

“Electronic nose”-type chemosensory systems for detection of gaseous poisonous substances

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Abstract. The work is devoted to a study of the detection sensitivity and selectivity of a series of simulants of gaseous poisonous substances (PS). Two different sensor types were used, namely: 1) a quartz crystal microbalance (QCM), exhibiting a shift of the resonant frequency of quartz plates coated with calixarene thin layers, and 2) chemoresistive electrodes coated with layers of nanocomposites of intrinsically conducting polymers (ICP) changing their conductance under the influence of adsorbed gas molecules. The concentration of the analyzed volatile compounds varied within the range of 10 to 1000 ppm. The detection threshold ranged from 10 to 100 ppm depending on the analyzed substance for both transducer types. The response time was from 10 to 20 s for the QCM sensors and up to 1 minute for the ICP based sensors. The possibility of qualitative identification of poisonous substances in a wide concentration range by means of statistical analysis of the sensor array data is demonstrated.

Keywords: quartz crystal microbalance, chemoresistive electrodes, calixarenes, electrically conducting polymers, nanocomposites, organophosphorous and organochlorine compounds.

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1. Introduction

Repeated terrorist attacks and targeted poisoning of individuals by chemical warfare agents (CWAs), in particular by organophosphorous nerve agents or mustard gas [1], actualized the necessity of their fast and selective detection [2]. A lot of techniques such as mass-spectrometry (MS), gas chromatography (GC), electrochemistry, infrared and fluorescence spectroscopy, *etc.* [3, 4] are used to detect CWAs. However, these techniques, being very reliable and sensitive, are still time-consuming, complex and expensive. That is why simpler and cheaper detection methods using chemoresistive and gravimetric transducers were developed.

The operating principle of chemoresistors is based on variation of electrical resistance of a sensing material due to interaction with CWAs or their mimics [2, 5, 6]. Chemoresistive materials are in many cases associated with relatively simple synthesis and treatment procedures. At the same time, they enable extremely low CWAs detection limits in the ppm range and even down to

10...20 ppt [2–6]. Moreover, sensors based on such materials have low power consumption and do not require complex secondary equipment, thus allowing easy, fast and accurate measurements of their resistance. Typically, chemoresistive materials [7–9] used for detection of CWAs and other volatile organic compounds (VOC) are based on metal oxide semiconductors [10, 11], nanocomposites of dielectric polymers with carbonaceous or noble metal nanoparticles [12], intrinsically conducting polymers (ICP) [13–17] and their nanocomposites with dielectric polymers or with inorganic or carbonaceous nanoparticles.

ICP rank high among the sensing materials due to perfect combination of physical and chemical properties, such as efficient electronic π -conjugation, semiconductor or metallic behavior, easy preparation and use, chemical stability, synthetic versatility and high room-temperature sensitivity to VOC and, in particular, to CWAs [2, 5–6, 13–17]. Moreover, it was found recently that ICP nanocomposites, in particular core-shell nanocomposites

of polyaniline (PANI) and poly(3-methylthiophene) (P3MT) with such core materials as multiwall carbon nanotubes (MWCNTs) and poly(vinylidene fluoride) (PVDF), can be even more sensitive to some CWA simulants and VOC [18, 19]. The ICP based nanocomposite materials reversibly react with CWAs changing their conductivity (resistance) by adsorption of gas analytes due to the changes in the electronic state of the sensing ISP component and the physico-chemical interactions with the matrix component (spherical nanoparticles or nanotubes of inorganic materials and dielectric polymers) [20–22].

Another widespread sensor type is the gravimetric one based on the quartz crystal microbalance (QCM). In such sensors, the oscillation frequency of a quartz resonator changes with the change of the mass adsorbed on its surface. Sensors of this type are widely used for determining the thicknesses of deposited layers and monitoring gaseous [23] or liquid [24] media. Sensitive coatings for such sensors are often made of calixarene layers, which are capable of forming supramolecular complexes with gas molecules and therefore enable their selective detection. Consequently, calixarenes (CA) are promising materials for sensing and chemical technology applications [25]. Having molecular cavities of different structures and sizes, these compounds are suitable for creating efficient receptor platforms with specific adsorptive properties. CA can be immobilized as thin layers on a quartz resonator surface to produce the QCM sensor elements. Because of the sufficiently weak intermolecular interactions between the calixarene compounds and the analyte molecules, such sensors demonstrate fast sorption-desorption kinetics, which is important for chemical sensors intended, *e.g.*, for environment monitoring or detecting dangerous toxic substances. In particular, calix[4]arenes are promising for designing highly efficient selective adsorbents of volatile organic substances [26, 27]. A calix[4]arene molecule has a bowl-shaped macrocyclic structure that can be functionalized at both the lower and the upper rims. This provides a sufficiently rigid base for combining different functional groups and endowing the resulting molecule with the required selectivity properties.

The purpose of this work was to study the possibility of rapid detection and subsequent identification of toxic (poisonous) gases with the help of chemoresistive and quartz crystal sensor arrays using statistical methods of recognizing chemical patterns and the “electronic nose” technology.

2. Materials and methods

2.1. Characteristics of PS and CWA simulants

In this work, organophosphorous and organochlorine compounds with the molecular structure and physico-chemical properties close to those of real poisonous substances (PS) were used as the PS simulants. These compounds are not categorized as real PS due to certain differences in chemical structure, however, they can still be considered toxic. A brief list of the substances under

study is as follows (name of the substance, chemical formula and saturated vapor pressure at 20 °C are specified) [28]: dimethylmethyl phosphonate (DMMP, simulant of sarin agent), $C_3H_9O_3P$, 0.962 mm Hg; diethyl phosphite (DEP), $C_4H_{10}O_3P$, 10.5 mm Hg; trimethyl phosphate (TMP), $C_3H_9O_4P$, 0.85 mm Hg; 1,4-dichlorobutane (DCB), $C_4H_8Cl_2$, 4 mm Hg; dichloroethyl ether (chlorex), $(ClCH_2CH_2)_2O$, 0.7 mm Hg.

2.2. Chemoresistive electrodes with ICP nanocomposite coatings

Based on the results of the previous studies [18–21, 29] regarding the sensitivity of a series of chemoresistive ICP materials toward the above mentioned toxic substances in gaseous phase at concentrations of 10 to 1000 ppm, two types of chemoresistive nanocomposites, different in their nature, with the “core-shell” morphology of nanoparticles were chosen in this work, namely:

1) a nanocomposite consisting of polyvinylidene fluoride (PVDF) particles about 200 nm in size, covered with the shell of poly-3-methylthiophene (P3MT) doped with chloride anions (PVDF/P3MT), synthesized according to the method described in [18, 29]; and

2) a nanocomposite consisting of titanium dioxide particles about 20 nm in size, covered with the shell of polyaniline (PANI) doped with dodecylbenzenesulfonic acid (DBSA) ($TiO_2/PANI$), synthesized according to the method described in [30].

