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Quantitative gas mixture analysis using temperature-modulated micro-hotplate gas sensors: Selection and validation of the optimal modulating frequencies

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Abstract

The selectivity of metal oxide gas sensors can be improved by operating the sensors in a temperature-modulated mode. Although the selection of optimal modulating frequencies deserves accurate attention, this aspect has been generally overlooked. In this paper, a systematic method to determine which are the optimal temperature-modulation frequencies to solve a given gas analysis problem has been introduced, discussed in detail and fully validated for the first time. The optimization method is based on the use of multi-level pseudo-random sequences. These sequences share some properties with white noise and allow for the impulse response of the sensor–gas system to be estimated. Using this strategy, it is shown that the best temperature-modulating frequencies to discriminate and quantify gases using an array of four metal oxide gas sensors are identified. The process is illustrated solving a practical application: the quantitative analysis of acetaldehyde, ethylene, ammonia and their binary mixtures (monitoring climacteric fruit during cold storage). By using a multi-sinusoidal temperature-modulating signal, the frequencies of which are a reduced set of the optimal ones, the gases and gas mixtures were discriminated with a 100% success rate. In gas identification, features from the sensors' dynamic response extracted via the fast Fourier transform (FFT) were used together with a fuzzy ARTMAP neural network. After the identification process, the concentration of the different species was accurately predicted by PLS-based calibration models. These results compare favorably with the ones obtained when the sensor array was operated in a steady-state mode. The optimization method is shown to be consistent and effective, since the process of determining optimal modulation frequencies and the validation process were conducted using different metal oxide gas sensor micro-arrays (of the same type) and different measurement sets.
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1. Introduction

It is well known that metal-oxide semiconductor gas sensors still suffer from serious shortcomings. These are mainly related to their low selectivity and response drift [1]. Using response signals resulting from the operation of metal oxide gas sensors in a temperature-modulated mode has been, by far, the most studied dynamic method for improving their sensitivity and selectivity and for counteracting response drift [2–10]. Despite the improvements reported in the last years, semiconductor gas sensors are hardly ever used in quantitative gas analyzers. Their typical applications are found in alarm-level monitors.

The sensitive layers of metal oxide gas sensors are made up of particles (particle size can range from nanometers up to microns) and atmospheric oxygen is adsorbed on their surfaces. Oxygen adsorbates abstract electrons from the conduction band of the sensing material, which results in the development of Schottky potential barriers at the grain boundaries. The response of semiconductor gas sensors to a reducing species implies a change in the concentration of adsorbed oxygen species. On the other hand, oxidizing species can interact with the sensor surface in a variety of ways; for example, interacting directly with the surface and

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forming negatively charged ionosorbed species or in competition with ionosorbed oxygen or oxygen ions for the adsorption sites available [11]. These changes modulate the height of the potential barriers and thus the conductance of the sensing layer. Characteristic conductance-temperature profiles arise because:

- There are different adsorbed oxygen species such as O^-, O^{2-}, and ${O_2}^-$ over the temperature range [6].
- Different gases have different optimum oxidation temperatures [1].
- Adsorption, desorption and diffusion rates (of oxygen species, reducing and oxidizing gases, and oxidation by-products) are temperature-dependent [12–14].

In this context, Sears and co-workers and also Nakata and co-workers were the first to introduce cyclic temperature variations as a way to enhance the performance of metal oxide gas sensors. In their earliest works, they concluded that temperature modulation altered reaction kinetics at the sensor surface [6,8]. A recent study, where a model based on surface kinetics that accounts for the interaction of CO and temperature-modulated metal oxide gas sensors was developed, further supports these conclusions [15]. Temperature modulation leads to response patterns that are characteristic of the species present in a gas mixture [6,8], which allows for measuring multivariate information from every single sensor. An appropriate extraction of this multivariate information helps improving selectivity. Furthermore, it has been shown that transient response patterns are less affected by drifts or changes in ambient temperature and humidity than the steady-state sensor response [16].

With the development of microsystems technology, the availability of micro-machined substrates for metal oxide gas sensors implied that sensors had their operating temperature-modulated in a more efficient way. In micro-hotplate gas sensors, the active film lays on a thin membrane with a thermal response in the range of milliseconds, which compares favorably with the thermal response of seconds found in conventional sensors (e.g. Taguchi type sensors). Many authors have introduced different methods to process the multivariate information from temperature-modulated micro-hotplate sensors [16–23]. Although the results reached using thermal modulation have been very promising, in all the works cited above the frequencies used to modulate sensor temperature are based on a non-systematic trial and error procedure. This is not the best way to ensure that the optimal modulating frequencies are used for each specific application.

Recently, we introduced a method borrowed from the field of system identification, to systematically study the effect of modulation frequencies in the discrimination and quantification ability of metal oxide gas sensors. This method is based on the use of pseudo-random maximum-length sequences to modulate the working temperature of gas sensors. It allows an optimal set of modulating frequencies to be determined for a given gas analysis problem [24,25]. In other words, the method allows for identifying specific frequencies that most enhance sensor selectivity.

In this paper, for the first time, we further develop and fully validate the method for optimizing the choice of temperature-modulating frequencies. The problem envisaged to illustrate the process is the building of calibration models for the analysis of acetaldehyde, ethylene, ammonia and their binary mixtures using metal oxide micro-hotplate gas sensors. These species were chosen, since the first two are related to the quality of climacteric fruit during cold storage and the third one reveals the occurrence of a leak in the refrigeration system.

The organization of the paper is as follows: Section 2 describes how pseudo-random sequences can be generated, used in system identification and how the method can be extended to systematically study temperature-modulated gas sensors. Section 3 describes the micro-hotplate sensors used, the experimental set-up and the different measurements performed. In Section 4, the optimization process is applied to find a reduced set of modulation frequencies to discriminate among the different gases or mixtures and to estimate their concentration. The process of frequency selection is fully validated by running new measurements using different micro-hotplate sensors (same type than the ones used for frequency selection). During these measurements, the working temperature of the new sensors is modulated using a multi-sinusoidal signal. The temperature-modulating signal is made up of some of the frequencies found to be optimal in the frequency selection step. This ensures that an honest and accurate validation of the optimization process is possible. To do so, identification and calibration models are built based on the multi-sinusoidal temperature modulation and their performance is compared against the one of models based on the static sensor response. Finally, Section 5 outlines the conclusions of this work.

2. Gas/sensor system identification by multi-level pseudo-random sequences

2.1. Generation of multi-level pseudo-random sequences

Pseudo-random sequence signals have been used as test signals in system identification for many years. The most common application is the identification of linear systems using pseudo-random binary sequences (PRBS), which have excellent correlation properties for this purpose [24]. Like PRBS, multi-level pseudo-random sequences (MLPRS) are periodic, deterministic signals, and have an autocorrelation function similar to white noise. One of the main reasons for considering signals with more than two levels is that they can provide a better estimate than binary sequences of the linear dynamics of a process with non-linearity and they can also be of use in the identification of the non-linear characteristics themselves [26].

The pseudo-random sequence signals considered here are based on maximum-length q-sequences, the generation and properties of which were described by Zierler [27]. The relevant theory behind MLPRS is based on the algebra of finite fields [28,29]. When q (the number of levels) is a prime, the digits of the sequence are the integers 0, 1, . . ., $(q-1)$ and the sequence can be generated by a q-level, n-stage shift register with feedback to the first stage consisting of the modulo q sum of the outputs of the other stages multiplied by coefficients $a_1, \ldots, a_n$ which are also the integers 0, 1, . . ., $(q-1)$. The length (or period)

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