Anodic alumina sensor for water activity monitoring in food materials

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Abstract. Water activity is a parameter that characterizes the hydration state of a particular substance and the extent of water binding therein. Many food system technology aspects are related to food system hydration, hence water activity (Aw) measurements can become widely used in technological application. However, widespread implementation of water activity monitoring is hampered by the lack of available measuring instruments. This article provides the examples of potential water activity use in food industry and proposes a method of water activity measurement with a piezoelectric quartz sensor coated with a porous alumina layer.

1. Introduction

Water activity is a parameter that directly characterizes the hydration state of a particular substance and the extent of water binding therein. Many food system technology aspects are related to food system hydration, hence water activity (Aw) measurements can become widely used in technological application [1,2]. Water activity monitoring is most widely used in the production of long-shelf life products to avoid microbiological deterioration [3-5]. However, widespread implementation of water activity monitoring is hampered by the lack of available measuring instruments. This article proposes and studies a piezoelectric quartz sensor with a deposited porous alumina layer for measuring water activity. Requirements for accuracy and sensitivity of the sensor can be set on the basis of a specific food industry problem to be resolved using water activity monitoring. Determination of the extent of sugar hydrolysis can be taken as an example. Simple yet reliable measurement of the extent of sugar hydrolysis is quite a priority in various food industry sectors. For example, glucose and fructose as the products of enzymatic hydrolysis of starch or sucrose can be determined either by chemical methods using expensive reagents or by high performance liquid chromatography using most sophisticated equipment [6]. An alternative to these methods is the reagent-free express method of measuring water activity in solutions that does not require any sophisticated equipment. Sucrose solutions with a concentration range of 30-90% were hydrolyzed by heating in the presence of citric acid. At a sucrose concentration of 55%, water activity after hydrolysis decreases from $A_w1 = 0.91$ to $A_w2 = 0.84$. With an increase in sucrose concentration, the difference between the values of $A_w1$ and $A_w2$ rises. The results can be explained by an increase in the number of water binding sites after sugar hydrolysis.

Sensitivity of water activity measuring instrument can be evaluated on the basis of water activity measurements in sugar and sugar hydrolyzate solutions. Thus, to determine the degree of hydrolysis with an error of 2%, water activity should be measured with an accuracy of 0.2%. To the best of the
authors’ knowledge, water activity measuring instruments are not commercially manufactured in Russia. So there is a need for a simple but sufficiently accurate instrument enabling such measurements. The value of water activity is determined by the formula:

\[ p_w = p(p_0)^{-1} \]

where \( p_w \) is water vapor equilibrium pressure in a food system, \( p_0 \) is pure water vapor pressure (at the same temperature).

As follows from the definition, to measure water activity, we should place the sample in a confined space, keep it there until the thermodynamic equilibrium in the system is reached, and measure relative air humidity, which will be equal to water activity. Thus, a special relative air humidity sensor is the key element of the water activity measuring instrument. The principle of operation of such a sensor can be a change in the natural frequency of the piezoelectric crystal when a thin layer of substance is deposited on its surface [7]. Obviously, if such layer is a polymolecular water layer deposited on the surface from air, the resonator surface should actively interact with water. Therefore, it is proposed to modify the resonator surface by applying a thin alumina film. Quantum-mechanical calculations show that the binding energy of water molecules with \( \text{Al}_2\text{O}_3 \) cluster is significantly higher than the respective binding energy with \( \text{SiO}_2 \).

2. The object of the study. Materials and methods

A method of high-frequency magnetron sputtering was selected to deposit coating on the quartz resonator.

Magnetron sputtering of \( \text{Al}_2\text{O}_3 \) was carried out under Argon (10-1 Pa) at a magnetron power density of 40–70 W·cm\(^{-2}\). A grounded metal stage with a piezoelectric resonator mounted on it and satellite plates (n-type Si (111), NaCl crystals) were located at a distance of 5-10 cm from the erosion zone of the \( \text{Al}_2\text{O}_3 \) source. The sputtering time was 20-40 minutes, the temperature of the metal stage, depending on its position, had a value of 100-200°C. Silicon substrates and NaCl crystals were in thermal contact with the stage.