Chemosensors with these two specific types of sensitive coatings turned out to be the best, consistently and reproducibly exhibiting the largest magnitudes of the relative response to the analyzed substances vapors. We consider below in detail their sensory characteristics in both standalone configuration and as a part of a sensor array. The latter is important since such sensors can provide the most significant contribution to the recognition of toxic substances by the “electronic nose” technology.

The technological and methodological advantages of nanocomposites stem from their relatively high sensitivity to harmful volatile compounds, possibility of controlling electrophysical characteristics (conductivity, spectral properties), and low specific weight, combined with the ease of synthesis and low cost. Besides, ICP nanocomposites possess improved sensory characteristics (stability, sensitivity) as compared to pure intrinsically conducting polymers [18, 19, 29].

The nanocomposite layers were dropcasted from their 0.5...2% (w/v) dispersions in chlorobenzene [31] onto the raster gold electrodes formed on the glass-ceramic substrates by thermal evaporation in vacuum (Fig. 1). Each sensor element contained 20 pairs of raster electrodes $1050 \times 20 \mu m$ in size, separated by $20 \mu m$ gaps. The obtained nanocomposite sensitive layers had an area of approximately $2 mm^2$. Two identical sensor elements were simultaneously prepared on each substrate. The resistances of the obtained sensor elements with the deposited sensitive layers were in the range of 20 Ohm to 20 kOhm.

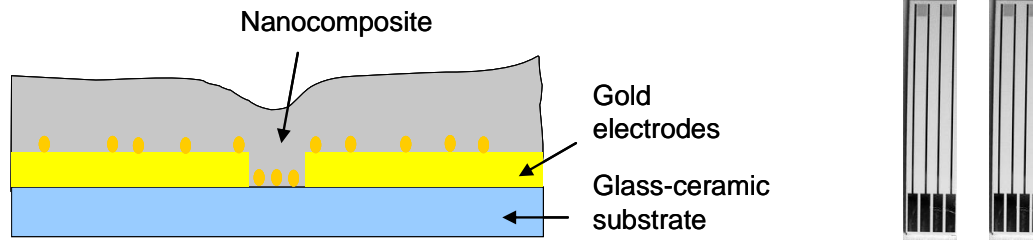


Fig. 1. Chemoresistive sensor with raster gold microelectrodes covered with the ICP nanocomposite layer.

The magnitude of the sensor response to a target gaseous analyte was defined as the change in the value of direct current flowing through each chemoresistor at a certain applied excitation voltage. The physical value actually measured in the experiments was the voltage at the transducer output. This voltage is directly proportional to the current flowing through the sensor, which in turn is proportional to the conductivity of the sensitive layer. The current was measured by an opamp-based current-to-voltage converter connected to the analog-to-digital converter (ADC) with the effective resolution of 11 bits and the 5 V input range. The excitation voltage and the amplifier transimpedance (current-to-voltage conversion ratio) were tuned individually for each sensor type to provide the ADC input voltage within the 2...4 V range in order to minimize the dynamic range loss. Because of the substantial scattering of electric parameters of different chemoresistive sensors, the recorded response values were converted into the relative changes of the sensor resistance:

$$\delta R = \frac{R - R_0}{R_0} = \frac{U_0 - U}{U}, \quad (1)$$

where R and U are the sensor resistance and the voltage at the converter output after exposition to analyte, and R_0 and U_0 are the initial values of resistance and output voltage in the absence of analyte vapors, respectively.

Exposition to gas-air mixtures of the individual analyte vapors was performed using an injection system [18, 19]. The response of the sensor elements was recorded for 2 min, and the airtight Teflon chamber was repeatedly purged with the room air afterwards. The desired concentration of analyte in the air-vapor mixture was obtained by successive dilution of the saturated vapor (collected at 20 °C) with the room air at the relative humidity of approximately 30%. For the majority of organophosphorous and organochlorine PS simulants, the concentrations of 100, 200, 500 and 1000 ppm were used. However, if a particular sensitive layer exhibited high sensitivity to specific simulants, lower concentrations of 10 and 50 ppm were additionally prepared.

2.3. Piezoelectric quartz crystal microbalance

The principle of operation of a QCM sensor element consists in measuring the shift in the oscillation frequency of a quartz resonator caused by the adsorption of molecules from the surrounding medium on the quartz surface. As the molecules accumulate on the surface, the oscillation frequency decreases. The dependence of the change in the oscillation frequency of the quartz resonator Δf on the adsorbed mass Δm is described by the well-known Sauerbrey equation [32]:

$$\Delta f = - \frac{2f_0^2}{A\sqrt{\rho_q\mu_q}} \Delta m, \quad (2)$$

where Δf is expressed in Hz, f_0 is the fundamental frequency of quartz (MHz), Δm is the mass adsorbed on the surface (g), A is the surface area (cm²), $\rho_q = 2.648$ g/cm³ is the quartz density, and $\mu_q = 2.947 \cdot 10^{11}$ g/cm·s² is the quartz elastic modulus. The sensors used in this work had circular effective surface with the diameter of 4 mm. The described method provides a fairly high sensitivity of about 1 ng/Hz for an AT-cut quartz resonator having the resonant frequency of 10 MHz. The standard radio engineering 10 MHz AT-cut quartz crystals, 8 mm in diameter, were used as the resonators. To create a highly sensitive and selective QCM sensor, the surfaces of the quartz resonators were covered with the thin sensitive layers. The relation (2) holds within the limits up to 1% of the frequency shift relative to the fundamental one, provided the sensitive film is thin and dense and the analyzed medium is not viscous.

For measuring and recording sensor responses to the adsorbed organic substance vapors, an 8-channel chemosensory system developed at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine was used. An original software was developed for measurement process control and data acquisition. Technical details of the system design and the measurement process are described in [27]. The experiments were conducted at the normal conditions (20 °C, 760 mm Hg). Prior to the measurements, all sensor elements were individually tested using a single-channel QCM-sensor transducer designed for the express-testing of the operability of each sensor and determination of the “effective thickness” of the sensitive layers.

The required concentrations of the PS simulants were obtained using the in-house developed gas mixture generator based on a diffusion tube [33]. The prepared mixtures were injected into a 9 ml chamber with the sensor array installed inside it. Using the multichannel system, the response kinetics was recorded simultaneously for all sensor elements and sequentially for each analyte at a given concentration. The response magnitude was defined as the maximum deviation of the resonator oscillation frequency from its initial value. To ensure the equal measurement conditions and prevent the influence of previous experiments, the chamber was purged with clean air after each measurement.

