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Drift compensation of the electronic nose in the development of instruments for out-of-laboratory analysis

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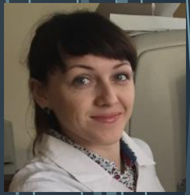

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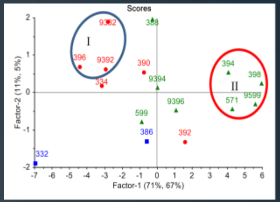
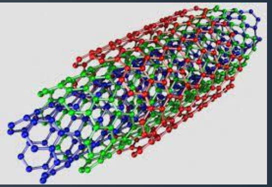
Drift in piezoelectric gas sensors

1. Reasons for long-term drift:
   1. Gradual temperature and humidity changes
   2. Background influence (air of a room for open detection)
   3. Changes in sorption properties of modifiers

Mathematical processing



New materials



2. Reasons for short-term drift:
   1. Abrupt changes of temperature or humidity
   2. Interfering background influence
   3. Device malfunctions

Exclude of outliers and development of corrections

Accuracy and correctness of decision-making procedure

The goal of this research

The development of a technique for drift compensation of the signals of mass-sensitive piezoelectric quartz sensors during operation in the open detection cell and frontal input of the gaseous phase over biosamples with a significant water content.

1. Technique of drift compensation to account background shifts, temperature changes ($\pm$ 2°C)
2. Algorithm of assessing of changes in sorption properties of modifiers (stability of sorbents)
3. The application this technique for analysis of blood samples (possibility of program realization)

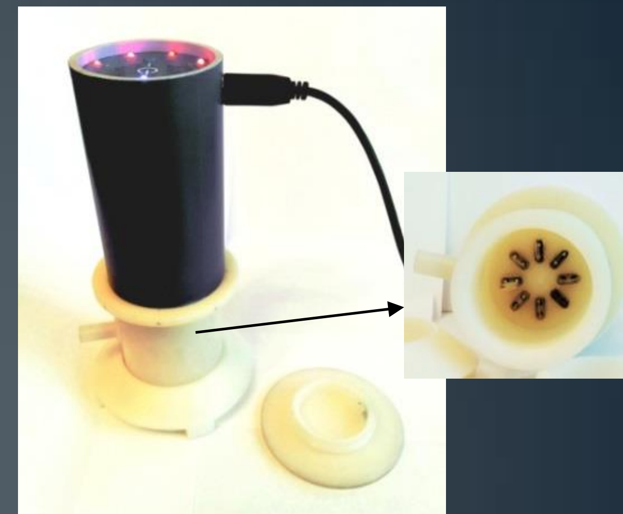
For biosamples with a significant water content, distilled water is proposed as the standard.

Materials, methods and objects

Modifier of piezoelectric quartz resonator electrodes:

- Sensors 1, 8 – carboxylated carbon nanotubes of different mass (1-4 mcg), CNT1, CNT2
- Sensors 2, 7 – phases of nitrate of zirconium oxide of different mass (2-4 mcg), Zr1, Zr2
- Sensor 3 – Dicyclohexano-18-Crown-6, DCH-18C6
- Sensors 4, 5 – biohydroxyapatite phases of different mass (2-4 mcg), HA1, HA2
- Sensor 6 – polyethylen glycol succinate, PEGSc

Portable E-nose “Diagnost-Bio-8”



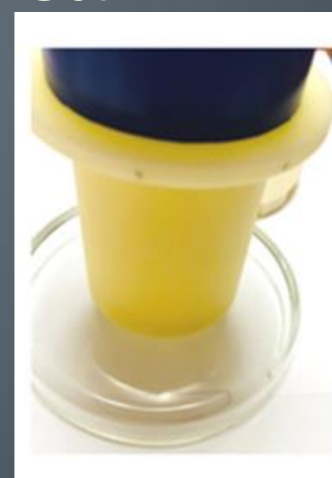
The objects: 1) Blood samples (n=31); 2) distilled water samples (n=75).

