



Measurements of helium permeation in Zerodur glass used for the realisation of quantum pascal

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ABSTRACT

In the new optical pressure standard Ultra-Low Expansion glass cavities were proposed to measure helium refractivity for a new realisation of the unit of pressure, pascal. However, it was noticed that the use of this type of material causes some difficulties. One of the main problems of ULE glass is the pumping effect for Helium. Therefore, instead of ULE, Zerodur glass was proposed as a material for the cavity. This proposal was given by the Vacuum Metrology team of the Physikalisch-Technische Bundesanstalt - PTB in the QuantumPascal project. In order to calculate the flow of helium gas through Zerodur glass one has to know the permeation constant K . Moreover, the modelling of time dependency of the flow requires the knowledge of diffusion constant D as well. The relation between them is given by $K = S \cdot D$, where S is the solubility of Helium in glass. In our research work we measured permeation of helium gas in Zerodur. Measurements were performed in the temperature range 80 °C – 120 °C. Based on our results, we consider that the Zerodur material has potential to be used as cavity material for the new quantum standard of pressure.

Section: RESEARCH PAPER

Keywords: Permeation; helium; diffusion; vacuum; metrology

Citation: Ardita Kurtishaj, Ibrahim Hameli, Arber Zeqiraj, Sefer Avdiaj, Measurements of helium permeation in Zerodur glass used for the realisation of quantum pascal, Acta IMEKO, vol. 11, no. 2, article 27, June 2022, identifier: IMEKO-ACTA-11 (2022)-02-27

Section Editor: Sabrina Grassini, Politecnico di Torino, Italy

Received August 3, 2021; In final form March 1, 2022; Published June 2022

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1. INTRODUCTION

Pressure is traditionally defined as force per unit area. Therefore, to realise the unit of pressure - pascal, the most apparent method is to apply a known force to a known surface. Essentially, this is how pressure is defined since 1640, when Evangelista Torricelli invented the mercury barometer [1]. Nonetheless, since pressures in the vacuum range do not exert great forces, it becomes more convenient to formulate pascal as the amount of energy per unit volume [2]. Consequently, at low pressures, pascal is realized through the law of ideal gases, utilizing the optical measurement of gas density [3]. One of the methods that serves for the latter purpose, relies on Fabry-Perot optical cavities for the measurement of refractivity of the gas being used [4], [5].

Cavities made out of Ultra-low expansion (ULE) glass were initially proposed to measure helium refractivity for the new realisation of pascal [1], [4], [6]. However, the usage of this material has shown some difficulties, as reported in references [2] and [7]. One of these difficulties is the permeability of helium

into the cavity material. For this reason, the 18SIB04 QuantumPascal EMPIR project - "Towards quantum-based realisations of the Pascal" - proposed the testing of Zerodur as potential cavity material.

To estimate whether Zerodur is more suitable than the ULE glass, different studies are being made, such as the one reported in reference [8]. This evaluation requires the modelling of gas transport dynamics in the material. Such modelling, on the other hand, requires knowledge of diffusion and permeability coefficients. Therefore, as collaborators in the above-mentioned project, we have studied the permeability of Helium into the Zerodur material.

The measurements were performed in the temperature range 27 °C – 120 °C. Determined values of helium gas permeability in the Zerodur sample are given in the temperature range 80 °C – 120 °C.

