

Development of the colorimetric sensor array for detection of explosives and volatile organic compounds in air

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ABSTRACT

In the framework of the research project 'Xsense' at the Technical University of Denmark (DTU) we are developing a simple colorimetric sensor array which can be useful in detection of explosives like DNT and TNT, and identification of volatile organic compounds in the presence of water vapor in air. The technology is based on an array of chemo-responsive dyes immobilized on a solid support. Upon exposure to the analyte in suspicion the dye array changes color. Each chosen dye reacts chemo selectively with analytes of interest. A change in a color signature indicates the presence of unknown explosives and volatile organic compounds (VOCs).

We are working towards the selection of dyes that undergo color changes in the presence of explosives and VOCs, as well as the development of an immobilization method for the molecules. Digital imaging of the dye array before and after exposure to the analytes creates a color difference map which gives a unique fingerprint for each explosive and volatile organic compound. Such sensing technology can be used to screen for relevant explosives in a complex background as well as to distinguish mixtures of volatile organic compounds distributed in gas phase. This sensor array is inexpensive, and can potentially be produced as single use disposable.

Keywords: colorimetric sensor array, DNT, chemo-responsive dyes, volatile organic compounds, color difference map, principal component analysis.

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1. INTRODUCTION

Nowadays international terrorism creates public concern in various forms, situations and places. New technology must be developed to easily detect a variety of illegal chemicals, substances, drugs and explosives

carrying by suspects as well as hidden in mails, luggage and vehicles. Another requirement is that the technologies should be portable, rapid, highly sensitive, specific (minimal false positives), and low cost.

One of the most traditional and common technology that involves the detection and classification of volatile organic compounds in the gas phase is electronic nose [1-3]. The electronic nose is the device that combines a chemical-sensing and pattern-recognition systems; in nature it could be the sensing organ of an animal like the nose of a bomb-sniffing dog. The sensor can recognize specific molecules and can be applied in many areas of research, such as food quality analysis, medical diagnostics, explosives and toxins detection, and environmental monitoring. Further, the sensor has shown high capability for detecting explosives, such as ammonium nitrate, mineral explosives, and DNT in low concentrations [4]. Nevertheless, the traditionally applied electronic nose technique has limitations due to the detection problems at low analyte concentrations, at high or low temperature and humidity.

Information about volatile organic compounds presented in the gas phase may be provided by the colorimetric sensor array technology. Suslick et al. described the application of the colorimetric sensor array, which measures volatile organic compounds in the gas phase [5, 6] as well as different organic compounds in the liquid phase [7, 8]. This sensor was able to monitor different VOCs in real-time; compounds were able to represent the common organic functionality such as: amines, carboxylic, strong acids, thiols, ketones, aldehydes, etc. Traditionally, chemically responsive dyes are immobilized on a hydrophobic membrane manually or using split-pin contact printing technique. Suslick et al. has designed the sensor array based on the application of three successive dye classes: Lewis acid/base dyes (i.e. metal ion containing dyes), Brønsted acid-base indicators, and dyes with large permanent dipoles (i.e. zwitterionic solvatochromic dyes). In the presence of the specific target dyes were able to change their colors; such identification method provided a color pattern for each specific analyte. The changes in color is the result of the selective interaction between molecules and atoms, such as dipolar and multipolar interactions, acid-based interaction, van der Waals interaction and physical adsorption [9]. The colorimetric sensor array technique presented by Suslick et al. showed the great potential for real-time monitoring of analytes such as amines, carboxylic acids, and thiols with extended sensitivity below 6-60 ppm [5].

In our group we are developing a simple colorimetric sensor array which can be useful in detection and identification of explosives like DNT and TNT, and also VOCs in air. The technology relies on an array of a new class of chemo-selective dyes immobilized on a solid support. We are working towards the selection of molecules that undergo color changes in the presence of explosives, as well as development of an immobilization method for the molecules. Our current colorimetric sensor array contains 15 chemically responsive dyes immobilized on a silica gel membrane. Upon exposure to the analyte in suspicion the dye array changes color. A change in a color signature indicates the presence of unknown explosives and VOCs. Each chosen dye reacts chemo-selectively with analytes of interest. Digital imaging of the dye array before and after exposure to the analytes creates a color difference map which composes a unique fingerprint for each analyte. Such sensing technology can be used as a screening method for relevant explosives in a complex background as well as distinguish mixture of VOCs distributed in gas phase.

