VORONEZH STATE UNIVERSITY OF ENGINEERING TECHNOLOGIES

DEVELOPMENT OF CHEMICAL SENSOR BASED ON DEEP EUTECTIC SOLVENTS AND ITS APPLICATION FOR MILK ANALYSIS

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PREPARATION OF DEEP EUTECTIC SOLVENTS

THE GOAL – TO INVESTIGATE THE SORPTION PROPERTIES OF THIN FILMS BASED ON HYDROPHILIC DEEP EUTECTIC SOLVENTS (CHOLINE+POLYALCOHOLS) AND THEIR APPLICATION TO THE ANALYSIS OF THE GAS PHASE OF MILK.
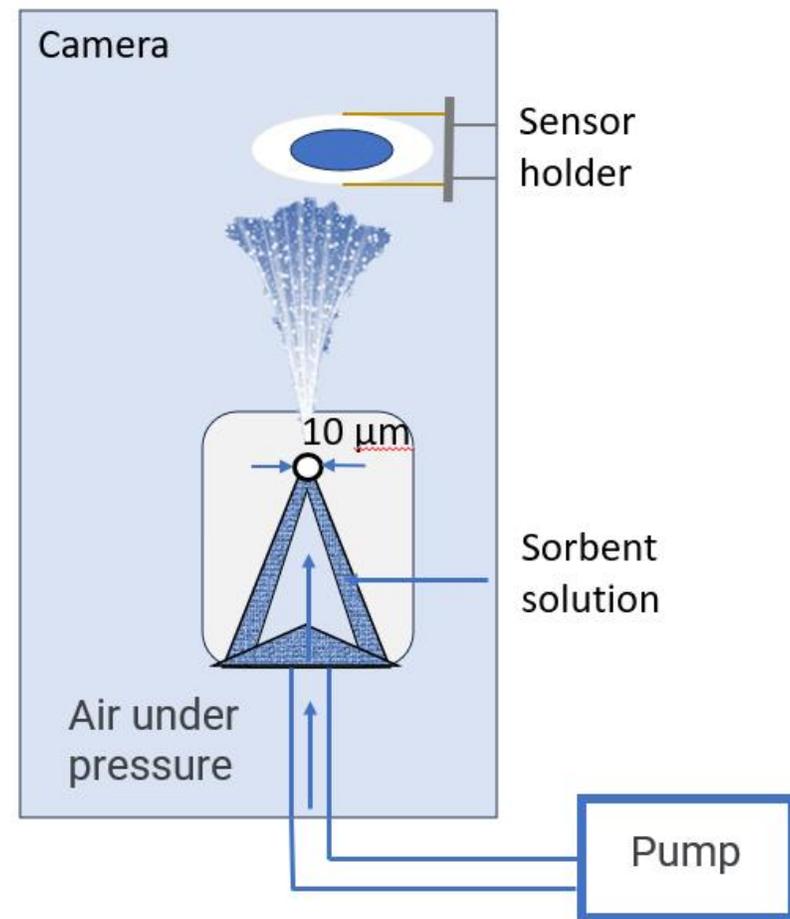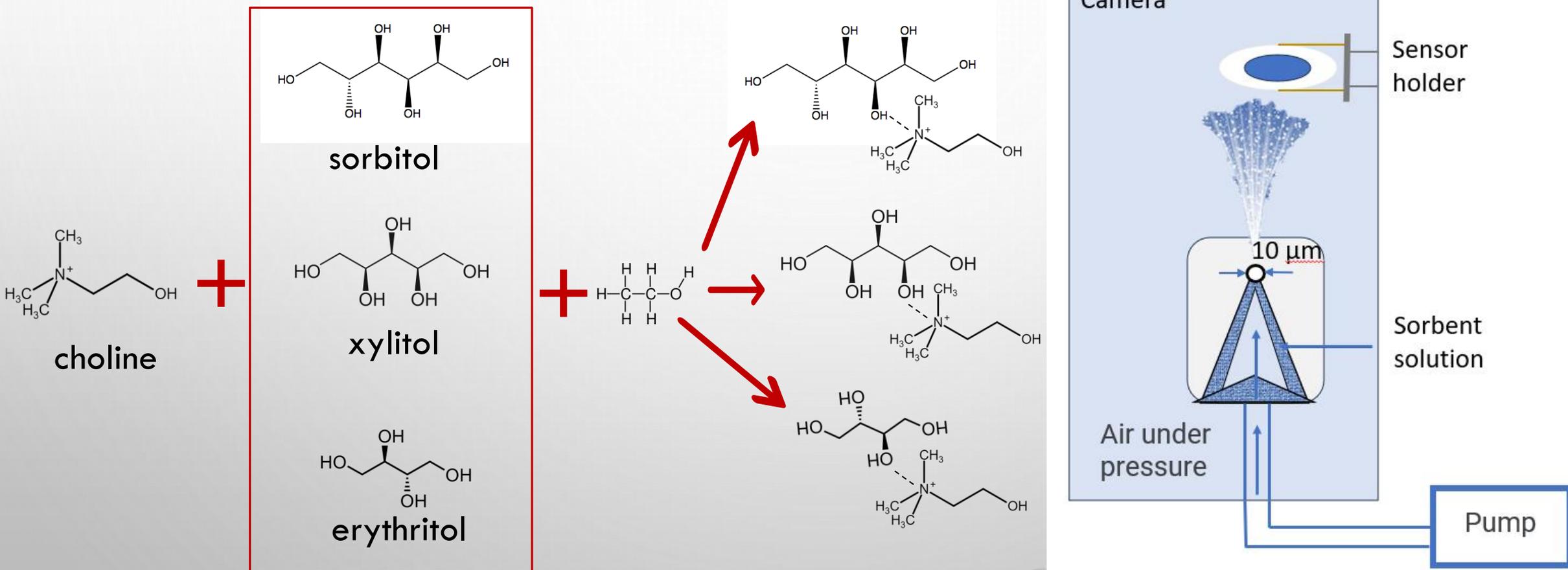
Scheme of an experimental setup for spray coating method

DEVICE FOR GAS ANALYSIS – ANALYZER "MAG-8"