Time period: 3 month (October-December 2019)

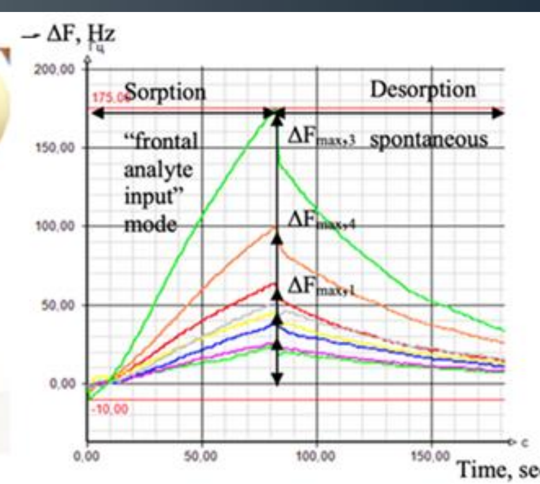
Temperature variation: 20 – 25 °C

Humidity variation: 40 – 45%

Background (air of a room): slight changes due to disinfection and ventilation of the laboratory



The measurement of a blood sample



The output curves of sensors signals during measurement

Signal processing for drift compensation

Implementation of specific signals $\bar{F}_i$:

$$\bar{F}_i = \frac{\Delta F_{max,i}(for\ sample)}{\Delta \bar{F}_{max,i}(for\ water)}$$

the ratio of sensor signals (ΔF_{max}, Hz) when measuring a sample to their corresponding average signals (n=3) when measuring of water samples on the same day

Verification of proposed technique by classification: two classes "water" and "blood" by linear discriminant analysis with the preliminary processing by principal component analysis (PCA-LDA, significance level 0.05). (CAMOSoftware, Unscrambler v.10.0.0 (trail version), Norway).

1) By original maximal sensor responses $\Delta F_{max,i}$, Hz
2) By specific signals $\bar{F}_i$
3) Using component correction by principal component analysis

Daily average original signals ($\Delta F_{max,i}$, Hz) and specific signals (F_i) of sensors for distilled water samples

NN	Sensor coatings		Time from the starting point of the experiment, days							$\overline{X}$*	SD*
			1	2	5	10	20	30	60		
Temperature in the laboratory, ° C			22,0	20,0	21,0	23,0	24,0	24,5	25,0	23.1	1.86
1	CNT1	max	22	21	19	28	18	27	19	21	5,5
		sp	1.02	0.98	0.98	1.01	0.99	1.00	1.02	1.00	0.13
2	Zr1	max	114	101	97	122	76	103	84	92	22
		sp	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.11
3	DCH18C6	max	107	92	100	115	76	113	100	96	22
		sp	1.00	1.00	1.00	1.00	1.01	1.00	1.00	1.00	0.10
4	HA1	max	138	119	106	159	85	116	104	109	29
		sp	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.13
5	HA2	max	49	43	41	53	30	44	39	40	10
		sp	1.01	1.01	1.00	1.00	1.00	1.00	0.99	1.00	0.12
6	PEGSc	max	43	52	55	59	39	60	53	49	11
		sp	1.01	1.01	1.00	0.99	1.01	0.99	1.00	1.00	0.10
7	Zr2	max	77	70	68	82	60	91	70	71	16
		sp	1.01	1.00	1.00	1.00	1.01	0.99	1.00	1.00	0.11
8	CNT2	max	136	110	74	118	74	98	67	91	25
		sp	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.12

$\overline{X}$ is average values of indicators, SD – standard deviation.

Assessing of sensor array stability

Method: Exponentially Weighted Moving Average (EWMA) control charts

Variables: standardized specific signals by the average value equal to 1,00 for all the sensor signals and by standard deviation for each sensor in accordance with data sampling for the first 25 operation days (0,10-0,13).

For sensor array (8 sensors):

Central tendency: values of variable (mean vector of standardized specific sensor signal values) - parameter Z_i :

$\boldsymbol{Z}_i = \boldsymbol{x}_i + 1(-\lambda)\boldsymbol{Z}_{i-1}$, λ is empiric coefficient, it is equal to 0,2, $\mathbf{x}_i$ – matrix string of specific sensor signals.

