Composite Coatings of Piezoelectric Quartz Sensors Based on Viscous Sorbents and Casein Micelles

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***Abstract*—**The development of new sensitive coatings for sensors is one of the key directions in the development of sensor technologies. Recently, there has been a trend towards the creation of multicomponent coatings for sensors, which make it possible to increase the sensitivity, and specificity, and improve the performance properties of sensors. When analyzing samples with a complex matrix of biological origin, the inclusion of micelles of bioactive substances (amino and nucleic acids, peptides, proteins) in the composition of the sensor coating can also increase useful analytical information. The purpose of this work is to evaluate the analytical characteristics of composite coatings of piezoelectric quartz sensors based on medium-molecular viscous sorbents with incorporated micellar casein concentrate during the sorption of vapors of volatile organic compounds. The sorption properties of the coatings were studied by piezoelectric quartz microbalance. Macromolecular compounds (dicyclohexyl-18-crown-6, triton X-100, lanolin, micellar casein concentrate) were used as sorbents. Highly volatile organic compounds of various classes (alcohols, acids, aldehydes, esters) and water were selected as test substances. It has been established that composite coatings of sensors with the inclusion of micellar casein are more stable and selective to vapors of highly volatile compounds than to water vapors. The method and technique of forming a composite coating using molecular viscous sorbents does not affect the kinetic features of VOC sorption. When casein micelles are used, the features of kinetic sorption depend on the matrix of the coating.

***Keywords*—**Composite coating, piezoelectric quartz microbalance, sensor, volatile organic compounds.

I. Introduction

THE development of new sensitive sensor coatings is one of the mainstream in the creation of sensor devices and technology based on them. In the recent 20 years, there has been a tendency to create multicomponent coatings of sensors, which allow to increase sensitivity and specificity, and improve the operational properties of sensors [1], [2]. Promising devices for practical application are miniature sensor ones based on various types of transducers [3], including electrochemical, optical and acoustic wave sensors [4]. For the analysis of gas medium using sensor technology, a wide range of semiconducting materials has been used, including oxides, polymers, carbon nanomaterials, and other heterostructures [5]. Also, other developing areas are the use of chemical capacitors [6], nanofibers with gold nanoparticles [7], manganese [8], and metal oxides [9] to create miniature systems for the determination of gases and vapors. In terms of cost, responsiveness and sensitivity, gas sensors based on piezoelectric quartz microbalances are promising for solving a wide range of problems, such as food analysis and clinical diagnostics. At the same time, compounds of different natures are used as coatings: polymer films, macromolecular compounds, inorganic compounds, carbon nanotubes and other nanostructures [10], [11]. The development of complex coatings for piezoelectric quartz sensors is also underway [2], [12].

When using biosensors, which are characterized by higher specificity in the analysis of biological objects, various compounds are used as coatings, such as DNA, aptamers, antigens, antimicrobial peptides [13]-[15]. It is also reported about the use of olfactory peptides in the analysis of food for the presence of pathogenic microorganisms [16]. Unfortunately, biosensors require special storage and analysis conditions and have a short lifetime. The use of antimicrobial peptides partially solves the problem of storage and lifetime; however, the analysis conditions remain rather harsh and complex [15]. One possible option for improving the analytical characteristics of gas chemical sensors for the analysis of samples with a biological origin, which have a complex composition, is to introduce amino and nucleic acids, peptides, and proteins in micellar form into the coating of the sensors. The aim of this research is to evaluate the analytical information obtained from piezoelectric quartz sensors coated with composite materials composed of viscous sorbents and micellar casein concentrate. The assessment is based on the sorption of vapors of volatile organic compounds.

II. Materials and Methods

The study of sorption of volatile compounds was carried out in static mode and injection of equilibrium gas phase over volatile compounds in a cell for eight piezoelectric sensors on the analyzer "MAG-8" with special software, in which during measurement, the responses of sensors ($-\Delta F$, Hz) are recorded with a resolution of 1 s, as so-called chronofrequency grams. The time of sorption of equilibrium gas phase was 80 s; the full time of one measurement 180 s. More details of the measurement mode and the device are described in [17].

