VORONEZH STATE UNIVERSITY OF ENGINEERING TECHNOLOGIES

APPLICATION OF PIEZOELECTRIC SENSORS WITH POLYCOMPOSITE COATINGS FOR ASSESSING MILK QUALITY INDICATORS

ANASTASIIA SHUBA,
EKATERINA ANOKHINA,
RUSLAN UMARKHANOV,
EKATERINA BOGDANOVA,
INNA BURAKOVA

CSAC 2023
The 2nd International Electronic Conference on Chemical Sensors and Analytical Chemistry

The work was supported by the Russian Science Foundation grant № 22-76-10048.

GOALS

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.

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

- treatment of ultrasound 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 °C for two hours (3);
- adding 2 ml of hydrogen peroxide and keeping at room temperature for 2 hours (4).

METHODS ANALYSIS OF MILK

- **Mass fraction of dry solids** in the samples (Binder ED 53 oven (BINDER Inc., Tuttlingen, Germany)
- **Mass fraction of fat** - by the Gerber acid method,
- **Mass fraction of total protein** - by formol titration,
- **Density** - by areometric method,
- **Titratable acidity** - by titrimetric method with phenolphthalein indicator [19],
- **Purity group** - by gravimetric method,
- **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.
- **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).
- **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. 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) by dispersion spraying.

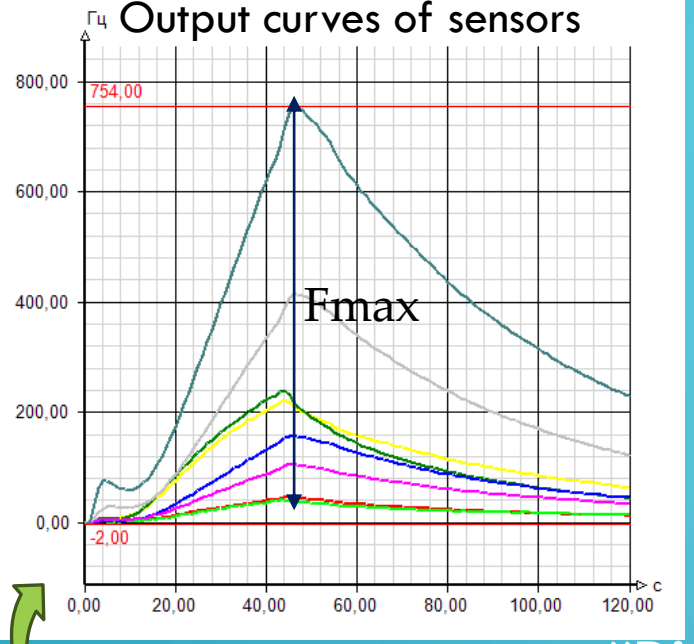
CHARACTERISTICS OF SENSOR COATINGS

Sensor number	Coating (1/2)	Solvent	Mass, μg	Specific mass sensitivity, S_f [Hz•cm³/μg²]			
				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