Statistic quantity T_i^2 of multivariate EWMA for sensors array: $T_i^2 = \boldsymbol{Z}_i' \sum_{Z_i}^{-1} \boldsymbol{Z}_i$, $\sum_{Z_i}$ –is covariance matrix

Parameter H = upper control limit (UCL) = 20,79.

Variability: $\mathrm{CL} = b_1|\Sigma|$, $\mathrm{UCL(LCL)} = |\Sigma|\left(b_1 \pm 3b_2^{\frac{1}{2}}\right)$

For each sensor:

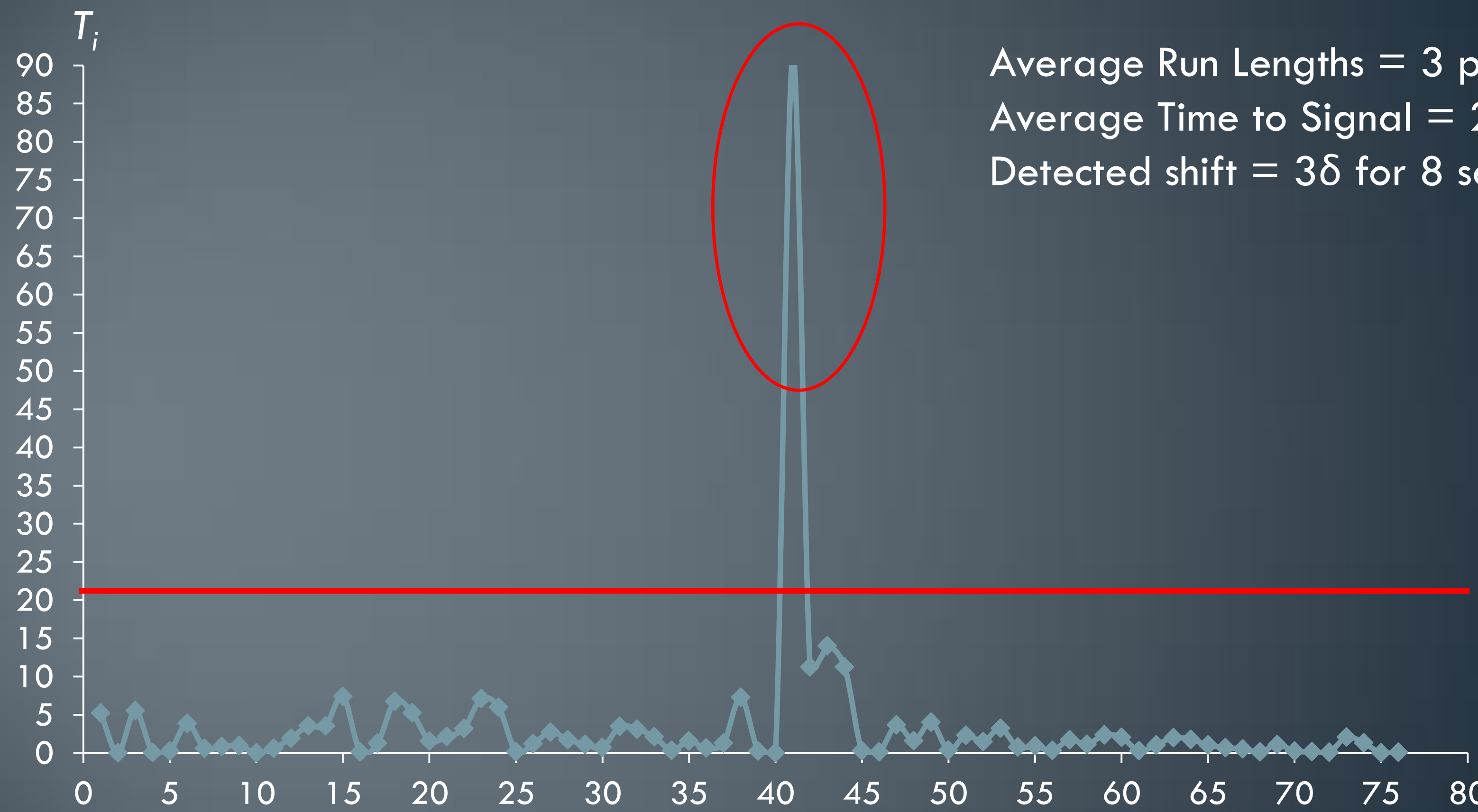
Central tendency: values of standardized specific signals - parameters z_i , $z_i = x_i + 1(-\lambda)z_{i-1}$

