecular densities and monolayer formation times at various pressures for N₂ molecules at 20 °C.^[19]

The mean free path can be derived from the Maxwell-Boltzmann distribution when the particles are assumed as hard spheres with a kinetic diameter d . The mean free path is then given as^[16]

$$\lambda = \frac{k_B T}{\sqrt{2} \pi d^2 p}. \quad (6)$$

The mean free path is descriptive concept even for macroscopic phenomena. Properties like viscosity and thermal conductivity become less influential when the mean free path decreases. This is particularly pronounced in gas flow properties.

Gas flow

Gas flow characteristics present an important part in vacuum technology. When a chamber is evacuated, the initial gas inside has to flow from the chamber to the pumps that are often connected by pipes of varying lengths that resist the flow. Three different flow regimes are generally applied in vacuum technology and the Knudsen number K_n can differentiate these regimes quantitatively with^[16]

$$K_n = \frac{\lambda}{d}, \quad (7)$$

where λ is the mean free path and d is the limiting dimension of the chamber or tube. Table 3 shows regimes according to the Knudsen number.

$K_n < 0.01$	viscous flow
$0.5 > K_n > 0.01$	transitional flow
$K_n > 0.5$	molecular flow

Table 3: Flow regimes distinguished by the Knudsen number.^[18]

A low Knudsen number indicates that the pressure is high and the mean free path of the particles is much lower than the chamber's dimensions and particle-particle collisions are dominant. This is called viscous flow because the gas behaves as a continuum. A high Knudsen number implies that particles rarely interact with each other and predominantly collide with the chamber walls. A macroscopic flow behaviour can only be estimated as an average of a single particle behaviour. This regime is called molecular flow. The medium regime, where mutual collisions of particles happen about as often as with the chamber walls, is called transitional flow or Knudsen flow.^[18]

Conductance

To understand gas flow and pressure distribution in vacuum systems the concept of conductance is needed. It gives a quantitative measure of the ease of flow of a vacuum component. The higher the conductance is the easier the gas flows through the component. The following equations apply in the molecular flow regime. The definition of conductance is^[20]

$$C = \frac{q_{th}}{p_1 - p_2}, \quad (8)$$

where p_1 is the upstream pressure, p_2 is the downstream pressure and q_{th} is the throughput, which gives the quantity of gas that flows through the component within given time interval, often expressed in units of $\frac{\text{hPa}\cdot\text{l}}{\text{s}}$. The conductance is analogous to the electrical conductance, so the effective conductance of N vacuum components connected in series is:^[20]

$$\frac{1}{C_{\text{series}}} = \sum_{n=1}^N \frac{1}{C_n} \quad (9)$$

and for components that are parallel the effective conductance is^[20]

$$C_{\text{parallel}} = \sum_{n=1}^N C_n. \quad (10)$$

The conductance of vacuum components depends on the flow regime. For example in a viscous flow the conductance is proportional to the mean pressure whereas in molecular flow the conductance of the component is independent of the pressure. Here we restrict to molecular flow regime that is present in high and ultra high vacuum systems. Sometimes in these systems a very low conductance with known value is applied in order to measure the throughput more precisely. Conductance of an orifice depends on the surface size A and mean thermal velocity and it is given as^[21]

$$C = A \sqrt{\frac{k_B T}{2\pi m}}, \quad (11)$$

where m is the mass of the molecule. Table 18 in Appendix B shows conductances at 25 °C for the most common residual gas molecules for an orifice with 1 cm diameter.

Pumpdown

Pumping speed S describes the pump's capability to remove gas from the vacuum system. It has the same units as conductance and because pumps are often connected to the vacuum systems via some component with a conductance, the effective pumping speed S_{eff} can be expressed as^[16]

$$\frac{1}{S_{\text{eff}}} = \frac{1}{S_{\text{pump}}} + \frac{1}{C_{\text{eff}}}, \quad (12)$$

where S_{pump} is the actual pumping speed of the pump and C_{eff} is the conductance of the components between the pump entrance and the chamber. Usually the conductances are practically impossible to determine analytically and therefore simulations or measurements are required to determine the conductance or the effective pumping speed. Even when the conductance is known, the backstreaming of particles from the downstream part can occur. In this case the actual pumping speed S_{act} in molecular flow regime can be measured with the pressures on both sides of the component as^[18]

$$S_{\text{act}} = C \left(1 - \frac{p_1}{p_2} \right), \quad (13)$$

where p_1 is the pressure on the downstream side and p_2 is the pressure in the upstream part. The pressures p_1 and p_2 are not considered here as being close to the component with a conductance, but some distance away where the conditions are isotropic^[20]. Throughput q_{th} is somewhat easier concept to visualize as it gives the quantity of gas pumped away in a unit time. It relates to pumping speed and pressure as^[16]

$$q_{\text{th}} = Sp. \quad (14)$$

With these equations, it is possible to derive a general equation for pressure in a simple vacuum system with a total gas load Q_t , volume V and pump with an effective pumping speed S_{eff} as^[16]

$$V \frac{dp}{dt} = Q_t - pS_{\text{eff}}. \quad (15)$$

This equation is basically a conservation of mass equation. It states that the net change of quantity of gas in the system equals the gas load that is coming to system minus the quantity of gas being pumped away in units of $\frac{\text{hPa}\cdot\text{l}}{\text{s}}$. The gas load Q_t includes factors like outgassing, leaks and virtual leaks, that are leaks of trapped gas from some volume within the vacuum chamber, thus giving a false signal of a leak from atmosphere. Outgassing Q means the release of gas from a material and it is explained in more detail in chapter 2. Under the assumption of no leaks, outgassing is the main limiting factor in reaching lower pressures. Often the term outgassing rate q is more useful as it is more informative regarding to the surface area A of which the outgassing originates:

$$Q = qA. \quad (16)$$

With outgassing rate, it is easier to compare materials and design applicable components by minimising the use of high outgassing materials. The outgassing rate is expressed in units of $\frac{\text{hPa}\cdot\text{l}}{\text{s}\cdot\text{cm}^2}$ in this work so that results are comparable to literature and CERN databases. Conversion to $\frac{\text{Pa}\cdot\text{m}}{\text{s}}$ is possible by multiplying units of $\frac{\text{hPa}\cdot\text{l}}{\text{s}\cdot\text{cm}^2}$ by a factor of thousand. The pumpdown of a vacuum system to UHV range requires several stages. First, the volume of gas in the chamber has to be evacuated. At this stage, the gas load Q_t is assumed negligible and equation 15 can be integrated to yield

$$p = p_0 \exp\left(-\frac{St}{V}\right), \quad (17)$$

where p_0 is the initial pressure. In the first phase the pressure drop is exponential to pressures of 10^{-4} to 10^{-3} hPa until the assumption of negligible gas load is no longer valid. If the vacuum system is leak tight, outgassing becomes the main source of gas load.

2 Theory of outgassing

Outgassing means the spontaneous evolution of gas from a solid or liquid in a vacuum. This complicated vacuum phenomenon includes several processes: release of gas from the surface, diffusion from the bulk and permeation through the walls of the vacuum vessel. Further source of outgassing comes from materials that have a high vapour pressure resulting in vaporisation or sublimation of atoms or molecules^[22]. All of these phenomena limit the lowest achievable pressure, increase the pump-down time and present a source of impurities in experiments and industrial processes. Outgassing depends on the material, surface area, the physical and chemical nature of the surface, porosity, thickness, temperature, surface treatments, pump-down time and the history of the sample. For example, most metal samples kept at atmosphere before vacuum use, will release mainly water vapor, which extends the pumpdown time to the desired pressure significantly. Outgassing is often distinguished^[17] from desorption which means the release of gas from the surface of the material.^[16,17]

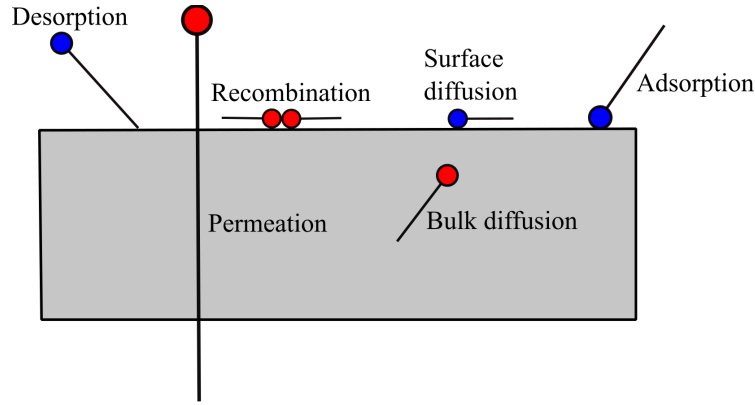


Figure 4: Phenomena contributing to outgassing.

The intrinsic outgassing rate describes the quantity of gas leaving per unit time per a unit of geometric surface area. In this definition, the term geometric surface area means the visible area without any corrections for surface roughness, machine finish or porosity. The measured outgassing rate usually differs from the intrinsic outgassing rate because of readsorption on the surface of the vacuum system. The readsorption rate depends on the gas species, surface areas, materials of the system and also on the measurement method^[17]. Readsorption is always present in conventional measurement methods. However, the measured rates can nearly equal the intrinsic outgassing rates under particular conditions. For example Komiya et al.^[23] have used a direct-molecular-beam method to measure directly the particles coming from the sample using a quadrupole mass spectrometer isolated from the rest of the vacuum chamber by a cylindrical cryocollimator and a coaxial cover cooled with liquid nitrogen. The method is rarely applied because of its complexity and the requirement for cryogenic cooling.^[17,22]

2.1 Desorption

The initial outgassing in a vacuum system is mostly from desorption of adsorbed gases. The kinetic approach to adsorbed gas species on the surface explains the desorption process. Desorption occurs when an adsorbed gas species can escape the adsorption well by acquiring enough energy from the thermal vibrations of the surface atoms. Thus, the adsorption of gases to surfaces needs to be understood in order to explain desorption. Adsorption is generally divided into physisorption and chemisorption according to the strength of the interaction between the gas species and the surface. In physisorption the interaction is due to van der Waals forces, so the interaction is weak and the binding energies are typically 10 - 100 meV per molecule or atom. The adsorption is defined conventionally as chemisorption if the binding energy is over 0.5 eV. In this case, the gas atom or molecule can form chemical bonds with the surface atoms.^[19]

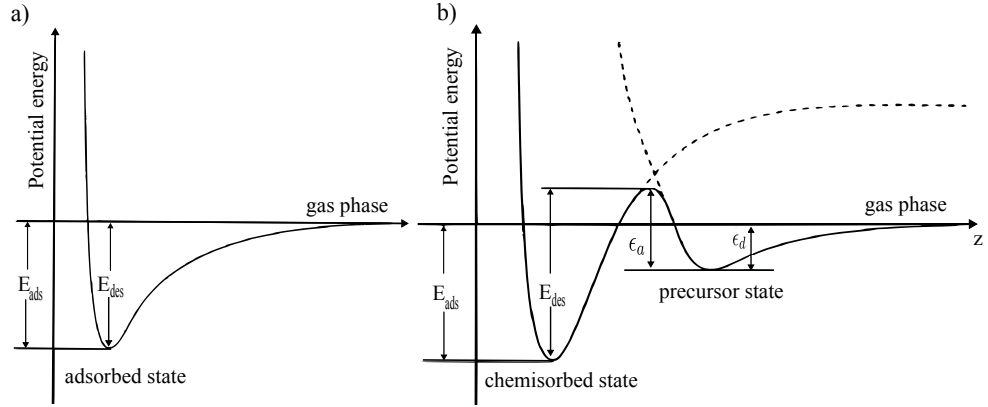


Figure 5: Potential energy diagrams for a) simple non-activated adsorption and b) precursor-mediated activated chemisorption. Figure drawn based on graphics from source^[19].

Chemisorption often involves a precursor state, in which the adsorbate is first trapped in a lower potential well before it enters the final adsorption state. The transition from the precursor state to the chemisorbed state may also include the dissociation of the molecule into atomic species. The states are separated by an activation barrier as seen in figure 5. If the barrier ϵ_a is higher than ϵ_d the process is called activated chemisorption and for $\epsilon_a < \epsilon_d$ it is called non-activated chemisorption. The adsorbed species have to surmount the desorption energy E_{des} in order to leave the surface. The desorption rate r_{des} , which has the same unit as outgassing rate, can be written as^[19]

$$r_{des} = \sigma_{des} f_{des}(\theta) \exp\left(\frac{-E_{des}}{k_B T}\right), \quad (18)$$

where σ_{des} is a desorption coefficient that takes into account steric and mobility factors and $f_{des}(\theta)$ is the coverage dependent function. Assuming identical adsorption sites without interactions between the adsorbates, the desorption rate is described by the Polanyi-Wigner equation^[19,22]

$$r_{des} = k_{0,n} \theta^n \exp\left(\frac{-E_{des}}{k_B T}\right), \quad (19)$$

where k_n the desorption rate constant and n is the kinetic order. For $n = 0$, the desorption rate is coverage independent so it is constant at given temperature. In the first-order kinetics the rate is directly proportional to θ and the rate constant can be approximated by the atomic frequency of the crystal lattice $k_{0,1} \approx 10^{13} \frac{1}{s}$. From here it is possible to estimate the residence time τ of a particle on the surface as^[19]

$$\tau = \frac{1}{k_{0,1}} \exp\left(\frac{E_{\text{des}}}{k_B T}\right). \quad (20)$$

From equation (20) it is possible to infer that adsorbates with low desorption energy will be desorbed rapidly after the pumpdown begins. These physisorbed gases usually include oxygen and nitrogen molecules in stainless steel vacuum systems. Strongly bound gases have very long residence times and therefore don't contribute to the outgassing significantly. Gases that belong in the intermediate range pose a much bigger concern since they can not be expelled from the surface in a reasonable time. These gases include water vapour, most organic species and weakly chemisorbed species such as CO and CO₂^[18]. In reality the surface is more complex and contains many adsorption sites presenting many desorption energies. This explains e.g. why water desorption follows a power law with an exponent close to unity.^[22]

2.2 Diffusion

Diffusion presents another relevant outgassing mechanism besides desorption after most of the physisorbed and chemisorbed species have been desorbed. The amount of adsorbed particles is much smaller than the amount of dissolved particles because the number of sites available to dissolved particles in the bulk is large compared to the sites at the surface so diffusion poses a more persisting concern^[16]. Diffusion means the movement of particles from high concentration regions to low concentration regions. Particles can jump between interstitial sites, lattice defects or along the grain boundaries. Every jump requires an activation energy E_{diff} . The net movement of particles is described by the Fick's first law:^[16]

$$\vec{j}_{\text{diff}} = -D \nabla \rho, \quad (21)$$

where $\vec{j}_{\text{diff}}$ describes the number of particles flowing through a unit area during a unit time interval, ρ is the number density of absorbed particles and coefficient of diffusion D is

$$D = D_0 \exp\left(-\frac{E_{\text{diff}}}{k_B T}\right), \quad (22)$$

where D_0 is the maximal diffusion coefficient. Fick's second law describes how the concentration changes over time as

$$\frac{\partial \rho}{\partial t} = D \nabla^2 \rho. \quad (23)$$

Hydrogen atoms are very small and light so they have a high solubility in most metals^[22]. Thus, significant amounts of hydrogen from the atmosphere can dissolve into the bulk when it is molten during the production

process. In vacuum, the hydrogen diffuses out and is usually the main source of gas in baked UHV systems^[16]. Hydrogen is dissolved as single atoms in metals and once they reach the surface, they must be recombined to leave the surface as molecular hydrogen. Assuming instant recombination, diffusion in vacuum chamber walls can be modelled with the classical example of a thin metal sheet in a vacuum with a thickness $2d$, uniform initial number density, and boundary condition $\rho(\pm d) = 0$ at $t = 0$ s. Jousten^[16] provides the solution for the flow of atoms j_{diff} to the surface as

$$j_{\text{diff}}(\pm d) = \frac{2D\rho_0}{d} \sum_{i=0}^{\infty} \exp\left(-\frac{(2i-1)^2\pi^2}{4d^2}Dt\right), \quad (24)$$

where ρ_0 is the initial number density. The value $t_c = \frac{4d^2}{\pi^2 D}$ describes the characteristic time constant for diffusion and equation (24) can be simplified as:^[16]

$$j_{\text{diff}}(\pm d) \approx \frac{2D\rho_0}{d} \exp\left(-\frac{t}{t_c}\right), \text{ for } t \gg \frac{t_c}{2}, \quad (25)$$

$$j_{\text{diff}}(\pm d) \approx \frac{2D\rho_0}{d} \sqrt{\frac{\pi t_c}{16t}}, \text{ for } t \ll \frac{t_c}{2}. \quad (26)$$

From equations (22), (25) and (26) we see that diffusion is strongly temperature dependent. The depiction is of course valid for other materials and molecules. For example, water molecules have high solubility and mobility in polymers so diffusion becomes quickly the prevalent outgassing mechanism.^[16,24]

The diffusion models apply if desorption from the surface is far more quicker than diffusion from the bulk. This is called diffusion limited outgassing. However, for hydrogen to desorb from the surface, it needs another hydrogen atom to recombine and desorb^[22]. If the amount of free-moving hydrogen on the surface is small, recombination becomes less probable and recombination step would be the limiting factor in outgassing rates. In this case, the assumption of zero surface density is inaccurate, and the diffusion equations have to be solved with a boundary condition where the surface density and recombination are taken into account.^[16]

2.3 Permeation

The diffusion process only considers the movement of particles from the bulk of the solid to the surface and from there to vacuum. However, in a typical vacuum system the other side of the surface is also exposed to air, so it is important to consider which gas species could penetrate the walls and propagate into the vacuum. This phenomenon is called permeation and it includes three steps: the adsorption of a particle usually on the high-pressure side, diffusion to the other side of the vessel wall and desorption from the surface. If permeation is diffusion limited, the permeation rate j_{perm} depends on the adsorption kinetics. Gas molecules like N_2 and H_2O do not dissociate on the surface and the permeation rate is^[16]

$$j_{\text{perm}} = \frac{K_s D}{2d} (p_{\text{atm}} - p_{\text{vac}}), \quad (27)$$

where K_s is the solubility that describes the materials' ability to get certain types of gases from the surroundings and has a similar form as the diffusion constant:^[16]

$$K_s = K_{s0} \exp\left(-\frac{E_s}{k_B T}\right). \quad (28)$$

If the molecules dissociate on the surface, like hydrogen molecules, then the permeation rate is

$$j_{\text{perm}} = \frac{K_s D}{2d} \left(\sqrt{p_{\text{atm}}} - \sqrt{p_{\text{vac}}} \right). \quad (29)$$

Assuming diffusion limited permeation, the stationary permeation rate of atmospheric hydrogen to a vacuum system with 2 mm walls at 23 °C is about $8.1 \times 10^{-15} \frac{\text{hPa}}{\text{s cm}^2}$ [25], which compared to typical outgassing rates is very low. It should be noted that surface effects e.g. recombination limit the permeation additionally and that the surface oxide layer also plays a significant role as a barrier in metals [25]. Permeation is of concern mostly in very thin walled vacuum systems or with systems having viewports. [16]

2.4 Mitigating outgassing

It is necessary to inhibit or temporarily increase one of the processes contributing to outgassing in order to reduce it. As we saw in chapter 2.1, desorption increases rapidly by elevating the temperature. Therefore, temporarily increasing the temperature from about 100 °C up to 400 °C is a standard procedure, called bakeout, in vacuum systems to expel the adsorbed particles from the surface resulting in lower outgassing rates once the system is cooled down. Concurrently, the bakeout also increases the diffusion that lowers the amount of dissolved particles in the bulk and once the system is cooled down the number density settles to a lower value at the surface. [16]

For unbakeable UHV components or materials the surface treatments are the most preventive measures that can be taken. Cleaning processes are an integral part of vacuum technology and suitable cleaning has been devised for many materials. Majority of these processes use organic solvents that pose safety and environmental hazards and new procedures are constantly under testing for UHV components [26]. Surface treatments can also aim to reduce the roughness by machining or electropolishing as smooth surfaces provide less adsorption sites. Adsorption of gases can also be mitigated for already installed components and vacuum systems by venting with an inert gas before exposing them to atmospheric gases [10].

Mitigating hydrogen outgassing in metals is of special interest since they are the most commonly used materials in UHV systems. Hydrogen outgassing rates can be reduced somewhat by in situ bakeouts. Elevated temperatures increase the diffusion of hydrogen which leads to the depletion of hydrogen from the bulk. Even greater improvement can be obtained applying an ex situ high temperature treatment in a vacuum furnace. At CERN, this treatment known as vacuum firing is typically carried out at 950 °C for 2 hours [27]. Another option to vacuum firing is a medium-temperature air-bakeout. Park et al. [28] reported 30 % lower outgassing rates for air-baked samples compared to in-vacuum baked for 1.65 mm thick stainless steel tubes. Diffusion during the heat treatments obviously reduces the outgassing in both cases, but the difference can be partly attributed to the formation of thick, iron-rich oxide layer, which acts as a barrier [28].

Lastly, some reports [29] of unusual outgassing results from stainless steel samples question whether diffusion limited or recombination limited models are satisfactory. Berg [30] also highlights the role of hydrogen traps in metals. Heterogeneities, such as dislocations and grain boundaries, can hold a significant amount of hydrogen even though they comprise less than 0.1 % of the lattice sites [30].

3 Vacuum instrumentation

This chapter offers an introduction to relevant vacuum instrumentation. A special emphasis is given to instrumentation used in the measurement systems described in chapter 4. General information about vacuum pumps, pressure gauges and residual gas analysers are given. Specific information and data such as description of the calibration procedure and sensitivity factors are given in the appendices A, B and C.

3.1 Vacuum pumps

Vacuum pumps are used to obtain and maintain the vacuum in the chamber. The pumpdown from atmospheric pressure to ultra high vacuum means a pressure change of over 13 orders of magnitude, which is beyond the pumping capacity of any single pump. This means that the pumpdown process happens in stages, where different kinds of pumps are used according to their properties and pumpdown stage. The pumps can be categorized roughly to transfer pumps that remove gas molecules permanently from the system and to capture pumps that retain the gases by condensation, sorption or other mechanism within the system.^[18]

Primary pumps

Primary pumps are used for the initial evacuation from atmosphere to about 10^{-3} hPa - 10^{-1} hPa. The most common type in CERN is the rotary vane pump, which is a transfer pump that uses a rotating vane that traps, compresses and transfers the gas from the inlet port to the outlet port where it exits the pumping cycle through an exhaust discharge valve. The distance between the vane and the pump wall is typically sealed with oil that can be supplied by an integrated oil pump. The experimental systems described in chapter 4 use a two-stage rotary vane pumps so that the first pump stage is backed by a second stage which increases the performance. Furthermore, the pressurized oil is fed only to the low vacuum stage, which enhances the performance and reduces backstreaming of oil vapor into the system. In case of a power cut, the rotary vane pumps are connected in series with a safety valve.^[31]

Turbomolecular pumps

Turbomolecular pumps (often abbreviated as turbopump) transport gases out of the system by giving momentum to the particles in a preferred direction so they are also transfer pumps. Turbopumps require a primary pump since they can only be utilised below 1 hPa and as the name implies they operate best in the molecular flow regime down to 10^{-10} hPa^[19]. The transport of particles is achieved by rapidly rotating blades with a certain pitch so that particles gain momentum towards the outlet. The speed of the blade must be comparable to the particle speed, otherwise the particle may pass without being struck, therefore the rotation frequency is usually in the range of 900–1500 Hz. Between the sets of rotating blades are stationary stator blades and each of these rotor-stator pair forms a compressor stage. The total compression ratio is optimised by having an open blade configuration at the inlet providing high pumping speed, and compact blade structure closer to the outlet. After the pressure reaches a range below 10^{-10} hPa, turbopumps may begin to limit the achievable vacuum because their compression ratio for hydrogen is quite low. At this stage it is possible to isolate the pump from the system with a valve.^[18]

Sputter-ion pumps

Sputter-ion pumps, commonly referred as ion pumps, belong to the capture pump category and they can reach pressures in the range of 10^{-11} hPa. The major advantages of ion pumps is their ability to pump different gases, cleanliness and the ability to withstand high temperature bakeouts. Their pumping mechanism relies on both sputtering of a getter material in a gas discharge and implantation of ions from the gas discharge. The normal diode configuration of an ion pump consists of two cathode plates made of titanium, which are situated close to the open ends of the short stainless steel anode tubes. A magnetic field in the range of 0.1 T to 0.2 T is applied parallel to the tube's axes and a voltage of about 6 kV is applied between the cathodes and the anodes.^[16,19]

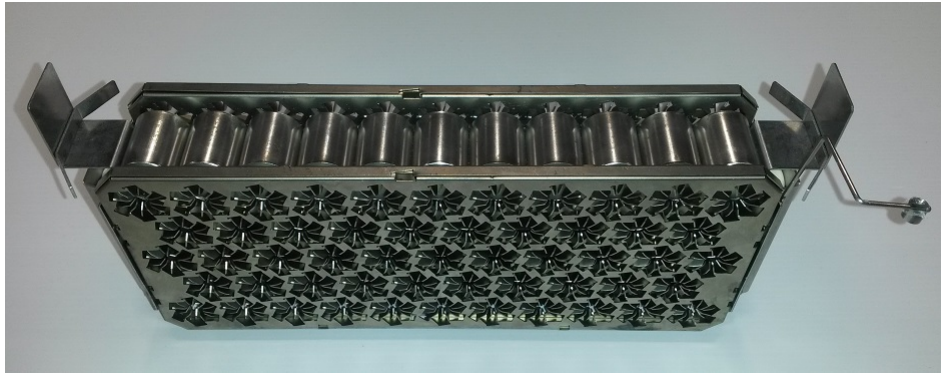


Figure 6: Arrangement of the anode tubes in the ion pump

The pumping is initiated by electrons emitted from the cathode plates which accelerate in the electric field and begin to move in helical trajectories towards the anode tubes due to the magnetic field. This trajectory increases the chances that the electrons hit and ionize residual gas molecules. The ionized molecules are accelerated by the electric field and strike the titanium cathode where they can penetrate the crystal structure up to 10 atomic layers depending on the size of the implanted molecule. Some ions, especially noble gas ions, can be reflected by the cathode if they become neutralized, but they can still be implanted at other spots due to their remaining high kinetic energy. During this process, the implanted ions sputter some of the cathode lattice atoms. These atoms can be deposited on the surrounding surfaces, primarily on the anodic tubes, where they form a getter film as pure titanium is very reactive. This getter effect is the prevalent pumping effect in an ion pump under normal HV conditions. Nevertheless, the implantation process is essential particularly for noble gases that are non-getterable.^[16]

Titanium sublimation pumps

Titanium sublimation pumps (TSP) are a very common type of evaporable getter pumps. The pumps contain titanium filaments, which can be heated to the sublimation temperature of the titanium with a high current of about 40-50 A. The sublimed titanium deposits on the chamber walls and forms a film of clean and chemically reactive titanium.^[32]

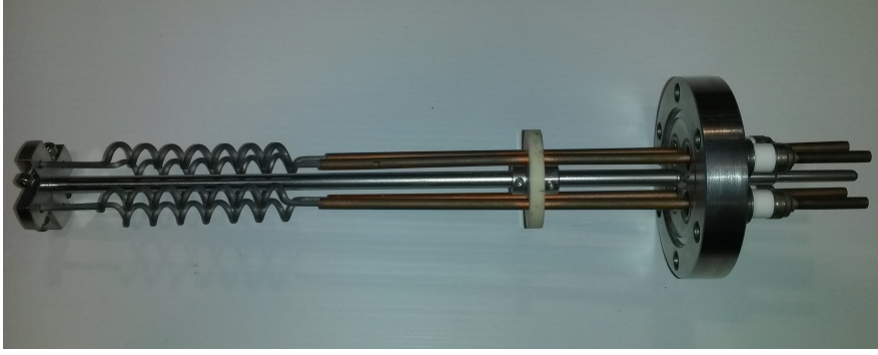


Figure 7: Titanium sublimation pump with 4 filaments.

The produced film can pump considerable amounts of residual gas due to different chemical reactions with titanium. Hydrogen molecules can dissociate on the surface and may diffuse into the bulk whereas water can dissociate to hydrogen atoms while the remaining oxygen atom forms titanium oxide. However, inert gases like methane and noble gases do not react with titanium and are therefore not pumped. Because of this titanium sublimation pumps are often used together with ion pumps. After a certain amount of gas reacts with the titanium film, the pumping speed is reduced and a new sublimation of titanium is required. The sublimation period depends largely on the gas load of the system and the presence of other pumps.^[32]

Non evaporable getter coating

Non evaporable getter (NEG) coatings developed at CERN^[33] are similar to titanium sublimation pumps, but as the name implies the getter material is not evaporated on the surfaces. Instead, the coating is applied ex situ to the chamber walls, where it can chemically bind most of the gases present in UHV. However noble gases and hydrocarbons are not pumped by the NEG, which means that NEG has to be used in conjunction with other pumps. The commonly used composition for NEG coating is an alloy of titanium, zirconium and vanadium.^[34]

The sticking factors are different for every gas and vary for specific gases due to the differences in surface roughness. For hydrogen the sticking factor varies from 0.6 to 3×10^{-2} corresponding to pumping speeds per area from 0.25 to $1.3 \frac{1}{\text{s cm}^2}$, while for CO it varies from 5 to $10 \frac{1}{\text{s cm}^2}$. At room temperature hydrogen is the only gas that can diffuse into the bulk, while other gases remain on the surface. The gases remaining on the surface decrease the sticking factors as the surface saturates. Especially CO can saturate the surface completely and inhibit the pumping of other gases completely. NEG also saturates upon exposure to air which leads to a formation of an oxide layer. Pumping speeds can be recovered by NEG activation upon which the NEG is heated to high temperatures under vacuum. During this process the gases on the surface dissolve into the bulk of the getter. This exposure-activation cycle is called aging of the NEG since it eventually fills the bulk with the gases and permits only a limited lifetime for the NEG.^[33]

3.2 Pressure gauges

Various methods for pressure measurement are needed as none of the methods cover the entire pressure ranges. The criteria for selecting a pressure gauge in addition to pressure range also depends on the required accuracy and repeatability. Pressures in the low vacuum region can still be measured directly on the basis of force, but other methods are required below 1 hPa^[21]. Properties that depend on the gas density can be utilised.

