

A NEW METHOD FOR DETERMINING WATER ADSORPTION PHENOMENA ON METAL SURFACES IN A VACUUM

NOVA METODA ZA DOLOČANJE ADSORPCIJE VODNE PARE NA KOVINSKIH POVRŠINAH V VAKUUMU

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Prejem rokopisa – received: 2013-04-25; sprejem za objavo – accepted for publication: 2013-12-23

A new method for measuring the amount of adsorbed water vapor on different technical metal surfaces in vacuum systems after exposure to water vapor has been developed. The method is based on a measurement of the pressure – time response after the sudden introduction of a constant gas flow into the vacuum chamber. For non-adsorbing gases the pressure approaches the equilibrium value with a time constant τ that is equal to $\tau = V/S$, where V is the volume of the system and S is the effective pumping speed for a given gas. For adsorbing a gas like water vapor the approach of the pressure to the equilibrium value is delayed due to the adsorption of molecules on the surfaces of the vacuum system. The method was evaluated using aluminum foils with different surface areas. The measured data were modeled using the Langmuir, Freundlich and Temkin isotherms. The measured water coverage on the stainless-steel and aluminum surfaces was less than one monolayer for pressures ranging from 8×10^{-5} mbar to 1×10^{-2} mbar. The best fit to the measured coverage was obtained when using the Freundlich isotherm.

Keywords: water vapor, adsorption, surface coverage, adsorption isotherm

Razvita je bila nova metoda merjenja adsorbirane količine vodne pare na različnih tehničnih površinah v vakuumskih sistemih. Metoda temelji na merjenju časovnega odziva tlaka po nenadnem uvajanju konstantnega toka plina v vakuumsko komoro. Za pline, ki se ne adsorbirajo, se tlak približa ravnotežni vrednosti s časovno konstanto τ , ki je enaka $\tau = V/S$, kjer je V volumen sistema in S efektivna hitrost črpanja za dani plin. Pri plinu, ki se adsorbira, kot je na primer vodna para, je bližanje tlaka ravnotežni vrednosti zadržano zaradi adsorpcije molekul na površini vakuumskega sistema. Metoda je bila ocenjena s folijami iz aluminija, ki so imele različne velikosti površine. Izmerjeni podatki so bili modelirani z Langmuirjevo, Freundlichovo in Temkinovo izotermo. Za tlake od 8×10^{-5} mbar do 1×10^{-2} mbar je bilo izmerjeno pokritje z vodo na površini nerjavnega jekla in na površini aluminija manj kot ena monoplast. Najboljše ujemanje izmerjenega povprečja je bilo doseženo s Freundlichovo izotermo.

Ključne besede: vodna para, adsorpcija, pokritje površine, adsorpcijska izoterma

1 INTRODUCTION

Water vapor adsorption on the inner surfaces of vacuum systems after exposure to the ambient atmosphere is one of the major problems for most processes carried out in an unbaked vacuum system, and frequently determines the pump-down time to reach ultra-high-vacuum conditions. When a vacuum system is exposed to the ambient atmosphere the water vapor can be adsorbed in several monolayers¹. The amount of adsorbed water vapor on the surfaces of vacuum systems depends on the characteristics and treatment of the material surface, the partial pressure of the water vapor in the atmosphere and the exposure time. A better knowledge of the amount adsorbed and the behavior of the water vapor on the material surface is one of the main contributions to solving the problem of the pump-down time. The amount of adsorbed water vapor on the surfaces of different materials has been studied by several authors using different methods. Minxu Li and H. F. Dylla²⁻⁴ measured the amount of adsorbed water vapor on an electro-polished stainless-steel surface after exposure to

various water vapor pressures and duration times. They calculated the amount of adsorbed water vapor by integrating the desorption flux. Another interesting method, known as the radioactive tracer technique, was also used to determine the amount of adsorbed water vapor on the technical surfaces of metals.⁵⁻⁷ On the other hand, P. A. Redhead^{8,9} studied the effect of adsorption-desorption processes on the pump-down behavior for both monolayer and multilayer adsorption. He reported that the amount of adsorbed water vapor can be expressed as a function of the pressure using a suitable adsorption isotherm.

