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Interactive Wireless Sensor for Remote Trace Detection and Recognition of Hazardous Gases

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INTERACTIVE WIRELESS SENSOR FOR REMOTE TRACE DETECTION AND RECOGNITION OF HAZARDOUS GASES

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INTERACTIVE WIRELESS SENSOR FOR
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OF HAZARDOUS GASES

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I dedicate this work to WKU Physics Department, Dr. Vladimir Dobrokhotov and Dr. Keith Andrew for helping me accomplish my research. Also, I dedicate this thesis to my friend Dewayne Sowell who helped greatly acquiring data for my project.

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PREFACE

This manuscript is the outgrowth of a three semester course which has been researched for few years at the Applied Physics Institutes and graduate studies in Physics and Homeland Security. Interactive Wireless Sensor capable of localization of hazardous gases has emerging applications in homeland security, law enforcement, emergency response, defense command and control. In fact, detection of hazardous gases is vital for many applications, including emergency disaster scenarios, preventing leakage of hazardous gas pipelines and detecting hazardous gas coming out of bomb from a longer distance. While research in this area is progressing, limited resources are available to support graduate students and researchers: More specifically, a limited number of books have been published in this area, and the existing books do not have sufficient depth to be considering a manuscript.

This manuscript presents a detail research of emerging techniques, and introduces advanced remotely control wireless practical methods in localization and positioning of hazardous gases. It will also allow any working engineer or graduate student to quickly come up to speed on a specific topic. The script in this manuscript will also help university professors to teach the fundamentals of wireless localization of poisonous gases in graduate schools worldwide. The intended audience thus includes graduate students, researchers, and industry.

The interactive wireless sensor that’s been created is based on wireless sensor, microchip, Potentiometer and ZigBee. This system will improve the level of detecting hazardous gases and reduce accident in the place where lot of hazardous gases is being used.

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INTERACTIVE WIRELESS SENSOR FOR
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The interactive wireless sensor detects many hazardous gases such as Hexane, Propane, Carbon monoxide and Hydrogen. These gases are highly toxic and used in different kinds of manufacturing industries, domestic purpose and so on. So, building a sensor that can detect this kind of gases can save the environment; prevent the potential for explosion, and endangering human life. In long term, interactive wireless sensor can also prevent the financial losses that might occur due to the hazardous incident that might occur due to these toxic gases.

Hexane is a colorless, strong gas which inhaled in significant amounts by a person then he may suffer with hexane poisoning and suffocation. It also causes skin burns when exposed in high concentrations. Propane, carbon monoxide and hydrogen can easily freeze in room temperature, if in contact with eye, it could permanently damage eye or cause blindness. The advantage of this wireless sensor is the use of artificial olfactory system (electronic nose) that can be taught to detect these hazardous gases. This sensor has a unique molecular combination of analysts, impurities and background that corresponds to a gas leak. It consists of a chemiresistor, such as an array of conductometric sensors, and a mechanism analyzing the data in real time. A smell-print is composed of many molecules which reaches receptor in the human nose. When a specific receptor receives a molecule, it sends a signal to the brain where the smell is identified

and associated with that particular molecule. Similar manner, albeit substituting sensors for the receptors, and transmitting the signal to a machine learning algorithm for processing, rather than to the brain.

This wireless gas leak sensing system consists of microchip Pic 32, integrated electronic nose, automated data analysis unit, power supply, and communications. The communication channel will use the ZigBee link, or the cellular links, or other specific frequency wireless link. The time-stamped and position-stamped sensor measurement data are transmitted to the central computer in predetermined periods of time. The data will be stored in the computer database for possible future analysis of the gas leak development process.

Introduction

An electronic nose (e-nose) is a biologically inspired device that identifies and analyses chemical compounds in gaseous environments [1-3]. It consists of a mechanism for chemical detection, such as an array of electronic sensors, and a mechanism for pattern recognition, such as a neural network. The sensor array consists of broadly tuned, non-specific sensors that are treated with a variety of odor-sensitive biological or chemical materials. Odors are composed of molecules, each having a specific shape and size. Each of these molecules has a correspondingly shaped and sized receptor in the human nose. When a specific receptor receives a molecule, it sends a signal to the brain and the brain identifies the smell associated with that particular molecule.

Electronic noses based on the biological model work in a similar manner, substituting sensors for receptors and transmitting the signal to a program for processing, rather than to the brain. An odor stimulus generates a characteristic fingerprint (or smellprint) from the sensor array. Patterns or fingerprints from known odors are used to construct a database and train a pattern recognition system to classify and identify unknown odors. Thus, electronic nose instruments are comprised of hardware components to collect and transport odors to the sensor array as well as electronic circuitry to digitize and store sensor responses for signal processing.