Mass sensitivity of piezoresonator was determined by spraying a thin Al layer on the surface by thermal evaporation in vacuum. The layer thickness was measured by atomic force microscopy (AFM). The mass sensitivity value was 1200 Hz/\( \mu \)G, while the theoretical value calculated according to the well-known Sauerbrey equation [17] is 750 Hz/\( \mu \)G. The difference between experimental and theoretical values is due to the contribution of the resonator peripheral region to the experimentally determined value, while the Sauerbrey equation describes a problem with a coating applied only on the metal electrode region.

3. Results and discussion

The dependence of piezoelectric crystal frequency on relative air humidity was determined by injection of air with required humidity into the vessel with the resonator. Using the above resonator mass sensitivity data, the obtained dependence was converted into the isotherm of water sorption on alumina (Figure 1).

For theoretical description of such adsorption, a model that takes into account the change in the interaction energy of water molecules in the adsorption layers depending on the layer number is proposed. The model makes it possible to explain the features of the obtained sorption isotherms. From the experiment it follows that most of the metal electrode surface is occupied by a deposited film, which adsorbs water much more actively than the initial surface. Let us consider the interaction of the surface with water. Let the probabilities of the molecule addition to the previous i-th layer be \( p_i \), \( q_i = 1 - p_i \) (the first layer is the surface). Then let us make a large partition function taking into account that until the “cell” of the previous layer is filled the corresponding “cell” of the next layer cannot be filled. For n layers we get:
\[ Z = \sum_{N_1+N_2+\cdots+N_{n+1}=N} \frac{N!}{N_1!N_2!\cdots N_{n+1}!} q_1^{N_1} (p_1q_2)^{N_2} (p_1p_2q_3)^{N_3} \cdots (p_1\cdots p_nq_{n+1})^{N_{n+1}} e^{\mu\beta(0N_1+N_2+\cdots+nN_{n+1})} \]

where \( \beta = 1/kT \), \( \mu \) is energy needed to extract a molecule from a gas.

The partition function corresponds to the distribution of molecules when \( N_1 \) positions are not occupied in the first layer, \( N_1 + N_2 \) positions in the second layer, etc. We write the partition function in the form:

\[ Z = \left( q_1 + p_1q_2 e^{\mu\beta} + p_1p_2q_3 e^{2\mu\beta} + \cdots + \prod_{i=1}^{n} p_iq_{n+1} e^{n\mu\beta} \right)^N . \]  

(1)

We introduce the notation:

\[ \frac{q_i}{p_i} = \alpha p_i, \quad e^{\mu\beta} = \alpha P . \]

It is known [12] that \( \alpha = \frac{1}{kT} \left( \frac{h^2}{2\pi m kT} \right)^{3/2} \).

We note that in the problem under consideration \( q_{n+1} = 1 \). Then (1) takes the form:

\[ Z = \left( \sum_{m=1}^{n+1} \prod_{i=1}^{m-1} \left( \frac{q_i}{p_i} \right) q_m P^{m-1} \right)^N = \left( \prod_{i=1}^{n+1} q_i \right)^N \left( \prod_{m=1}^{n+1} \left( \frac{P}{p_i} \right) \prod_{j=m+1}^{n+1} 1/q_j \right)^N \]

where \( P \) parameters are given in pressure units.

The average number of adsorbed molecules is determined by the expression:

\[ \overline{N} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z = P \frac{\partial}{\partial P} \ln Z . \]
Let us write down the expressions for the fraction of occupied positions \( \theta = \frac{N}{N} \) for various values of \( n \):

\[
\theta_1 = \frac{P}{P + P_1},
\]

\[
\theta_2 = \frac{P_2 P + 2P^2}{P_1(\alpha^{-1} + P_2) + P_1 P + P^2},
\]

\[
\theta_3 = \frac{P_2 (\alpha^{-1} + P_1) P + 2P_1 P^2 + 3P^2}{P_1(\alpha^{-1} + P_2)(\alpha^{-1} + P_1) + P_3(\alpha^{-1} + P_1) P + P_3 P^2 + P^3}.
\]

The value of \( \theta n \) is the average number of molecules in \( n \) layers located above one "cell" on the surface with the area corresponding to the size of 1 water molecule.