$\mathrm{UCL(LCL)} = \mu_0 \pm L\sigma\sqrt{\frac{\lambda}{(2-\lambda)}[1-(1-\lambda)^{2i}]}$, coefficients λ =0,2, L =2.962, μ_0=0, σ – variance of z_i

Variability: exponentially weighted mean square (EWMS) error s_i , $s_i^2 = (x_i - \mu)^2 + 1(-\lambda)s_{i-1}^2$

$$\mathrm{UCL} = \sigma_0\sqrt{\frac{\chi 2_{\nu,\alpha/2}}{\nu}},\quad \mathrm{LCL} = \sigma_0\sqrt{\frac{\chi 2_{\nu,1-(\frac{\alpha}{2})}}{\nu}},\quad \nu = (2-\lambda)/\lambda$$

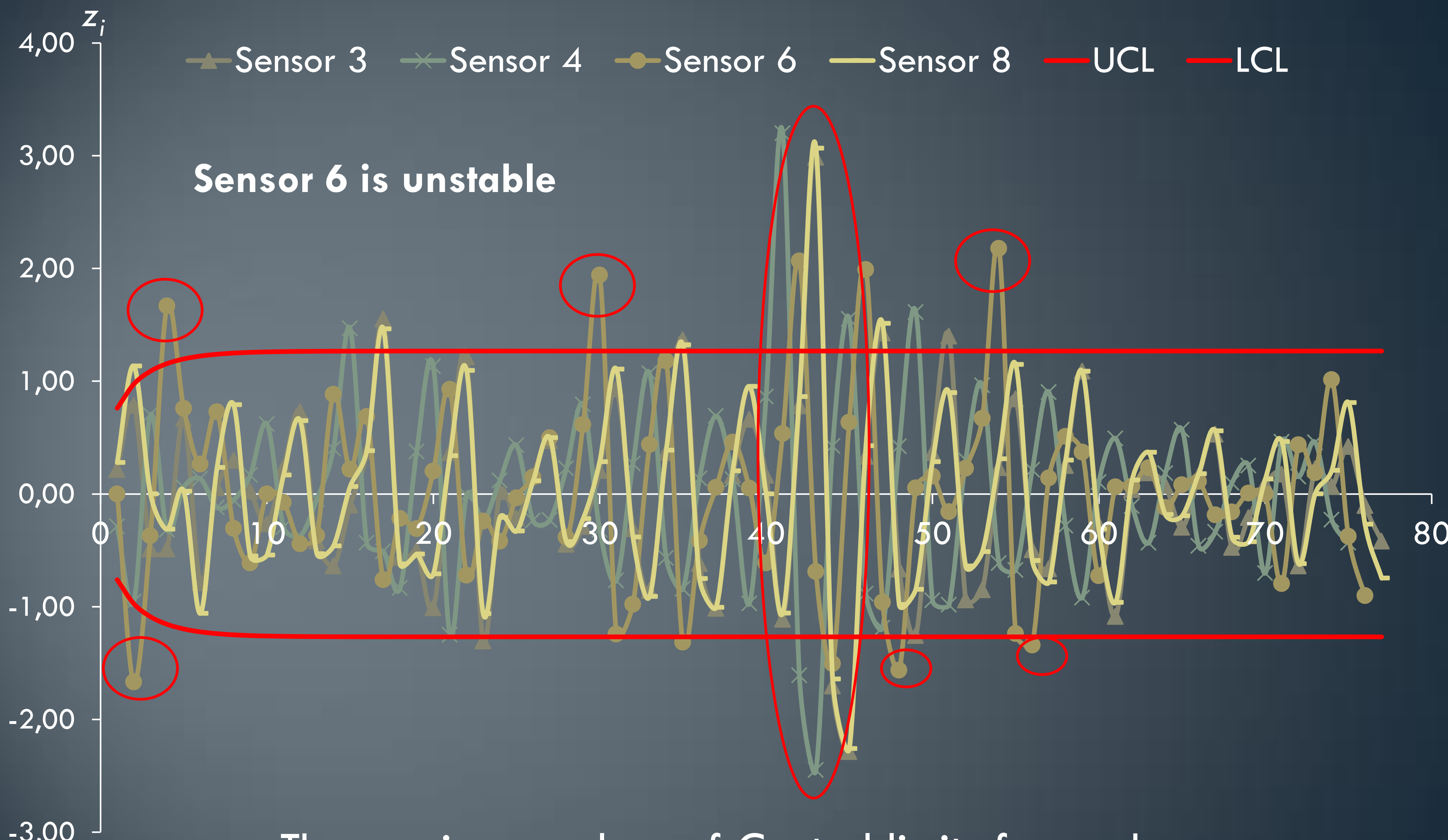
MEWMA control chart for sensor array



Average Run Lengths = 3 per day
Average Time to Signal = 2,5 h
Detected shift = 3δ for 8 sensors