A Pirani gauge consists of a metal filament in vacuum which is connected to the outside electrical circuit. The filament can be heated by an electrical current and a thermocouple or a resistance thermometer can be used to measure the temperature of the filament. The filament loses heat depending on the pressure due to thermal conductivity. The higher the pressure the higher is the rate at which the filament loses heat to the residual gas. Therefore, the equilibrium temperature of the filament is dependent on gas pressure and because the resistance of the wire is temperature dependent, pressure can be estimated with the electrical circuit.^[21]

In ultra high vacuum conditions conventional pressure gauges can not be used because of very low gas densities. Ionization gauges measure the pressure indirectly by ionizing the gas molecules. There are two common types of ionization gauges compatible to measure pressures in the UHV range. In the hot cathode gauge (HCG) thermionic cathode emits electrons that are accelerated to the ionizing space. In the cold cathode gauges (CCG), the ionization of residual gas is caused by a electron plasma trapped and maintained by crossed electric and magnetic fields. In both gauges the collection of the positive ions and the resulting ion current in the circuit is measured to determine the pressure. The pressure reading is gas dependent because the gases have different ionization probabilities. Each gauge type has their own operation characteristics with assets and liabilities, hence careful consideration is required to select the most suitable gauge for the purpose of the system.^[35]

Cold cathode gauge

Cold cathode gauges use crossed electric and magnetic fields to sustain a gas discharge. The gauges in essence consists of an anode and a cathode. A high voltage of 2–6 kV is applied between the electrodes. A gas discharge ignites when an electron releases from the cathode by field emission, or any by other event such as cosmic ray or radioactive decay. The discharge builds up until new electrons are repelled by the space charge. The discharge is essentially pure electron plasma at pressures below 10^{-4} hPa. The ions generated by the discharge are slow in comparison and are quickly captured by the cathode. This current is proportional to pressure, which is the basis of cold cathode pressure measurement. The current depends on ionization probabilities and the displayed pressure is therefore gas dependent. The gas correction factors are given in table 4.^[21,35]

Gas	C
Air, N ₂ , O ₂ , CO	1.0
He	5.9
Ne	4.1
H ₂	2.4
Ar	0.8

Table 4: Cold cathode gauge IKR070 conversion factors with the formula: $p_{\text{eff}} = Cp_{\text{disp}}$.^[36]

In CERN, the term penning is sometimes used for cold cathode gauges even though the measuring principle in most gauges relies on the inverted magnetron principle. This is also the case in the experimental systems where cold cathode gauge of type IKR070 from Pfeiffer are used, which are capable to measure pressures in the range of 10^{-11} hPa^[36]. The inverted magnetron is assembled so that the anode pin is in the middle of the measurement volume and surrounded by the cylindrical cathode. A permanent magnet cylindrical ring is placed parallel to the pin outside the measurement chamber. This design increases significantly the electron paths and probability to ionize gas molecules.^[21]

Cold cathode gauges present fewer problems with outgassing as there are no hot filaments in the gauge. Degassing is also not necessary since there is no internal heating to cause local thermal outgassing. A pumping effect is a problem as gases are gettered on the surface of the cathode and falsify the measurement signal. However, the measured pumping speeds for CCGs are low compared to HCGs.^[35]

Bayard-Alpert gauge

Bayard-Alpert gauge (BAG) is a type of hot cathode ionization gauge. Electrons are emitted from the heated cathode filament and accelerated with a voltage of approximately 100 V towards a cylindrical anode mesh shown in figure 8. During the acceleration the electrons can collide and ionize the residual gas molecules. In the center of the anode is a thin wire functioning as a collector with the same potential as the anode. The measured collector current is used to determine the pressure. The emission current can be measured with the anode circuit, which can be used to evaluate the sensitivity of the gauge as it is proportional to the ion current.^[16,21]

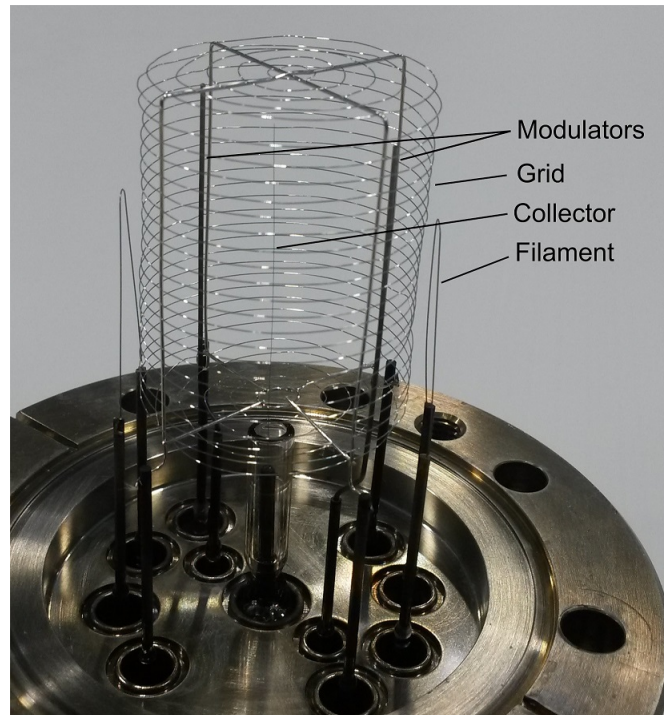


Figure 8: CERN Bayard-Alpert gauge configuration. The gauge has two filaments, but only one of them is activated during operation.

Measurement uncertainties arise from the pumping effect, X-ray effect or ESD ions. The pumping effect occurs when chemically active gases react with the hot filament^[38]. Electrons striking the anode grid cause x-rays to be emitted. Some of the X-rays strike the collector which causes photoelectric effect and the resulting current falsifies the collector current. Gas molecules that are adsorbed on the anode grid can be desorbed and ionized by the striking electrons. The energetic ESD ions can strike the collector and falsify the collector current. Both the X-ray and ESD effects can be minimised to certain extent by decreasing the collector thickness. ESD effect can also be mitigated by degassing the grid by electron bombardment during a bakeout.^[21,37,38]

Collector	Tungsten, $\phi = 0.05$ mm
Grid	Pt/Ir, $\phi_G = 35$ mm, wire $\phi = 0.13$ mm
Modulators	Molybdenum, $\phi = 0.7$ mm
Filament	Tungsten, $\phi = 0.18$ mm
Grid & Modulator potential	150 V
Filament potential	50 V
Collector potential	0 V

Table 5: Typical BAG specifications at CERN.^[39]

The CERN modulated BAGs have been developed in the 1970's to maximise the sensitivity and reduce the X-ray current^[39]. The modulators are used to determine in situ X-ray current and thus they allow a low pressure limit down to the upper range of 10^{-13} hPa^[39]. Table 5 presents the typical dimensions and operating potentials for the BAGs used at CERN. BAGs are more stable and accurate compared to cold cathode gauges, and BAGs are often used as a reference gauge for calibration^[21,35]. The BAGs used at the accumulation system were calibrated before installation. The sensitivity factors for H_2 and N_2 are $S_{N_2} = 38.2$ A/hPa and $S_{H_2} = 16.2$ A/hPa so H_2 equivalent pressures are a factor of 2.34 higher.

3.3 Residual gas analyzer

Residual gas analyzers (RGA) are used to measure the partial pressures of different gases in the vacuum systems. An RGA typically consist of an ion source, mass analyzer, detector and control and data-acquisition electronics. For UHV applications the open ion source design is similar to a total pressure gauge as it uses electron impact for ionizing the residual gas molecules. A filament is heated to temperatures where thermionic emission occurs. The electrons are accelerated from the filament towards the anode grid and pass through the mesh structures to the ionization region. The resulting ions are extracted by ion focus lenses to the mass analyzer.^[41]

The most common type of mass analyzer is the quadrupole mass analyzer (QMS). It consists of four parallel cylindrical rods, usually with a circular shape, arranged 90° apart from each other as seen in figure 9. An alternating electric field is used to separate the ions. A voltage in the form of $U + V \cos \omega t$ is applied to the rods that is a combination of direct voltage U and a high-frequency alternating component V . This causes the entering ions to oscillate perpendicularly to the axis of the four rods. The motions of the ions are described by Mathieu differential equations, which have two categories of solutions. The first solutions describe stable situation, where the ions pass through the rods as the amplitude of the oscillation remains within distance of the rods. Other solutions are referred as unstable, because the amplitude of the oscillations increases continuously. This results the ions hitting the rods where they neutralize and are eventually pumped away.^[16]

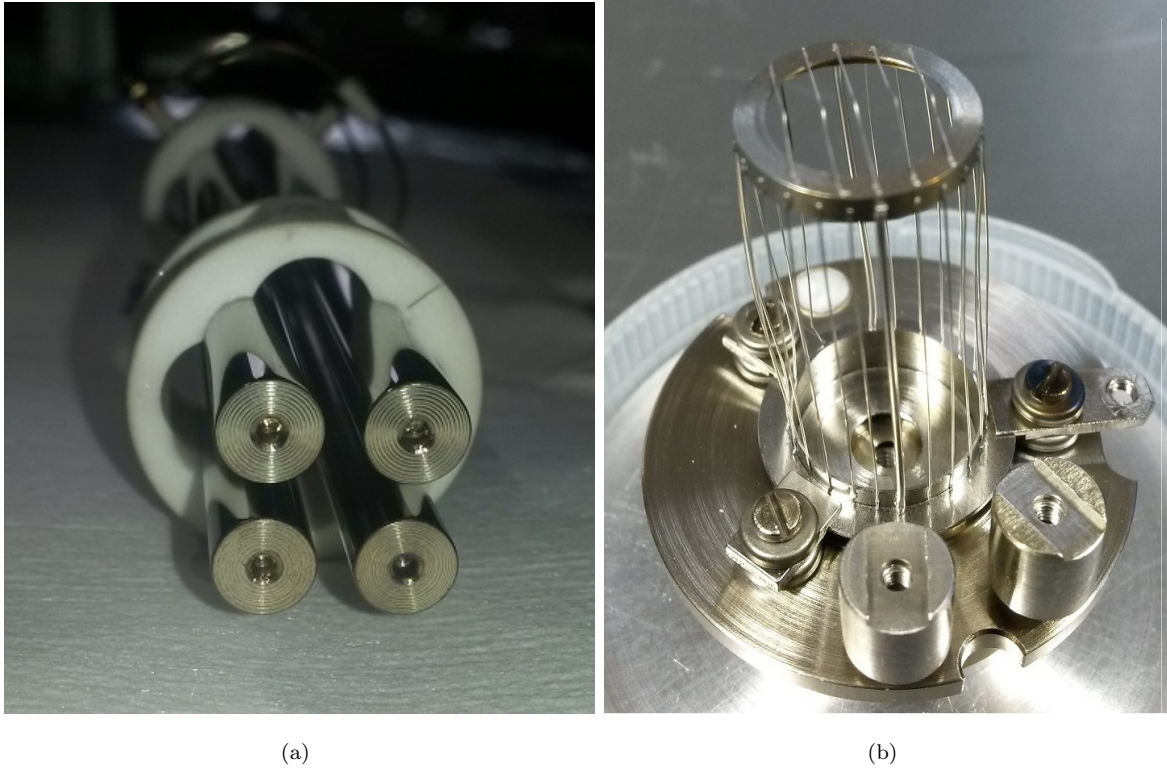


Figure 9: a) QMS cylindrical rods and b) an ion source without the filaments.

The remaining ions that passed the rods are guided for detection. In the simplest method, the ions strike a Faraday collector, where they ion neutralize and the resulting current is proportional to the partial pressure of the gas. If the pressure is very small, the resulting current might be below the detection limits and an amplifying element is required to measure the partial pressure. A secondary electron multiplier (SEM) accelerates the ions to strike a conversion dynode that releases secondary electrons. The secondary electrons strike another dynode, that has secondary electron yield higher than one. Several stages of these dynodes in succession guarantee very high current gains.^[41]

The term mass analyzer is somewhat misleading as it actually separates the ions by their mass-to-charge ratio m/Q . This characteristic of the analyzer and the ionization process can result in many different outcomes, three of which principally form the final residual gas spectrum. The most common outcome is the removal of a single electron resulting in the parent ion that represents exactly the corresponding mass in the spectrum. Secondly, molecules like CO and CO₂ can fragment when the chemical bond between the atoms break. This gives rise to a fragmentation pattern that is unique to each molecule, the RGA and the system if it contains other ionizing instruments. Thirdly, the atoms or molecules may be ionized twice without fragmentation in which case it shows in the spectrum with half of the mass of the actual atom or molecule. The sum of these effects determines the residual gas spectrum in the RGA. Since double ionization is relatively rare in clean UHV systems, most ratios are with a charge value of one electron and hence literature often presents the measurements in atomic mass units. The convention is applied in this work as well, whenever it is reasonable to assume that the molecule or fragment is ionized only once.^[40]

The RGA can be operated in two modes. An analog scan can sweep over the entire mass range and give information about the gas composition in the system. The multiple ion detection (MID) mode can track only the selected masses, but the advantage of the MID scan is that it is much faster in comparison, and events, such as pressure bursts, can be traced more accurately. The electron impact type ionizer that is used in almost

every RGAs usually causes more than one kind of ion from a single molecule. Multiple ionization, isotopic composition and molecular fragmentation has to be counted in. All of these contribute to the mass spectrum and the peak heights must be interpreted with this knowledge. A table of fragmentation patterns is provided in appendix A. The total ion current I at mass m can be summed as:^[41]

$$I_m = \sum_g \alpha_{m,g} s_g p_g, \quad (30)$$

where p_g is the partial pressure of the gas in the system, s is the sensitivity factor for gas g and $\alpha_{m,g}$ gives the probability of the gas to fragment to mass m . It is necessary that the RGA itself doesn't contribute to the gas composition in the UHV system for accurate analysis. For this reason, RGAs often have a degassing function that can be applied during a bakeout to get rid of contaminants.

3.4 Variable leak valve

A very controlled flow of gas is required for example to calibrate the RGA or to keep the pressure under certain limits to protect sensitive instruments during a controlled pressure burst from a temporarily separated chamber. For these purposes, a variable leak valve (Agilent, model 951-5106) is used in both of the systems. The valve allows to control gas flows in the order of $10^{-10} \frac{\text{hPa l}}{\text{s}}$. This is accomplished with a movable piston with an optically flat sapphire that can close a leak tight seal with a captured metal gasket. The movement of the piston allows to control the gas flow.^[42]

3.5 Temperature control of the systems

Temperature control of the systems for bakeouts and keeping a stable temperature during the measurements is accomplished and monitored using various kinds of equipment. Temperature monitoring is performed using type E thermocouples. The thermocouple is attached with kapton tape to the desired place of monitoring, which is typically the flanges of the instruments or the vacuum chamber body. In the case of sample chambers, the thermocouple is attached to the chamber body that is well in contact with the samples. The thermocouples are connected with a bakeout rack that controls the heating wires, bands, jackets and collars that are wrapped around the chambers and flanges. All of the parts are also insulated with fiber glass, aluminum foil and tape to keep the temperature distribution as uniform as possible. The systems are also kept above room temperatures to eliminate the effects coming from the fluctuation of temperature inside the laboratory.

3.6 Sample chambers

Both of the sample chambers used in the systems described in chapter 4 are vacuum fired 316L DN63 stainless steel chambers with two vacuum fired 316LN ConFlat flanges. However, the flanges are 10 mm thick and therefore the effect of 2 hours of vacuum firing at 950 °C is less efficient compared to the sample chamber body that is thinner. To remove and insert samples one of the flanges needs to be removed. A new silver coated copper gasket is used to close the sample chamber. When the flanges are tightened together the knife-edges penetrate into the copper gasket providing a leak tight and bakeable metal-to-metal seal.

4 Experimental methods for outgassing studies

This chapter introduces the two experimental systems and their operating principles, measurement methods and results and error analysis.

4.1 Accumulation system

Outgassing resulting from small samples, well baked or UHV compatible materials can often fall below the detection limits of the pressure gauges. In order to determine low outgassing rates, the method of accumulation can be used. In this method the sample is isolated from the rest of the system by a leak valve in a separate vessel. When the valve is closed, gas releasing from the sample accumulates in the sample chamber for a given time until the leak valve is opened and the quantity of gas accumulated is measured with pressure gauges and residual gas analyzer. It is important to note that this method differs from the rate-of-rise method, which is often called confusingly as the accumulation method as well. The rate-of-rise method also accumulates gas, but it measures the pressure change within the chamber where the gas accumulates.^[22]

The accumulation method can be used reliably only if the outgassing rate is constant during the accumulation time and readsorption by the sample and the sample chamber is negligible. This is often the case with well baked metal samples when hydrogen outgassing is dominant. Because the gas accumulates in a separate chamber, the usual problems with gauges can be ignored since in this method the gauge does not affect on the quantity of gas accumulated and accumulation time can be extended to obtain gauge sensitivity.^[16]

Experimental setup

The experimental setup is shown in figure 10. Parts of the system have been labelled according to their functions. The 10 mm orifice separates the pumping chamber, where all the pumps are connected, and the measurement chamber that includes the RGA and BAG which measure the pressure burst from the sample chamber. There is also a BAG on the pumping chamber to estimate the pumping speed of the orifice and cross-check the validity of the other BAG. The sample chamber and the flanges have been vacuum fired at CERN. The chamber with the NEG strips has also been produced at CERN.

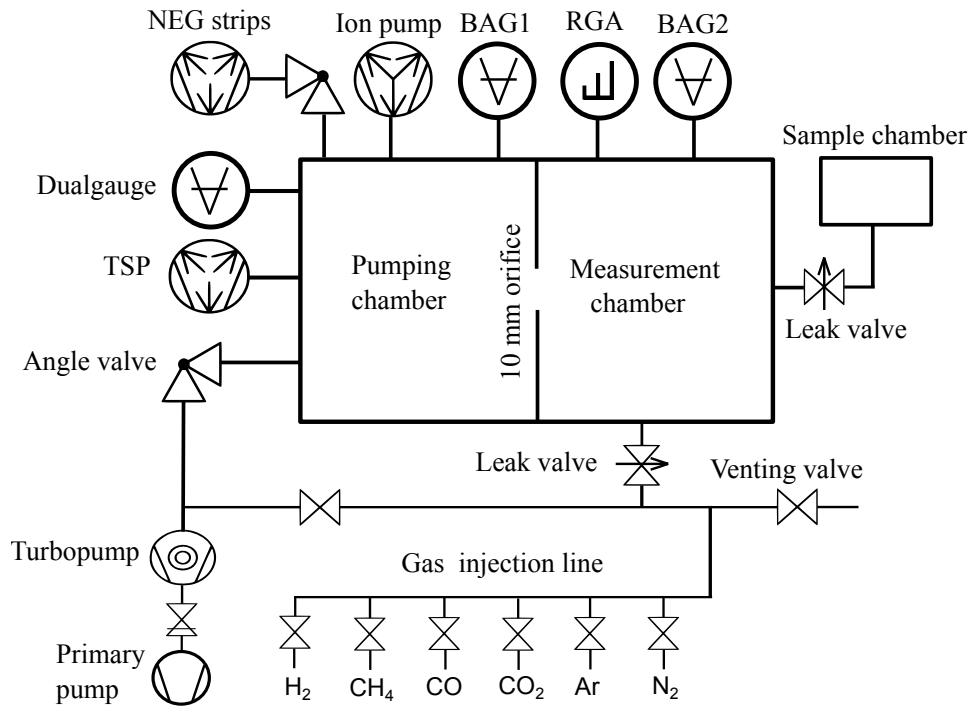


Figure 10: Schematic of the accumulation system.

The schematic in figure 10 has been simplified for clarification. For example the NEG strips are on top of the pumping chamber and the titanium sublimation pump is behind a bend so that the titanium filaments are not in a direct line of sight with any of the important instruments in order to protect them from the sputtered titanium. Furthermore, the BAG2 and the RGA are not positioned side by side and the overall geometry of the system resembles a Fischer-Mommsen dome^[43]. The dimensions and the positions in the measurement chamber have been selected in such a way that the BAG2, RGA, gas injection valve and the valve to the sample chamber are at equal distances away from each other so geometrical considerations are not needed in analysing the results.

Measurement procedure

The measurement procedure can be summarized roughly as:

1. Replace the samples while keeping the variable leak valve closed and the rest of the system at UHV.
2. Turn off instruments and close the angle valve to the turbopump.
3. Vent the system with nitrogen.
4. Begin pumping through the turbopump and simultaneously open the leak valve to the sample chamber.
5. Leak detect the sample chamber. Continue pumpdown for 24 hours.
6. Begin system bakeout for 24 hours.
7. Lower the bakeout temperatures and degass the RGA, BAGs, TSP and the ion pump.
8. Cooldown to 25 °C. Turn on the ion pump at 120 °C.
9. At about 60 °C sublime titanium for the first time and close down the turbopump valve.
10. Leak test sample chamber and the valve. Wait at least 48 hours before starting the accumulation test.
11. Perform 6 accumulation tests at each temperature: 25 °C, 60 °C, 100 °C, 150 °C and 200 °C.
12. Cooldown the sample chamber and close the variable leak valve.

13. Open the sample chamber CF flange to perform a leak test for the variable leak valve.
14. Return to step 1.

Step 4 ensures minimal air-exposure to the system from the air-vented sample chamber. During the bakeout step, the system is heated according to table 6. If NEG activation is performed, the angle valve to the NEG strips is opened for the bakeout step 6, NEG strips are heated accordingly and the 2nd phase is prolonged for 24 hours.

Part	1st phase T ($^{\circ}\text{C}$)	2nd phase T ($^{\circ}\text{C}$)	3rd phase T ($^{\circ}\text{C}$)
BAG1 and BAG2	300	150	25
Dualgauge and turbopump	140	140	25
RGA	300	180	25
NEG strips (optional)	180	250	25
Other parts	250	150	25

Table 6: Bakeout temperatures of the different parts. Heating rate for every component is set to $50\text{ }^{\circ}\text{C/h}$, but large parts heat and cool slower.

The turbopump is separated from the system after the bakeout as it presents a source of outgassing at low pressures and a contamination risk in case of a powercut. The base pressure in the pumping chamber after a bakeout is typically about 2.7×10^{-11} hPa and about 1.5×10^{-10} hPa in the measurement chamber. TSP is used typically after each accumulation test. Accumulation times vary from few hours to several days and shorter times can be used at higher temperatures. During the accumulation tests, only the sample chamber is heated and the temperature is monitored with two thermocouples attached to the side of the sample chamber. Every time the temperature is elevated, the first accumulation test at that temperature is delayed until the next day to guarantee enough time for the samples to heat as well.

Theory

Pumping equation (15) states that the change in the quantity of gas per unit of time in the system equals the quantity of gas leaving the system and the quantity of gas coming to the system as

$$-V \frac{dp}{dt} = pS_{\text{eff}} - Q_t,$$

where V is now the volume of the measurement chamber, p is pressure, S_{eff} is the effective pumping speed through the orifice, and Q_t is the gas load from the sample chamber. When the variable leak valve is opened, the accumulated gas is released and figure 11 shows how the pressure rises momentarily in the measurement chamber until the excess gas is pumped.

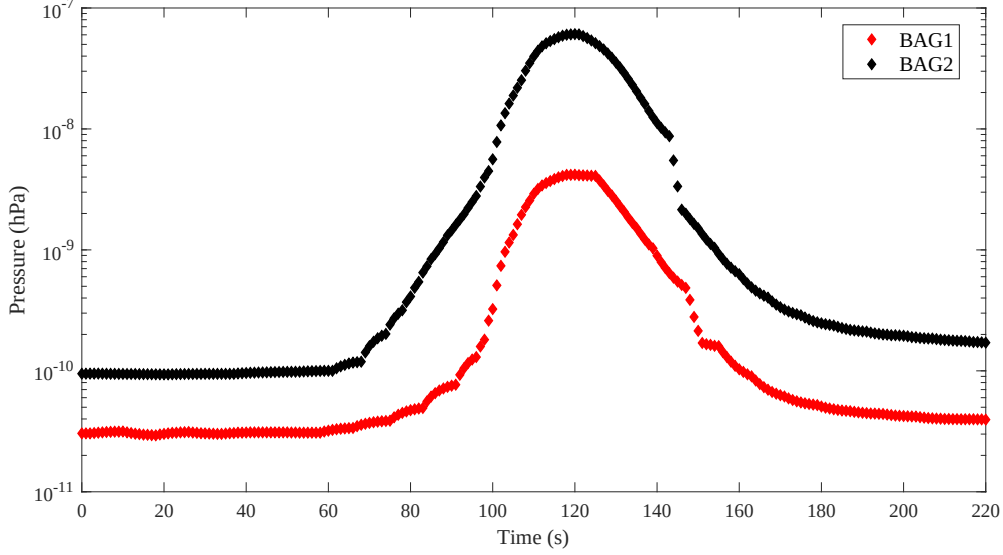


Figure 11: Accumulation test: opening of the variable leak valve at $t \approx 60$ s. BAG2 measures the pressure rise in the measurement chamber while BAG1 helps to check the pumping speed.

According to the pumping equation (15) we can calculate the quantity of gas released from the sample chamber by integrating both sides:

$$-V \int_{t_1}^{t_2} \frac{dp}{dt} dt = S_{\text{eff}} \int_{t_1}^{t_2} p dt - \int_{t_1}^{t_2} Q_t dt, \quad (31)$$

where t_1 denotes the time at the beginning of the opening and t_2 the point where the gas has been pumped. Ideally the pressure change $\frac{dp}{dt}$ is zero at the beginning and at the end so that the quantity of gas $\int_{t_1}^{t_2} Q_t dt$ denoted with q_{accu} is

$$q_{\text{accu}} = S_{\text{eff}} \int_{t_1}^{t_2} p dt. \quad (32)$$

The peak areas can be numerically integrated with the trapezoidal rule. The effective pumping speed in the measurement chamber can be approximated due to the 10 mm orifice between the two chambers. The effective pumping speed of a system with an orifice and a pump is given by

$$\frac{1}{S_{\text{eff}}} = \frac{1}{S} + \frac{1}{C_{\text{orifice}}}. \quad (33)$$

And if the pumping speed is high for all the gases it can be approximated as $S_{\text{eff}} \approx C_{\text{orifice}}$. It is also possible to measure the effective pumping speeds for the gases during gas injections using the BAGs and the RGA. The procedure and results are described in more detail in appendix B. The outgassing Q of the samples and the sample chamber can now be calculated as

$$Q = \frac{q_{\text{accu}}}{t_{\text{accu}}}, \quad (34)$$

where t_{accu} is the accumulation time. The total outgassing rate q of the samples is thus

$$q = \frac{Q - Q_{\text{BG}}}{A_{\text{samples}}}, \quad (35)$$

where Q_{BG} is the background outgassing of the sample chamber and A_{samples} is the surface area of the samples. Further analysis can be made with an RGA that can measure the gas specific outgassing rates. Figure 12 shows an example of a multiple ion detection (MID) scan performed during the opening the variable leak valve.

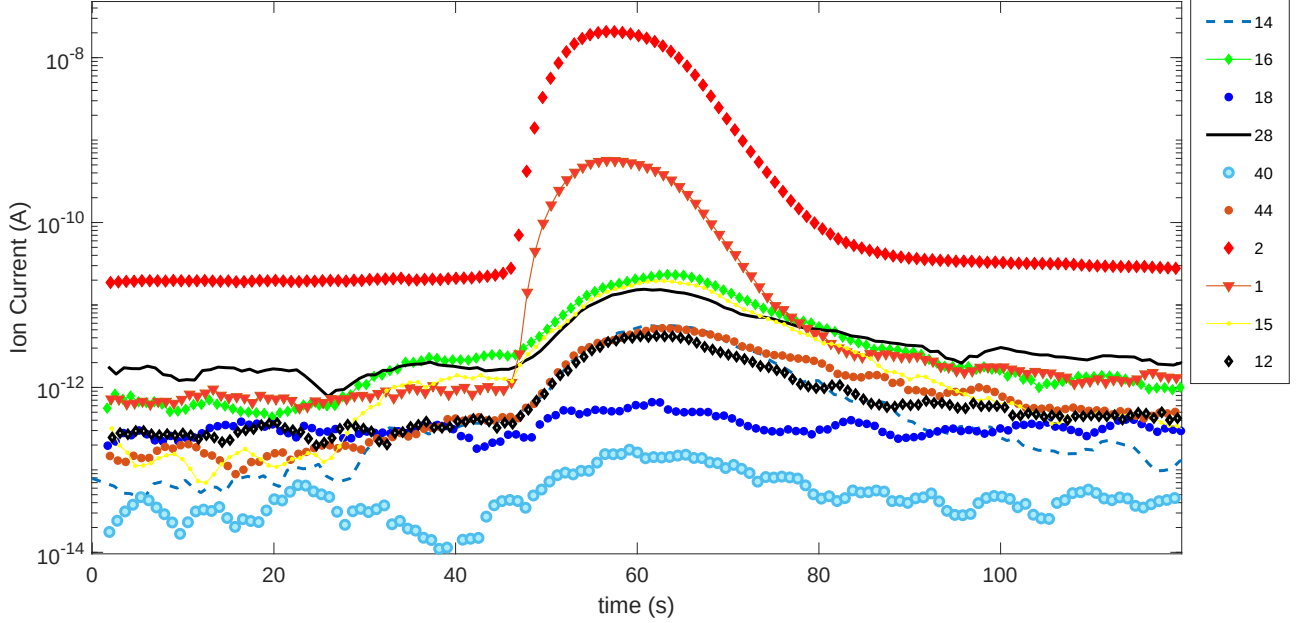


Figure 12: Example of a MID scan during the opening at $t \approx 45$ s. The legend on the right shows the measured mass-to-charge ratios. Insignificant gases have been removed from the plot for clarity.

RGA measures ion currents, so the pressure term in equation (32) is replaced by the measured ion current I and converted to pressure by dividing with the sensitivity factor s as

$$q_{\text{accu}} = S_{\text{eff}} \int_{t_1}^{t_2} \frac{I}{s} dt. \quad (36)$$

The sensitivity factors are obtained by calibrating the RGA. The procedure and results are presented in appendix A. Furthermore, the gas specific pumping speeds must be used to obtain gas specific outgassing rates. The pumping speeds could be evaluated with equation (11), but with this system it is possible to directly measure them during a gas injection because both sides of the orifice have BAGs. This procedure and results are presented in more detail in appendix B.

RGA analysis takes into account the fragmentation patterns as was explained in chapter 3.3. For example CO_2 fragments to masses 28, 16 and 12 which correspond to ions: CO^+ , O^+ and C^+ . This is why CO_2 contribution to the CO integral q_{accu} must be subtracted to obtain the ion current coming only from CO. Similarly, both CO and CO_2 fragment to mass 16, which corresponds also to the CH_4^+ ion. Therefore methane

is tracked by mass 15, which comes from the fragmentation of methane ions with quite high relative intensity j_{rel} . The ion current of methane is thus evaluated as

$$I(\text{CH}_4^+) = \frac{I(15)}{j_{\text{rel}}(\text{CH}_4 \rightarrow \text{CH}_3^+)}. \quad (37)$$

Hydrogen pressures can be estimated directly from the measured ion current since only He^{2+} ion has the same mass-to-charge ratio and can be ignored. The measured relative intensities are given in table 17 in appendix A.

Results and error analysis

For each measurement the error is estimated with the propagation of uncertainty due to errors in pressure, pumping speed, sensitivity factors, accumulation time and sample surface area. The total error after a 6 measurements is then calculated with the method of least squares. The background error analysis follows the same principle, but error analysis is needed for the measured outgassing Q . For the outgassing rate q the error in background also needs to be included. Because the variables are independent and measured independently, propagation of uncertainty can be used to estimate the error of the outgassing Q in individual measurements i as

$$\sigma_{Q,i}^2 = \left(\frac{\partial Q_i}{\partial S_{\text{eff}}}\right)^2 \sigma_{S_{\text{eff}}}^2 + \left(\frac{\partial Q_i}{\partial t_{\text{accu}}}\right)^2 \sigma_{t_{\text{accu}_i}}^2 + \left(\frac{\partial Q_i}{\partial \iota}\right)^2 \sigma_{\iota_i}^2, \quad (38)$$

where σ_{ι} is the error of the pressure integral over time. For total outgassing rates, the error is due to uncertainty in pressure. For the specific gases, the error is due to the error in sensitivity factors, which are mostly due to uncertainties in pressure. A pressure error of 20 % was chosen based on literature^[21,38,35] and also because the BAGs were last calibrated many years ago. The measured pumping speeds S_{eff} and errors are given in appendix B. The error in the accumulation time $\sigma_{t_{\text{accu}}}$ is negligible so equation (38) simplifies to

$$\sigma_{Q,i} = \sqrt{\frac{\iota_i^2 \sigma_{S_{\text{eff}}}^2 + S_{\text{eff}}^2 \sigma_{\iota_i}^2}{t_{\text{accu}_i}^2}}, \quad (39)$$

where the error σ_{ι} is simply 20% of the integral $\iota = \int_{t_1}^{t_2} p \, dt$ when estimating the total nitrogen equivalent outgassing with the BAG. For the specific gases the pressure integral is $\iota = \int_{t_1}^{t_2} \frac{I}{s} dt$ so the uncertainty for ion current and sensitivity factors are included as

$$\sigma_{\iota} = \frac{\sqrt{s^2 \sigma_{\iota_1}^2 + \iota_1^2 \sigma_s^2}}{s^2}, \quad (40)$$

where ι_1 is the current integral and s is the sensitivity factor. The σ_{ι_1} is estimated also as 20 % of the integral. Outgassing rate errors $\sigma_{q,i}$ for each measurement i can be estimated similarly with equation (35) as:

$$\sigma_{q,i}^2 = \left(\frac{\partial q_i}{\partial S_{\text{eff}}}\right)^2 \sigma_{S_{\text{eff}}}^2 + \left(\frac{\partial q_i}{\partial t_{\text{accu}}}\right)^2 \sigma_{t_{\text{accu}}}^2 + \left(\frac{\partial q_i}{\partial Q_{\text{BG}}}\right)^2 \sigma_{Q_{\text{BG}}}^2 + \left(\frac{\partial q_i}{\partial A_{\text{sample}}}\right)^2 \sigma_{A_{\text{sample}}}^2 + \left(\frac{\partial q_i}{\partial \iota}\right)^2 \sigma_{\iota_i}^2, \quad (41)$$

$$\sigma_{q,i} = \sqrt{\frac{\iota_i^2 \sigma_{S_{\text{eff}}}^2 + S_{\text{eff}}^2 \sigma_{\iota_i}^2}{t_{\text{accu}_i}^2 A_{\text{sample}}^2} + \frac{\sigma_{BG}^2}{A_{\text{sample}}^2} + \left(\frac{Q_i}{A_{\text{sample}}^2} - \frac{S_{\text{eff}} \iota_i}{t_{\text{accu}_i} A_{\text{sample}}^2} \right)^2 \sigma_{A_{\text{sample}}}^2}. \quad (42)$$

Method of least squares gives the estimator as^[44]

$$q = \frac{\sum_{i=1}^N \frac{q_i}{\sigma_{q,i}^2}}{\sum_{j=1}^N \frac{1}{\sigma_{q,j}^2}} \quad (43)$$

and the estimator error as^[44]

$$\sigma_q = \frac{1}{\sqrt{\sum_{i=1}^N \frac{1}{\sigma_{q,i}^2}}}, \quad (44)$$

where N is the number of measurements. Note that this error analysis for q does not count for systematic or other errors which are discussed in chapter 5. The outgassing rates are expected to follow an Arrhenius temperature dependence $q = q_0 \exp\left(-\frac{E_{\text{act}}}{k_B T}\right)$. Thus the measured outgassing rates at different temperatures can be used to estimate the activation energy E_{act} by simple linear least squares method when the logarithm is taken as

$$\ln q = \ln q_0 - \frac{E_{\text{act}}}{k_B T}, \quad (45)$$

so a linear fit in a $(\ln q, \frac{1}{T})$ plot has an intercept of $\ln q$ and a slope of $\frac{E_{\text{act}}}{k_B}$, where the activation energy can be obtained by multiplying with the Boltzmann constant. The uncertainties $\sigma_{\ln q} = \frac{\sigma_q}{q}$ can be used as weights and to estimate the error of the slope.

