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Application of Piezoelectric Sensors with Polycomposite Coatings for Assessing Milk Quality Indicators†

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Abstract: Milk is an important and necessary food product for reducing morbidity in the human body. There are numerous falsifications of milk and dairy products in this regard. At the same time, one of the most time-consuming indicators of raw milk is microbiological parameters. The purpose of this research is to study the gas phase of raw milk samples using piezoelectric sensors with polycomposite coatings to predict its physicochemical or microbiological properties. The sorption of volatile compounds onto the coatings based on chitosan, micellar casein concentrate with polymeric sorbents was studied. This array was employed to analyze the gas phase over raw milk samples. It has been evaluated physicochemical indicators of milk (content of fat, protein, solid substances; acidity) and microbiological indicators (total microbial count; the presence of mold, yeasts, pathogenic microorganisms). The influence of several factors on the composition of volatile compounds in milk was evaluated using the output data of sensors. There are injector and frontal mode of input gas phase into the detection cell, the processing of milk samples by ultrasound and microwave radiation, the introduction of glucose and hydrogen peroxide additives into samples. It has been established statistically significant correlations between the sensor output data and the physicochemical or microbiological indicators of raw milk samples. The regression model was constructed using partial least squares regression to predict the total microbial count of milk based on the output data of piezoelectric sensors with composite coatings, with an appropriate error.

Keywords: chemical piezoelectric sensors; polycomposite coating; volatile compounds; milk; microbiological indicator

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1. Introduction

Milk and dairy products are included in the list recommended for mandatory consumption by the FAO and WHO, and they are of great importance in the diet of the population [1,2]. However, milk processing is costly for several reasons. Furthermore, raw milk is a favorable nutrient medium for various microorganisms, including pathogenic ones, and can be easily contaminated by them [3].

The routine analysis of raw milk for pathogenic bacteria and spoilage microflora is a widely accepted method to guarantee food safety and quality. However, detecting the presence of microorganisms in milk, before they multiply exponentially, is not easy. The analysis of total bacterial count in raw milk requires a duration of several hours, and the confirmation of the presence of pathogenic microorganisms necessitates several days [4]. Consequently, an urgent trend is the development of an express, cheap and highly sensitive method for assessing the microbiological safety of raw milk, comparable with traditional direct inoculation methods. Among these techniques, the usage of gas sensors holds

considerable potential, as the occurrence of distinctive volatile compounds in the gas phase over milk can serve as an indicator for evaluating microbiological parameters [5–7]. Previously, attempts have been made to use gas sensors and their arrays to determine early spoilage of milk [8], estimate shelf life and other indicators [9–13], and identify milk from cows with mastitis [14]. Therefore, the development of techniques for employing gas sensors to evaluate the microbiological characteristics of milk is a promising area of investigation.

The paper describes the investigation of the gas phase over raw milk samples using piezoelectric sensors with polycomposite coatings, including the pretreatment of samples, in order to assess the physicochemical or microbiological properties of milk.

2. Materials and Methods

The objects of research were samples of raw cow's milk obtained from various farms at different seasons, cooled immediately after milking to T=(4 ± 2)^{0}C and delivered to the laboratory for no more than 3 hours of storage.

2.1. Determination of physical and chemical properties of the milk

Mass fraction of dry solids in the samples was determined by drying [15] in a Binder ED 53 oven (BINDER Inc., Tuttlingen, Germany) to constant mass at T=(105±2)^{0}C; the mass fraction of fat - by the Gerber acid method [16], mass fraction of total protein - by formol titration [17], density - by areometric method [18], titratable acidity - by titrimetric method with phenolphthalein indicator [19], purity group - by gravimetric method [20], sizes of milk fat globules - by microscopy (microscope "Altami Bio 1", Altami Ltd., Saint Petersburg, Russia; Canon camera adapter, Canon Inc., Tokyo, Japan) at a magnification x1200 using Gorjaev's count chamber. All used chemicals were of analytical grade quality (Stock Company “Lenreactiv”, Saint-Petersburg, Russia). The experimental studies of each sample were carried out 3–5 times. The number of repetitions of each experiment to determine one value was three times. Calculations were performed using mathematical statistics using the XLSTAT application (Lumivero, Denver, USA) for Microsoft Office 365 Family (Microsoft Corporation, WA, USA). Data were expressed as mean±standard deviation for normally distributed data. The significance of the findings was determined by utilizing the P-value, which was less than or equal to 0.05.