We have developed a special method for measuring water vapor adsorption on the inner surfaces of vacuum systems with the amount of adsorbed water vapor being less than one monolayer. We made the first measurements in an empty chamber, and then in the same chamber loaded with samples of aluminum foil that had different surface areas. The amount of adsorbed water vapor on the sample surface was calculated by subtracting the amount adsorbed on the walls of the empty chamber from the amount adsorbed in the

chamber with the sample. The measured data were analyzed according to the surface-area dependence of the adsorbed amount. The measured results of the amount of adsorbed water vapor on the surfaces of the vacuum chamber after exposure to various water vapor pressures are compared to the modeling results using several different adsorption isotherms (i.e., the Langmuir isotherm, Freundlich isotherm, and Temkin isotherm).

2 EXPERIMENTAL

2.1 Measurement setup

A schematic of the experimental setup is shown in **Figure 1**. The sample chamber (SC) has a volume of 0.66 L and an inner surface area of 760 cm². It is equipped with a capacitance diaphragm gauge (CDG1) and a spinning rotor gauge (SRG). The SC is connected through a vacuum valve V_0 to a turbomolecular pump (TMP) that has a pumping speed of 60 L s⁻¹ for N₂. Between the SC and the valve V_0 there is an orifice that is made by drilling a hole in a blank Cu gasket for a CF40

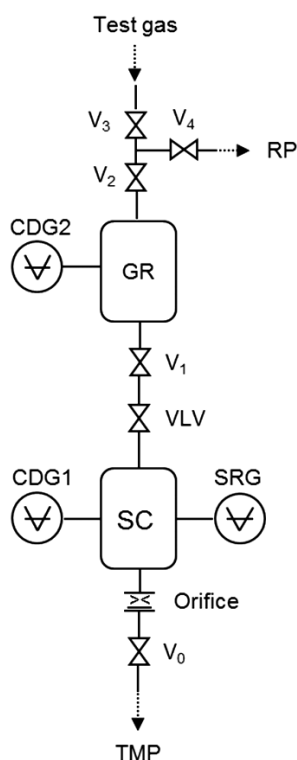


Figure 1: Measurement system for studies of the adsorption of water vapor on metal surfaces in a vacuum: CDG1 – capacitance diaphragm gauge (0.1 mbar FS), CDG2 – capacitance diaphragm gauge (100 mbar FS), SRG – spinning rotor gauge, GR – gas reservoir, SC – sample chamber, TMP – turbo molecular pump, RP – rotary pump, VLV – variable leak valve, V_0 , V_1 , V_2 , V_3 , V_4 – all-metal valves

Slika 1: Merilni sistem za študij adsorpcije vodne pare na površino kovin v vakuumu: CDG1 – kapacitivni membranski merilnik tlaka (0,1 mbar FS), CDG2 – kapacitivni membranski merilnik tlaka (100 mbar FS), SRG – viskoznostni merilnik z lebdečo kroglico, GR – rezervoar plina, SC – komora z vzorcem, TMP – turbomolekularna črpalka, RP – rotacijska črpalka, VLV – ventil s spremenljivim pretokom, V_0 , V_1 , V_2 , V_3 , V_4 – kovinski ventili

flange. The dimensions of the orifice are diameter 5.3 mm and thickness 2 mm. On the other side, the SC is connected to a gas reservoir (GR) through a vacuum valve (V_1), and a variable leak valve (VLV). The GR is equipped with a capacitance diaphragm gauge (CDG2) and connected to both a rotary pump (RP) and a gas source through the valves V_2 , V_3 and V_4 . All the chambers are made of austenitic stainless steel AISI 304L. All the joints are based on Conflat flanges and Cu gaskets. The valves are bakeable all-metal type. The inner surfaces have the standard finish of commercial Conflat-type fittings.

2.2 Measurement method

The SC was pumped by TMP1 for several minutes to reach a pressure of 1×10^{-6} mbar. The pressure was measured by the SRG. The previously evacuated GR was filled with nitrogen gas to a pressure in the range from 10 mbar to 20 mbar. A conductance of the VLV was adjusted to an appropriate value to get a desired pressure in the SC. After that the GR was evacuated again with the valve V_1 opened. Then V_1 was closed and GR was filled with water vapor (or another gas) through V_2 and V_3 . After that the V_2 was closed and the valve V_1 was quickly opened.