Over the last decade, electronic nose technologies have undergone important developments from a technical and commercial point of view. A few interesting engineering solutions for electronic noses became possible only recently thanks to the development of microelectronics prototyping platforms. Also, the pattern recognition and

decision making algorithms are constantly evolving. To date, the classical methods of recognition of electronic signatures include Linear Discriminant Analysis (LDA), Quadratic Discriminant Analysis (QDA) and various Neural Network techniques, intended to separate the classes of analytes in multi-dimensional hyperspace [4]. However, frequently these methods require too much computational power at high sampling rate. Also, the training procedure for LDA can be overcomplicated, since the electronic signature of a smell can dramatically evolve at different concentration levels. Finally, because of the limited amount of chemicals in the training dataset, the interpretation of mixtures and unknown chemicals is questionable and unreliable.

In this work a wireless integrated sensory unit with a statistical pattern recognition algorithm, based on the array of metal oxide sensors incorporated into the Microchip Pic32 electronic prototyping platform is presented. The discussed design and algorithm have multiple attractive features, such as: simplicity of manufacturing and training, high speed of operation, and predictability of response to mixtures and unknown vapors. The developed integrated sensory unit is simple in design and low in cost, which together with its wireless capabilities makes it suitable for distributed wireless network for chemical mapping of the areas of interest.

Chapter 1: Description of Technology

Unlike many other analytical techniques, an electronic nose does not try and separate all the chemical components within a sample, but it perceives a sample as a whole, creating a global fingerprint. For example, the smell that emanates from coffee has many hundreds of different chemical components, but the human biological olfactory system (and the electronic nose) simply identifies the total chemical composition as coffee. In an electronic nose, the headspace from a sample (i.e. the gases emanating from a sample) are delivered to an array of chemical sensors. As each sensor is different in some way, (usually broadly tuned to a different chemical group) each sensors response to a sample is different. These responses can then be used to form a chemical fingerprint of a sample. The response is seen as a change in electrical properties (normally resistance) of the sensor. Specialized software then identifies the sample from this fingerprint. Pattern recognition algorithms and/or neural network hardware are used on the output signals arising from the electronic nose to classify, identify, and where necessary quantify, the vapor or odors of concern. This response is much like the way the mammalian olfactory sense produces diagnostic patterns and then transmits them to the brain for processing and analysis. This approach does not require development of highly specific recognition chemistries. Instead, this approach requires a broadly responsive array of sensors that is trainable to the target signature of interest and then can recognize this signature and deliver it to the sensing electronics in a robust fashion for subsequent processing by pattern recognition algorithms (Figure 1).

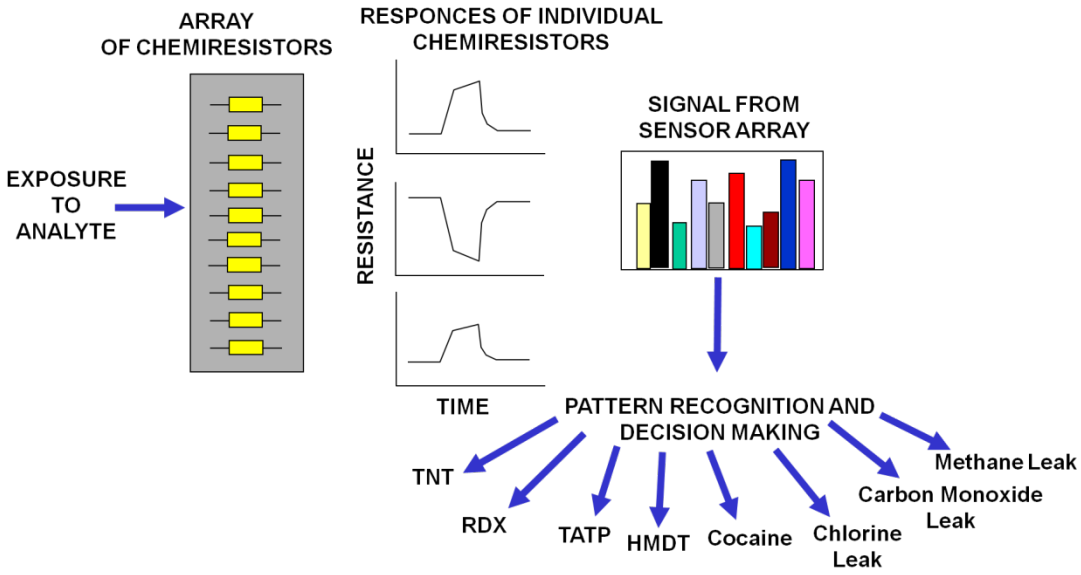

Figure 1: Principle of operation of an integrated chemical sensor (electronic nose).