4.2 Throughput system

The throughput system is dedicated to test outgassing of unbaked samples. The outgassing is determined at five temperatures subsequently and measured for 100 hours at each temperature. The gas composition can be qualitatively analysed in addition. The throughput system measures the outgassing with the throughput method. In this method, the chamber and the samples are pumped through an orifice of known conductance and the pressure difference on both sides of the orifice is measured. In the case of small orifice with very high outgassing samples, it is often assumed that the pressure drop is so great that the second gauge on the downstream side is not needed, and the pumping speed of the orifice can be evaluated as the conductance of the orifice. Compared to the accumulation method, the throughput method allows to measure the outgassing rate as a function of time. This is particularly applicable for unbaked samples where the main outgassing component is water.

Experimental setup

The experimental setup is shown in figure 13. The system requires two separate pumping groups for different tasks. The main turbopump (1) is used during the measurements and the second turbopump (2) is only used during a bakeout and the initial sample chamber evacuation after sample insertion. The samples are replaced by opening the CF flange to the sample chamber. Measurements can be made using the RGA and cold cathode gauge. The small orifice helps to estimate the effective pumping speed. The total surface area of the system is about 0.2 m^2 , not including the pumps behind angle valves (1) and (3).

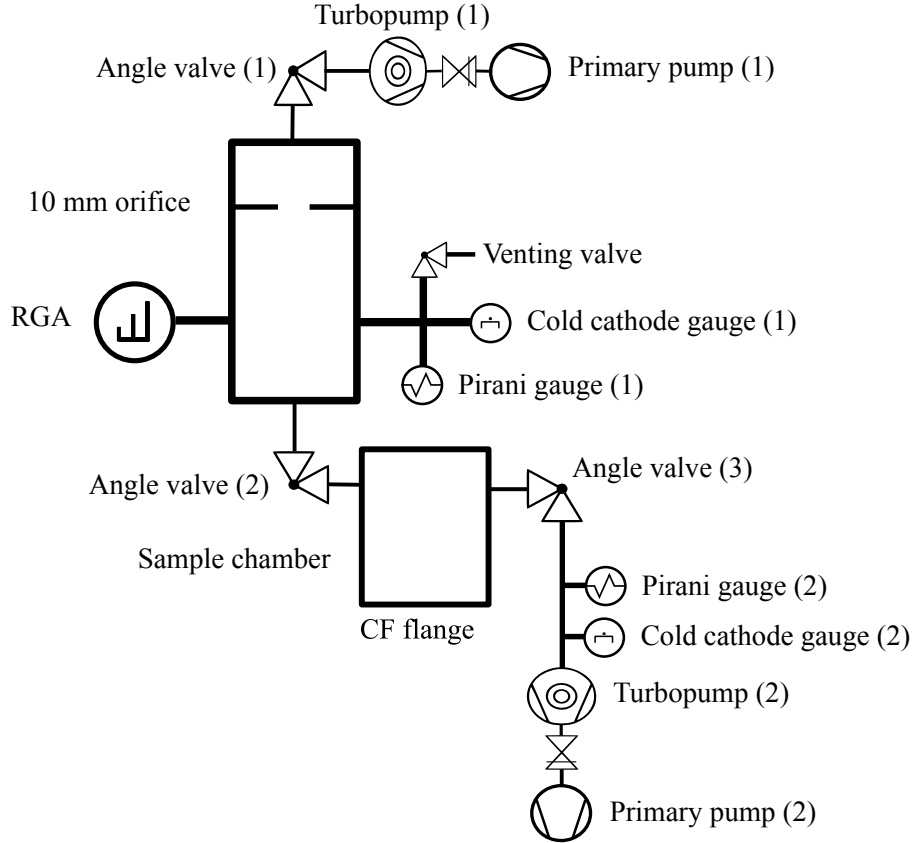


Figure 13: Schematic of the throughput system.

Measurement procedure

Normal measurement procedure involves several steps. First, the sample chamber and most of the system are baked 24 hours at 250 °C, RGA is baked at 300 °C and pressure gauges and turbopump at lower temperatures. Also, the pumping group that is used to evacuate the sample chamber from atmosphere, is baked at 120 °C. The system is cooled down to 30 °C and at least 24 hours is waited until the angle valve to the sample chamber is closed and samples inserted by opening a CF flange on the side of the sample chamber. After that, the angle valve (3) is opened and the sample chamber is evacuated with the pumping group for 6 hours. During this time, the closed CF flange is leak tested with helium leak detector connected to the pumping group. Then, the angle valve (2) to the system is opened and the valve (3) to the pumping group is closed.

Hundred hours of pumping is measured at five temperatures: 30 °C, 60 °C, 100 °C, 150 °C and 200 °C. Only the sample chamber is being heated with a ramping rate of 50 °C/h to each temperature. RGA scans are also performed at regular intervals to analyse the gas evolution over time and temperature. After the measurements, the sample chamber is cooled down and leak tested again. The samples are removed and the measurement procedure can begin from the start again. The full cycle of steps can be summarized as:

1. Bakeout the entire system.
2. Cooldown and degass the RGA at 150 °C. Continue cooling down to 30 °C and wait 24 hours.
3. Close the angle valve (2) to the sample chamber and insert the samples.
4. Pumpdown the sample chamber for 6 hours and leak test the CF flange.
5. Open the angle valve (2) to the system and close the angle valve (3).
6. Measurements at five different temperatures.
7. Cooldown the sample chamber and leak test the sample chamber flanges.
8. Close the angle valve (2) and remove the samples.
9. Close the CF flange and pumpdown the sample chamber through angle valve (3).
10. Close angle valve (3) and open angle valve (2).
11. Return to step 1.

The steps 4 and 9 ensure that the rest of the system is rarely exposed to high pressures under normal operation, and therefore RGA sensitivity factors should not drift significantly between measurements. The exact pumpdown time in step 9 is inconsequential since this step is only used to enable the opening of the angle valve (2) without producing a high gas burst to the RGA. After that, the entire system is baked for 24 hours. The successfulness of the bakeout is estimated with an RGA scan and the pressure reading. The base pressure of the system after a bakeout is typically below 1.5×10^{-10} hPa.

Results analysis

Before measuring samples it is important to determine the background outgassing of the system with a blank measurement in which everything is performed normally, but without a sample in the sample chamber. This allows to subtract the background from the measurements. Two major sources of background can be identified: the air-vented sample chamber and the rest of the system that has been protected by the angle valve from air during the sample insertion. The background coming from the latter obviously increases when the sample chamber is opened to the rest of the system and it is included in the background measurement as well. This is why it is impossible to determine the outgassing rate of the sample chamber solely, but this doesn't matter

since the relevant quantity for background subtraction is the outgassing Q_{BG} . When the procedure is repeated with samples, the measured Q_{BG} can be used for background subtraction to determine the outgassing rate of the samples as

$$q_{\text{samples}} = \frac{Q - Q_{\text{BG}}}{A_{\text{samples}}}. \quad (46)$$

The background measurement to some degree takes into account the effect of readsorption and subsequent desorption from the system walls, but the influence of readsorption is discussed later in chapter 5 in more detail.

Conductance and pumping speed considerations

Since this system is used only for high outgassing samples, two gauges on either side of the orifice are not needed as pressure on the side of the turbopump can be estimated much lower than on the sample chamber side and therefore the pumping speed of the orifice S can be estimated as

$$S \approx C_{\text{orifice}}, \quad (47)$$

where C_{orifice} is the calculated conductance of the orifice. The RGA and the cold cathode gauge are relatively close to the orifice leading to the turbopump. However the sample chamber is slightly further and is separated from the rest of the system with an angle valve. Since all the flanges and pipes are DN63 sizes it is important to consider the effect of conductance to the outgassing values. Because of the conductance C_{sys} of the pipes and angle valve, the pressure p_{sc} in the sample chamber is higher and it can be evaluated from the equations (8) and (14) as

$$p_{\text{sc}} = \frac{Sp}{C_{\text{sys}}} + p, \quad (48)$$

where p is the pressure close to the orifice. To calculate the outgassing, the effective pumping speed S_{sc} at the sample chamber entrance is needed. This can be estimated by the system conductance and orifice pumping speed and calculated according to equation (9) as

$$S_{\text{sc}} = \frac{SC_{\text{sys}}}{S + C_{\text{sys}}}, \quad (49)$$

and the outgassing Q_{sc} of the sample chamber is

$$Q_{\text{sc}} = p_{\text{sc}}S_{\text{sc}} = \frac{Sp + pC_{\text{sys}}}{C_{\text{sys}}} \frac{SC_{\text{sys}}}{S + C_{\text{sys}}} = Sp. \quad (50)$$

So the outgassing of the sample chamber can simply be evaluated by the measured pressure near the orifice and the pumping speed of the orifice. This is valid if readsorption is negligible and the most dominant source of outgassing in the system is from the sample chamber and not from the system walls.

Error analysis

The uncertainty for outgassing is due to uncertainties in pressure and pumping speed. CCGs are considered to be less accurate than HCGs^[35]. Accuracy is typically in the range of $\pm 25\%$ ^[21] and hence the uncertainty here is roughly estimated as 30 % of the gauge reading. The pumping speed error in this case can be estimated as conductance error of the circular orifice which depends on temperature and the orifice diameter d according to equation (11) where $A = \frac{\pi d^2}{4}$. The pumping speed uncertainty is

$$\sigma_S^2 = \left(\frac{\partial C}{\partial T}\right)^2 \sigma_T^2 + \left(\frac{\partial C}{\partial d}\right)^2 \sigma_d^2, \quad (51)$$

$$\sigma_S = \frac{d}{8} \sqrt{\frac{k_B \pi}{2m_0 T} (d^2 \sigma_T^2 + 16 T^2 \sigma_d^2)}. \quad (52)$$

Assuming a manufacturing error of 0.1 mm for the orifice diameter d and a temperature uncertainty of 1.7 °C, we get an uncertainty of $\sigma_S \approx 0.19$ l/s for nitrogen molecules. This presents a relative pumping speed error of about 2 %, which is small in comparison to the assumed pressure uncertainty.

The uncertainty in outgassing rate can also be estimated by the propagation of uncertainty and it must take into account the uncertainties in background measurement and in the sample surface area as:

$$\sigma_q^2 = \left(\frac{\partial q}{\partial Q}\right)^2 \sigma_Q^2 + \left(\frac{\partial q}{\partial Q_{BG}}\right)^2 \sigma_{Q_{BG}}^2 + \left(\frac{\partial q}{\partial A}\right)^2 \sigma_A^2 \quad (53)$$

The error due to sample surface is negligible compared to the aforementioned uncertainties so the equation simplifies to

$$\sigma_q = \frac{1}{A} \sqrt{\sigma_Q^2 + \sigma_{Q_{BG}}^2} \quad (54)$$

and for high outgassing samples the uncertainty due to background is also expected to be insignificant.

5 Uncertainty considerations

This chapter examines the errors and effects that inherently affect the measured outgassing results, but can not be quantitatively assessed in the error analyses.

5.1 Temperature errors

Outgassing rates depend exponentially on temperature so any variation on temperatures is going to change the outgassing rates significantly. Type E thermocouple accuracy is $\pm 1.7^\circ\text{C}$ within the used temperature range. Both sample chambers had second thermocouples on the side of the chamber to check that the primary thermocouple was functioning. First thing to note is that even though the sample chamber is uniformly heated and well insulated, the temperatures of the samples and the temperature uniformity differ to some degree.

Another issue worth considering is the influence of temperature to the measured values as gas that is released at higher temperatures is expected to have a lower number density according to the ideal gas law, so that the RGA and ionization gauges would show lower pressures. However, in both accumulation and throughput systems the gas molecules have to travel a considerable distance before they are measured. In both of the systems the sample chambers are separated from the ionization gauges and RGA by an angle valve with relatively low conductance so the molecules hit the walls multiple times before reaching the ionization regions. Every hit with the wall reduces the kinetic energy of the molecule by a fraction α that is known as the accommodation coefficient. Most of the impinging molecules remain on the surface briefly. Then they desorb with cosine spatial distribution and with energy distribution corresponding the surface temperature so the accommodation coefficient for most gases and surfaces is typically near to unity. Therefore the molecules are expected to reach the wall temperatures, and no errors should be expected from the difference of temperatures between the sample chamber and the rest of the system.^[16,45,53]

5.2 Epistemic uncertainties

Some phenomena affecting the results are hidden or can not be reasonably quantified. This chapter introduces some of the main effects that need to be mentioned.

Readsorption

Readsorption is perhaps the most inherent effect in the systems that is difficult to quantify. The measured outgassing rates are always somewhat lower than the intrinsic outgassing rates because of readsorption. The difference between the two rates have been known for decades, but most published papers rarely even mention it or the relevant system parameters.^[48]

Readsorption particularly influences the throughput system and the venting system described in appendix G. Unbaked samples are expected to outgas particularly water, that has a relatively high sticking factor on stainless steel^[22], thus making readsorption of the desorbed molecule more probable. For the accumulation system, which measures baked samples that are predominantly outgassing hydrogen, the effect of readsorption is not substantial since hydrogen readsorption rate on stainless steel has been observed to be negligible. Tests with rate-of-rise method have shown hydrogen pressure rises to be linear up to 10^3 hours^[48,49] in stainless steel chambers indicating the absence of readsorption.

Redhead^[48] has considered the effects of readsorption to outgassing measurements. With the throughput method the conservation of mass requires that the number of molecules released from the surface must equal to

the sum of molecules being pumped, readsorbed and to the change of number of molecules in the volume stated as

$$A_0 q_i = A q_m + A I s + N V \frac{dp}{dt}, \quad (55)$$

where q_i is the intrinsic outgassing rate, q_m is the measured outgassing rate, I is the impingement rate, s is the sticking factor, and N is the number of molecules. Here a distinction between outgassing surface A_0 and the readsorbing surface A is made, because in the throughput system the main source of gas is the sample. The measured outgassing rate is^[48]

$$q_m = \frac{I a}{A_0}, \quad (56)$$

where a is effective pumping area. In a stationary state $\frac{dp}{dt} = 0$, so equation (55) gives

$$A_0 q_i = I a + A I s, \quad (57)$$

$$q_i = \frac{a + A s}{A_0} I = \frac{I a}{A_0} \left(1 + \frac{A s}{a} \right), \quad (58)$$

$$\frac{q_m}{q_i} = \frac{a}{a + A s}. \quad (59)$$

Here we see that the term A_0 is irrelevant and the equation (59) applies generally to systems where the outgassing and readsorption surfaces are the same. Figure 14 shows the measured and intrinsic outgassing ratios as function of sticking factor for two systems with different total surface areas.

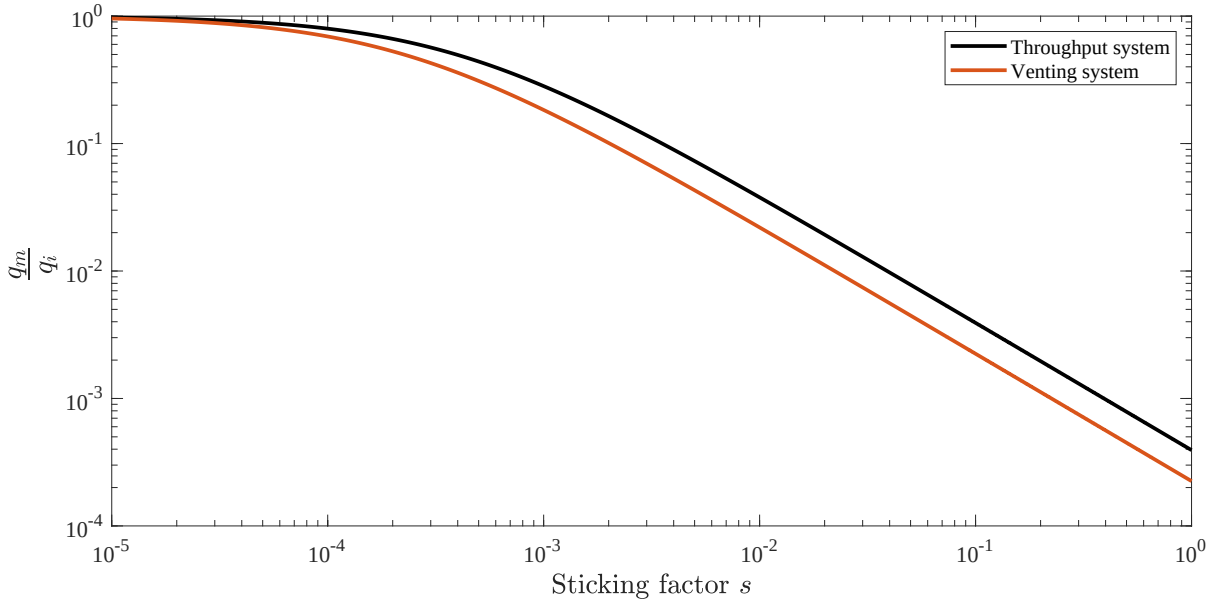


Figure 14: The ratio of measured and intrinsic outgassing rates as a function of sticking factor for two systems with total surface areas of 2000 cm² and 3500 cm².

Sticking factors in the range of 10^{-3} and 10^{-1} have been reported for water on stainless steel^[22], which indicates lower measured outgassing rates by a factor ranging from 3 to 250. However the sticking factor is dependent on surface coverage and decreases as the coverage increases. Therefore, it is difficult to estimate quantitatively the ratio of measured and intrinsic outgassing rates when the surface coverage and pressure are at equilibrium.^[48]

This effect should not be regarded as a flaw in the measurement procedure, because it is present in most vacuum systems inherently, but as a remainder that attention is required when applying outgassing results from one system to another with very different pumping, surface and sticking parameters. For this reason, the figure 14 can be used to estimate the difference between the measured and intrinsic outgassing rates, which could be used to estimate the measured values in another system.

RGA induced effects

The RGA is a source of gas in both systems and it also alters the residual gas composition so its effects to the measurements need to be considered. In the accumulation system the RGA is situated outside of the sample chamber and does not contribute to the accumulating gas as it is only used to measure the pressure burst after the accumulated gas is being released. The main nuisance of the RGA in the accumulation system comes from the tungsten filament, which has an operating temperature of about 1800 °C^[16]. This heats the nearby surfaces, which increases thermal outgassing in these areas thus increasing the background pressure of the measurement chamber. Since the accumulation time can be extended long enough to give a significant pressure rise, the effects of the RGA in the accumulation system can be disregarded.^[16]

In the throughput system the RGA is situated with the sample chamber so its effects are much more evident. As with the accumulation system, the hot filament also induces thermal outgassing. Because the filament material is yttria-coated iridium, which has an operating temperature of about 1200 °C,^[16] the gas load coming from thermal outgassing is smaller in this case. The hot filament can also induce many unwanted chemical reactions on the filament surface. Since the sample chamber and the samples are unbaked, the most concerning reactions comes from water vapor. When water comes into contact with yttria it can release small amounts of oxygen. Furthermore, water can also induce the formation of hydronium (H_3O^+) as ionized water molecules react with other ions and molecules in the ion source.^[16]

In addition, the emitted electrons from the filament can hit the nearby surfaces, notably the grid of the RGA, and cause electron stimulated desorption (ESD). The main desorbed ions that contribute to the residual gas spectrum are H^+ , O^+ , F^+ and Cl^+ . These ions are easily distinguished by altering the RGA's ion energy setting, because the ESD ions desorb from the surface with a relatively high kinetic energy that enables their passage through the mass analyser, leaving only the ESD ions visible in the residual gas spectrum when the ion energy parameter has been changed^[16]. During the first background measurement with the throughput system, a relatively high peak of 19 was observed, which was attributed to F^+ coming from ESD with some presence of H^+ and O^+ as well. Over time, approximately within two tests, these peaks vanished and as they were confirmed to come from the ESD of the RGA their presence was only disturbing the residual gas spectrum and it did not affect the measured outgassing rates.^[16,50]

Because the throughput system was used to measure very high outgassing samples, the gas load contribution coming from the RGA is apparent only in the background measurements and after the sample chamber is cooled down after the tests. Partly because of the latter reason, the measurements after cooldown are excluded from the results. The RGA contribution was measured occasionally by switching the filament off and measuring the

pressure drop with the cold cathode gauge. After an entire system bakeout at pressures below 10^{-9} hPa, the pressure drop was observed to be as high as 50 %. However, closer to the typical measurement pressure ranges 10^{-8} – 10^{-6} hPa, the pressure drop was less than 6 % and an average outgassing of about $Q_{\text{RGA}} = 9 \times 10^{-9} \frac{\text{hPa l}}{\text{s}}$ was estimated. Because this is already included in the background measurement, the RGA contribution requires no further attention.

Cold cathode gauge effects

Depending on the conditions and previous use of the cold cathode gauge, it can either release or pump gas. If the gauge has been exposed to contaminants or has been operated at high pressures for long periods of time the electrodes may not be clean and the gauge can release gases. However if the electrodes are clean, the pumping effect is prevalent.^[52]

Since the systems are well baked before the measurements and operated for several days, the most concerning effect is the pumping of gases of the new gauges. Mukugi et al.^[52] observed that the pumping speed depends on the pressure. In the range of 10^{-6} – 10^{-7} hPa the highest pumping speed was measured as 0.1 l/s. When UHV range was reached the pumping speed reduced below 0.01 l/s. Other literature values also support low pumping speeds, for example Peacock et al.^[35] reported values in the range of 2.4×10^{-2} – 3.3×10^{-2} l/s at a pressure of 6×10^{-7} hPa. Kendall et al.^[51] measured temporary CCG pumping speeds in the 0.1 - 0.3 l/s range after a large pressure increase, but observed that the pumping speed dropped significantly within several hours and concluded that pressure measurement errors due to CCG pumping effect in normal conditions are negligible.

6 Samples

Particle accelerators are generally operated in the HV or UHV range so the most common requirement for the materials used in accelerators are their low outgassing rates. Depending on the application, other properties like mechanical strength and similar thermal expansion compared to other materials in the system are required. The materials must be easy to form to the desired shape, for example by machining, and joining the materials by welding, brazing or by other means is sometimes essential. High energy particle accelerators place more demanding requirements for materials compared to ordinary industrial vacuum systems because of synchrotron radiation, scattered particles, electron cloud and impedance requirements. Also, for the interaction points the material should be transparent to radiation.^[54]

Since a bakeout is necessary to achieve low pressures quickly, the materials must be able to endure repeated high temperature cycles without losing essential mechanical properties such as leak tightness. In addition, it should possess negligible vapour pressure at these temperatures. Thus, the most common materials used for the vacuum chambers are stainless steel, aluminium and copper. For electrical components and feedthroughs insulating materials are required. For these reasons, many types of materials are needed in the vacuum systems and careful selection and testing of materials and surface treatments is essential in the design of vacuum systems and components. The next chapters introduce the samples and explain the reasons for testing the materials. The samples were kept at room temperature wrapped in aluminium foil in an airtight bag before the tests.^[54]

6.1 Vespel SP-1

Engineering polymers are excellent candidates when high insulation or high temperature operation in UHV are needed with mechanical properties comparable to metals. Vespel SP-1 is an unfilled polyimide. Vespel SP-1 provides excellent mechanical properties and electrical and thermal insulation and for these reasons it has been used as a reference material for a quite some time^[55]. When the material is used as a vacuum seal, it can be used continuously at 250 °C before it begins to lose mechanical properties and up to 450 °C for a short duration without permanent damage^[55]. Water solubility is reported^[24] as 0.24 %.^[24,55]

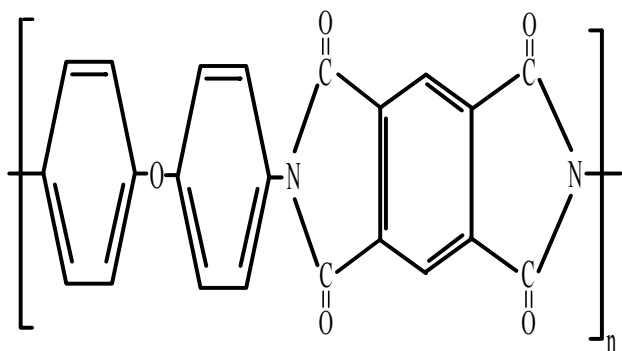


Figure 15: Chemical structure of Vespel SP-1. Figure based on source^[24].



Figure 16: Vespel SP-1 sample inside the throughput system sample chamber.

The sample was tested as received from the manufacturer (DuPont). The diameter of the sample was 50.8 mm and thickness 5 mm.

6.2 Polyetheretherketone (PEEK)

Polyetheretherketone (PEEK) is an organic thermoplastic polymer. It is one of the few plastics that is somewhat compatible with UHV systems where it can be used^[56] as a seal or as an electrical or thermal insulator. It has excellent mechanical and chemical resistance properties at elevated temperatures up to 250 °C^[56]. PEEK has a glass transition temperature around 143 °C and it melts around 340 °C^[55]. The main advantage compared to Vespel SP-1 is its lower cost and lower water solubility of 0.06 %^[24] that would predict lower initial outgassing.

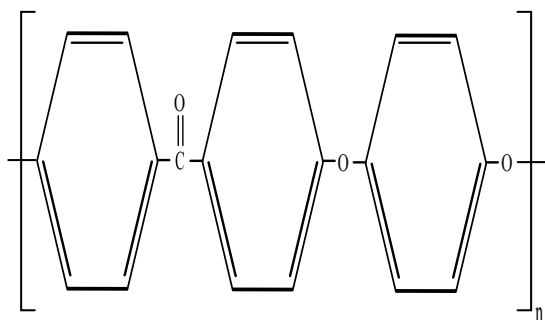


Figure 17: Chemical structure of PEEK. Figure based on source^[24].



Figure 18: 100 mm × 50 mm and 1 mm thick PEEK sample sheet.

The sample was provided by GoodFellow in a 100 mm x 100 mm semicrystalline sheet that was polished on one side and dull on the other side. The sheet was cut in half by machining and only one half with a total surface area of 103 cm² was tested. Before insertion to the sample chamber the sheet was wiped lightly with ethanol soaked cleaning cloth.

6.3 Macor

Macor is a registered trademark for a machinable glass ceramic made up of fluorophlogopite mica in a borosilicate glass matrix. The composition is approximately 46 % silica, 17 % magnesium oxide, 16 aluminum oxide, 10 % potassium oxide, 7 % boron trioxide and 4 % fluorine. According to the manufacturer, Macor can withstand high temperatures up to 1000 °C and the coefficient of thermal expansion is similar to most metals. It works as an insulator with high voltages and temperatures. Macor can be precisely machined with ordinary metal working tools and joining with other metals is usually possible with brazing. Since Macor exhibits no porosity and acceptable outgassing rates, it can be considered for ultra high vacuum systems where Macor is typically used as an electrical insulator in feedthroughs or as a coil support.^[57]

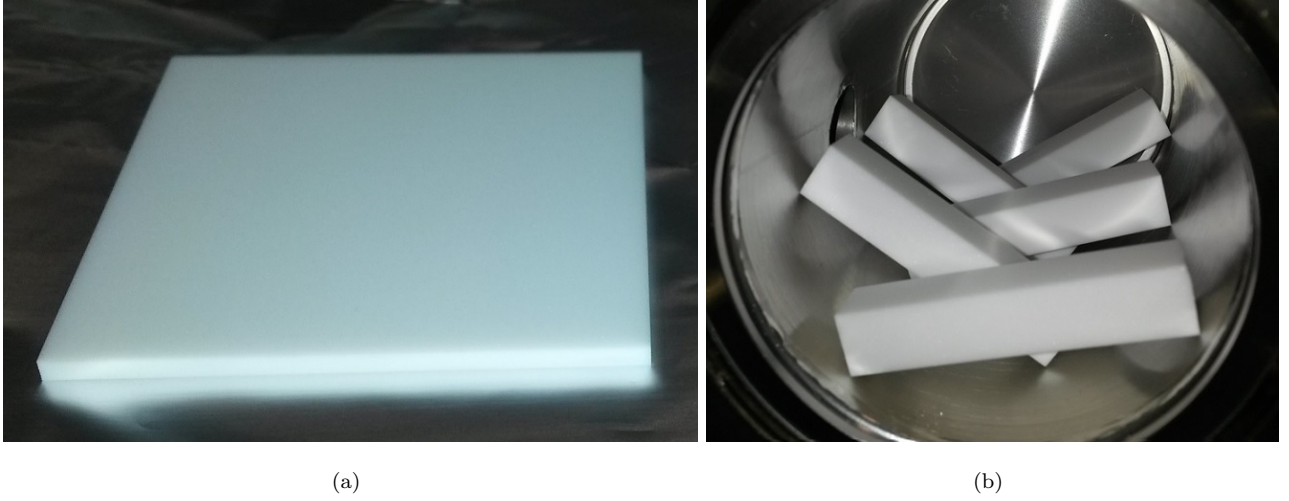


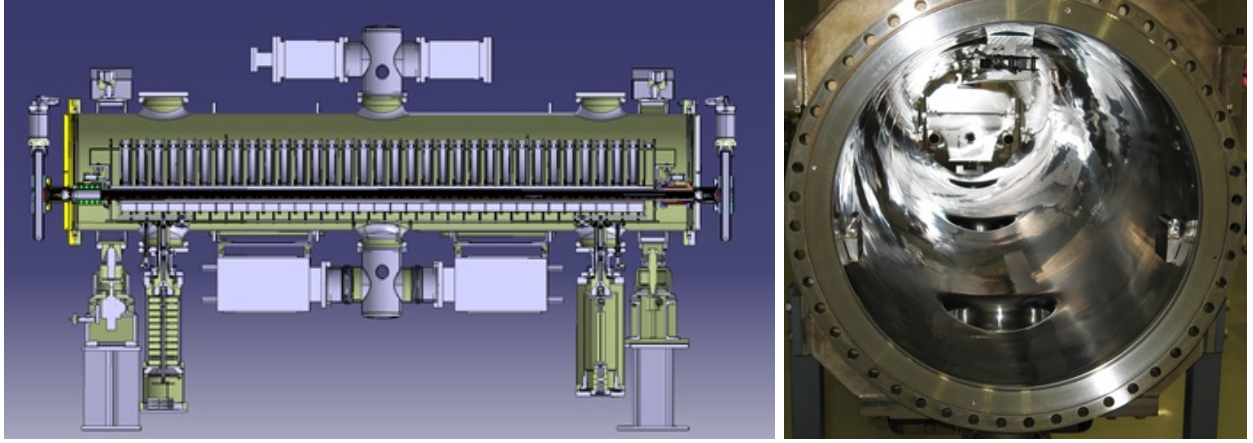
Figure 19: (a) One of the Macor plates on aluminum and (b) Macor rods in the sample chamber.

Samples were inserted in systems as received from RS Components. Different samples were tested on each system to measure the outgassing rates before and after bakeout. The two Macor plates tested on the throughput system had a thickness of 2 mm and a total surface area of 108 cm². The rods tested on the accumulation system were 50 mm long with a side length of 10 mm totalling a surface area of 110 cm².

6.4 Plasma sprayed 100 % fine alumina coating on stainless steel 304L

Alumina (Al₂O₃) is a commonly used ceramic in vacuum instruments such as cold cathode gauges due to its relatively low outgassing rates and insulating properties. It can be coated on stainless steel with e.g. thermal spraying methods such as plasma spraying. Plasma spraying applies a high-temperature plasma jet to heat up the coating precursor (i.e. alumina). The heated and high speed particles impinge on the substrate surface and rapidly cooldown forming a coating. Plasma spraying can provide thick coatings to large areas with high deposition rate compared to other coating processes such as physical vapor deposition, electroplating or chemical vapor deposition.^[59]

The motivation to measure the outgassing rates of alumina coating originates from the necessity to improve the cooling of the injection kicker magnets for the HL-LHC upgrade and the coating is considered for the inner surface of the vacuum chamber to increase the absorption of thermal radiation. The two fast pulsed kicker magnets are used to rapidly switch the path of the particle beam. The kicker magnets allow the injection of 450 GeV beam coming from the SPS to the LHC equilibrium orbit. The total deflection needed for the injection is 0.85 mrad. For this demanding task, the magnets are required to produce an integrated kick strength of 1.3 Tm^[63]. The uniform magnetic fields are produced with a rise time of 0.9 μs and they can be maintained up to 7.86 μs.^[60,61]



(a)

(b)

Figure 20: (a) Layout of the kicker magnet: 33 cells with a NiZn ferrite core placed between high voltage plates. Ceramic capacitors are sandwiched between each high voltage plate and a grounded plate^[63]. (b) Vacuum tank for the kicker magnets without any coating applied. Courtesy of Lorena Vega Cid from the Accelerator Beam Transfer group.