Abrupt changes in background or standard properties

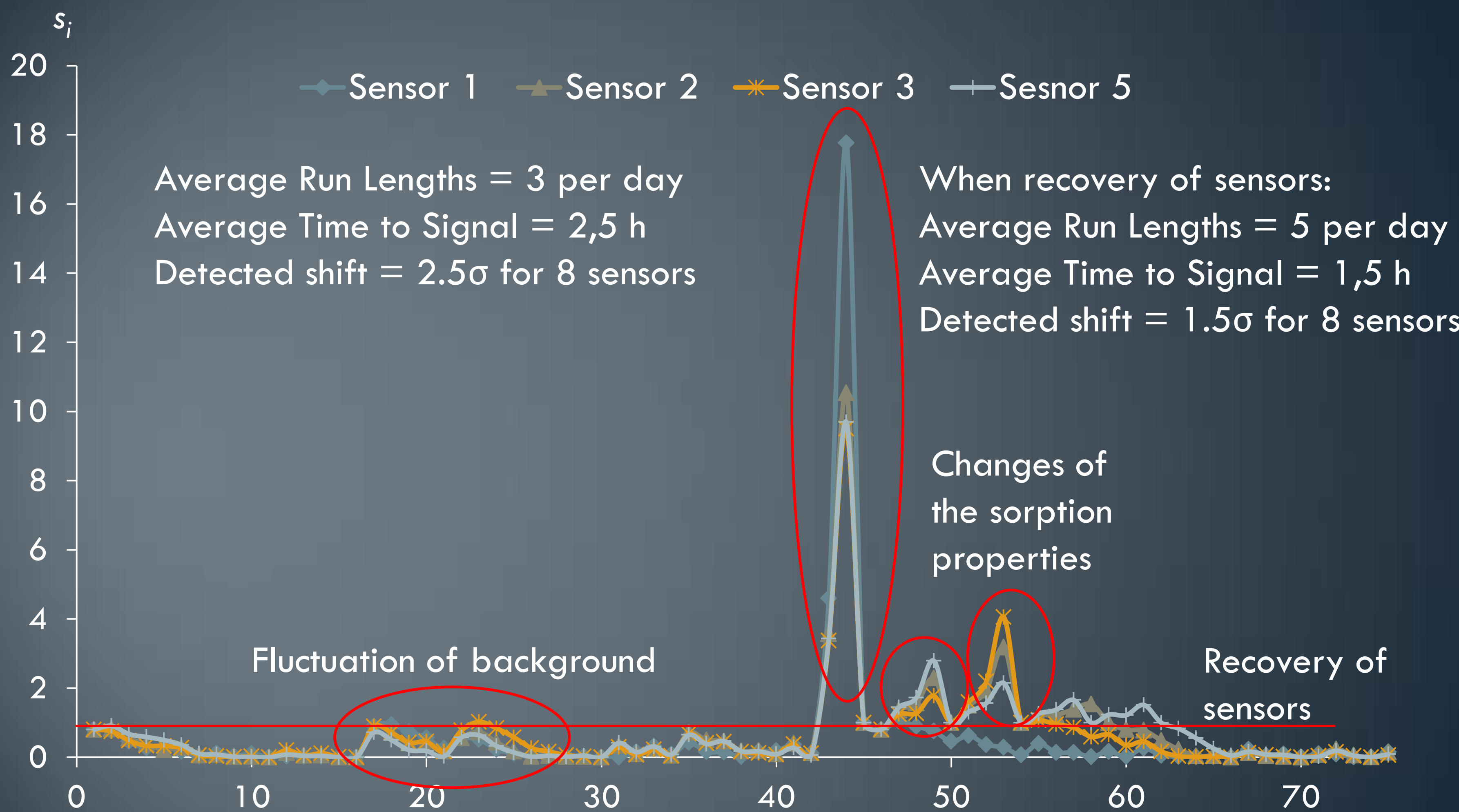
EWMA control chart