Chemiresistors are used as building blocks for integrated chemical sensors (electronic noses). A chemiresistor is a device whose electrical resistance can be modulated by molecular adsorption on its surface. Typically, the changes in resistance are proportional to the partial vapor pressure in the atmosphere; hence a chemiresistor converts the concentration of chemicals in the atmosphere into a measurable corresponding electrical signal. A chemiresistor is constructed from a thin layer of vapor-sensitive material placed between conducting leads. One of the best chemically sensitive materials ever utilized is tin oxide (SnO_2) nanoscale compound. The sensing mechanism by metal oxides is primarily based on the activation of the atmospheric oxygen on the semiconductor surface. Consequently, the catalytic reactions of gaseous species with oxygen sites on the surface induce charge transfer from the surface to the bulk, which changes the electrical resistance of the device.

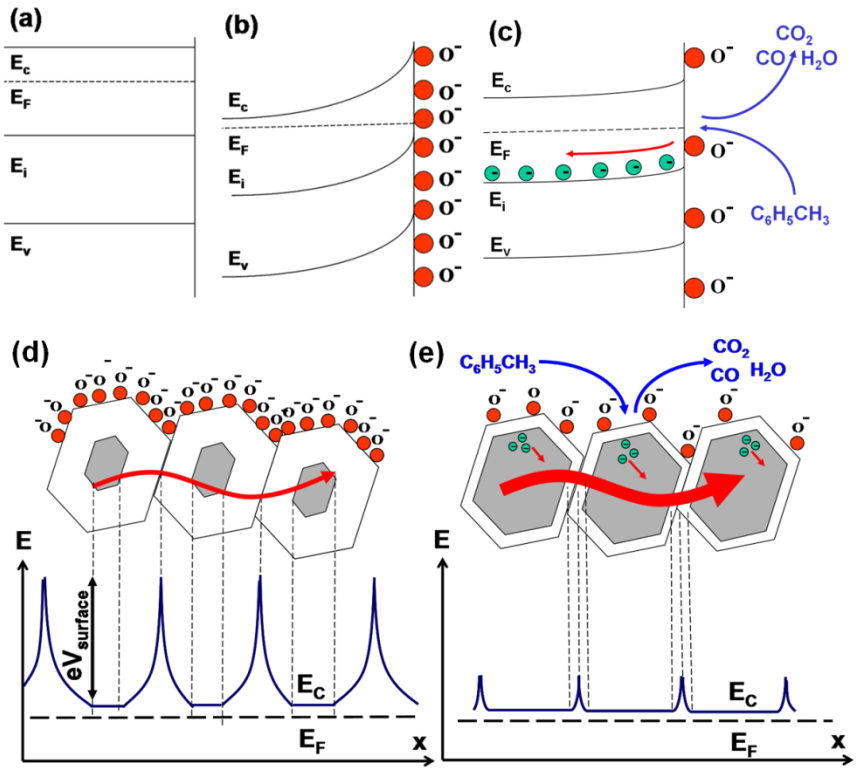

Figure 2: Top: Energy band diagrams of (a) bulk SnO_2, (b) at the surface of SnO_2 with O^- termination and (c) upon exposure to toluene. **Bottom:** Schematic energy-level diagrams of the polycrystalline SnO_2 layer (d) prior to exposure to toluene and (e) after exposure and subsequent oxidation of toluene.

A generalized model of sensing is shown in the Figure 2. At intrinsic n-type SnO_2 (Fig. 2(a)), once exposed to the ambient air, dissociates and ionizes atmospheric oxygen. Ionized oxygen on the surface acts as "traps" for electrons swept from the bulk, (i.e. subsurface), which induces energy band bending as the surface is approached. The net effect is the formation of a depletion layer near the surface of the SnO_2 nanocrystal (Fig. 2(b)). Upon exposure to a gaseous analyte, O^- is stripped from the surface of SnO_2 due to the catalytic oxidation of analyte, thereby releasing "trapped" electrons back into the

bulk. Introduction of electrons reduces the width of the depletion layer causing an increase in conductance of the SnO_2 (Fig. 2(c)). This type of sensors is self-refreshing: oxygen species regenerate on the surface of SnO_2, when the vapor pressure of the analyte drops.