A series of calix[4]arenes with different functional groups were used as the sensitive materials. Calixarenes were synthesized at the Institute of Organic Chemistry, NAS of Ukraine using the methods described in [34]. The calixarene sensitive layers were immobilized by spin-coating or drop-spreading from a 1 mg/ml solution of calixarene in chloroform. After evaporation of the solvent, a mostly homogeneous film with the thickness defined by the solution concentration was formed on the surface. All prepared sensor elements had similar "effective thicknesses" of the sensitive layers. According to (2), this corresponded to the shift of the base frequency in the range of 5000 to 6000 Hz, thus ensuring similar ranges of the response magnitudes for the sensors having different sensitive layers.

In previous experiments [27], three the most sensitive and selective calixarene types were identified to be CA1050, CA1089 and CA1091. Structural formulae of these macromolecules are shown in Fig. 2.

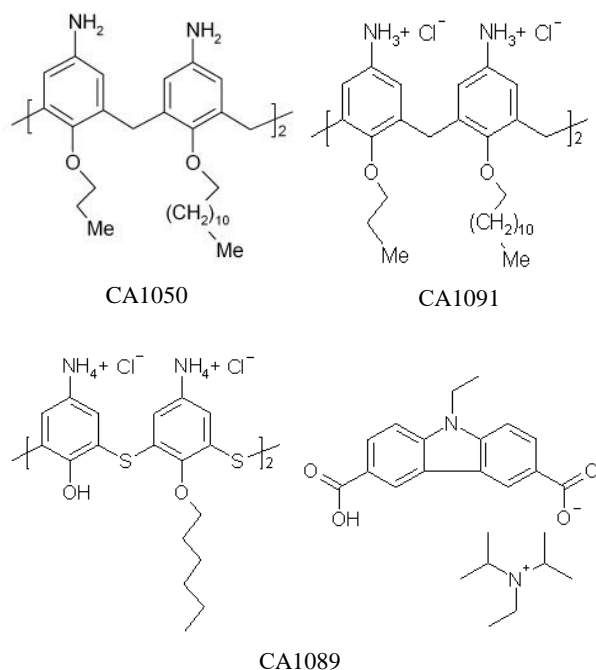


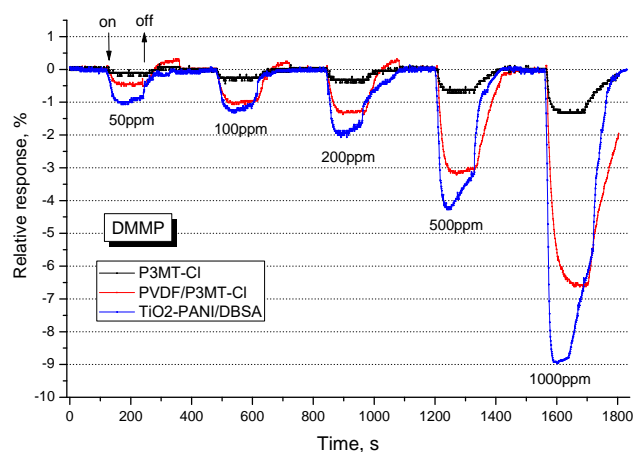
Fig. 2. Structural formulae of calixarene types CA1050, CA1089 and CA1091, which were used as the sensitive layers for QCM sensors.

3. Results and discussion

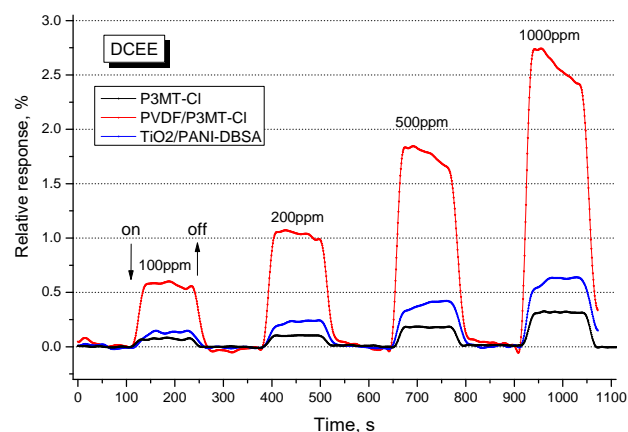
3.1. Sensitivity and selectivity of ICP nanocomposites to poisonous substance simulants

Fig. 3 shows typical consecutive responses of the chemoresistive sensors with the sensitive layers of the PVDF/P3MT and TiO₂/PANI nanocomposites as well as pure P3MT, to the organophosphorous DMMP (a) and organochlorine DCEE (b) vapors with concentrations increasing from 50 (100) to 1000 ppm. Note that the chemosensor with the pure P3MT layer was included in the experiments in order to compare its sensory characteristics with those of the hybrid nanocomposite materials.

As can be seen from the response kinetics, the reaction to the both analyte vapors is sufficiently fast with the response times of about 20 to 30 s. Recovery of



(a)



(b)

Fig. 3. Consecutive responses of the chemosensors based on the PVDF/P3MT and TiO₂/PANI nanocomposites as well as pure P3MT film to (a) 50, 100, 200, 500 and 1000 ppm concentrations of DMMP (original signals with noise tracks), and (b) 100, 200, 500 and 1000 ppm of DCEE (the response curves are smoothed using the FFT filter for irregular data processing with the averaging window size parameter set to 10 points).

different sensors by purging with air is somewhat slower so that the relaxation process may take several minutes. The rapidity and reversibility of the adsorption-desorption processes point to low interaction energy between the analyte molecules and the sensitive layers, namely on the order of a few kT units.

It is important to mention that the magnitudes of the responses of the pure P3MT based chemosensors to DMMP and DCEE (see Fig. 3) are significantly lower than those of the nanocomposite-based sensors (it also holds true for other tested analytes). This suggests considerably better sensory properties of the ICP nanocomposites as compared to the pure P3MT probably due to the specific interactions between the core materials and P3MT shells [18].

The concentration dependences of the responses of the PVDF/P3MT and TiO_2 /PANI nanocomposite-based chemosensors to the target analytes in the concentration range of 100 to 1000 ppm (Fig. 4) confirm the varying sensitivity and correspondingly pronounced selectivity of these sensors.