The pressure rise within the SC after the sudden introduction of gas was measured by CDG1 and SRG. For the inert gas, which has no interaction with the surface, the pressure rise of gas within the SC can be calculated from the basic quantities: volume of the SC, effective pumping speed, and gas flow into the SC.

By applying the ideal gas law and assuming that the gas temperature remains constant, the flux balance yields the basic differential equation:^{10,11}

$$V \frac{dP}{dt} = Q_m - SP \quad (1)$$

where Q_{in} is the gas flow into the SC, S is the effective pumping speed, t is the time, and V is the volume of the SC. If Q_{in} and S are constant (independent of pressure and time), then the solution of Eq. (1) gives a simple expression for the pressure rise $P(t)$ in the SC:

$$P(t) = \frac{Q_m}{S} \left(1 - s^{-\frac{V}{S}t} \right) \quad (2)$$

The pressure rise in the SC is characterized by the time constant τ which is only a function of the SC volume V and the effective pumping speed S (it is independent of the gas flow Q_{in}):

$$\tau = \frac{V}{S} \quad (3)$$

Since τ depends only on the system parameters V and S , it can be called the system time constant. The gas flow together with the effective pumping speed determines the equilibrium pressure P_{eq} in the SC:

$$P_{\text{eq}} = \frac{Q_{\text{in}}}{S} \quad (4)$$

By introducing Eq. (3) and Eq. (4) into Eq. (2), the latter can be rewritten as:

$$P(t) = P_{\text{eq}} \left(1 - e^{-\frac{t}{\tau}} \right) \quad (5)$$

Eq. (5) represents the pressure rise until the volume of the SC becomes filled with gas up to the equilibrium pressure. For a gas, which can adsorb on the surface, the pressure rise in the SC cannot be described by Eq. (5) because a certain number of gas molecules from the gas flow Q_{in} can be trapped on the inner surface of the SC and do not exit through the orifice. The amount adsorbed depends on the equilibrium pressure and the inner surface area of the SC. Therefore, the system time constant of gases that have an interaction with the surface will be prolonged to an actual time constant τ' . This τ' is not only a function of the SC volume and the effective pumping speed, since it is also influenced by the adsorption of gas molecules on the inner surface of the SC. Equilibrium is achieved when the surface becomes saturated with adsorbing molecules and the flux of the adsorbed and the flux of the desorbed molecules equalize.

Figure 2 shows the normalized measured pressure rise in the case of a sudden introduction of water vapor at a constant flow rate into the SC. It can be compared to the normalized estimated pressure rise for the case of non-adsorbing gas having the same flow rate, which can be calculated by Eq. (5). The area between the two curves in **Figure 2** represents the number of adsorbed molecules in the SC that did not exit through the orifice. This area can be calculated as the difference between the

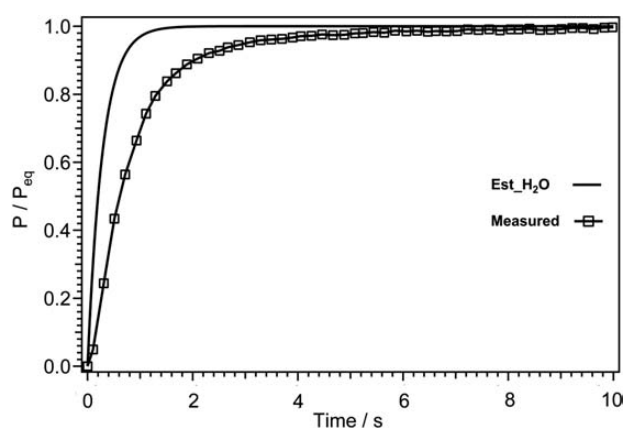


Figure 2: Example of normalized pressure rise until the volume becomes filled to an equilibrium pressure for water vapor. Measured pressure rise is compared to the estimated pressure rise (Est_H₂O) with the assumption that the H₂O has no interaction with the surface.