The main reason of interest for this coating is to improve the cooling of the ferrite yokes. Even though the kicker magnets are pulsed only 12 times to fill the LHC, the beam circulates through the apertures of these magnets for several hours. This results in significant beam induced heating of the ferrite yokes. If the Curie temperature $125\text{ }^{\circ}\text{C}$ is reached, the yokes will lose the ferromagnetic properties. This prevents injection to the LHC until the ferrites are cooled down, which can take several hours. For the HL-LHC upgrade the beam intensity will increase which in turn increases the beam induced heating. Thus additional measures to improve the cooling of the ferrites are needed.^[61,63]

Because of the design of the kicker magnet and UHV vacuum conditions, cooling is mainly by thermal radiation between the yokes and the vacuum tank. Currently the most limiting factor for the radiative cooling is the low emissivity of the stainless steel vacuum tank. Therefore, several coatings for the inside of the vacuum tank are under consideration, one of which is the plasma sprayed alumina coating. The coatings have emissivities in the range of 0.7 to 1.0 in wavelength range from $6\text{ }\mu\text{m}$ to $22\text{ }\mu\text{m}$.^[61,62]

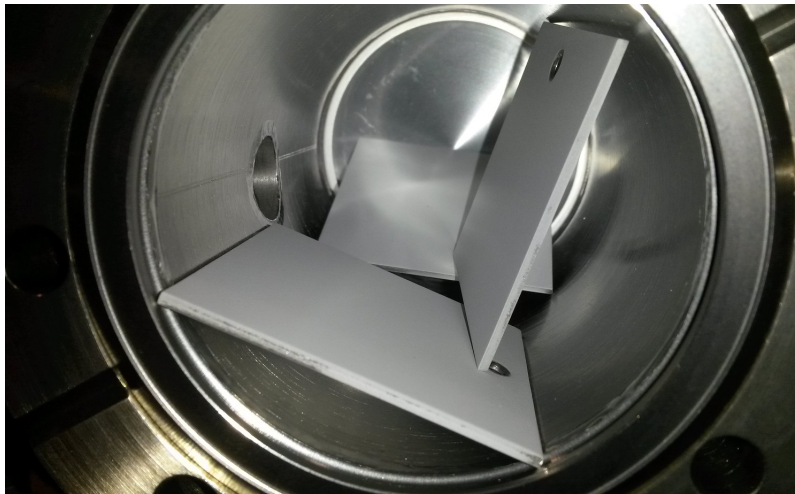


Figure 21: The three samples positioned inside the sample chamber in the accumulation system.

The samples were cleaned with Net-Inox^[64] as the treatments and cleaning applied is required to be the same as for the tanks. The drilled holes were made to hold the samples during the treatment. The total surface area of the samples was $162 \pm 2 \text{ cm}^2$ and each sample had a thickness of 2 mm. The thickness of the coating is unreported, but it is less than $300 \text{ }\mu\text{m}$.

6.5 Tungsten 99.95 %

Different types of tungsten alloys are often used or considered for collimation systems^[65] to prevent beam induced quenches and to protect the machine components against unavoidable beam losses. Tungsten is also a commonly used filament material for RGAs and pressure gauges^[16].

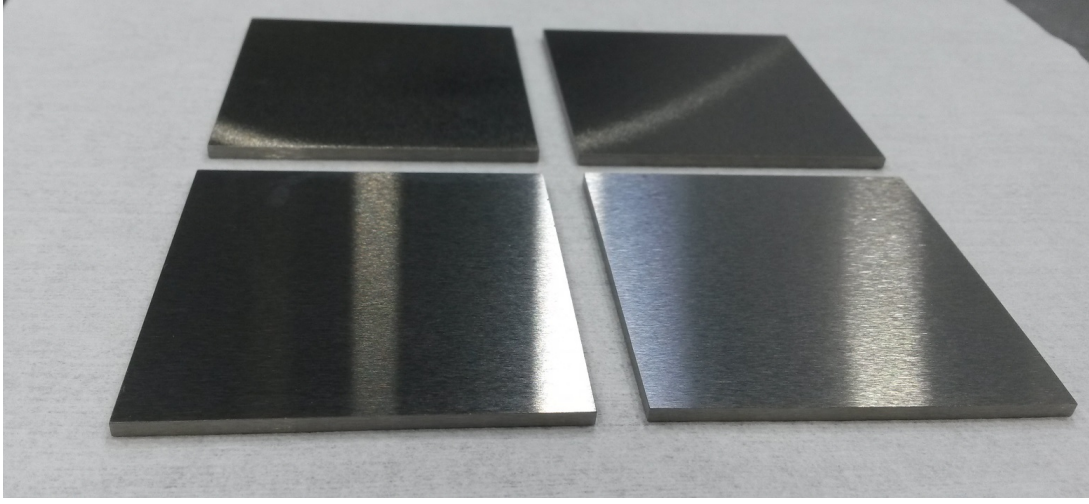


Figure 22: The four tungsten samples. Sample dimensions: $50 \text{ mm} \times 50 \text{ mm}$, thickness 2.0 mm.

Four tungsten (CAS 7440-33-7) samples were used from GoodFellow with a purity level 99.95%. The most common impurities according to the manufacturer are molybdenum (150 ppm), lead ($<50 \text{ ppm}$), silicon ($<50 \text{ ppm}$) and carbon (30 ppm). They were received from the company as rolled from the metal forming process. The samples were cleaned with a common metal finishing detergent NGL 17.40.

6.6 Graphite R 8500

Graphite is a commonly applied material for high vacuum systems with high temperature processes^[66]. In the accelerators, graphite blocks have been used in beam dumps and collimators^[67]. In the LHC very fast and large gradients of temperature with peak temperatures over $1000 \text{ }^\circ\text{C}$ inside the material can be expected if the beam is misdirected by an accident. Therefore, the absorbing materials for the blocks in the collimators have been selected based mainly on their thermal shock resistance capabilities.^[70]

The outgassing rates of graphite grades generally depend on impurities, cleaning and overall history of the samples, but compared to metals, the outgassing of graphite is more dependent on porosity, density, thickness as well as the method of graphitization^[66]. Graphite has a porous structure so gases from the atmosphere or substances from the cleaning procedure can penetrate deep into the bulk^[53]. The initial outgassing of graphite is expected to present long hydrocarbon chains, that are residues of the materials used in the compaction process^[67]. Due to poor vacuum properties, graphite grades are generally avoided unless a proper treatment is

applied. Vacuum properties can be improved by a high temperature heat treatment, which can expel most of the long hydrocarbon chains^[67].



Figure 23: One of the four identical graphite samples. Sample dimensions: 75 mm $\times$ 50 mm, thickness 10 mm.

For outgassing measurements, a graphite block of grade R 8500 from SGL Carbon was chosen. It is a general purpose grade that is formed by isostatic pressing. Four samples were cut from the graphite block by electroerosion. During the process the block was immersed in water. After the cutting, the samples were processed with ultrasonic cleaning with an ethanol solvent. One of the samples was tested as received from the cleaning on throughput system. Two of the samples were given a heat treatment at 1000 °C for 2 hours in a vacuum furnace and one of them was tested on the throughput system.

7 Results

This chapter presents the outgassing rate results from the two systems described in chapter 4. The pressures and outgassing rates are nitrogen equivalent and conversion from units of $\frac{\text{hPa l}}{\text{s cm}^2}$ to $\frac{\text{Pa m}}{\text{s}}$ is obtained by multiplying the former by a factor of thousand. The convention of referring to the mass-to-charge ratio simply as mass (in atomic mass units) is followed whenever it is reasonable to assume single ionization.

7.1 Throughput system results

The outgassing rate evolution over time at five different temperatures for unbaked samples are presented here. Gas evolution over time is also shown along with the curve. The RGA results are presented with a unit of ion current as complicated fragmentation patterns and inaccurate or unknown sensitivity factors make general quantitative analysis impossible. Fortunately, estimates for hydrogen and water sensitivity factors were obtained from RGA calibration and minimum χ^2 estimation described in appendix C. The ratio $\frac{s(\text{H}_2)}{s(\text{H}_2\text{O})}$ of the sensitivity factors for SEM scans were in the range of 6–12. At least six times lower water sensitivity was also observed in Faraday mode. These factors help to distinguish the most dominant gas as in most of the measurements either hydrogen or water was the highest or second highest ion current.

Test	Analog scan mode	Sample thickness (mm)	Sample surface area (cm ²)
1st background	SEM 1400 V	—	—
Macor	SEM 1400 V	2	108
PEEK	Faraday	1	103
Vespel SP-1	Faraday	5	48.5
Graphite	Faraday	10	100
Heat treated graphite	SEM 1000 V	10	100
2nd background	SEM 1000 V	—	—

Table 7: Chronological order of the tests, respective scan modes and sample surface areas.

Note that RGA ion currents of different tests are directly comparable only if the same mode and voltage was used. Table 7 shows the scan mode for each test. The first background measurement was used for Macor, PEEK, graphite and Vespel SP-1 and the second one was used for the heat treated graphite. Because the gas composition in some cases is quite complex, or not exactly known, the N₂ equivalent pumping speed (9.4 l/s) of the orifice was used regardless of the highest ion current to calculate all the outgassing rates as recommended [17].

Background tests

Outgassing Q is measured for the background tests as that is used for the background subtraction with samples. The first background measurement was done before any samples were tested and the second was the last measurement with the system to check if any change in background had occurred while the samples were tested. Figure 24 shows the outgassing Q for both of measurements as well as the evolution of ion currents, which can be used to qualitatively assess the gas evolution. The temperature was increased in steps as shown in the insert in figure 24(a).

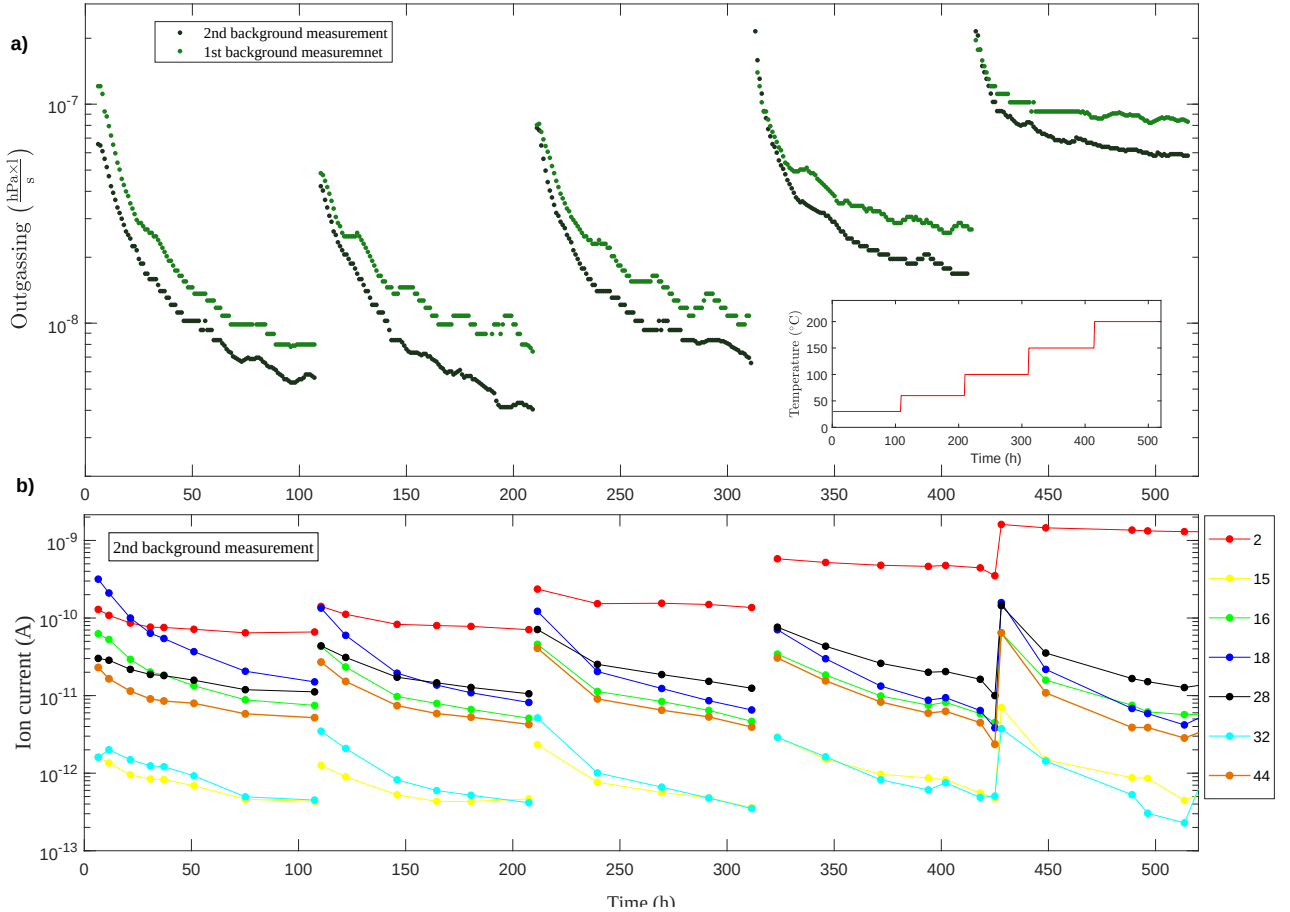


Figure 24: a) Outgassing Q of both background measurements at each temperature over time. b) Ion currents of the prevalent gases collected from the SEM 1000 V analog scans taken intermittently during the second background measurement. The points are connected to guide the eye.

The small difference between the two is explained by the fact that during the tests, the sample chamber was baked over 1000 hours at temperatures over 150°C and over 10 entire system bakeouts were also performed between the tests. Note that it is not reasonable to estimate outgassing rates for the sample chamber, since one is not able to differentiate sources of outgassing in a background measurement, which in this case includes the sample chamber and the rest of the system.

Because of the higher sensitivity factor for hydrogen, water clearly dominates the initial outgassing as expected. At higher temperatures water outgassing is also significant, but decreases quite rapidly compared to hydrogen outgassing, which is prevalent particularly at 150°C and 200°C . The presence of methane should be estimated from mass 15, as the mass 16 includes the fragmentation of water, CO and CO_2 . Because mass 15 is quite low, the third most contributing gas in the system is either CO or CO_2 .

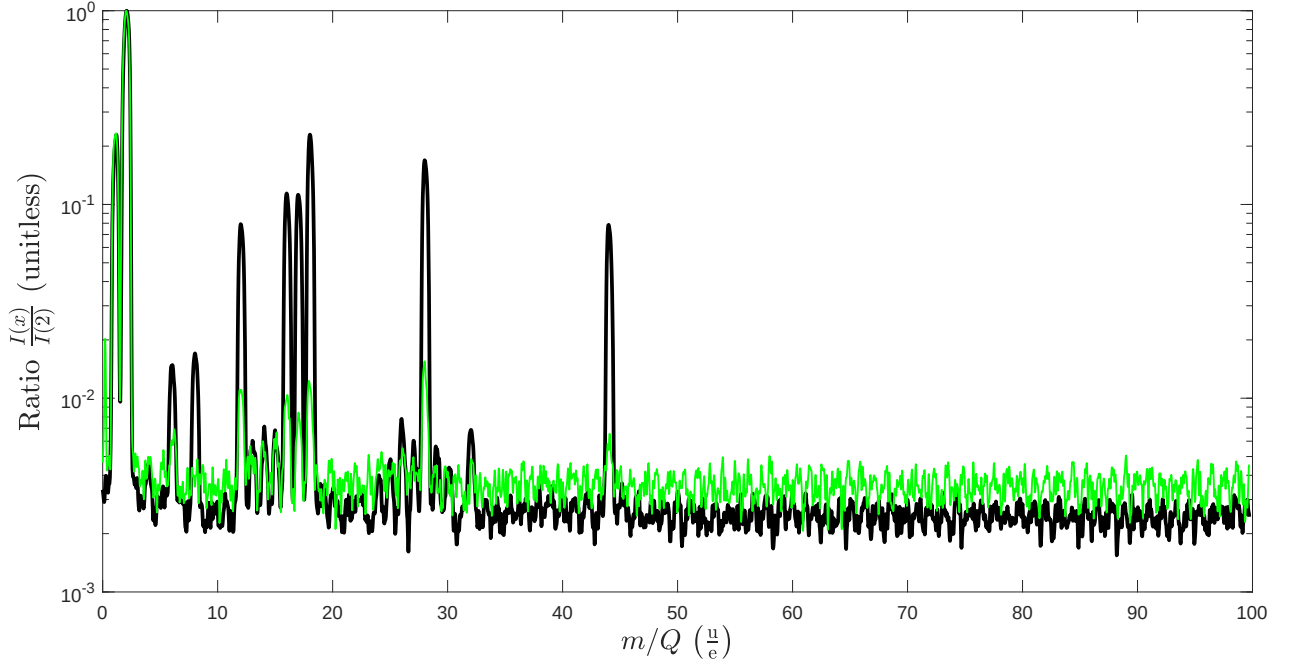


Figure 25: Normalised analog scan after a resetting bakeout (green) showing the cleanliness of the system and another scan (black) after the sample chamber has been exposed to air for the background measurement.

Figure 25 shows a clean system after a successful resetting bakeout at a pressure of 1.5×10^{-10} hPa. Water peak is almost a factor of 100 lower compared to hydrogen peak and no peaks at masses over 50 are present. The second scan (in black) is after the sample chamber has been exposed to air in order to simulate the measurement after the placement of samples. This scan was done after 106 hours of pumping at 30 °C, so it corresponds to the point at $t = 106$ h in figure 37(b) where the outgassing is $Q = 5.8 \times 10^{-9} \frac{\text{hPa l}}{\text{s}}$ at a pressure of $p = 6.2 \times 10^{-10}$ hPa.

Macor

Macor outgassing rates are presented in figure 26. The pressure in the system was initially a factor of 10 higher and stayed relatively high in comparison to the background measurement. At 200 °C the outgassing rate decreases quite rapidly and if the measurement would have been continued longer the background may have become more prominent.

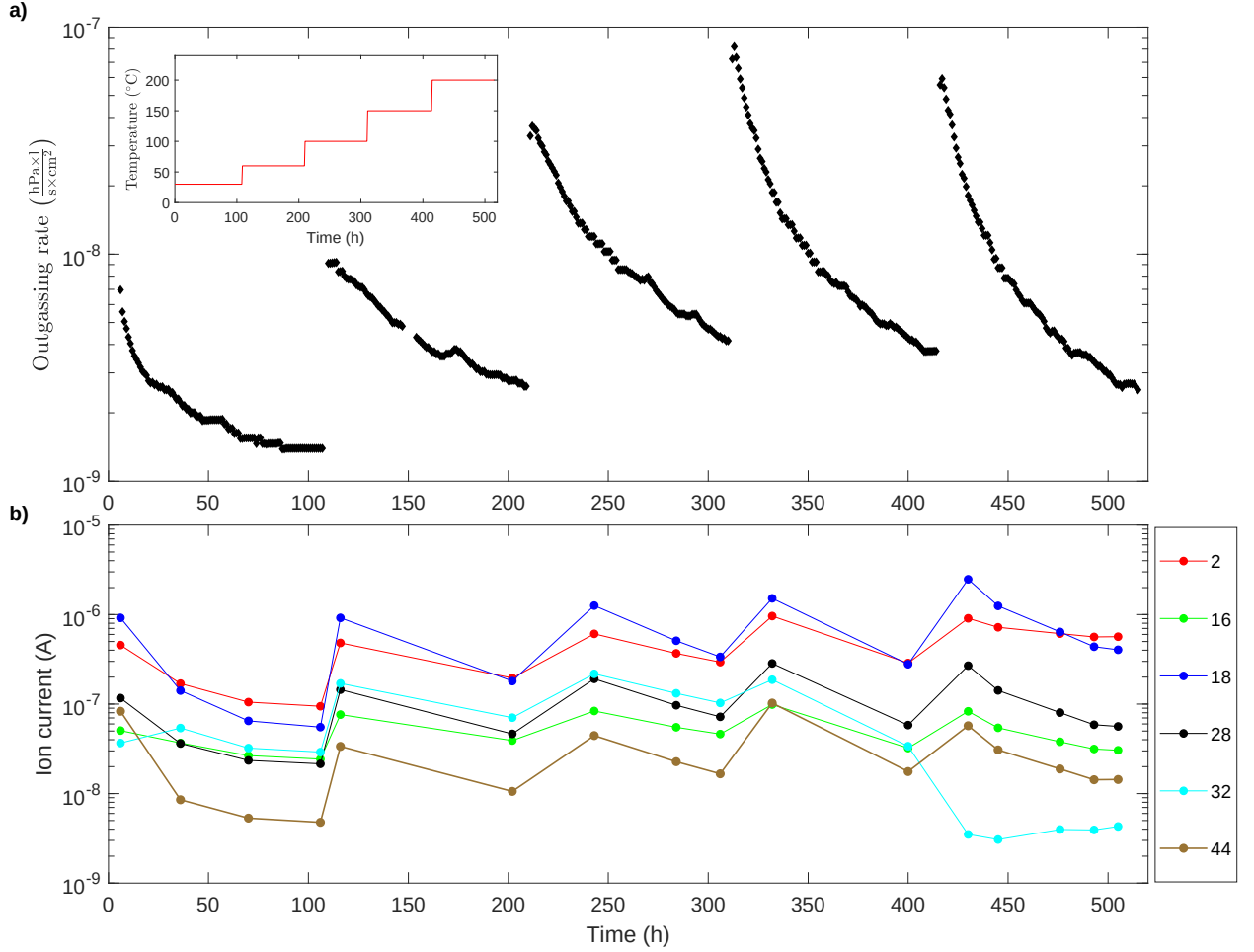


Figure 26: (a) Macor outgassing rate as a function of time and temperature. (b) Macor gas evolution over time compiled from analog scans (SEM 1400 V) taken at random time intervals.

Water outgassing at 30 °C resembles the water outgassing trend of the background measurement, but at higher temperatures it remains high compared to hydrogen and to the background measurement where hydrogen is the primary component. Therefore, water outgassing is highest at every scan in each temperature. CO and CO₂ outgassing are also more prevalent compared to the background measurement. Methane was not observed to any significant extent as mass 15 is scaled out of the plot and the observed mass 16 can be attributed mostly to the fragmentation of water and CO.

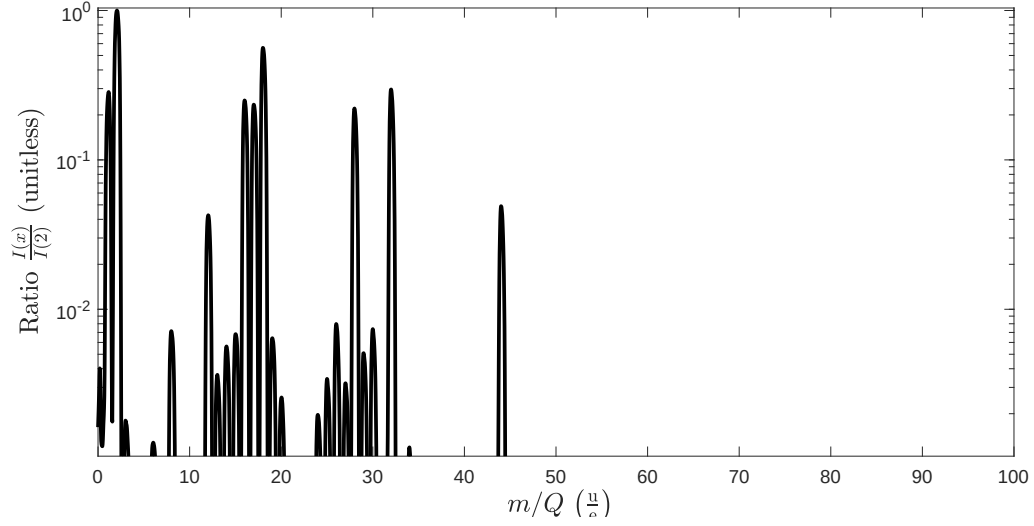


Figure 27: Macor normalised analog scan (SEM 1400 V) after 106 hours of pumping at 30 °C.

Figure 27 shows an analog scan after 106 hours of pumping. The presence of peak at mass 32 is peculiar, but not unexpected as this peak was also present and slightly higher during the first background measurement. It is either a byproduct of the RGA or a minor contamination in the system. Over time it faded from the scans as the RGA was kept on for hundreds of hours or the impurities were eventually removed.

PEEK

Figure 28 presents the outgassing and gas evolution of the prevalent components over time and temperature. A very high outgassing rate is apparent and the PEEK sheet was the primary cause for the high pressure in the system that ranged from 1.9×10^{-5} hPa to 3.4×10^{-7} hPa during the test even though the sample surface area was less than 3 % of the total system area.

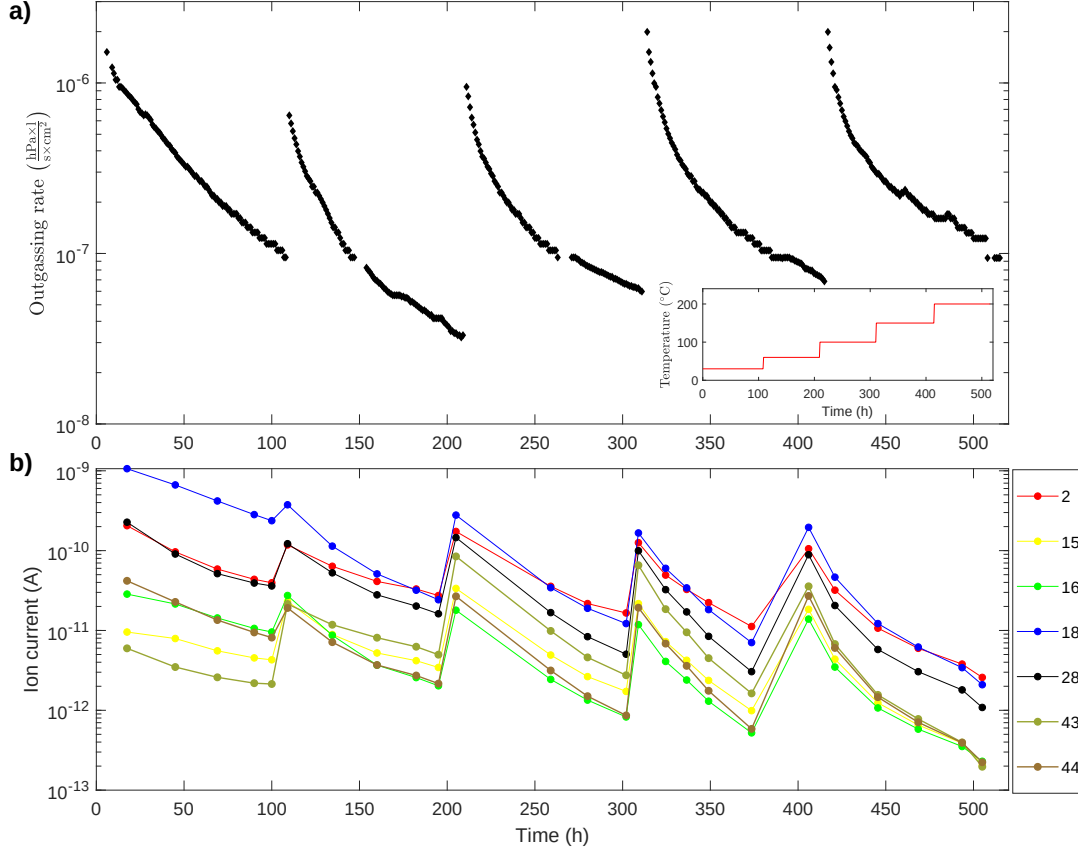


Figure 28: (a) PEEK outgassing rate as a function of time and temperature. (b) Ion currents compiled from analog scans (Faraday mode) of the most prevalent outgassing components.

Water vapour has the highest ion current at 30 °C and at 60 °C until it decreases to the level of hydrogen ion current at 180 hours. At higher temperatures water ion current starts as the highest component, but it decreases much faster compared to hydrogen and is eventually surpassed by hydrogen ion current. Despite hydrogen ion current being higher at some time intervals, water outgassing is higher at all times in each temperature due to the different sensitivity factors. No acceptable fits were found for entire time intervals at any temperature. For the first 24 hours, a power fit $q = at^b$ with an exponent of $b = -0.49$ was found, which is in agreement with the diffusion model described by equation (26), but later values at 30 °C showed a more exponential-like trend.

CO and CO₂ are clearly present in the scans, but since the sensitivity factors are not known, it is difficult to assess their contribution. The ion current at mass 15 indicates the presence of methane as well. The presence of mass 43 at higher temperatures is unexpected, especially at 150 °C and 200 °C it presents the fourth highest ion current.

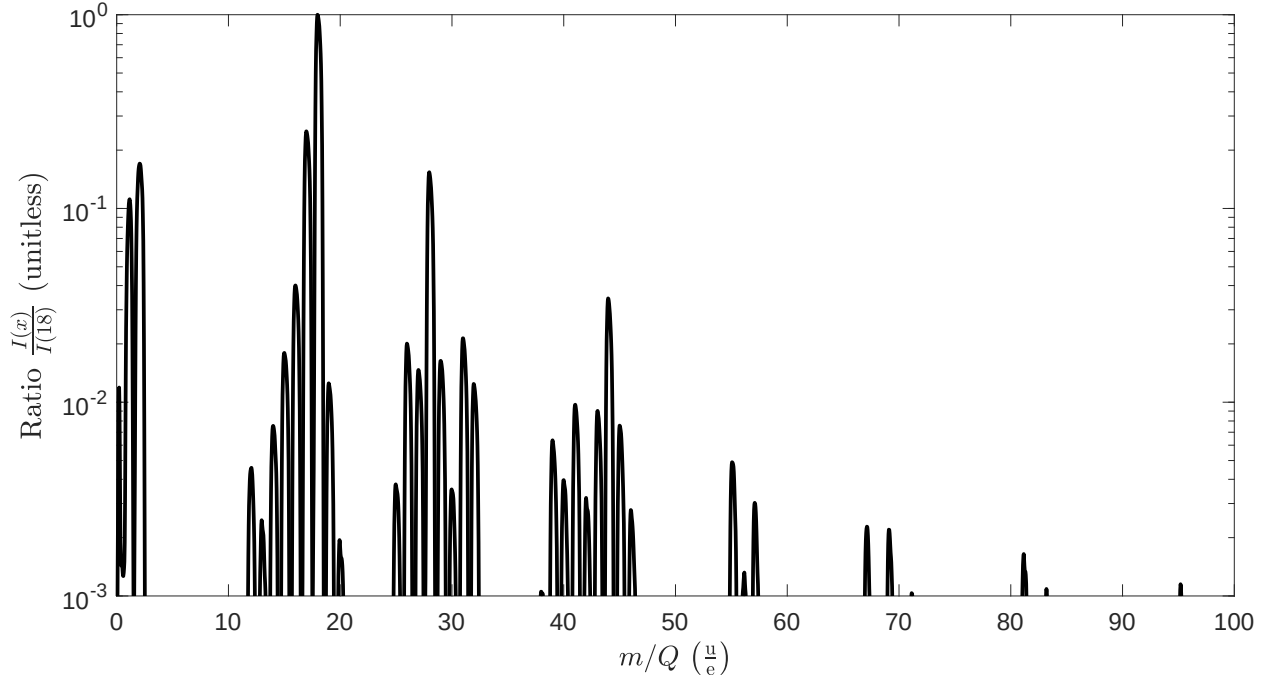


Figure 29: Faraday scan of PEEK after 100 hours at 30 °C

Figure 29 presents the normalised Faraday scan after 100 hours of pumping at 30 °C. The peak at mass 43 and some peaks at higher masses are also observed that could indicate a minor presence of oils in the system. The experiment had no powercuts or any sudden pump stops, that could explain a possible oil contamination so the source for the peaks remains ambiguous. After the measurements the sample was removed from the sample chamber and it was slightly bent according to the curvature of the sample chamber and had also acquired a brownish colour with some visible differences on the surface as well. This was somewhat unexpected as PEEK should have^[24] excellent chemical and mechanical properties up to 250 °C. However, it is uncertain if any of the important properties changed significantly.

Vespel SP-1

Vespel SP-1 also exhibited very high outgassing and pressures. When the valve separating the sample chamber was opened the first pressure reading was $p = 1.3 \times 10^{-5}$ hPa, so the cold cathode gauge was turned off for the day which explains the missing values from the first 28 hours in figure 30. The outgassing rate decreases quite rapidly at higher temperatures and at the end of the measurement the Vespel SP-1 sample showed lower outgassing rate even though the sample is 5 times thicker than PEEK.