2. MATERIALS AND METHODS

The vacuum system, in which the measurements were made, consists of two separate volumes (high-pressure volume V_1 and

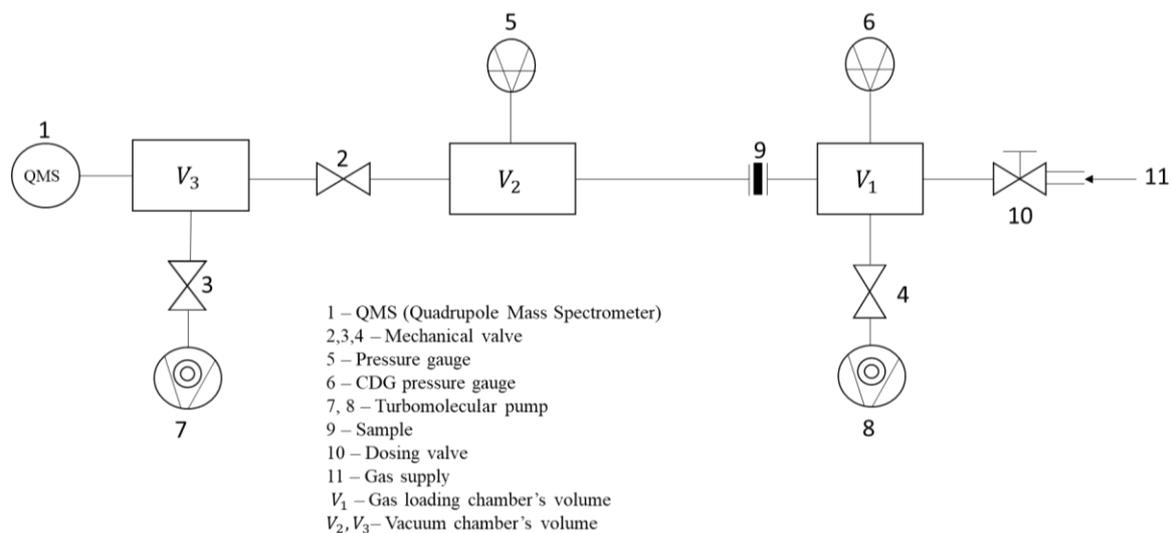


Figure 1. Schematic representation of the vacuum system used to study the permeability of Helium gas into the Zerodur material.

low-pressure volume $V_2 + V_3$, as shown in Figure 1) having in common the sample wall. Each of these volumes has its own vacuum pump, vacuum gauge and valves. In this setup, gas diffuses through the thin sample wall directly into the chamber where the quadrupole mass spectrometer was mounted. The vacuum chamber's material is stainless steel, the valves used are KF valves with stainless steel body and elastomer seal, whereas the pumps used in this research work are Pfeiffer turbopumps.

With this vacuum system, we investigated the diffusion of helium in a Zerodur sample. The sample (a squared plate with a thickness of 0.2 cm and an area of 2.27 cm²) was received by the Physikalisch-Technische Bundesanstalt in Berlin (charge number "105080201"). Aluminium joints, ISO-KF flanges and elastomer O-rings were used to mount the sample into the system. The O-rings were used to prevent He permeation and were placed on both sides of the sample, whereas KF flanges were placed next to the O-rings and then were tightened using aluminium joints.

To regulate and control the temperature we used HTC-5500/5500PRO Temperature control unit and heating tapes. The sample was wrapped several times with heating tapes, which were then wrapped with aluminium foil. Such sample insulation provided temperature regulation of about ± 1 °C. Temperature changes were recorded using a thermocouple connected to the LabVIEW software.

Before running measurements with the investigated sample, a leak test was performed, to make sure there was no He leakage through the elastomer parts of our system. During the measurements, the following procedures were pursued: The high-pressure chamber and the vacuum chamber were evacuated with the aid of two turbomolecular pumps. When the vacuum chamber had been pumped down to 10⁻⁴ Pa, helium gas was admitted to the high-pressure side of the mounted sample, at a pressure of 1.32·10⁵ Pa and temperature 27.1 °C. Data on the He partial pressure and the chemical composition of the gas species in the vacuum system were obtained by Pfeiffer's PrismaPro QMG 250 F1 Quadrupole Mass Spectrometer, QMS. Data recording and analysis was done using QMS software - PV MassSpec. The QMS was factory calibrated, nonetheless, its calibration expired by the time we conducted the study.