Slika 2: Primer naraščanja normaliziranega tlaka, dokler se ne napolni volumen do ravnotežnega tlaka vodne pare. Izmerjeno naraščanje tlaka je primerjano z ocenjenim naraščanjem tlaka (Est_H₂O) s predpostavko, da H₂O nima interakcije s površino.

two integrals, ($I_1 - I_2$), where I_1 is the time integral of the estimated pressure rise given by:

$$I_1 = P_{\text{eq}} \int_0^t (1 - e^{-\frac{t}{\tau}}) dt \quad (6)$$

and I_2 is the time integral of measured pressure rise $P_m(t)$ within the SC given by:

$$I_2 = \int_0^{t_{\text{eq}}} P_m(t) dt \quad (7)$$

Integration starts from the time when the V_1 is opened and needs to be continued over a sufficiently long period t_{eq} until the equilibrium of the measured pressure in the SC is reached. The number of adsorbed molecules N_{ad} on the inner surface area of the SC is calculated according to:

$$N_{\text{ad}} kT = S(I_1 - I_2) \quad (8)$$

where k is the Boltzmann constant, T is the absolute temperature and S is the effective pumping speed.

To evaluate this measurement method a measurement with water vapor in the empty SC was performed. In this way the adsorption on the chamber walls was determined. After that the sample of aluminum foil (99.6 % Al, 0.19 % Fe, 0.17 % S) was inserted into the SC. Measurements were performed on three samples that were cut from the same sheet of foil but having a different surface area, being 5, 10 and 25 times larger than the inner surface area of the SC.

The total number of adsorbed molecules is the sum of the adsorbed molecules on the inner surface of the SC (background) N_{ad}^b and the adsorbed molecules on the aluminum foil surface $N_{\text{ad}}^{\text{Al}}$:

$$N_{\text{ad}}^t = N_{\text{ad}}^b + N_{\text{ad}}^{\text{Al}} \quad (9)$$

N_{ad}^b and N_{ad}^t are calculated from the measured pressure rise using Eq. (8). The surface coverage of water vapor on the geometrical area can be calculated according to:

$$\theta = \frac{N_{\text{ad}}}{n_{\text{mono}} A} \quad (10)$$

where θ is the surface coverage, n_{mono} is the surface density of water molecules for a monolayer coverage on a flat surface ($\approx 10^{15} \text{ cm}^{-2}$) and A is the geometrical surface area.

2.3 Adsorption isotherms

The measured results were modeled using the Langmuir, Freundlich and Temkin adsorption isotherms, which are discussed in detail by Redhead⁸. The Langmuir isotherm is based on the simplest model, which assumes that the rate of adsorption is proportional to the number of empty adsorption sites, and the heat of adsorption is constant $q = q_0$. The relationship between pressure and coverage in this isotherm can be described by equation:

$$\theta = \frac{(ap)^{\frac{1}{n}}}{1+(ap)^{\frac{1}{n}}} \quad (11)$$

where p is the pressure, $n = 1$ for non-dissociative molecules, and $n = 2$ for dissociative molecules, and a is a constant that can be described as follows:

$$a = \frac{s_0 v \tau_0}{N_m} \exp \frac{q}{RT} \quad (12)$$

where s_0 is the sticking probability on an empty adsorption site, τ_0 is the period of oscillation of the molecule normal to the surface ($\approx 10^{-13}$ s), v is the specific arrival rate of molecules at the surface, N_m is the number of molecules for a monolayer coverage, q is the heat of adsorption and R is the universal gas constant.

The Freundlich isotherm can be derived by taking Langmuir assumptions and using a logarithmic variation of the heat of adsorption with the coverage as $q = -q' \ln \Theta$. The relation between the pressure and the coverage can be described by equation:

$$\theta = kp^\beta \quad (13)$$

where k and β are constants.

