

ANALYSIS OF THE OUTGASSING IN AN OPTICAL PRESSURE STANDARD

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Abstract:

Outgassing effects in a Fabry-Perot cavity based optical pressure standard (OPS) developed at NIM were studied at low pressures using a pressure rising method. The pressure rising curves were recorded by the OPS and a calibrated pressure transducer simultaneously. The pressure values assessed by the OPS were dependent on the gas refractivity parameters and deviated from the transducer values. From the difference, the effective molar polarizability of the accumulated gases was deduced and found to be close to the parameter of water vapour and increased with time. It supported that the accumulated gas in the OPS was composed of water vapor from outgassing and a small amount of air from leakage. To lower the outgassing effects, an external large vacuum chamber was attached to the OPS manifold. Finally, the pressure increase rate was reduced to ~ 50 mPa/h for a period of ~ 140 h, and ~ 27 mPa/h for the first 20 h.

Keywords: optical pressure standard; outgassing; refractometry; molar polarizability

1. INTRODUCTION

Pressure measurement has been widely used in industrial production, biomedicine, aerospace and other fields. Conventional pressure standards mainly include mercury manometers and piston gauges. However, the mercury manometers have disadvantages of large volume, complex operation process, toxic working medium. The traceability of the piston gauge effective area mainly depends on the high-precision measurements of its diameter and profile, which is difficult to achieve.

A Fabry-Perot cavity (FPC) based refractometer as an optical pressure standard (OPS) is a very promising new realization of the pascal due to the high precision and zero-chain traceability [1], [2]. Such kinds of OPS have attracted broad research interests [3]-[7]. The OPS assesses pressure from the refractivity of gas, thus it is highly sensitive to the gas species [8]. High purities of the used gases are of great importance to achieve the highest performance of the OPS. Bottled gases in high

purity together with a clean and tight vacuum system are indispensable. However, outgassing can adversely affect the gas purity. The OPS is typically designed with a small gas-filling volume, which allows to reduce the pV -work and shortens the time needed for thermal equilibrium [9], [10]. The outgassing effect is more prominent in a small volume and limits the low-pressure performance of the OPS. In this paper, the outgassing in an OPS developed at the National Institute of Metrology (NIM), China [6] was analysed by the so-called pressure rising method. The pressure rise was measured by the OPS and a calibrated pressure transducer simultaneously. The output of the OPS was based on the nitrogen parameters and showed a continuously enlarged difference to the pressure transducer with elapsed time. Effective molar polarizability of the accumulated gas was determined according to the measured pressure differences, and the results point out that the accumulated gas was mostly water vapor from outgassing and a small amount of air from leakage.

The outgassing/leakage effects in a vacuum system can be characterized by the static pressure increase rate (SPIR). The SPIR can be reduced by using a larger vacuum chamber. In this work, we proposed a convenient method to reduce the outgassing/leakage effects in the present OPS, which is to connect an external large vacuum chamber (ELVC) to the OPS manifold. This method doesn't alter the present OPS setup. Hence, the thermodynamic performance also doesn't change. Using the ELVC, the SPIR in the whole system was significantly reduced to ~ 50 mPa/h for a period of ~ 140 h, and ~ 27 mPa/h for the first 20 h.

2. EXPERIMENTS

The OPS developed at NIM has been described elsewhere [6]. Two tuneable diode lasers at a wavelength of 633 nm were frequency locked to the FPC, and their frequencies were used to assess the pressure. The uncertainty of this OPS was reported to be $[(0.13 \text{ Pa})^2 + (23 \cdot 10^{-6} p)^2]^{0.5}$ ($k = 2$). The outgassing effect had been observed during the pressure comparison against a primary piston gauge

and had been corrected by an extrapolation method. To investigate the outgassing quantitatively, the pressure rising curve of the vacuum system after closing the relevant valves was recorded with the OPS and a pressure transducer (Yokogawa, resonant silicon gauge, RSG) simultaneously at low pressures. The pressure transducer had been calibrated by a force-balanced pressure gauge (Fluke, FPG8601) with an uncertainty of 0.5 Pa ($k = 2$) for pressures below 1 kPa.