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

For EGP input

USB-connecting with PC

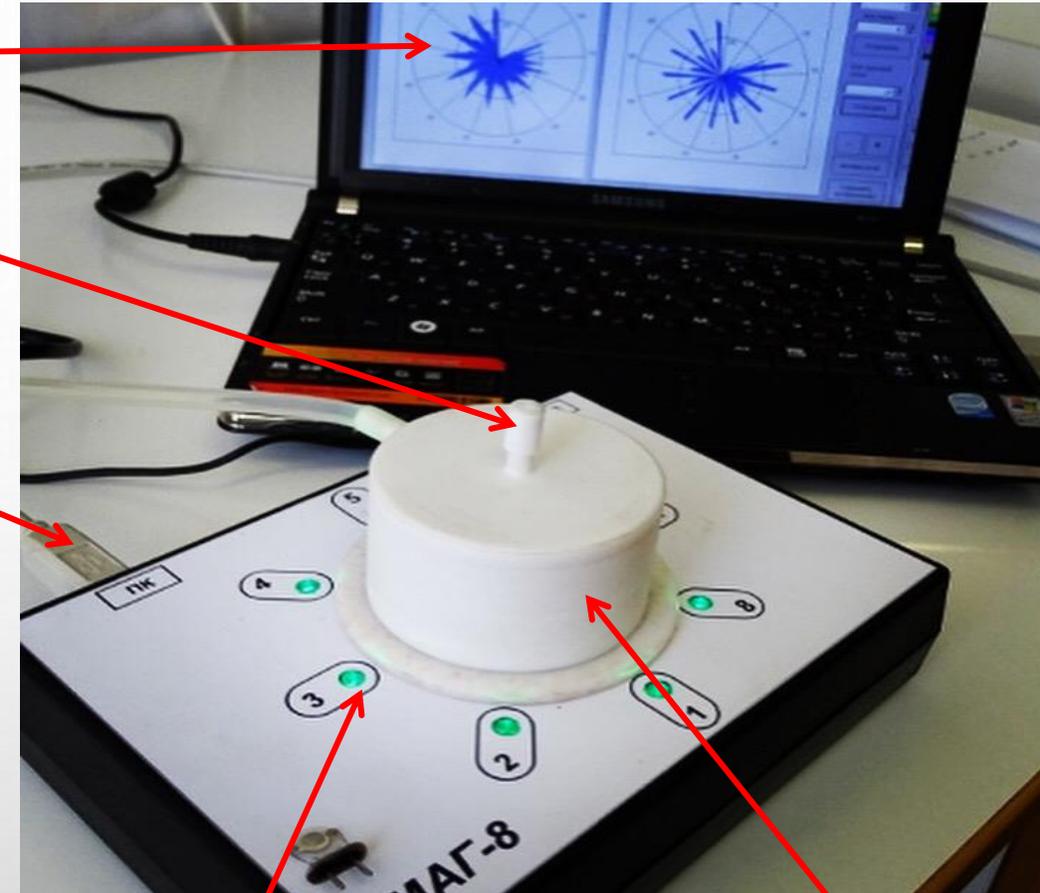| Coating	Mass*, μg
Choline+erythritol	8,81
Choline+xylitol	8,58
Choline+sorbitol	15,47
Choline+erythritol+ASO**	5,29
Choline+xylitol+ASO	4,56
Choline+sorbitol+ASO	5,71

*- calculated by Sauerbray equation

**- amorphous silicon oxide (ASO)

Studied **volatile compounds**: alcohols (ethanol, butanol, isobutanol, isopentanol), carboxylic acids (formic, acetic, butyric), ketones (acetone, butanone-2), acetaldehyde, ethyl acetate and water.
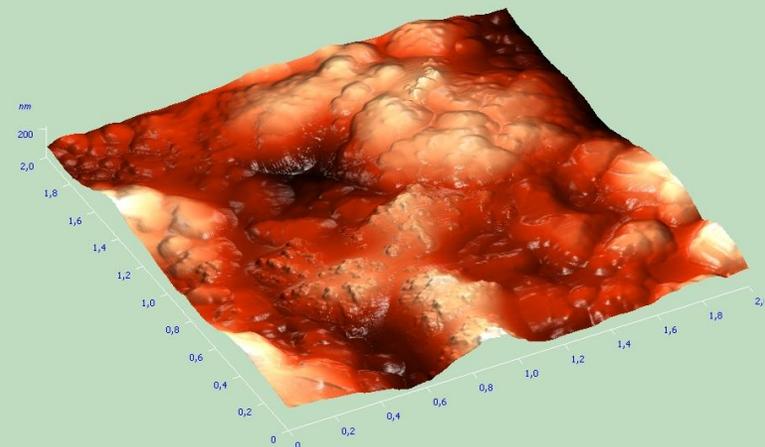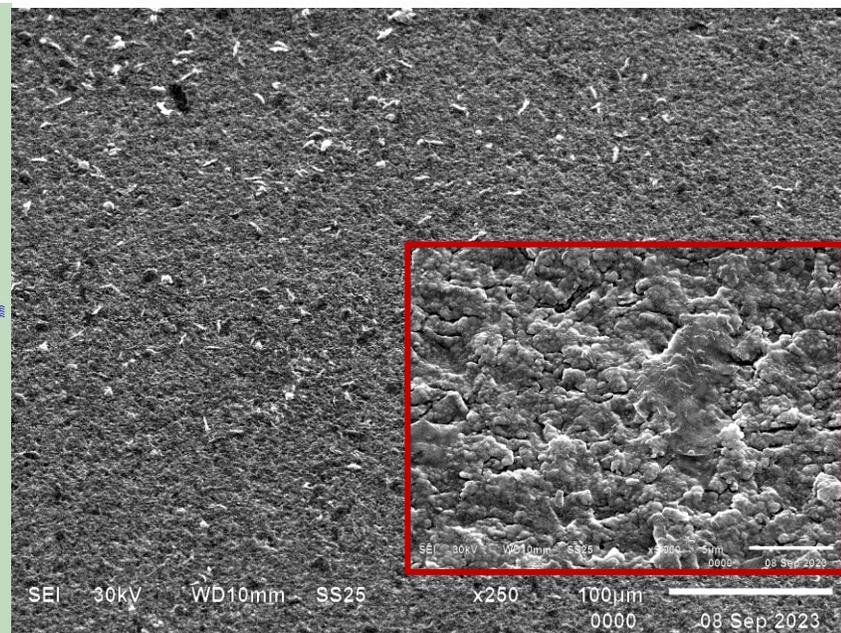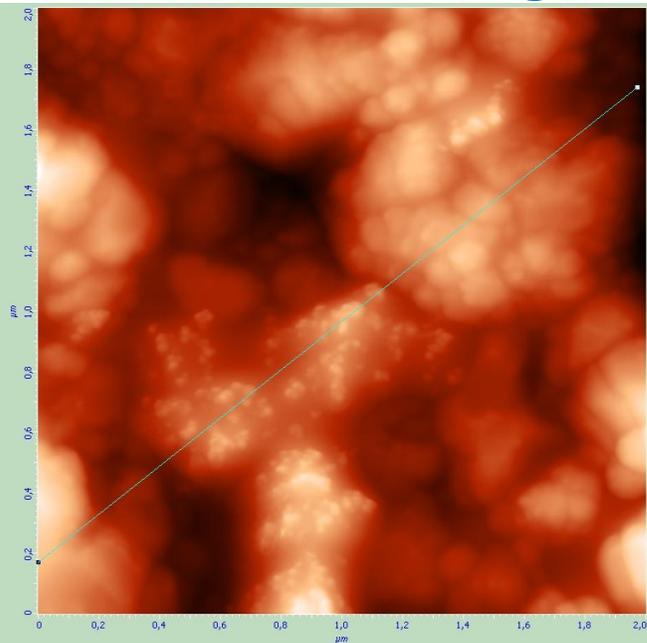
Indicator of working

