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Robust Advanced Sensor System for Determination of Volatile Organic Compounds (VOC)

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Abstract

Nowadays more and more health risks are increasing. Beside the viruses, there are also other particles which have an impact on the human well-being. The so called volatile organic compounds (VOCs) are substances in the air and can be harmful in high concentrations. Therefore, the detection of VOC value is particularly important.

Keywords

Electronic Nose, Volatile Organic Compounds, Sensor Fusion, Ionization, Excitation, Machine Learning, Robust Data Mining Algorithm, Photocatalysis, VOC Characterization, Embedded System

1. Introduction

This paper describes an advanced sensor system to determine VOCs based on of a state observer during a controlled photocatalytic change process. The sensitivity of the measurement setup is shown using in this case for three different alcohols that were investigated and determined.

The motivation of this project is to determine a previously measured diffusion behavior of a VOC in a real application-oriented environment. The given framework has been purposefully chosen to be less than ideal, meaning that many noise factors can affect the determination of the VOC. A robust data mining algorithm and the use of different sensors (sensor fusion) as well as the photocatalytic excitation of the VOC are the core of the system.

Low-cost industrial sensors and embedded microcontrollers are used, with the goal of making the system industrially usable later on. The setup is clearly different from an analytical or diagnostic system as typically used in research and in the laboratory in the spectroscopy of gases.

For photocatalysis, a UVA LED with a TiO_2 filter is used [1],[4]. Through this, the VOC is changed in its chemical properties and conductivity by the ionizing radiation. An industrial VOC sensor is used to measure the change in VOCs. This is a metal-oxide sensor with a controllable heating element. The conductivity of the MOX sensor [2],[9],[10],[17] can also be affected by the controlled heating element. Ionization changes the conductivity of the surface of the VOC sensor and shows a different behavior for each VOC. Other sensors, such as temperature and humidity sensors, are used to detect changes in the state of the environment and draw conclusions about this measurement. The sensors work as one overall system through what is known as sensor fusion.

In order to draw conclusions about the measurements made, a developed data mining algorithm is used. This uses the integrated measurement database to make a distinction between previously learned and stored data and the measured data in the determination.

In further investigations, other VOCs with different diffusion behavior than alcohols were determined using the same principle. The findings from the project are to be used in follow-up projects in the development of an electronic nose.

2. Motivation

The determination of Volatile Organic Compounds (VOC) is becoming increasingly important in many applications such as environmental measurement technology, industrial measurement technology, medical technology or air quality measurement. The aim of the project is to determine VOCs in a non-ideal measurement environment outside a defined atmosphere where uncontrolled diffusion processes can also take place. Industrially manufactured semiconductor-based sensors to detect or measure VOC, pressure, temperature and humidity form the basis for recording the physical and chemical variables of the setup. The project focuses on the development of a robust data mining algorithms that can determine the VOC with a limited number of training data and a reduced number of measurement data with the goal to realize data processing and data analysis on an embedded MCU [3]. Another goal of the project is to influence the dynamic range of a relative MOX-based VOC sensor using photocatalysis at different concentrations of VOC in the air with the aim of improving the sensitivity and selectivity of the sensor system. The problem statement is complex because training (Machine Learning ML) and detecting VOC is a VUCA problem. Thus, the stated goal of the project: Getting best possible estimation of the hidden variables in impedance-based VOC sensing in a non-ideal and nonlinear system

3. Basic knowledge

A. *The bond energy in reaction*

The reaction enthalpies can be estimated using average bond enthalpies. This calculation method is not accurate, but when more detailed data is not available, it can be used as an estimate.

