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Gas Uptake of 3-D Printed Acrylonitrile Butadiene Styrene (ABS) Using a Vacuum Apparatus Designed for Absorption and Desorption Studies

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Abstract

We describe a vacuum apparatus for determining the outgassing rate into vacuum, the diffusion coefficient, and the amount of gas absorbed for various materials. The diffusion coefficient is determined from a model applied to time-dependent desorption data taken using a throughput method. We used this method to determine the diffusion coefficient, D , for H₂O in 3-D printed acrylonitrile butadiene styrene (ABS). We found $D_{\text{H}_2\text{O}} = 8.3 \times 10^{-8} \text{ cm}^2/\text{s} \pm 1.3 \times 10^{-8} \text{ cm}^2/\text{s}$ ($k = 1$; 67% confidence interval) at 23.2 °C. This result was compared to the diffusion coefficient determined another by a gravimetric method, in which the sample weight was monitored as it absorbed gas from the atmosphere. The two methods agreed to within 3%, which is well within the uncertainty of the measurement. We also found that at least 80% of the atmospheric gas (air) absorbed by the ABS is water. The total amount of all atmospheric gas absorbed by ABS was about 0.35% by weight when exposed to ambient air in the laboratory, which was at a pressure of 101 kPa with a relative humidity of 57% at 22.2 °C.

I. INTRODUCTION

The amount and type of gas that a solid material absorbs and subsequently desorbs, in addition to the rate at which absorption and desorption takes place, is an important material property critical for many practical applications. Outgassing rates, for example, largely determine a material's suitability for vacuum or space applications. Perhaps more importantly, the suitability of a material for applications in gas sensing, for gas filters, or for

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gas storage strongly depends on the ability of the material to uptake or desorb gas. There are several properties commonly used to characterize a material's ability to absorb and desorb a gas: solubility, permeability, diffusion, and outgassing. Our vacuum apparatus can be used to determine the diffusion coefficient and outgassing rate. The diffusion coefficient, D (m^2s^{-1}) describes the time it takes for gas to diffuse through a solid. The outgassing rate Q ($\text{Pa L cm}^{-2} \text{s}^{-1}$) describes the desorption of gas from a solid or, more precisely, the flux or throughput of gas leaving the solid per unit area. This quantity is particularly useful for vacuum applications, and can be due to surface desorption, bulk diffusion, or permeation. The total amount of gas absorbed expressed as a fraction of the material mass (% of mass) is useful for gas storage and other applications, and, in general, will depend on the temperature and the gas pressure to which the material is initially exposed. In this work, we describe a relatively simple apparatus for determining the outgassing rate into vacuum, the diffusion coefficient, and the amount of gas absorbed for various materials.

For a test case, we selected 3-D printed acrylonitrile butadiene styrene (ABS). ABS is one of the most common materials used in 3-D printing. ABS has fairly high absorption and outgassing rates for atmospheric gases. This allowed us to compare the results obtained by the vacuum apparatus against those obtained by letting the sample absorb atmospheric gas (air) and measuring a mass change with a laboratory scale. In addition, 3-D printing is a relatively new technology with promising applications. Absorption and desorption data on 3-D printed ABS will be useful for determining its viability for use in vacuum, space science, embedded sensors, and a wide variety of present and future applications. Sorption, diffusion, and permeation constants are known for ABS.^{1,2} Measurements on ABS also give us a good baseline for planned future studies on other 3-D printed materials, particularly composites. For example, researchers are presently experimenting with 3-D printed ABS containing inorganic TiO_2 nanoparticles to enhance various mechanical and chemical properties.³

We chose to use atmospheric gas for this study; future studies will include single-species gases. Studying the absorption of atmospheric gases is of obvious practical importance since materials are typically handled in atmospheric conditions before being placed in vacuum or used in other ways. ABS is a useful test case for our vacuum apparatus and will be an important baseline for future studies of gas absorption properties of other 3-D printed materials.