The Temkin isotherm may be derived using the Langmuir isotherm, which assumes that the heat of adsorption decreases linearly with increasing coverage as $q = q_0 (1 - \alpha \Theta)$, where α is a constant. The relationship between pressure and coverage can be described by the equation:

$$\theta = A \ln(\beta p) \quad (14)$$

where A and β are constants:

$$A = \frac{RT}{q_0 - q_1}, \beta = \frac{1 + \frac{p}{p'} \exp \frac{q_0}{RT}}{1 + \frac{p}{p'} \exp \frac{q_1}{RT}} \quad (15)$$

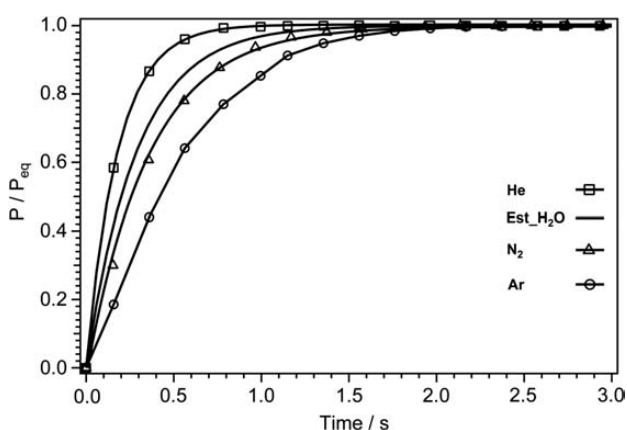


Figure 3: Normalized pressure rise until the volume becomes filled to an equilibrium pressure for gases: He, N₂, Ar and estimated pressure rise for water vapor (Est_H₂O) with the assumption that H₂O has no interaction with the surface

Slika 3: Normaliziran tlak naraščaja, dokler se volumen ne napolni do ravnotežnega tlaka za pline: He, N₂, Ar in ocenjeni tlak vodne pare (Est_H₂O) naraščaja s predpostavko, da H₂O nima interakcije s površino

where $p' = N_m/s_0\tau_0v$, q_0 is the heat of adsorption at $\theta = 0$ and q_1 is the heat of adsorption at $\theta = 1$.

3 RESULTS AND DISCUSSION

The measurement method was validated with non-adsorbing gases: He, N₂ and Ar. **Figure 3** shows the normalized measured pressure rise for helium, nitrogen and argon as a function of time. Also added is the normalized estimated pressure rise of H₂O that would be observed when no water molecules are adsorbed on the surfaces. The normalized pressure is equal to the measured or estimated pressure divided by the equilibrium pressure: $P(t)/P_{eq}$.

The calculated system time constants τ_{gas} for the gases He, N₂ and Ar are shown in **Table 1**. The constants were obtained by fitting Eq. (5) to the measured values. The system time constant for a given gas depends on the effective pumping speed (Eq. (3)), which is gas dependent. Since the orifice conductance is significantly smaller than the pumping speed of the turbo-molecular pump, the effective pumping speed is mainly determined by the orifice conductance.

Table 1: Measured time constants t_{gas} for different gases, time constants ratio t_{gas}/t_{N_2} and square root of the ratio of molecular masses

Tabela 1: Izmerjena časovna konstanta t_{gas} za različne pline, razmerje časovnih konstant t_{gas}/t_{N_2} in kvadratnega korena razmerja molekulskih mas

Gas	t_{gas}/s	t_{gas}/t_{N_2}	$(M_{gas}/M_{N_2})^{1/2}$
He	0.17	0.49	0.38
N ₂	0.35	1.00	1.00
Ar	0.43	1.23	1.20

In the molecular regime, the orifice conductance is inversely proportional to the square root of the molecular mass of the gas. Therefore, the ratio of the system time constants τ_{gas}/τ_{N_2} should be equal to:

$$\frac{\tau_{gas}}{\tau_{N_2}} = \sqrt{\frac{M_{gas}}{M_{N_2}}} \quad (16)$$

where t_{N_2} is the system time constant for nitrogen, M_{N_2} is the molecular mass for nitrogen, and M_{gas} is the molecular mass of the gas. **Table 1** shows that τ_{Ar}/τ_{N_2} is close to the expected value. There is an enlarged difference for τ_{He}/τ_{N_2} . The main reason for this deviation is the very fast pressure rise in the case of He, so that the time response of CDG1 is too slow for an accurate measurement. Close agreement for the ratio of the system time constants for N₂ and Ar with Eq. (16) justifies the use of Eq. (16) to estimate the system time constant for H₂O for the hypothetical case of non-adsorbing water molecules.