A bond dissociation energy BDE is defined by

$$XY \rightarrow X + Y \tag{1}$$

with BDE=ΔH

In this process, the adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\Delta H = \Sigma(\text{bonds broken}) + \Sigma(\text{bonds formed}) \tag{2}$$

The combustion of ethanol in gas-phase as an example:

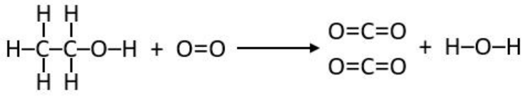

Table 1 Bond Energy

Bond	ØEnergy (kJ/mol)	Quantity
C–C	348	+1
C–H	413	+5
C–O	358	+1
O–O	463	-1
O=O	495	+1
C=O	799	-4

The Energy: $\Delta H = -393$ kJ/mol (± 5-10%)

B. *Plank-Einstein Relation*

This relationship clarifies that the energy of a photon is proportional to its frequency.

$$E = h\nu = h(c/\lambda) \tag{3}$$

If one molecule absorbs only one photon, the total energy absorbed by one mol of molecule:

$$E = N_A h\nu \tag{4}$$

E : photon energy
ν : photon frequency
λ : wavelength
h : Planck constant, $6.62607015 \times 10^{-34}\ (J \cdot s)$
c : speed of light, $299792458\ (m/s) \approx 3 \times 10^{8} (m/s)$
N_A : Avogadro constant, $6.022140 \times 10^{23} (mol^{-1})$

$$E = \frac{N_A hc}{\lambda} \approx \frac{6.022 \times 6.626 \times 3 \times 10^{-3}}{\lambda(m)} \approx \frac{1.1971 \times 10^{8}}{\lambda(nm)}$$

The energy must meet the needs of the reaction. And by adjusting the light source can be used as a way to increase or decrease energy.

C. *Photocatalysis*

Titanium dioxide (TiO_2) is used as a catalytic material and added to the chemical reaction to carry out a photo-assisted catalytic reaction [19],[20],[21],[22]. In this photocatalytic reaction requires permanent exposure to light of a suitable wavelength to generate the excited catalyst state (K*). The light energy (hν) is a necessary condition for the reaction to proceed.

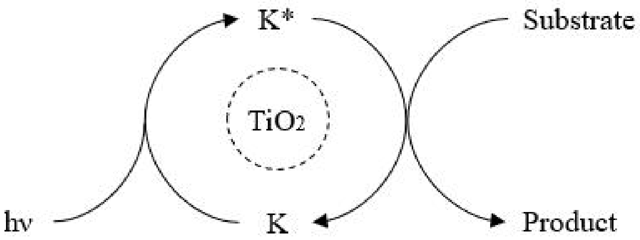

Fig. 1. Sketch of a catalytic photoreaction, TiO2 as a catalyst

In one mechanism of the oxidative reaction, the positive holes react with the moisture present on the surface and produce a hydroxyl radical. The reaction starts by photo-induced exciton generation in the titanium dioxide surface.

$$TiO_2 + h\nu \rightarrow TiO_2 + h^+ + e^- \qquad (5)$$

Oxidation reactions due to the photocatalytic effect:

$$h^+ + H_2O \rightarrow H^+ + \bullet OH \qquad (7)$$

Reduction reactions due to the photocatalytic effect:

$$e^- + O_2 + H_2O + H^+ \rightarrow 3\bullet OH \qquad (6)$$

The intermediate product hydrogen peroxide (H_2O_2) and negative Oxygen (O_2^-) are also generated in the reaction. Ultimately, the hydroxyl radicals are generated in both reactions. These hydroxyl radicals are very oxidative and not selective with a redox potential E0 = +3.06V [12]

D. *Decomposition of organic matter*

When the energy of the photon is greater than the energy gap requirement of the catalytic material, the photocatalytic reaction can be activated. For example, the photon energy should be greater than the energy gap 3.2eV of the typical TiO_2 anatase. Through a photocatalytic reaction mediated by titanium dioxide, organic molecules can be decomposed into harmless substances water and carbon dioxide.

Consider the practical application, usually ultraviolet light source will be used as the source of effective activating light radiation energy.