The purpose of this report is, therefore, twofold: First, to describe a vacuum apparatus that can be used to determine outgassing rates and diffusion coefficients; Second, to report the outgassing rate and water diffusion coefficient, $D_{\text{H}_2\text{O}}$, for 3-D printed ABS at room temperature when exposed to atmospheric gas. Our vacuum apparatus utilizes two techniques for determining outgassing rates: the rate-of-rise method and the throughput method. In the throughput method, the total quantity of gas evolved from a sample is determined from the integrated time-dependent pressure change in the apparatus due to outgassing of the sample. Similar techniques (also referred to as gas-burst methods) have been applied for the calibration of vacuum instruments,⁴ for the determination of water outgassing from a stainless steel chamber,⁵ for the calibration of getter pumps,⁶ and for the determination of water coverage on technical surfaces.⁷ In the present work, data from the throughput method is modeled to determine $D_{\text{H}_2\text{O}}$ and the total gas desorbed. The diffusion

coefficient thus determined is compared to that obtained by a simple gravimetric method: recording the weight change of the material as it absorbs gas from the atmosphere, thus providing an independent test of our results.

II. EXPERIMENTAL

A. Overview of apparatus

A schematic of the apparatus is shown in Figure 1. The apparatus was designed to determine amount and rate at which a sample desorbs gas using two different measurement techniques. First, a rate-of-rise method was used to measure the outgassing rate of the sample within the sample chamber (SC). In this case, the SC is isolated from the rest of the system by closing valves V_0 and V_1 , and the resulting pressure rise in the SC due to outgassing of the sample is measured. Second, a throughput method was used to determine the amount of H_2 , H_2O , N_2 , and other species that evolved from the sample as a function of time. In this method, gas desorbed from the sample was allowed to exit the SC by opening valve V_0 . Desorbed gas flowed through an orifice into the measurement chamber (MC), and was finally removed from the apparatus by a turbomolecular pump connected to the MC. A quadrupole mass analyzer (also commonly known as a residual gas analyzer or RGA) and a total pressure gauge (an ionization gauge) were used to record both the total pressure and partial pressure of various gases in the MC as a function of time. The total gas absorbed by the sample was then determined by integrating the ion gauge signal multiplied by the effective pumping speed of the turbo pump. The analysis and uncertainties associated with the two measurement techniques will be described in detail in the following sections. In this section, we describe the overall apparatus and sample preparation techniques common to both methods. The gravimetric method is covered in II.d.

The apparatus was constructed of standard vacuum components and evacuated by a turbomolecular (turbo) pump backed by a dry scroll pump. All components were made of 304 stainless steel with knife-edge (CF) seals and copper or silver-plated copper gaskets, and the valves were of all-metal construction. All vacuum components between the turbo pump and the valve V_1 were initially degassed by baking at a temperature in the range of 400 °C to 450 °C in dry air free of volatile organic compounds for a period of 2 weeks. This medium-temperature bake significantly reduces the outgassing of H_2 which diffuses from the bulk of the stainless steel. A standard tee with tube inner diameter of approximately 3.5 cm serves as the sample chamber (SC). A spinning rotor gauge (SRG) was used to determine the pressure in the sample chamber. The SRG was also used to determine the outgassing rate of the SC walls, and of the ABS sample, as described below. A valve, V_0 , was used to isolate the SC from the measurement chamber (MC) which was directly connected to the main turbo pump. In addition, a small orifice, approximately 0.6 cm in diameter, was fitted between the SC and the MC. The orifice reduced the pressure from the SC to the MC in an analytically predictable way such that a calibrated ionization gauge (IG) of known accuracy, and a residual gas analyzer (RGA) could be used to measure the gas desorbed from the sample.

The outgassing rate of the SC was characterized by first baking the empty system under vacuum at a temperature of approximately 103 °C for 3 days, which was sufficient to remove most of the water absorbed on the SC walls. Then, using rate-of-rise method, the

outgassing rate of the SC was determined to be 1.9×10^{-9} Pa L/cm² s at 23 °C. The volume of the SC was determined to be 243.2 cm³ using a static expansion method. The SC background outgassing rate can then be subtracted from the measured outgassing rate of a sample.

The sample was allowed to absorb atmospheric gas by resting in ambient laboratory conditions for 350 hours, and then measured by the following procedure:

1. Isolate the SC from the main vacuum system by closing V_0 , ionization gauge and RGA remain in ultra-high vacuum ($<10^{-7}$ Pa).
2. Place sample in SC.
3. Evacuate the SC with the portable pumping system (at $t = 0$, valves V_1 and V_2 are open).
4. Allow gas to flow through the MC where it is sensed by the ion gauge and RGA (at approximately $t = 120$ s, when $p < 20$ Pa, V_1 is closed and V_0 is open).