Detection cell with piezoelectric sensors

3

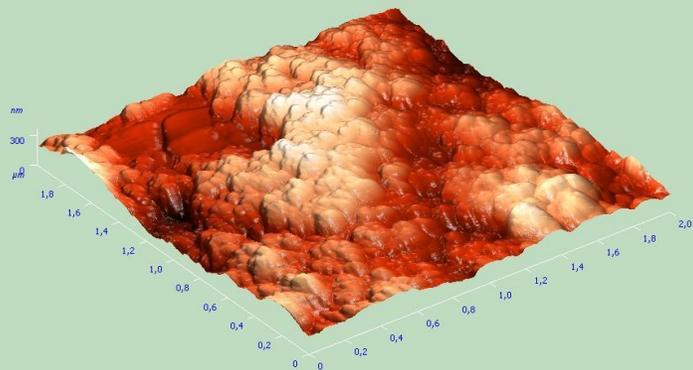# Microstructure of coatings based on DESs
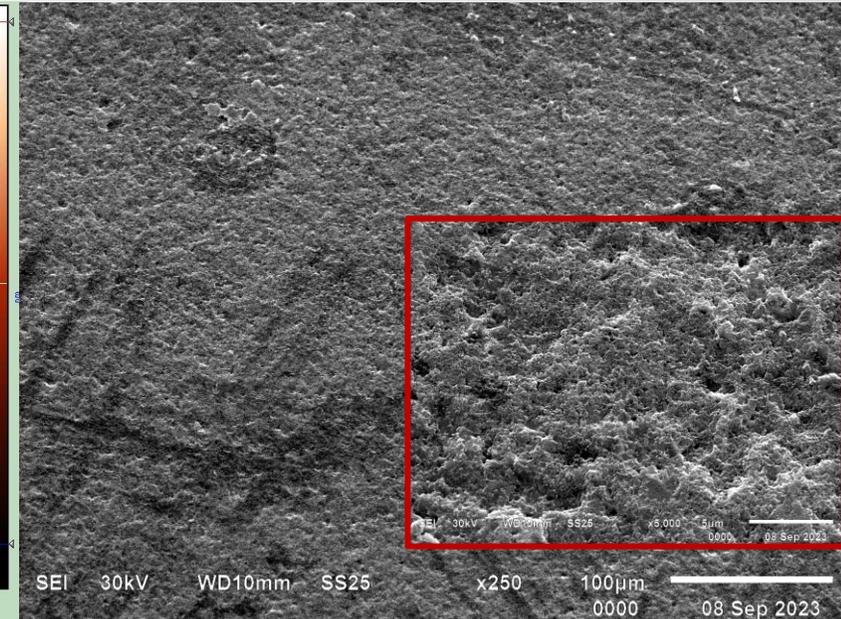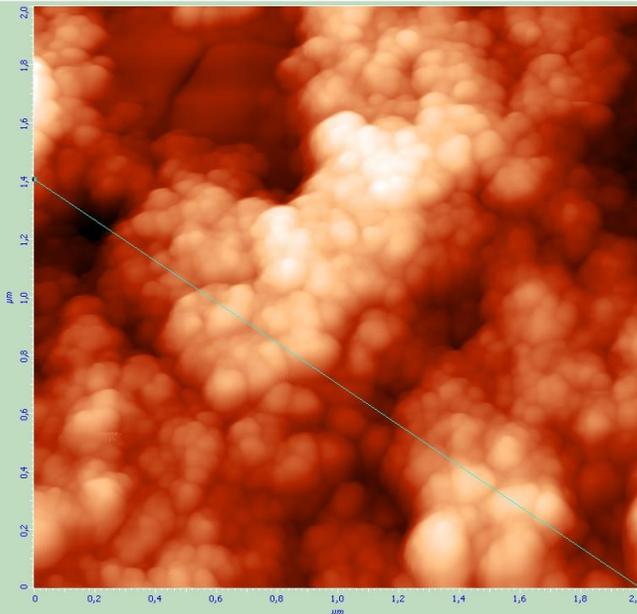