for each sensor



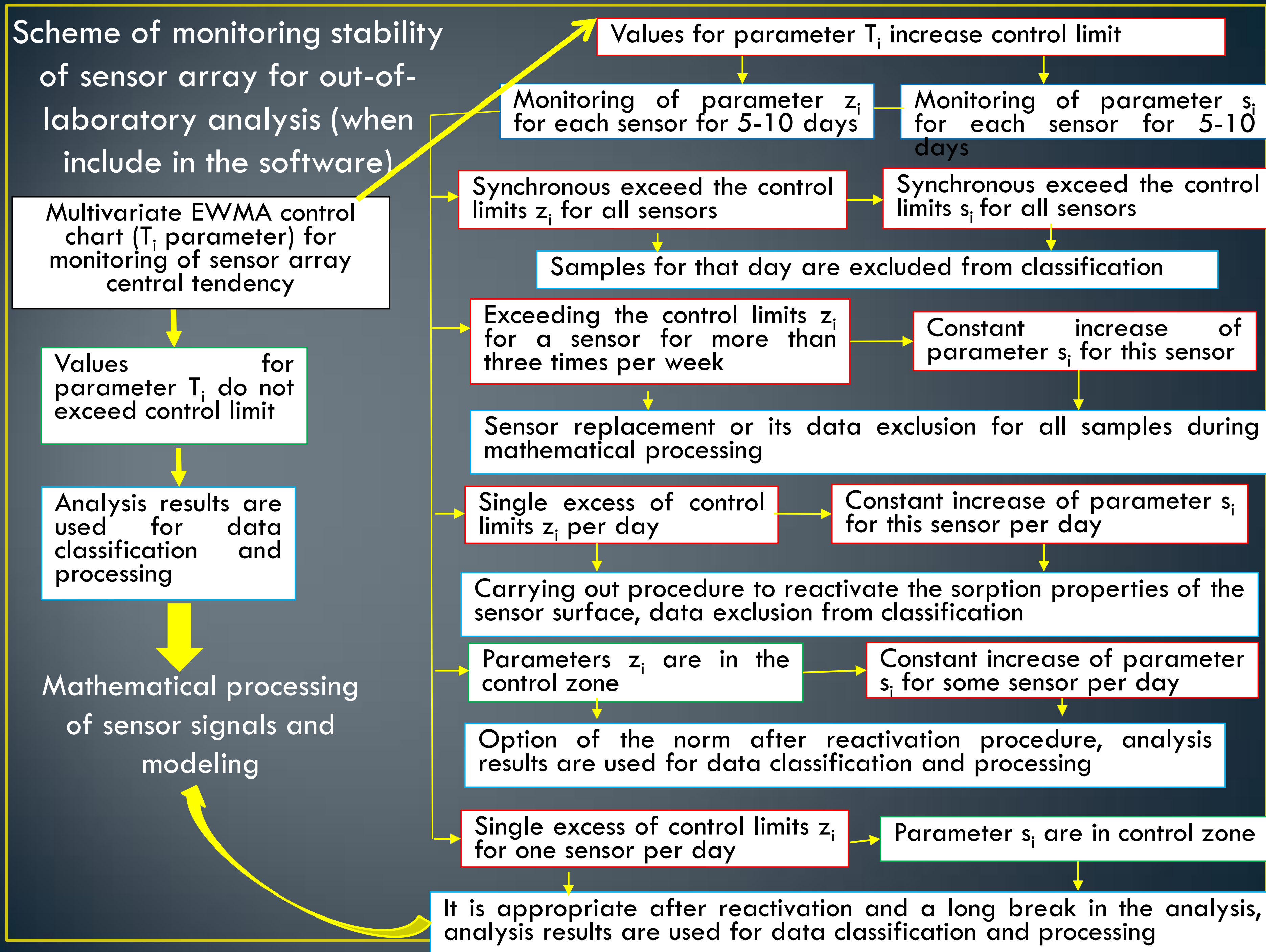
The maximum values of Control limits for each sensor