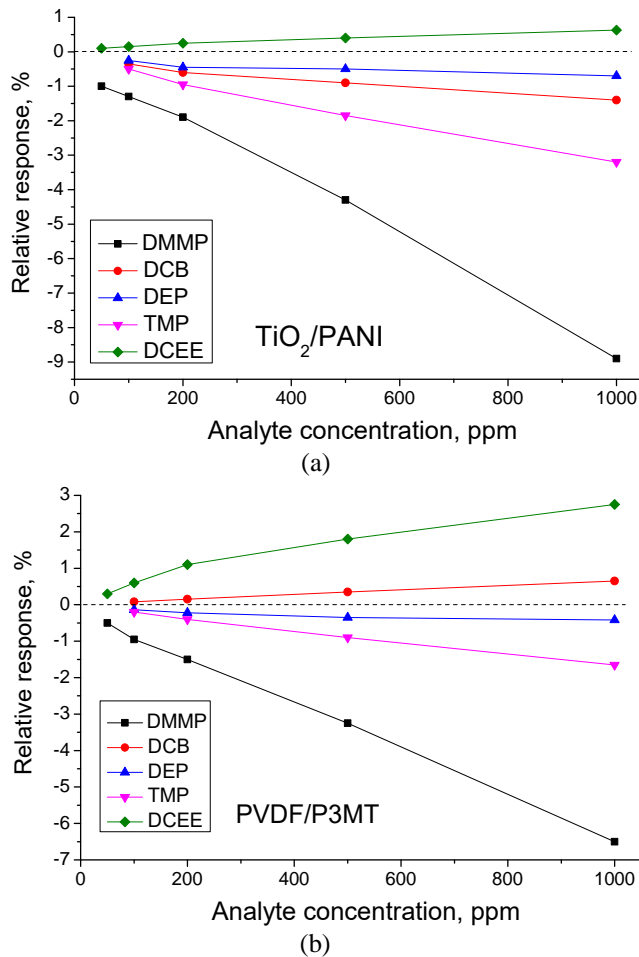


Fig. 4. Concentration dependences of the responses of the chemoresistive sensors based on TiO_2 /PANI (a) and PVDF/P3MT (b) nanocomposites to the organophosphorous and organochlorine simulants of poisonous compounds in the concentration range of 100 to 1000 ppm.

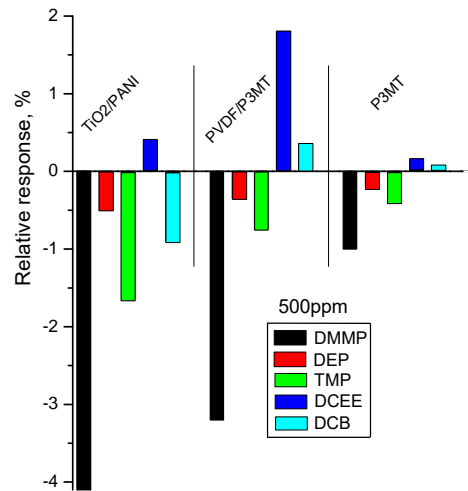


Fig. 5. Summarized diagram of the responses of the chemosensors with TiO_2 /PANI and PVDF/P3MT nanocomposite layers as well as with pure P3MT layer to the target analytes at the concentration of 500 ppm.

The sensitivity and selectivity of the sensors under study are well illustrated by the overall diagram of responses to each of the target analytes at a fixed concentration of 500 ppm (Fig. 5).

As can be seen from Fig. 5, the chemoresistive sensors with TiO_2 /PANI and PVDF/P3MT nanocomposite layers exhibit maximum sensitivity to the DMMP vapor. As compared to nanocomposites, pure P3MT demonstrates generally low sensitivity to all the tested analytes. It is also clear from Figs. 4 and 5 that the nanocomposite sensors are selective in regard to separation of organophosphorous and organochlorine compounds, since the responses to these two classes of substances have opposite signs. It is also worth noting that the PVDF/P3MT composite shows the most pronounced selectivity.

3.2. Study of the sensitivity of QCM sensor elements with calixarene sensitive layers to poisonous substance simulants

Fig. 6 shows typical kinetic dependences of the responses of the sensors with calixarene sensitive coatings to different concentrations of the analytes injected into the sample chamber.

It can be seen that the sensor responses settle within a few seconds. The only exception are the responses of the sensor with the CA1089 film showing some broadening of the front edge. Such broadening is typical for the interactions of this calixarene compound with virtually all of the studied analytes. This peculiarity of the response kinetics, common for the interactions with different compounds, is likely related to the specific CA1089 calixarene structure, which is the most sophisticated among the calixarene types used in this work. Formation of supramolecular complexes in such

systems is difficult to predict even using dedicated molecular simulation software. Recovery of the sensors by purging with air until the output signal reaches its initial level is also relatively fast, indicating presence of weak non-covalent bonds formed through interaction between the analyte molecules and the calixarene compounds.

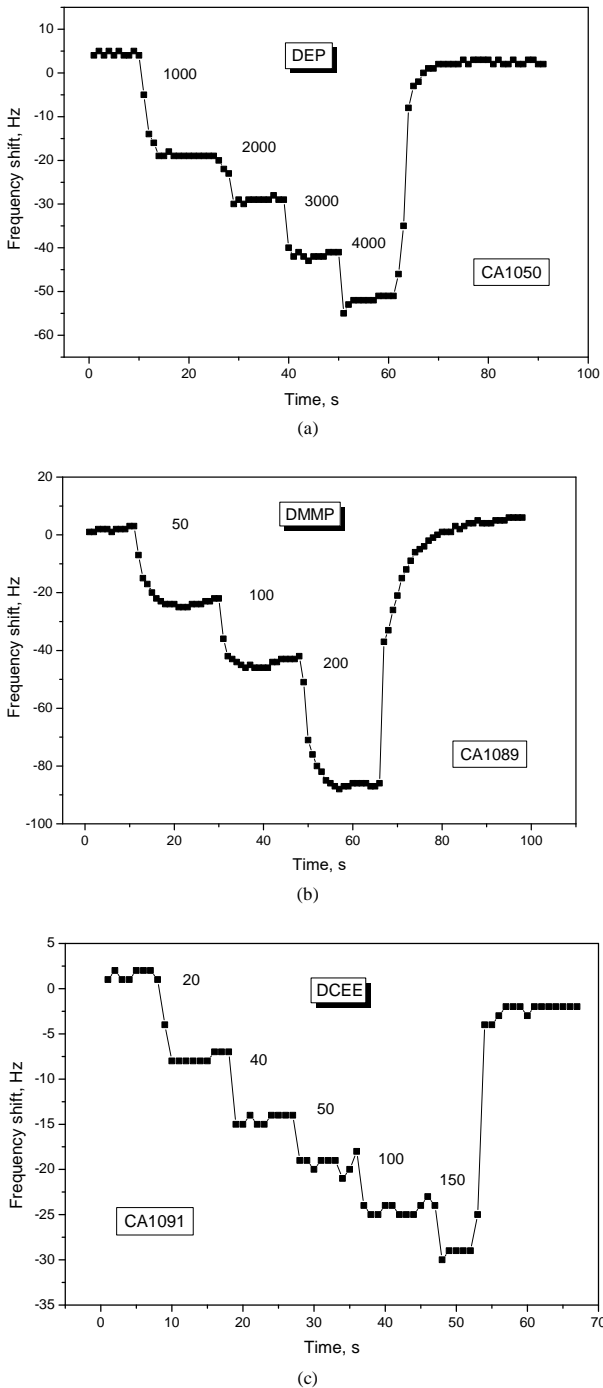


Fig. 6. Kinetic dependences of the sensor responses to successive injection of DEP (a), DMMP (b) and DCEE (c) vapors into the sample chamber. Numbers on the plots denote the respective analyte concentrations in ppm.