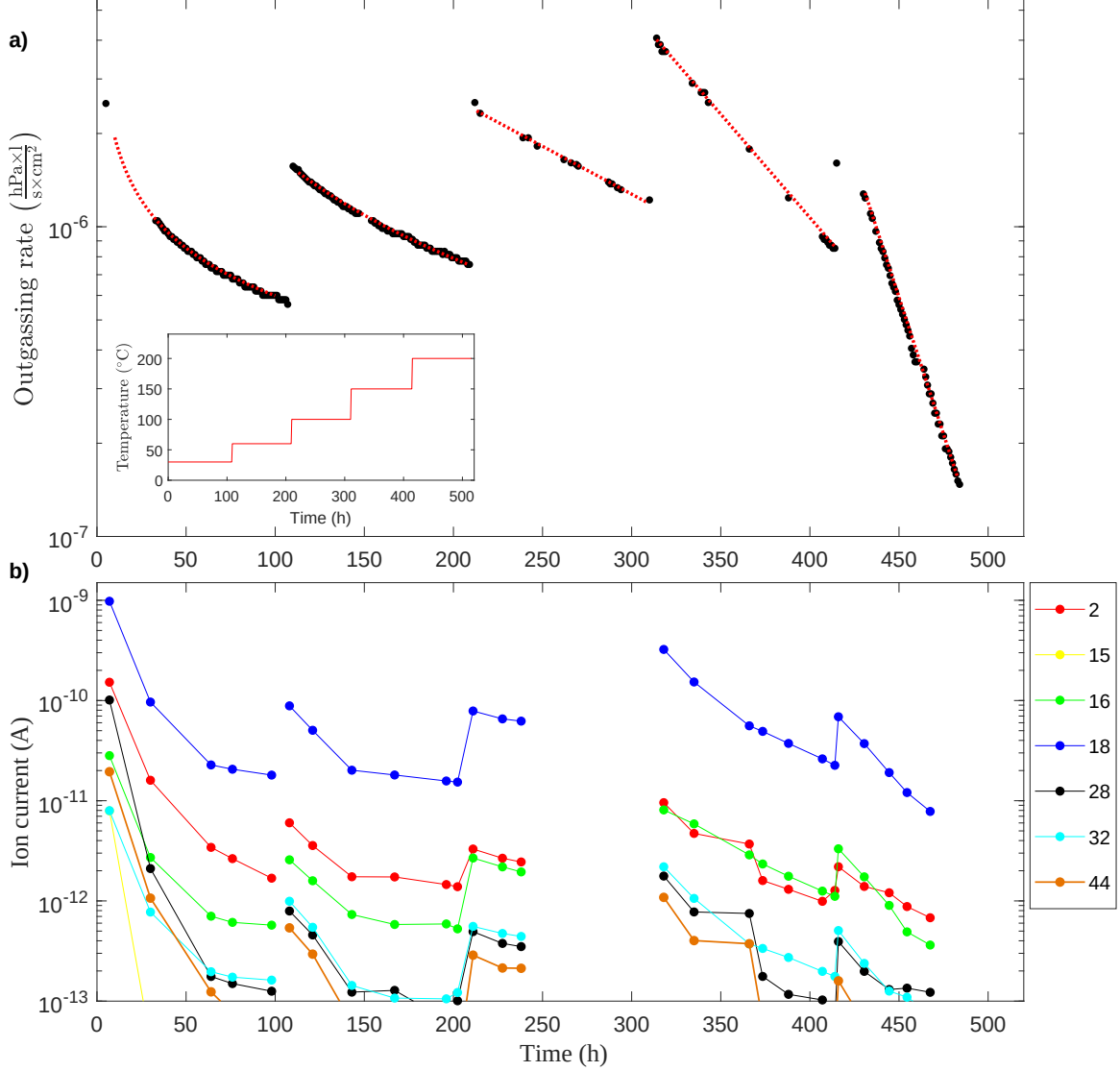


Figure 30: a) Vespel SP-1 outgassing rate at each temperature over time and their respective fits. Pressure readings at 100 °C and 150 °C were taken intermittently to protect the cold cathode gauge from the high pressure. b) Ion currents of the most prevalent outgassing components collected from Faraday scans.

Water outgassing is distinctly dominant throughout the entire test. The ion current at mass 16 is completely attributable to the fragmentation of water to oxygen ions. Mass 15 is scaled out so methane is not present in any significant amounts. The ion current for CO initially starts high, but diminishes quickly to negligible levels along with the ion current for CO₂. The ion current at mass 32 follows the water ion current quite accurately with an average ratio of 0.78 %. Thus the ion current in this case could be a byproduct of the RGA as water vapour reacts with the yttria coated hot filament releasing oxygen.

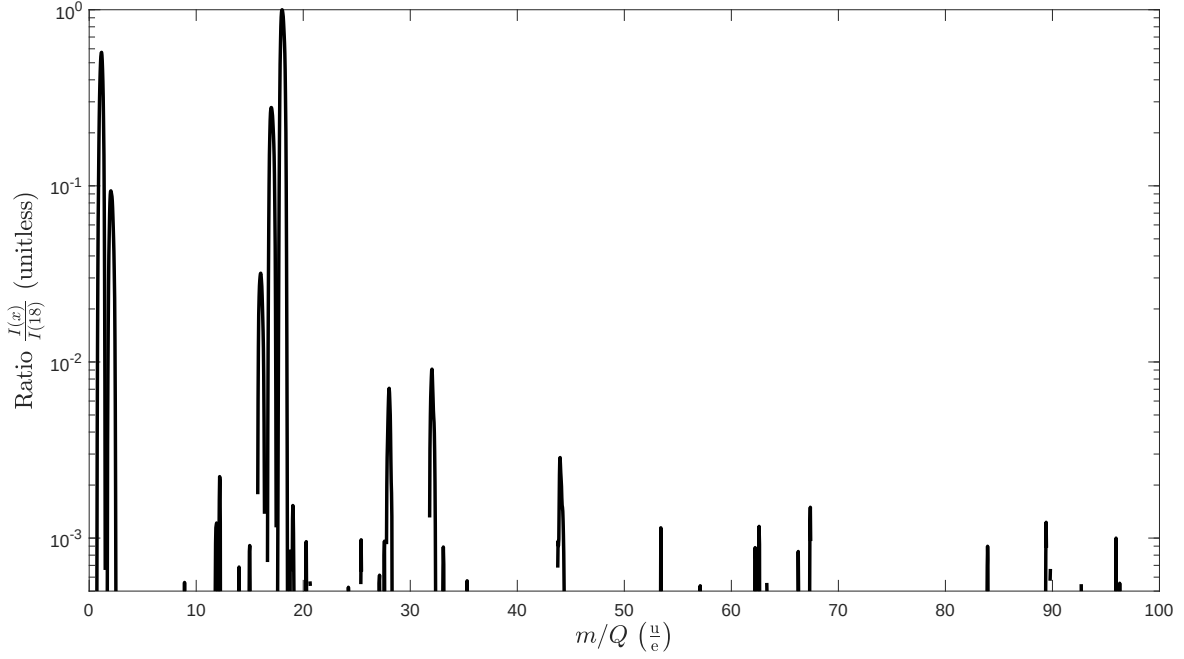


Figure 31: Faraday scan of Vespel SP-1 after 98 hours of pumping at 30 °C highlights the prevalence of water. Some minor peaks are visible at masses over 50, but they are almost a thousandfold smaller in comparison to water.

Temperature (°C)	Fit model	$a \left(\frac{\text{hPa l}}{\text{s cm}^2} \right)$	b (unitless)	R^2
30	$q = at^b$	5.799×10^{-6}	-0.4917	0.9985
60	$q = at^b$	4.528×10^{-4}	-1.205	0.9895
100	$q = a \exp(bt)$	1.069×10^{-5}	-0.007112	0.9982
150	$q = a \exp(bt)$	5.601×10^{-4}	-0.01575	0.9985
200	$q = a \exp(bt)$	43.81	-0.04035	0.9989

Table 8: Nonlinear least square fit coefficients for Vespel SP-1 outgassing rate at each temperature.

Because the outgassing is so prevalently water, suitable fits were found for the entire time interval at each temperature. The fits are included in figure 30 and the coefficients are compiled in table 8. Outgassing rate at 30 °C can be characterized by a power fit with an exponent of $b = -0.49$, which is compatible with the diffusion model described by equation (26). The powerfit at 60 °C is somewhat arbitrary since the exponent b is dependent on the time that the sample was at previous temperature. By shifting the values at 60 °C by 74 hours towards the start of the pumpdown, an exponent $b = -0.516$ ($R^2 = 0.995$) was obtained, which indicates an outgassing mechanism described again by equation (26). No suitable power fits were found in this manner at higher temperatures. The coefficients b in the exponential fits do not change by shifting the time and they could be used according to equation (25) to estimate the diffusion energy E_{diff} for water with an Arrhenius plot, but more values are required for an accurate fit.

Graphite

The big and thick graphite sample increased the system pressure by an average factor of 140 at 30 °C and the rate of decrease at each temperature has similar trends compared to the background measurement. Outgassing rates are presented on figure 32. The results at 200 °C are omitted since the test had to be stopped and instrumentation turned off as a precaution to a power cut.

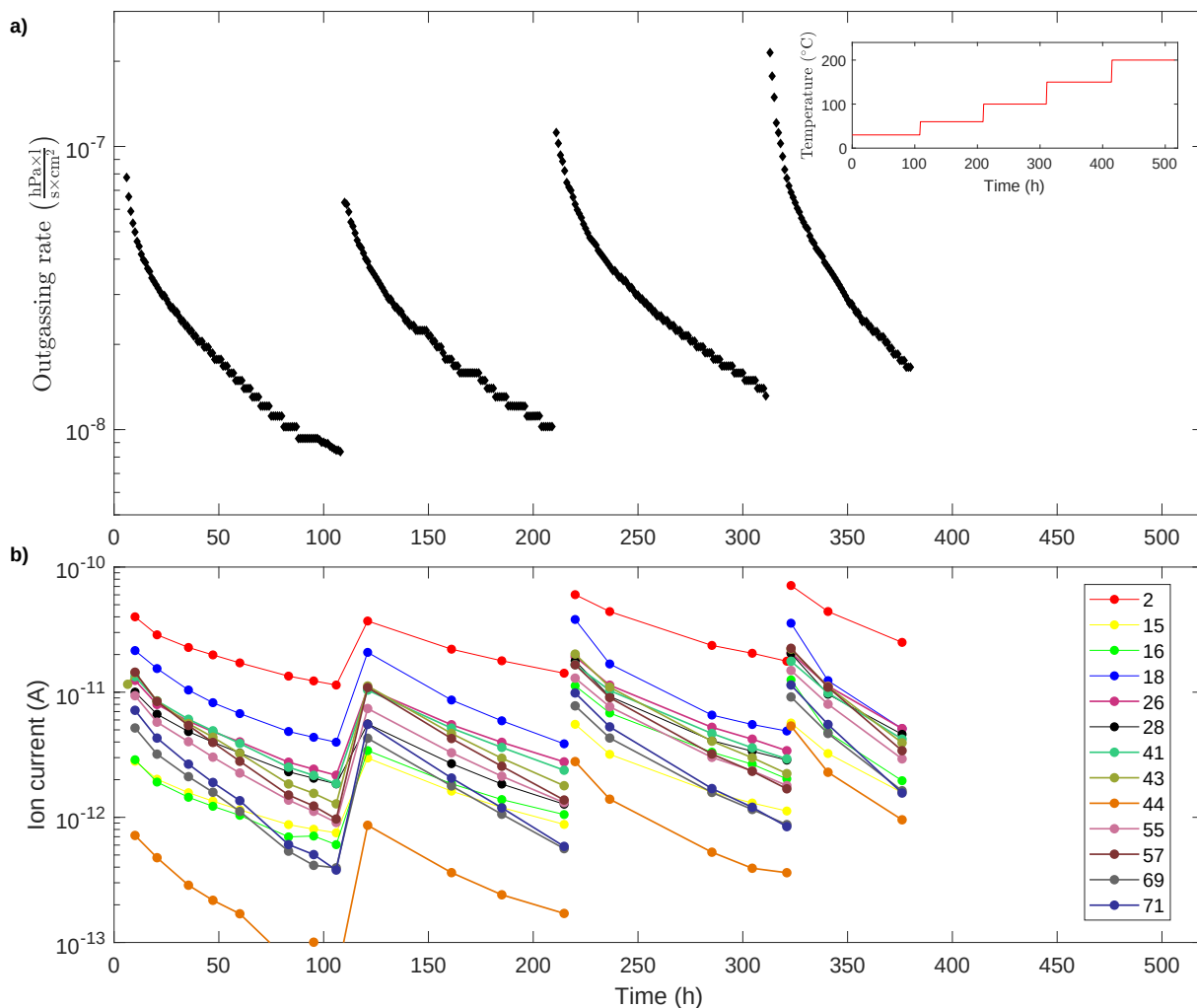


Figure 32: a) Outgassing rate of graphite as a function of time at the shown temperatures. b) Ion currents (Faraday mode) of the most prevalent outgassing components as a function of time and temperature.

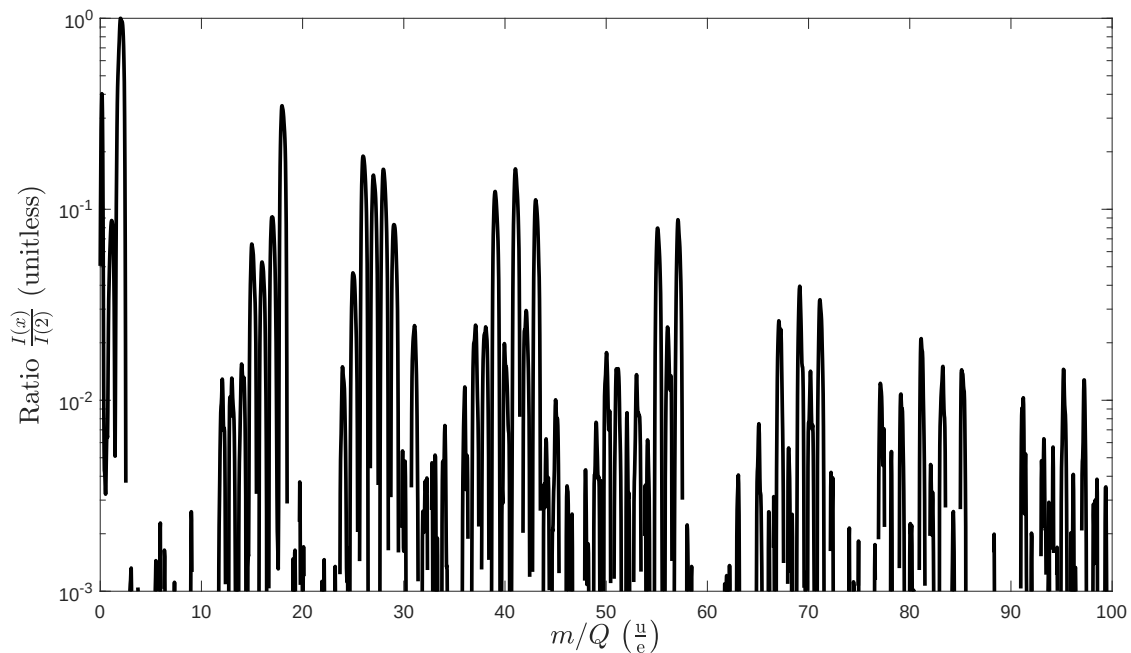


Figure 33: Normalised RGA scan of graphite after 106 hours at 30 °C

An analog scan in figure 33 reveals a plethora of peaks even at higher masses. These are most likely due to the long hydrocarbon chains coming from the manufacturing process mentioned in chapter 6. The presence of these peaks makes even qualitative analysis difficult and highlights the necessity for a treatment that could remove the hydrocarbon residues. The significant peaks were also monitored as a function of time and they are compiled in figure 32(b). Hydrogen and water ion currents are clearly highest, with the exception of water ion current dropping at 200 °C.

Heat treated graphite

Initially the heat treated graphite sample showed 12–20 times lower pressures at 30 °C and also decreased faster in comparison to the untreated graphite sample. After 100 hours of pumping at 30 °C, the pressure was about 55 times lower. Thus this was the only sample that was near to the background outgassing as seen in figure 34. For this reason, the uncertainties propagated from the estimated gauge error of 30 % have been included together with the outgassing rate in figure 35.

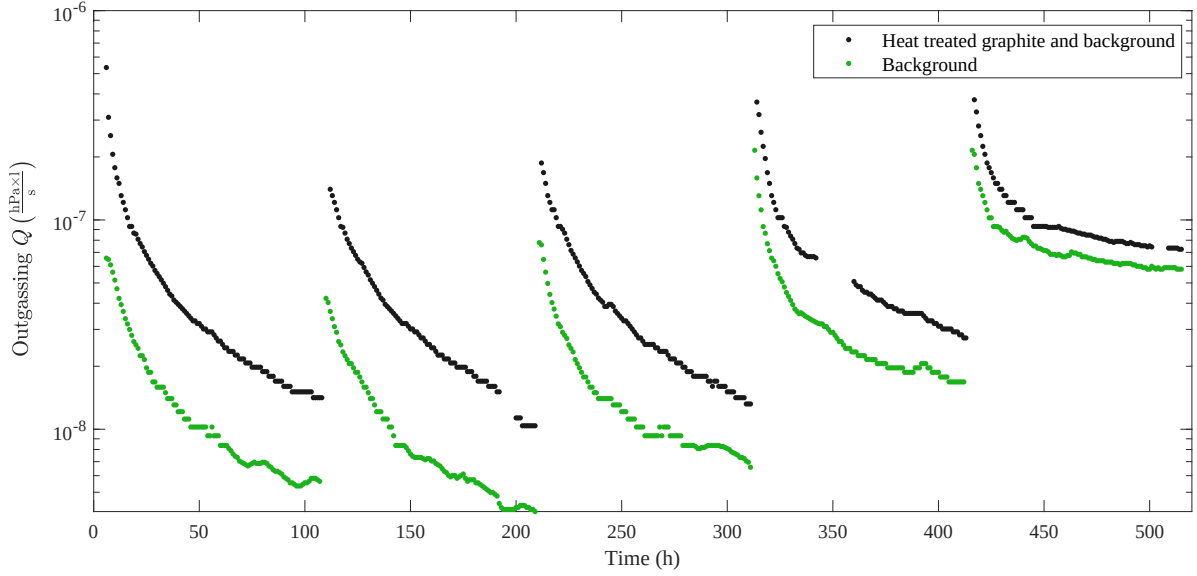


Figure 34: Heat treated graphite and background outgassing Q compared to the second background measurement.

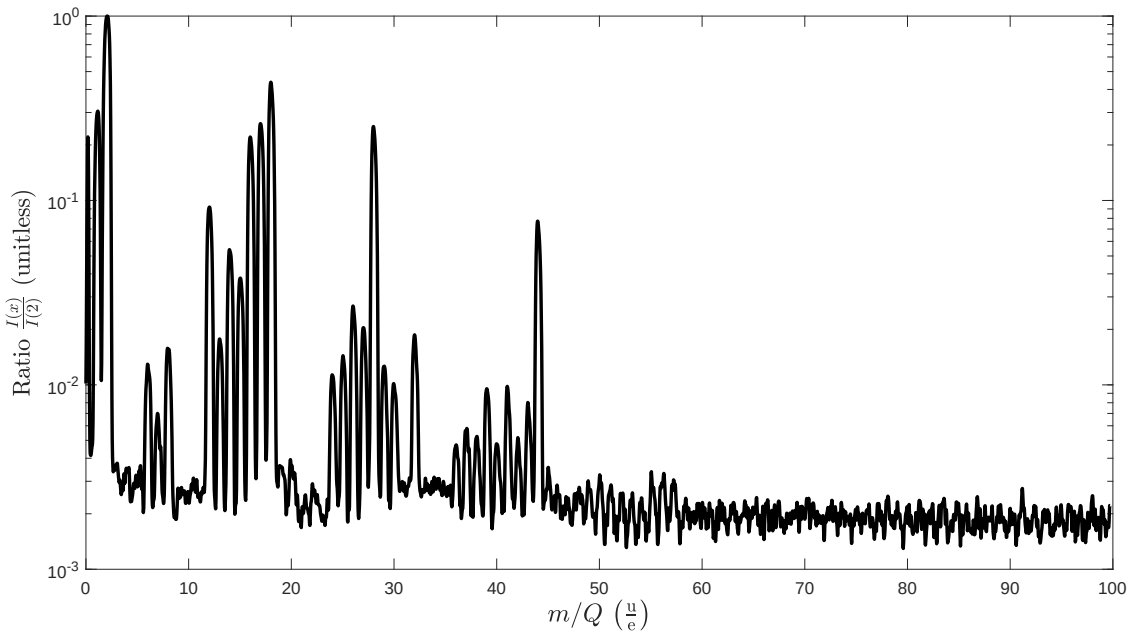


Figure 35: Normalised RGA scan of heat treated graphite after 106 hours at 30 °C showing the improved vacuum performance after heat treatment. There are no significant peaks at masses over 44, so the heat treatment expelled the long hydrocarbon outgassing components effectively.

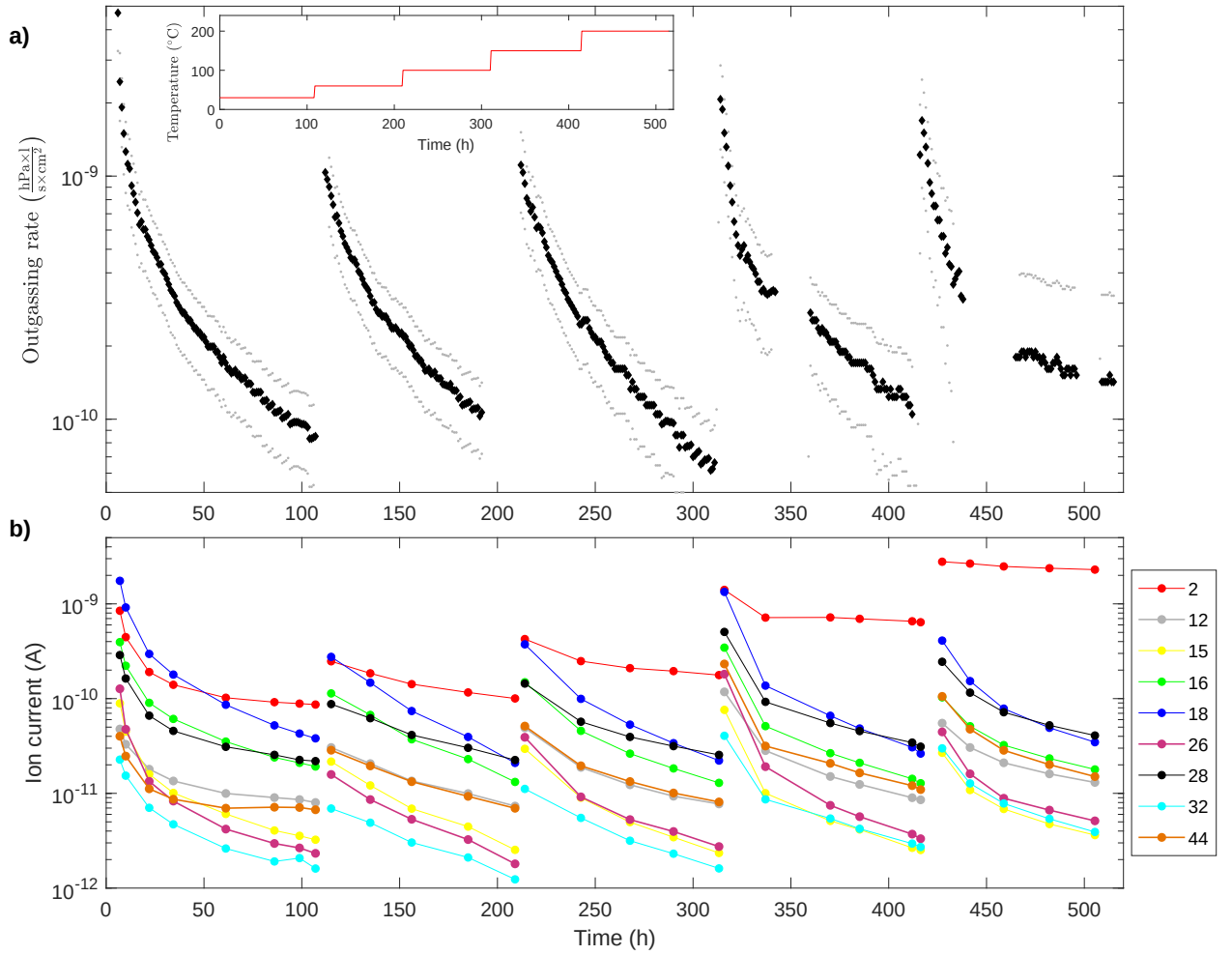


Figure 36: a) Heat treated graphite outgassing rate as a function of time and temperature. This plot also includes the estimated uncertainties because the outgassing was so close to the background b) Ion currents (SEM 1000V) of the most prevalent outgassing components as a function of time and temperature.

Contrary to the analog scans before the treatment, water ion current is highest in the beginning and even at 60 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$ it starts as the highest ion current, but decreases quite rapidly in comparison to hydrogen ion current. Nevertheless, outgassing of water is initially the highest at the first four temperatures and probably at 200 $^{\circ}\text{C}$ as well, because the hydrogen ion current could be attributed mostly to the background. The trends of competing hydrogen and other outgassing components is visible on the total outgassing rate plot, especially at 150 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$, where two phases can be distinguished. At first, the outgassing rate decreases rapidly as water and CO outgassing decreases. Then the total outgassing rate levels as the rate of decrease slows down for water and CO outgassing.

Discussion of results

Outgassing studies of important technical materials have been made for many decades and a lot of outgassing measurements can be found in literature. However, the results vary considerably^[71] for the same material even when the same measurement method is used. This difference seen even with the same method and same material is partly attributable to the difference between intrinsic and measured outgassing rates that depends on the readsorption surface, sticking and pumping parameters of the system^[48]. These parameters are rarely mentioned in the studies that only report the measured outgassing rates^[48]. But perhaps even more importantly, other factors like thickness, temperature, surface treatments, manufacturing processes and overall sample history influence the outgassing as well. Literature studies for the samples were found, but direct comparison of outgassing rates should be done with caution because of the aforementioned factors.

Figure 37 compiles the outgassing rates of the samples. The polymers presented the highest outgassing rates as expected. Water outgassing was significant for all the samples, particularly for polymers where it presented the highest outgassing rate at all times at each temperature. The prevalence is hard to quantify exactly due to the high uncertainties in the sensitivity factors for water and hydrogen. Vespel SP-1 water outgassing was found to be consistent with the simplified diffusion models. PEEK presented a lower outgassing rate for most of the time partly because of its lower water solubility and thickness, but the rate of decrease at high temperatures was faster for Vespel SP-1 despite its thickness.

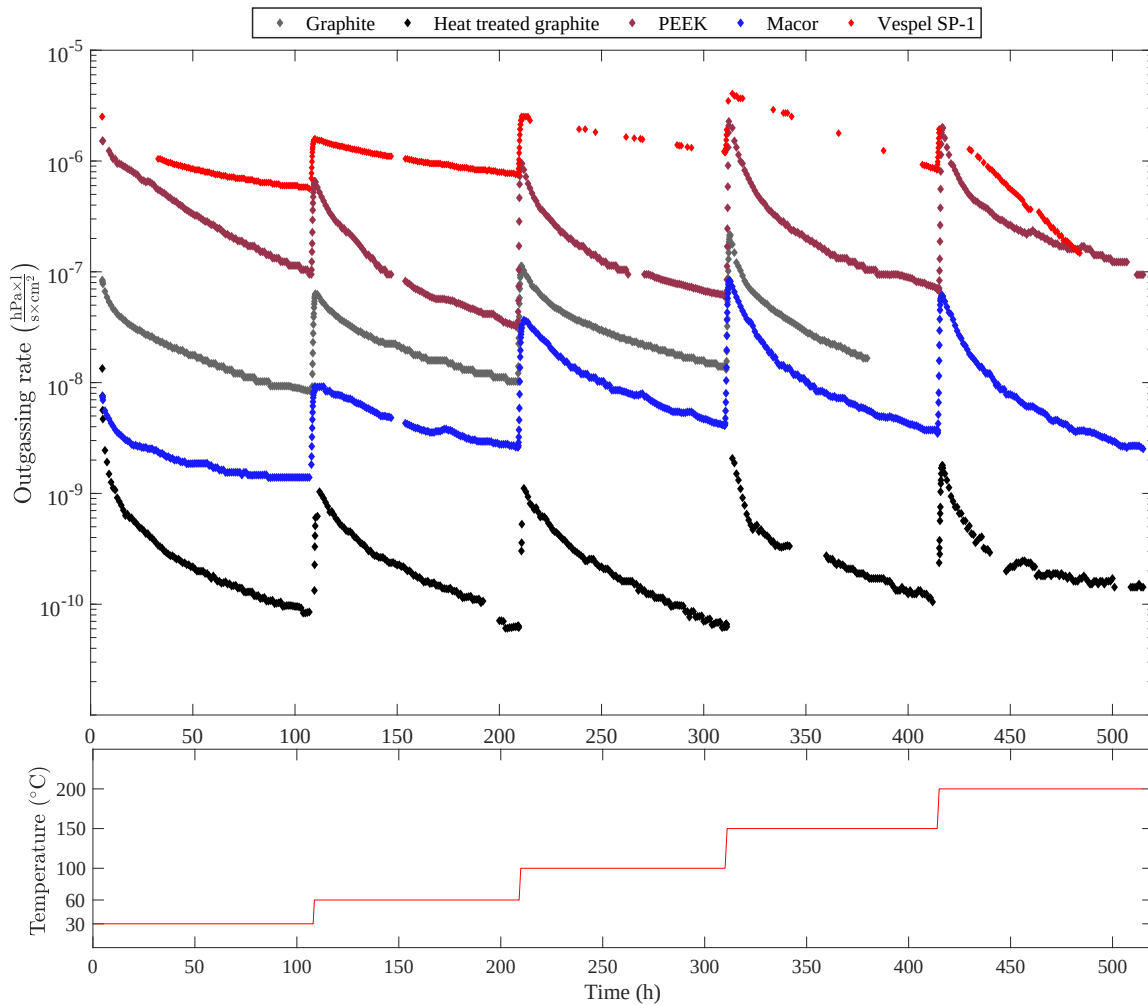


Figure 37: Outgassing rates of the samples.

The outgassing rate uncertainties are attributable to the pressure error as explained in chapter 4.2 and can be estimated roughly as 30 % with one exception: the heat treated graphite sample exhibited quite low outgassing and with this sample the background subtraction was relevant and thus the propagated error was included in figure 35. In many cases, outgassing at elevated temperatures starts at the same level, or sometimes even at lower levels, compared to previous temperatures. An obvious explanation is that some of the gas has already been outgassed. The amount of gas that has left the system can be estimated roughly as $\int_{t_0}^t Q dt$, that should also include the 6 hours of pre-pumpdown of the sample chamber.

Graphite exhibited quite high outgassing without a heat treatment and the long hydrocarbon chains are distinctly present in the analog scans. A heat treatment at 1000 °C expelled the hydrocarbon chains and lowered the outgassing rate significantly. This is in agreement with literature^[67] where an unreported graphite grade was also given a heat treatment at 1000 °C. After an exposure to air and a regular in-situ bakeout at 300 °C, the outgassing rate is reported^[67] as quite similar to "usual metallic vacuum components" and the long hydrocarbon chains were also expelled. Watanabe et al.^[46] also reported very small gas uptake of graphite during exposure to air after the heat treatment.

The published outgassing rates for Vespel SP-1 vary on a large scale. Battes et al. have measured the outgassing rates of PEEK, Macor and several Vespel SP-1 plates. The tests were based on the difference method, which is a modified version of the throughput method. The outgassing rates of the unbaked samples were measured subsequently at three temperatures for 100 hours. The results are presented in table 9.^[71,72,73]

Sample	Sample thickness (mm)	N ₂ equivalent total outgassing rate ($\frac{\text{hPa l}}{\text{s cm}^2}$)		
		100 h at 20 °C	100 h at 100 °C	100 h at 200 °C
Vespel SP-1	0.79	6.53×10^{-7}	6.82×10^{-8}	2.33×10^{-9}
Vespel SP-1	1.5	5.61×10^{-7}	7.56×10^{-7}	$< 5.00 \times 10^{-9}$
PEEK	1	8.90×10^{-8}	4.94×10^{-10}	1.16×10^{-9}
Macor	3.9	6.4×10^{-10}	1.8×10^{-9}	1.1×10^{-9}

Table 9: Literature values for polymers^[73] and Macor^[72]. Macor values were read from a digitalized plot.