During the time that the ion gauge data were collected, V_0 was periodically closed to stop the flow from the SC into the MC, so that the outgassing rate in the SC could be monitored using the rate-of-rise method. This procedure only took a few minutes and valve V_0 was reopened immediately after the measurement. It caused no error in the total gas evolved as determined by the IG, since the subsequent pressure burst was recorded by the ion gauge and therefore this periodic check of SC outgassing had no effect on the measurement of the total integrated flow. This periodic pressure rate-of-rise measurement of the SC provided a check on the gas flow seen by the ion gauge: The gas flow in the SC with all valves closed is related to the pressure rate-of-rise $\dot{p}_{SC}$ by $\dot{p}_{SC}V = \dot{n}RT$, where V is the volume of the SC.

B. ABS Sample and Sample Preparation

The ABS sample was a rectangular cuboid of dimensions of 6.0 mm $\times$ 48.0 mm $\times$ 24.9 mm and a mass of approximately 6.5 grams (before loading with gas). Prior to gas loading, the ABS sample was degassed by baking in vacuum for three days at 103 °C, which is just below the 105 °C glass transition temperature. After degassing, the sample was exposed to ambient gas in the laboratory atmosphere for 350 hours. The pressure in the laboratory was an average 100.6 kPa and varied by $\pm 8.0\%$ ($k=1$), with a relative humidity of 56.6% ($\pm 1.0\%$) at 22.23 °C (± 0.21 °C), which is equivalent to a partial pressure of water of about 1.5 kPa. In future experiments, the sample can be saturated with singular gases such as H₂ or CO₂ by placing the sample in the SC, baking the sample to drive out water and other atmospheric gases, and filling the SC with gas from a gas manifold attached to V_2 .

C. Measuring the gas absorbed using the throughput method

Immediately following the initial evacuation of the SC, the valve V_0 was opened so that the remaining gas in the SC and subsequent gas desorbing from the ABS passed through the orifice into the MC, where it was removed from the system by the turbo pump. The pressure signal was recorded by the ion gauge and various partial pressures were recorded by the RGA. The gas flow $\dot{n}$ (mol/s) produced from ABS outgassing flows through the orifice, into the MC, and eventually into the turbo-pump with pumping speed S (L/s). The pressure p_{MC}

in the MC is related to the gas flow by $p_{MC}S = \dot{n}RT$. All of the gas from the SC that passes through the orifice into the MC contributes to the total pressure in the MC and is detected by the ionization gauge. The gas flow from the ABS sample is shown in Fig. 2. Also shown is the background gas flow, which was determined with the SC empty but otherwise under identical conditions as with the ABS sample in the chamber. The background signal is more than two orders of magnitude smaller than the ABS signal. The time integrated pressure gives the total amount of gas evolved from the ABS and can be understood as follows. The total amount of gas evolved from the ABS is given by

$$n = \int \dot{n}(t) dt = \frac{S}{RT} \int p_{MC}(t) dt \quad (2)$$

for a constant effective pumping speed S . Pressures in the MC chamber remained well within the constant pumping speed range of the turbo pump.

Ionization gauge pressure readings are sensitive to gas species. We carried out our analysis assuming that the pressure p_{MC} is entirely due to water. This assumption is supported by the RGA traces shown in Figure 3. The first trace, 3(a), is the background taken 2 minutes before the valve V_0 was opened. The background shows a dominant H_2 peak and water being the second dominant gas. RGAs are typically more sensitive to H_2 than other gases, and we determined that the relative sensitivity of H_2 to N_2 for our RGA was approximately 6. The relative sensitivity of other common gases such as H_2O are typically within 20% of N_2 .⁸ Figs. 3(b) – 3(d) are background subtracted RGA traces taken at 30 s, 10 hr, and 100 hr after the valve was opened. The water cracking fraction in an RGA is typically 100:21:2 for atomic mass unit peaks of 18, 17, and 16, and therefore we can assume that the peaks seen at these masses are due to water. These traces show water as the dominant peak, but becoming smaller at 100 hrs while still remaining more than 85% of the total gas in the system. The RGA traces show that at least 86% of the gas desorbed from the ABS is water for the first 170 hours and, from Fig. 2, that 85% of the gas was desorbed. Therefore we conclude that at least 80% of p_{MC} is due to water, and the remaining 20% could be a combination of H_2O , H_2 , or possibly other gases, although the later contribution is likely to be insignificant.