The pressure rising data were logged starting from a nitrogen pressure of ~ 10 Pa, instead of a background vacuum. This is to keep a good thermal connection between the FPC and the chamber housing it, thus temperature gradients can be minimized. The data were collected over a period of ~ 740 h until a final pressure of ~ 500 Pa was reached, as shown in Figure 1. The trend of the pressure rising curves is a typical outgassing type.

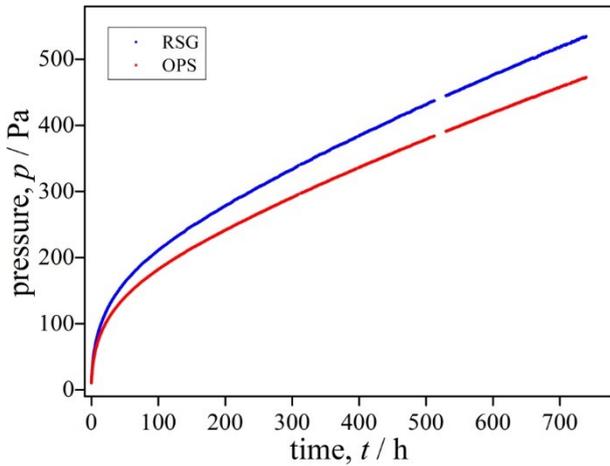


Figure 1: Pressure rising curves recorded by the RSG and OPS

3. RESULTS AND DISCUSSION

The working equation for the OPS to calculate pressure has been described elsewhere [3], [6]. For pressures below 1 kPa, the following equation can be used with adequate accuracy.

$$p_{\text{OPS}} = \frac{2 R T}{3 A_R} \left(1 + \frac{2 R T d_m}{3 A_R} \right) \frac{\Delta v}{v}, \quad (1)$$

where R is the molar gas constant, A_R is the molar polarizability of the working gas, T is the gas temperature in kelvin, d_m is the pressure distortion coefficient of the FPC ($-\frac{\delta L}{L}/p$, the fractional change in the cavity length per pascal), and $\frac{\Delta v}{v}$ is the fractional change in the unwrapped locking frequency of the FPC with phase-shift correction being considered [11]. The data of the OPS plotted in Figure 1 were based on the dynamic polarizability of nitrogen gas. At a wavelength of 633 nm it has a value of $A_{R,N_2} =$

$4.446139(32) \text{ cm}^3/\text{mol}$ [3]. The apparent OPS-based pressure values were gradually lower than the RSG pressure values and became even lower over time. This indicates that the accumulated gas in the vacuum system has smaller molar polarizability than nitrogen.

Although the composition of the accumulated gas might include several gas species, its impact on the assessed OPS pressures can be considered as caused by a single gas with effective molar polarizability, $A_{R,\text{eff}}$. Using the data shown in Figure 1, $A_{R,\text{eff}}$ at time t can be deduced as:

$$A_{R,\text{eff}}(t) = A_{R,N_2} \cdot \frac{p_{\text{OPS}} - p_{\text{OPS}}(t=0)}{p_{\text{RSG}} - p_{\text{RSG}}(t=0)} \cdot \left[1 + \frac{2 R T d_m}{3 A_{R,N_2}} \frac{p_{\text{RSG}} - p_{\text{OPS}}}{p_{\text{OPS}} - p_{\text{OPS}}(t=0)} \right]. \quad (2)$$

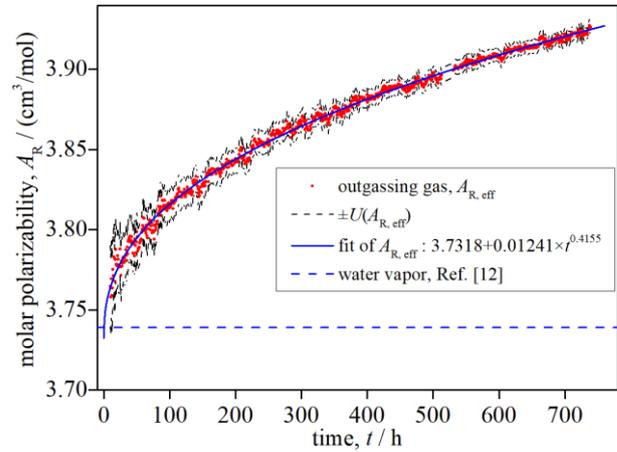


Figure 2: Effective molar polarizability of the accumulated gas over time calculated from Eq. (2) (red dots), its estimated uncertainty (black dash lines), its model fit curve (blue line), and the molar polarizability of pure water vapor for reference (blue dash line).

