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A novel odor filtering and sensing system combined with regression analysis for chemical vapor quantification

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ABSTRACT

An advanced odor filtering and sensing system based on polymers, carbon molecular sieves, micro-ceramic heaters and metal oxide semiconductor (MOS) gas sensor array has been designed for quantitative identification of volatile organic chemicals (VOCs). MOS sensor resistance due to chemical vapor adsorption in filtering material and after desorption are measured for five target VOCs including acetone, benzene, ethanol, pentanal, and propenoic acid at distinct concentrations in between 3 and 500 parts per million (ppm). Two kinds of regression methods specifically linear regression analysis based on least square criterion and kernel function based support vector regression (SVR) have been employed to model sensor resistance with VOCs concentration. Scatter plot and Spearman's rank correlation coefficient (ρ) are used to investigate the strength of dependence of sensor resistance on vapor concentration and to search optimal filtering material for VOCs quantification prior to the regression analysis. Quantitative recognition efficiency of regression methods have been evaluated on the basis of coefficient of determination R^2 (R-squared) and correlation values. MOS sensor resistance after vapor desorption with carbon molecular sieve (carboxen–1012) as filtering material results the maximum values of R-squared ($R^2 = 0.9957$) and correlation ($\rho = 1.00$) between the actual and estimated concentration for propenoic acid using radial basis kernel based SVR method.

1. Introduction

Olfaction is one of the significant senses of mammalian for their survival. Over the past few decades researchers are concentrating on development of smart sensing device by following the functioning mechanism of mammalian olfactory system. This device is introduced as artificial olfaction also referred as Electronic Nose (E-nose). Currently it is widely used as an effective chemical vapor sensing device in food, health, security and safety applications, etc. [1–3] Chemical sensor array and pattern recognition methods are the most emphasized domains of present E-nose research [2,3]. Sensor array tries to mimic the activities of olfactory receptor (OR) neurons of biological nose, while pattern recognition methods function for sensor array signal processing analogous to olfactory cortex of brain. Foremost constrains that effect the sensing efficiency of E-nose are low sensitivity, selectivity, stability, life time and power consumption, noise and drift of chemical sensors and lack of optimized pattern recognition methods. Several research groups have been continually actioned for the development of highly sensitive and selective metal oxide semiconductor (MOS) sensors and optimized pattern recognition methods to miniaturize the limitations of E-nose. Some of the recent advancement are summarized as follows: E-nose based on tin oxide nanowires (performs better than thin film based sensors for ethanol-water mixture recognition) [4], laser irradiation (enhances sensitivity, signal to noise ratio and discrimination efficiency for olive oil identification) [5], metal oxide nanotechnology [6], TiO_2 nanohelix array (increases sensor response 10 times and decreases detection limit 5 times) [7], temperature modulated MOS sensors [8], plasma treated MOS sensor array (enhances recognition efficiency by 5%) [9] etc., chaos based neural network (improves vapor identification efficiency by 26%) [10], statistical techniques for sensor array optimization [11,12], interferences reduction by using pattern recognition [13], odor mixture's responses prediction [14], denoising and preprocessing [15–17], data fusion [18] (improves chemical vapor recognition efficiency by 10–30%), etc. Still there are indispensable disparities between biological and E-nose that need to reduce, to build more sensitive artificial olfaction system.

In addition to the sensing and signal processing, other parts of biological nose which must be modeled in E-nose are: inhaling system for pumping and filtering system for separation of odor

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molecules; axons, response measurement and collection system, etc. Amongst them filtering plays a significant role for recognition of simple as well as complex odors. In biological nose long hair, cilia and mucus layer function for odor filtering. Long hairs separate larger dust particles from the odor molecules while the minor particles are filtered out by the cilia. After that the mucus layer contributes in chromatographically filtering, by dissolving odor molecules in specific peptides and enzymes [19]. Although being a vital part of biological nose, we hardly notice research report in literature intended on modeling of separate filtering system for E-nose. For instance olfactometry along with ammonia and hydrogen sulphide gas detection tubes are used by Willers et al. [20] to investigate the odor filtration (efficiency 80%), Iskandarani modeled a low pass filter for odors using multi-gap sensors [21], and Imahashi et al. [22] have reported molecular imprinted polymers based odor filters for E-nose in which odor molecules are filtered due to their size and polarity. Filtering can play a significant role in odor recognition by E-nose analogous to the biological nose.