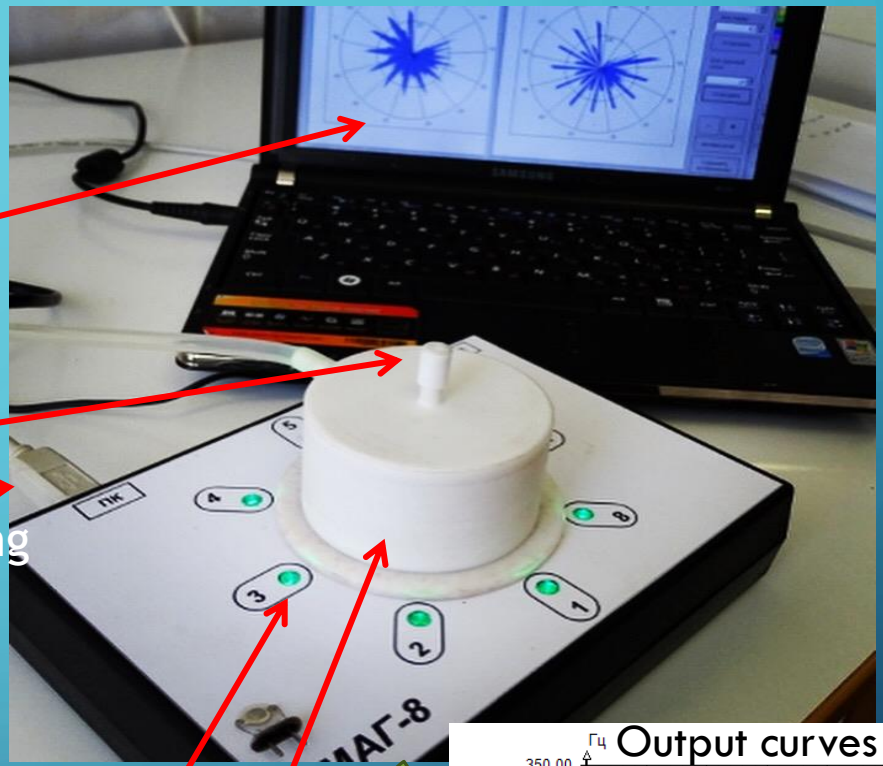
* - 18C6 – dicyclohexane-18-crown-6, DHC – dihydroquercetin, CMC – concentrate micellar casein, PVP – polyvinylpyrrolidone, PEG-2000 - polyethylene glycol 2000.

Volatile compounds for training of sensors: alcohols (ethanol, butanol, isobutanol, isopentanol), carboxylic acids (formic, acetic, butyric), ketones (acetone, butanone-2), acetaldehyde, ethyl acetate and water.

USING E-NOSES



"MAG-8"



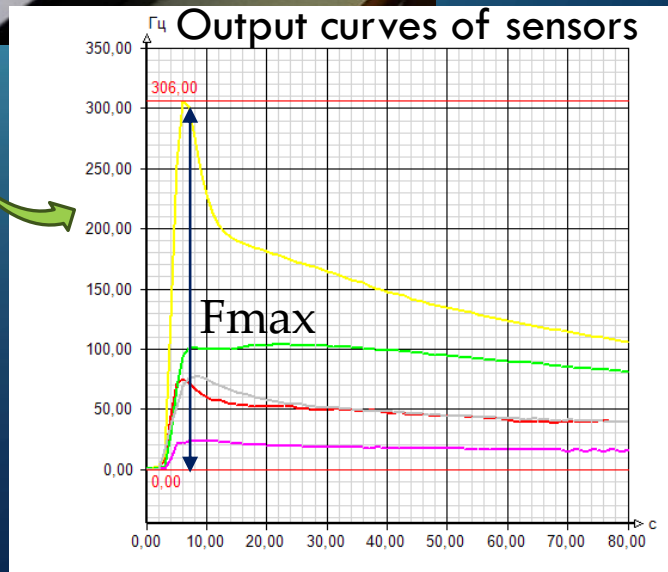
Device with software for recording and processing of output data from sensors

For EGP input USB-connecting with PC

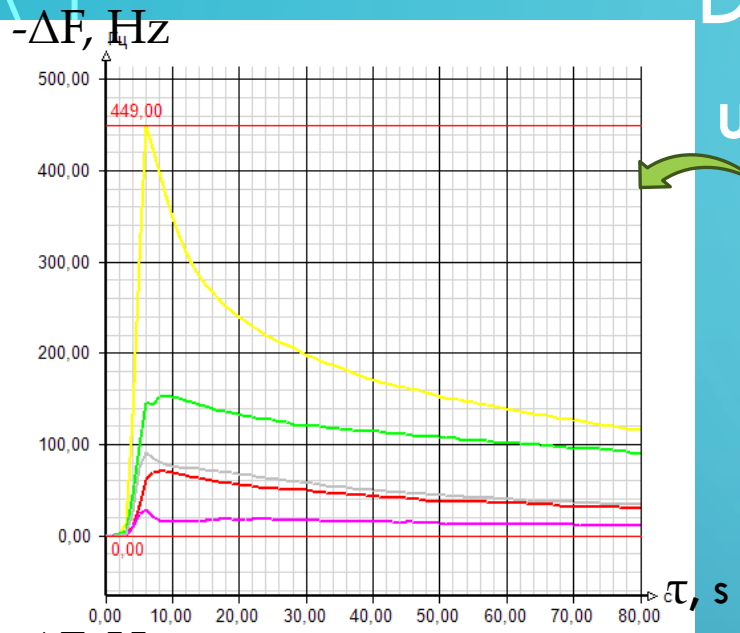
"Diagnost-Bio-8"