Figure 2 shows the calculated $A_{R,\text{eff}}$ over time. Its uncertainty was dominated by the uncertainty of RSG and was estimated to be 0.25% \sim 0.1% from time 100 h to the end. High-accuracy water vapor refractivity has been reported by Schödel *et al.* [12], and the result produces the molar polarizability of water vapor at 633 nm to be $3.739 \text{ cm}^3/\text{mol}$ with an uncertainty of 0.05% ($k = 1$). The determined $A_{R,\text{eff}}$ for the accumulated gas is a little bit higher than that for water vapor. It makes sense to infer that the accumulated gas in the vacuum system is a mixture of water vapor desorbed from surfaces and air from leaks, while the water vapor accounts for the largest share. According to this assumption, the molar polarizability of water vapor can be deduced by the model fit of $A_{R,\text{eff}}$ at $t \rightarrow 0$ h. A power increasing model, $a + b t^c$, was chosen, and the fitting results were $a = 3.7318, b = 0.01241, c = 0.4155$. The residuals of the fit were within

$\pm 0.01 \text{ cm}^3/\text{mol}$. We concluded that for 633 nm the result for water vapor is $A_{R,H_2O} = 3.73(1) \text{ cm}^3/\text{mol}$. It is in good agreement with Ref. [12], although it has a larger uncertainty.

As shown in Figure 2, the molar polarizability of accumulated gas $A_{R,eff}$ gradually increases over time from the initial value which is close to the molar polarizability of water vapor. The reason is that with the growth of time, the air is constantly leaking into the vacuum chamber and the molar polarizability of air at 633 nm $A_{R,air} = 4.357 \text{ cm}^3/\text{mol}$ [13] is larger than that of water vapor. The verification is carried out through further data processing and analysis, which are described in more details below.

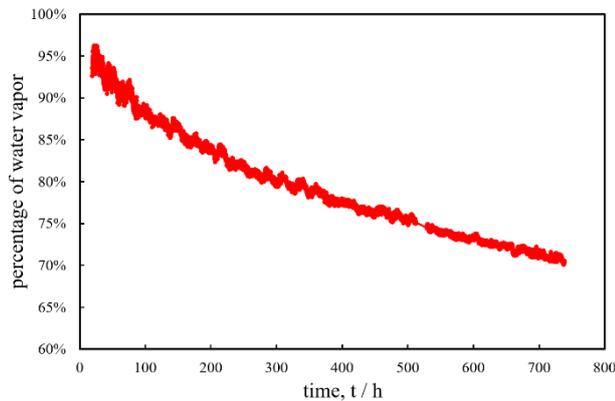


Figure 3: The percentage of water vapor in the accumulated gas.

According to the determined $A_{R,eff}$ of the accumulated gas, the molar polarizability of water vapor at 633 nm A_{R,H_2O} and the molar polarizability of air at 633 nm $A_{R,air}$, the percentage of water vapor in the accumulated gas can be calculated, as shown in Figure 3, and the partial pressure of water vapor and air over time is deduced, as presented in Figure 4. A linear model is used to fit the leakage process of air over time, and the results reveal that the air leakage process in the OPS satisfies a linear relationship, and the leakage rate is $\sim 206 \text{ mPa/h}$, which is consistent with common sense that the air leakage process is a stable cumulative linear effect.

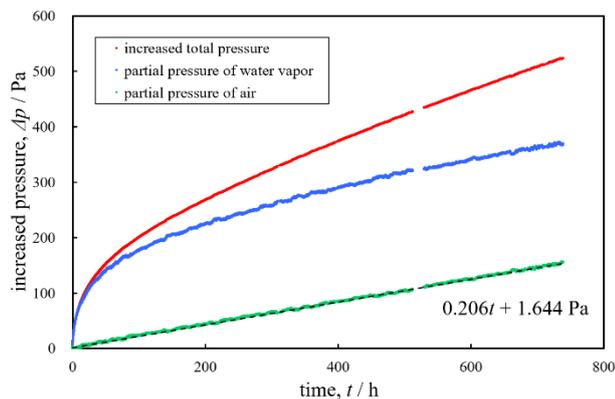


Figure 4: Partial Pressure of water vapor (blue line) and air (green line) in the accumulated gas (red line) over time.