The aforementioned depletion effect and chemiresistor sensitivity can be amplified by using a SnO_2 polycrystalline nanoscale compound. Specifically, the diffusion of molecular species between the neighboring nanocrystals, as opposed to depletion of free carriers over the entire surface of an individual SnO_2 nanocrystal, creates stochastic contact potentials at grain boundaries (Figure 2(d)). 3-D molecular adsorption over the entire surface of the nanocrystal increases the global sensitivity of the polycrystalline compound. The contact potential can be viewed as a tunneling barrier to electrons, which in our case is modulated by the catalytic reactions with analytes (Figure 2(e)). A combination of several chemiresistors, each providing a different sensitivity spectrum, a so-called sensor array, delivers signal patterns characteristic for the gases to which the array is exposed. To achieve the difference in sensitivity spectrum of individual sensors in the array, several techniques of the surface functionalization can be applied. Currently, one of the most efficient techniques is the treatment of oxides with various catalytic nanoparticles.

Chapter 2: Experimental Design.

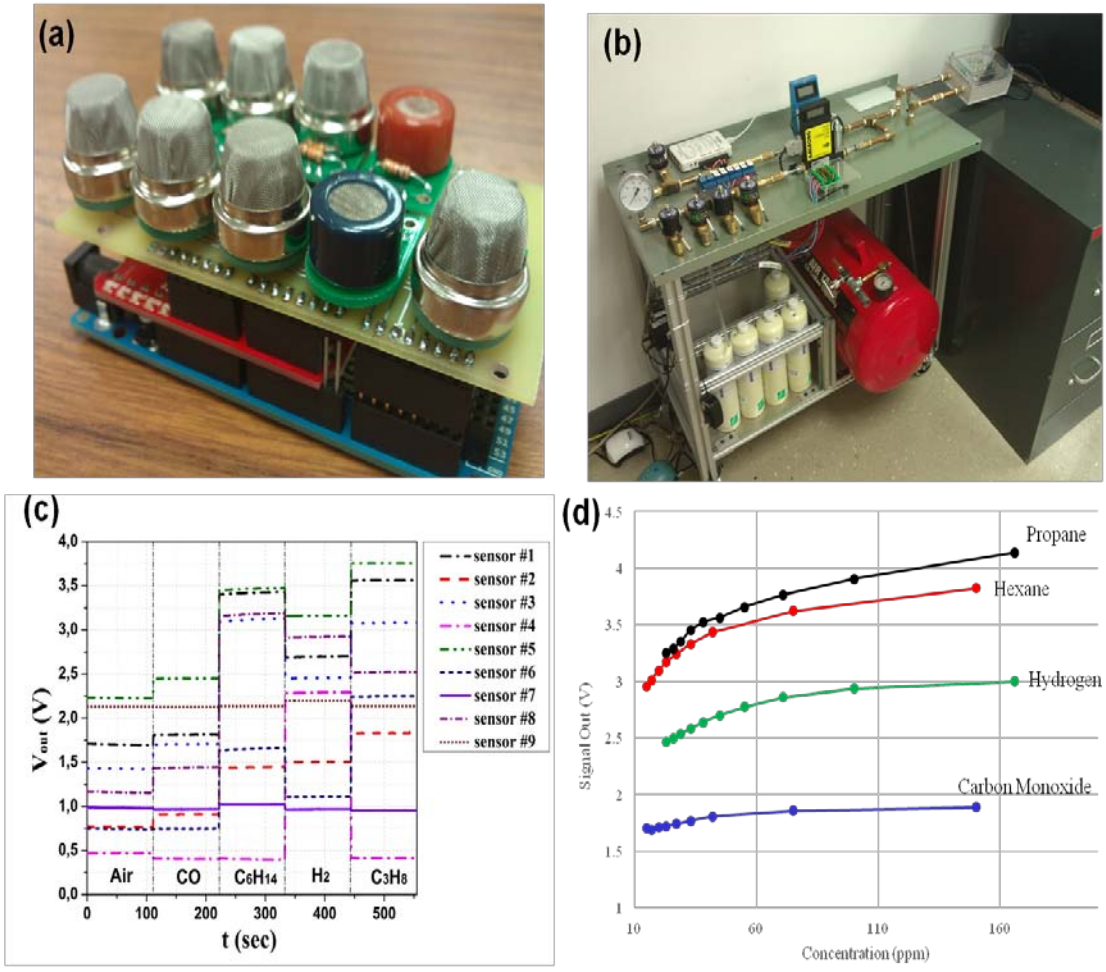

Figure 3. (a) Integrated multi-sensory systems based on SnO_2 gas sensors developed at the Applied Physics Institute (b) calibration and testing system, (c) integrated response of a multi-sensory system, (d) MQ-2 sensor output signal upon exposure to different gases as a function of concentration.