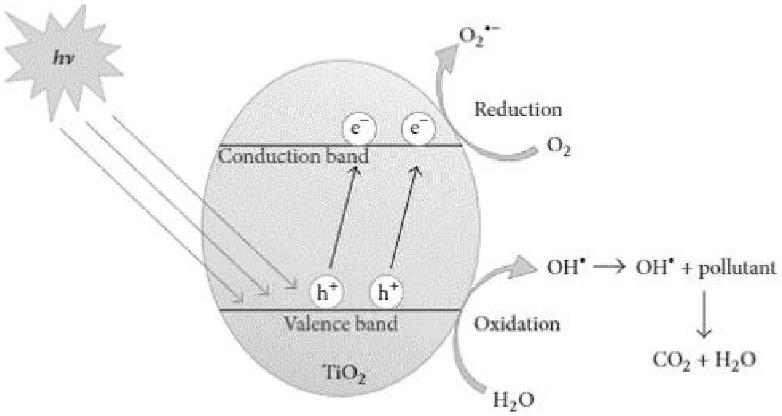

Fig. 2. General mechanism of the photocatalysis [13]

When designing an application, it is also necessary to pay attention to some factors in the reaction, such as the light intensity in the reaction, the catalytic material, the contact area, the surface adhesion, the temperature, etc. which can all affect the efficiency of photocatalysis [5],[8].

E. *Metal oxide gas sensor*

Briefly introduce the principle of a gas sensor based on tin dioxide (SnO_2) as the sensing material. The electrons from the conduction band of SnO_2 are captured by oxygen atoms adsorbed on its surface, and the electrochemical reactions occurs. The difference in the products (O_2^-, O^- and O^{2-}) depend on temperature. The chemical adsorption process can be explained by the following reactions: [14]

$$O_2\,(gas) \leftrightarrow O_2\,(ads) \tag{7}$$

$$O_2\,(ads) + e^- \leftrightarrow O_2^-\,(ads)\ (T<150°C) \tag{8}$$

$$O_2^-\,(ads) + e^- \leftrightarrow 2O^-\,(ads)\ (150°C<T<400°C) \tag{9}$$

$$O^-\,(ads) + e^- \leftrightarrow O^{2-}\,(ads)\ (T>400°C) \tag{10}$$

When SnO_2-sensor contacts with the measured gas, its resistance will change according to the oxidation or reduction characteristics of the gas. The sensing mechanism of the SnO_2-sensor reacting with these gases can be represented by the following desorption process, where O^- is taken as an example: [15]

$$C_2H_5OH + 6O^-\,(ads) \rightarrow 2CO_2 + 3H_2O + 6e^- \tag{11}$$

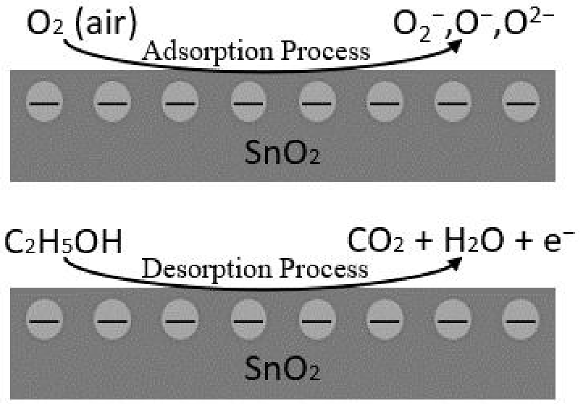

Fig. 3. The gas sensing mechanism of SnO_2-Sensor

4. Design of measuring plattform

F. *MOx based VOC Sensor*

The gas sensor used in the project is an industrially manufactured MOx based sensor with digital interface. The technology provides a complete, easy-to-use sensor system on a single chip with a digital I^2C interface and a temperature-controlled micro-heating plate that provides a humidity-compensated VOC-based indoor air quality signal. The output signal can be processed directly by an embedded MCU to translate the raw signal into a VOC index as a robust measure of air quality. The sensing element is very robust to contaminating gases found in real-world applications and allow for good long-term stability and low drift and variation from part to part.