In the case when \( P_i = P_1 \), i.e. the probabilities are the same for all layers, we have:

\[
\theta_n = P \left( \frac{n\alpha^{-1} P^{n-1} - (n+1)P^n}{P_1(\alpha^{-1} + P_1)^n + (\alpha^{-1} - P)P^n} + \frac{1}{\alpha^{-1} + P_1 - P} \right).
\]

From (5) it follows that \( \lim_{p \to \infty} \theta_n = n \). This relation holds in the general case and corresponds to physical ideas about phase transition. We note that phase transition will occur when pressure \( P \ll P_1 \). With this in mind, formula (5) for large values of \( n \) corresponds to the polynuclear adsorption equation.

When studying adsorption processes, the formulas for \( \theta_n \) allow one to determine the number of layers participating in the adsorption process and determine their characteristics. For calculations, it is convenient to pass to dimensionless variables \( x_i = \frac{\alpha P_i}{P} = \frac{q_i}{\alpha P}, \quad x = \alpha P \).

Then the adsorption isotherm curve in a three-level scheme is determined from formula (4):

\[
f(x) = 19 \frac{x(x_2 + x_3x_1 + 2x_3x + 3x^2)}{x_1(1 + x_2 + x_3 + x_3x_1) + x(x_2 + x_3x_1) + x^2x_3 + x^3},
\]

where coefficient 19 is determined experimentally as a value corresponding to the formation of a monolayer.

Quantum-mechanical calculations in the framework of the Hückel method for water molecules on \( \text{Al}_2\text{O}_3 \) surface lead to the binding energy \( |E_1| = 122.35 \text{ kJ mol} \). Knowing this value, we calculate \( x_1 = 0.37 \cdot 10^{-21} \) at a temperature \( T = 298 \text{ K} \). After sequential optimization by parameters \( x_i (i > 1) \), the following results were obtained. Assuming that the adsorption process occurs in one or two layers (formulas (2) and (3)), the obtained dependence \( f(x) \) is qualitatively different from experimental results. For three layers on \( \text{Al}_2\text{O}_3 \) surface, dependence (6) is shown in Figure 1. The values of the parameters are \( x_1 = 1.0 \cdot 10^{-14}, x_2 = 8.6 \cdot 10^{-16} \). For four water layers, parameters \( x_3 \) and \( x_4 \) are not determined by experimental data approximation. Using the indicated parameter values, we determine binding energies for each of the layers: \( E_2 = 79.61 \text{ kJ / MOL}, E_3 = 28.91 \text{ kJ / MOL} \). The sequence of filling the layers is determined by their binding energy with the previous layer.

To increase the sensor sensitivity, it is necessary to increase the surface area on which water can precipitate. For this, porous alumina can be applied to a quartz resonator. Porous films can be formed on aluminum surface by anodic oxidation, i.e. treatment of aluminum, which is the anode, in an electrolyte exposed to electric field. Predominance of aluminum substrate dissolution over competing
processes (for example, oxide growth and dissolution) leads to the formation of porous films with high specific surface [9,11,13]. The pore diameter as well as the thickness and porosity of the film depend on oxidation conditions: electrolyte composition, oxidation time, current density [8,10].

In this research, hydration of anodic oxide on aluminum surface was studied by electrophysical and thermogravimetric methods.

Porous Al₂O₃ films on the surface of a piezoelectric crystal were obtained by thermal evaporation of aluminum in vacuum, followed by anodic oxidation. Anodic oxidation was carried out in a 10% sulfuric acid solution at a current density of 0.5 A / cm² for 5-10 min. After oxidation, the sample was washed with distilled water.

Since the silver electrode is destroyed during anodic oxidation, it was etched before thermal spraying. And after anodic oxidation, a thin aluminum layer was sprayed onto the surface of the formed Al₂O₃. Al layer served as a quartz resonator electrode.

Average pore diameter in the obtained films was determined based on the study of samples by transmission electron microscopy. For this, carbon-tungsten replicas with a thickness of about 80 nm were sprayed on the sample in vacuum. The thickness of replicas was measured by piezoelectric quartz weighing. The resulting replicas were studied using an EMV-100 transmission electron microscope.