Indicator of working

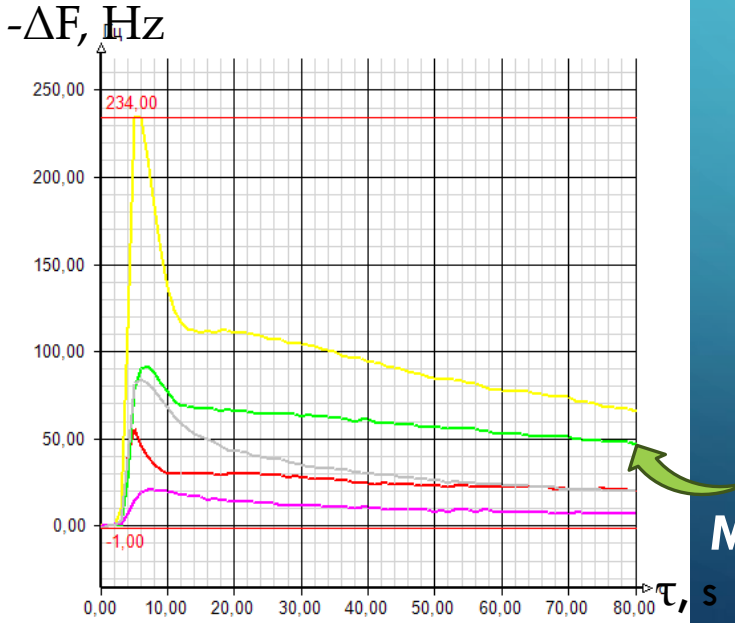
Detection cell with piezosensors



CHRONOFREQUENCYGRAMS OF SENSORS DURING MEASUREMENTS

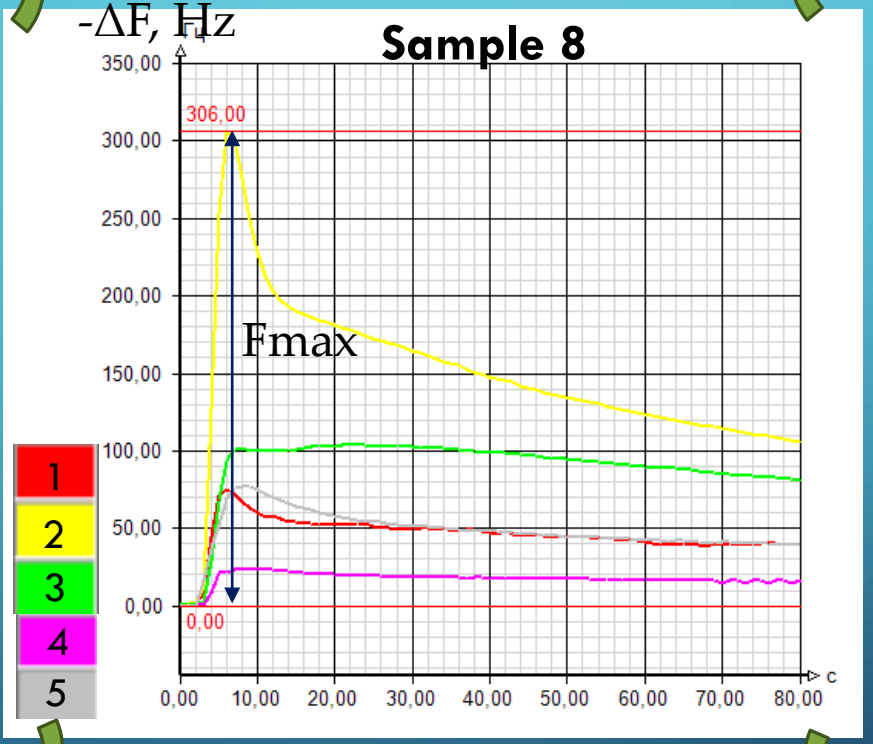


Ultrasound (1)