The measured Macor values at 100 °C and 200 °C are close to the literature values and about a factor of 2.3 higher in both cases. Even though lower values were measured for the thicker sample at 20 °C, Battes et al.^[73] found that the outgassing rate for a thinner polymer sample decreased much more rapidly particularly at higher temperatures. This observation and the obvious experimental differences explain why the measured Vespel SP-1 sample with the throughput system presents higher values at 100 °C and 200 °C compared to this literature study. The PEEK samples however have the same thickness, but the values at higher temperatures are factors of 80 and 120 times higher.

The differences between the polymers could also come from the different grades that are available on the market and the lacking information on their differences^[71]. Manufacturers often enhance processing by applying internal procedures that have an influence on the outgassing behaviour^[71]. Thus comparison is of limited use and own outgassing measurements for the specific material type could be the only solution.

7.2 Accumulation system results

Results presented here are nitrogen equivalent which in practice means that these results could estimate the reading of a nitrogen calibrated gauge in a system that is made from the tested material with a known surface area and the gas specific pumping speeds are also known in this system. Conversion to hydrogen equivalent outgassing rates can be obtained by multiplying the results by a factor of 2.34. Here, the exact gas composition is known due to the calibrated RGA and the gas specific pumping speeds are also used. A SEM voltage of 1400 V was used for all the analog and MID scans to comply with the RGA calibration. The terms "total outgassing" or "total outgassing rate" refer to the values measured by the BAG. Ideally, the gas specific outgassing rates measured by the RGA should add up to the value measured by the BAG. Results are plotted as a function of inverse absolute temperature $1/T$ because the expected exponential trend should be more apparent in this manner and the exponent conveys information about the activation energies.

Test	Bakeout time (h) at 250 °C	Bakeout time (h) at 150 °C
1st background	36	2
Alumina coated SS304L	39	2
Tungsten	24	22
2nd background	24	22
Macor	24	21

Table 10: Chronological order of the tests and the respective bakeout times.

Table 10 shows the tests and bakeout times at each temperature. Two background measurements were made. The first one was made after a new variable leak valve was installed to the system and before any of the samples were tested and the second background was measured two tests later. The first background test was used for alumina coated stainless steel samples and the second was used for tungsten and Macor samples, because the bakeout times are similar and also because this way the background tests are right before or after the sample tests.

Background tests

Figure 38 presents a normalised analog scan of the entire system demonstrating a typical residual gas spectrum of a clean UHV system. Analog scans were always performed up to a mass of 100, but never showed any peaks after mass 44. Figure 39 shows the small difference between analog scans of the entire system scan and the scan after the sample chamber has been isolated from the rest of the system.

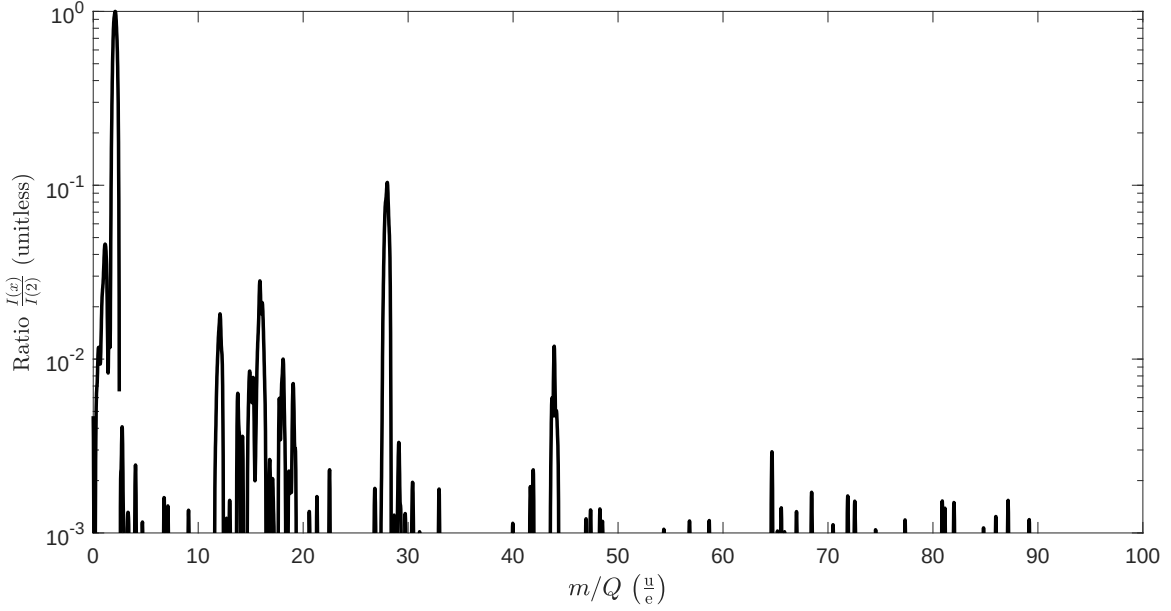


Figure 38: Normalised analog scan with SEM voltage 1400 V of the system at a pressure of $p = 7.8 \times 10^{-11}$ hPa.

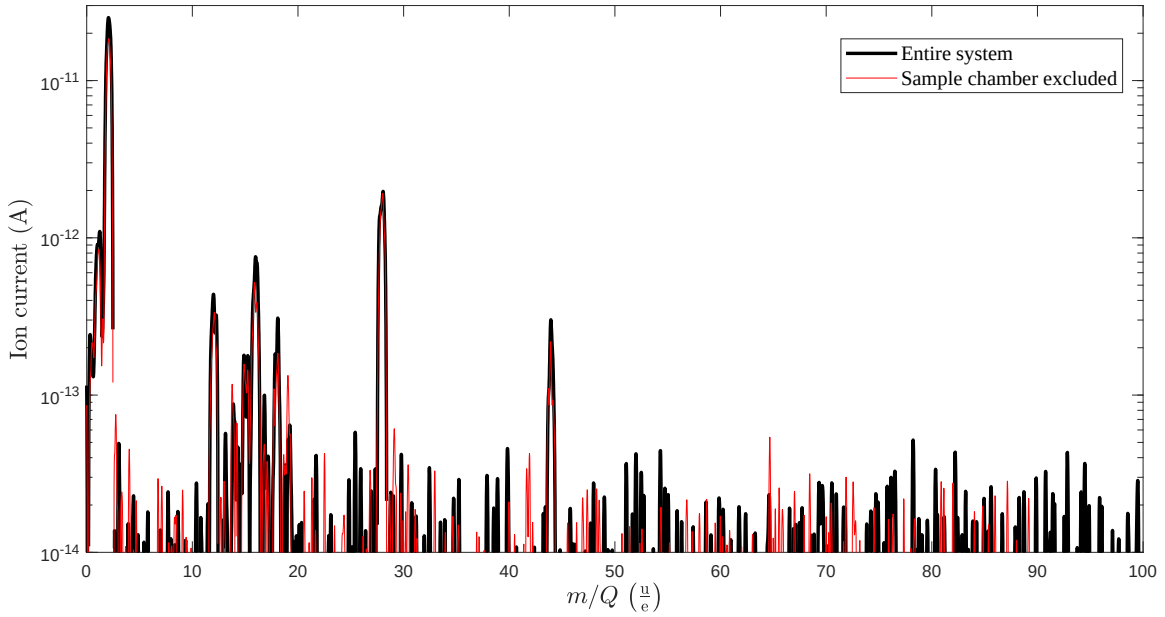


Figure 39: Comparison of scans with the variable leak valve open after bakeout for 2 days and a scan with the valve closed 66 h at pressures of $p = 7.3 \times 10^{-11}$ hPa and $p = 6.5 \times 10^{-11}$ hPa. Note that the scan is not normalised.

It is already evident from figure 39 that the sample chamber contribution to the system pressure is quite minimal and therefore accumulation tests are required to determine the outgassing of the sample chamber. The results compiled from the accumulation tests are presented in figure 40.

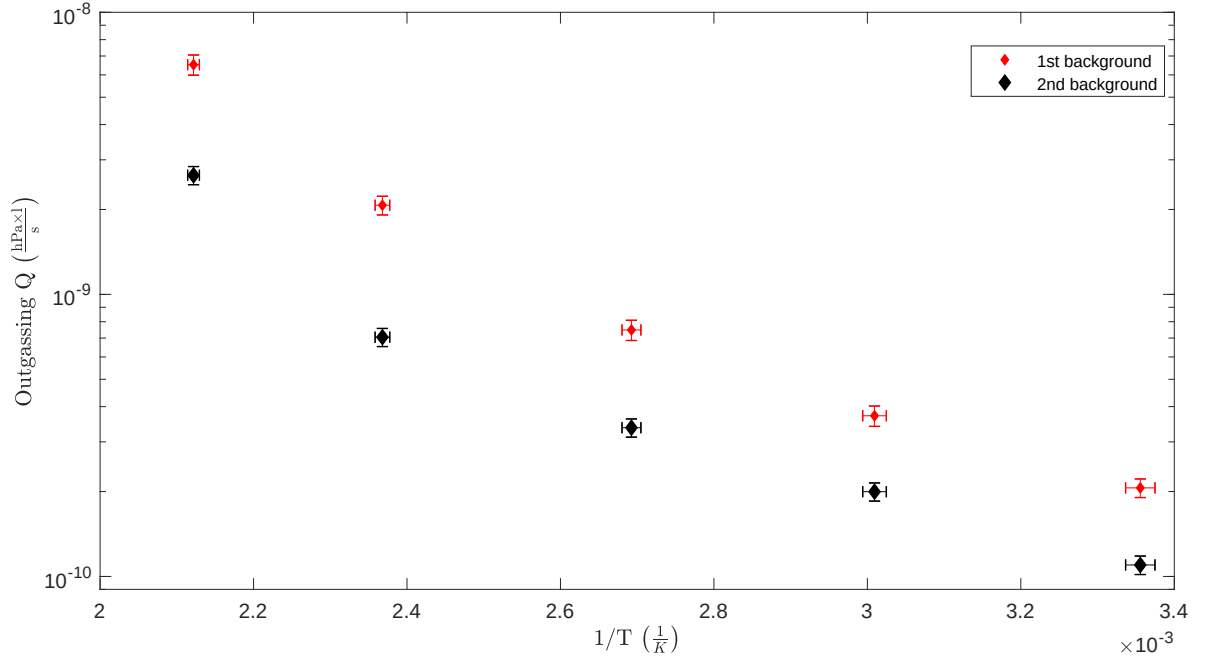


Figure 40: Total outgassing comparison of the first and second background tests.

Note that the background results are given in units of outgassing $\frac{\text{hPa}\cdot\text{l}}{\text{s}}$ because these are the values that are used for background subtraction with samples. Outgassing rates could be evaluated by dividing the results by the sample chamber surface area (278 cm^2), but this is not very useful or meaningful because the outgassing comes from two sources. The vacuum fired sample chamber should present quite low outgassing, but the new variable leak valve also has a small volume on the sample chamber side, and it is not possible to differentiate the two sources from another.

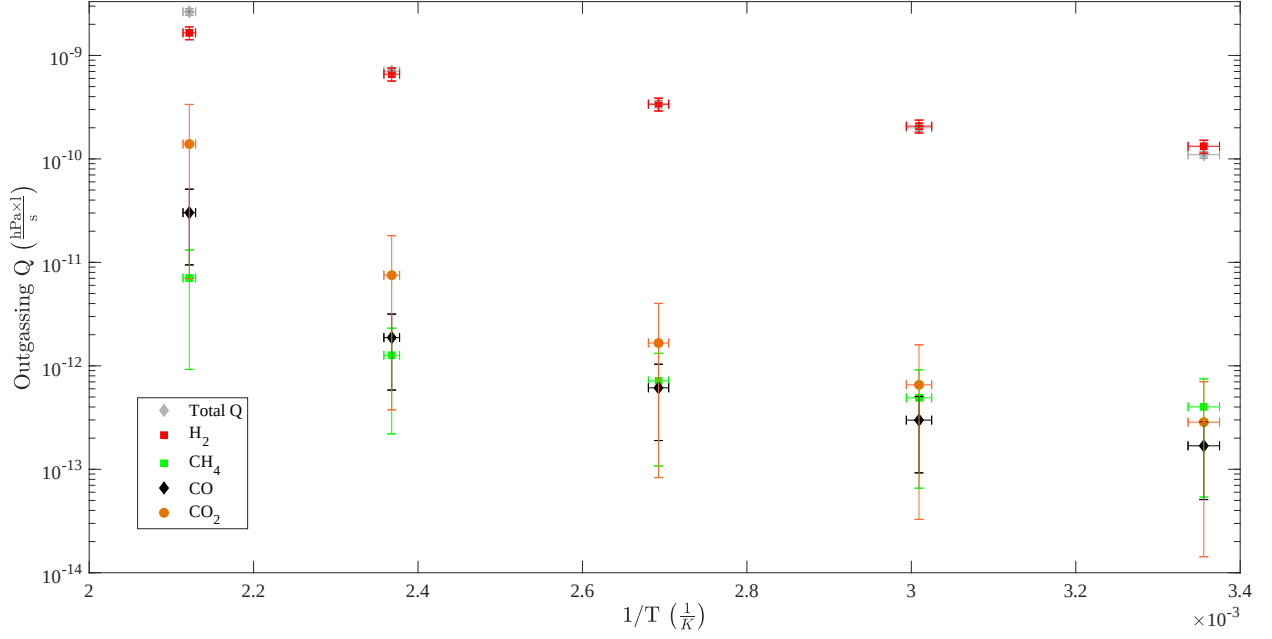


Figure 41: Total outgassing of the 2nd background test measured by the BAG and the gas specific outgassing measured by the RGA.

Temperature (°C)	Total Q ($\times 10^{-10}$)	H ₂ ($\times 10^{-10}$)	CH ₄ ($\times 10^{-12}$)	CO ($\times 10^{-13}$)	CO ₂ ($\times 10^{-13}$)
25	2.1 ± 0.2	2.1 ± 0.3	1.0 ± 0.5	3.5 ± 2.2	$3.4 \pm \begin{smallmatrix} 3.5 \\ 3.4 \end{smallmatrix}$
60	3.8 ± 0.3	3.7 ± 0.5	1.5 ± 0.8	6.6 ± 4.2	$6.4 \pm \begin{smallmatrix} 7.9 \\ 6.4 \end{smallmatrix}$
100	7.4 ± 0.6	7.6 ± 1.1	2.2 ± 1.3	12 ± 8	$14 \pm \begin{smallmatrix} 18 \\ 14 \end{smallmatrix}$
150	21.1 ± 1.6	20.2 ± 2.7	5.5 ± 2.8	37 ± 21	$50 \pm \begin{smallmatrix} 60 \\ 50 \end{smallmatrix}$
200	66 ± 5	61 ± 9	13 ± 9	270 ± 190	$800 \pm \begin{smallmatrix} 1100 \\ 800 \end{smallmatrix}$

Table 11: Outgassing Q ($\frac{\text{hPa}\cdot\text{l}}{\text{s}}$) and the error estimates of the first background test at each temperature.

Temperature (°C)	Total Q ($\times 10^{-10}$)	H ₂ ($\times 10^{-10}$)	CH ₄ ($\times 10^{-13}$)	CO ($\times 10^{-13}$)	CO ₂ ($\times 10^{-13}$)
25	1.2 ± 0.1	1.3 ± 0.2	5.4 ± 3.5	1.8 ± 1.2	$3 \pm \begin{smallmatrix} 4 \\ 3 \end{smallmatrix}$
60	2.0 ± 0.2	2.1 ± 0.3	5.9 ± 4.3	3.0 ± 2.1	$7 \pm \begin{smallmatrix} 9 \\ 7 \end{smallmatrix}$
100	3.4 ± 0.3	3.4 ± 0.5	8.2 ± 6.1	6.3 ± 4.2	$17 \pm \begin{smallmatrix} 23 \\ 17 \end{smallmatrix}$
150	7.0 ± 0.5	6.7 ± 0.9	13 ± 11	19 ± 13	$80 \pm \begin{smallmatrix} 110 \\ 80 \end{smallmatrix}$
200	26.6 ± 2.0	16.6 ± 2.4	70 ± 60	300 ± 210	$1400 \pm \begin{smallmatrix} 2000 \\ 1400 \end{smallmatrix}$

Table 12: Outgassing Q ($\frac{\text{hPa}\cdot\text{l}}{\text{s}}$) and the error estimates of the second background test at each temperature.

The first background test presented factors of 1.8 and 1.9 higher total outgassing at 25 °C and at 60 °C, and about two to three times higher outgassing at higher temperatures compared to the second background test. The difference between the tests is explainable by the several bakeouts the system and the sample chamber went between these tests. The sample chamber was baked hundreds of hours at temperatures up to 250 °C between the background tests. The bakeouts probably lowered mostly the outgassing of the variable leak valve volume within the sample chamber.

Plasma sprayed 100 % fine alumina coating on stainless steel 304L

Figure 42 shows the outgassing rate estimates for the alumina coated SS304L samples and table 13 compiles the values. The total outgassing of the samples and background at 25 °C was about 25–30 % higher compared to the background, but the outgassing increased more at higher temperatures. At 200 °C the total outgassing was about 25 times higher compared to the background. This is why relative errors at 25 °C are larger in comparison to higher temperatures.

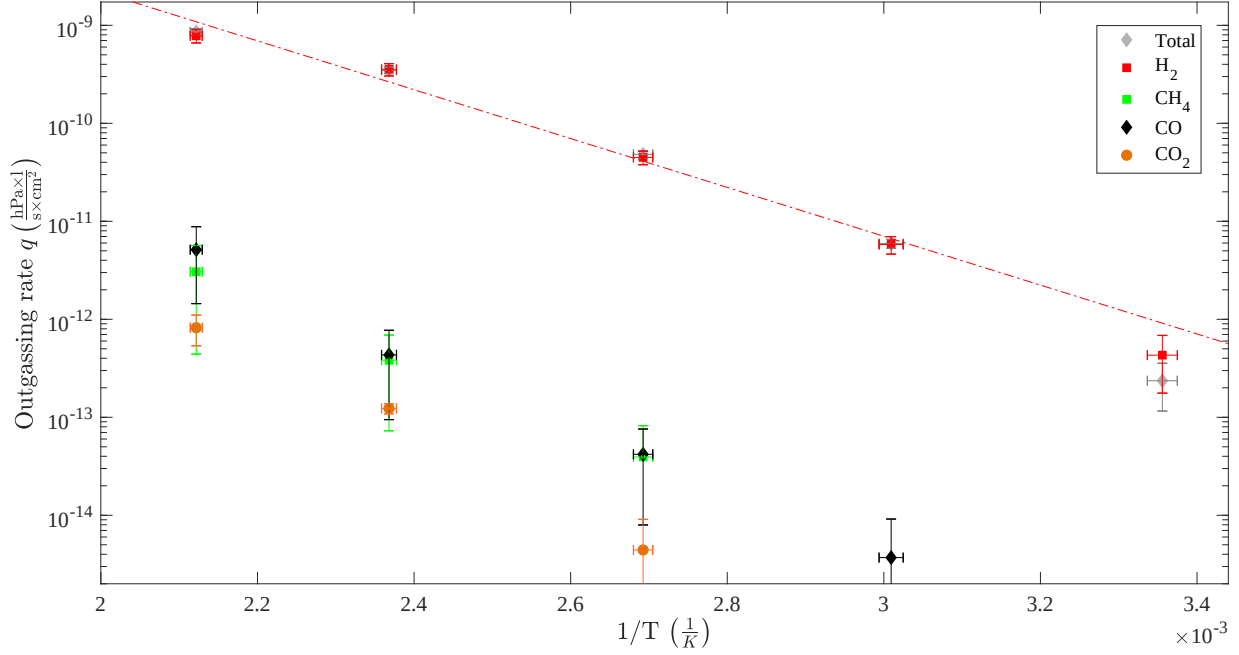


Figure 42: Outgassing rates of the gases and the fit for hydrogen outgassing rate.

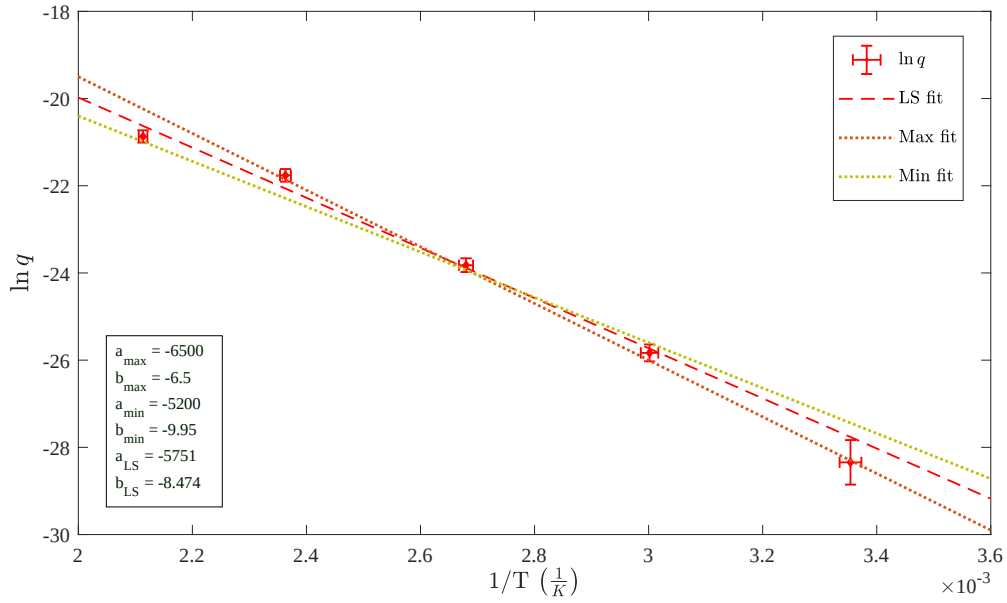


Figure 43: Linear least squares fit $\ln q = a/T + b$ for hydrogen outgassing rate data and the visually estimated minimum and maximum fits.

Outgassing is hydrogen dominant at each temperature. The activation energy was estimated as $E_{\text{act}}(\text{H}_2) \approx 0.50 \pm 0.06$ eV with the linear transformation method described in chapter 4.1 and the error was estimated from the slopes in figure 43 by the minimum-maximum method. The value can be compared to the diffusion energy of type 304 stainless steel reported as 0.57 eV by Ishikawa and Nemanic^[69]. The energy is lower, but given the rather large uncertainty it is possible that the outgassing originated also by diffusion from the substrate. CO and CH₄ errors are higher in comparison to CO₂ errors because the background outgassing for these gases were closer. Table 13 includes the values and error estimates. The outgassing rates measured by the BAG and the RGA are very consistent and within error limits at each temperature.

Temperature (°C)	Total ($\times 10^{-13}$)	H ₂ ($\times 10^{-13}$)	CH ₄ ($\times 10^{-13}$)	CO ($\times 10^{-13}$)	CO ₂ ($\times 10^{-13}$)
25	2.3 ± 1.2	4.9 ± 2.5	—	—	—
60	60 ± 6	60 ± 12	—	$0.04 \pm \begin{smallmatrix} 0.95 \\ 0.04 \end{smallmatrix}$	—
100	480 ± 40	450 ± 70	0.4 ± 0.4	0.4 ± 0.3	0.04 ± 0.04
150	3480 ± 260	3540 ± 510	3.9 ± 3.1	4.4 ± 3.4	1.2 ± 0.2
200	9200 ± 700	8600 ± 1200	33 ± 26	53 ± 37	7.1 ± 2.9

Table 13: Coated alumina outgassing rates q ($\frac{\text{hPa l}}{\text{s cm}^2}$) at five temperatures.

T (°C)	Standard deviations σ ($\frac{\text{hPa l}}{\text{s cm}^2}$)				
	Total ($\times 10^{-13}$)	H ₂ ($\times 10^{-13}$)	CH ₄ ($\times 10^{-13}$)	CO ($\times 10^{-13}$)	CO ₂ ($\times 10^{-13}$)
25	1.52	1.58	—	—	—
60	6.62	7.47	—	0.01	—
100	15.6	9.27	0.02	0.03	0.003
150	173	145	0.24	0.18	0.07
200	2070	2370	5.57	7.35	1.78

Table 14: Standard deviations of the measured outgassing rates shown in table 13.

Table 14 gives the standard deviations of the measurements for comparison. Note that the highest and lowest values have been removed when calculating the standard deviations just as with the error estimates. The values for each measurement are given in appendix F table 26. The error estimates for hydrogen are always larger compared to the total outgassing rate error estimates as the error propagates due to the uncertainties in the sensitivity factors and pressure integral.

Macor and tungsten

Four tungsten plates with a surface area of 216 cm² and five Macor rods with a surface area of 110 cm² were tested. Both tests showed low outgassing as seen in figure 44 that also includes the second background test for comparison.

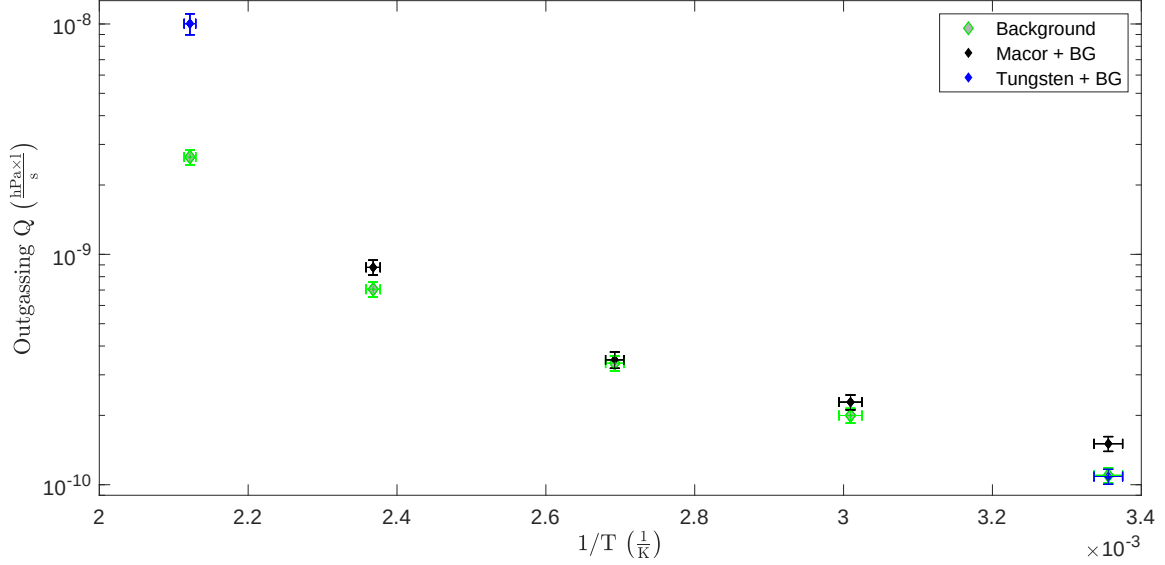


Figure 44: Comparison of total outgassing between Macor and tungsten samples with the 2nd background test.

Because the outgassing is so close to the background measurement, it is more reasonable to estimate maximum possible outgassing rates, except for tungsten at 200 °C, as it is noticeable from the background. The estimates are given in table 15.

Temperature (°C)	Macor ($\times 10^{-13} \frac{\text{hPa l}}{\text{s cm}^2}$)	Tungsten ($\times 10^{-13} \frac{\text{hPa l}}{\text{s cm}^2}$)
25	< 5.2	< 2.7
60	< 9.1	—
100	< 15	—
150	< 32	—
200	—	330

Table 15: Macor and tungsten outgassing rates.

The maximum outgassing rates for the samples were estimated by assuming an outgassing of 50 % of the background, as samples with outgassing higher than $\frac{Q_{BG}}{2}$ would have been surely distinct in the tests. At 60 °C and 100 °C only tentative tests were made with tungsten samples to check if it was worth to measure at these temperatures. Since the tests showed very low outgassing rates, the measurements were cancelled and only at 200 °C a clear difference allowed to estimate the outgassing rate.

Discussion of results

Contrary to the throughput system, readsorption requires less attention as hydrogen was the most dominating gas in each test and is known to exhibit negligible readsorption on stainless steel surfaces^[48,49]. The main concern was the relatively high background, that prevented accurate results for Macor and tungsten. Two background tests were made about 5 months apart. The first one was used for the first sample tested and the second one for the two last samples as they also had similar bakeout times. The difference between the two backgrounds is explainable by the bakeouts that the system, and particularly the lately installed variable leak valve, went through between the tests.

Occasionally the RGA sensitivity factor for hydrogen was checked with a gas injection and no significant drift in the sensitivity was observed. This is confirmed also from the comparison of the RGA results with the results measured by the BAG, which cross-validate each other conveniently. It is apparent that the precision of the RGA is quite good. Even for CH₄, CO and CO₂, that presented low ion currents, the standard deviations are quite small at each temperature. But good precision does not imply good accuracy or reproducibility for subsequent tests. This is why the complementary error analysis was provided given the errors in pumping speeds, sensitivity factors and pressure, of which the BAG and RGA error of 20 % predominates. Therefore, the error estimates are generally larger than the standard deviations, particularly for residual gases CH₄, CO and CO₂, that presented low ion currents. The error estimates related to BAG are smaller than those of the RGA as the errors do not propagate as much. At lower temperatures the error estimates are just slightly higher than the standard deviations for hydrogen and BAG results.

Errors related to other uncertainties are harder to quantify. For example any changes in the background are excluded from the error analysis, but this didn't affect too much the outgassing rate estimates for the alumina coated samples, that showed higher outgassing compared to the background particularly at higher temperatures, or the maximum rates estimated for tungsten and Macor as a quite high assumption of 50 % of the background outgassing was used for the calculations. Furthermore, the background subtractions were used for adjacent tests, so any changes that might have occurred were smaller than the difference between the two background tests.

8 Conclusions

The main objective of this work was to determine outgassing rates of different materials that were either baked or unbaked. The outgassing was subsequently measured at elevated temperatures as well. The results can be used for design and vacuum simulations to estimate the pressure in a system when the surface area, thickness, temperature, pumping speeds and other relevant factors are known. It is the user's responsibility to apply the results in a way that the outgassing from the chosen materials is compatible with the system parameters to ensure a sufficiently low pressure. Keeping the pressure low is of paramount importance in accelerator vacuum systems in order to avoid many undesirable effects due to the beam.

The unbaked samples presented high outgassing rates as expected. Water outgassing was significant, particularly for polymer samples, that showed the highest outgassing rates. Vespel SP-1 was found to follow the simple diffusion models at each temperature. The vacuum performance of graphite improved significantly with an ex situ heat treatment at 1000 °C, which lowered the outgassing considerably and removed hydrocarbon residues. Comparison with literature is difficult due to differences in measurement methods, samples, cleaning procedures, temperatures and also because of the inherent uncertainties present in any outgassing measurement method. Regardless, Macor values were found to be similar and Vespel SP-1 and especially PEEK showed higher outgassing rates compared to the few studies found with similar measurements. A bakeout is advisable for all the materials, especially for polymers that showed rapid decreases in outgassing at elevated temperatures.

The baked samples were found to have low outgassing rates. Especially with tungsten and Macor samples the outgassing was hardly distinguishable from the sample chamber background even though the samples had reasonable surface areas in comparison. Therefore upper limits were estimated for the outgassing rates. Most of the sample chamber's outgassing came most likely from the new variable leak valve part that had not been vacuum fired unlike the sample chamber. The alumina coated SS304L samples were distinct from the background and estimates for the outgassing rates were measured at five temperatures yielding an estimate of 0.50 ± 0.06 eV for the activation energy.

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Appendix A

Calibration of the RGA

This appendix describes an in situ calibration procedure and results against a calibrated total pressure gauge for the accumulation system RGA QMG 700 Analytical Mass Spectrometer with QMA 125 Analyzer from Inficon with tungsten filaments. Calibration is needed to enable quantitative analysis of the residual gas spectrum. The calibration provides the sensitivity factors s that can be used to convert the measured ion currents to partial pressures. The word calibration is used here even though the RGA itself is not adjusted.^[40]

The basic procedure is to inject a chosen gas in the system and measure the ion current and total pressure as a function of time. These measurements can be combined to a plot of ion current as a function of total pressure. The slope of this curve is the sensitivity factor s_g . The calibration for the accumulation system was done with H_2 , CO , CO_2 , CH_4 , N_2 and Ar . These are the main gases of interest since most samples and the sample chamber outgas them, except Ar and N_2 which are injected because argon peaks can be used for leak detection and N_2 is a standard for expressing total pressures.

Only clean gases were injected in the system. A baked injection line was used and the level of impurities were reduced by flushing the injection line several times with the selected gas. Gas injection to the chamber was controlled with a variable leak valve. The pressure in the chamber was increased in steps by a factor of 2–5, allowing 2 to 10 minutes (depending on the gas) for stabilization before reading the pressure and the ion current. Ion current was measured for the significant masses i.e. 2, 15, 16, 18, 28, 40, 44 and the masses expected from the fragmentation pattern of the injected gas. Figure 45 shows a MID scan during a gas injection and figure 46 shows the pressure during the same injection.