To investigate helium diffusion through the Zerodur sample we used two main methods. The first method aimed to determine permeation, diffusion and solubility coefficients by recording He

partial pressure increase in the vacuum chamber vs. time, until steady state is achieved. After the steady state is reached, the permeated amount of substance vs. time graph is a straight line. The intercept of this straight line with the time axis can be used to calculate the diffusion coefficient, D [9]. The permeation coefficient, K , can be determined from the helium gas flow in the steady state, the known thickness and area of the sample used, and the known pressure in the high-pressure chamber, as described in reference [9]. The relation between the diffusion and permeation coefficient is given by $K = S \cdot D$, where S is the solubility of He in glass. Therefore, with the known diffusion and permeation coefficients, solubility coefficient can be calculated as well. The second method is a modification of the so-called accumulation method, which is described in detail below.

Following the two methods, our study lasted 70 days. From the first day to the twelfth day the sample was kept at a temperature of 27 °C. Then, for the next nineteen days, temperature was raised and adjusted to be 50 °C. Fourteen consecutive days temperature has been changed to 80 °C, then the next nine days to 110 °C, the next seven days to 115 °C and the last nine days to 120 °C.

To reduce the noise in the recorded signal, dwell time was changed from 32 ms to 1024 ms on the 49th day of the study. Also, due to the reduction of He pressure in the high-pressure volume, on the 66th day of the study pressure was increased from 8.87·10⁴ Pa to 1.31·10⁵ Pa. On the 69th day of the study He gas was pumped from the high-pressure volume, to finally record changes in the He signal.

3. RESULTS AND DISCUSSION - MODIFIED ACCUMULATION METHOD

With the previously described procedure, He signal was recorded after its permeation into the Zerodur sample. Graphs presented at Figure 2 display some of the measurements of this signal (representing the partial pressure of He, in Pa) at different times and temperatures during the study.

As can be noticed from the graphs listed in Figure 2, even with the increased dwell time, the recorded He signal was still very low. This may be because He permeability in Zerodur material is so small that it cannot be recorded with our experimental scheme. Therefore, we have conducted