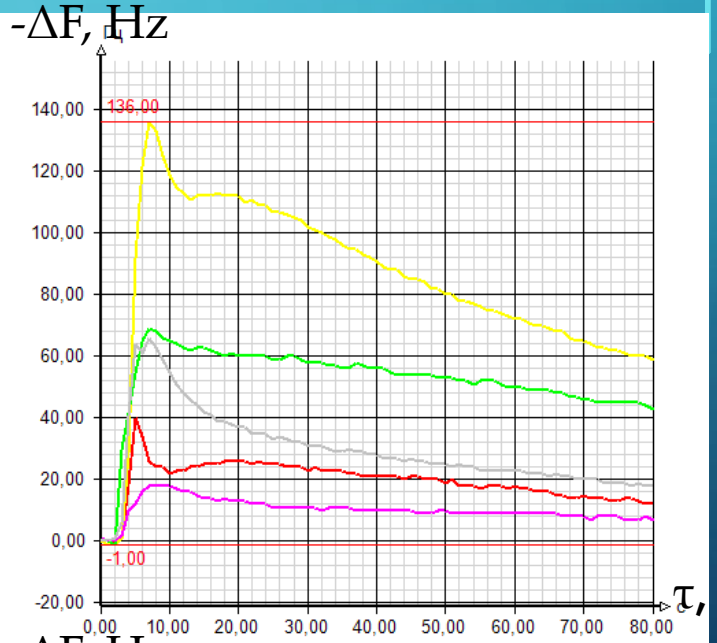
Microwaves (2)

$$\beta_i=(\Delta F_{max,i}-\Delta F_{80s,i})/(80-\tau_{max,i})$$

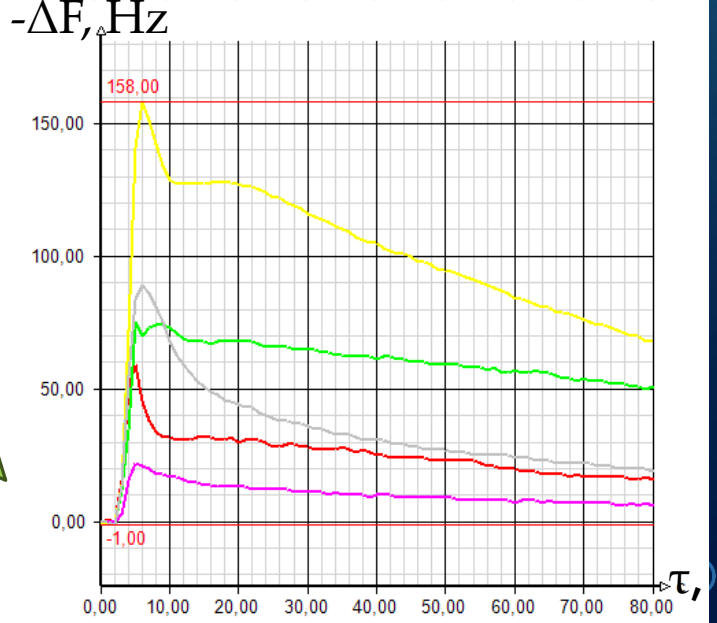


Raw milk

+$C_6H_{12}O_6$(3)



+H_2O_2 (4)



