Talanta 78 (2009) 840–845

Contents lists available at ScienceDirect

Talanta

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

Sensor array data profiling for gas identification

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ARTICLE INFO

Article history:
Received 21 August 2008
Received in revised form 17 December 2008
Accepted 22 December 2008
Available online 15 January 2009

Keywords:
Gas sensor
Transient response
Classification
Volatile organic compounds

ABSTRACT

The paper presents a new method of qualitative identification of gas. It is based on a dynamic response of sensor array with the emphasis on the processing of discrete measurement data. The information needed for identification of test samples is obtained in course of profiling the data from calibration measurements. This operation consists of the following steps: classification of data sets, selection of representative data sets, parameterization of classifiers associated with representative data sets and determination of data records. In our work Discriminant Function Analysis was used for data classification. The information saved in data record describes: the sequential number of discrete measurement, combination of gas sensors in this measurement which are best for classification of calibration samples, and the parameters of associated classifier. They are identifiers of gas class. The procedure of data record determination itself is time consuming. However this operation will be performed only at the stage of the development of the measurement instrument and when its malfunction is diagnosed. The routine use of the instrument will be restricted to gas identification task, which only utilizes the results of profiling.

The identification of unknown gas is performed on the base of data records and measurement data obtained for this gas. Data records guide the preparation of data sets, separately for each class of gases. These data sets are used as input of the discriminant functions which have parameter values also indicated by data records. It was shown in the present contribution, that the qualitative identification of nine test gas samples (vapors of ethanol, acetic acid and ethyl acetate in air) with our method was very accurate and fast.

1. Introduction

Among various types of analytical instruments, the devices based on gas sensors offer a number of interesting features. Unfortunately, they suffer also from serious shortcomings such as low selectivity, high sensitivity to humidity, drift and slow response [1]. These disadvantages are still unsolved in spite of extensive studies.

Various attempts are made to improve the measuring characteristics of sensor devices. One approach focuses on perfecting the performance of single gas sensors. This method exploits: chemical properties of the active materials, physical parameters of the sensing layer, surface modification, sensor design, physical and chemical modification of the sample (before it contacts with the chemical sensitive layer) and mode of sensor operation [2–4].

The alternative approach is based on arrays which consist of gas sensors with partially overlapping selectivity to a measured gas. Such arrays yield specific patterns of responses when different gas molecules are in contact with the sensors [5]. These responses can be analysed using well known pattern recognition algorithms. The analysis of the response signals from the sensor array can provide both qualitative and quantitative information regarding the composition of measured mixture [6].

Usually, the responses of applied sensors (especially commercial ones) to various substances are only slightly different. Therefore, the performance of arrays depends not only on the properties of individual gas sensors, but on their combinations and array size (number of sensing elements) in particular. The inadequate choice of gas sensors can potentially result in insufficient information or it can lead to noise and information redundancy [7]. For these reasons, the selection of the optimal set of gas sensors is necessary for engineers and designers of sensor systems [8–10]. A considerable efforts have been made recently to solve this problem.

Currently developed sensor arrays are mostly dedicated to strictly defined gas mixtures. The selection of gas sensors addresses the particular application and it is performed at the stage of sensor system design. Optimisation takes advantage of statistical methods, which are applied for the analysis of measured calibration data sets. Various multivariate techniques such as principal component analysis, cluster analysis, genetic algorithms, artificial neural networks and others are used to achieve this goal [11–14].

The alternative to sensor arrays dedicated to strictly defined chemical species are devices of more universal applicability. These

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doi:10.1016/j.talanta.2008.12.055

arrays require to use a broad spectrum of sensing elements, so that large number of gases could be measured by one sensor array. Due to progress in sensor technology the construction of relatively cheap arrays, consisting of many sensing elements is already possible. It allows to expand the scope of applicability of measuring systems based on gas sensors. However, a large size of such systems complicates measuring procedure, increases calibration effort and time demand for data collection and processing. Addressing these aspects is very important from the practical point of view.

This paper describes an effective method of qualitative identification of gases using sensor array which consisted of many sensors. They were not selected with a particular application in mind, but they covered as broad range of substances as possible in a partially selective manner. The dynamic mode of sensor array operation was applied in our work, but the conception could be extended to other operation modes. The proposed method was based on the idea of data profiling. The data was obtained during calibration measurements and its profiling was carried out in respect of the classification of measured gases. In course of profiling operation, data records were determined. They were structures, which were designed for the purpose of identification of unknown gas samples based on test measurements.

To show the details of this method an example of array consisting of 15 gas sensors was considered for identification of several unknown gas samples. These were vapors of one of the following substances: ethanol, acetic acid or ethyl acetate in air. Concentrations of volatile organic compounds (VOCs) in tested gases were various. We believe, that the presented method will provide a useful tool for designers and users of sensor systems.