2.2. Determination of microbiological indicators

Microbiological indicators (the quantity of mesophilic aerobic and facultative anaerobic microorganisms QMAFAnM, the quantity of yeasts and molds) were determined using microbiological inoculation on universal nutrient media (plate count agar, Sabouraud agar, Obolensk, Russia) according to standard methods describing in GOST [4,21]. QMAFAnM was estimated using three dilutions of milk (from 10^6 to 10^4). The raw milk sample was diluted in 10 times to quantify the yeast and mold.

Furthermore, molecular genetic studies were carried out to determine the possible presence of opportunistic bacteria: enterohemorrhagic E. coli (EHEC); Salmonella spp.; and Listeria monocytogene. Total deoxyribonucleic acid (DNA) was isolated from the obtained samples using the Proba-GS commercial kit (DNK-Technology, Moscow, Russia) according to the manufacturer's protocol. The concentration was then measured for each sample using a Qubit fluorimeter (Thermo Fisher Scientific, USA) and a commercial Qubit™ dsDNA Quantification Assay Kits (Thermo Fisher Scientific, USA). The detection of enterohemorrhagic E. coli (EHEC), Salmonella spp., and Listeria monocytogene was conducted using commercial reagent kits by detecting the DNA of these bacteria using the polymerase chain reaction method. The reaction mixture components and amplification conditions were chosen according to the manufacturer's protocol.

2.3. Analysis by sensor array

The study of the gas phase over milk samples was carried out on the device "MAG-8" (OOO "Sensors - New Technologies", Russia) with piezoelectric quartz sensors and injector input of gas phase [22]. The surface of electrodes of a quartz resonator with a base frequency of 14,0 MHz were coated by composite films consisting of several sorbents (designation - ½) based on chitosan (degree of deacetylation 2,1, pH = 5,1 – ammonium nitrate, Mr=30–35 kDa). The solutions of sorbents in suitable solvents were prepared with concentration 10 mg/ml and mixed in proportion 1:1 by volume. Coatings were formed by dispersion spraying from solutions of sorbent mixtures [23]. Prior to analyzing the gas phase over milk, the sensor array underwent training on volatile organic compounds of various classes, including alcohols, ketones, ethyl acetate, acetaldehyde, carboxylic acids (analytical grade, Reakhim LLC) and bidistilled water, in order to evaluate their sorption characteristics (Table 1). Estimation of effectiveness of sorption by the composite coatings was assessed using specific mass sensitivity [24].

Table 1. Several characteristics of sensor coatings.

Sensor Number	Coating (1/2)	Solvent	Mass, μg	Specific mass sensitivity, S_f [Hz cm^3/μg^2]			
				Butanoic Acid	Butanone-2	Isopentanol	Acetaldehyde
1	18C6*/Chitosan	Toluene	28.7	26.4	1.55	1.70	0.42
2	DHC/Chitosan	Ethanol	14.7	10.4	1.76	4.04	1.38
3	CMC/ Chitosan	Ethanol	12.5	5.03	0.24	1.26	0.61
4	PVP/ Chitosan	Acetone	12.0	1.12	0.28	0.80	0.21
5	PEG-2000/ Chitosan	Acetone	3.41	26.9	1.43	15.2	2.64

* - 18C6 – dicyclohexane-18-crown-6, DHC – dihydroquercetin, CMC – concentrate micellar casein, PVP – polyvinylpyrrolidone, PEG-2000 - polyethylene glycol 2000.