The colorimetric sensor array is a rapid detection method; the signal is achieved within 30-60 sec. Another advantage of this technique is that the colorimetric sensor array is inexpensive approach, and can potentially be produced as single use disposable.

2. MATERIALS AND METHODS

2.1 Reagents:

Analytes that has been exposed to our sensor: acetone, acetic acid, dichlorethane, 2,4-dinitrotoluene (DNT), formic acid, hydrochloric acid, methanol, propanol, toluene were from Sigma (St. Louise, MO, USA). Ethanol was ordered from Solveco Chemicals AB (Dramstadt, Germany). All chemicals were analytical grade and used without further purification.

For the colorimetric sensor array, 15 different compounds were selected from the new class of chemicals, and used as the chemo-responsive dyes. Stock solutions of dyes (4 mM in dichloroethane) were freshly prepared and stored in a lightproof flask before use.

2.2 Colorimetric sensor array:

A colorimetric sensor array was designed using the 15 selected dyes. Dyes were immobilized onto silica gel Kieselgel 60F₂₅₄ plates (Merck KGaA, Germany) in the working volume of 1 μ l. Since mass transport and time response are correlated values, saturated conditions of analytes (acetone, acetic acid, DNT, formic acid, hydrochloric acid, methanol, ethanol, propanol, and toluene) were prepared. Detection of acetone, acetic acid, formic acid, hydrochloric acid, methanol, ethanol, propanol, and toluene were performed at 24° C. DNT was detected at the elevated temperature of 100° C.

The experiments were of 2 minute duration. Pictures were scanned through an ordinary flatbed scanner (Epson V750-M Pro Perfection scanner) immediately after immobilization of dyes and after exposure of analytes. Pictures were obtained at 600 dots per inch in RGB color format.

2.3 Data processing:

In order to extract the color code from each dye the position of each dye on the image must be located. The exact procedure that was used is described in a technical report [10]. Each dye is represented using the red, green, and blue color scheme. In this model every color is provided as red, green, and blue color (RGB); RGB values are given in the 0-255 integer range. The minimum intensity of the color gives black (0;0;0) and maximum white color (255;255;255). After the dye was located and converted to RGB values, we calculated the median value of each. We used the median instead of the mean in order to be more robust to noise and outliers.

A traditional difference map was obtained from the values of red, green or blue colors after exposure minus the value of red, green or blue color before the exposure. Since the RGB color scheme does not allow negative values the absolute difference was taken. Further in order to enhance the visibility of the colors difference maps the RGB values were first scaled with a factor 5 and then shifted by 10. The instances where the difference map (before scaling) resulted in a color value lower than 3 the pixel was rounded down to a color value of 0. However, elimination of negative values and the need for scaling in order to make the differences visible imply that color the difference map does not produce unique representations and further that sign-information is lost. As an alternative we suggest to use bar plots where each bar represents the cumulative density function (cdf) of difference values.

2.4 Statistical analysis of data.

Data obtained with the colorimetric sensor array has been evaluated by using the principal component analysis (PCA) method [9]. PCA is a simple, non-parametric method which is relevant to extract data among different analytes into the minimum number of dimensions. In order to apply the method the difference maps must be represented as a matrix. As described earlier, each difference map can be represented using 45 color numbers hence each difference map corresponds to a vector in a 45 dimensional space (each map contains 15 dyes and each dye yields 3 values). We then construct a data matrix where each column corresponds to a difference map. PCA was applied to this data matrix.

3. RESULTS AND DISCUSSION

It is well known that mass transport is a limiting factor for many assays that effects on the assay response. However, the colorimetric sensor array was indicated as a relatively fast method where the significant color changes were observed within 2 minutes under ambient conditions. Color change patterns manifest the presence of a specific or given targets, in other words, observed color change patterns indicate a particular vapor of the individual analyte.

Suslick et al. demonstrated the capability of the colorimetric sensor array to sense different analytes even a mixture of analytes. The colorimetric sensor array had ability to monitor in real-time 100 different VOCs with various organic functionalities: including primary, secondary, tertiary, and aromatic substituents of amines, arenes, alcohols, aldehydes, carboxylic acids, esters, hydrocarbons, ketones, phosphines, and thiols [9]. As has been mentioned in the introduction part this group has successfully used three classes of dyes: Lewis acid or base dyes (i.e. metal ion containing dyes), Brønsted acidic or basic dyes (i.e. pH indicators), and dyes with large permanent dipoles (i.e. zwitterionic solvatochromic dyes). The specific interaction between molecules and atoms, such as dipolar and multipolar interactions, acid-based interaction, van der Waals interaction and physical adsorption cost the changes of the colors [9].

