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# Light-Tunable Hybrid Organic-Inorganic Nanostructured Layers for Virtual Sensor Arrays †

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**Abstract:** Electronic nose (EN) is a most advanced technology for classification and identification of complex gaseous mixtures. The idea is to use a small set of low-selective sensors instead of huge number of specific ones. The response of such an array is a chemical image (CI) which is a mathematical (or graphic) representation of an analyte. The ability of an EN system to distinguish different mixtures is defined by its ability to produce unique CI. The latter is defined, and limited, first of all, by the sensor's adsorption properties. We propose the approach to increase the versatility of low-selective sensor arrays by using virtual sensors. By "virtual sensor" in this case we mean a sensor able to change its adsorption properties in conditions of illumination. Within this scenario, we were able to successfully distinguish between homologous alcohols (methyl, ethyl, and isopropyl) using organic-inorganic nanostructured sensitive layers based on ZnO nanoparticles and phthalocyanines (Pc). The performance of quartz crystal microbalance sensors with hybrid nanostructured organic-inorganic layers is increased in comparison with single-Pc ones. Using illumination allowed to obtain additional responses considered as virtual sensors. The both factors played the decisive role in the successful discrimination of alcohols.

**Keywords:** virtual sensors; chemical sensors; electronic nose; ZnO nanostructures; organic-inorganic nanostructured materials

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## 1. Introduction

Electronic nose (EN) is an advanced technology for fast identification of complex gaseous mixtures in such areas as food quality, environmental monitoring, counterfeit determination, medical diagnostics etc. The basis of an EN instrument is an array of cross-selective chemical sensors typically combining physical transducer and a chemical sensitive layer. Contrary to the approach when selective sensors are used, an array of low-selective sensors gives the response which can be interpreted as chemical image (CI) of the analyte. CI is a kind of graphic or mathematic representation of the analyte in the response space.

The functionality of such arrays is determined mostly by the adsorption properties of the sensitive layers. Each multisensor array is targeted to solve only a limited set of tasks and it will not be effective in other areas. This is one of the main problems limiting the wide spread of EN systems.

There are two most perspective approaches for overcoming the limited application area of low-selective sensors arrays. Both of them are concerned with the development of new sensing materials with advanced properties. The first approach lies in the development of new sensitive layers with improved sensitivity, repeatability and long-term stability. One of the most effective ways to implement this is to combine organic materials, which provide the necessary selectivity profile, with nanostructured inorganic ones.

The second approach is controlling of adsorption properties of sensor coatings, in other words, creation of virtual sensors. A virtual sensor—is a response of the same sensor operating in different conditions [1].

We propose to combine both approaches. Nanostructured organic-inorganic sensitive layers based on ZnO nanoparticles and three different phthalocyanines: metal free ($H_2Pc$), copper (CuPc) and lead (PbPc) phthalocyanines were created. We studied the adsorption properties of these layers and the possibility to control them by means of illumination. The combination of phthalocyanines with ZnO gave increased responses and improved reproducibility of experimental results. The use of illumination of the obtained sensor coatings made it possible to further improve the recognition ability of the arrays, as well as to obtain additional virtual sensors from which new adaptive arrays can be built for various tasks.

The significant increase of classification efficiency of the array based on hybrid organic-inorganic layers comparing with single-layer phthalocyanine sensors and additional benefits of virtual sensor approach is demonstrated on the example of classification of three alcohols: ethanol, methanol and isopropanol. As these compounds have similar physico-chemical properties they are quite a complicated target for classification by systems based on low-selective sensors. Therefore, the successful recognition of alcohols is a result that convincingly demonstrates the effectiveness of the used approaches.

## 2. Materials and Methods

The ZnO suspension was prepared as it described here [2]. The solutions were deposited on one of the electrodes of quartz crystal microbalance (QCM) sensors [3]. Then, Pc films were deposited by thermal evaporation of powder of metal free, copper and lead phthalocyanines (Sigma Aldrich) in vacuum.