The features of sorption of volatile compounds on the composite coatings is presented in [25]. The time taken to measure the sorption equilibrium gas phase over pure compounds and samples of raw milk (20 ml) was 80 seconds. In a software of "MAG-8", the values of the frequency of the piezoelectric sensor during the sorption of the volatile compounds were recorded with a frequency of 1 s, according to which the maximum sensor signal ($\Delta F_{max, i,}$ Hz) were obtained.

Four methods of processing raw milk samples were investigated to intensify the release of volatile compounds:

- treatment of ultrasonic with a power of 50 W for 3 minutes (1)
- microwave treatment (2450 MHz) with 800 W for 30 s (2)
- addition of 2 g of glucose and keeping at 37 ºC for two hours (3);
- adding 2 ml of hydrogen peroxide and keeping at room temperature for 2 hours (4).

Sterile samplers with a volume of 100 ml with milk samples after treatment were kept in the laboratory before gas phase analysis at room temperature (25.2 ± 1.0ºC). Additionally, the frontal input mode of the gas phase over milk samples was studied using the odor analyzer "Diagnost-Bio-8" (Ltd. "Sensino", Kursk, Russia) [26] with the same array of sensors. The regime of measurement was 40s- sorption, 80s – desorption.

Based on the sensor signals after the measurement, the parameters β were calculated. The more detail about this parameter will be presented in [27]. The Pearson correlation coefficient was used to evaluate the association between the sensor's output data and physical, chemical, and microbiological characteristics, and its statistical significance was assessed using the Student's t-criteria [28]. The data matrix was processed using the module for Microsoft Excel and Unscrambler X 10.0.1 (CamoSoftware AS, Oslo, Norway) by the partial least squares regression with full cross-validation.

3. Results

The physical and chemical properties of the samples were determined (Table 2). It was established that they conformed with requirements of regulatory documents for raw milk in the Russian Federation [29], except for samples No. 7, 9, 11–13. These samples had a mass fraction of total protein below minimum 2.8% and a titratable acidity below the standardized 16 ^{0}T. All samples have the first group of purity. No opportunistic bacteria were found in the milk samples. The values of all estimated physical and chemical properties of raw milk samples, including the size of fat globules, are presented in the Appendix A, Table A1–A2.

Table 2. The physical and chemical properties of raw milk samples.

No	Mass fraction of Dry Solids, %	Mass Fraction of Fat, %,	Mass Fraction of Total Protein, %	Titratable Acidity, ^{0}T	QMAFAnM*, CFU/ml	Quantity of Yeast CFU/ml	Quantity of Mold CFU/ml
1	16.02 ± 0.12	7.5 ± 0.3	3.46 ± 0.15	19 ± 0.5	10,000,000	100,000	0
2	12.22 ± 0.13	3.8 ± 0.1	3.74 ± 0.10	20 ± 0.5	4,000,000	10,000	0
3	13.36 ± 0.08	4.8 ± 0.1	3.45 ± 0.10	19 ± 0.5	4,500,000	1000	10
4	15.15 ± 0.14	7.5 ± 0.5	3.26 ± 0.10	15 ± 0.5	340,000	0	0
5	11.63 ± 0.13	3.5 ± 0.1	3.01 ± 0.10	19 ± 0.5	2,400,000	1500	160
6	11.77 ± 0.11	3.1 ± 0.1	3.30 ± 0.15	19 ± 0.5	590,000	650	900
7	10.83 ± 0.09	3.9 ± 0.1	2.40 ± 0.10	15 ± 0.5	4,640,000	5680	0
8	12.31 ± 0.12	3.7 ± 0.1	3.10 ± 0.15	18 ± 0.5	98,000,000	8004	60
9	11.41 ± 0.06	3.2 ± 0.1	2.00 ± 0.05	15 ± 0.5	480,000	0	10
10	12.14 ± 0.10	4.1 ± 0.1	2.88 ± 0.10	16 ± 0.5	5,700,000	34,200	300
11	11.72 ± 0.07	3.4 ± 0.1	1.16 ± 0.10	15 ± 0.5	42,000,000	1800	0
12	10.92 ± 0.09	3.3 ± 0.1	1.35 ± 0.10	11 ± 0.5	2,000,000	2300	10
13	11.44 ± 0.11	3.6 ± 0.1	2.59 ± 0.15	17 ± 0.5	3,400,000	17,400	10
14	15.07 ± 0.15	6.5 ± 0.3	3.07 ± 0.10	16 ± 0.5	39,000,000	100,000	0

