Wrocław University of Technology

Assessment of VOCs in air using sensor array under various exposure conditions

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LABORATORY of SENSOR TECHNIQUES

Outline

- Introduction;
- Experimental;
- Sensor signal and features;
- Qualitative assessment of VOCs;
- Quantitative assessment of VOCs;
- Conclusions.

Introduction

Volatile organic compounds (VOCs) are one of the most important groups of air pollutants.

They occur in outdoor (ambient), indoor and workplace air.

Potential health and environmental problems resulting from the use of VOCs have prompted the requirement to identify and determine the concentration of these chemical species.

Introduction

A wide range of instruments have been developed for the measurement of VOCs e.g.:

- photoionization detectors (PIDs);
- flame ionization detectors (FIDs);
- infrared analyzers;
- Fourier-transform infrared spectrometers (FT-IR spectrometers);
- gas chromatographs with appropriate detector (usually FID or tuned mass spectrometer MS or other mass-selective detector).

Introduction

The available methods are:

- too expensive;
- time-consuming;
- they require trained and experienced personnel.

Introduction

There is a strong demand for a new type of cost effective devices, particularly for:

- continuous measurements;
- performed in real time;
- using on-line, *in situ* or remote mode of operation.

Introduction

In practice, less accurate but simpler, quicker and more convenient methods are entirely satisfactory and desirable for:

- routine laboratory analysis,
- emission determination,
- industrial processes examinations,
- safety monitoring,
- surveillance and homeland security.

Introduction

There are different research strategies which can be used for the development of these novel methods.

One of them is based on a semiconductor gas sensor technology.

Introduction

Advantages

- long life time;
- sensitivity at ppm level;
- small size;
- low cost;
- convenient in use.

Introduction

Disadvantages

- relatively high power consumption;
- lack of long-term reproducibility and stability;
- sensitivity to poisoning and ambient conditions;
- insufficient selectivity.

Introduction

Sensor array consists of at least several different sensors with broad and partially overlapping sensitivity to the gas under test.

The selectivity of each sensing element is admittedly low, but the combination of responses of different sensors presents a characteristic pattern that can be treated as a unique ‘signature’ (“electronic fingerprint”) of individual chemical species.

Introduction

Measurement characteristics of devices based on the sensor array are dependent on the sensing mechanism of semiconductor gas sensors which is complex and involves:

- diffusion;
- chemisorption;
- desorption;
- catalytic reactions;
- electronic conductions.

Introduction

These phenomena are affected by:

- concentration and physical/chemical properties of an analyte;
- working parameters of the sensors;
- operation mode;
- sampling method.

Introduction

Working parameters of the sensor, operation mode and method of sampling determine conditions of a sensor exposure to gas under test.

The magnitude and shape of the signal are influenced by exposure conditions.

The measurement abilities of sensor systems are dependent on the conditions of a sensor exposure to analyte.