To create sensors, piezoelectric quartz resonators with a base frequency of 14.0 MHz and silver electrodes were used (Piezo LLC, Moscow). To create composite coatings, viscous

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macromolecular compounds (Table I) and a concentrate of micellar casein were used as sorbents. Micellar casein concentrate (CMC) is a complex product of dairy production, while its composition is quite complex, but about 85% are casein micelles in their native form with varying degrees of dispersion from 0.1 µm to 200 µm. Detailed characteristics of composition and dispersion of the concentrate of micellar casein are presented in [18].

TABLE I
CHARACTERISTICS OF SORBENTS FOR SENSITIVE SENSOR COATINGS

Name	Abbreviation	CAS number	Producer	Solvent
Dicyclohexane-18-crown-6	DCH-18C6	16069-36-6	Sigma-Aldrich, Germany	Toluene
Triton-X100	TX-100	9036-19-5	Sigma-Aldrich, Germany	Toluene
Lanolin	-	8006-54-0	Sigma-Aldrich, Germany	Chloroform
Concentrate of micellar casein	CMC	-	Molvest, Russia	Ethanol

The composition coating of viscous sorbents and casein micelles was formed by layer-by-layer application from sorbent solutions (designation of coating "sorbent1/sorbent2"). First, a coating of viscous sorbent was formed by drop-casting. The process of forming coatings on the electrodes of piezoelectric quartz resonators is described in detail in [19]. Then, casein micelles were applied to the formed coating by finely dispersed spraying of the CMC suspension with pre-filtration from a homemade device, while the size of the micelles did not exceed 10 µm. The composite coating from CMC and lanolin was also formed from a mixture of sorbent solutions (volume proportion – 1:1) of lanolin and micellar casein, since lanolin has good emulsifying properties and increases the solubility of casein in ethanol (designation of coating "sorbent1+sorbent2").

The vapor sorption of volatile compounds on the coatings from single selected sorbents (monocoating) is also investigated to differentiate the features of sorption on composite coatings. The viscous sorbents were deposited also by drop-casting method. In this case, coatings from CMC were applied by dip-coating method. The volume of sorbent solution was varied to form the mass of the coating in the optimal interval for the stable generation of an acoustic wave. The masses of the obtained coatings, calculated by the Sauerbray equation [20], are presented in Table II.

TABLE II
MASSES OF SENSITIVE SENSOR COATINGS

Monocoating	Mass, µg	Composite coating	Mass 1st sorbent, µg	Mass 2nd sorbent, µg
DCH-18C6	20,6	DCH-18-C-6/CMC	4,97	3,12
TX-100	9,15	TX-100/CMC	3,17	2,27
Lanolin	13,0	Lanolin/CMC	6,05	7,79
CMC	4,23	Lanolin+CMC	13,6	

As the operational characteristics of piezoelectric sensors, several indicators were evaluated:

1. Noise, as a shift in the initial frequency of oscillation (F_0, Hz) of the piezoelectric quartz sensor in 10 minutes ($\Delta F_{10\ min}$, Hz), can be determined by the chronofrequency grams;
2. Drift ($\Delta F_{10cycles}$, Hz) is a change in the initial frequency of oscillation (F_0, Hz) of the piezoelectric quartz sensor after the desorption of the compound for ten sorption-desorption cycles ($F_{10cycles}$, Hz), taking into account the noise in the system. Drift is calculated according to (1):

$$\Delta F_{10cycles} = F_0 - F_{10cycles} \quad (1)$$

3. Stability (*Stab,* %) is a decrease in the mass of the newly formed sorbent film (m_f^{15}, µg) relative initial one (m_f^0, µg) for 1 hours of active operation (12-15 sorption-desorption cycles). The stability is calculated according to (2):

$$Stab = (1 - \frac{m_f^0 - m_f^{15}}{m_f^0}) \times 100\% \quad (2)$$

The following parameters were selected as parameters for assessing sorption characteristics:

1. Specific mass sensitivity (S_m^{sp}, Hz×cm³/µg²) of microweighting of vapors of substances with *i*-ng thin coating films by (3):

$$S_{m,i}^{sp} = \frac{\Delta F_{max}}{m_f^0 \cdot C}, \quad (3)$$

where ΔF_{max} – maximum shift in the initial frequency of oscillation of the piezoelectric quartz sensor during the sorption time, Hz; *C* – concentration of volatile compounds into detection cell of analyzer, calculated by the Antoine equation [21] and Mendeleev-Clapeyron equation, µg/cm³.