*- the number of CFU is calculated as the arithmetic mean value when counting on Petri dishes with different dilutions if it was possible or from appropriate dilution.

The changes in gas phase over milk samples after treatment estimated based on relative change the sensor signals (Δ_i) (Table A3). It has been established statistically significant correlations between the sensor output data and the physicochemical or microbiological indicators of raw milk samples (Table 3).

Table 3. Pearson correlation coefficient (r) between sensor data and properties of milk.

Mass fraction of Fat, %,	Mass Fraction of Total Protein, %	Quantity of Mold CFU/ml
β_5 (0.344)[1]	$F_{max,2}$ (0.377)	$F_{max,4(1)}$ (0.572)
Quantity of yeast CFU/ml	$F_{max,2(3)}$ (0.414)	$\beta_{4(1)}$ (0.460)
$\beta_{5(3)}$ (0.402)	$F_{max,3(3)}$ (0.449)	$F_{max,1(3)}$ (0.402)
Titratable acidity, ^{0}T	$F_{80s,3(3)}$ (0.432)	$F_{80s,4(4)}$ (0.544)
$F_{max,3(3)}$[2] (0.382)	$F_{max,3(4)}$ (0.424)	$F_{80s,5(4)}$ (0.530)
$F_{80s,3(3)}$ (0.395)	$F_{80s,3(4)}$ (0.384)	$\Delta_{3(1)}$ (0.865)
		$\Delta_{1(3)}$ (0.595)

[1] - the correlation coefficient is statistically significant at $p<0.05$, when calculating the correlation coefficient, each repetition of measurements of milk sample were taken into account as a new sample.

[2]- $F_{max,3(3)}$ – in brackets noticed the type of treatment, for example, that means the signal of 3rd sensor during measurement of milk sample after addition of the glucose.

The significant correlation between the signal of sensor 2 after microwave treatment with logarithm of QMAFAnM was observed ($r = 0.551$, $t = 2.287 > t_{(0.05, 12)} = 2.178$).

The regression models were constructed using the data sensors before and after the threatments to predict the mass fraction of total protein and quantity of mold. The errors of models were less than 20 %. The regression model was used to predict QMAFAnM, but the prediction error was rather high, and the appropriate error (6%) was archived when including the additional parameters.

4. Discussion

During experimental studies, a correlation was found between the mass fraction of fat in the sample and the size of their fat globules (Table A1). In samples with a high content of milk fat (No. 1, 2, 4, 8, and 14), the presence of very large fat globules was noticed, what affects the sensor signals to a greater extent during the frontal gas phase input into the detection cell.

There is an increase or decrease in volatile compounds in the gas phase over milk samples, depending on the treatment type and the initial composition of milk. So, when ultrasound influence milk, the amount of all detectable volatile compounds in the equilibrium gas phase for most samples decreases to 60%. Nonetheless, for certain samples (Table A3, No.3, 8, and 13), there is a significant increase in the quantity of organic acids in the equilibrium gas phase in comparison to milk samples (a rise in the signals of sensors No.1–3 by 16-56%), which is attributed to the ratio of the mass fraction of fat, protein, and total microbial count. The most noticeable positive signal changes were observed after the addition of hydrogen peroxide into the milk. The most significant effect was observed in sample No.8, which can be associated with a bacteriostatic effect on microorganisms and the simultaneous oxidation of milk fats and proteins. It was found that changes in the gas phase over milk samples after ultrasound treatment are associated with the amount of fungi and mold in raw milk. The addition of glucose and hydrogen peroxide also affects the composition of the gas phase, which is connected to microbiological indicators, titratable acidity, and protein fraction.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1.