Electronic microphotographs of replicas are shown in Figure 2.

![Figure 2. Microstructure of anodic oxide obtained by anodizing Al in aqueous sulfuric acid solution (magnification 60,000).](image-url)
A system of hillocks with typical dimensions of ~ 80 nm is visible in Figure 2. When spraying replicas on porous materials, carbon penetrates into the pores to a certain depth. As a result, the surface of replicas is covered with hillocks. Therefore, the size of hillocks is equal to the size of pores.

The resonator frequency shift as a function of relative humidity is shown in Figure 3a.

![Graph](image)

**Figure 3.** Dependence of the frequency shift of piezoelectric crystal with a layer of anodic alumina on the relative air humidity (a); typical dependence of sorbed water mass on relative air humidity for porous structures in the case of capillary condensation (b).

Since \( \Delta f \) is proportional to the mass of water deposited on the resonator, the sorption isotherm will be the same as in Figure 3a.

Typical sorption isotherms of porous bodies with pore sizes larger than 1 nm is shown in Figure 3b.

The cd region corresponds to complete filling of capillaries with condensed adsorbate.

Relative humidity \( \varphi_k \) corresponding to a sharp increase in adsorbed matter mass depends on the pore diameter and is determined by the Kelvin equation:

\[
\phi = \exp \left( -\frac{2\mu V_1 \delta}{\sigma r_k RT} \right)
\]

where \( \mu \) is the liquid molar mass, \( \sigma \) is the surface tension coefficient thereof, \( r_k \) is the capillary radius, \( T \) is the temperature, \( V_1 \) is the specific volume of liquid.

The value of \( \varphi_k \) calculated by this equation for a pore diameter of 80 nm is \( \varphi_k = 0.98 \). This means that the cd region (Figure 3b) of anodic alumina sorption isotherm (Figure 3a) is very small and falls within the measurement error. Sorption isotherms of capillary-porous bodies in the ab region correspond to polymolecular adsorption isotherms. That is, at least up to a relative water vapor pressure of 0.9-0.95 the effect of capillary condensation in anodic alumina pores can be neglected.
Figure 4. Dependence of the capacitance of aluminum-anodic alumina structure on relative air humidity (test signal frequency is 1000 Hz).

Figure 5. Dependence of the capacitance of Al-anodic alumina structure on relative air humidity (test signal frequency is 1 MHz).

Studies of Al-Al₂O₃-thin Al layer structures by capacitive methods reveal a significant frequency dispersion of the capacitance of these samples at high air humidity (Figure 4 and Figure 5).

In [19], the dependence of the dielectric constant ε of α-Fe₂O₃ on relative air humidity was determined in the frequency range of the measuring signal from 100 Hz to 100 kHz. Until the formation of the first monolayer is completed, ε remains constant and small in comparison with ε of water. When the second monolayer is formed, a sharp increase in ε is revealed at low frequencies. This suggests that molecules in the first layer of physically adsorbed water are stationary. In [20], electrical conductivity of γ-Al₂O₃-dilute HCl solution system was measured, based on which it was concluded that water structuring near the surface favors the displacement of electrolyte from the surface layer.

Measurements of anodic oxide capacitance (Figure 5) show that the dielectric constant calculated from the formula:

\[ \varepsilon = \frac{Cd}{\varepsilon_0 S} \]  

at high frequencies (with complete wetting of the material) \( \varepsilon = 12 \), which can be explained by the contribution of Al₂O₃ to the total dielectric constant. For the case of low frequency, \( \varepsilon \approx 500 \), which is significantly higher than the dielectric constant of water. Therefore, the frequency dispersion of dielectric constant cannot be explained analogously [20] to the difference in the relaxation time of the first and last monolayers, since in this case ε would not exceed ε of water.

In addition, according to the calculations [21] based on the moment of inertia of a water molecule fixed on the surface by an oxygen atom, the dielectric constant of water monolayer at radio frequencies remains high (ε = 81.04) and drops sharply only in the infrared region of spectrum.

Using this information, the observed physical phenomena can be given the following interpretation. It is known [14] that anodic Al₂O₃ consists of two layers – a thick porous layer and a thin solid layer, the so-called “barrier”, bordering on the metal. Let there be impurity ions on the walls of oxide pores. With increasing air humidity and with the formation of polymolecular water layers on pore walls, these ions, in accordance with [19], are displaced from the surface layer and solvated in polymolecular water layers.