2. Specific selectivity coefficient $K_{s,i}^{sp}$ by (4):

$$K_{s,i}^{sp} = \frac{S_{m,i}^{sp}}{S_{m,j}^{sp}}, \quad (4)$$

where *i,j* – are the number of coating, *i≠j*

3. The shape of the output sorption curves of volatile substances on the coatings – chronofrequency grams, saving into the special software.

The compounds belonging to different classes of organic compounds were selected as volatile compounds (LLC Reachem, Russia, classification p.a.) for testing the obtained coatings. They are alcohols (ethanol, butanol, isobutanol, isopentanol), acids (formic, acetic, butyric), ketones (acetone, butanone-2), acetaldehyde, ethyl acetate and water. These compounds were selected because they are both native compounds for food and volatile markers of microbiological contamination with pathogenic microorganisms [22]-[26].

III. RESULTS AND DISCUSSION

When developing new coatings for their practical use, the performance characteristics of the sensors are important, allowing to predict the lifetime of the coating and the service life of the sensors. The obtained operational characteristics of the developed sensors are presented in Table III, which are determined by chronofrequency grams and calculated by (1) and (2).

It is established that the coating of CMC is unstable and loses more than 10% of its mass per day of operation. At the same time, when CMC is included in composite coatings, the stability increases to 98%. Also, for composite coatings, the drift and noise are significantly less than for the corresponding monocoatings of viscous sorbents, which can be explained by the structuring of the viscous coating around the casein micelles due to hydrophobic interactions, which further stabilizes the coating.

TABLE III
OPERATIONAL CHARACTERISTICS OF PIEZOELECTRIC SENSORS WITH COMPOSITE COATINGS

Covering	Stability, %	ΔF_{10min}, Hz	$\Delta F_{10cycles}$, Hz
DCH-18C6	98,1	28	880
TX-100	97,7	19	463
Lanolin	99,3	6	185
CMC	88,8	53	1048
DCH-18-C-6/CMC	98,1	12	416
TX-100/CMC	98,8	11	137
Lanolin/CMC	100,0	6	84
Lanolin+CMC	99,9	2	18

One of the important analytical characteristics for evaluating the comparison of the properties of thin films of sorbents is their sensitivity. In the case of piezoelectric quartz sensors, the change in the signal of which is proportional to the mass of the substance on the surface of the electrodes of the resonator, it is convenient to use specific mass sensitivity as such a characteristic. The specific mass sensitivity during sorption of vapors of volatile compounds on the coatings, calculated by (4), is presented in Table IV.

TABLE IV
SPECIFIC MASS SENSITIVITY OF COMPOSITE AND MONOCOATINGS OF SENSORS TO VAPORS OF VOLATILE COMPOUNDS

Coating	Acetic acid	Butyric acid	Butanone-2	Acetaldehyde	Ethylacetate
DCH-18C6	0.85	80	7.3	1.	0.60
TX-100	1.1	50	8.4	1.4	0.69
Lanolin	0.13	5.8	5.9	0.8	0.52
CMC	25	35	2.0	3.3	5.6
Lanolin+CMC	0.16	1.1	3.7	0.59	0.17
Lanolin/CMC	0.25	0.98	3.7	0.32	0.20
DCH-18C6/ CMC	1.0	16	4.3	1.4	0.21
TX-100/CMC	2.1	11	5.3	1.44	0.32

It was found that the specific mass sensitivity of microweighting of acetic acid vapors on composite coatings is greater than on monocoatings. At the same time, the specific mass sensitivity of vapors of other volatile compounds on composite coatings is less than on monocoatings. This indicates the fact that adding casein micelles to the coating increases their hydrophilic properties, so for less polar compounds, the number of available adsorption sites on the coating surface is reduced. However, when analyzing real objects using the sensors and their arrays, not only the sensitivity is important, but also the selectivity of microweighting of vapors of substances. Fig. 1 shows the calculated specific selectivity coefficients for studied coatings.