The aim of the work

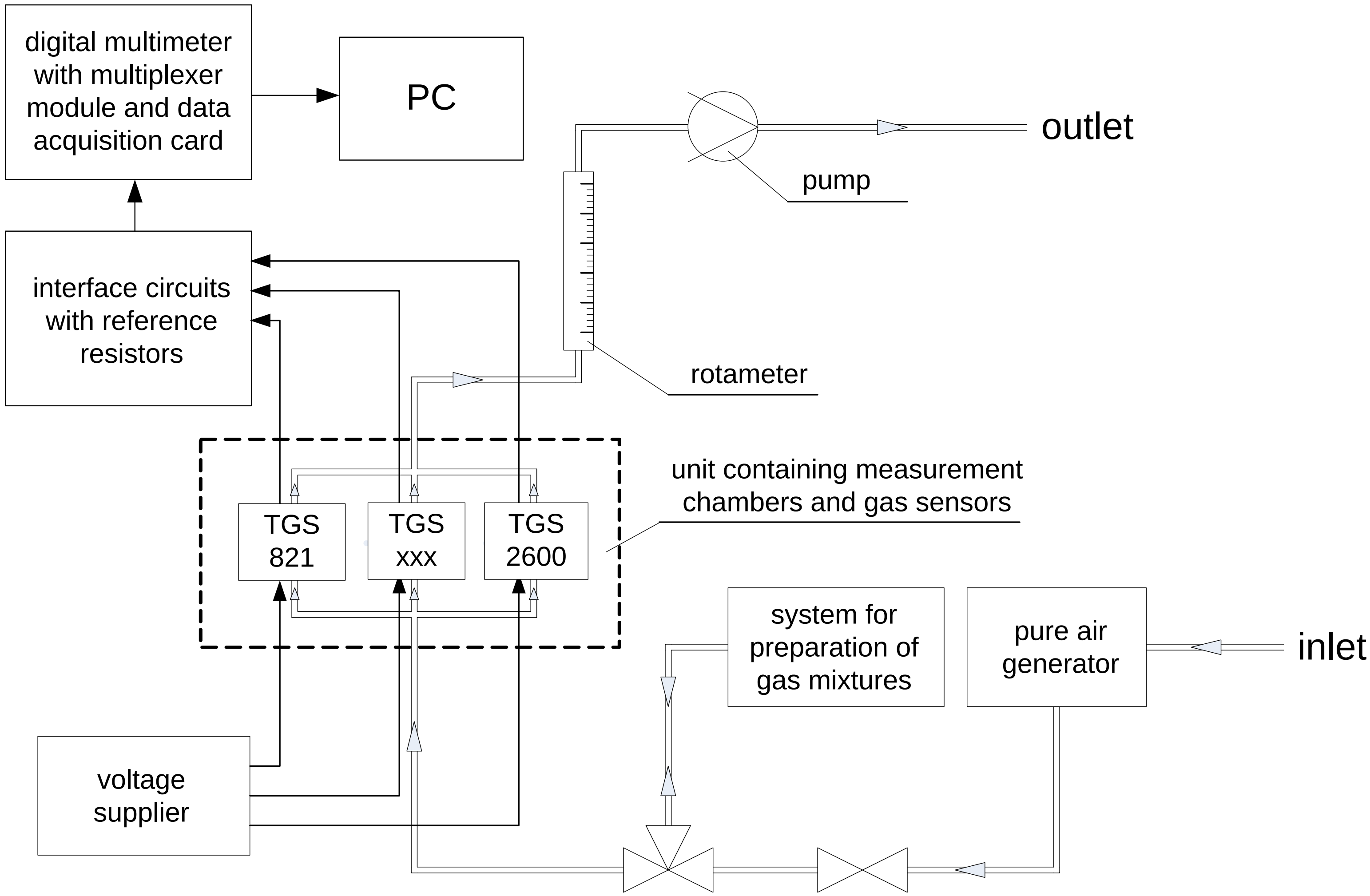
The aim of this work was to determine the influence of exposure conditions on classification and quantification abilities of sensor array.

Chemicals

The following compounds were chosen as analytes of interest in this work:

- cyclohexane (21-249 ppm);
- hexane (17-204 ppm);
- heptane (15-183 ppm);
- octane (14-165 ppm);
- benzene (25-302 ppm);
- ethylobenzene (18-220 ppm);
- toluene (21-255 ppm);
- xylene (18-222 ppm);
- water (493-26443 ppm).