Using Eq. (2), and assuming that all of the gas evolved is water, the integrated mass change was determined and is shown in Fig. 4. A three dimensional diffusion model was fit to the data (details given in the appendix). This is shown in Fig. 4 for a diffusion constant of $8.3 \times 10^{-8} \text{ cm}^2/\text{s}$.

The uncertainty in the determined diffusion coefficient has four main components: the ion gauge pressure, the temperature, the effective pumping speed for water, and the uncertainty of the fit. The ion gauge pressure reading uncertainty has two main components: the calibration uncertainty, which we determined to be 2% ($k = 1$)⁹, and the gas composition. As discussed above, the majority of the evolved gas is H_2O , we estimate that the lack of knowledge of gas composition contributes 10% ($k = 1$) to the total uncertainty contributes. We estimate the temperature uncertainty to be 3% ($k = 1$) and the effective pumping speed to

be 5% ($k = 1$). Finally, the statistics of the model fit are 4% ($k = 1$), yielding a final uncertainty of about 12% ($k = 1$).

D. Measuring outgassing rates using the rate-of-rise method

Outgassing rates were determined by observing the rise in pressure in the SC using an SRG. Between 10^{-5} Pa and 0.2 Pa the gauge operates in the free molecular flow regime and the effective accommodation coefficient (inverse calibration factor) is constant. This was sufficient for measuring the background outgassing of the SC, however, with the ABS sample in the SC, the large outgassing rate of the ABS forced the chamber pressure to quickly rise above 0.2 Pa. Between 0.2 Pa and 2 Pa the effective accommodation coefficient is not constant but may be described by a simple linear model.^{10,11} We did not use the SRG above 2 Pa in this work.

In general, outgassing rates of materials are given by $Q = \dot{p}V/A$, where $\dot{p}$ (Pa/s) is the pressure rise within a container of volume V caused by the outgassing of a material of area A . When the ABS sample was in the SC, the pressure rise indicated by the SRG is due the combined outgassing of the ABS and the SC: $\dot{p} = \dot{p}_{ABS} + \dot{p}_{SC}$. The outgassing rate of the ABS is determined by combining the general expression for outgassing with the pressure rise in the SC:

$$Q_{ABS} = \frac{V}{A_{ABS}}(\dot{p} - \dot{p}_{SC}) \quad (1)$$

The uncertainty of the outgassing measurement is 15% ($k = 1$) and is dominated by the reproducibility. The pressure uncertainty contributed about 3% ($k = 1$) and the area and volume uncertainty contributed about 1% each. The total nominal surface area of the ABS sample A_{ABS} is 3.2 cm², which was measured with a caliper, with an uncertainty of 0.03 cm². This is a macroscopic measurement which does not take into account the surface roughness. The particular 3-D printed ABS object used in this study had a much rougher surface area than is typical of unformed ABS or ABS objects produced by injection molding. Using a focus variation instrument, we found that the true area is at least 1.4 times the projected area. The volume of the SC, V , was determined to be 243.2 cm³ by a static expansion method with an uncertainty of 1% ($k = 1$).

Fig. 5 shows the pressure rise due to outgassing of the sample as a function of time. From the slope of the line, we obtain an outgassing flow of about $Q_{ABS}A_{ABS} = 5.8 \times 10^{-4}$ Pa L/s. In principle, this flow should be equal to that determined by the throughput method. In fact, for water, it represents only a lower limit to the true outgassing rate. The pressure rate-of-rise does not take into account gas that is reabsorbed by the ABS or chamber walls as the pressure rises in the SC. For the outgassing flow of the background gas, determined using the SRG, the outgassing flow is mostly H₂. In that case, re-absorption by the surfaces is insignificant and the H₂ outgassing flow of 2.6×10^{-7} Pa L/s is consistent with that determined by the throughput method.

E. Measuring the gas absorbed using the gravimetric method

The ABS sample was degassed in the SC as discussed in Section IIb, and subsequently placed on a mass scale with an accuracy of 0.1 mg. The time between venting, removing the ABS sample from the SC, and placing on the scale was approximately 2 minutes. The atmospheric and environmental conditions were as described in Section IIb. The mass gain of the ABS sample as a function of time is shown in Fig. 6. The total mass gained was about 0.36% of the ABS weight. The data were fit to a similar diffusion model as described in the preceding section. A diffusion coefficient of $8.1 \times 10^{-8} \text{ cm}^2/\text{s}$ (23.2 °C) was used to fit the data in Fig. 6. This diffusion constant determination agrees with that determined using the throughput method to within 3%, which is well within the uncertainty of the measurement (note that the uncertainty of the gravimetric method is also dominated by the gas species composition, and is therefore on the same order as that of the throughput method, or about 12%). The close agreement between these two numbers supports the assumption that it is mostly water that is absorbed from the atmosphere.