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Conflicts of Interest: The authors declare that they have not conflict of interest.

Appendix A

Table A1. The physical and chemical properties of raw milk samples.

No	Mass Fraction of Dry Solids, %	Mass Fraction of Fat, %,	Mass Fraction of Total Protein, %	Density, kg/m^3	Titratable Acidity, ^{0}T	Purity Group
1	16.02 ± 0.12	7.5 ± 0.3	3.46 ± 0.15	1025 ± 0.5	19 ± 0.5	I
2	12.22 ± 0.13	3.8 ± 0.1	3.74 ± 0.10	1031 ± 0.5	20 ± 0.5	I
3	13.36 ± 0.08	4.8 ± 0.1	3.45 ± 0.10	1032 ± 0.5	19 ± 0.5	I
4	15.15 ± 0.14	7.5 ± 0.5	3.26 ± 0.10	1024 ± 0.5	15 ± 0.5	I
5	11.63 ± 0.13	3.5 ± 0.1	3.01 ± 0.10	1028 ± 0.5	19 ± 0.5	I
6	11.77 ± 0.11	3.1 ± 0.1	3.30 ± 0.15	1030 ± 0.5	19 ± 0.5	I
7	10.83 ± 0.09	3.9 ± 0.1	2.40 ± 0.10	1030 ± 0.5	15 ± 0.5	I
8	12.31 ± 0.12	3.7 ± 0.1	3.10 ± 0.15	1027 ± 0.5	18 ± 0.5	I
9	11.41 ± 0.06	3.2 ± 0.1	2.00 ± 0.05	1028 ± 0.5	15 ± 0.5	I
10	12.14 ± 0.10	4.1 ± 0.1	2.88 ± 0.10	1028 ± 0.5	16 ± 0.5	I
11	11.72 ± 0.07	3.4 ± 0.1	1.16 ± 0.10	1028 ± 0.5	15 ± 0.5	I
12	10.92 ± 0.09	3.3 ± 0.1	1.35 ± 0.10	1027 ± 0.5	11 ± 0.5	I
13	11.44 ± 0.11	3.6 ± 0.1	2.59 ± 0.15	1028 ± 0.5	17 ± 0.5	I
14	15.07 ± 0.15	6.5 ± 0.3	3.07 ± 0.10	1026 ± 0.5	16 ± 0.5	I

Table A2. Fat globule size distribution in raw milk samples.

No	% Content of Fat Globules in the Size of μm		
	0.01-10.00 μm	10.01-20.00 μm	>20.01 μm
1	99.89 ± 0.030	0.07 ± 0.005	0.04 ± 0.003
2	62.88 ± 0.090	36.20 ± 0.020	0.92 ± 0.007
3	82.83 ± 0.040	17.16 ± 0.009	-
4	82.55 ± 0.025	9.76 ± 0.008	7.69 ± 0.004
5	89.17 ± 0.031	10.83 ± 0.009	-
6	87.26 ± 0.024	12.74 ± 0.006	-
7	99.94 ± 0.021	0.06 ± 0.0017	-
8	75.33 ± 0.037	23.79 ± 0.009	0.88 ± 0.005
9	93.74 ± 0.042	6.26 ± 0.008	-
10	100.00 ± 0.010	-	-
11	100.00 ± 0.008	-	-
12	100.00 ± 0.009	-	-
13	100.00 ± 0.011	-	-
14	99.77 ± 0.022	0.18 ± 0.003	0.05 ± 0.002

Table A3. Relative changes in sensor signals ($\Delta_{i(j)}=(F_{max,i} - F_{max,i(j)})/F_{max,i}$) after treatments.