The resonant frequency of QCM sensors decreases when its mass is increased: so, if an analyte is adsorbed on the surface, the oscillation frequency decreases and is recorded by the frequency meter. The difference between initial frequency and that measured in the current time in the course of adsorption is the measuring parameter F. The maximum frequency shift reached when the adsorption-desorption processes on the sensor's surface came into the equilibrium is the response amplitude $\Delta F$.

Ethanol, methanol and isopropanol were obtained from Sigma Aldrich. The concentration of analytes was 28,000 ppm.

Typical measurement procedure involved the following stages. Initially, blowing dry air went through the gas chamber until the transducer frequency was stabilized (±2 Hz). Then a sample has been injected using the dynamic dilution to get a desired analyte concentration. After the signal's saturation was achieved, blowing dry air through the gas chamber was used to remove vapor residue until the QCM frequency returned to its initial value.

Agilent Technology LEDs with central wavelengths of 472 nm and 615 nm were used for illumination of the sensor's surfaces. These regions of spectra were chosen considering the spectral properties of both Pcs and ZnO. The strongest mutual influence of the organic and inorganic components of the hybrid structure was observed here. Indeed, illumination within the "window" of Pc's absorption spectra (472 nm, 21,186 $cm^{-1}$) generates states with partial charge transfer, which can significantly affect the features of electrostatic interactions at the interface "ZnO-Pc". Excitation within a high-intensity phthalocyanines' Q band (615 nm, 17,886 $cm^{-1}$) makes it possible not only to maintain a high population of excited states using low-power sources, but also to modify their electron density distribution [4].

The classification of the experimental data was performed by the cluster analysis method in the fuzzy logic format [5]. The calculations were performed in the S-Plus environment by Math. Soft Inc. The advantage of this method is the presence of a quantitative assessment of classification efficiency: the silhouette width (SW). This parameter reproduces the degree of belonging of an object to a certain cluster [6].

Normalized to unity amplitudes of sensor responses (1) were used as the initial data for analysis in the S-Plus. $F_{norm}$ were used for chemical images representation as well.

$$F_{norm} = \frac{F_n}{\sum F_n} \quad (1)$$

Reproducibility of the responses was evaluated by the coefficient of variation Cv, which is the ratio of the standard deviation to the mean value, taken as a percentage.

## 3. Results and Discussion

The cluster analysis results for the array of sensors with $H_2Pc$, CuPc and PbPc layers (without ZnO underlayers) are presented on Figure 1. Each point on the plot (Figure 1, left) represents a measurement result: a cumulative array response for one or another analyte transformed for the best graphic representation. Each bar on the diagram (Figure 1, right) represents a silhouette width for corresponding response. Here and after the numbers on the silhouette plot correspond to: 1, 2, 3—to the methanol, 4, 5, 6—ethanol, 7, 8, 9—isopropanol.

As it is seen from the silhouette width plot (in the right) the wrong classification takes place: negative SW values indicate that the data most likely belong to another cluster. Therefore, this array cannot be used for reliable classification of such analytes.