Choline+sorbitol
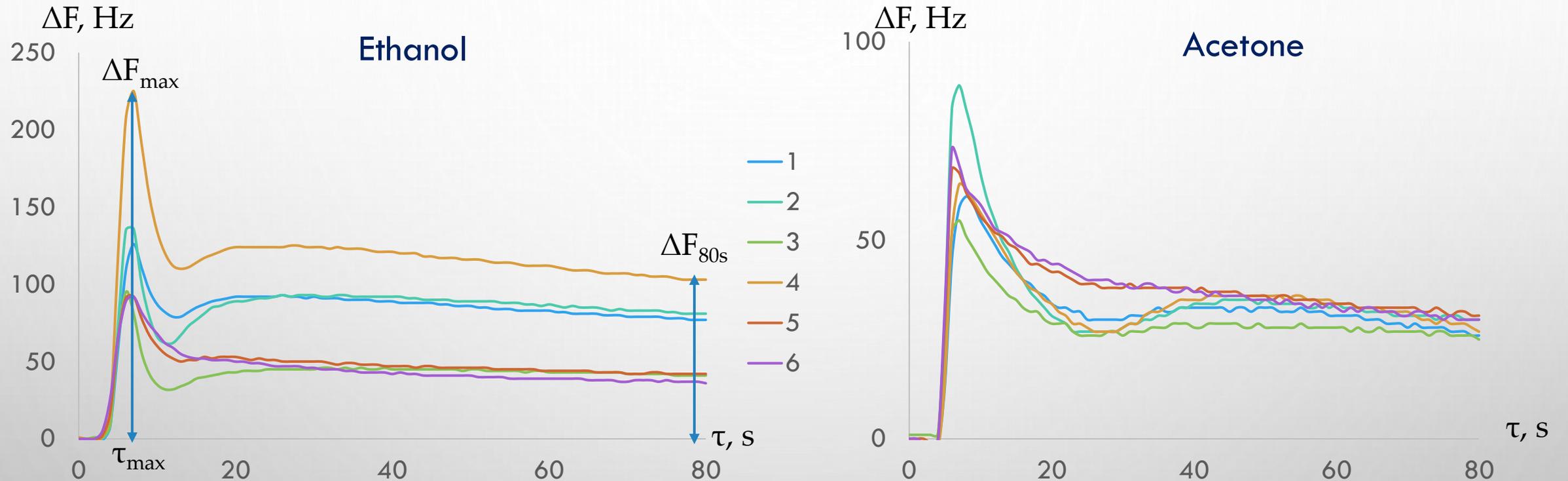
Sa=33,46 nm   Ssk=0,207   Ska=0,230

Choline+sorbitol+ASO

Sa=39,67 nm   Ssk=0,209   Ska=0,155

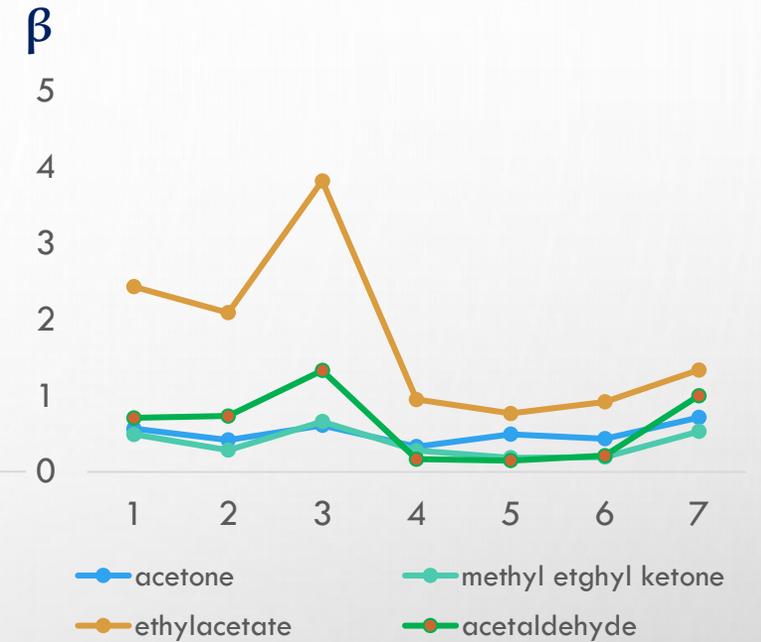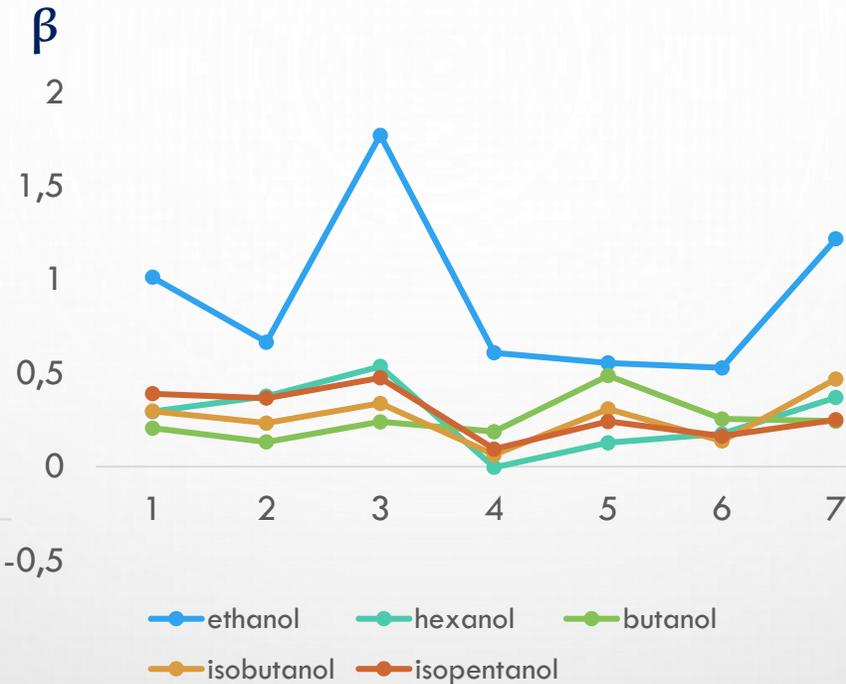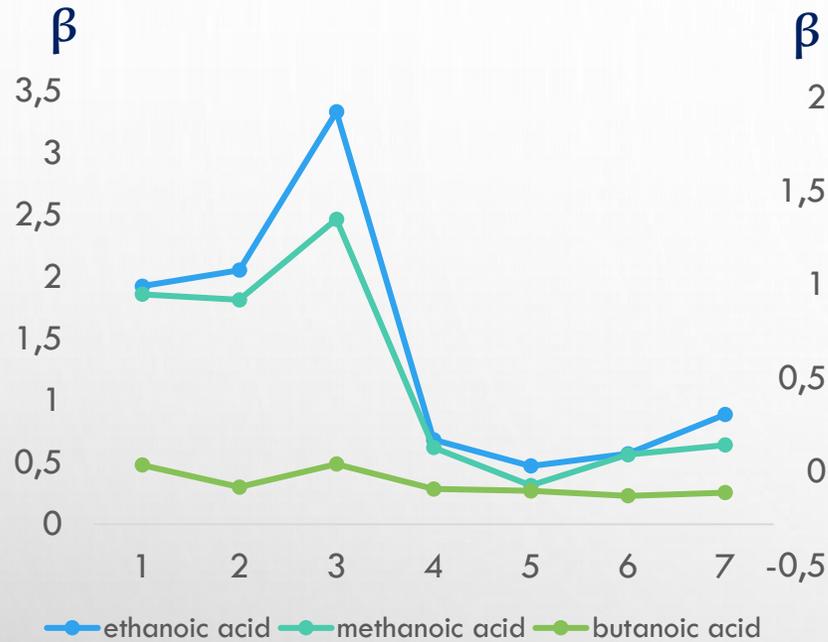# Chronofrequencygram of VOC sorption on sensors with coatings based on DESs

