Sensors and Actuators B 214 (2015) 225–233

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Discrimination and quantification of volatile organic compounds in the ppb-range with gas sensitive SiC-FETs using multivariate statistics☆

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ARTICLE INFO

Article history:
Available online 18 March 2015

Keywords:
Indoor air quality
Temperature modulation
Linear Discriminant Analysis
Partial Least Squares
Trace level detection

ABSTRACT

Gas sensitive field effect transistors based on silicon carbide, SiC-FETs, have been studied for indoor air quality applications. The selectivity of the sensors was increased by temperature cycled operation, TCO, and data evaluation based on multivariate statistics. Discrimination of benzene, naphthalene, and formaldehyde independent of the level of background humidity is possible by using shape describing features as input for Linear Discriminant Analysis, LDA, or Partial Least Squares – Discriminant Analysis, PLS-DA. Leave-one-out cross-validation leads to a correct classification rate of 90% for LDA, and for PLS-DA a classification rate of 83% is achieved. Quantification of naphthalene in the relevant concentration range, i.e., 0–40 ppb, was performed by Partial Least Squares Regression and a combination of LDA with a second order polynomial fit function. The resolution of the model based on a calibration with three concentrations was approximately 8 ppb at 40 ppb naphthalene for both algorithms.

Hence, the suggested strategy is suitable for on demand ventilation control in indoor air quality application systems.

1. Introduction

In today's society, people spend most of their time, up to 85%, indoors where fresh air exchange is limited. Due to that, the quality of indoor air has become a major issue in the last years. The most commonly used indicator for indoor air quality, IAQ, is carbon dioxide, CO_2, which causes fatigue at elevated concentrations around 1000 ppm and can be measured using infrared, IR, absorption. However, the air quality is also strongly affected by volatile organic compounds, VOCs, which pose a serious health risk even at very low concentrations of a few parts-per-billion, ppb [1–3]. Lack of fresh air can lead to sick building syndrome, SBS, with symptoms like acute discomfort, headache, dizziness, difficulties in concentrating, respiratory problems like asthma, skin irritation, and hypersensitivity to odors and tastes [4,5].

The French Agency for Food, Environmental and Occupational Health & Safety, AFSSET, suggested in 2006 the first guidelines for limiting the emission of VOCs [6]. In more recent studies, e.g., by the European project INDEX [7] and French Indoor Air Quality Observatory, OQAI, priority lists of air pollutants with an undeniable health impact were suggested. Target VOCs of high relevance are benzene, naphthalene, and formaldehyde.

Benzene is present both indoors and outdoors; however, indoor air concentrations are generally higher than outdoors [3]. Typical indoor sources are furniture, heating and cooking systems, building materials, dyes, and paints, whereas outdoors benzene is released mainly from petrochemical industry, traffic, and gas stations. The concentration of benzene is significantly higher in homes of people who smoke. It was reported that ambient air concentrations vary from sub-ppb (approx. 1 $\mu g/m^3$) in rural areas to low ppb (5–20 $\mu g/m^3$) in urban areas, or even to tens of ppb in source impacted areas [8,9]. Benzene is classified as carcinogenic to humans and according to the World Health Organization, WHO, there is no safe level of exposure. However, the French decree n.

☆ Selected papers presented at EUROSENSORS 2014, the XXVIII edition of the conference series, Brescia, Italy, September 7–10, 2014.

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http://dx.doi.org/10.1016/j.snb.2015.03.016
0925-4005/

2011–1727 (December 2, 2011) has established an exposure limit for public buildings of 1.5 ppb in 2013 and 0.6 ppb by 2016 [10].

Naphthalene is also used in paints and the production of insecticides. It outgases from consumer products and other sources today are cigarette smoke and incomplete combustion processes (e.g., vehicle and air traffic, residential heating, etc.). Health effects are mostly respiratory tract lesions, but naphthalene is also classified as a possible carcinogenic [3,11,12]. In Germany, guidance limit levels of 0.01 mg/m^3, i.e., 3.5 ppb (guide level I), and of 0.03 mg/m^3, i.e., 5.7 ppb (guide level II) are suggested [11]. If guide level II is reached or exceeded, immediate action is required as this concentration could pose a health hazard [13].

Formaldehyde is one of the most well-known VOCs and very common in both indoor and outdoor air. Typical sources are outgassing of building materials, consumer products, and textiles. In particular, outgassing from wood-based materials (among others pressed wood products), glues, e.g., from laminate floors, and coatings including wallpaper are a major concern [14]. Exposure to formaldehyde leads to sensory irritations, especially of the eyes. The WHO has classified formaldehyde as carcinogenic for humans and recommends a short-term exposure limit of 81 ppb [3].

In order to reduce the exposure to VOCs in indoor air, heating, ventilating, and air-conditioning, HVAC, systems are usually used. However, a significant amount of energy is required to operate these systems. It was reported that approximately 40% of primary energy is consumed for heating and air conditioning. Thus, on demand ventilation has potential to improve the quality level and efficiency of such systems considerably. In order to operate such systems effectively, sensors and sensor systems able to measure the air quality, i.e., the amount of pollutants such as VOCs, are required. It has been demonstrated that gas sensitive field effect transistors based on silicon carbide are suitable candidates for indoor air quality measurement systems [15,16].