CNT1	Zr1	DCH18C6	HA1	HA2	PEGSc	Zr2	CNT2
± 1.01	± 1.24	±1.27	±1.25	±1.22	±1.06	±1.18	±1.22

Monitoring Variability of each sensor



The most stable sensors with coating from carboxilated carbon nanotubes



Scheme of monitoring stability of sensor array for out-of-laboratory analysis (when include in the software)
Multivariate EWMA control chart (T_i parameter) for monitoring of sensor array central tendency
Values for parameter T_i do not exceed control limit
Analysis results are used for data classification and processing
Mathematical processing of sensor signals and modeling
Values for parameter T_i increase control limit
Monitoring of parameter z_i for each sensor for 5-10 days
Monitoring of parameter s_i for each sensor for 5-10 days
Synchronous exceed the control limits z_i for all sensors
Synchronous exceed the control limits s_i for all sensors
Samples for that day are excluded from classification
Exceeding the control limits z_i for a sensor for more than three times per week
Constant increase of parameter s_i for this sensor
Sensor replacement or its data exclusion for all samples during mathematical processing
Single excess of control limits z_i per day
Constant increase of parameter s_i for this sensor per day
Carrying out procedure to reactivate the sorption properties of the sensor surface, data exclusion from classification
Parameters z_i are in the control zone
Constant increase of parameter s_i for some sensor per day
Option of the norm after reactivation procedure, analysis results are used for data classification and processing
Single excess of control limits z_i for one sensor per day
Parameter s_i are in control zone
It is appropriate after reactivation and a long break in the analysis, analysis results are used for data classification and processing

Accuracy and correctness of sample classification into 2 classes by PCA-LDA models for original and specific sensor signals.

Variables	Accuracy of PCA-LDA model using training set of sample, %		Correctness of classification of blood samples from test set, %	
	Initial	After stability assessment	Initial	After stability assessment
Original signals, ($\Delta F_{max,i}$, Hz)	90,4	96,2	0	0
Specific signals, ($\overline{F_i}$)	94,2	95,2	33,3	80,0
Signals after CC-PCA	-	-	8	10

Proposed algorithm of stability assessment and drift correction could be applied for various sensor system with selection of appropriate standard for purpose of investigation.

Training set: sensor array data for 64 samples (19 blood samples and 45 water samples) for the first one and a half month of operation (October-November).
Test set: sensor array data for 42 samples (12 blood samples and 30 water samples) for the next period of operation (November-December).

Summary

1. For biosamples with a significant water content (urine, perspiration, exhaled air condensate, saliva, etc.), distilled water is an appropriate standard.
2. The proposed method for sensor signal drift compensation consists in dividing the sensor signals for blood samples onto corresponding average signals for standard sample (3 times measured during the day).
3. The scheme for assessing the sensor array stability has been offered using Exponentially Weighted Moving Average control charts.
4. ARL = 3 – 5 measurement per day, ATS=1.5 – 2.5 hours.
5. The scheme can be utilized as an additional module in the device software for routine out-of-laboratory analysis
6. The most stable coatings when measuring water and blood samples are carboxylated carbon nanotubes (sensors 1 and 8).
7. Error classification of 42 samples from the test set onto two classes constituted 15% with significance level of 0.05.

Thank you for your attention!

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