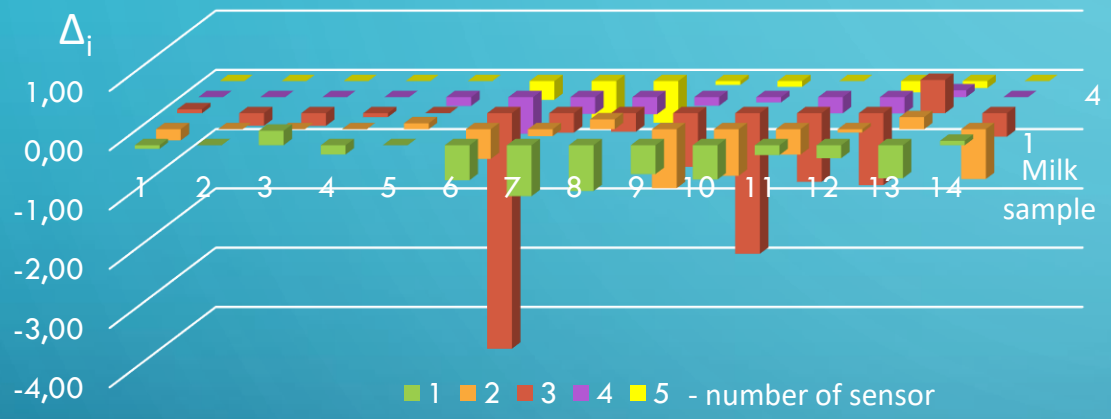
THE PHYSICAL, CHEMICAL AND MICROBIOLOGICAL PROPERTIES OF RAW MILK SAMPLES

No	Mass fraction of dry solids, %	Mass fraction of fat, %,	Mass fraction of total protein, %	Titratable acidity, °T	QMAFAnM*, CFU/ml	Quantity of yeast CFU/ml	Quantity of mold CFU/ml	% content of fat globules in the size of μm		
								0.01-10.00 μm	10.01-20.00 μm	>20.01 μm
1	16.02±0.12	7.5±0.3	3.46±0.15	19±0.5	10000000	100000	0	99.89±0.030	0.07±0.005	0.04±0.003
2	12.22±0.13	3.8±0.1	3.74±0.10	20±0.5	4000000	10000	0	62.88±0.090	36.20±0.020	0.92±0.007
3	13.36±0.08	4.8±0.1	3.45±0.10	19±0.5	4500000	1000	10	82.83±0.040	17.16±0.009	-
4	15.15±0.14	7.5±0.5	3.26±0.10	15±0.5	340000	0	0	82.55±0.025	9.76±0.008	7.69±0.004
5	11.63±0.13	3.5±0.1	3.01±0.10	19±0.5	2400000	1500	160	89.17±0.031	10.83±0.009	-
6	11.77±0.11	3.1±0.1	3.30±0.15	19±0.5	590000	650	900	87.26±0.024	12.74±0.006	-
7	10.83±0.09	3.9±0.1	2.40±0.10	15±0.5	4640000	5680	0	99.94±0.021	0.06±0.0017	-
8	12.31±0.12	3.7±0.1	3.10±0.15	18±0.5	98000000	8004	60	75.33±0.037	23.79±0.009	0.88±0.005
9	11.41±0.06	3.2±0.1	2.00±0.05	15±0.5	480000	0	10	93.74±0.042	6.26±0.008	-
10	12.14±0.10	4.1±0.1	2.88±0.10	16±0.5	5700000	34200	300	100.00±0.010	-	-
11	11.72±0.07	3.4±0.1	1.16±0.10	15±0.5	42000000	1800	0	100.00±0.008	-	-
12	10.92±0.09	3.3±0.1	1.35±0.10	11±0.5	2000000	2300	10	100.00±0.009	-	-
13	11.44±0.11	3.6±0.1	2.59±0.15	17±0.5	3400000	17400	10	100.00±0.011	-	-
14	15.07±0.15	6.5±0.3	3.07±0.10	16±0.5	39000000	100000	0	99.77±0.022	0.18±0.003	0.05±0.002