Suslick et al. described the wide application of the colorimetric sensor array in the many areas of research. Reported applications in the detection of ammonia from exhaled breath and the presence of *Helicobacter pylori* that causes chromatic inflammation (gastritis) [11]; *E.coli*, *Staphylococcus aureus* as an indicator of the food freshness; *Moraxella catarrhalis* that causes bronchitis, pneumonia and meningitis, the detection was based on the measurements of CO₂ produced by microorganisms during growth [12]. Examples are the determination of the ethanol rate and organic compounds in the beer [8] and sugar in soft drink samples [13].

Using the similar detecting principle and a new class of chemo-responsive dyes, we were able to apply the colorimetric sensor array not only for screening volatile organic compounds, like acetone, acetic acid, ethanol, formic acid, hydrochloric acid, methanol, propanol, and toluene, but also for the first time, for probing of explosives, like DNT in the gas phase.

For fabrication of the colorimetric sensor array 15 chemically responsive dyes were immobilized on a solid support, silica gel membrane, as shown in Figure 1. After the exposure of DNT the chemo-selective dye array changed color (Fig. 1). The changes in a color signature indicate the presence of explosives or VOCs. Almost each chosen dye reacted chemo-selectively with the analyte of interest. The resulting colorimetric sensor was used for the analysis vapor of acetone, acetic acid, ethanol, formic acid, hydrochloric acid, methanol, propanol, and toluene. For each analyte average color change profile was obtained and shown in Figure 2. Digital imaging of the chemo-selective dye array before and after exposure can be used for generating of the color difference map by pixel subtraction. A difference map is able to compose a unique fingerprint for each analyte.

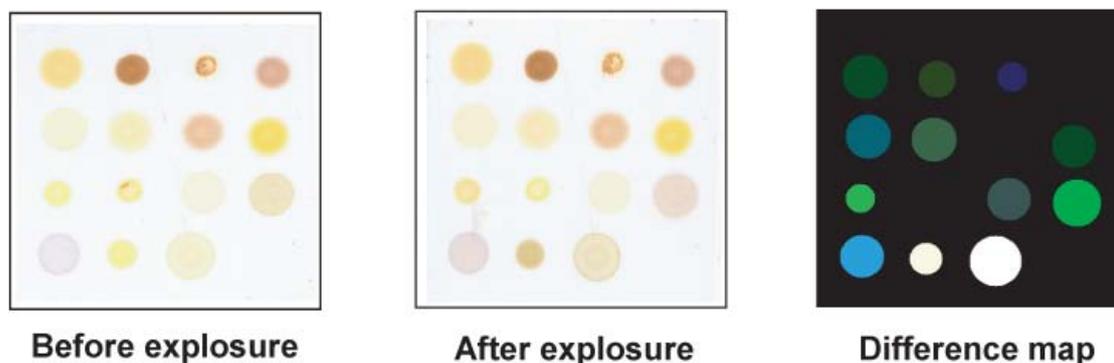


Figure 1. A difference map of the colorimetric sensor array obtained before and after the exposure of DNT in the gas phase. The image was generated after the mathematical analysis of the color changes. A difference map presents the difference in absolute value of RGB colors obtained from the absolute value of red, green or blue color after the exposure of DNT minus the absolute value of red, green or blue color before the exposure of DNT.

Even without the statistical analysis it was possible to observe the color changes after the explosion of analytes. The mathematical analysis is described in the material and method section. The analysis demonstrates the familiar similarity in the response among compounds with common organic properties: alcohols, organic and inorganic acids, ketones and arenes. The strong signal was obtained in the presence of acids, the color-changes profile shows the significant different between inorganic and organic acids (Fig. 2). By using the chemo-selective dye array was possible to identify closely related alcohols; some dyes selectively changed color in the presence of methanol, ethanol and propanol