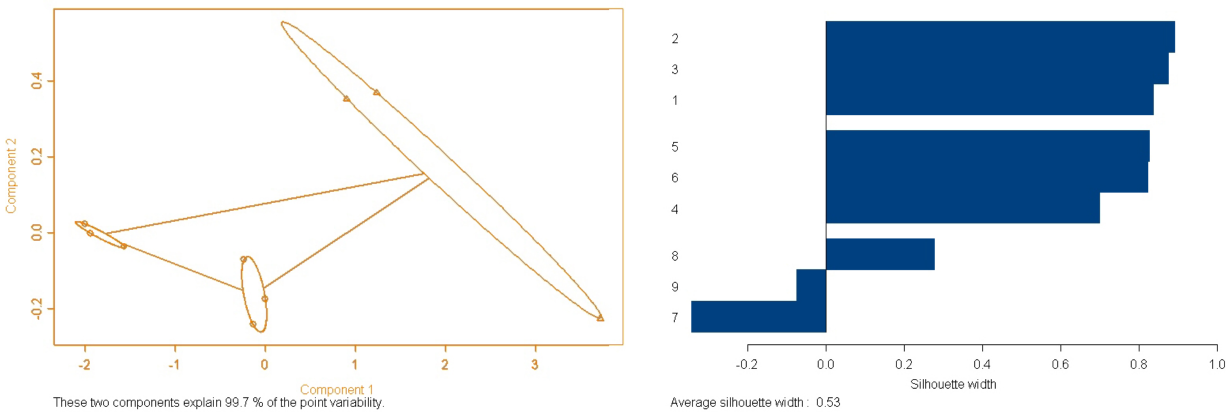


**Figure 1.** Classification of methyl, ethyl and isopropyl alcohols by sensor array based on QCM sensors with $H_2Pc$, CuPc and PbPc coatings. The classification failed as there are negative values of silhouette width.

The main reasons of failed classification in this case are obvious if analyze the data presented on Figure 2a. On the left, the response amplitudes are presented while on the right there are chemical images of the alcohols built as the normalized responses of three sensors ($F_{norm}$). Although the CIs look quite different and it seems that the classification should be good, low responses values and insufficient reproducibility (Cv is 25–54%) played their decisive role in failed classification.

The situation is totally different when the hybrid ZnO-Pc nanostructured layers are used. As it is seen from Figure 2b, the response amplitudes increased by 5–10 times. The Cv decreased to 2.5–9.2%). This has allowed to classify the alcohols despite of somewhat increased similarity of chemical images.

Another noteworthy result is change of sensors functionality comparing to pure Pc films. Indeed, three-sensor arrays based on Pc and ZnO-Pc films, form different response patterns for the same analytes. This means that combination of Pc with ZnO nanostructures results not only in the increase of sensitivity and reproducibility, but gives us new sensors with different adsorption properties.