Most published reports are based on class identification of volatile organic chemicals (VOCs) by E-nose response analysis [1,2]. Apart from the class identification of VOCs, their qualitative identity (concentration) is also required independently or simultaneously in several practical applications. For instance in air quality monitoring of atmosphere, indoor, air craft and space craft, to decide the threshold level of poisonous gas emission from industries and automobiles, to establish disease biomarker VOCs and in health monitoring of patient during medical treatment, to check the freshness of food product and beverages, in cosmetic industry and many more. Several approaches to establish the quantitative identity of VOCs have been researched. For instance, concentration estimation of VOCs by response analysis of MOS sensor array using ANN method (95% quantification rate for ethanol, o-xylene and toluene) by Llobet et al. [23], Pardo et al. (90–95% quantification rate for CO and NO_2) [24] and Lee et al. (quantification of ethyl alcohol, toluene, methyl alcohol, acetone, and benzene) [25], regression analysis method for concentration estimation of acetone, benzene, ethanol, isopropanol and methanol by Khalaf et al. [26], simultaneous qualitative and quantitative recognition of ethanol, ethyl acetate, ethyl caproate and ethyl lactate using ANN and function approximation model by Gao et al. [27] and Daqi et al. [28], nonlinear polynomial model for quantification of six VOCs by Huang et al. [29], etc. A few reports are based on application of support vector regression (SVR) for concentration estimation of VOCs, apart from Song et al. [30] for quantitative identification of methane, hydrogen and their binary mixtures by response analysis of Fe_2O_3 sensor array (correlation value 0.99), hybrid genetic SVR model for indoor car air quality monitoring (with average prediction error 10% for five VOCs including formaldehyde, benzene, CO, NO_2 and toluene) by Tien et al. [31], etc. Though the optimization of SVR method particularly the kernel functions and their allied parameters, for concentration estimation of VOCs have not been noticed in published literature.

This study is inspired from the need to design the filtering system for E-nose and optimized regression analysis methods for concentration estimation of VOCs by E-nose response analysis. We have modeled a separate odor filtering unit using polymers, carbon molecular sieves and micro ceramic heaters. Sensing system is based on 8-element MOS sensor array. There is a specific filter for each of the MOS sensor and packed in a closed chamber in such a way that the odor molecule passes through the filter before getting exposed to the sensor surface. The proposed E-nose system incorporates high selectivity features of polymers, molecular sieves and high sensitivity of MOS sensor. This makes it different from earlier reported E-nose systems. We have employed scatter plot and correlation analysis approaches for selection of optimal filtering material. In addition an optimized pattern recognition approach is established for concentration estimation of VOCs. This is done by using the PCA, liner regression analysis and non-linear SVR methods. The optimum SVR model is built by variation in types of kernel functions and their affiliated parameters. The novel E-nose system is combined with optimized regression analysis method for response processing after that used for concentration estimation of five target VOCs of medical and forensic significance. The target VOCs are acetone, benzene, ethanol, pentanal and propenoic acid. The rest part of the paper is organized as follows. Section 2 presents the detail description of target VOCs and proposed E-nose system including the odor filtering, sensor response measurement and regression analysis methods. Analysis output of regression methods are discussed in Section 3. Findings of study and future research scope are concluded in Section 4. R program code for the regression methods are given in Appendix A.

2. Experimental details

2.1. Materials and instruments

Polydimethylsiloxane (PDMS), polyvinyl chloride (PVC) with dioctylphthalate (DOP) as plasticizer and carbon molecular sieves including carboxens – 1021 and 1012 (micropore diameter 5–8 Å and 19−21 Å, respectively) (purchased from Sigma–Aldrich, Japan) are used as odor filtering materials. Odor filters are designed by coating the filtering materials over the surface of micro ceramic heaters (MS–M5) (purchased from Sakaguchi Corp., Japan). MOS sensors TGS 2600 (from Figaro, Japan) are used in odor sensing unit. Separate odor filters are prepared for eight MOS sensors by coating PDMS with uniform thickness and scratched shapes, PVC with DOP concentration 5%, 10% and 15%, pure PVC, carboxens – 1021 and 1012 over the surface of eight micro ceramic heaters, respectively. Each of the filters is packed individually with a MOS sensor in a metallic cubical cell (5.9 cm × 3.7 cm × 2 cm) with VOCs inlet along the filter and outlet after sensor. VOCs are get filtered according to their size and diversity in interaction with chemoselective polymers and carbon molecular sieves. Thereafter MOS sensors respond to the filtered and dislodged VOCs from the filtering materials. LabVIEW program (from National Instrument, Japan) is used to control the heater current, cleaning of filtering and sensing chamber and flow rate of VOCs simultaneously.

2.2. Target chemicals and vapor generation

This study targets efficient quantitative recognition of five VOCs, reported as significant biomarker in human body odor. Human body odor consists of complex matrix of thousands of VOCs belonging to numerous chemical classes such as aldehydes, alcohols, amines, ketones, acids, ethers, hydrocarbons, esters, sulphides, etc. In present study we have selected VOCs from five chemical classes including ether, hydrocarbon, alcohol, aldehyde and acid (one chemical from each class). The target VOCs are acetone, benzene, ethanol, pentanal, and propenoic acid (purchased from Sigma–Aldrich, Japan). Detail descriptions of VOCs are compiled in Table 1 [32–46]. Vapor generator permeater PD-1B2 (purchased from GASTEC, Japan) is used to generate the standard concentrations of target VOCs. Pure dry air (passing air through cleaning vials) is used as dilution gas in permeater. Flow rate of diluting gas is controlled in between 0.2 and 2 L/min. Generated vapors are collected in Tedlar$^{(R)}$ gas sampling bags of capacity one liter (purchased from GL Science, Japan). Variations in flow rate of diluting gas in between 0.4 – 1.36, 0.25 – 1.33, 0.53 – 1.59, 0.26 – 1.20, and 0.23 – 1.82 L/min generate concentrations of target VOCs in between 150 – 500, 50 – 260, 35 – 105, 4 – 18, and 40 – 320 parts per million (ppm) for acetone, benzene, ethanol, pentanal and propenoic acid, respectively (Table 1). After vapor generation and