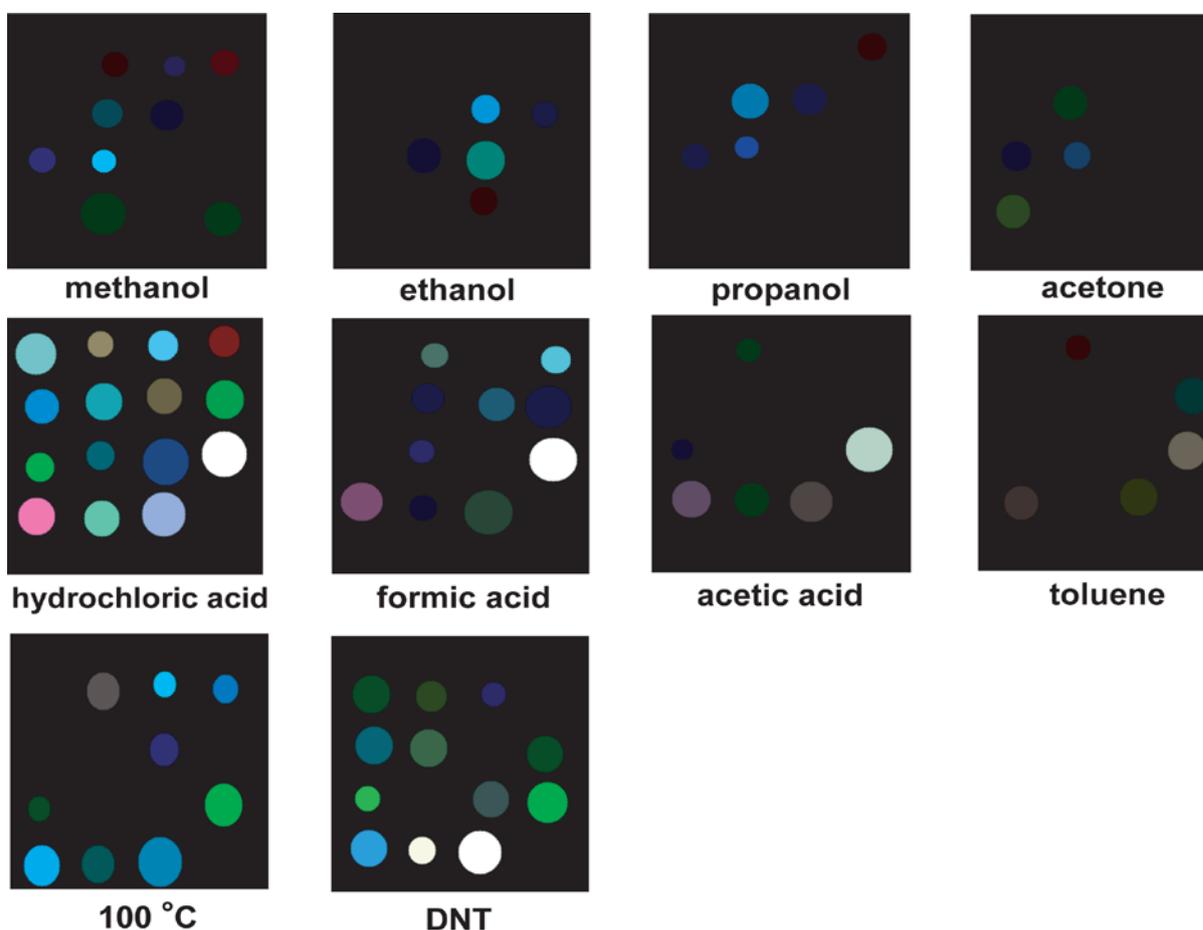


Figure 2. Difference maps of the colorimetric sensor array obtained in the presence of volatile organic compounds and DNT in the gas phase; saturated analyte vapor at room temperature. Images were generated after the mathematical calculations of the color changes; and presented as the difference map obtained from the absolute values of RGB values of each dye spot before and after the exposure of the targets.

Since explosives have the low vapor pressure at the room temperature [14, 15], to increase the analyte vapor DNT was heated up to 100 °C. The same working principle will be used in the commercialized sensor. The slide with the ordinary immobilized dyes was also heated up at the same elevated temperature; those results were used as a control. Results obtained from the analysis presented in the Figure 2. According to the evaluated data, the chemo-selective dyes not only were able to detect specific analytes, also they were able to change the color pattern specifically at the high temperature. This phenomenon can be also investigated and applied for the development of the thermo-sensor that can be used together with the chemo-selective sensor.