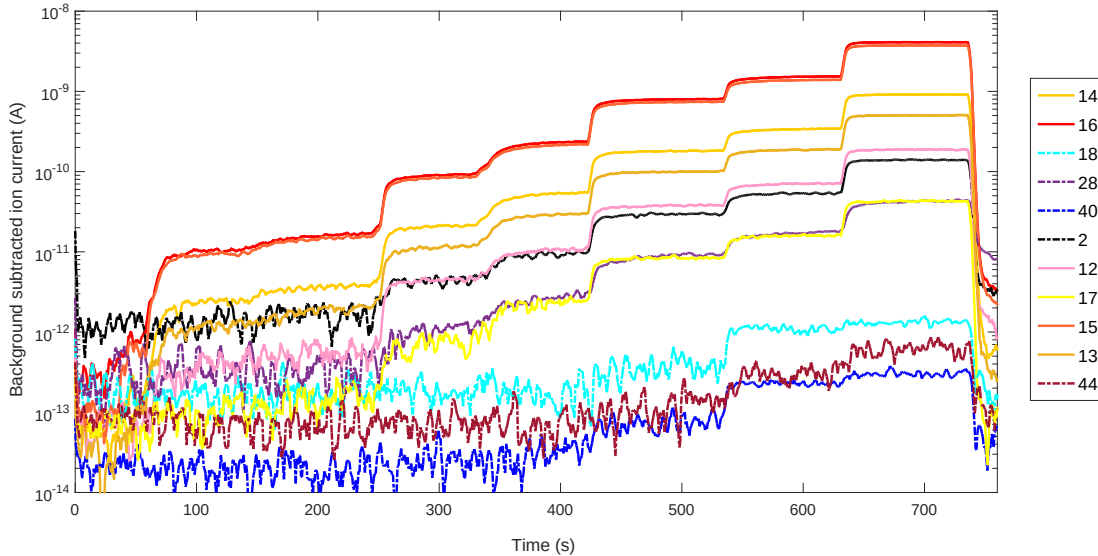


Figure 45: RGA ion current as a function of time during a methane injection. All the relevant gases were monitored and insignificant gases have been removed from the plot for clarity. Masses related to the fragmentation of methane molecule are marked with solid lines and gases not related to methane are marked with dashed lines. The other gases can be used to measure the impurities in the injection.

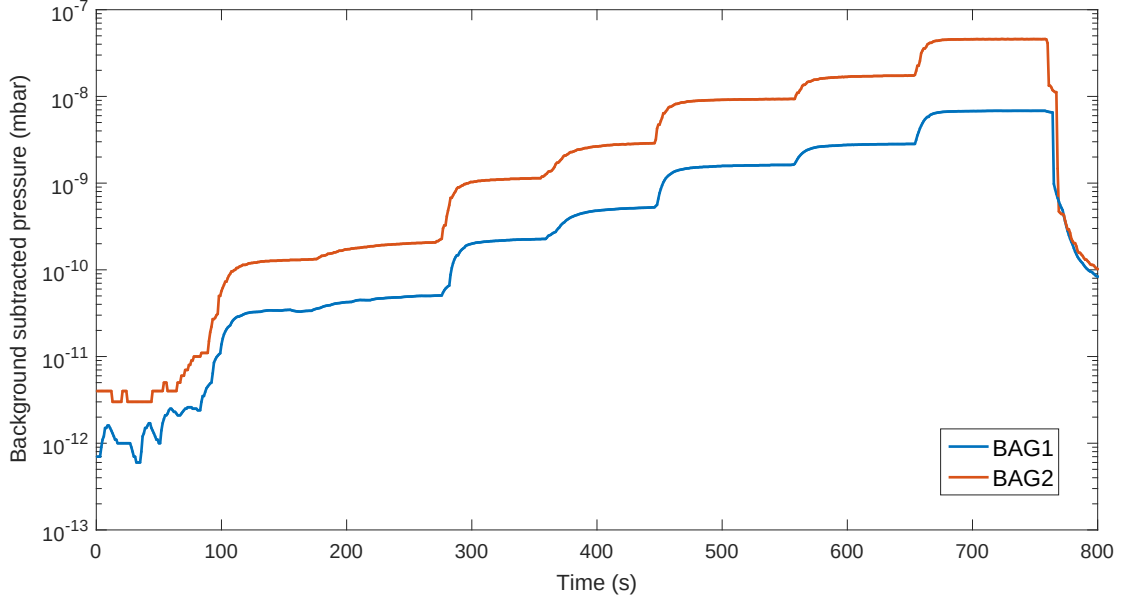


Figure 46: BAG1 and BAG2 pressures during the injection. The base pressures $p_1 = 3.7 \times 10^{-11}$ hPa and $p_2 = 1.4 \times 10^{-10}$ hPa of the system has been subtracted.

The RGA was calibrated in SEM mode with a voltage of 1400 V in the pressure ranges of 10^{-10} – 10^{-7} hPa since this is the pressure range of the accumulation tests. At low pressures the injected gas is not dominant. The sensitivity factors are therefore determined from points when the injected gas ion current is prevalent. After the gas injection the vacuum chamber and injection lines were left to be pumped for several hours until this procedure was repeated with another gas.

Gas	Mass (u)	Sensitivity factor (A/hPa)
Hydrogen (H ₂)	2	0.58 ± 0.02
Methane (CH ₄)	16	0.092 ± 0.004
Carbon monoxide (CO)	28	0.120 ± 0.003
Carbon dioxide (CO ₂)	44	0.059 ± 0.002

Table 16: RGA calibration results against the BAG2. Errors are given as the standard deviation of the measured ratios $s_n = \frac{I_n}{p_n}$.

Table 16 shows the obtained sensitivity factors for the different gases. It should be noted, that even though the mass-to-charge ratios are given as integers, the peaks are shifted in the RGA scans. For example, the highest current for hydrogen occurs at $m/Q = 2.08$. The ion current is taken at this value and the value was also used later with the accumulation tests. Shifts were monitored throughout the other tests as well. Table 17 shows the fragmentation patterns for the injected gases.

Gas	$m/Q \left(\frac{u}{e}\right)$	Relative intensity (%)
CO	28	100
	16	6.6
	12	13.7
CH ₄	17	1.7
	16	100
	15	91.2
	14	22.6
	13	12.4
	12	4.8
N ₂	29	0.6
	28	100
	14	22.4
H ₂	2	100
	1	2.4
CO ₂	45	Below sensitivity
	44	100
	28	44
	22	Below sensitivity
	16	32
	12	0.4
Ar	40	100
	20	21

Table 17: The measured fragmentation patterns with a SEM voltage of 1400 V.

Appendix B

Pumping speeds in the accumulation system

This appendix describes how the gas specific pumping speeds were measured for the accumulation system. The pressure difference across the orifice affects the actual pumping speed according to equation (13) and it can be measured for the relevant gases. Since there is no second RGA at the pumping side of the system, the pumping speeds for different gases can not be estimated during each accumulation test separately. However, it is possible to measure the gas specific pumping speeds with the two BAGs during a gas injection. These measurements were done during the RGA calibration when different gases were injected from the measurement chamber side to calibrate the RGA. Since the injected gas is dominant, as confirmed by the RGA, the pressure difference across the orifice measured by the two BAGs can be used to evaluate the pumping speeds as a function of BAG2 pressure. The results are given in table 18.

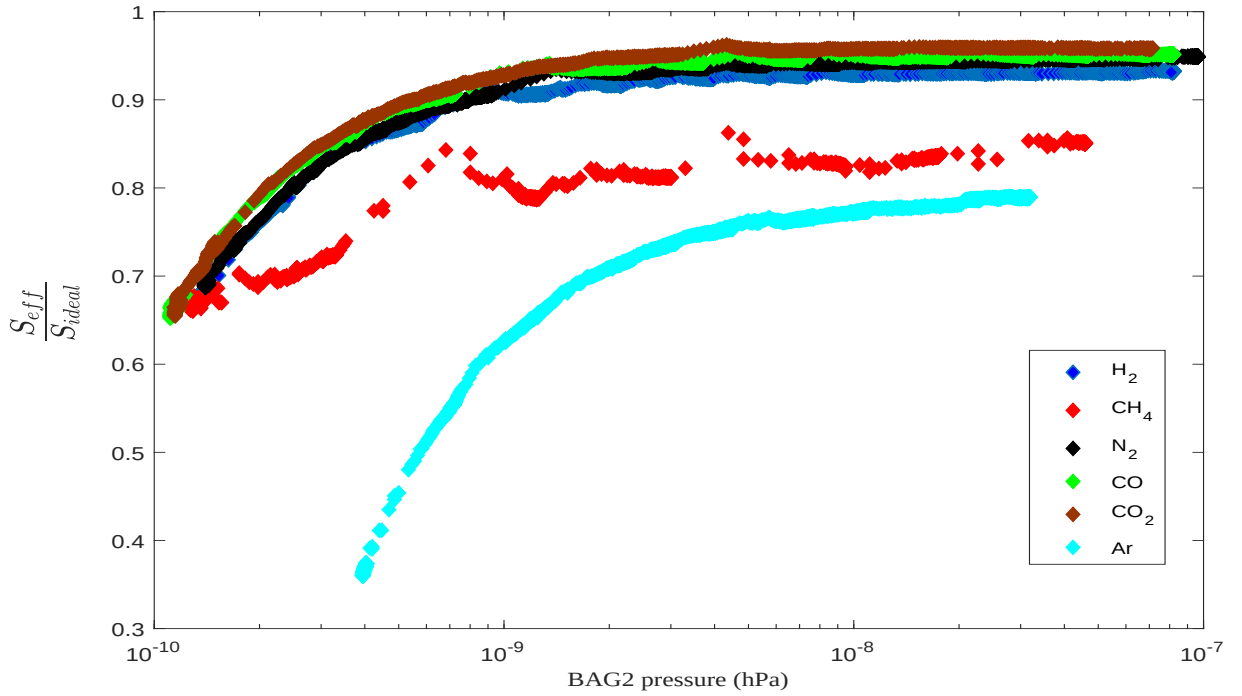


Figure 47: The ratio of effective pumping speed S_{eff} and ideal pumping speed S_{ideal} as a function of BAG2 pressure for different gases.

Figure 47 shows that the measured pumping speeds are close to the ideal pumping speeds estimated as the conductance of the orifice with the exception of Argon, which as a noble gas is pumped inefficiently by the pumps. Since Argon is rarely present during the accumulation tests in significant quantities, a lower pressure injection up to 3×10^{-8} hPa was done quickly due to the risk of saturating the ion pump. Methane as an inert gas is also pumped less efficiently and shows some peaks caused by handling the injection valve too quickly.

During the initial phase of the injection the injected gas is not dominant in the system. Also, the pressures at the different sides of the orifice are initially in the same order of magnitude so the pumping speed of the orifice is very small, which is not the case during the accumulation test. For these reasons the effective pumping speed for different gases were evaluated as an average in the range $10^{-8} - 10^{-7}$ hPa, which is also the prominent

range during the controlled pressure burst from the accumulation tests.

Gas	Mass (u)	Conductance (l/s)	Measured pumping speed (l/s)	$\frac{S_{\text{measured}}}{S_{\text{ideal}}}$
Hydrogen (H ₂)	2	34.8	29.7 ± 0.7	0.94
Methane (CH ₄)	16	12.3	10.5 ± 0.5	0.85
Carbon monoxide (CO)	28	9.3	8.81 ± 0.14	0.95
Nitrogen (N ₂)	28	9.3	8.70 ± 0.13	0.95
Carbon dioxide (CO ₂)	44	7.4	7.11 ± 0.09	0.96

Table 18: Molecular conductances of different gas species at 25 °C with a 1.0 cm diameter orifice calculated from equation (11) and the fraction of ideal and measured pumping speeds for the different gases.

The uncertainty of the measured pumping speed S_{eff} was calculated by the propagation of uncertainty with equation (13) as:

$$\sigma_{S_{\text{eff}}}^2 = \left(\frac{\partial S_{\text{eff}}}{\partial p_1} \right)^2 \sigma_{p_1}^2 + \left(\frac{\partial S_{\text{eff}}}{\partial p_2} \right)^2 \sigma_{p_2}^2, \quad (60)$$

$$\sigma_{S_{\text{eff}}} = \sigma_p C_g \frac{p_1}{p_2} \sqrt{2}, \quad (61)$$

where C_g is the ideal orifice conductivity for each gas species and its uncertainty due to uncertainty in size has been neglected as it is small in comparison to the estimated pressure uncertainties $\sigma_{p_i} = \sigma_p p_i$, where σ_p is 20% for both gauges^[38,35].

Appendix C

Throughput system RGA calibration

This appendix describes briefly the calibration of the QME200 Balzers Prisma quadrupole mass spectrometer in the throughput system.

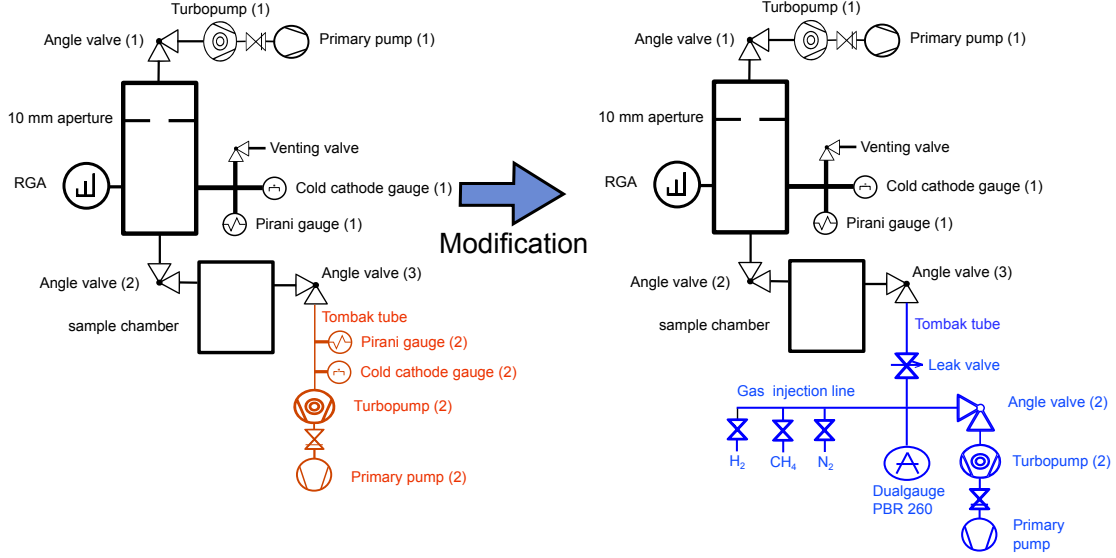


Figure 48: System modification for RGA calibration. This setup allowed the bakeout of the gas injection system and the gas received by the RGA and cold cathode gauge came from the sample chamber as in the tests.

Calibration for the selected gases was done with the method described in appendix A. In this case the available gases were hydrogen, methane and nitrogen, and the latter two injections were not pure enough to determine the sensitivity factors. Hydrogen sensitivity factors were estimated both in Faraday and SEM = 1000 V mode as $s_F(\text{H}_2) = (6.2 \pm 1.1) \times 10^{-4} \text{ A/hPa}$ and $s_{\text{sem}}(\text{H}_2) = 0.40 \pm 0.05 \text{ A/hPa}$. Even though no other gases were used for calibration, other sensitivity factors may be obtained if only one or two of them are significant with hydrogen by χ^2 -minimisation as

$$\chi^2 = \sum_{k=1}^N \frac{\left(p_k - \left(\sum_{j=1}^n \frac{I_{jk}}{s_{jk}} \right) \right)^2}{p_k}, \quad (62)$$

where p_k is the measured pressure, I_{jk} is the measured ion current of gas component j during the measurement k and s_{jk} is the estimated sensitivity factor that can be optimised to minimise the χ^2 with a Matlab script. Fortunately, either hydrogen or water, or both, are often the only dominant gases. Such is the case during the initial pumpdown of the system or during tests with high outgassing materials. Multiple measurements with different samples were used to estimate the water sensitivity factor $s_{\text{sem}}(\text{H}_2\text{O}) = 0.05 \pm 0.01$ and the ratio $\frac{s_{\text{sem}}(\text{H}_2)}{s_{\text{sem}}(\text{H}_2\text{O})}$ of the sensitivity factors were in the range of 6–12. Due to the lack of background measurements done in Faraday mode, only upper and lower bounds could be estimated for the water sensitivity factor in Faraday mode as $10^{-5} \text{ A/hPa} < s_F(\text{H}_2\text{O}) < 10^{-4} \text{ A/hPa}$.

Appendix D

Polymer tests with the accumulation system

Polymers were also tested on the accumulation system. However, the tests encountered problems caused by a faulty variable leak valve and a proper background measurement for the valve and sample chamber was left out when a new variable leak valve was replaced to the system. A few things can still be inferred based on analog scans since polymers are very high outgassing materials.

Vespel SCP-5000

Vespel SCP-5000 is an unfilled polymer that has better mechanical properties and lower water absorption compared to Vespel SP-1. Two samples with a diameter of 5.8 cm, thickness 0.5 cm and a total surface area of 120 cm² were inserted in the sample chamber and baked thoroughly for 16 hours at 120 °C and 137 hours at 250 °C. Tests were made at 25°C, 50 °C, 75°C, 100 °C and 125 °C. Table 19 shows the estimated outgassing rates.

Temperature (°C)	Outgassing rate ($\times 10^{-10} \frac{\text{hPa l}}{\text{s cm}^2}$)
25	< 1
50	2
75	6
100	20
125	70

Table 19: Nitrogen equivalent outgassing rates at each temperature evaluated with the throughput method so these results are susceptible to the uncertainties related with this method.

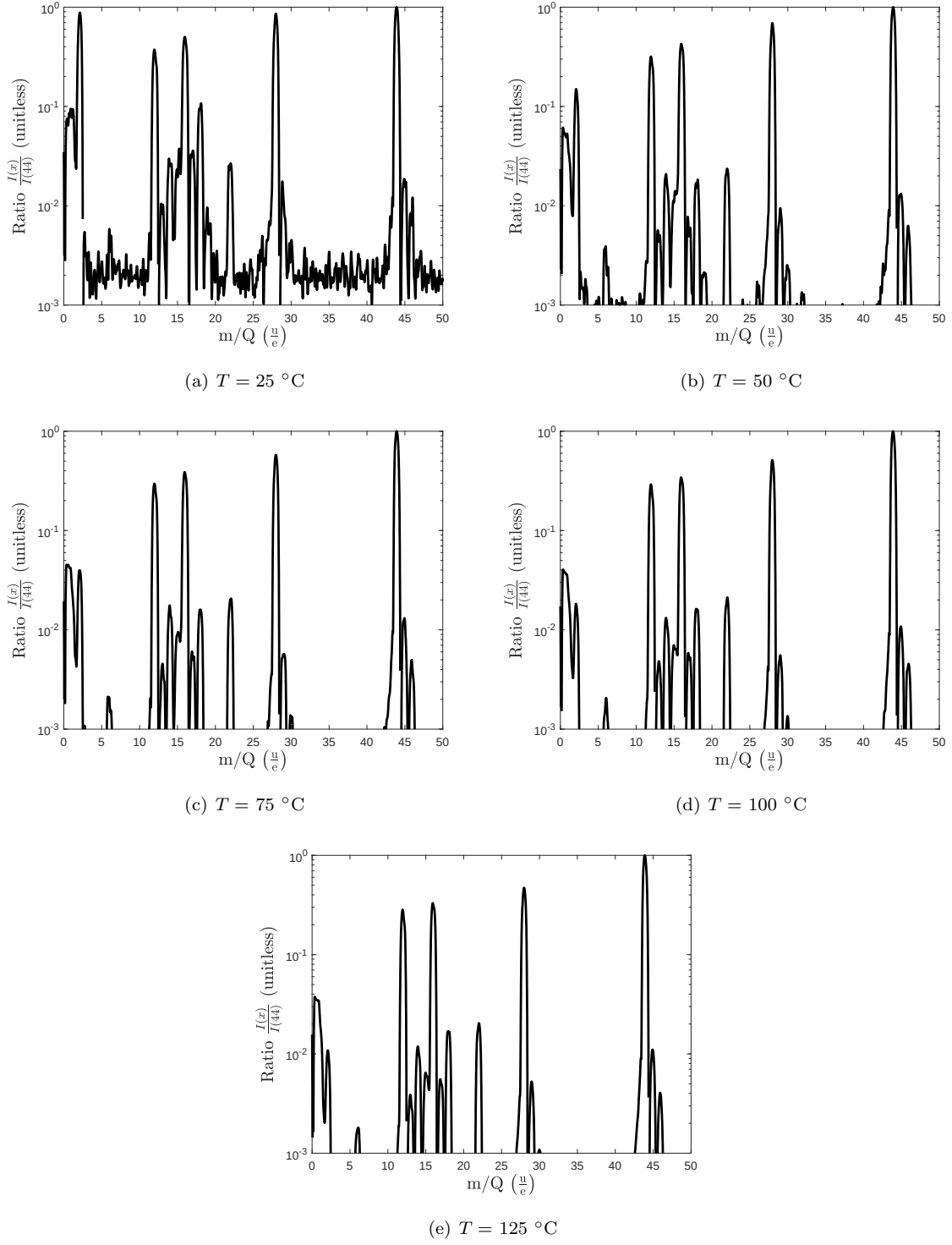


Figure 49: VespeI SCP-5000 normalised analog scans at each temperature.

Figure 49 shows that CO_2 outgassing is dominant at each temperature and increases relatively fast compared to the other gases at higher temperatures. No significant peaks were observed at masses higher than 50.

Vespel SP-1

Five Vespel SP-1 samples with a diameter of 50.8 mm and thickness 5 mm and a total surface area of 242.6 cm² were inserted in the accumulation system. These samples were also very thoroughly baked for 18 hours at 210 °C and 94 hours at 250 °C. Figure 50 shows the normalised analog scans.

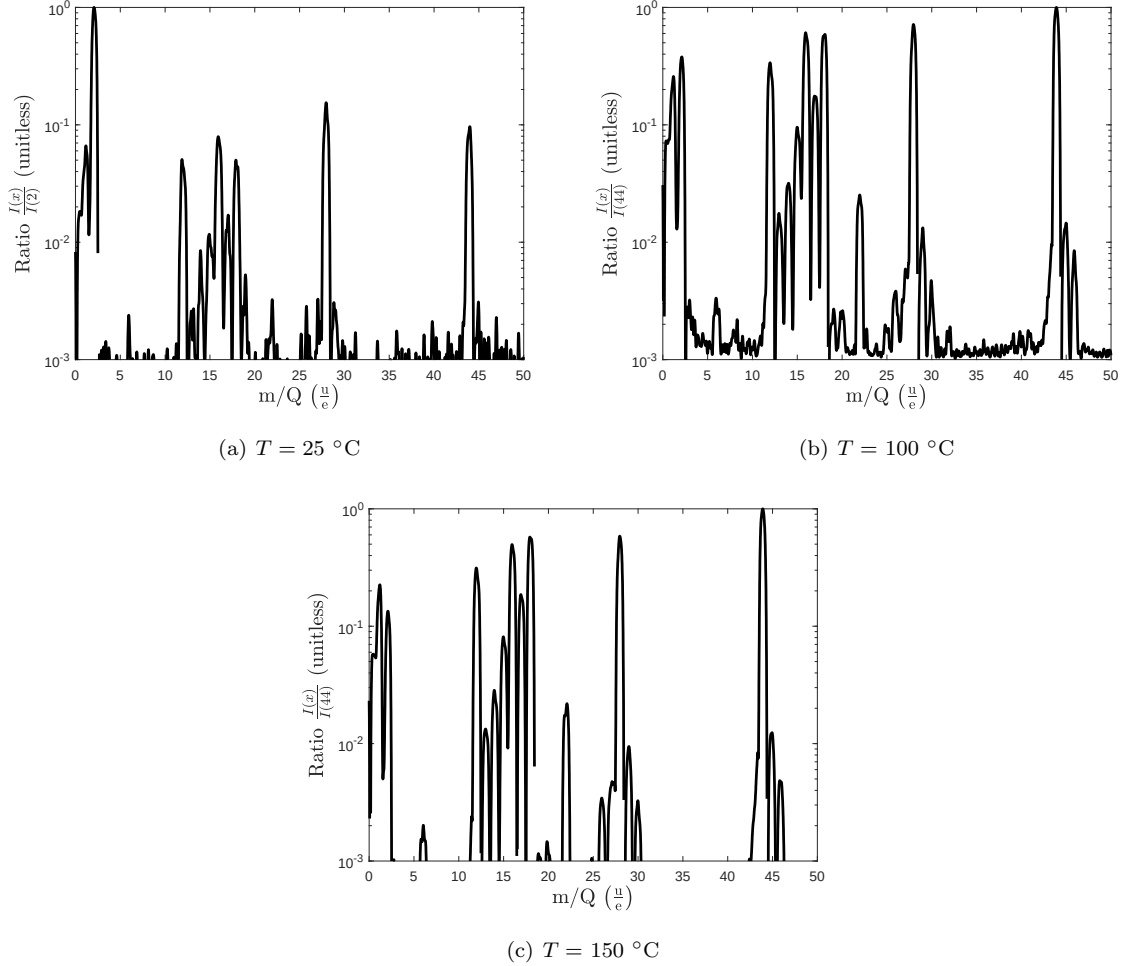


Figure 50: Vespel SP-1 normalised analog scans at each temperature. The scans are normalised according to the highest peak, which at 25 °C is hydrogen and later CO₂. No significant peaks were observed at masses higher than 50.

CO₂ outgassing after a thorough bakeout is obviously substantial with both samples (note that CO₂ has the lowest sensitivity factor $s(\text{CO}_2) = 0.059$ and hydrogen the highest $s(\text{H}_2) = 0.58$). Furthermore, hydrogen outgassing is prevalently due to the background. This was determined by comparing analog scans when the variable leak valve was open or closed. Closing the variable leak valve resulted in a significant pressure drop, but hydrogen peak remained almost at the same level. Furthermore, CO₂ fragments to CO and CH₄ with relative ion current intensities of 44 % and 32 % so the second highest outgassing component in most cases is actually water. Omitting the one exception in figure 50(a), CO₂ outgassing presents distinctly the highest outgassing at every scan. It is possible that the long bakeout causes the diffusion of most of the light and fast molecules that leaves a relatively high concentration of CO₂ molecules which contribute to the outgassing later.

Temperature (°C)	Outgassing rate ($\times 10^{-11} \frac{\text{hPa l}}{\text{s cm}^2}$)
25	1
100	10
150	60

Table 20: Nitrogen equivalent outgassing rates at each temperature evaluated with the throughput method.

Table 20 shows the estimated outgassing rates for Vespel SP-1. The value at 25 °C is comparable to the values found in literature^[73], which are presented in table 21.

Thickness (mm)	Outgassing rate ($\times 10^{-11} \frac{\text{hPa l}}{\text{s cm}^2}$)
0.79	0.37
2.36	6.72

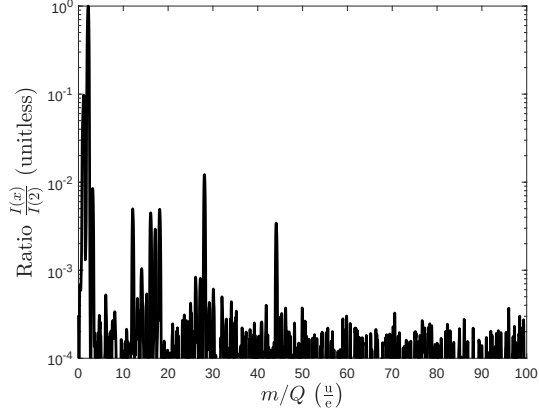
Table 21: Nitrogen equivalent outgassing rates for Vespel SP-1 found in literature at room temperature after a bakeout. The samples were baked 100 hours at 100 °C and subsequently 100 hours at 200 °C.^[73]

The measured value at 25 °C seems reasonable considering the differences in sample thickness's, bakeout times and temperatures. In comparison with the unbaked sample tested with the throughput system, at 100 hours the unbaked but otherwise similar sample presented about 60000 higher outgassing rate at 30 °C. A prolonged bakeout at 250 °C is thus advisable for Vespel SP-1.

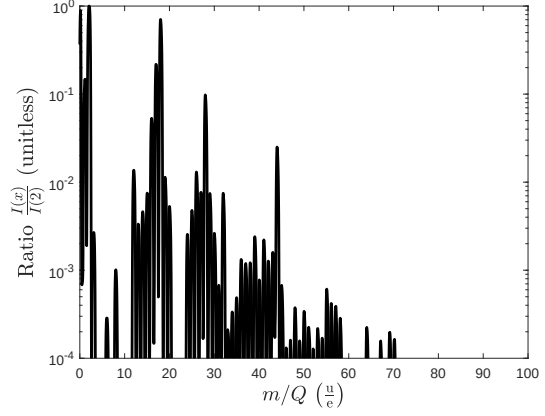
Appendix E

Throughput system analog scans

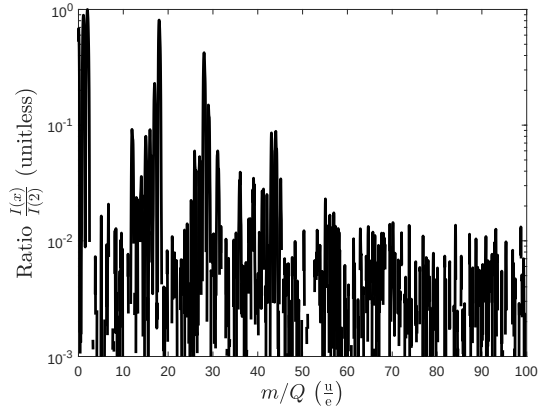
This appendix includes analog scans performed at the end of each test. The relevant peaks of these scans are already accounted in the figures of the results chapter, but for transparency the entire analog scans are included here.



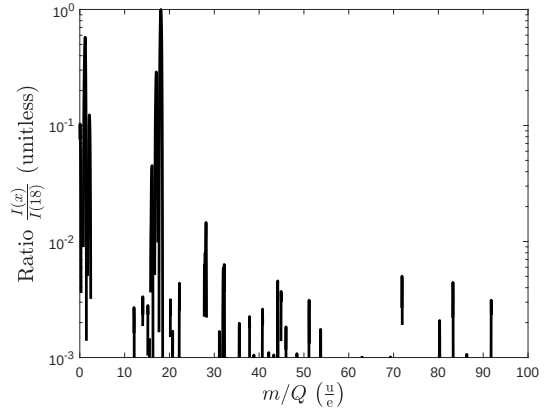
(a) 2nd background after 94 h at 200 °C (SEM 1000V)



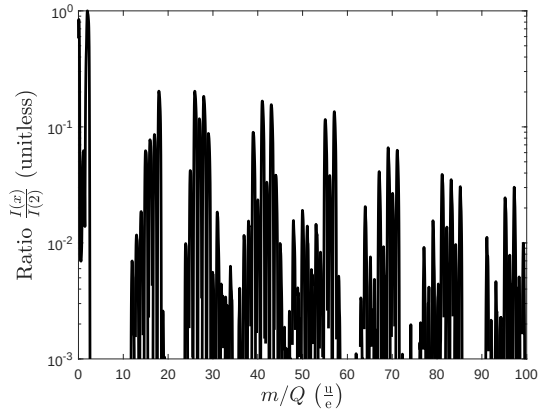
(b) Macor 99 h at 200 °C (SEM 1400V)



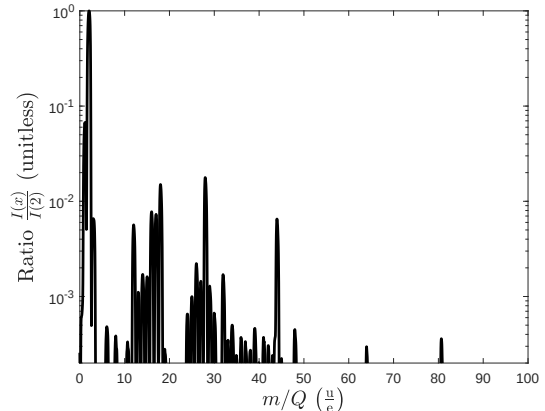
(c) PEEK 99 h at 200 °C (Faraday)



(d) Vespel SP-1 62 h at 200 °C (Faraday)



(e) Graphite 53 h at 150 °C (Faraday)



(f) Heat treated graphite 86 h at 200 °C (SEM 1000V)

Figure 51: The last analog scans of the tests taken at the highest temperature after hundreds of hours of bakeout at different temperatures.

Appendix F

Accumulation system measurements

This appendix includes the results from each accumulation test. Note that the units of outgassing ($\frac{\text{hPa}\cdot\text{l}}{\text{s}}$) are used except for the alumina coated SS304L results. Highest and lowest values have not been removed from the tables.