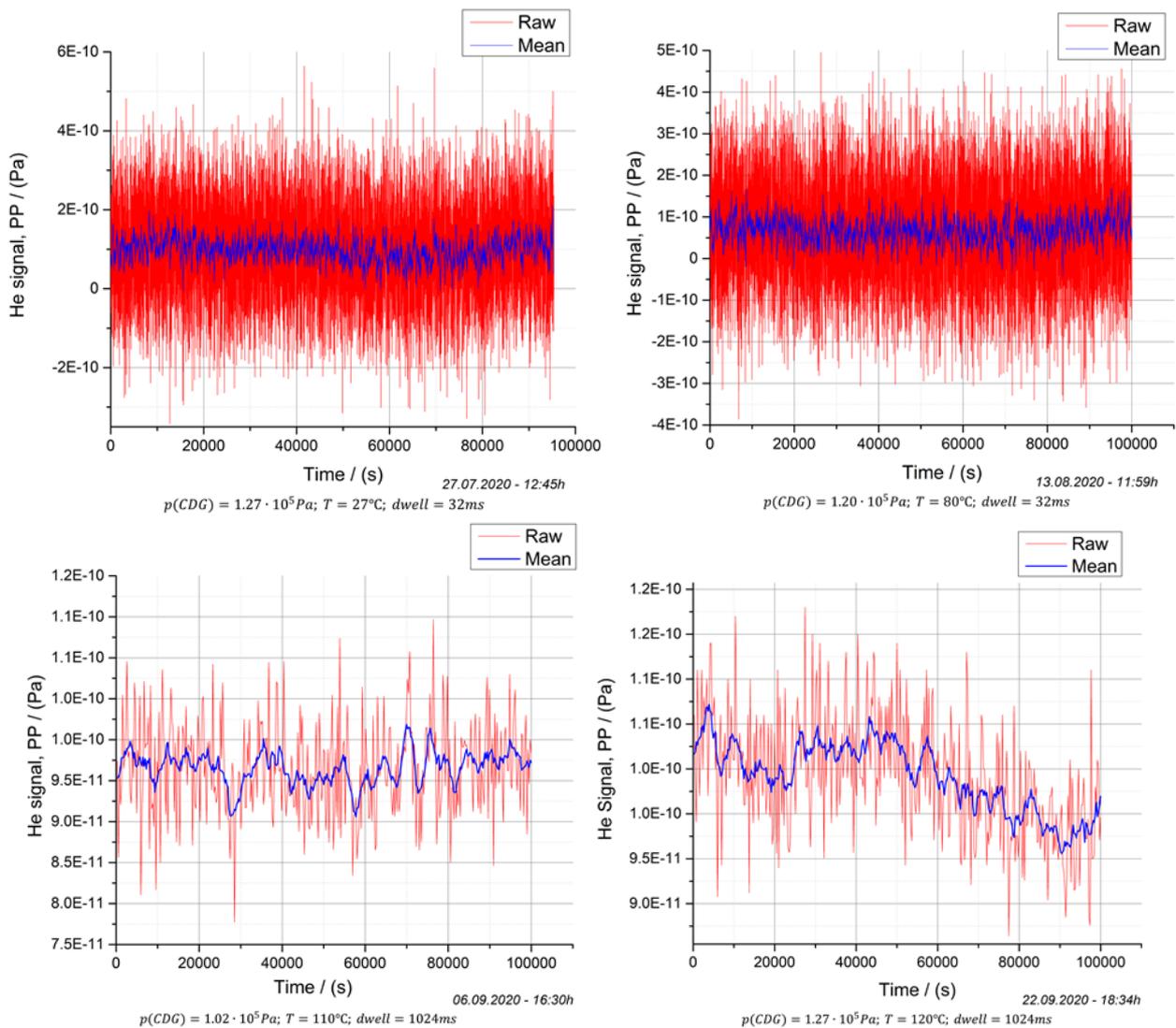


Figure 2. Recorded He signal at different times and temperatures during the study. $p(\text{CDG})$ indicates the He pressure at the high-pressure volume, measured with the Capacitance Diaphragm Gauge – CDG. In addition to the date of measurements recording, the start time of their registration and dwell time are marked as well.

measurements with a modified version of the accumulation method as well [10].

To record measurements by this method, the valve separating the pump and the vacuum system (valve 3, in Figure 1), closes. This enables the accumulation of helium gas that has permeated the sample and allows a longer time for the QMS to record the signal, before it is pumped. While keeping valve 3 closed, the total pressure is monitored in the full range gauge (gauge 5, Figure 1).

As soon as pressure reaches a value of 10^{-2} Pa the valve opens to prevent damage to the QMS filament. This procedure is repeated several times, for different times and temperatures. In the meantime, we tried to conduct measurements with the same method, while keeping valve 2 closed (the valve separating volume V_2 from volume V_3 , in Figure 1). This enables for the gas that permeates the Zerodur sample to not glide into the vacuum chamber where the QMS is located, and it allows us to make comparisons between the signal recorded in these two states. If after closing valve 2 the signal value drops, it indicates that the recorded helium signal is actually the one permeating the sample.

Since no significant values of the helium signal were recorded up to the temperature of 80°C , the results of the measurements conducted with the accumulation method are presented for the temperatures of 80°C , 110°C , 115°C and 120°C .