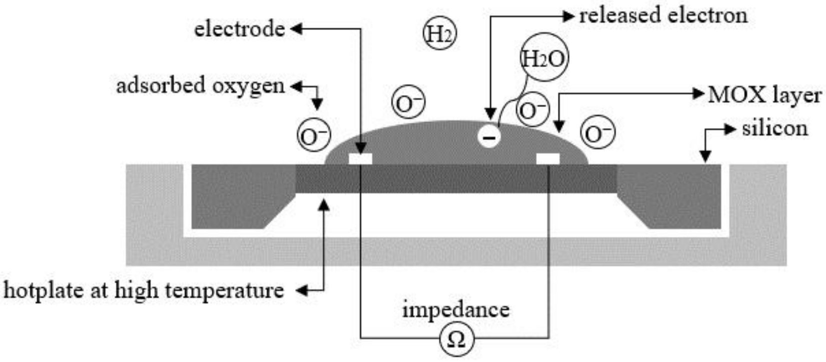

Fig. 4. Measure principle of gas sensor SGP41[18]

G. *Design of the demonstrator*

The measuring system was installed in a non-hermetically sealed metal chamber with a volume of 30 liters, consisting of a controlled and pulsed UV-LED light source, a TiO_2 photocatalytic filter [6],[7],[16] and a sensor arrangement of four sensors consisting of a VOC sensor, temperature sensor, humidity sensor and pressure sensor, which are marked as complex impedances in Fig. 5. The VOC-air mixture flows past the UV-LED, through the TiO_2-photocatalytic filter. The diffusion is supported by a fan. The data mining process for training and data analysis have a total of four phases. In phase 1, the sensor signals are measured and processed without VOC and without UV light source. In phase 2, the sensor signals are measured without VOC with UV light source. In phase 3, the sensor signals are measured with VOC and with UV light source. In phase 4, the sensor signals are measured with VOC without UV light source. The data mining process was performed all VOCs. The following VOCs were trained and measured: 0.05ml German red wine, 0.05ml French red wine and 0.05ml vodka. To support the diffusion of the VOCs, the liquids were applied to a paper tissue and placed on the bottom of the measurement chamber.

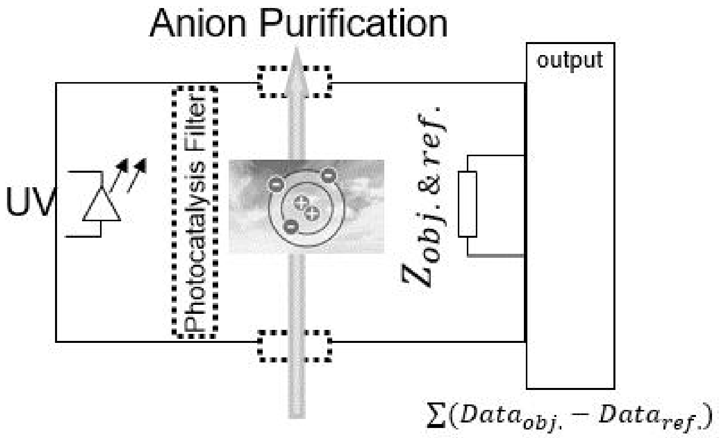

Fig. 5. Simplified schematic of the Measurement Setup

H. *Hardware*

The hardware of the sensor measurement system (Fig.7) consists the sensor unit with the 4 sensors, an embedded MCU board with Arduino interface, a programmable high-speed modulator and a controlled high-speed LED current driver, a Quad-UV LED array with heat sink and thermal monitoring by an NTC. The fan is controlled by a PWM modulated switching transistor.

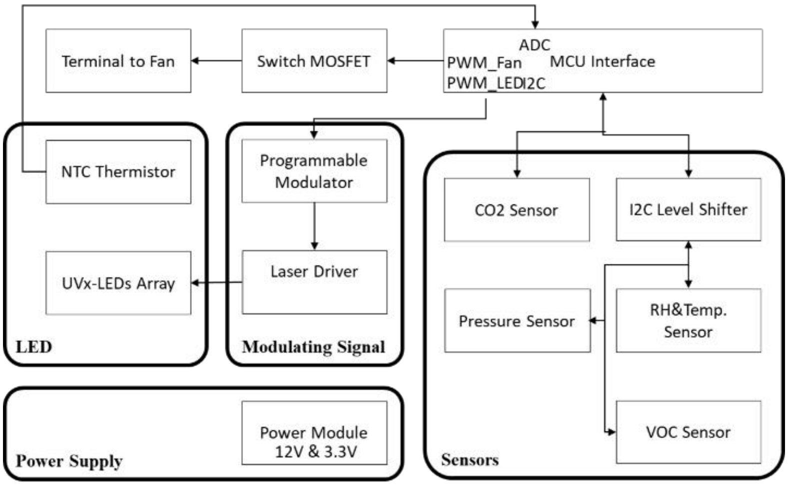

Fig. 7. Block diagram of functional modules

Fig.8 shows the arrangement of the UV light source with side openings to support VOC circulation in the measurement chamber. The sensor unit was placed on the right side. The photocatalytic filter, the fan together with the mechanical holder have been disassembled here.