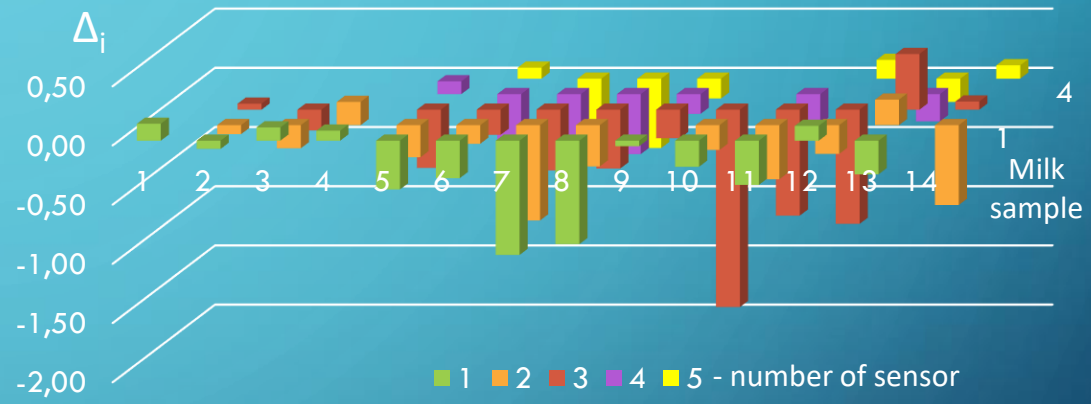
*- the number of CFU is calculated as the arithmetic mean value when counting on Petri dishes with different dilutions if it was possible or from appropriate dilution.