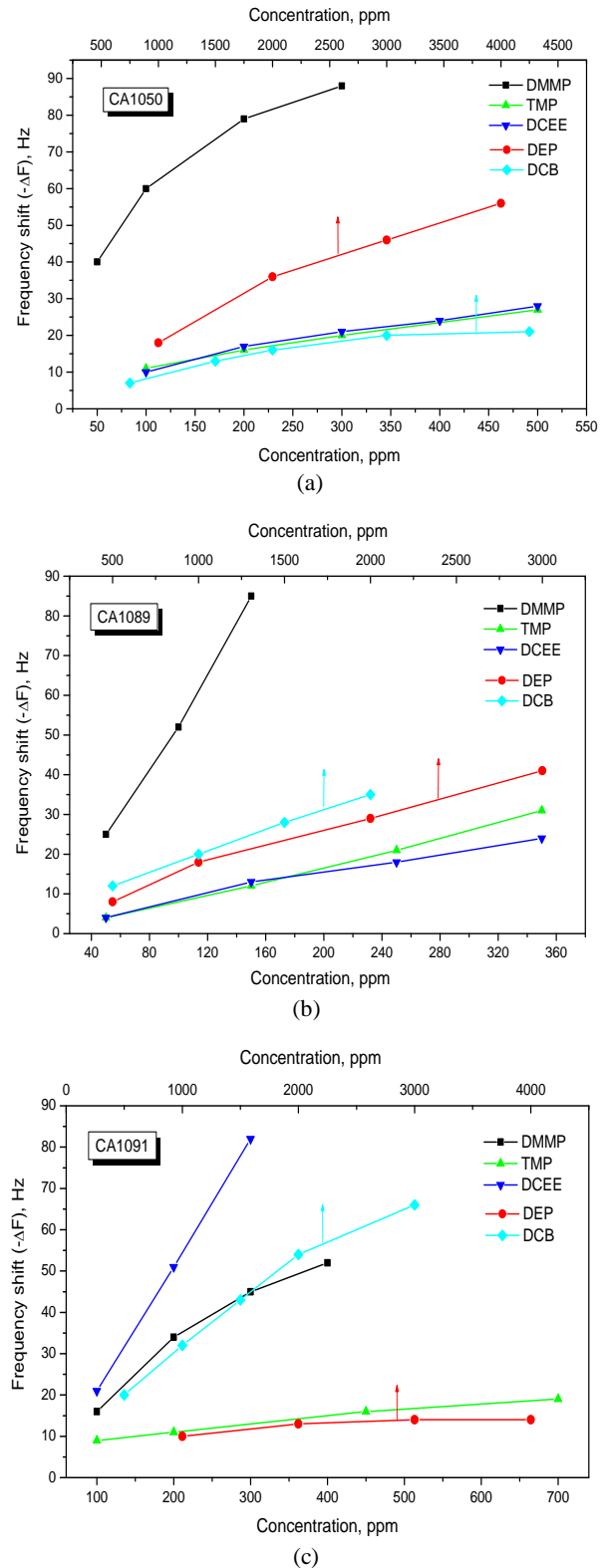


Fig. 7. Concentration dependences of the responses of the calixarene-based chemosensors with the sensitive layers of CA1050 (a), CA1089 (b) and CA1091 (c) exposed to the indicated PS simulants in the concentration range of 50 to 4000 ppm. The plots of the DMMP, TMP and DCEE responses correspond to the bottom concentration scale, and the plots of the DEP and DCB responses (marked with the up arrows) correspond to the top concentration scale.

Fig. 7 shows the dependences of the responses of the sensors based on calixarene compounds CA1050, CA1089 and CA1091 on the concentrations of the injected into the sample chamber target analyte (DMMP, DEP, TMP, DCB and DCEE) vapors in the range of 50 to 4000 ppm. It has to be noted that the sensitivity of the studied sensors to different analytes was noticeably different. In particular, the sensitivity to DMMP, TMP and DCEE was higher than to DEP and DCB. Hence, the respective plots in the corresponding figures are separated by the concentration ranges indicated on the bottom and top axes.

As can be seen from the plots, the calixarene types CA1050 and CA1089 show high and selective sensitivity to organophosphorous compounds. At this, CA1050 exhibits stronger response to DMMP, while CA1089 to DEP. High sensitivity to organochlorine compounds is also exhibited by the CA1091 calixarene, but it is less sensitive to organophosphorous analytes.

It is also worth noting that the response magnitude is determined by both the nature of the interaction between the analyte molecules and the sensitive layer, and the analyte concentration. It has to be taken into account that the saturated vapor pressure at normal conditions is close to 10 mm Hg for DEP, while for DMMP and TMP it is only about 1 mm Hg. At the same time, the chemosensor responses to DMMP turned out to have noticeably larger magnitudes than to DEP. This indicates that the sensitivity as well as selectivity of the chemosensors is determined mainly by the chemical structure of the sensitive compounds – calixarenes.

The minimum detectable concentrations of the analytes by the QCM sensors (the detection thresholds) are listed in Table.

For a better general depiction of the sensitivity pattern, the responses of the three selected sensor types to the diluted by a factor of 10 saturated vapor of each of the target analytes are summarized in the bar plots in Fig. 8.

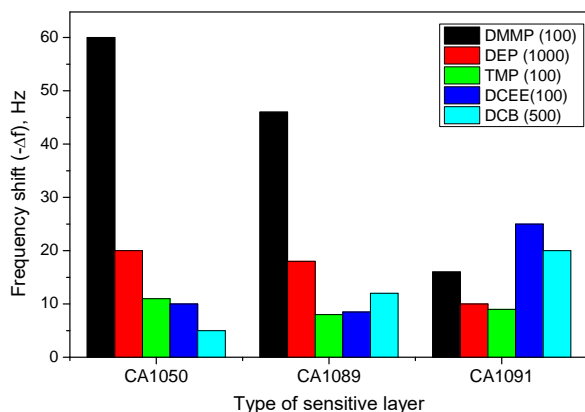


Fig. 8. Bar plots of the responses of an array of QCM sensors with CA1050, CA1089 and CA1091 calixarene sensitive layers to the injected vapors of all the studied PS simulants at the concentrations corresponding to a tenfold dilution of the saturated vapors of the respective analytes.

Table. Detection thresholds (in ppm) of the sensors with calixarene films.

Analyte \ CA type	DMMP	DEP	TMP	DCEE	DCB
CA1050	<10	750	80	80	1200
CA1089	10	500	70	75	350
CA1091	20	1000	80	10	200

The response plots clearly demonstrate sufficiently high selectivity of the used sensors with respect to the poisonous compound simulants. In particular, CA1050 exhibits the best sensitivity toward DMMP, and CA1091 toward DCEE, respectively.