No	$\Delta_{1(1)}$	$\Delta_{2(1)}$	$\Delta_{3(1)}$	$\Delta_{4(1)}$	$\Delta_{5(1)}$
1	−0.06	−0.19	0.07		
2	*		−0.21		
3	0.24		−0.21		
4	−0.15		−0.07		
5	0.00	0.10	0.00	−0.15	
6	−0.59	−0.50	−3.97	−0.62	−0.32
7	−0.86	−0.12	−0.33	−0.28	−0.69
8	−0.77	0.17	−0.31	−0.29	−0.70
9	−0.49	−0.99	−0.91	−0.15	−0.06
10	−0.58	−0.79	−2.37	−0.09	−0.10

11	−0.16	−0.43	−1.16	−0.27	0.00
12	−0.22	−0.06	−1.21	−0.28	−0.19
13	−0.56	0.20	0.56	0.11	−0.12
14	0.08	−0.84	−0.40		
No	$\Delta_{1(2)}$	$\Delta_{2(2)}$	$\Delta_{3(2)}$	$\Delta_{4(2)}$	$\Delta_{5(2)}$
1	0.14				
2	−0.07	−0.08	0.05		
3	0.11	−0.19	−0.18		
4	0.08	0.20			
5	−0.41	−0.27	−0.49	0.11	
6	−0.32	−0.16	−0.21	−0.52	0.09
7	−0.96	−0.80	−0.51	−0.50	−0.57
8	−0.87	−0.35	−0.50	−0.51	−0.59
9	−0.05		−0.24	−0.17	−0.17
10	−0.22	−0.21	−1.67		
11	−0.37	−0.46	−0.89	−0.25	
12	0.13	−0.24	−0.96		0.16
13	−0.28	0.22	0.47	−0.23	−0.20
14		−0.67	0.07		0.11
No	$\Delta_{1(3)}$	$\Delta_{2(3)}$	$\Delta_{3(3)}$	$\Delta_{4(3)}$	$\Delta_{5(3)}$
1	−0.37	−0.09	0.10		
2	−0.17	−0.06	−0.11		
3	0.37	0.13	−0.27		
4					
5	−0.39	−0.14	−0.48	−0.28	
6	−0.65	−0.53	−0.45	−0.07	
7	−0.35	−0.06		−0.28	−0.38
8	−0.29	0.21		−0.29	−0.40
9	−0.20	−0.39	0.22	0.08	
10	−0.43	−0.52	−2.19	−0.14	−0.08
11	−0.12	−0.74	−1.74	−0.14	0.11
12	0.13	0.12	−0.43	−0.13	
13	−0.36	0.35	0.49		−0.39
14	0.07	−0.17	−0.27	0.26	0.26
No	$\Delta_{1(4)}$	$\Delta_{2(4)}$	$\Delta_{3(4)}$	$\Delta_{4(4)}$	$\Delta_{5(4)}$
1	0.12	0.16	0.16		
2	0.13	0.12	0.10		
3	0.35	0.14	−0.09		
4		0.15	0.18		
5	0.10	0.21	−0.20	−0.07	−0.17
6			−0.52	0.09	−0.07
7	−0.39	−0.63	−0.07	−0.17	−0.25
8	−0.33	−0.22	−0.06	−0.18	−0.27
9	0.18	−0.14	0.42	−0.08	
10	−0.24	0.13	−1.90		0.17
11		−0.42	−1.26	−0.05	0.22
12	0.65	0.48	−0.29	−0.17	0.30
13	0.04	0.20	0.51	−0.28	−0.11
14		−1.04		0.12	0.11

*-the values lower 0.05 is absent in the table because of insignificant difference from 0.

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