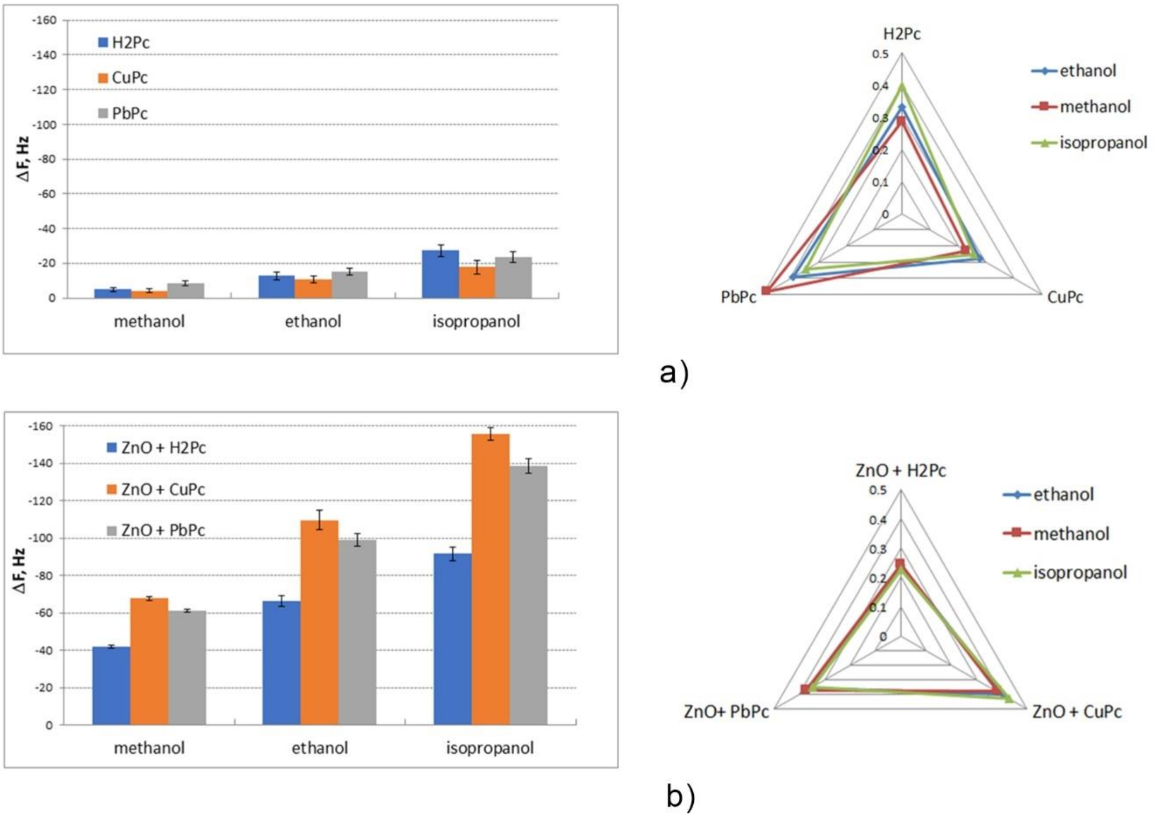


**Figure 2.** Response amplitudes (**left**) and chemical images (**right**) of methyl, ethyl and isopropyl alcohols for QCM sensors arrays: (**a**) based on $H_2Pc$, CuPc and PbPc sensitive layers; (**b**) based on hybrid ZnO-$H_2Pc$, ZnO-CuPc and ZnO-PbPc layers.

The results of classification of three alcohols by the array based on ZnO-$H_2Pc$, ZnO-CuPc and ZnO-PbPc sensors are presented on Figure 3. Figure 3a—the classification without illumination, Figure 3b,c—classification of the results obtained from sensors illuminated by 472 nm and 615 nm LEDs respectively.

The data obtained from the array of ZnO-Pc sensors are classified adequately (SW value is 0.77), but the classification of data obtained during illumination is much better. Indeed, as can be seen from Figure 3b,c, the clusters are spaced at greater distances, and the objects within each cluster are more compactly located. The best classification is for illumination in the 472 nm region. The SW value for this case is 0.91.

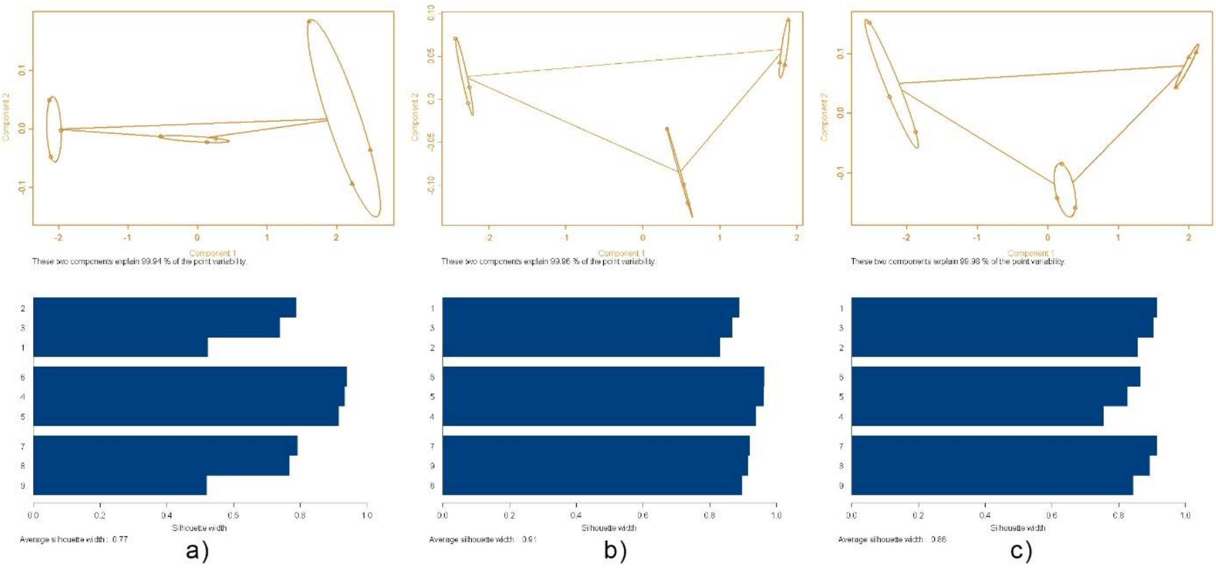


**Figure 3.** Classification of methyl, ethyl and isopropyl alcohols by sensor array based on QCM sensors with hybrid ZnO-H2Pc, ZnO-CuPc and ZnO-PbPc layers; (**a**) without illumination; (**b**) under illumination in 472 nm region; (**c**) under illumination in 615nm region.