Next, the outgassing effect of water vapor is further analysed. The power model is used to fit the release process of water vapor, P_w represents the partial pressure of water vapor, as shown in Figure 5. It is consistent with common sense that the water vapor outgassing process is a stable cumulative nonlinear effect.

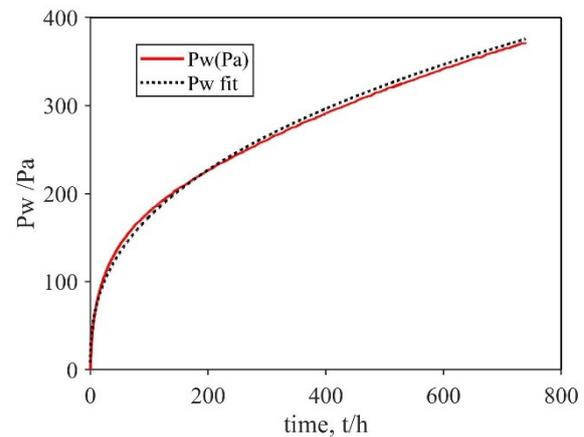


Figure 5: Partial pressure of water vapor over time (red line) and its fitness results (black dots).

On the basis of this, the outgassing rate of water vapor is calculated with the derivation formula and the results are shown in Figure 6. It is obviously seen that the outgassing rate of water vapor is significant at the beginning, but with the growth of the time, it decreases sharply and stabilizes gradually after 100 h. The corresponding logarithm representation is given in Figure 7, and the fitting result by the linear model is presented in black dots.

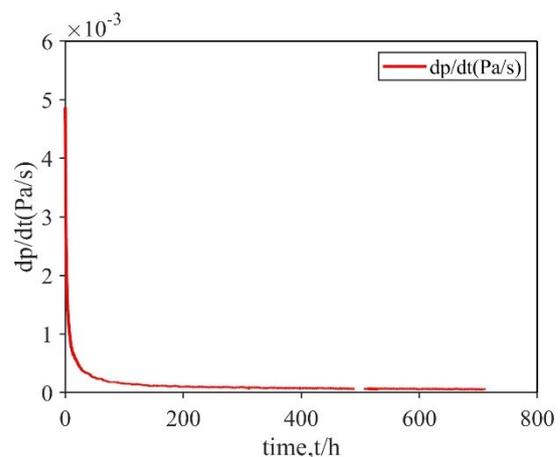


Figure 6: Outgassing rate of water vapor over time.

The outgassing rate of water vapor obeys a power law of the form $Q = Q_0 t^{-\alpha}$, where α is typically near 1 for metal surfaces [14] and near 0.5 for polymers [15]. According to the fitting result shown in Figure 7, α is 0.65 in our case, which

indicates the outgassing was mostly from the O-ring seals.

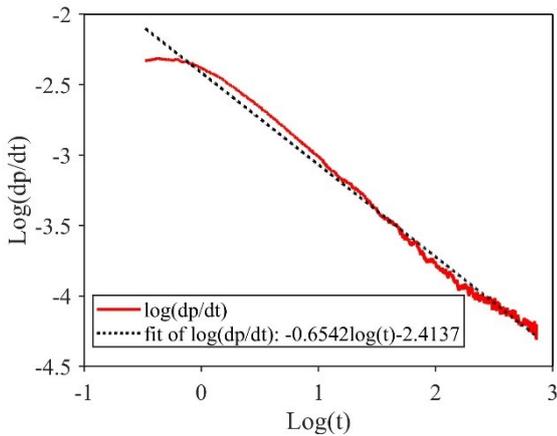


Figure 7: Outgassing rate of water vapor over time plotted in logarithm scale.