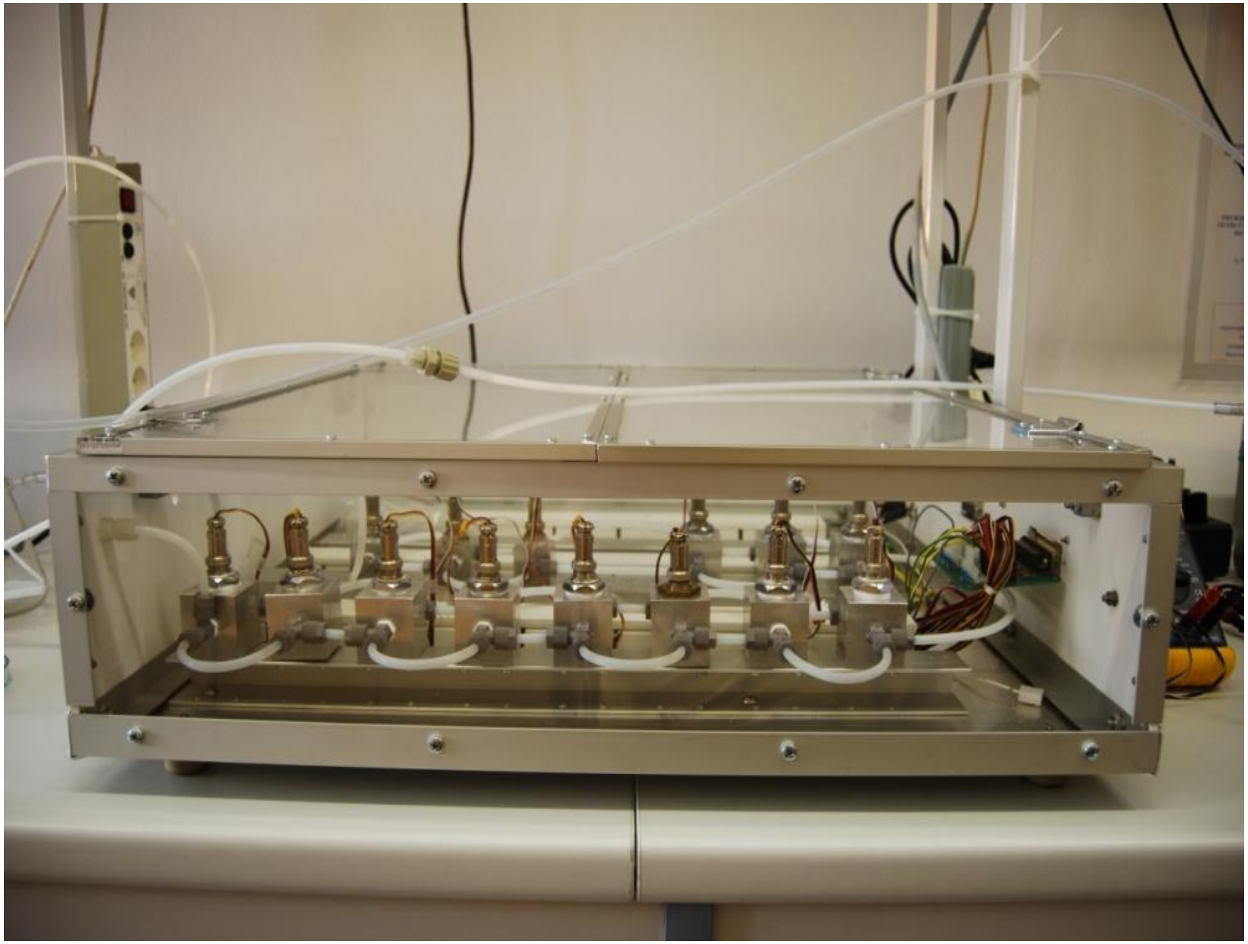
Experimental setup



Gas sensors

All measurements were performed with the use of sensor array equipped with a set of fifteen commercially available Taguchi Gas Sensors made by Figaro Engineering Japan: TGS800, TGS821, TGS822, TGS824, TGS825, TGS826, TGS880, TGS883, TGS2104, TGS2106, TGS2201 (2 sensors), TGS2600, TGS2602, TGS2620.

Sensor array



Sensor array

Sensor array

Sensor chamber

Each sensor was mounted inside its own, specially designed, airtight, flow-type test chamber made of aluminum.

Chambers were provided with two ports for the gases (inlet and outlet) and a head with wires.

Sensor chamber

The chambers were connected in parallel using Teflon-tubing.

Such configuration allowed for the simultaneous exposure of sensors to the same test gas.