An example of a conventional multi-sensory system developed by the Applied Physics Institute at Western Kentucky University is shown in the Figure 3(a). It is based on the array of metal oxide gas sensors manufactured by Hanwei Eletronics. Nine SnO_2-

based sensors (2×MQ-2A, MQ-3, MQ-4, MQ-5, MQ-6, MQ-7, MQ-8, MQ-9) were incorporated into Microchip Pic32 electronic prototyping platform for simultaneous measurements. The sensing mechanism of metal oxides is based on the activation of atmospheric oxygen on the surface at high temperatures. Consequently, the catalytic reactions of gaseous species with oxygen sites on the surface induce charge transfer from the surface to the bulk, which changes the electrical resistance of the device. Standard voltage divider configuration was utilized for the output signal readings. The switching between the sensors was enabled through an embedded multiplexer. Wireless communication with the computer was enabled through a XBee Pro 60 mW unit with the baud rate 9600 bits/sec. Discrimination between the individual sensors in the array was achieved thanks to the variations in chemical composition of the porous SnO_2 interactive layers. The measurements were conducted in the flow-chamber under atmospheric pressure [Figure 3(b)]. The system is equipped with a gas manifold with multiple flammable gas sources. A needle valve was used to regulate gas flow and in the chamber.

Chapter 3: Pattern Recognition and Decision Making

Several pattern recognition algorithms for electronic noses have been tested throughout the course of this work. Besides the standard techniques, such as Linear Discriminant Analysis, Quadratic Discriminant Analysis and neural network techniques, a few novel methods have been developed, such as a spectral method and a statistical method, which have been applied to electronic noses for the first time by our group. In the statistical method, the training dataset was obtained in the form of calibration curves A(C) (amplitude vs. concentration). An example of the calibration curves for sensor MQ-2 is shown in the Figure 3(d). From the training A(C) curves, a set of inverted C(A) (concentration vs. amplitude) fit-functions was generated. A complete set necessary for pattern recognition includes $n \times m$ functions $C_{ij}(A)$, where $i=1..n$ is a sensor number and $j=1..m$ is a number of a tested chemical in the training dataset. Once the sensor array is exposed to the unknown gas, the sensors in the array respond with amplitudes A_1, A_2,... A_n. By substituting these amplitudes into the functions $C_{i1}(A_i)$, $C_{i2}(A_i)$,..., $C_{im}(A_i)$, where $i=1..n$, we obtain m arrays of numbers:

$$\begin{pmatrix} \boldsymbol{C_{11}(A_1)} \\ \boldsymbol{C_{21}(A_2)} \\ \boldsymbol{C_{31}(A_3)} \\ \boldsymbol{C_{41}(A_4)} \\ \boldsymbol{C_{51}(A_5)} \\ \boldsymbol{C_{61}(A_6)} \\ \cdot \\ \cdot \\ \cdot \\ \boldsymbol{C_{n1}(A_n)} \end{pmatrix}, \begin{pmatrix} \boldsymbol{C_{12}(A_1)} \\ \boldsymbol{C_{22}(A_2)} \\ \boldsymbol{C_{32}(A_3)} \\ \boldsymbol{C_{42}(A_4)} \\ \boldsymbol{C_{52}(A_5)} \\ \boldsymbol{C_{62}(A_6)} \\ \cdot \\ \cdot \\ \cdot \\ \boldsymbol{C_{n2}(A_n)} \end{pmatrix}, \ldots \begin{pmatrix} \boldsymbol{C_{1m}(A_1)} \\ \boldsymbol{C_{2m}(A_2)} \\ \boldsymbol{C_{3m}(A_3)} \\ \boldsymbol{C_{4m}(A_4)} \\ \boldsymbol{C_{5m}(A_5)} \\ \boldsymbol{C_{6m}(A_6)} \\ \cdot \\ \cdot \\ \cdot \\ \boldsymbol{C_{nm}(A_n)} \end{pmatrix}, \quad (1)$$