4. REDUCTION OF THE OUTGASSING/LEAKAGE EFFECTS

The relatively large outgassing/leakage effects observed were mainly due to the O-ring seals used in the vacuum chamber, which housed the FPC. A fundamental way to solve this problem is replacing the O-ring seals with metal seals and bake out. However, the OPS vacuum chamber should be redesigned and reconstructed. Here, we proposed a convenient method to reduce the outgassing/leakage effects in the present OPS system. An external large vacuum chamber (ELVC) was connected to the OPS by long gas tube as shown in Figure 8. The ELVC has a volume of ~ 3.1 L, and was made from stainless steel and sealed by all-metal seals. A capacitance diaphragm gauge (CDG, 1 Torr, MKS690) is also connected to the manifold to measure the SPIR. The additional volume of ELVC can efficiently reduce the SPIR and improve the performance of the OPS at low pressures. Since the OPS is almost thermal isolated from the outside manifold and ELVC, thermodynamic effects in the OPS and ELVC caused by the filling and pumping of gas are independent from each other.

The pressure rising curve was again measured by the CDG, and the results were shown in Figure 9. Comparing to Figure 1, the SPIR has been largely reduced. With the ELVC, the SPIR was ~ 50 mPa/h for a measured period of ~ 140 h, and was ~ 27 mPa/h for the first 20 h. This result is close to that measured in the OPS developed by other team [16].

To demonstrate the effectiveness of the ELVC method, comparison between the OPS and the CDG will be carried out in the near future.

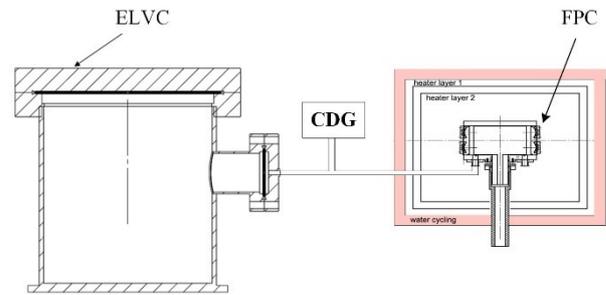


Figure 8: Schematic of the ELVC method to reduce the outgassing/leakage effects in the OPS.

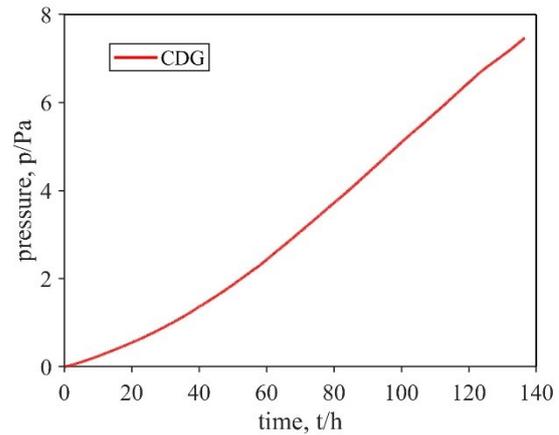


Figure 9: Pressure rising curve for the OPS with ELVC.

5. SUMMARY

An OPS developed at NIM has realized pressure measurements in the low pressure range down to 10 Pa. As reported before [6], the uncertainty was $[(0.13 \text{ Pa})^2 + (23 \cdot 10^{-6} p)^2]^{0.5}$ ($k = 2$), which was demonstrated in the pressure range from 20 kPa to 100 kPa by comparison against a primary piston gauge. The uncertainty at low pressures was limited by outgassing effects. The outgassing features for the vacuum system of the OPS were studied using the so-called pressure rising method with an initial pressure of 10 Pa of nitrogen. A calibrated RSG was used to record the unbiased pressure value. The effective molar polarizability of the accumulated gas was deduced from the apparent OPS pressure and the RSG reading, and was found to be close to the parameter of water vapor. The result supported that the pressure increase in the OPS system was mainly caused by the outgassing of water vapor, and by a minor leak inside the vacuum system. The outgassing of water vapor followed a power law of the form $Q = Q_0 t^{-\alpha}$, where α is ~ 0.65 . This indicated that the outgassing was mainly due to the O-ring seals.

The ELVC method was proposed to reduce the outgassing/leakage effects in the OPS system. It doesn't change the OPS setup and its thermodynamic performance. The ELVC was connected to the OPS by long gas tube, hence they were almost thermal isolated between each other.

With the ELVC connected to the OPS manifold, the pressure increase rate was largely reduced to ~ 50 mPa/h for a period of ~ 140 h, and ~ 27 mPa/h for the first 20 h. The performance of the improved OPS system at low pressures will be further studied by comparison against the CDG in the near future.

6. ACKNOWLEDGEMENTS

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