III. DISCUSSION AND SUMMARY

The goal of this work was twofold: to describe and test an apparatus for studying the gas absorption and desorption properties of materials and to determine the uptake properties of 3-D printed ABS for atmospheric gases. The close agreement between H₂O diffusion coefficient results using the gravimetric and throughput methods ($8.1 \times 10^{-8} \text{ cm}^2/\text{s}$ and $8.3 \times 10^{-8} \text{ cm}^2/\text{s}$, respectively) validates the uncertainty of the vacuum apparatus. The fact that the agreement between the two methods is, in fact, much closer than the measurement uncertainty points to correlated errors between the methods. The same model was used to fit the data in both measurements, and the uncertainty in the gas composition is correlated between the two methods.

It is interesting to compare the H₂O diffusion coefficients determined here with those for fluoroelastomer compounds commonly used for seals in vacuum systems. These have diffusion coefficients which range from $2.4 \times 10^{-7} \text{ cm}^2/\text{s}$ to $8.3 \times 10^{-8} \text{ cm}^2/\text{s}$.¹² Thus water diffusion through ABS is similar to typical elastomer seals in high-vacuum systems. In addition, Viton O-rings have reported water reabsorption varying from 0.07% to 0.38% by weight.¹³ This is also similar to the present results for ABS.

Water absorption for 3-D printed ABS has also been reported by NASA.¹³ They report that 3-D printed ABS re-absorbs water by 0.25% of the sample weight for a sample baked to 125 °C for 24 hours, and then exposed to air at 50% relative humidity for 24 hours. In the present work, the 3-D printed ABS sample absorbed 0.15% of its weight in water at 24 hours, and 0.36% after 350 hours. The difference between the two measurements are likely due to differences in the printing process or, in addition, the NASA sample may have exceeded the glass transition temperature causing a change in the water uptake properties. It should also be noted that the sample in the NASA study was greater than 275 mg, which is much larger than in the present study.

The total amount of gas absorbed as determined by the gravimetric method differed from the total gas desorbed determined using the throughput method by nearly 40%. This difference

is due to gas desorbed during the initial pumpdown of the SC using the portable pump, which was not detected by the ionization gauge in the MC. We also cannot disregard the possibility that a faster diffusion coefficient may govern the initial desorption, but is missed in our model because the data is missing. This gas was also not detected by the RGA, but does not change our conclusion that most of the gas absorbed by the ABS from the atmosphere was water because our measured $D_{\text{H}_2\text{O}}$ is larger than that for the other primary atmospheric constituents. Diffusion coefficients for atmospheric gases such as N_2 and O_2 at 20 °C, for example, have been measured to be $0.889 \times 10^{-8} \text{ cm}^2/\text{s}$ and $3.33 \times 10^{-8} \text{ cm}^2/\text{s}$, respectively.² If these gases were present in the ABS, it would have taken longer for them to desorb than H_2O ; yet significant signals of these gases were not seen in the RGA trace. We anticipate smaller uncertainties for future studies which involve single gases because the gas composition will be known. In that case, the sample can be loaded into the vacuum system, baked, and the gas loading can be performed within the vacuum apparatus. However, studying the gas uptake for atmospheric gases allowed us to compare the diffusion coefficients determined using a gravimetric method to those using a throughput method in the vacuum apparatus. In addition, gas uptake of atmospheric gases is of great practical value and is an important consideration for 3-D printed materials.

The rate-of-rise method is an excellent method for determining outgassing rates for non-condensing gases such as H_2 or N_2 . However, for condensing gases such as H_2O , it can provide only a lower limit to the outgassing rate unless a model is applied to the data which takes gas re-absorption into account. This technique will be effective for planned future studies involving H_2 uptake in materials.

