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Analysis of the dynamic features of metal oxide sensors in response to SPME fiber gas release

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ABSTRACT

In this study a metal oxide sensor array is exposed to a time-dependent amount of gas inside the sensor chamber of negligible "dead" volume. Special parameters of the response kinetics are used for multi-parametric featuring of volatile organic compounds (VOCs). The composition of the atmosphere in the chamber varies due to the time-dependent release of the VOCs from a solid phase micro-extraction (SPME) fiber into the flow of synthetic air. Four types of volatile compounds, namely acetone, acetic acid, acetaldehyde and butyric acid, that are known being frequently emitted from infected wounds, are tested in this study. The explorative data analysis (EDA) of the features is performed for the sensor outputs obtained at different carrying gas flow rates and the VOC amounts. Influence of specific aspects of the SPME based sampling on the sensor outputs is estimated. It is demonstrated by the PCA results that the target compounds cannot be distinguished below 3–4 ppm if only the sensor outputs based on the signal magnitudes are used for the featuring of VOCs (static-compatible features). The dynamic features add significant information and allow a better discrimination of the volatile compounds. The classification of the target volatile compounds can additionally be improved by precise control of the VOCs expansion in the chamber in the dynamic exposure approach.

1. Introduction

Various attempts are made to mimic natural olfaction in development of electronic noses (e-nose). Though the sensors are the key elements in the gas recognition systems it is also important to improve the methods and modules used for gas sampling and delivery, signal preprocessing and data analysis. For example, some attempts are made to mimic the human nose mucosa which provides a kind of chromatographic separation of the volatile organic compounds (VOCs) across the olfactory epithelium [1,2]. VOCs are separated in time according to their water solubility value and this adds further information to the odor processing centers (olfactory bulb and cortex) for the recognition of odor patterns. This new approach expands the opportunities of adapting the intentional variation of gas concentration for obtaining the dynamic response of gas sensors to gas in practical devices. Until now, this attractive method of the dynamic response analysis is typically studied in the gas test systems creating a concentration step by a valve-switcher [3], a moving gas outlet [4], fluidic valve [5], pre-concentrator with variable temperature [6] and so on. Analysis of the features obtained by the original approaches, for example, based on the temporal evolution of the conductance [7], the response time [8], Fourier and wavelet descriptors, integrals and derivatives [9], a short-time Fourier transform [5], proved that the capability of the recognition system to classify the gases improves notably. It was demonstrated [10] that the promising results can even be obtained by a real-time analysis in long-term rapidly varied gas concentration surrounding if the optimized gas sensor fusion architecture is developed.

The discriminatory information hidden in the dynamic response is typically defined by both the characteristics of the fundamental processes and arrangement of the detection system. This is because the kinetics of chemical sensor response to gas depends on the time-dependent processes happening at the sensor surface and in the atmosphere as well as on the experimental parameters such as dimensions of sensor chamber, the dead volume, the rate and duration of injection of target gas. Understanding fundamental aspects of the processes that determine the gas injection and delivery to the sensors is therefore a key step for developing new approaches in dynamic response mode in e-noses.

The present study aims to describe the methodological aspects that can be important for odor featuring and identification when a variation of gas concentration is produced in the gas test system by an emission of the target VOCs from the solid phase micro-extraction (SPME) fiber. This approach is particularly useful in practical applications when the direct access to a smell source

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is restricted or hardly feasible as, for example, sampling of the headspace air over the burn wounds in the clinical conditions in our FP6 STREP project WOUNDMONITOR. Living infectious agents in wounds, such as bacteria, are a source of smell since their metabolism produces a complex pattern of VOCs [11–13]. Since the pattern of volatile products should depend on the growth of bacteria it can be possible to monitor the wound state by analyzing the headspace air above the wound. The SPME approach allows testing the e-nose technology by the procedures similar to the standard clinical tests and excludes unwanted intrusion into the healing process.

Considering the possibility to split the qualitative and the quantitative description of the wound smell by using transient response parameters demonstrated in our recent work [14], this study aims to describe the influence of the controllable parameters of the SPME injection method on the results of the feature extraction and the data analysis. Therefore, in this paper, we show how transient features extracted from the response of MOX sensors in a particular e-nose setup with negligible dead volume and axial symmetry together with an SPME sampling enhances VOC quantification at several concentrations. Differently from other studies, we concentrated here more on a thorough search of the optimal sampling parameters (flow, SPME exposure time) for the extracted features, than on the choice of the successive classifier. Performances have been gauged with PCA plots obtained by the explorative data analysis (EDA).