The normalized measured pressure rises in the SC as a function of time at various equilibrium pressures of water vapor P_{eq} are shown in **Figure 4**. The normalized estimated pressure rise is also added in **Figure 4**. The

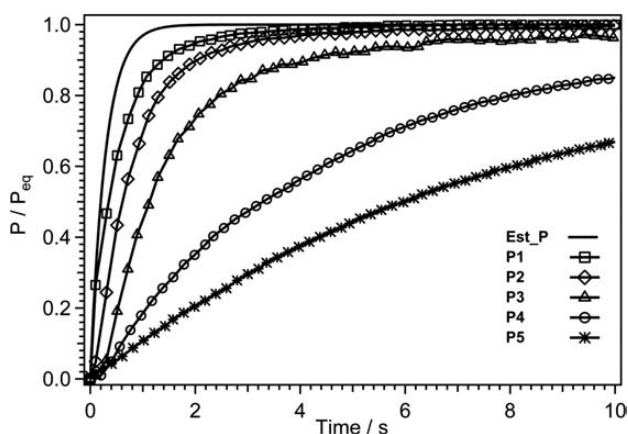


Figure 4: Normalized measured pressure rise until the volume becomes filled with water vapor to the equilibrium pressure P_{eq} ($P1 = 1.03 \times 10^{-2}$ mbar, $P2 = 5.21 \times 10^{-3}$ mbar, $P3 = 1.93 \times 10^{-3}$ mbar, $P4 = 5.67 \times 10^{-4}$ mbar and $P5 = 8.29 \times 10^{-5}$ mbar), and H_2O estimated pressure rise (Est_P) with the assumption that H_2O has no interaction with the surface

Slika 4: Normaliziran izmerjeni tlak narašča, dokler se volumen ne napolni z vodno paro do ravnotežnega tlaka P_{eq} ($P1 = 1,03 \times 10^{-2}$ mbar, $P2 = 5,21 \times 10^{-3}$ mbar, $P3 = 1,93 \times 10^{-3}$ mbar, $P4 = 5,67 \times 10^{-4}$ mbar in $P5 = 8,29 \times 10^{-5}$ mbar) in ocenjen tlak H_2O (Est_P) raste s predpostavko, da H_2O nima interakcije s površino

estimated pressure rise $P_e(t)$ is calculated by Eq. (5) using the estimated system time constant for water vapor that would be observed if there was no adsorption of water molecules on the chamber walls. **Figure 4** shows that the $P(t)/P_{eq}$ curves are different for different P_{eq} and it is evident that the actual time constant τ' increases with decreasing P_{eq} in the SC.

The adsorbed amount of water vapor $N_{ad}kT$ on the inner surface area of the empty SC (background) for different equilibrium pressures, calculated using Eq. (8),

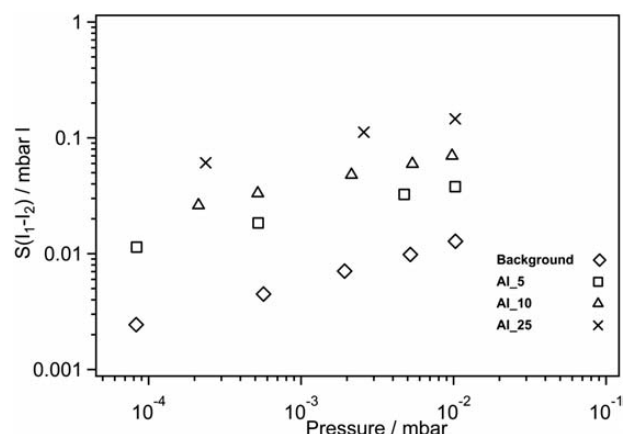


Figure 5: Adsorbed amount of water vapor (in mbar l) vs. H_2O equilibrium pressure, in the case of an empty chamber with an inner surface area 760 cm^2 (background) and the chamber filled with samples of aluminum foil having different surface areas ($A(\text{Al}_5) = 3800 \text{ cm}^2$, $A(\text{Al}_{10}) = 7600 \text{ cm}^2$ and $A(\text{Al}_{25}) = 19000 \text{ cm}^2$)