According to the statistical analysis the overlap in the response for different analytes is insignificant (Fig.3). Figure 3 show the PCA plot for the 1st to the 2nd principal components (PC) for a few select of the analytes. Using principal components 1 and 2 we see that 100 °C, HCl, acetic acid, toluene and DNT, groups tightly into clusters. Acetone, methanol, ethanol and propanol however are all grouped into the same cluster, but the cumulative density function analysis enables us to distinguish between these 4 analytes as well (Fig. 4). A cluster classification method such as simple as k-means should be able to perform well on these clusters.

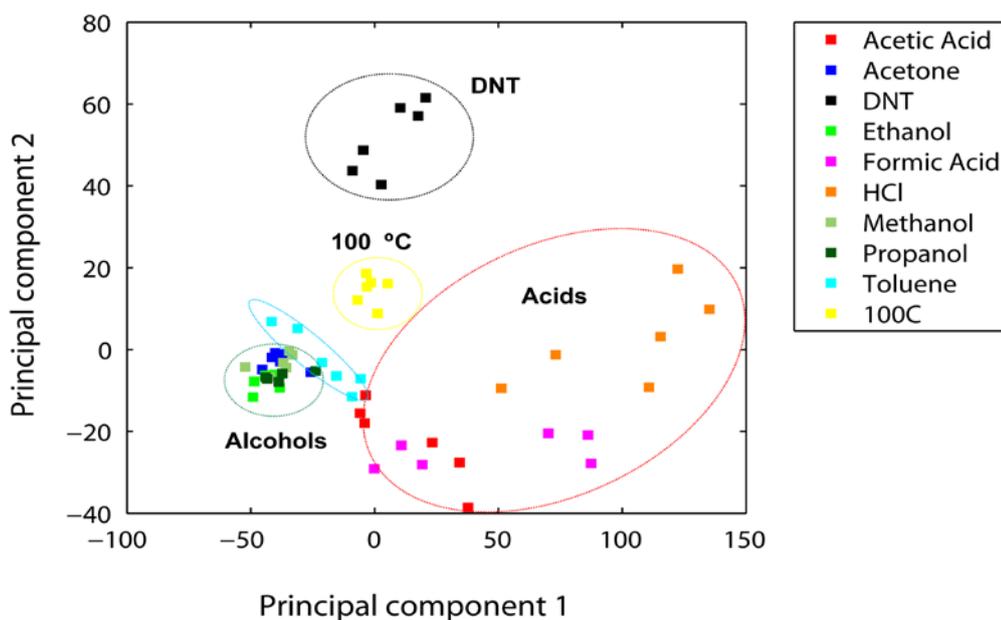


Figure 3. The Principal Component Analysis of the colorimetric sensor array obtained from the response results of VOCs and DNT, at saturated vapor pressure.

However, as mentioned earlier, the traditional approach to drawing color difference map as in Fig 1 and 2, eliminates of negative values and requires scaling in order to make the differences visible. The information can instead be shown as bar plots (Fig. 4). The Figure 4 shows 45 bars for four analytes: acetone, ethanol, methanol and propanol, one for each extracted color code. The bars are grouped by dye and the dyes are scanned horizontally starting from the left most dye – i.e. the first 3 bars represent the RGB values of the first dye (the top left) and so forth. This type of plot offers some advantages over the traditional difference map analysis as no scaling is needed and negative values can be plotted as well. In the case of repeated experiments the results can be encoded into a bar plot as well. Figure 4 shows results from acetone and methanol based on 6 repeats and ethanol and propanol based on 5 repeats. Each bar is drawn as the cumulative density function (cdf) - a well known function from statistics. In the case of 5/6 repeats we have 5/6 numbers per color index. The cdf has an initial value of 0 (in the area below the bars the value of the cdf is 0) and once n event(s) has occurred it will change its value to n/N, where N is to total amount of events. The value of the cdf is marked by a color. Further details can be found in the technical report [10]. A color signature obtained after the mathematical survey indicates that by using the colorimetric sensor array it is possible to determinate differences not only among various group of chemicals and also distinguish the individual analyte within the same chemical group.