RELATIVE CHANGES (Δ_i) IN SENSORS SIGNALS AFTER TREATMENT OF MILK SAMPLES

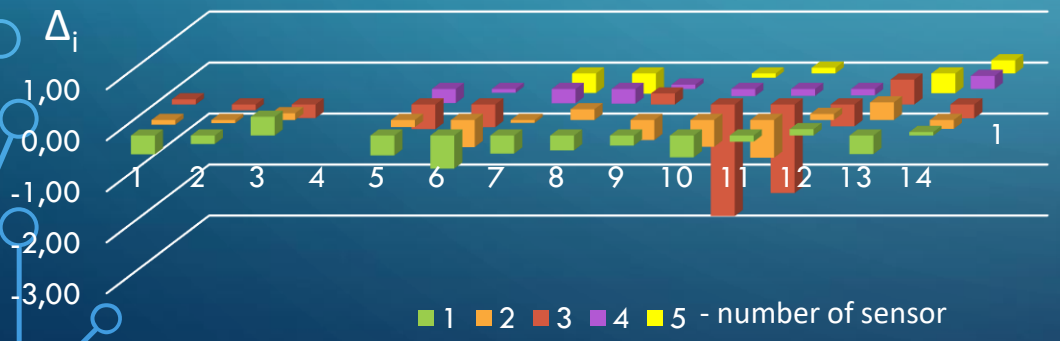
Ultrasound



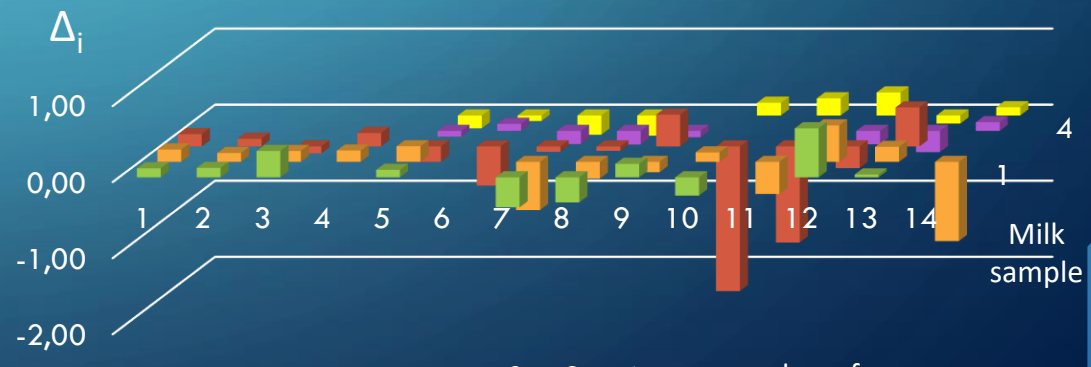
Microwaves



Glucose



Peroxide



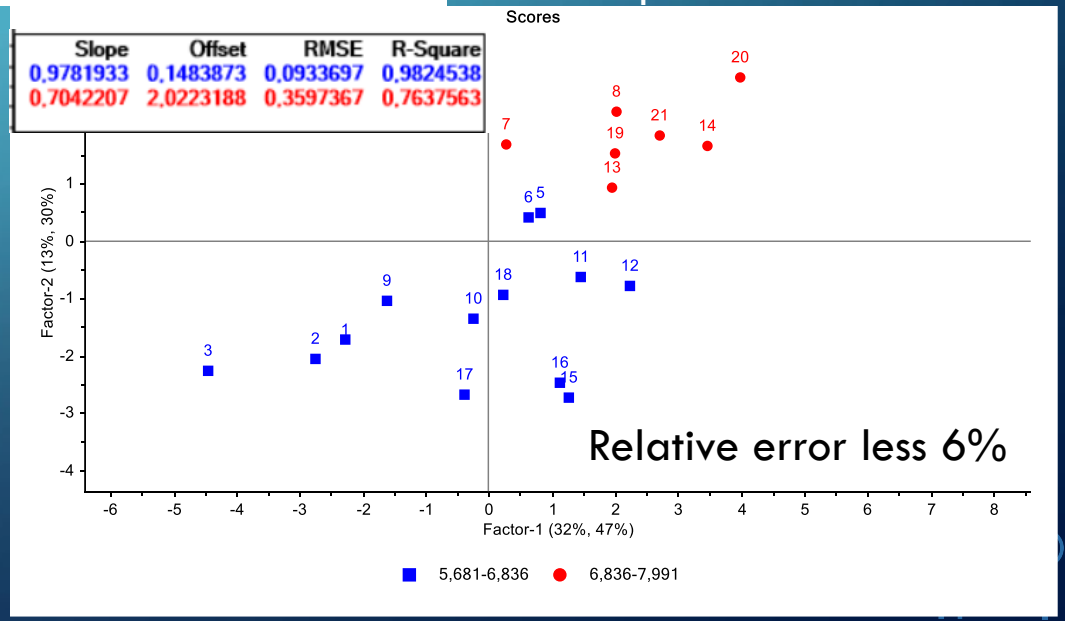
PEARSON CORRELATION COEFFICIENT (R) BETWEEN SENSOR DATA AND PROPERTIES OF MILK

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, °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)

PLS-model to predict total microbial count (lg(CFU)) for milk samples based on sensors parameters

[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.



CONCLUSIONS

- A correlation was found between the mass fraction of fat in the sample and the size of their fat globules. 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.
- The use of frontal input of the gas phase of milk increases sensor signals on average by two times. A significant moderate correlation was established between sensor signals and the content of fungi and yeast in milk samples.
- It has been established that pre-treatment of milk samples increases the degree of correlation between sensor output data and milk quality indicators. The most dramatic changes are associated with ultrasonic treatment of milk, the amount of all detectable volatile compounds in the equilibrium gas phase for most samples decreases to 60%. The addition of glucose has the greatest effect on the release of gaseous metabolites by yeast; ultrasound treatment increases the degree of correlation of sensor signals with the fungi concentration in milk samples. The most significant changes in the gas phase after various processing methods characterize the milk samples with the lowest total protein content and high QMAFAnM (samples № 11, 12). When processing milk samples with microwaves, a significant correlation was established between the signal of the sensor with the DHC/chitosan film and QMAFAnM.
- 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.

THANK YOU FOR YOUR ATTENTION

Contacts of authors:

Anastasiia Shuba
shuba1nastya@gmail.com
shuba@vsuet.ru
+79204031622
(Telegram, Whatsapp)

Anokhina Ekaterina
katya_anoh@mail.ru

Umarkhanov Ruslan
Rus_270487@mail.ru
+79204031622
LLC “SNT” (producer of devices)
http://E-nose.ru

Bogdanova Ekaterina
ek-v-b@yandex.ru

Burakova Inna
vitkalovai@inbox.ru