An example of recorded measurements is shown in Figure 3. The first three measurements represent the helium signal recorded by the accumulation method when valve 2 is open while the last three measurements indicate the helium signal recorded by the accumulation method when valve 2 is closed. Thus, by comparing the recorded measurements, with valve 2 open or closed, the Helium gas flow can be determined. With the known gas flow, the coefficient of permeability can be determined utilizing the known mathematics of the problem. The latter has been discussed in many articles and books, such as [11], [12], and [13]. Here we refer to reference [9] where the gas flow q , through a plane sample with pressure gradient Δp , cross-sectional area A and thickness l , is given by:

$$q = K A \frac{p - p_0}{l}, \quad (1)$$

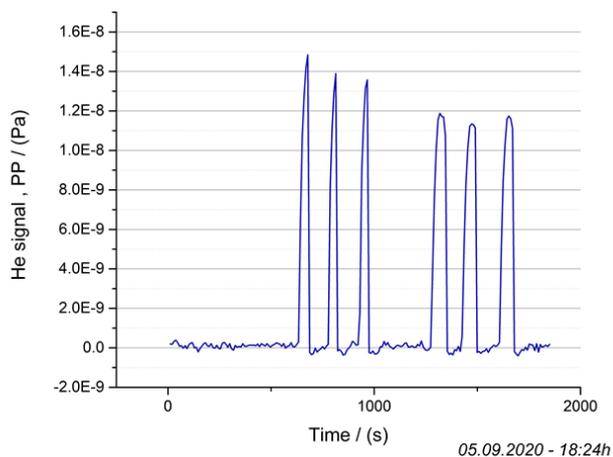


Figure 3. An example of the data conducted with the accumulation method at temperature 110 °C. The first three measurements represent the helium signal recorded by the accumulation method when valve 2 is open while the last three measurements show the helium signal recorded by the accumulation method when valve 2 is closed.

where K is the permeability coefficient, p is helium pressure in the high-pressure volume and p_0 is the helium partial pressure in the low-pressure volume. As the low-pressure side of our sample is a high vacuum, it was assumed that the partial pressure of helium at this side is zero. The volume of the low-pressure part of the system was determined by gas expansion method [14]. The sample surface and thickness were determined geometrically.

Values of the permeability coefficient for different temperatures and at different study times are listed in Table 1.

4. CONCLUSIONS

After 70 days of studying the helium permeability in the Zerodur material, the stationary state of the diffusion process was not recorded. This is because, the helium signal is so weak that it cannot be fully recorded with our vacuum system. As it was not possible to analyse the stationary state of helium diffusion in the Zerodur material, the time constant was not recorded, and consequently the helium diffusion coefficient in the Zerodur material was not determined.

On the other hand, with the accumulation method, we determined the helium permeability coefficient in the Zerodur material, for different temperatures. To our knowledge, there are no data in literature concerning the helium permeability in Zerodur. From the obtained results we estimate that the value of this coefficient is quite low and that it does not change much with increased temperature. For this and for the fact that the time constant of this material is observed to be long, we can conclude that Zerodur material has the potential to be used as cavity

Table 1. Determined values of the permeability coefficient of helium gas in the Zerodur sample, for different temperatures.

Date and time of commencement of data registration	Temperature T in °C	Permeation coefficient K in cm^2/s
31.08.2020 - 12:51h	80	$1.12 \cdot 10^{-15}$
05.09.2020 - 18:24h	110	$1.30 \cdot 10^{-14}$
08.09.2020 - 17:20h	110	$1.59 \cdot 10^{-14}$
09.09.2020 - 17:18h	115	$2.09 \cdot 10^{-14}$
12.09.2020 - 15:27h	115	$5.20 \cdot 10^{-14}$
19.09.2020 - 15:54h	120	$6.47 \cdot 10^{-14}$

material for the quantum standard of pressure measurement. Overcoming other problems regarding the performance of refractometers is among the objectives of the "QuantumPascal" EMPIR project.

ACKNOWLEDGEMENT

The research equipment in our laboratory was financed by USA embassy in Kosovo and the Ministry of Education, Science and Innovation of Kosovo. We also thank Prof. Lars Westerberg from Uppsala University for providing us with some of the vacuum components used in this research.

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