T ($^{\circ}\text{C}$)	t_{accu} (h)	Outgassing ($\frac{\text{hPa}\cdot\text{l}}{\text{s}}$)				
		Total (BAG)	H_2	CH_4	CO	CO_2
25	45.63	1.02E-10	1.39E-10	5.16E-13	1.87E-13	9.99E-14
	30.00	1.01E-10	1.39E-10	5.90E-13	1.79E-13	1.60E-13
	16.66	1.18E-10	1.35E-10	8.27E-13	1.85E-13	2.04E-13
	24.20	1.16E-10	1.30E-10	5.61E-13	1.74E-13	1.66E-13
	5.25	1.24E-10	3.79E-11	1.33E-12	1.10E-12	5.39E-13
	70.58	9.92E-11	1.17E-10	2.39E-13	1.42E-13	7.82E-14
Standard deviation:		1.05E-11	3.92E-11	3.69E-13	3.80E-13	1.69E-13
200	2.66	1.01E-08	2.65E-09	9.71E-11	4.89E-10	9.45E-10
	64.50	1.06E-08	2.19E-09	1.16E-10	5.16E-10	1.02E-09
	18.66	9.58E-09	2.25E-09	9.99E-11	4.67E-10	8.81E-10
Standard deviation:		4.90E-10	2.51E-10	1.05E-11	2.44E-11	6.97E-11

Table 22: Tungsten outgassing measurements without background subtraction at the two temperatures.

T ($^{\circ}\text{C}$)	t_{accu} (h)	Outgassing ($\frac{\text{hPa l}}{\text{s}}$)				
		Total (BAG)	H_2	CH_4	CO	CO_2
25	62.66	1.62E-10	2.06E-10	7.20E-13	2.45E-13	4.52E-13
	30.42	1.34E-10	1.72E-10	5.28E-13	2.31E-13	5.25E-13
	22.84	1.45E-10	1.79E-10	6.10E-13	2.53E-13	5.61E-13
	15.42	1.80E-10	1.82E-10	7.68E-13	2.57E-13	6.09E-13
	6.00	1.73E-10	1.71E-10	1.55E-12	4.22E-13	8.86E-13
	16.25	1.35E-10	1.88E-10	6.56E-13	2.58E-13	5.43E-13
Standard deviation:		1.97E-11	1.31E-11	3.74E-13	7.12E-14	1.51E-13
60	63.55	2.48E-10	2.67E-10	3.65E-13	3.89E-13	9.12E-13
	6.00	2.57E-10	2.59E-10	1.44E-12	4.86E-13	1.33E-12
	15.86	1.99E-10	2.27E-10	6.08E-13	3.63E-13	8.96E-13
	24.50	2.31E-10	2.48E-10	5.20E-13	3.79E-13	8.51E-13
	28.25	2.24E-10	2.48E-10	4.53E-13	3.43E-13	7.85E-13
	16.00	2.30E-10	2.30E-10	5.87E-13	3.69E-13	8.04E-13
Standard deviation:		2.03E-11	1.56E-11	3.92E-13	5.03E-14	2.03E-13
100	65.00	4.12E-10	4.06E-10	5.22E-13	7.37E-13	2.18E-12
	4.84	3.68E-10	3.36E-10	1.64E-12	8.76E-13	2.39E-12
	39.75	3.55E-10	3.40E-10	5.16E-13	6.65E-13	1.85E-12
	22.75	3.09E-10	3.55E-10	6.29E-13	6.72E-13	1.89E-12
	22.10	3.31E-10	3.44E-10	6.57E-13	7.11E-13	1.80E-12
Standard deviation:		3.92E-11	2.85E-11	4.76E-13	8.56E-14	2.54E-13
150	25.10	9.67E-10	8.49E-10	1.90E-12	4.14E-12	1.24E-11
	22.02	9.67E-10	8.76E-10	1.76E-12	3.75E-12	1.19E-11
	14.33	9.44E-10	9.19E-10	2.01E-12	3.90E-12	1.15E-11
	46.03	9.07E-10	8.17E-10	1.54E-12	3.26E-12	1.15E-11
	83.90	8.22E-10	7.11E-10	1.44E-12	2.97E-12	1.15E-11
	18.25	7.54E-10	6.76E-10	1.67E-12	3.23E-12	1.01E-11
Standard deviation:		8.72E-11	9.56E-11	2.15E-13	4.55E-13	7.74E-13

Table 23: Macor outgassing measurements without background subtraction at each temperature.

T (°C)	t_{accu} (h)	Outgassing ($\frac{\text{hPa l}}{\text{s}}$)				
		Total (BAG)	H ₂	CH ₄	CO	CO ₂
25	89.50	1.87E-10	2.12E-10	5.84E-13	2.96E-13	1.73E-13
	25.91	1.85E-10	1.98E-10	7.56E-13	3.15E-13	2.91E-13
	18.00	2.09E-10	2.30E-10	1.03E-12	3.70E-13	3.78E-13
	8.16	2.29E-10	2.3E-10	1.63E-12	4.25E-13	5.80E-13
	15.00	2.12E-10	2.22E-10	1.12E-12	3.41E-13	3.26E-13
	5.00	2.28E-10	1.94E-10	1.847E-12	4.35E-13	5.19E-13
	64.66	1.98E-10	2.04E-10	5.13E-13	2.83E-13	1.82E-13
Standard deviation:		1.70E-11	1.50E-11	5.11E-13	6.00E-14	1.56E-13
60	15.05	4.02E-10	4.08E-10	1.48E-12	6.90E-13	6.84E-13
	18.30	4.87E-10	4.80E-10	1.39E-12	7.12E-13	6.75E-13
	7.16	4.20E-10	3.99E-10	1.98E-12	7.05E-13	7.49E-13
	38.50	3.52E-10	3.55E-10	1.07E-12	5.30E-13	4.59E-13
	4.50	3.32E-10	3.31E-10	2.82E-12	6.94E-13	8.71E-13
	63.75	3.23E-10	3.20E-10	6.81E-13	4.72E-13	3.81E-13
Standard deviation:		6.20E-11	5.95E-11	7.49E-13	1.04E-13	1.83E-13
100	39.20	7.30E-10	7.27E-10	1.56E-12	1.128E-12	1.23E-12
	7.03	7.23E-10	7.7E-10	3.27E-12	1.41E-12	1.73E-12
	15.75	7.61E-10	7.85E-10	2.06E-12	1.15E-12	1.31E-12
	23.00	7.46E-10	7.55E-10	1.80E-12	1.12E-12	1.22E-12
	4.03	8.90E-10	9.38E-10	4.31E-12	1.65E-12	1.96E-12
	64.50	6.90E-10	6.89E-10	1.33E-12	1.02E-12	1.01E-12
Standard deviation:		6.9E-11	8.56E-11	1.16E-12	2.39E-13	3.58E-13
150	16.12	2.22E-09	2.19E-09	4.90E-12	3.82E-12	5.19E-12
	24.00	2.19E-09	2.11E-09	5.14E-12	3.96E-12	5.04E-12
	29.00	2.11E-09	2.03E-09	5.16E-12	3.94E-12	5.02E-12
	15.58	2.11E-09	1.98E-09	4.814E-12	3.43E-12	4.91E-12
	6.00	2.07E-09	2.05E-09	7.33E-12	3.95E-12	5.43E-12
	64.91	2.02E-09	1.89E-09	2.41E-12	2.21E-12	2.69E-12
	1.66	1.86E-09	1.94E-09	1.20E-11	3.43E-12	6.09E-12
Standard deviation:		1.19E-10	1.02E-10	3.026E-12	6.28E-13	1.06E-12
200	22.33	7.06E-09	6.50E-09	1.58E-11	3.05E-11	9.38E-11
	16.25	6.78E-09	6.27E-09	1.32E-11	2.83E-11	8.53E-11
	30.00	6.46E-09	5.97E-09	1.21E-11	2.62E-11	8.23E-11
	17.50	6.54E-09	6.19E-09	1.1941E-11	2.59E-11	7.73E-11
	4.50	6.404E-09	6.01E-09	1.3227E-11	2.57E-11	6.87E-11
	63.55	6.07E-09	5.79E-09	1.1953E-11	2.62E-11	8.02E-11
Standard deviation:		3.39E-10	2.49E-10	1.49E-12	1.91E-12	8.32E-12

Table 24: 1st background measured Q at each temperature.

T ($^{\circ}\text{C}$)	t_{accu} (h)	Outgassing ($\frac{\text{hPa}\cdot\text{l}}{\text{s}}$)				
		Total (BAG)	H_2	CH_4	CO	CO_2
25	66.48	9.04E-11	1.28E-10	6.86E-13	1.27E-13	2.15E-13
	24.00	1.03E-10	1.21E-10	5.18E-13	1.67E-13	3.96E-13
	20.00	1.06E-10	1.22E-10	5.48E-13	1.86E-13	3.65E-13
	30.00	1.06E-10	1.25E-10	4.26E-13	1.92E-13	3.27E-13
	15.80	1.60E-10	1.62E-10	6.79E-13	2.27E-13	4.33E-13
	70.00	1.44E-10	1.61E-10	2.54E-13	1.83E-13	2.34E-13
Standard deviation:		2.71E-11	1.95E-11	1.63E-13	3.29E-14	8.78E-14
60	16.50	1.87E-10	1.98E-10	6.86E-13	3.290E-13	7.66E-13
	30.00	1.83E-10	1.91E-10	4.46E-13	3.06E-13	6.64E-13
	22.92	2.04E-10	2.28E-10	5.39E-13	2.65E-13	6.17E-13
	15.05	2.10E-10	2.03E-10	7.05E-13	2.98E-13	6.96E-13
	5.47	2.19E-10	2.31E-10	1.41E-12	3.84E-13	9.652E-13
	64.66	2.04E-10	2.07E-10	3.42E-13	2.63E-13	5.15E-13
Standard deviation:		1.40E-11	1.64E-11	3.81E-13	4.49E-14	1.53E-13
100	16.00	3.46E-10	3.57E-10	9.88E-13	6.84E-13	1.91E-12
	30.00	3.64E-10	3.56E-10	8.06E-13	7.260E-13	1.78E-12
	22.25	3.13E-10	3.27E-10	6.72E-13	6.01E-13	1.66E-12
	16.25	3.11E-10	3.34E-10	8.08E-13	6.16E-13	1.60E-12
	5.45	3.81E-10	3.46E-10	1.65E-12	6.32E-13	1.78E-12
	63.58	3.27E-10	3.18E-10	5.06E-13	5.09E-13	1.42E-12
Standard deviation:		2.85E-11	1.58E-11	3.99E-13	7.47E-14	1.71E-13
150	16.00	7.45E-10	7.04E-10	1.56E-12	2.07E-12	8.33E-12
	6.25	6.79E-10	6.86E-10	2.13E-12	2.09E-12	7.91E-12
	22.52	6.97E-10	6.24E-10	1.26E-12	1.95E-12	7.71E-12
	18.16	7.01E-10	6.97E-10	1.38E-12	1.96E-12	7.55E-12
	45.80	7.17E-10	6.52E-10	1.10E-12	1.69E-12	7.13E-12
	66.08	6.99E-10	6.17E-10	1.03E-12	1.67E-12	6.84E-12
Standard deviation:		2.27E-11	3.76E-11	4.04E-13	1.83E-13	5.33E-13
200	15.30	2.72E-9	1.69E-9	7.10E-12	3.20E-11	1.51E-10
	6.08	2.53E-9	1.61E-9	7.06E-12	3.07E-11	1.31E-10
	23.00	2.63E-9	1.63E-9	6.37E-12	2.86E-11	1.51E-10
	18.00	2.65E-9	1.69E-9	6.63E-11	2.80E-11	1.43E-10
	2.66	2.68E-9	1.67E-9	8.27E-12	3.45E-11	1.21E-10
	46.50	2.66E-9	1.64E-9	6.42E-12	2.94E-11	1.52E-10
Standard deviation:		6.27E-11	3.24E-11	2.42E-11	2.43E-12	1.27E-11

Table 25: 2nd background measured outgassing Q at each temperature.

T (°C)	t_{accu} (h)	Outgassing rate ($\frac{\text{hPa l}}{\text{s cm}^2}$)				
		Total (BAG)	H ₂	CH ₄	CO	CO ₂
25	24	8.89E-14	3.75E-13	1.16E-14	3.32E-16	-
	19.23	1.96E-13	5.93E-13	2.29E-15	2.85E-16	-
	30.00	1.93E-13	3.41E-13	-	-	-
	15.50	4.47E-13	6.62E-13	6.70E-16	2.92E-16	-
	5.66	9.12E-13	7.26E-13	1.09E-15	5.46E-16	-
	71.33	3.80E-14	1.53E-13	-	-	-
Standard deviation:		3.28E-13	2.2E-13	5.20E-15	1.25E-16	-
60	30.13	5.86E-12	5.67E-12	3.11E-15	4.71E-15	-
	16.66	6.98E-12	7.07E-12	1.78E-15	4.76E-15	-
	6.42	7.45E-12	7.69E-12	4.81E-15	4.98E-15	-
	15.00	5.82E-12	6.03E-12	-	3.43E-15	-
	24.25	5.46E-12	5.35E-12	-	3.25E-15	-
	66.77	4.93E-12	4.53E-12	-	2.42E-15	-
Standard deviation:		9.54E-13	1.16E-12	1.51E-15	1.03E-15	-
100	24.03	4.61E-11	4.20E-11	4.83E-14	4.57E-14	4.12E-15
	20.03	4.93E-11	4.59E-11	4.16E-14	4.43E-14	4.74E-15
	10.42	4.64E-11	4.39E-11	3.63E-14	3.94E-14	2.98E-15
	3.33	5.05E-11	4.48E-11	3.91E-14	4.54E-14	548E-15
	15.08	4.81E-11	4.58E-11	3.61E-14	3.94E-14	2.98E-15
	6.00	4.99E-11	4.73E-11	3.82E-14	3.93E-14	4.31E-15
Standard deviation:		1.85E-12	1.84E-12	4.55E-15	3.17E-15	5,90E-16
150	24.03	3.58E-10	3.49E-10	4.30E-13	4.96E-13	1.31E-13
	1.33	4.13E-10	4.12E-10	4.20E-13	4.54E-13	1.37E-13
	15.00	3.48E-10	3.61E-10	3.85E-13	4.44E-13	1.19E-13
	5.00	3.61E-10	3.70E-10	3.94E-13	4.56E-13	1.25E-13
	8.07	3.23E-10	3.36E-10	3.62E-13	4.16E-13	1.13E-13
	2.84	3.15E-10	3.27E-10	3.33E-13	3.75E-13	1.07E-13
Standard deviation:		3.49E-11	3.03E-11	3.61E-14	4.08E-14	1.10E-14
200	8.08	1.69E-9	1.46E-9	5.94E-12	7.42E-12	9.61E-13
	0.41	1.21E-9	1.20E-9	3.20E-12	6.16E-12	1.57E-12
	1.00	8.57E-10	8.48E-10	2.33E-12	4.35E-12	6.02E-13
	4.50	8.86E-10	7.64E-10	4.05E-12	5.53E-12	6.51E-13
	2.08	6.93E-10	6.46E-10	2.70E-12	4.48E-12	5.34E-13
	3.08	7.20E-10	6.28E-10	3.30E-12	4.89E-12	5.97E-13
Standard deviation:		3.80E-10	3.33E-10	1.29E-12	1.17E-12	3.95E-13

Table 26: Alumina coated SS304L outgassing rate q results and the standard deviations at each temperature.

Appendix G

Venting system measurements and results

This appendix provides the introduction, measurements and results of a third and smaller experiment that was used to measure the effect of different venting gases and venting times to the pumpdown curve after exposure to the gases. The venting system also relies on the throughput method to determine the outgassing rate. However, in this case, the sample is a vacuum fired 316L stainless steel tube and the outgassing rates are measured after the tube, and the rest of the system, has been exposed to different venting gases for a selected time. The motivation to perform pumpdown studies comes from the requirement to reach acceptably low pressures in a reasonable time after e.g. some mandatory maintenance during which parts of the vacuum systems are exposed to air or vented to atmospheric pressures as a precaution to prevent accidental air rushes or restrain the saturation of the NEG coatings and pumps.^[10]

Experimental setup

Figure 52 shows the experimental setup used. The test side of the system consists of the one meter long DN100 stainless steel tube, 316LN stainless steel transition flange that connects to a DN63 stainless steel T-piece, where the pirani and cold cathode gauges are mounted. The tube, flange and cross have been vacuum fired for 2 hours at 950 °C. The 10 mm circular orifice is a silver coated copper disk with a hole that functions as a gasket as well between the test side and the pumping side. The total area A of the test side of the system is approximately 3490 cm².

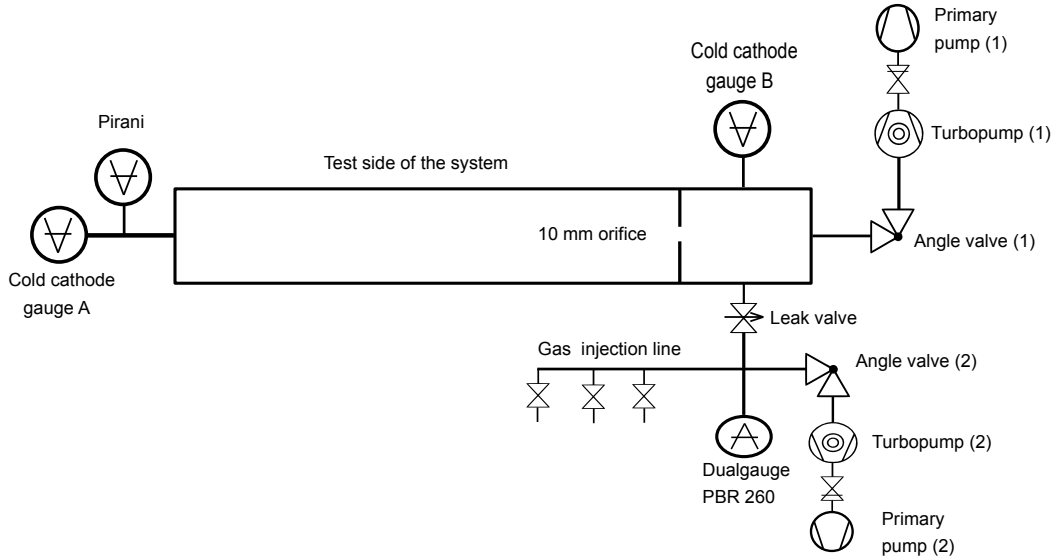


Figure 52: Venting system schematic.

The second cold cathode gauge on the other side of the orifice is used to measure the pressure on the pumping side. As the conductance of the DN100 tube is very high, the pressure reading at the end of the tube can be used together with the other cold cathode gauge to determine the actual pumping speed of the orifice. Hence the outgassing rate q of the test side of the system can be calculated with equations (13), (14) and (16) as

$$q = \frac{p_A(1 - \frac{p_B}{p_A})S}{A}, \quad (63)$$

where p_A is the pressure on the test side, p_B is the pressure on the pumping side and S is the pumping speed of the orifice. The injection system is connected to the system by a variable leak valve. The injection system has a pirani-Bayard-Alpert full-range gauge that is used to validate the successfulness of the bakeout and also to check the pressure during the injection of the selected gas.

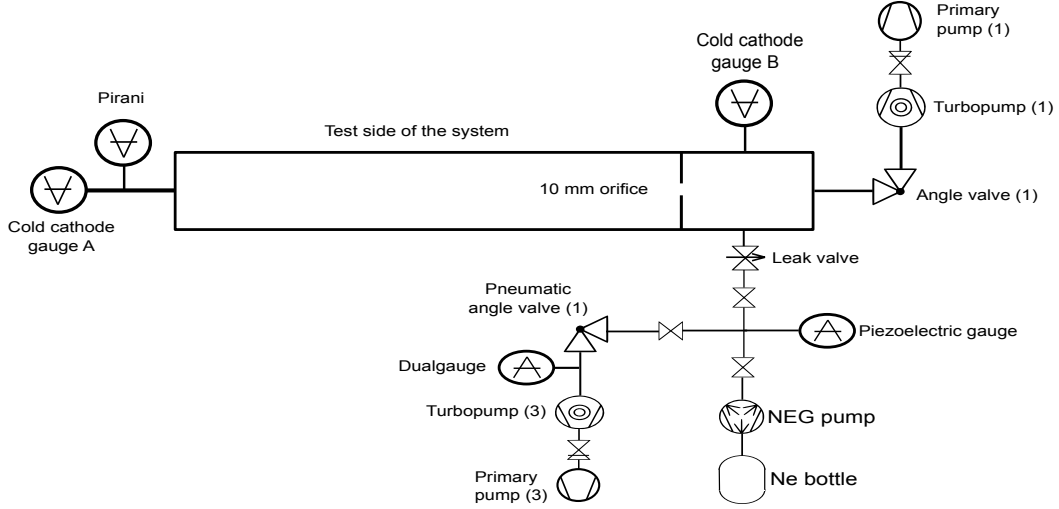


Figure 53: Mobile neon injection system connected to the pumpdown system.

For ultra pure neon venting the original injection system was replaced with a mobile neon injection system shown in figure 53. Mobile neon injection systems are commonly used in the LHC as they include pumps, bakeout instruments and most importantly a NEG filter that is used to remove the impurities from the neon gas before being injected to the LHC.

Measurement procedure

A consistent measurement procedure is crucial to obtain comparable results. Between each measurement the entire system is baked for 24 hours. Most parts are baked at 250 °C, except the Pirani and turbopump flanges, which are baked at temperatures of 140 °C and 120 °C respectively. After the bakeout the system is cooled down and 24 hours elapses before the next measurement. Then, the injection line is flushed three times with the selected gas unless it is air. Then the angle valve (2) is closed and the injection system is vented with the gas. Angle valve (1) is closed and the system is vented through the leak valve. The leak valve is closed after 30 minutes and the system is kept vented for the selected time. To start the pumpdown, the turbopump is first turned off and when the frequency of the turbopump has decreased 60 % the angle valve (1) is slowly opened and the pumpdown begins. This practice prevents any backstreaming from the primary pump and also effectively vents the turbopump with the selected gas as well. After the pressure has decreased to 10 hPa the turbopump is started again. Pirani gauge is turned off at $p = 10^{-4}$ hPa and the cold cathode gauges are turned on shortly after and the pumpdown curve is measured for 100 hours. During the venting and measurement the system is kept at 30 °C.

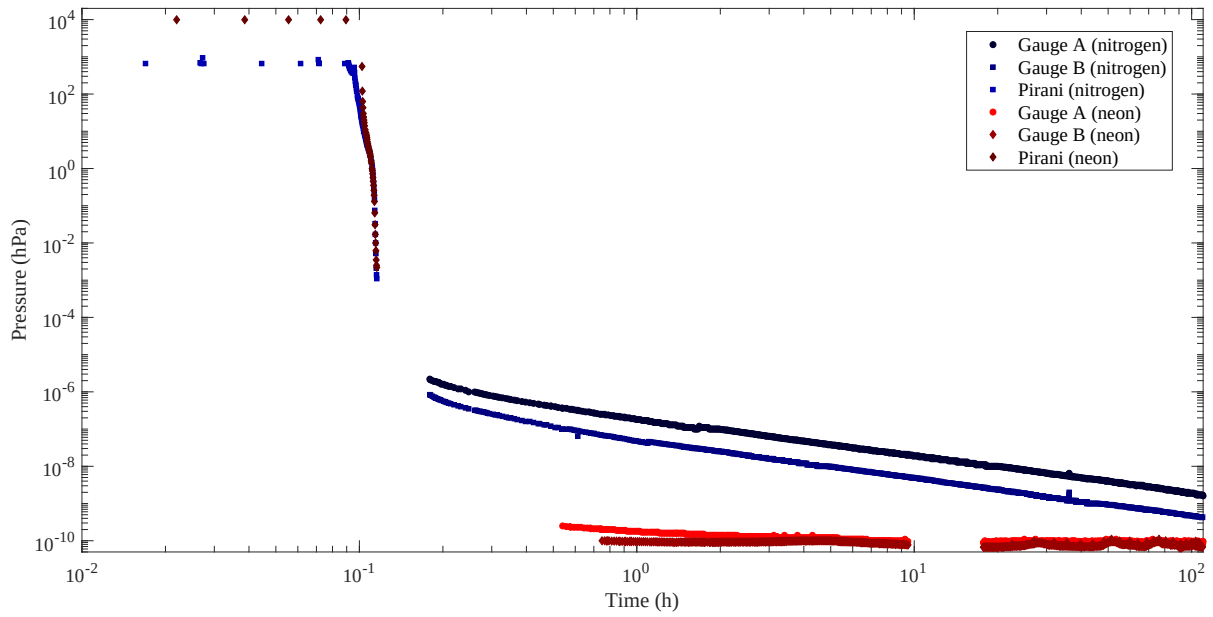


Figure 54: Measurements of the pumpdown curve after 168 hour venting with nitrogen and 24 hour venting with ultra pure neon.

Figure 54 shows two measurements. The first 10 minutes of the pressure readings are excluded when calculating the outgassing rate. Both injections were vented to atmospheric pressure, but the pirani shows larger reading for neon venting because of different sensitivity factors. Therefore the neon venting pressure was checked with piezoelectric gauge that displays gas independent readings.

Venting gases

The most apparent choice of venting gas is atmospheric air as most of the vacuum systems are frequently exposed to air. Atmospheric air contains about 1 % of water vapour at sea level and because of this air ventings are undesirable due to adsorption water on technical surfaces^[58]. Therefore, the system is preferably vented with a gas that has a low binding energy. Nitrogen is a commonly used gas due to its low price and availability. However in LHC, even better gases with very high purity are required. Of all the noble gases neon is the only one without significant downsides. Helium is generally used for leak detection, so any residues of helium remaining in the chamber reduces the sensitivity of the leak detection. Argon is inappropriate for the same reason as it is a signature peak of leaks in the residual gas spectrum. Krypton and xenon are heavier gases and have high scattering cross-sections so any amount left in the beam pipes would results in harmful beam-gas interactions.^[10,47]

Impurities	Nitrogen (ppm)	Neon (ppm)
H ₂ O	<1	<2
O ₂	<5	<1
H ₂	<0.1	<2
CO	<0.5	<0.2
CO ₂	<0.2	<0.2
CH ₄	<0.1	–
N ₂	–	<4
He	–	<20
Noble gases	<50	–

Table 27: Nitrogen (Carbagas, purity 99.9997 %) and neon (Carbagas, purity 99.999%) gas specifications.

Table 27 shows the impurities of the gases stated by the manufacturer. Impurities in the neon gas are expected to be removed by the NEG filter excluding noble gas impurities.

Results and conclusions

The system was vented to 1000 hPa with one exception: one air venting with $p = 0.1$ hPa ($p_{\text{H}_2\text{O}} \approx 10^{-3}$ hPa) was carried out to see the effect of reduced venting pressure. Also, one venting was done with two gases: first the system was vented with nitrogen and subsequently with air to see how much the preceding nitrogen venting lowered outgassing in comparison to direct air venting.

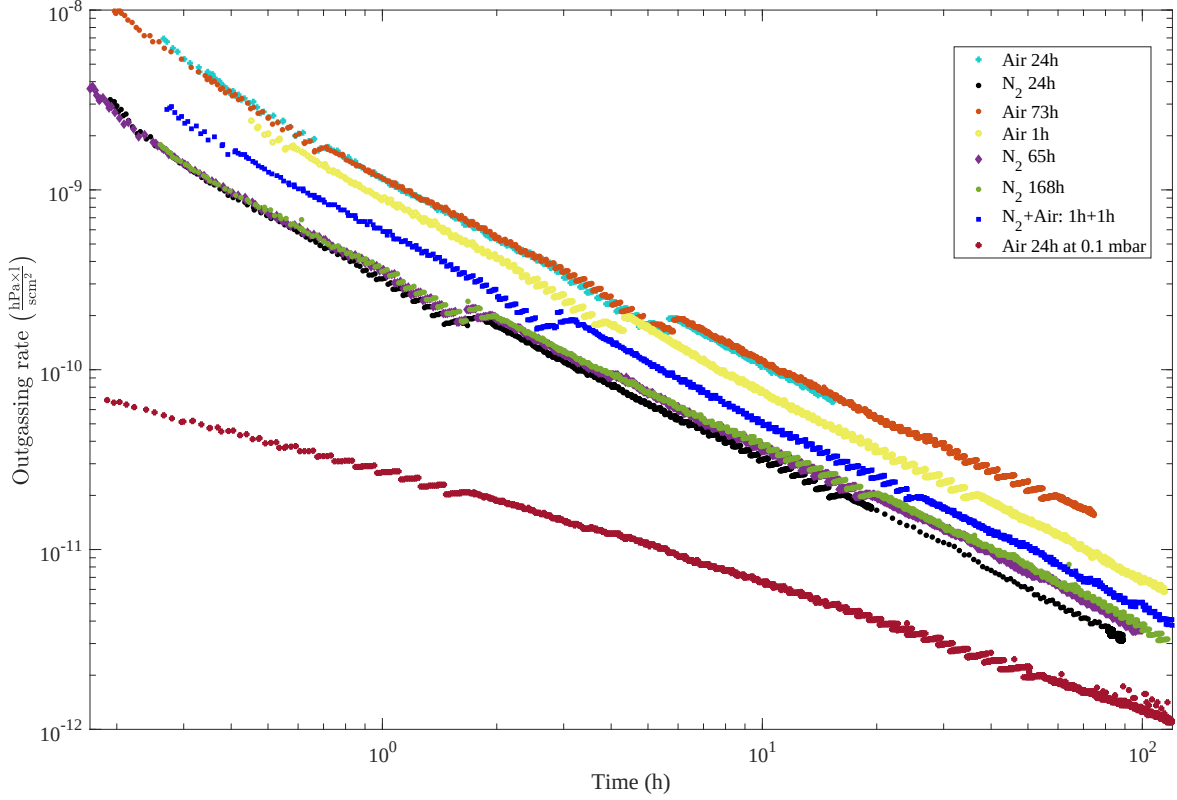


Figure 55: Outgassing rates after the venting gas injections.

Figure 55 shows the obtained outgassing rates given as nitrogen equivalent. Ultra pure neon injection is excluded from the plot as the pressure dropped close to the system's base pressure very soon after the pumpdown begun as seen in figure 54. This verifies that the ultra pure neon filtering procedure is indeed very effective and also validates the experimental procedure as it shows that no oil backstreaming occurs from the primary pump to the system during the short shutdown period of the turbopump at the beginning of the pumpdown.

The results are consistent regards to the venting time so that a higher venting time resulted in slightly higher outgassing rates. The only negligible exception is the first hour of pumpdown after 73 hour air venting that is very slightly lower in comparison to the 24 hour air venting. Generally, the venting time didn't affect the outgassing rate considerably. At most, a factor of 2 between the 1 hour and 168 hour air venting was measured. The air and nitrogen pumpdown curves instead differ clearly from another and in between the curves is the successive nitrogen and air venting that shows that the physisorbed nitrogen inhibits water vapour adsorption resulting in lower outgassing in comparison to any of the air ventings. The low pressure air venting resulted in the lowest outgassing rate. Therefore even the nitrogen injections exposed the system to higher amount of water vapour or other impurities than the low pressure air venting.

Injection	$a \left(\times 10^{-10} \frac{\text{hPa} \cdot \text{l}}{\text{s} \cdot \text{cm}^2} \right)$	b	R^2
Air 73h	14	-1.08	0.983
Air 24h	12.2	-1.21	0.993
Air 1h	9.22	-1.06	0.998
N ₂ +Air: 1h+1h	6.29	-1.08	0.995
N ₂ 168h	3.91	-1.04	0.995
N ₂ 65h	4.33	-1.05	0.978
N ₂ 24h	3.80	-1.07	0.982
Air 24h at 0.1 hPa	0.262	-0.64	0.992

Table 28: Powerfit $q = at^b$ parameters for the studied injections. Injections are ordered from highest to lowest outgassing rate at $t = 24$ h.

Table 28 shows the respective power fits made to the pumpdown curves. The exponents are close to -1 as expected with the exception of the low pressure air venting that has significantly lower rate of decrease. Similar results are found in literature. Minxu Li and H.F. Dylla^[68] found that for stainless steel surface the outgassing rate after an exposure to water vapour depends on the duration, surface temperature and partial pressure of water during the exposure. They found that the exponent was smaller the lower the exposure pressure was or the higher the temperature was during the exposure. For example with $p_{\text{H}_2\text{O}} = 10^{-4}$ hPa, $T_{\text{exp}} \approx 37$ °C and $t_{\text{exp}} = 1$ h they obtained an exponent of $b \approx -0.7$. In addition they measured the outgassing rates after an exposure to N₂/H₂O-mixture. The simultaneous exposure to both gases did not affect water adsorption at all and the result was comparable to pure water exposure of the same quantity of water. A difference is indicative in figure 55 when the injections are successive, but further measurements with controlled or more precisely measured water vapour injections are required to draw more conclusions.