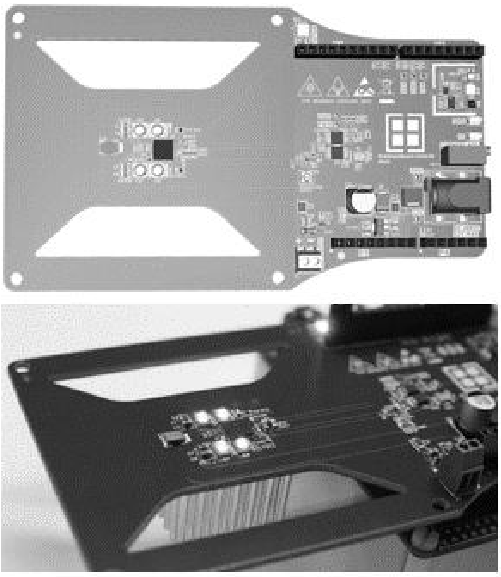

Fig. 8. 3D-PCB (top) and actual test device without photocatalytic filter and fan

5. Test and evaluation

I. Measurement date from VOC sensor

Fig. 9 shows the measurement results using the different phases - 1, 2, 4 and 5 with and without photocatalysis, here in comparison: air, vodka and German red wine. In phase 3, add a selected substance to be measured.

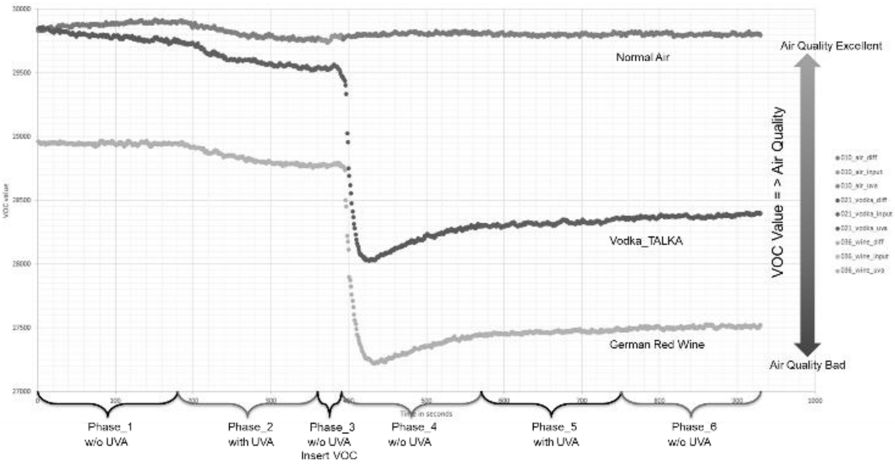

Fig. 9. VOC values (Air, Vodka and German red wine)

J. *Data mining on PC-based tool Orange3*

With the support of the data mining toolkit from Orange3, the training data as well as the measurement data were preprocessed and programmed according to the flowchart in Fig.11. A visualized plot is designed showing the differentiation between the three VOCs (Fig.10).