Slika 5: Adsorbirana množina vodne pare (mbar l) proti ravnotežnemu tlaku H_2O v prazni komori z notranjo ploščino površine 760 cm^2 (ozadje) in komorami, napolnjenimi z vzorci folije iz aluminija z različno velikostjo površine ($A(\text{Al}_5) = 3800 \text{ cm}^2$, $A(\text{Al}_{10}) = 7600 \text{ cm}^2$ in $A(\text{Al}_{25}) = 19000 \text{ cm}^2$)

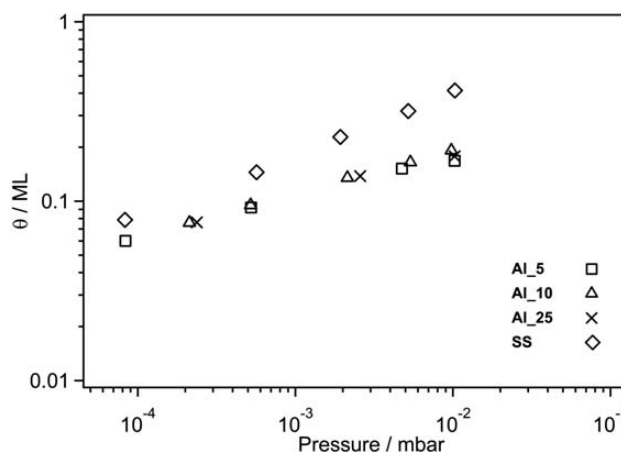


Figure 6: Surface coverage vs. H_2O equilibrium pressure for samples (Al_5 , Al_{10} and Al_{25}) having different surface areas, and for the chamber's inner surface (SS)

Slika 6: Pokritje površine v odvisnosti od ravnotežnega tlaka H_2O za vzorce (Al_5 , Al_{10} in Al_{25}) z različno velikostjo površine in za notranjo površino komore (SS)

is shown in **Figure 5**. The same procedure was then repeated in cases when samples of aluminum foil with different surface areas, being 5, 10 and 25 times larger than the chamber's inner surface area ($A(\text{Al}_5) = 3800 \text{ cm}^2$, $A(\text{Al}_{10}) = 7600 \text{ cm}^2$, and $A(\text{Al}_{25}) = 19000 \text{ cm}^2$), were sequentially placed in the SC. The calculated adsorbed amounts of water vapor for each of these cases are also shown in **Figure 5**.

Figure 5 shows that the amount of adsorbed water vapor on the surface of the SC increases with increasing equilibrium pressure and also with increasing sample surface in the SC. It is expected that the amount adsorbed is proportional to the sample surface. The amount

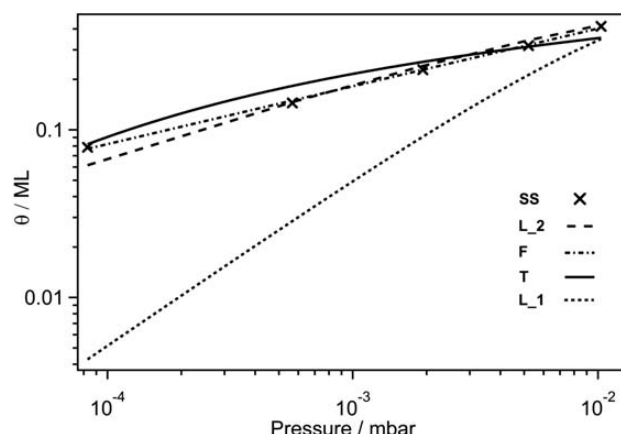


Figure 7: Surface coverage vs. H_2O equilibrium pressure for stainless-steel (SS) and model curves using Langmuir isotherm (L_2 , for dissociative adsorption $n = 2$), Freundlich isotherm (F), Temkin isotherm (T) and Langmuir isotherm (L_1 , for non-dissociative adsorption $n = 1$)