Array with number j represents the concentrations, reconstructed from responses of sensors, under assumption that the sensor array was exposed to analyte j from the training

dataset. In the idealized model, the exposure to analyte *j* means that all the elements of the array with number *j* are equal to each other and in the other (*m-1*) arrays the elements are different from each other. Physically, it means that the concentrations determined by each sensor (C_1, C_2,... C_n) obtained from the calibration curves using the integrated response to the unknown gas (A_1, A_2,... A_n) will be the same, if the assumption about the unknown gas is correct. In the mathematical model, *m* concentration arrays (1) represent *m* different assumptions, corresponding to the number of gases in the training dataset. In reality, if the unknown substance is *j*, the standard deviation of elements in the array with number *j* is the smallest among all the *m* arrays. The standard deviation σ_j can be calculated as:

$$\boldsymbol{\sigma_j = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(C_{ij}(A_i) - \overline{C}_j)^2}}\,, \qquad (2)$$

where $\boldsymbol{\overline{C}_j = \frac{1}{n}\sum_{i=1}^{n} C_{ij}(A_i)}$ is the average concentration that can be determined together with recognition.

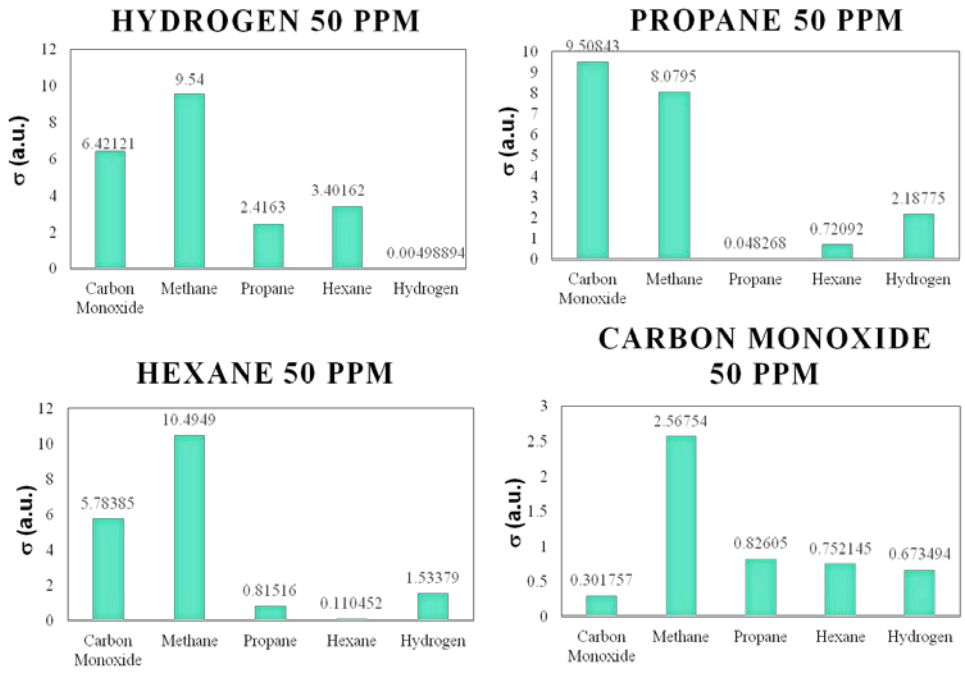

Figure 4. Standard deviation upon the exposure to various analytes. Minimum standard deviation corresponds to the detected analyte.

Histograms in Figure 4 illustrate the performance of the algorithm upon the exposure of the integrated system to hydrogen, propane, hexane and carbon monoxide. Minimum standard deviation in Figure 4 corresponds to a detected analyte. In our experiments the integrated sensor could recognize simple gases and measure their concentrations as fast as 120 times per minute. Under the laboratory conditions, the probability to recognize pure analyte was 100%, with an error in concentration measurement not exceeding 8%. Using mixtures, the system identified the component with the highest vapor pressure. For analytes not present in the training dataset, the system still picked the closest known analog.

Conclusions

The developed integrated wireless sensory system provides real-time recognition of gaseous analytes together with estimation of the analyte concentration. In contrast to standard recognition methods, the presented pattern recognition method is based on statistical analysis of the integrated sensor array response. The algorithm is simple and fast, so that the rate of decision making is only limited by the signal sampling rate. In addition to that, if the analyzed substance is unknown, the algorithm can choose the closest electronic signature from the training dataset. The developed integrated sensory unit is simple in design, low in cost, reliable and reproducible.

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