Sensors: 1 - choline + xylitol, 2 - choline + erythritol, 3 - ASO +choline+ erythritol, 4 - choline + sorbitol, 5 - ASO + choline + sorbitol, 6 - ASO + choline + xylitol

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

Kinetic parameter β

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

Sensors: 1 - choline + erythritol, 2 - choline + xylitol, 3 -choline + sorbitol, 4 - ASO +choline+ erythritol, 5 - ASO + choline + xylitol, 6 -ASO + choline + sorbitol, 7 - ASO

Relative change (%) in coating masses after 3 months of operation

choline + erythritol	choline + xylitol	choline + sorbitol	ASO +choline+ erythritol	ASO + choline + xylitol	ASO + choline + sorbitol	ASO
25	16	10	4,7	10	9,5	2,8

Specific mass sensitivity (S_m, Hz•cm^3/mcg^2) of coatings based on DESs to vapors of volatile compounds
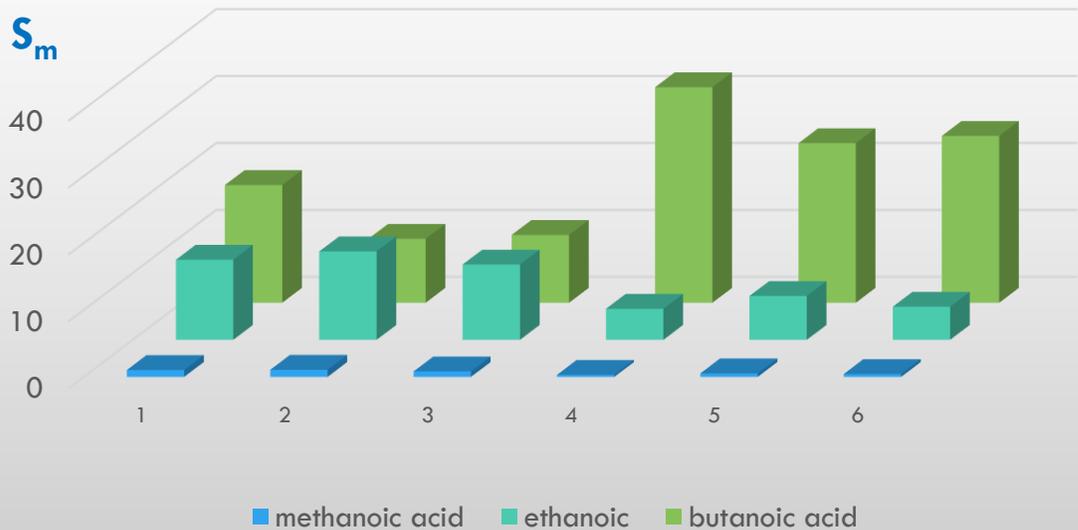

Sensors:
1 - choline + erythritol,
2 - choline + xylitol,
3 -choline + sorbitol,

Sensors:
4 - ASO +choline+erythritol
5 - ASO + choline + xylitol,
6 -ASO + choline + sorbitol,
7 - ASO

Sorption of aqueous mixtures of volatile substances
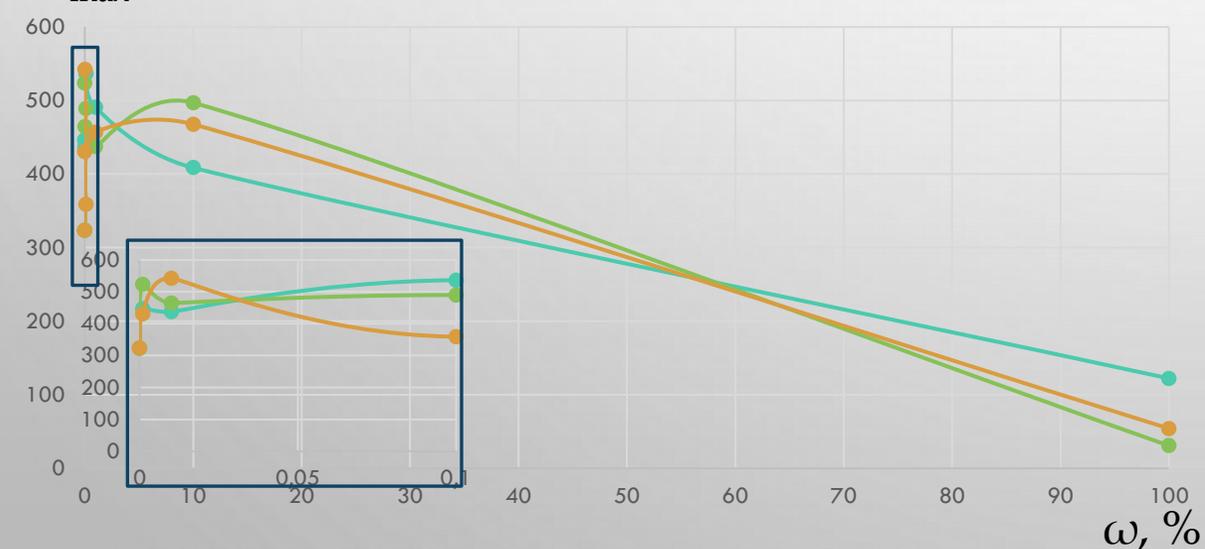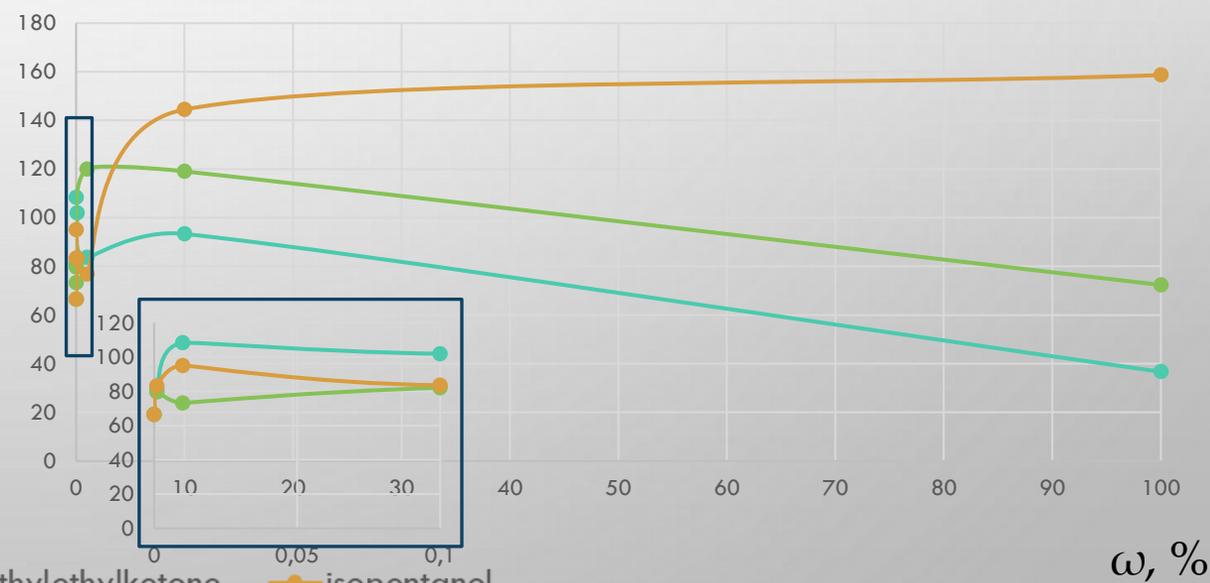
Microstructure of choline+sorbitol coatings after 6 month of operation