The present work demonstrates that water is the dominant gas absorbed from the atmosphere by 3-D printed ABS. Materials which strongly absorb atmospheric gas are often not considered good materials for use in high-vacuum. However, materials which can be easily degassed in a reasonable amount of time may still be considered appropriate for use in high-vacuum or ultra-high vacuum (UHV). We found that small samples of 3-D printed ABS may be suitable for high or even ultra-high vacuum use if it is degassed for 3 days at 100 °C. Care must be taken during bake-out because ABS has a glass transition at around 105 °C, which may limit the utility in some cases because UHV systems are often baked at temperature well in excess of 100 °C to remove water from the system. Considering that 3-D printing offers practicality, convenience, and flexibility in component design, the potential of these materials for use in vacuum opens up new possibilities and warrants further study.

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References

1. Marchese J, Garis E, Anson M, Ochoa NA, Pagliero C. *J of Membrane Science*. 2003; 221:185–197.
2. Sanaeepur H, Amooghin AE, Moghadassi A, Kargari A, Moradi S, Ghanbari D. *Polym Adv Technol*. 2012; 23:1207–1218.
3. Skorski M, Esenther J, Ahmed Z, Miller AE, Hartings MR. *Science and Technology of Advanced Materials*. 2016 in press.

4. Dobrozemsky R. Vacuum. 1990; 41:2109–2111.
5. Li M, Dylla HF. J of Vac Sci Technol A. 1993; 11:1702.doi: 10.1116/1.578482
6. Erjavec B, Setina J. J Vac Sci Technol A. 2011; 29:051602.doi: 10.1116/1.3626535
7. Sefa M, Setina J, Erjavec B. Vacuum. 2016; 131:201–208.
8. Malyshev OB, Middleman KJ. J Vac Sci Technol A. 2008; 26:1474.doi: 10.1116/1.2990856
9. Fedchak JA, Defibaugh DR. J Vac Sci Technol A. 2012; 30:061601. <http://dx.doi.org/10.1116/1.4750482>.
10. Fedchak JA, Arai K, Jousten K, Setina J, Yoshida H. Measurement. 2015; 66:176–183.
11. Berg, R., Fedchak, JA. NIST Special Publication 250–93. 2015. NIST Special Publication 250–93: NIST Calibration Services for Spinning Rotor Gauge Calibrations; p. 23
12. Šetina J, Sefa M, Erjavec B, Hudoklin D. Int J Thermophys. 2013; 34:412.doi: 10.1007/s10765-013-1422-2
13. Outgassing Data for Selecting Spacecraft Materials. <https://outgassing.nasa.gov>, Data Reference GSC35076 for ABS
14. Crank, J. The Mathematics of Diffusion. 2. Clarendon Press; Oxford: 1975. p. 2-4.

Appendix

Diffusion of gas in solids

In our experiment the ABS sample was a rectangular parallelepiped of size $l_x = 0.60$ cm, $l_y = 2.49$ cm and $l_z = 4.80$ cm in the direction x, y and z, respectively. The gas concentration C in the ABS sample is a function of thickness and time and it can be described by Fick's second law of diffusion:¹⁴

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right). \quad (\text{A1})$$

Eq. (A1) may be solved for specific boundary conditions. In the gravimetric measurement the sample was fully degassed, so that we have the initial condition $C(x, y, z; t = 0) = 0$. For $t > 0$ we have the boundary condition $C = 1$ for all faces. In the vacuum measurement the sample was fully saturated with gas: the initial condition was $C(x, y, z; t = 0) = 1$, and the boundary condition for $t > 0$ was $C = 0$ for all faces.

The total mass can be calculated as

$$m(t) = \int_{-l_x/2}^{l_x/2} \int_{-l_y/2}^{l_y/2} \int_{-l_z/2}^{l_z/2} C(t, x, y, z) dx dy dz. \quad (\text{A2})$$

Eqs. (A1) and (A2) can be solved numerically by a finite difference method (FDM). The FDM is based on dividing the sample (calculation domain) into a finite number of layers and replacing the partial derivatives in Eq. (A1) at layer boundaries with differential quotients, as described below:

For our sample the dimensionless variables are defined as

$$T = \frac{t}{\tau}, \quad \tau = \frac{l_x^2}{D}, \quad \dot{c} = \frac{C}{C_0}, \quad X = \frac{x}{l_x}, \quad Y = \frac{y}{l_x}, \quad Z = \frac{z}{l_x}, \quad (\text{A3})$$