Slika 7: Prekritje površine v odvisnosti od ravnotežnega tlaka H_2O za nerjavno jeklo (SS) in krivulje modela z Langmuirjevo izotermo (L_2 , za disociativno adsorpcijo $n = 2$), Freundlichovo izotermo (F), Temkinovo izotermo (T) in Langmuirjevo izotermo (L_1 , za nedisociativno adsorpcijo $n = 1$)

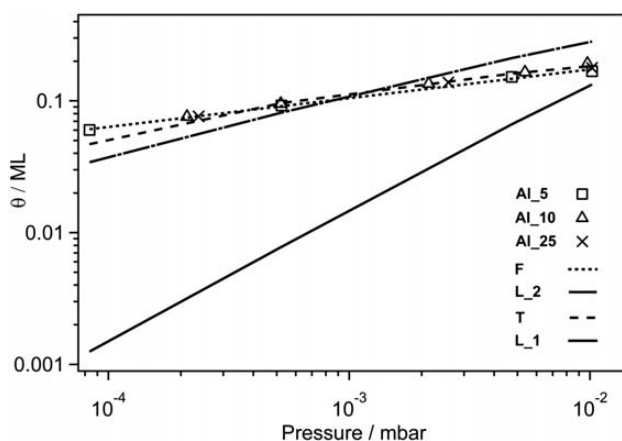


Figure 8: Surface coverage vs. H₂O equilibrium pressure for samples (Al_5, Al_10 and Al_25) having a different surface area and model curves using Langmuir isotherm (L_2, for dissociative adsorption $n = 2$), Freundlich isotherm (F), Temkin isotherm (T), and Langmuir isotherm (L_1, for non-dissociative adsorption $n = 1$)

Slika 8: Prekritje površine v odvisnosti od ravnotežnega tlaka H₂O za vzorce (Al_5, Al_10 in Al_25) z različno velikostjo površine in krivulje modela z Langmuirjevo izotermo (L_2, za disociativno adsorpcijo $n = 2$), Freundlichovo izotermo (F), Temkinovo izotermo (T) in Langmuirjevo izotermo (L_1, za nedisociativno adsorpcijo $n = 1$)

adsorbed on the Al samples can only be calculated by subtracting the background amount that is adsorbed on the chamber's inner surface (Eq. 9).

From the adsorbed amount and the known surface area the surface coverage can be calculated using Eq. (10). The surface coverage of the walls of the SC and the Al samples is shown in **Figure 6**. The values of the measured coverage of the samples of the same material, but with a different surface area are independent of the area. This proves the correctness of our measurement method. From **Figure 6** it can be derived that the surface coverage of the Al samples is on average 1.7 times lower than that of the SC.

The calculated surface coverage for each water vapor exposure pressure is modeled with the adsorption isotherms. **Figures 7 and 8** compare the measured surface coverage for the case of the stainless-steel surface of the SC and Al foils with a different surface area, with different adsorption isotherms (Eqs. (11), (13), and (14)). **Figures 7 and 8** show that the best fitting to the calculated surface coverage is the Freundlich isotherm, whereas the Temkin isotherm and the Langmuir isotherm

(for $n = 2$, dissociative adsorption) show a slightly larger deviation from the calculated surface coverage. There is a large deviation when fitting the Langmuir isotherm for the case of non-dissociative adsorption ($n = 1$).

4 CONCLUSIONS

We developed a special method for measuring the amount of adsorbed water vapor on metal surfaces. The method was tested with Al samples that have different surface areas. The measured amount of adsorbed water was proportional to the area. The results can be modeled with Langmuir, Freundlich and Temkin isotherms (in a rather narrow pressure range). The surface coverage curve of our measurement vs. H₂O exposure pressure had the best fit with the Freundlich isotherm. Fitting with the Langmuir isotherm ($n = 2$) suggested that we have a dissociative adsorption of water molecules.

Acknowledgement

The authors acknowledge the financial support of Slovenian Research Agency ARRS through the project P2-056 Vacuum Technique and Materials for Electronics.

The first author (M. Sefa) acknowledges the partial financial support by the European Union, European Social Fond. Operation was implemented in the framework of the Operational Programme for Human Resources Development for the Period 2007–2013.

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