3.3. Development of chemoresistive “electronic nose” for detection and identification of poisonous substance simulants

The chemoresistive sensors based on two nanocomposite types, PVDF/P3MT and TiO₂/PANI, were combined into a two-element sensor array to investigate the possibility of identification of the organophosphorous and organochlorine poisonous volatile compound simulants in a wide concentration range by using the statistical analysis methods for processing the data obtained from this array. For this purpose, applying the principal component analysis [35], the responses of the sensor array were visualized as so called “chemical images” of the studied analytes on a factor plane.

It has to be noted that the above mentioned method allows to reduce the dimensionality of the initial n -dimensional database of the sensor array responses down to two principal components PC1 and PC2, which can be represented on a plane. However, no dimensionality is reduced if a sensor array is composed of only two sensors (provided that each sensor response is represented by a single numeric value). That is, the principal components plane coincides with the sensor responses plane in this case. Instead, the PCA procedure results in rotation of a coordinate system in such a way that the new coordinate axes are aligned with the directions of the maximum scattering of the sensor responses. Principal components are characterized by the associated variance fraction, whose percentage value defines the completeness of the representation of the experimental data by the corresponding component. If the value of the total variance of both principal components is greater than 90%, such representation has high informational capacity. The points corresponding to the chemical image of an analyte form visually distinct areas on the principal components plane, and the absence of overlapping areas indicates high selectivity of a sensor array.

Fig. 9 shows a representation of the responses of the above mentioned sensor array on a principal components plane. It can be seen from this figure that DMMP (the simulant of Sarine CWA) is reliably distinguishable from all the other tested analytes. The organochlorine simulants DCB and DCEE are also well identified.

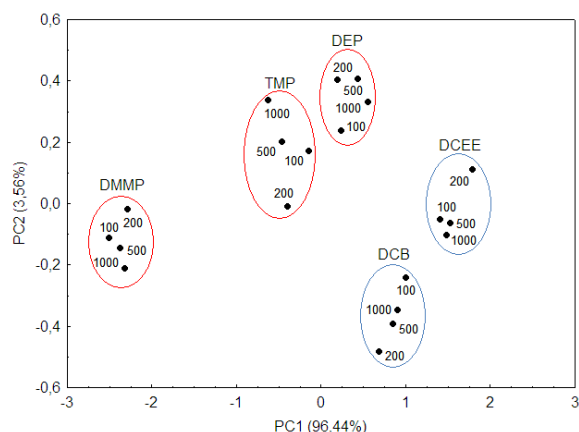


Fig. 9. Representation of chemical images of the five specified types of organophosphorous and organochlorine PS simulants at the concentrations of 100 to 1000 ppm on the principal components plane (sensors response plane). The images were obtained from the responses of a two-element sensor array based on the TiO_2/PANI and PVDF/P3MT nanocomposite layers.

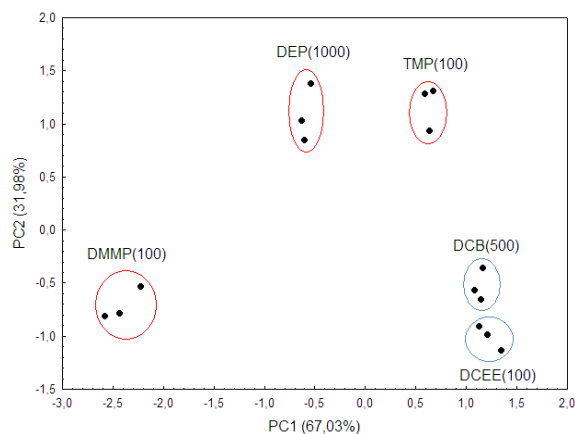


Fig. 10. Representation of the chemical images of the specified PS simulants at the concentrations corresponding to the tenfold dilution of the saturated vapor of the analytes. The images were obtained from the responses of a three-element sensor array based on the CA1050, CA1089 and CA1091 calixarene layers.

Identification of the DEP and TMP simulants is somewhat worse albeit still reliable since the images of the corresponding sensor responses are separated by a certain distance. It is shown therefore that use of two specified sensors in a sensor array enables successful identification of the tested simulants at any concentrations in the range of 10 to 1000 ppm. This shows its sufficient selectivity for recognition of all classes of the mentioned toxic substances. It is also worth mentioning that reliable identification of simulants is generally achievable using just two or three most sensitive elements in a sensor array. Further increase of the number of chemosensors does not substantially change the recognition quality of the chemical images of tested analytes.

Similar statistical calculations with the principal component analysis were also done for the QCM sensor array composed of the three studied sensor types with the CA1050, CA1089 and CA1091 calixarene sensitive layers. Fig. 10 presents the responses of this three-element sensor array for a single concentration of each analyte, corresponding to the tenfold-diluted saturated vapor, on a principal components plane.

It can be seen from the diagram that DMMP is the most separated from the rest of the analyzed substances. In general, all the organophosphorous simulants (DMMP, DEP and TMP) are well identifiable. The identifiability of the organochlorine simulants (DCB and DCEE) is somewhat worse. However, it is important to note the high selectivity of this sensor array regarding the discrimination of organophosphorous and organochlorine compounds as separate classes of toxic substances.

4. Conclusions

In this work, we studied the sensing behavior of the two types of transducers based on piezoelectric quartz crystal microbalance and chemoresistive electrodes coated with thin sensitive layers of calixarenes and of intrinsically conducting polymer nanocomposites, respectively, upon the influence of poisonous substance simulant molecules from the gas phase.

The advantages of chemoresistive sensors include relatively rapid response (response time of less than one minute), selectivity regarding the discrimination and identification of organophosphorous and organochlorine compounds separately as different classes of substances, small size, and simple transduction principle. The advantages of quartz crystal microbalance sensors include rapid response (tens of seconds), availability of cheap disposable sensor elements (commercial 10 MHz AT-cut quartz crystals), and portability of instrumentation combined with sampling system. More detailed summary on both types of studied transducers is as follows.

Conclusions on chemoresistors

◆ It was found that the studied chemoresistive sensors are sufficiently selective regarding the discrimination separately of organophosphorous and organochlorine compounds, exhibiting responses of opposite signs to these substance classes.

◆ The detection thresholds for the analyzed PS simulants ranged from 10 ppm (for DMMP and DCEE) to 100 ppm (for the rest of the simulants). The maximum relative response magnitude was about 4–5% at the concentrations of the tested compounds of the order of 100 ppm. The sensor response time was below 1 minute at this.

◆ It was demonstrated that an array of two chemoresistive sensors based on the PVDF/P3MT and TiO_2/PANI nanocomposites was able to reliably identify all five of the studied organophosphorous and organochlorine PS types in a wide concentration range, using the “electronic nose” approach.