New
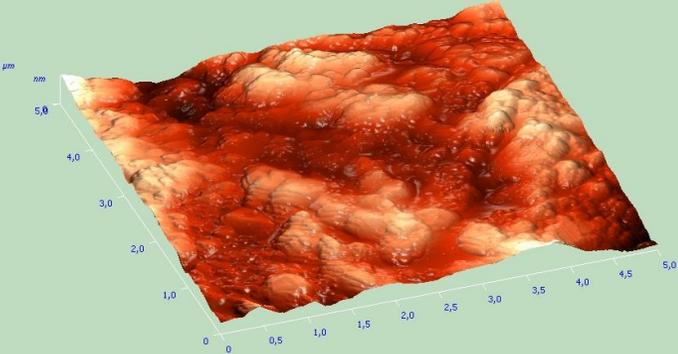
Sa=59,46 nm   Ssk=0,144   Ska=0,316
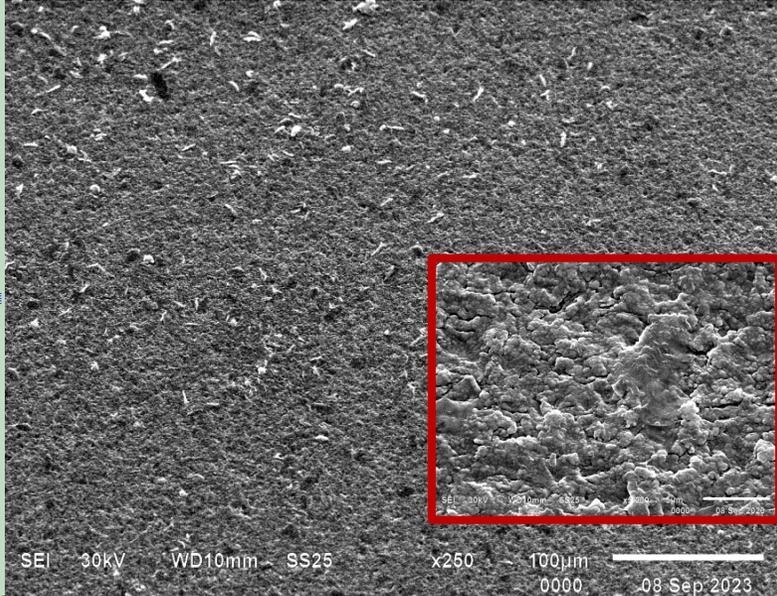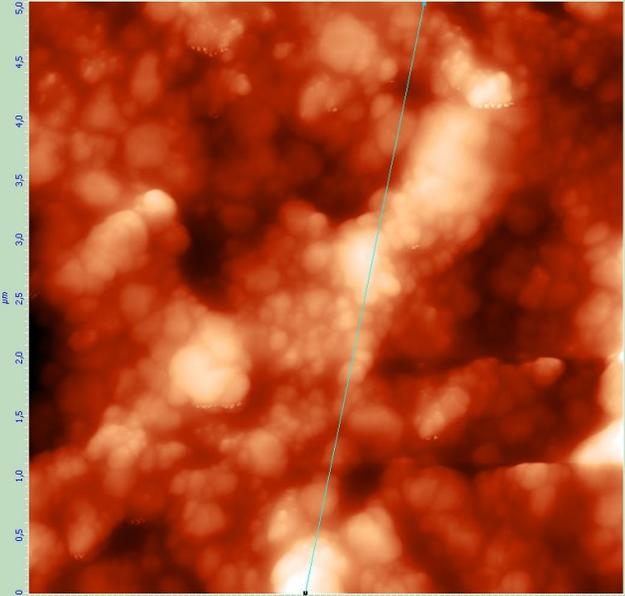
After operation
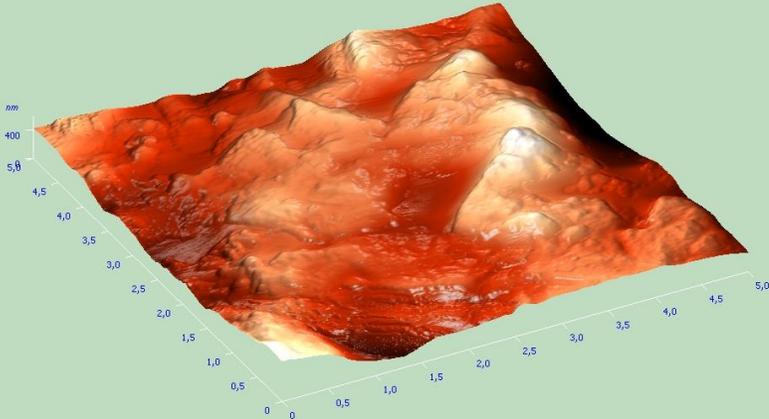
Sa=71,50 nm   Ssk=0,712   Ska=1,531
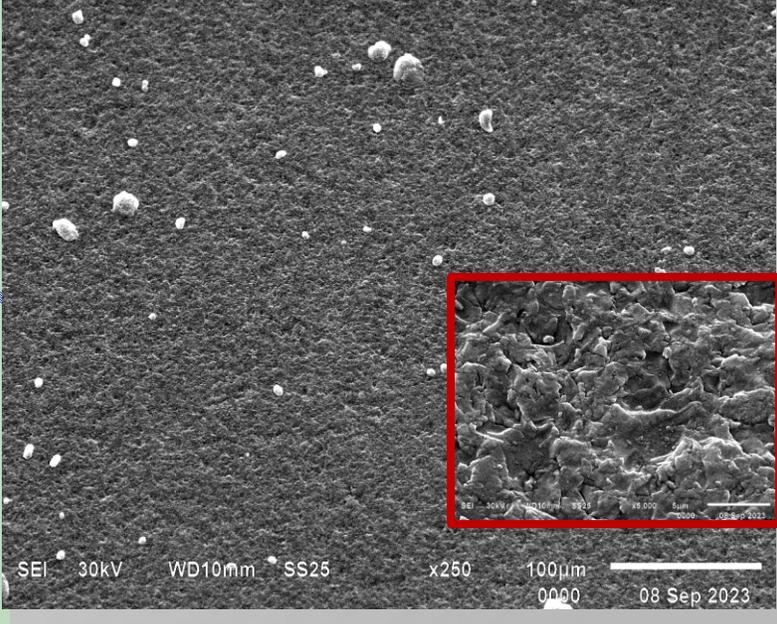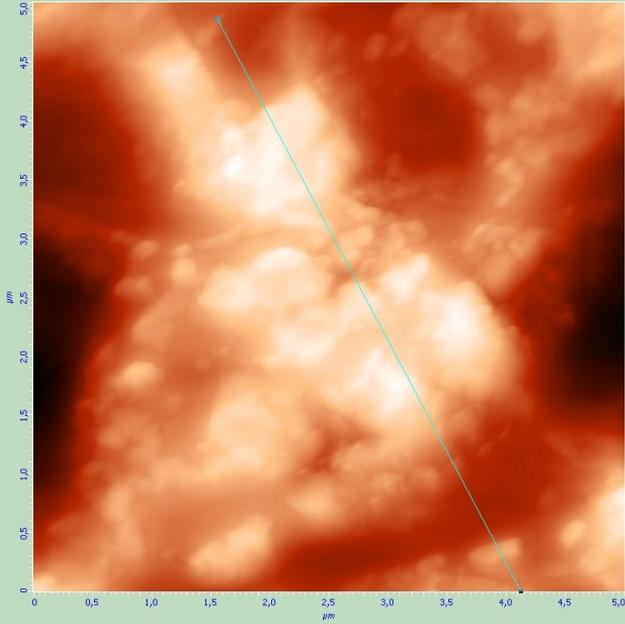
The physical and chemical properties of raw milk samples