It has been established that the coefficients of selectivity of composite coatings are comparable with the coefficients of selectivity of nanocoatings. The highest coefficients of selectivity are characteristic of a coating of lanolin and CMC applied from a mixture of sorbent solutions. In layer-by-layer coating of piezoresonator electrodes, the selectivity coefficients are largely determined by the properties of the coating that is applied by the second layer. Since the micellar casein concentrate is hydrophilic in nature, for polycomposite coatings based on CMC with layer-by-layer application, there is an increase in the selectivity coefficient of more polar compounds relative to non-polar compounds, for example, acetaldehyde compared to butanol (Fig. 1). At the same time, when forming a coating from a mixture of solutions, the selectivity coefficients of the coating are determined by the properties of the viscous sorbent. This is shown by the example of the selectivity coefficient of butanone-2 relative to water (Fig. 1).

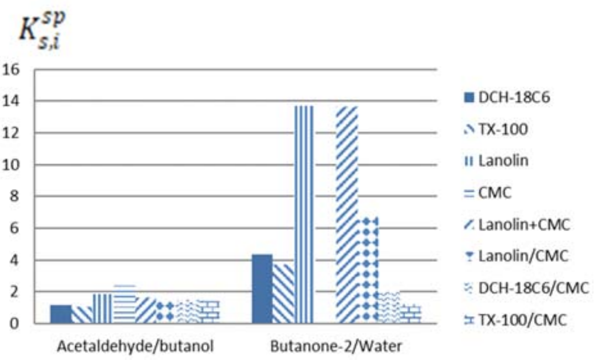

Fig. 1 Coefficient of sensitivity of sensor coatings to volatile compounds

However, when sensors analyze objects of complex composition, the kinetic features of the sorption of the volatile fraction of the sample are also important [27]. When studying the kinetics of sorption, the most informative indicators are chronofrequency grams. With the help of chronofrequency grams, it is possible to find out the changes in the sorption mechanism that occur when using different coatings on piezoelectric quartz transducer [28]. It is established that composite coatings with layer-by-layer application retain the characteristic features of sorption of individual coatings. So, with the sorption of isopentanol (Fig. 2), a slight desorption is maintained after maximum sorption at 5 seconds of injection.

Taking into account the fact that the sorption of volatile compounds on the CMC is characterized by saturation in the first seconds of sorption, it is possible to isolate analytical information related to both coatings after carefully investigation of chronofrequency grams, and thus use one sensor in arrays instead of two. An example of data processing of sensors with composite coatings is described in [29]. Thus, the proposed composite coatings based on micelles of casein can increase the hydrophilicity and surface area of coatings made of viscous sorbents and can be helpful to analyze biological and food objects with a high water content.

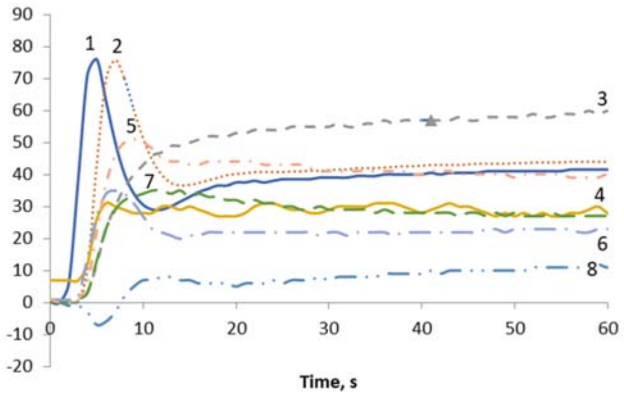

Fig. 2 Chronofrequency grams of piezoelectric sensors with composite and monocoatings during the sorption of isopentanol: 1-TX-100, 2-DCH-18C6, 3- Lanolin, 4-CMC, 5-DCH-18C6/CMC, 6-TX-100/CMC, 7-Lanolin+CMC, 8-Lanolin/CMC

IV. Conclusion

The sorption characteristics of composite coatings based on viscous sorbents with the inclusion of casein micelles depend on the method of formation. When forming a coating of their sorbent solutions, the sorption characteristics are determined by the properties of the viscous sorbent, with layer-by-layer application, the sorption characteristics reflect the features of the two phases included in the coating. The application of composite coatings of piezoelectric quartz sensors based on viscous sorbents and micellar casein concentrate to samples with a complex water-based matrix (food, biological samples) is promising because of their operation and selectivity characteristics. In the future, it is possible to optimize the phase ratio to regulate the required degree of hydrophilicity of the surface and amplify the signal due to casein micelles.

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