Then Eq. A1 becomes

$$\frac{\partial \dot{c}}{\partial T} = \frac{\partial^2 \dot{c}}{\partial X^2} + \frac{\partial^2 \dot{c}}{\partial Y^2} + \frac{\partial^2 \dot{c}}{\partial Z^2}, \quad (\text{A4})$$

Let the range in X , Y and Z be divided into intervals ΔX , ΔY and ΔZ and the time into intervals ΔT ,

$$T_n = n\Delta T, \quad (\text{A5})$$

$$X_i = i\Delta X, \quad -N_x \leq i \leq N_x, \quad \Delta X = \frac{l_x}{2N_x} \quad (\text{A6})$$

$$Y_j = j\Delta Y, \quad -N_y \leq j \leq N_y, \quad \Delta Y = \frac{l_y}{2N_y} \quad (\text{A7})$$

$$Z_k = k\Delta Z, \quad -N_z \leq k \leq N_z, \quad \Delta Z = \frac{l_z}{2N_z} \quad (\text{A8})$$

Let us denote

$$C'_{ijk}{}^{(n)} = C'(T_n, X_i, Y_j, Z_k), \quad M^n = M(t_n) \quad (\text{A9})$$

Eq. (A1) is approximated as

$$C'_{ijk}{}^{(n+1)} = C'_{ijk}{}^{(n)} + \Delta T \left(\frac{C'_{i+1,jk}{}^{(n)} - 2C'_{ijk}{}^{(n)} + C'_{i-1,jk}{}^{(n)}}{\Delta X^2} + \frac{C'_{i,j+1,k}{}^{(n)} - 2C'_{ijk}{}^{(n)} + C'_{i,j-1,k}{}^{(n)}}{\Delta Y^2} + \frac{C'_{i,j,k+1}{}^{(n)} - 2C'_{ijk}{}^{(n)} + C'_{i,j,k-1}{}^{(n)}}{\Delta Z^2} \right)$$

(A10)

Where $C'_{ijk}{}^{(n+1)}$ is known then $M^{(n+1)}$ is calculated according (A2) by the trapezium rule

$$M^{(n+1)} = \sum_{ijk} C'_{ijk}{}^{(n+1)} W_i W_j W_{ik} \quad (\text{A11})$$

$$W_i = \Delta X \begin{cases} \frac{1}{2} & \text{at } i = \pm N_x \\ 1 & \text{at } -N_x < i < N_x \end{cases} \quad (\text{A12})$$

In our modeling, two different meshes were used: mesh 1: $T = 10^{-4}$, $N_x = 20$, $N_y = 83$, $N_z = 159$; and mesh 2: $T = 0.25 \times 10^{-4}$, $N_x = 40$, $N_y = 166$, $N_z = 318$. The relative values of $M(t)/M_\infty$ are given in table 1. Reducing the number of layers in mesh had a very small effect. The maximum relative uncertainty was of 0.7%. So, we can conclude that numerical errors of modeling were negligible compared to other measurement errors.

FIG. 1. Schematic of the vacuum apparatus. V_0 , V_1 , V_2 , all-metal valves; SRG, spinning rotor gauge; CDG, capacitance diaphragm gauge; SC, sample chamber; RGA, residual gas analyzer; MC, measurement chamber; IG, ionization gauge.

FIG. 2.

Solid line: gas flow from the ABS sample as determined by the ionization gauge in the MC chamber. Dashed line: background gas flow from the apparatus determined by the ionization gauge without the ABS sample in the SC.

Fig. 3.

(a) The background residual gas analyzer (RGA) trace signal, i , taken before desorption measurements were begun. (b) – (c) RGA traces with the background trace subtracted taken at 30 s, 10 hrs, and 100 hrs, respectively.

Fig. 4.
The open circles represent the integrated data of Fig. 2. The solid line is a model of the data.

Fig. 5.

Open circles are SRG pressure data, solid lines are fits to the data. (a) is the pressure rise in the SC due to the background. (b) is the pressure rise in the SC due to ABS outgassing, roughly 10 minutes after exposed to atmosphere and loaded into the vacuum apparatus.

Fig. 6.

The open circles are the mass gained by the ABS sample as a function of time as determined by a mass scale. The solid line is a model of the data.

Table 1Relative mass $M(t)/M_{\infty}$ vs dimensionless time

T	$M(t)/M_{\infty}$	
	mesh 1	mesh 2
0.01	0.2914	0.2893
0.1	0.7727	0.7725
0.5	0.9971	0.9971