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	10000000	100000	0
2	12.22±0.13	3.8±0.1	3.74±0.10	20±0.5	4000000	10000	0
3	13.36±0.08	4.8±0.1	3.45±0.10	19±0.5	4500000	1000	10
4	15.15±0.14	7.5±0.5	3.26±0.10	15±0.5	340000	0	0
5	11.63±0.13	3.5±0.1	3.01±0.10	19±0.5	2400000	1500	160
6	11.77±0.11	3.1±0.1	3.30±0.15	19±0.5	590000	650	900
7	10.83±0.09	3.9±0.1	2.40±0.10	15±0.5	4640000	5680	0
8	12.31±0.12	3.7±0.1	3.10±0.15	18±0.5	98000000	8004	60
9	11.41±0.06	3.2±0.1	2.00±0.05	15±0.5	480000	0	10
10	12.14±0.10	4.1±0.1	2.88±0.10	16±0.5	5700000	34200	300
11	11.72±0.07	3.4±0.1	1.16±0.10	15±0.5	42000000	1800	0
12	10.92±0.09	3.3±0.1	1.35±0.10	11±0.5	2000000	2300	10
13	11.44±0.11	3.6±0.1	2.59±0.15	17±0.5	3400000	17400	10
14	15.07±0.15	6.5±0.3	3.07±0.10	16±0.5	39000000	100000	0