2. Experiments and methods

2.1. Sensors

The array of MOX sensors consists of commercial and laboratory made sensors. Commercial TGS type sensors (TGS2602, TGS2610) were included in the array. The laboratory made sensors were based on tin oxide thin films and were grown by two original methods, namely the rheotaxial (fused metal) growth and thermal oxidation technique (RGTO) developed in Brescia University and deposition of ultra-thin tin oxide films by dc-magnetron sputtering in the atmosphere of reactive gas (mixture Ar_2:O_2). The SnO_2 films were modified by catalytic metals Au, Pt, Pd and Ru. The sensor array was equipped within a tube-like test chamber of negligible dead volume. The diameter of the chamber was the same as the diameter of the tubing and equal to 6 mm. Details of the sensor technology and the dynamic test system were described in our previous reports, e.g. [15]. The only modification of this system in present study was the special module described below in this section.

2.2. Measurements

Sensors were exposed to strictly controlled amounts of the reference VOCs, namely acetone (CH_3COCH_3), acetic acid (CH_3COOH), butyric acid ($CH_3CH_2CH_2$–COOH), and acetaldehyde (CH_3CHO). The list of target VOCs was defined in the WOUNDMONITOR project based on the GC–MS tests on the headspace of infected wounds. VOCs concentrations can be set any between 0.1 and 10 ppm inside a mixing container.

SPME fiber was used for sampling and pre-concentration of the target VOCs fixed concentration of which was prepared in the air flow system using commercial permeation tubes obtained as special stainless steal containers from Φfine permeation tubes (Italy). During sampling, the SPME fiber was inserted in the tube-like section in the flow control system.

The sensor testing system was equipped with the special tube-like module that can be heated by an external heater. This module was connected to the inlet of the chamber. The SPME fiber was introduced into the module along the tube axis through the membrane sealing the testing system. A sketch of the test chamber with the module and the SPME fiber is illustrated in the insert in Fig. 1. Carrying synthetic air flew in the system at a constant rate. Depending on the experimental objectives the rate can be set at any value from 0 to about 200 ml per minute in our gas flow control system. It should be noted here that the surrounding temperature was about 20 °C and, based on the construction of the system, we neglected the compressibility of the flowing air.

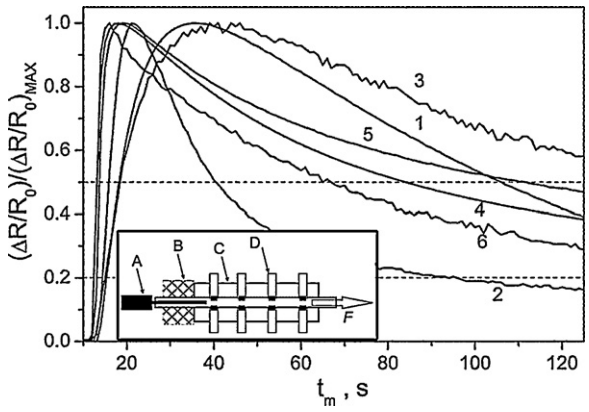

Fig. 1. Responses of the array of MOX sensors to the headspace air of *Staphylococcus aureus* culture injected by the SPME fiber into the testing system with constant flow of synthetic air $F = 32$ ml per minute. Insert: a sketch of the sensor chamber (C) with gas sensors (D), special evaporation module (B) and SPME fiber (A). The arrow (F) in the insert shows the flow of the carrying gas.

2.3. Signal processing and data analysis

The responses of sensors to the VOC were recorded at the constant sampling rate of 5 readings per second. We extract three kinetic features from the transients in Fig. 1: (1) the time at which the signal reaches its maximum (τ_{max}), (2) the length of the response defined by the time interval between the beginning of the signal rise and the almost clean air resistance (the deviation of the restored sensor resistance from the clean air resistance is allowed being less than ±20% of the total resistance response aiming to eliminate an influence of the signal noise) at the end of the transient signal (τ_1) and (3) the slope of the response calculated when the signal falls by factor e with respect to its maximum (δ_e). In addition to these features, the relative maximum response is also included in the set of the outputs of sensor array. The maximum response is defined by the signal at τ_{max} and is equal to $\Delta R = (R_g - R_0)/R_0$ where R_0 is the clean air resistance and R_g is the resistance in the air with the target gas at τ_{max}.

The feature sets obtained from the sensor responses were analyzed by the EDA software package that was described in a recent paper [16]. It comprises utilities for easy data manipulation (e.g. data sub-sampling, data set fusion) and plots customization.

3. Basic considerations

VOCs evaporation from the SPME fiber creates varying concentration of constituent compounds in any point inside the chamber. Since the gas channel is narrow (diameter is 6 mm and the chamber length 100 mm) it is reasonable to assume that the amount of VOC varies only along the chamber axis. The VOC package is broadened by the diffusion inside the chamber but still it seems reasonable to assume that the VOCs concentration is homogeneous orthogonally to the chamber axis. Neglecting the consumption of VOC by the sensors, we can expect the same amount of VOC at any of the sensors at individual short periods of the exposure. The momentary amount