Conclusions on QCM sensors

◆ It was found that some calix[4]arene derivatives among the tested films exhibit sufficiently high selective sensitivity and can be used therefore as the sensitive layers in chemosensory devices for detection of the studied PS simulants.

◆ The sensors based on CA1050 and CA1089 calixarenes were found to be most sensitive toward the organophosphorous compounds and the sensor based on CA1091 calixarene toward the organochlorine compounds, respectively. The detection threshold of these sensors for the analyzed PS was from 10 ppm (for DMMP and DCEE) to 100 ppm and more (for the rest of analytes), with the response time of about 10 to 20 s.

◆ It was demonstrated that an array of two or three QCM sensors of different types was able to reliably identify and discriminate between the organophosphorous and organochlorine poisonous substance classes using the “electronic nose” approach.

Due to the fast response to the changes in a gas environment, the developed chemosensory systems can be successfully applied to implement the portable alarm devices for detection of toxic gaseous substances in the air. At the same time, because of insufficient selectivity of the used sensors (their cross-sensitivity), it is appropriate to use their arrays to continuously monitor the environment. The result is provided in the form of qualitative identification of toxic molecules in the air after a necessary delay by applying the “electronic nose” technology.

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References

- De Cauwer H., Somville F.J.M.P., Joillet M. Neurological aspects of chemical and biological terrorism: Guidelines for neurologists. *Acta Neurol. Belg.* 2017. **117**. P. 603–611. <https://doi.org/10.1007/s13760-017-0774-y>.
- Zehra N., Kalita A., Malik A.H. *et al.* Conjugated polymer-based electrical sensor for ultratrace vapor-phase detection of nerve agent mimics. *ACS Sens.* 2020. **5**. P. 191–198. <https://doi.org/10.1021/acssensors.9b02031>.
- Kim K., Tsay O.G., Atwood D.A., Churchill D.G. Destruction and detection of chemical warfare agents. *Chem. Rev.* 2011. **111**. P. 5345–5403. <https://doi.org/10.1021/cr100193y>.
- Zeng L., Zeng H., Jiang L. *et al.* A single fluorescent chemosensor for simultaneous discriminative detection of gaseous phosgene and a nerve agent mimic. *Anal. Chem.* 2019. **91**. P. 12070–12076. <https://doi.org/10.1021/acs.analchem.9b03230>.
- García-Briones G.S., Olvera-Sosa M., Palestino G. Novel supported nanostructured sensors for chemical warfare agents (CWAs) detection. In: C. Bittencourt, C. Ewels, E. Llobet (eds) *Nanoscale Materials for Warfare Agent Detection: Nanoscience for Security. NMWAD 2017. NATO Science for Peace and Security Series A: Chemistry and Biology*. 2019. P. 225–251. Springer, Dordrecht. https://doi.org/10.1007/978-94-024-1620-6_11.
- Zhu R., Azzarelli J.M., Swager T.M. Wireless hazard badges to detect nerve-agent simulants. *Angew. Chem. Int. Ed.* 2016. **55**, Issue 3. P. 9662–9666. <https://doi.org/10.1002/anie.201604431>.
- Park S.Y., Kim Y., Kim T. *et al.* Chemosensitive materials for electronic nose: Progress, perspectives, and challenges. *InfoMat.* 2019. **1**, Issue 3. P. 289–316. <https://doi.org/10.1002/inf2.12029>.
- Kaushik A., Kumar R., Arya S.K. *et al.* Organic–inorganic hybrid nanocomposite-based gas sensors for environmental monitoring. *Chem. Rev.* 2015. **115**. P. 4571–4606. <https://doi.org/10.1021/cr400659h>.
- Potyrailo R.A. Multivariable sensors for ubiquitous monitoring of gases in the era of internet of things and industrial internet. *Chem. Rev.* 2016. **116**. P. 11877–11923. <https://doi.org/10.1021/acs.chemrev.6b00187>.
- Bigiani L., Zappa D., Barreca D. *et al.* Sensing nitrogen mustard gas simulant at the ppb scale via selective dual-site activation at Au/Mn₃O₄ interfaces. *ACS Appl. Mater. Interfaces.* 2019. **11**. P. 23692–23700. <https://doi.org/10.1021/acsami.9b04875>.
- Bigiani L., Zappa D., Maccato C. *et al.* Quasi-1D MnO₂ nanocomposites as gas sensors for hazardous chemicals. *Appl. Surf. Sci.* 2020. **512**. Art. id. 145667. <https://doi.org/10.1016/j.apsusc.2020.145667>.
- Chang C.P., Yuan C.L. The fabrication of a MWNTs–polymer composite chemoresistive sensor array to discriminate between chemical toxic agents. *J. Mater. Sci.* 2009. **44**. P. 5485–5493. <https://doi.org/10.1007/s10853-009-3766-3>.
- Cho S., Kwon O.S., You S.A., Jang J. Shape-controlled polyaniline chemiresistors for high-performance DMMP sensors: Effect of morphologies and charge-transport properties. *J. Mater. Chem. A.* 2013. **1**. P. 5679–5688. <https://doi.org/10.1039/C3TA01427D>.
- Yu H., Han H., Jang J., Cho S. Fabrication and optimization of conductive paper based on screen-printed polyaniline/graphene patterns for nerve agent detection. *ACS Omega.* 2019. **4**. P. 5586–5594. <https://doi.org/10.1021/acsomega.9b00371>.
- Lee J.S., Shin D.H., Jun J., Jang J. Multidimensional polypyrrole/iron oxyhydroxide hybrid nanoparticles for chemical nerve gas agent sensing application. *ACS Nano.* 2013. **7**. P. 10139–10147. <https://doi.org/10.1021/nn404353w>.
- Jun J., Lee J.S., Shin D.H. *et al.* Fabrication of a one-dimensional tube-in-tube polypyrrole/tin oxide structure for highly sensitive DMMP sensor applications. *J. Mater. Chem. A.* 2017. **5**. P. 17335–17340. <https://doi.org/10.1039/C7TA02725G>.