The improvement of classification efficiency in conditions of illumination is explained by further increase of reproducibility of data and by change of adsorption properties caused by light absorption.

The change of adsorption properties is summarized on the Figure 4. Here you can see the chemical images of three alcohols built on the basis of the whole experimental data set: the responses of three sensors operating without illumination and the same sensors under illumination by blue and orange light. It is seen from the diagram that not only the response magnitudes themselves but the response patterns are different. So, the selectivity profile of hybrid materials changes under illumination. Therefore, virtual sensors may be used as independent elements of multisensor arrays. In such a way, the obtained array is a basis for further optimization and finding the best set of sensors for a definite task. The difference with classic approaches when sensors are been selected to form an optimal array is that you don’t have to replace sensors in the experimental setup but just select the best illumination program. This opens the way for the development of tunable miniaturized EN systems with much wider application area.

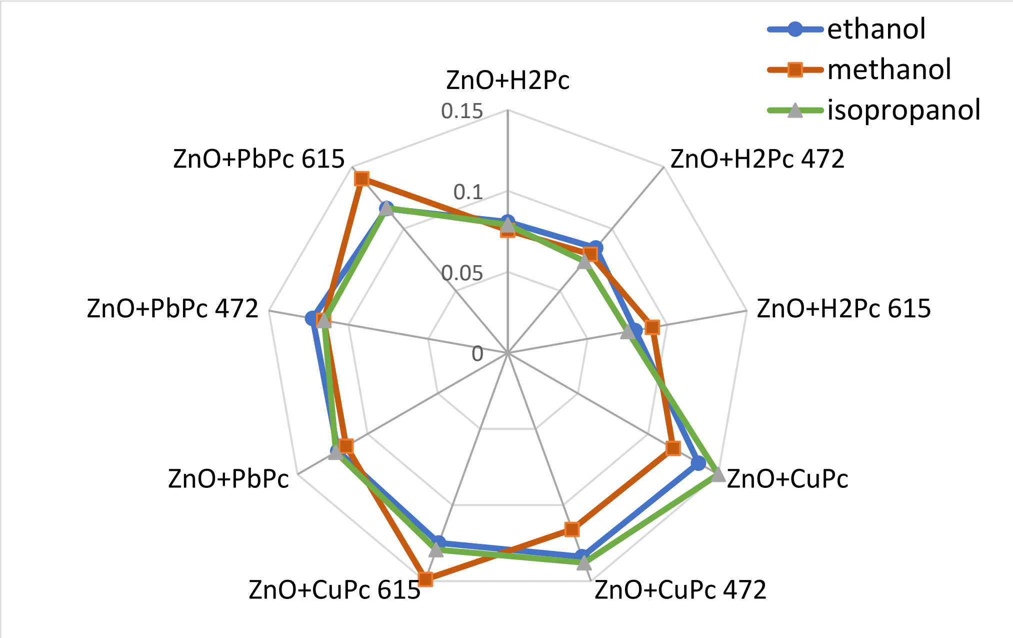


**Figure 4.** Chemical images of three alcohols built on the basis of responses of three sensors with ZnO-$H_2$Pc, ZnO-CuPc and ZnO-PbPc layers and virtual ones that are the same sensors operating under illumination by 472 nm and 615 nm LEDs.

## 3. Conclusions

The proper selection of sensing materials considering their photosensitive properties opens wide perspectives for the development of compact and versatile electronic nose systems with the possibility of their tuning for different tasks using illumination. Combining of organic and inorganic nanostructured materials allow increasing performance of individual sensors that gives an additional contribution in the classification performance.

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