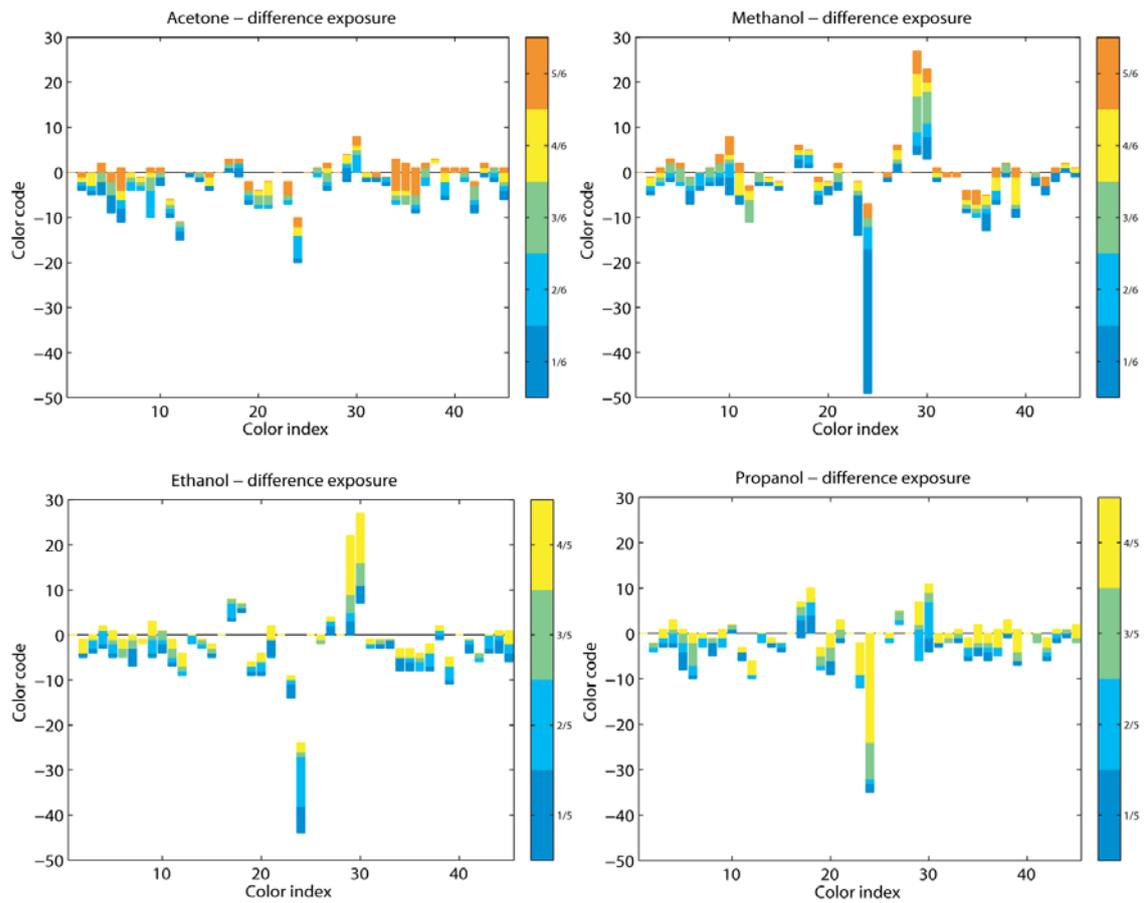


Figure 4. Analysis and comparison of the responses of the chemo-selective dyes after detection of acetone, methanol, propanol and ethanol using the cdf difference plots. Each bar represents the cumulative density function (CDF) of the color difference for a particular dye and color channel R,G,B.

4. CONCLUSION

In this paper the development of the colorimetric sensor array for effective and fast monitoring of explosives and volatile organic compounds has been described. Further an alternative visualization to color difference map, the cdf difference plot, was presented. Since the effective real-time surveys of VOCs and explosives in low concentrations under the ambient conditions are relatively scarce. This colorimetric sensor array can be applied for fast, precise screening of the most commonly used organic compounds and explosive in the real-time format and under the ambient conditions. In the future this array will be probed for detecting of different analytes in various concentrations and the kinetics of relevant reactions will be calculated.

This colorimetric sensor array can be also used for the detecting and identifying of different chemical compounds belongs to the different classes, like amines, alcohols, carboxylic acids, ketones, sulphides, and thiols. In the practical use the array can be modified for sensing of chemicals poisonous, toxins, illegal compounds, drugs, and narcotics. Also the sensor can be applied for screening of the spoilage and/or freshness in the food, of vapor poisoning compounds in plastic materials in industry or houses, and for detecting the environment.

However, the progress in this area could clearly be reached with the development of tools, which will combine inside different sensor system based on the application of classical methods and modern sophisticated techniques with capability for fast and precise detection of explosives and VOCs in real-time regime as well as quantify the type and place of hidden compounds.

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