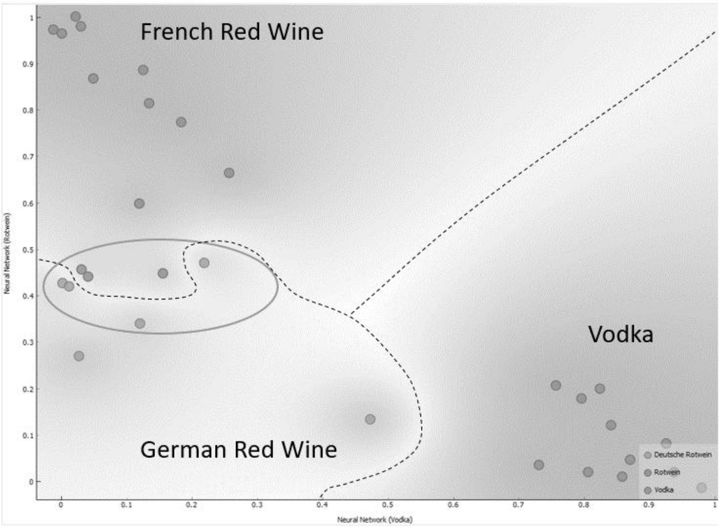

Fig. 10. Visualized plot of the VOC differentiation

K. *Embedded programming*

The digital data processing of the sensor raw data is performed by the embedded MCU board. Fig. 11 shows the flow chart of the data processing. The measurement phases described in Fig. 9 are the basis for the machine learning process. In the pre-processing of the data, first a filtering and then a difference calculation from the phase 5 and phase 2 in (Fig.9) takes place. This is followed by a normalization and standardization of the data and a check of the continuity of the measured data. This is important so that the eigenvalue matrix can be extracted. The data should be in a non-linear relationship, so the data should be decorrelated to then apply PCA (principal component analysis) to reduce multidimensionality. Then a training dataset and a test dataset with suitable data volume is created.

After that, the data will be imported into a TensorFlow-based multi-layer perceptron to train the network model. It is very important to set and adjust the appropriate activation function and number of iterations. By comparing with the prediction of the test set, parameters such as node weights are corrected. Too much emphasis on the loss function and too many iterative loops may result in over-fitting and reduce the accuracy of the test set, a reasonable trade-off need to be considered. Because of the limitation of the computing resources of the microcontroller, the model is trained on a network platform (Colab by Google), after training the parameters are extracted, programmed and flashed into the ARM-microcontroller.

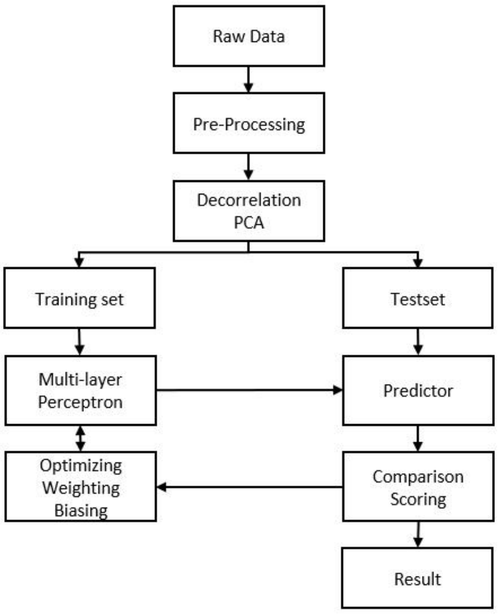

Fig. 11. Flow chart of the data processing

6. Conclusion and outlook

By using data mining algorithms, even with a very limited number of training data sets the determination of different VOCs is possible. The results show, that photocatalysis is a method to control the relaxation time of the VOC and the diffusion process. Due to the photochemistry and the molecular change of the VOC, it is not a VOC diagnosis or VOC analysis system. From the required hardware and cost perspective, it is one of the most cost-efficient ways to determine VOC by using a high-performance the proposed data mining algorithm. This is important for an industrial use case later on. The advanced sensor setup with UVA excitation can control the saturation behavior of a relative MOX-based VOC sensor. With a pulsed UV-LED array, it is possible to control the photocatalysis process, to be able to use an optimal dynamic range of the VOC sensor and to use a measurement range of the VOC sensor with a high sensitivity of the sensor fusion setup, e.g. to distinguish between different VOCs with a very limited test volume of 0.05ml. Further investigations and projects will follow by using synchronous double sampling with two VOC sensors, tiny machine learning by Tensorflow setup with multi-sensors and advanced design of excitation signals for the UV-LEDs in order to improve the sensitivity of the measurement setup.

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