Gas sensitive field effect transistors, FETs, have been studied for many years [17–19]. Besides silicon, which was used in the beginning, silicon carbide, SiC, is currently used as a substrate material as it offers the possibility for high temperature application (up to at least 800 °C for SiC [17]). Due to its chemical inertness, SiC is also a suitable material for sensors operating in harsh environments, e.g., directly in the exhaust stream of combustion engines [18].

Excellent gas sensitivity can be achieved by using catalytically active gate materials like palladium, platinum, or iridium for SiC-FETs. The sensing properties of the FET depend mainly on the material and its structure as well as on the operating temperature of the device. For a dense, homogenous layer of, e.g., palladium or platinum, hydrogen molecules adsorbing on the surface dissociate and rapidly diffuse through the dense metal layer. At the metal-insulator, which is SiO_2 in this work, interface hydrogen atoms form a polarized layer of hydroxyl groups influencing the density of mobile carriers in the channel of the transistor [19,20].

For the detection of non-hydrogen containing gases like carbon monoxide, CO, but also for ammonia, NH_3, a porous layer of, e.g., platinum is required which allows direct interaction with the oxide surface like spill over from the metal and detection of dipoles formed on the oxide surface. Additionally, three phase boundaries between metal, oxide, and gas have a higher catalytic activity which is very important for the gas response [21,22].

It was reported that the sensing mechanism of hydrogen and non-hydrogen containing gases can be explained by spill-over effects of adsorbed oxygen [23]. Reducing gases like CO would react with adsorbed oxygen and thereby lower the density of oxygen on the surface.

In order to enhance the performance of SiC-FET sensors dynamic operation, i.e., temperature cycled operation, TCO, can be used [24]. Temperature modulation gives rise to several advantages [25], among others the transient response of the sensor provides an unique response pattern or signature for each gas thereby increasing the selectivity.

In this work, the detection, discrimination, and quantification of three hazardous VOCs are presented using multivariate statistic tools, i.e., Linear Discriminant Analysis, LDA, Partial Least Squares Regression, PLSR, and Partial Least Squares – Discriminant Analysis, PLS-DA.

2. Experimental

In this section, the gas mixing apparatus for supplying ppb-level VOCs is briefly presented (cf. Section 2.1) followed by a description of the field effect transistor and its operating mode (cf. Section 2.2).

2.1. Apparatus for ppb-level supply of VOCs

Measuring in the low and sub-ppb ranges impose high requirements on the test equipment. For this purpose, a new gas mixing system was realized where the VOCs are supplied either by permeation ovens (VICI Dynacalibrator 150) or by a gas bottle in combination with an additional dilution stage. A detailed description of the used system and the setup can be found elsewhere [26]. In the used setup benzene and naphthalene were supplied by permeation tubes with oven temperatures for benzene and naphthalene of 30 °C and 70 °C, respectively. Formaldehyde was supplied by a gas bottle with a mixture of 50 ppm formaldehyde in nitrogen connected to a dilution stage. Dry synthetic air with a purity of 99.999% was used as carrier gas. However, it still contains contaminations with concentrations up to ten parts per million, ppm. Nevertheless, using the same carrier gas in all parts, i.e., for the permeation ovens and the dilution stage, these contaminations form a constant background and thus, do not affect the sensor response. The background contamination of the system was checked using gas chromatography–mass spectrometry, GC–MS, reference measurements [26].

For all experiments the continuous flow over the sensor was kept at a constant level of 200 ml/min which means that when a test gas is injected, the flow of the carrier gas is reduced accordingly. The total flow was monitored during the measurements by a mass flow meter downstream of the sensor. Humidification was realized by a temperature stabilized water bubbler through which a part of the carrier gas was passed.

2.2. Sensor setup and operation

For all measurements an n-channel depletion type SiC-FET supplied by SenSiC AB, Kista, Sweden was used (cf. Fig. 1). The catalytic gate metallization is porous platinum with a thickness of 25 nm. A detailed description of the sensor and the manufacturing process can be found elsewhere [19].

In order to allow precise heating of the sensor, the SiC chip is glued onto a ceramic heater (Heraeus GmbH, Germany). A Pt-100 temperature sensor was attached next to the sensor as temperature reference. The heater together with the SiC chip and the temperature sensor is spot-welded on a 16-pin TO8 header (cf. Fig. 1b). Electrical contacts to the transistor structures on the SiC chip are realized via gold wire bonding.

Sensor control and data acquisition were performed by a combined system (3S GmbH – Sensors, Signal Processing, Systems, Saarbrücken, Germany). The sensor temperature was controlled by an analog control circuit with a resolution of 1 °C. The sensor signal, i.e., the drain–source voltage, was measured by a 14 bit ADC with a measurement range of 0–6 V, resulting in a theoretical resolution of approx. 0.4 mV. The drain-source current was set with accuracy better than 1 μA. The acquisition rate for all measurements was 10 Hz.