Results of analysis of raw milk samples

Sensors parameter	Titratable acidity, °T	Sensor parameter	Quantity of mold CFU/ml	Sensor parameter	Quantity of yeast CFU/ml
$\Delta F_{max, \, choline+ \, sorbitol}$	0.609	$\Delta F_{80s, \, choline+sorbitol}$	0.643	$\Delta F_{max, \, choline+ \, erythritol+ASO}$	0.830
$\beta_{choline+sorbitol}$	0.679			$\beta_{choline+ \, erythritol+ASO}$	0.868
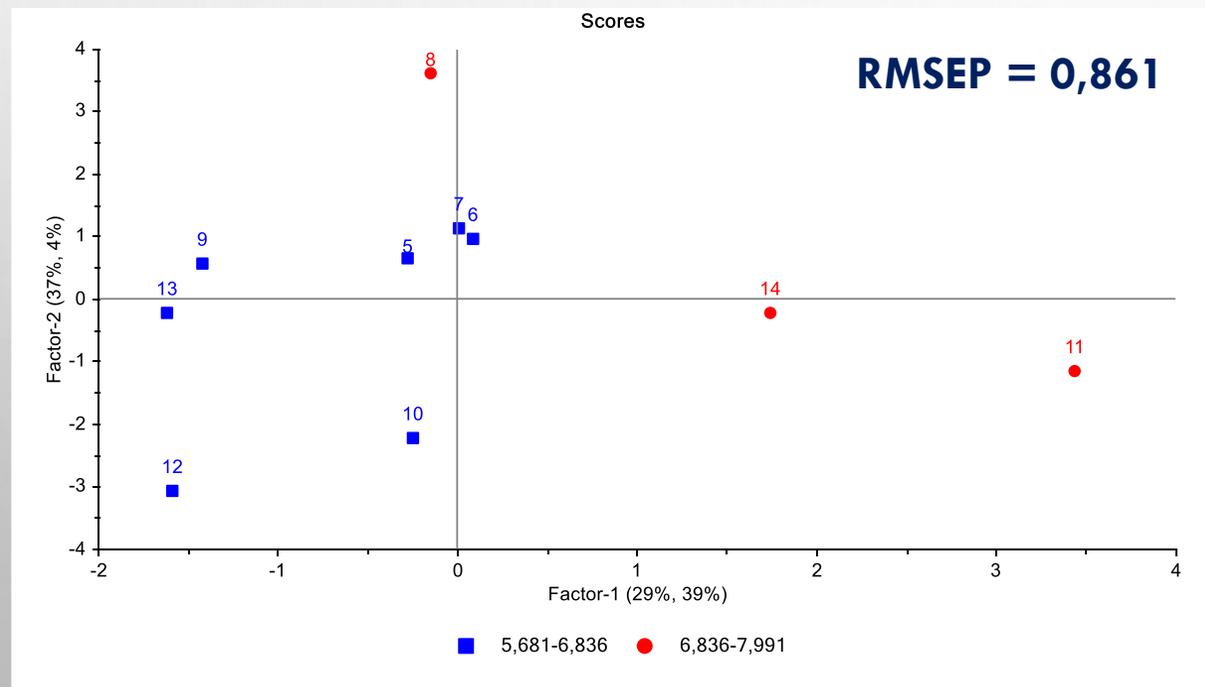
Scores plot of PLS-model to predict total microbial count (lg(CFU)) for milk samples based on sensors parameters

The most important variables are parameters of sensors with coating from choline+erythritol
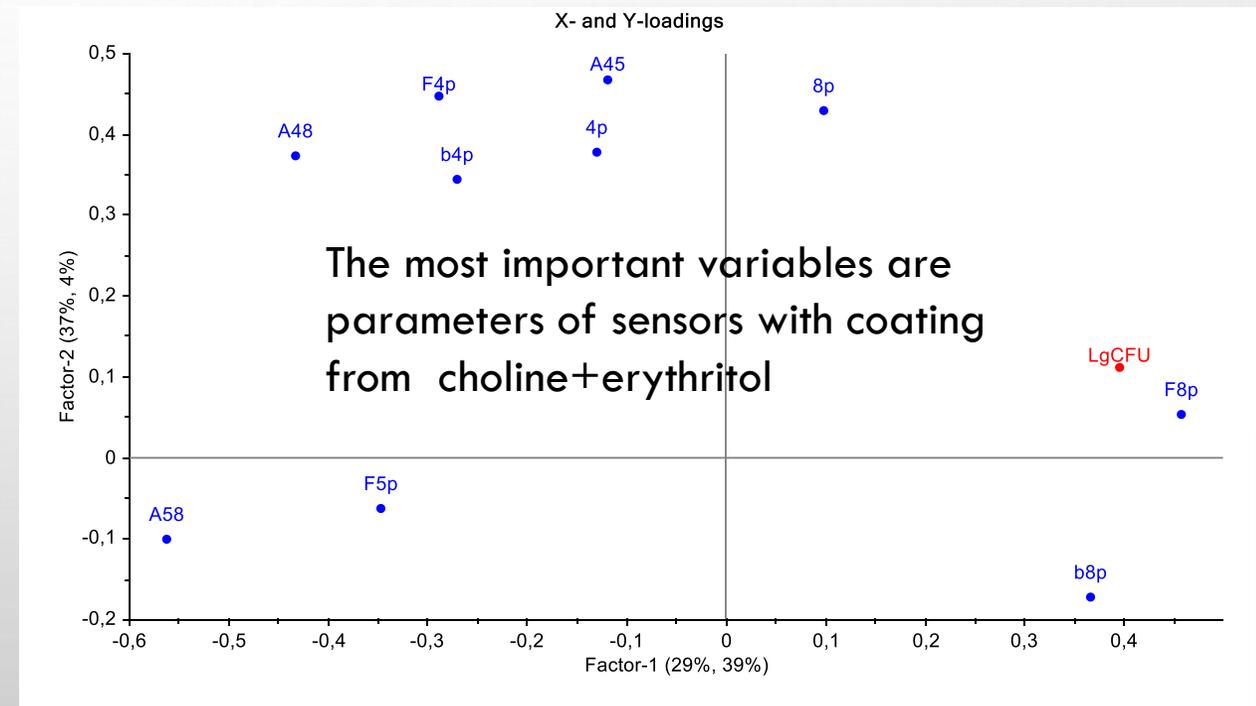
Loadings plot of PLS-model to predict total microbial count (lg(CFU)) for milk samples based on sensors parameters

CONCLUSION

⇒ Microstructural studies of sensor coatings based on deep eutectic solvents (choline + polyalcohols) have been carried out. It has been established that coatings based on DESs, together with amorphous silicon oxide, have a more developed surface and DESs is uniformly distributed over the surface, and the average roughness increases slightly. After 6 months of operation, the roughness of coating, contained the crystals of choline+polyalcohols, increases due to the increase in peaks and smoothing out of small roughness, including due to an increase in the size of DES particles (swelling when analyzing the gas phase over aqueous solutions).

⇒ The sorption of volatile compounds on piezoelectric quartz sensors coated with hydrophilic eutectic solvents has been studied. It has been established that the performance characteristics of coatings based on DESs with the addition of silicon oxide are improved compared to films made from DESs without additives. It has been established that the efficiency of sorption of volatile compounds is higher on coatings made of DESs with ASO than on coatings made from DESs alone; at the same time, the kinetic parameter decreases for almost all substances on the coatings and becomes closer to the values of the parameter for a coating of amorphous silicon oxide.

⇒ The study of the absorption of volatile vapors in the gas phase over aqueous solutions revealed that, for all films based on DESs, the sensitivity of microbalance of vapors of substances abruptly changes when the concentration of the substance in the solution reaches 0.1 or 1% by volume.

⇒ It has been shown that these sensors can be useful in the analysis of volatile compounds of milk associated with microbiological quality indicators.

THANK YOU FOR YOUR ATTENTION

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