2. Experimental

The schematic diagram of the experimental setup used in our work is presented in Fig. 1. This system was composed of the following elements: (1) pure air generator, (2) system for the preparation of gas mixtures (measured samples), (3) unit containing measurement chambers with gas sensors inside, (4) voltage supplier, (5) interface circuits containing reference resistors, (6) digital multimeter with multiplexer module and data acquisition card, and (7) PC with HP BenchLink Datalogger software.

Pure air generator (Horiba) consisted of compressor and cartridges filled with silica gel, activated carbon, soda lime and molecular sieve. Ambient air passing through these filters was purified and dried. The degree of purification was sufficient that the sensors applied in this work did not detect VOCs in the used air. Gas mixtures were prepared in the dedicated system by an evaporation method. Ethanol, acetic acid and ethyl acetate were chosen as gas mixture components of interest. Desired amounts of these compounds were continuously injected as a liquid into the heated vessel and then vaporized in a stream of air from Horiba generator. The flow rate of air was precisely adjusted and controlled by a mass flow controller. The system had the capability of generating different concentrations of volatile organic compounds using two-step dilution. The concentration of these substances in air was determined by dosage, airflow and dilution rate. The sensors were exposed to 38–610 mg/m^3 (18–297 ppm) of ethanol, 47–423 mg/m^3 (18–158 ppm) of acetic acid and 34–490 mg/m^3 (9–125 ppm) of ethyl acetate. In those ranges the concentrations of investigated mixtures followed approximately the geometrical progression with the ratio of two. This method of selection was justified by the logarithmic character of sensor response. Both, pure air generator and system for preparation of gas mixtures were designed for the dynamic and continuous supply of gases. They were connected by teflon tubes with the unit containing gas sensors.

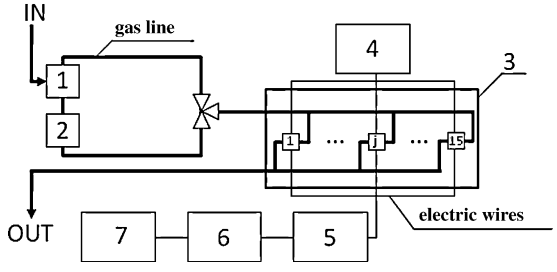

Fig. 1. Schematic diagram of the experimental setup. (1) Pure air generator, (2) system for the preparation of gas mixtures, (3) unit containing measurement chambers and gas sensors, (4) voltage supplier, (5) interface circuits containing reference resistors, (6) digital multimeter with multiplexer module and data acquisition card, and (7) PC with HP BenchLink Datalogger software.

In our work, measurements were performed using a parallel set of sensors with different sensitivities to volatile organic compounds. The array consisted of 15 commercially available Taguchi Gas Sensors made by Figaro Engineering Japan. The following TGS sensors were applied in this work TGS821, TGS822, TGS824, TGS825, TGS826, TGS880, TGS883, TGS800, TGS2201, TGS2201, TGS2106, TGS2104, TGS2602, TGS2620 and TGS2600. These devices were heated to a constant temperature, by applying voltage of 5 V to the sensor heater.

Sensors were placed inside cells with feed-through electrical wires used for electrical supply and measurements. Each sensor had its own small aluminium chamber. Since these elements were connected parallel, all sensors were exposed to the same gas mixture. The chambers were connected to a gas delivery system, voltage supplier and measuring module.

The transient response of gas sensor over time (a resistance change) was measured sequentially and converted into an output electrical signal (a voltage variations on the load resistance connected to the sensor). This operation was performed by means of interface circuits containing a series of reference resistors. The output signal was a sequence of raw voltage measurements that were related by time, used as an ordinal variable. The measured quantities were digitized and stored for further processing and analysis. The data acquisition board from Agilent was used to record the transient output of sensors. The sampling rate during data acquisition was one point per second (1 s^{-1}). Output signals generated by the data acquisition board were transmitted to PC.

Before each set of measurements, chambers containing sensors were cleaned with pure air. The measurement process involved two stages: exposition and regeneration. In the first step, the gas sample was allowed to continuously flow through the chambers. The total gas flow was set to 2 dm^3/min and it was kept constant. The exposition ran for 10 min. This time was sufficient to attain the steady state in signal output. After this step of experiment, regeneration of sensors was performed. In that phase, the whole system was flushed with a stream of pure air until readouts from sensors reached the level as before exposition.

3. Methods of measurement data analysis

Identification of test gas by the sensor array can be defined as the procedure that assigns a sensor array output to a class [15]. In other words, it allows to associate unknown mixture with one of the calibration patterns. In this paper, the class was defined as a group of gas mixtures featured by identical qualitative composition (chemical constitution). Substances in mixtures which belonged to one class could have different concentration values. However, quantification was not attempted at this stage of research. It is proposed here to perform the qualitative identification of unknown gas in mixture with air on the basis of dynamic responses of the sensor array and using data records obtained from calibration data profiling.