At low measuring signal frequencies, thin layers with a certain ion content are a conducting medium. In this case, the metal-electrolyte-oxide-metal system forms a capacitor with a dielectric gap equal to the thickness of the barrier layer. The capacity of such a capacitor, and, accordingly, the dielectric constant, are determined by the formula (7) and are expected to be very large, which is
observed experimentally. At high frequencies $\omega \gg 1/\tau$, where $\tau$ is the relaxation time of impurity ions, the ions do not have time to respond to changes in the electric field; therefore, the dielectric constant of the moisture layer in the pores becomes equal to $\varepsilon$ of water, and the sample capacity is determined by its porosity.

Measurements of the capacitance – voltage characteristics of the silicon – porous silicon structures performed in [15] as well as our studies of the Al – anodic Al$_2$O$_3$ systems show that at high frequencies ($f$ about 1 MHz), the capacitance of structures is determined by the water dielectric constant and film porosity.

Let us determine the number of monolayers of polymolecular adsorption on the pore walls of anodic oxide at a given air humidity. Since the study of anodic alumina by small-angle X-ray scattering methods together with electron microscopy [18] show that the pores in oxides are straight, cylindrical, the film will be modeled by a system of through cylindrical pores with a diameter equal to the average pore diameter in the anodic oxide film (80 nm).

Using the Sauerbrey equation, expressing the resonator frequency shift $\Delta f$ for porous film through the shift of the resonator frequency with a water monolayer on a flat surface of the deposited aluminum oxide $\Delta f_{\text{water}}$ and calculating the film pore surface area taking into account its porosity $k$, we obtain the dependence of the number $N$ of water monolayers adsorbed on the pore walls on the amount of resonator frequency shift:

$$N_m = \frac{\Delta f}{\Delta f_{\text{water}}} = \frac{\Delta f \cdot R}{2 \Delta f_{\text{water}} k d}$$

where $R$ is the radius of the pores of the film, $d$ is its thickness.

Dependence of the number of monolayers $N_m$ adsorbed on the walls of the pores of anodic oxide on relative air humidity $\varphi$ calculated by the formula (8) is shown in Figure 6.

![Figure 6](image)

**Figure 6.** Dependence of the number of H$_2$O monolayers adsorbed in porous anodic alumina on relative air humidity.

An estimate of the thickness $d_n$ of the surface water film on the pore walls of Al$_2$O$_3$ shows that at the maximum number of monolayers (21) $d_n = 6.4$ nm. This amount of water is clearly not enough to fill a pore with a diameter of 80 nm. Therefore, we can conclude that capillary condensation in the pores of anodic Al$_2$O$_3$ is not achieved even at air humidity close to 100%.

Let's compare the Al$_2$O$_3$ graph in Figure 6 with the isotherm of water sorption on an energetically heterogeneous silver- Al$_2$O$_3$ surface (Figure 1). Even taking into account the fact that Al$_2$O$_3$ may not
occupy the entire surface area of silver electrode, the adsorption of water on the pore walls of anodic oxide proceeds more intensively than on the surface of alumina deposited on a silver electrode. Elemental analysis of Al-anodic Al₂O₃ structures using the electron probe x-ray microanalysis (Table 1) showed that, in addition to aluminum and oxygen, sulfur also enters into the composition of anodic films. Based on the method of producing Al₂O₃ films, it can be assumed that sulfate ions remain in the water even after washing the obtained samples in water. Sulfate ions are among the most hydrated ones [16]; therefore, their presence enhances the adsorption of water on the pore walls of anodic oxide.

Table 1. The results of anodic alumina elemental composition study by electron probe x-ray analysis

| Element | Content % |
|---------|-----------|
| Al      | 42        |
| O       | 55        |
| S       | 3         |

4. Conclusion

Thus, a simple and commercially inexpensive yet extremely sensitive sensor for monitoring of water activity in food materials has been proposed and investigated. The sensitivity of the sensor is confirmed by the ability to detect tenths of a moisture monolayer on its surface.

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