17. Fennell J.F., Hamaguchi H., Yoon B., Swager T.M. Chemiresistor devices for chemical warfare agent detection based on polymer wrapped single-walled carbon nanotubes. *Sensors*. 2017. **17**. Article id. 982. <https://doi.org/10.3390/s17050982>.
18. Ogurtsov N., Bliznyuk V., Mamykin A. *et al.* Poly(vinylidene fluoride)/poly(3-methylthiophene) core-shell nanocomposites with improved structural and electronic properties of the conducting polymer component. *Phys. Chem. Chem. Phys.* 2018. **20**. P. 6450–6461. <https://doi.org/10.1039/C7CP07604E>.
19. Kukla O.L., Mamykin A.V., Pud A.A. *et al.* Nanostructured electroconductive composite materials for detecting phosphorus and chlororoganic substances. *Collection of scientific papers, X Int. sci. conf. "Functional basis of nanoelectronics"*. September 16–21, 2019, Kharkiv–Odesa, Ukraine. P. 70–73.
20. Kukla O.L., Mamykin A.V., Ogurtsov N.A. *et al.* Properties of the nanocomposite based on poly(3-methylthiophene). *Abstracts of 16th Int. conf. "Physics and technology of thin films and nanosystems" (ICPTTFN-XVI)*. May 15–20, 2017, Ivano-Frankivsk, Ukraine. P. 292.
21. Ogurtsov N., Bliznyuk V., Mamykin A. *et al.* Enhanced properties of the conducting polymer in the PVDF/poly(3-methylthiophene) nanocomposites. *Abstracts of 11th Int. conf. "Electronic processes in organic and inorganic materials" (ICEPOM-11)*. May 21–25, 2018, Ivano-Frankivsk, Ukraine. P. 56.
22. Myronyuk I.Ye., Mamykin A.V., Kukla O.L., Pud A.A. The doping degree effects in sensitivity of polyaniline and its coreshell composite with polyvinylidene fluoride to the volatile organic acids. *Abstracts of 11th Int. conf. "Electronic processes in organic and inorganic materials" (ICEPOM-11)*. May 21–25, 2018, Ivano-Frankivsk, Ukraine. P. 132.
23. Ballantine D.S., Martin S.J. White R.M. *et al.* *Acoustic Wave Sensors: Theory, Design and Physico-Chemical Applications*. Acad. Press, New York, 1997. P. 237.
24. Auge J., Hauptmann P., Eichelbaum F., Rosler S. Quartz crystal microbalance sensor in liquids. *Sensors and Actuators B*. 1994. **18–19**. P. 518–522. [https://doi.org/10.1016/0925-4005\(93\)00983-6](https://doi.org/10.1016/0925-4005(93)00983-6).
25. *Calixarenes*. Z. Asfari, V. Boehmer, J. Harowfield, J. Vicens (Eds.). Kluwer Academic Publishers, Dodrecht, 2001. P. 496–512.
26. Safina G., Gavrilova O., Ziganshin M. *et al.* recognition of chloroform by divergent polymorphic transitions in tert-butylthiacalix[4]arene tetrasubstituted with N-(2-hydroxyethyl)-carbamoylmethoxy groups in a lower rim. *Mendeleev Communications*. 2011. **21**, No 5. P. 291–292. <https://doi.org/10.1016/j.mencom.2011.09.022>.
27. Kazantseva Z.I., Koshets I.A., Drapailo A.B. *et al.* Sensory features of tiacalixarene films towards toxic and explosive volatile compounds. *Sensor Electronics and Microsystem Technologies*. 2021. **18**, No 3. P. 51–63. <https://doi.org/10.18524/1815-7459.2021.3.241064>.
28. Boublik T., Fried V. and Hala E. *The Vapour Pressures of Pure Substances*. Second Revised Edition. Amsterdam, Elsevier, 1984.
29. Ogurtsov N.A., Mamykin A.V., Kukla O.L. *et al.* The impact of interfacial interactions on structural, electronic, and sensing properties of poly(3-methylthiophene) in core-shell nanocomposites. Application for chemical warfare agent simulants detection. *Macromol. Mater. Eng.* 2022. **307**. P. 2100762. <https://doi.org/10.1002/mame.202100762>.
30. Mikhaylov S., Ogurtsov N., Noskov Yu. *et al.* Ammonia/amines electronic gas sensors based on hybrid polyaniline-TiO₂ nanocomposites. The effects of titania and the surface active doping acid. *RSC Adv*. 2015. **5**. P. 20218–20226. <https://doi.org/10.1039/C4RA16121A>.
31. Ogurtsov N.A., Pud A.A., Mamykin A.V., Kukla O.L. Conductive polymer composite based on poly-3-methylthiophene for sensor measurements. *Ukrainian patent for a utility model UA №131913*, publ. 11.02.2019, Bull. №3.
32. Sauerbrey G. Verwendung von Schwingquartzen zur Wagung dünner Schichten und zur Mikrowagung. *Z. Physik*. 1959. **155**. P. 206–222. <https://doi.org/10.1007/BF01337937>.
33. McKelvey J.M. and Hoelscher H.E. Apparatus for preparation of very dilute gas mixtures. *Analytical Chemistry*. 1957. **29**, Issue 1. P. 123–124. <https://doi.org/10.1021/ac60121a036>.
34. Kharchenko S., Drapailo A., Shishkina S. *et al.* Dibutyl phosphinoylmethoxythiacalix[4]arenes. Synthesis, structure, americium, europium and technetium extraction. *Supramolecular Chemistry*. 2014. **26** (10-12). P. 864–872. <https://doi.org/10.1080/10610278.2014.890198>.
35. Jurs P.C., Bakken G.A., McClelland H.E. Computational methods for the analysis of chemical sensor array data from volatile analytes. *Chem. Rev.* 2000. **100**. P. 2649–2678. <https://doi.org/10.1021/cr9800964>.

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- A.S. Pavluchenko:** formal analysis, data curation (partially), writing – original draft.
- Z.I. Kazantseva:** investigation, methodology, writing – original draft.
- I.A. Koshets:** formal analysis, investigation, methodology, writing – original draft.
- A.A. Pud:** conceptualization, resources, writing – original draft.
- N.A. Ogurtsov:** investigation, resources.
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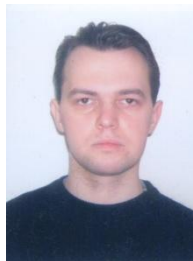
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Хемосенсорні системи типу „електронний ніс” для детектування газоподібних отруйних речовин

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Анотація. Робота присвячена дослідженню чутливості та селективності детектування ряду газоподібних імітаторів отруйних речовин (ОР) за допомогою двох типів сенсорних перетворювачів: 1) кварцового кристалічного мікробалансу (ККМ), що виявляє зсув частоти резонансу кварцових платівок, вкритих тонкими шарами каліксаренів, та 2) хеморезистивних електродів з шарами електропровідних полімерів (ЕПП), що змінюють електропровідність під впливом адсорбованих молекул газів. Концентрація аналізованих летких сполук варіювалася в межах від 10 до 1000 ppm. Поріг детектування в залежності від типу аналізованих речовин становив від 10 до 100 ppm для обох типів перетворювачів, швидкодія відгуків була в межах 10–20 с для ККМ сенсорів та до 1 хв для ЕПП сенсорів. Продемонстровано можливість якісної ідентифікації отруйних речовин у широкому діапазоні концентрацій за допомогою методів статистичного аналізу даних від сенсорного масиву.

Ключові слова: кварцовий кристалічний мікробаланс, хеморезистивні електроди, каліксарени, електропровідні полімери, наноконізити, фосфор- та хлорорганічні сполуки.