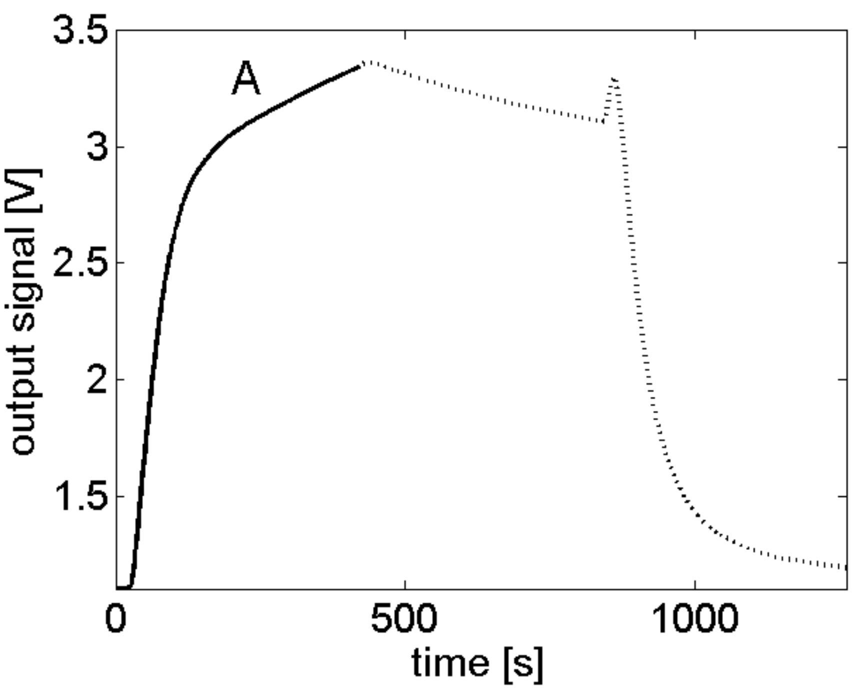
First type of exposure

First exposure was accomplished in dynamic conditions.

Sensors were exposed to a stream of air containing compound of interest.

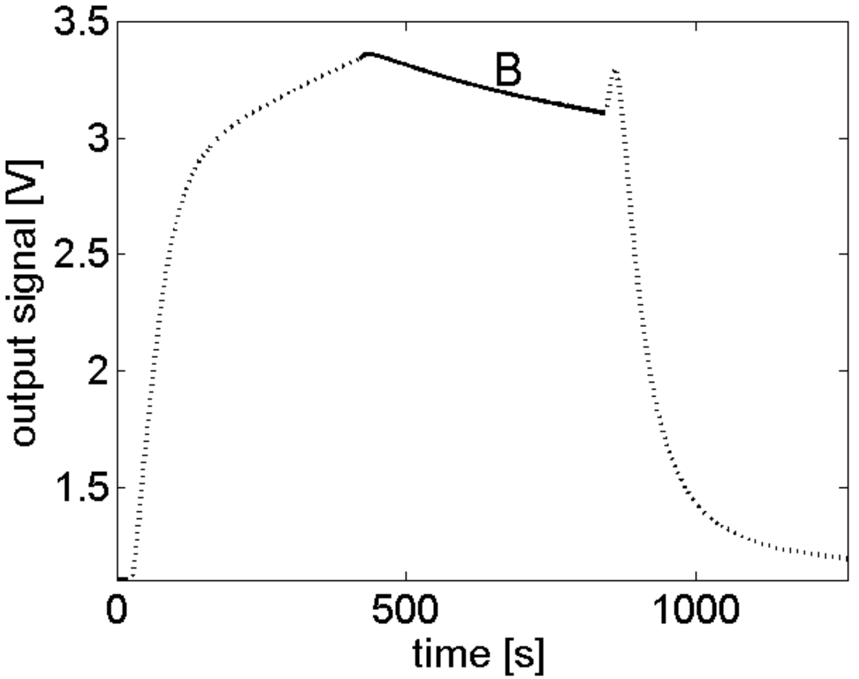
The gas flow through the experimental setup was continuous and kept at a constant rate.

The exposure time was usually sufficient to attain the gas equilibrium inside the sensor chambers.



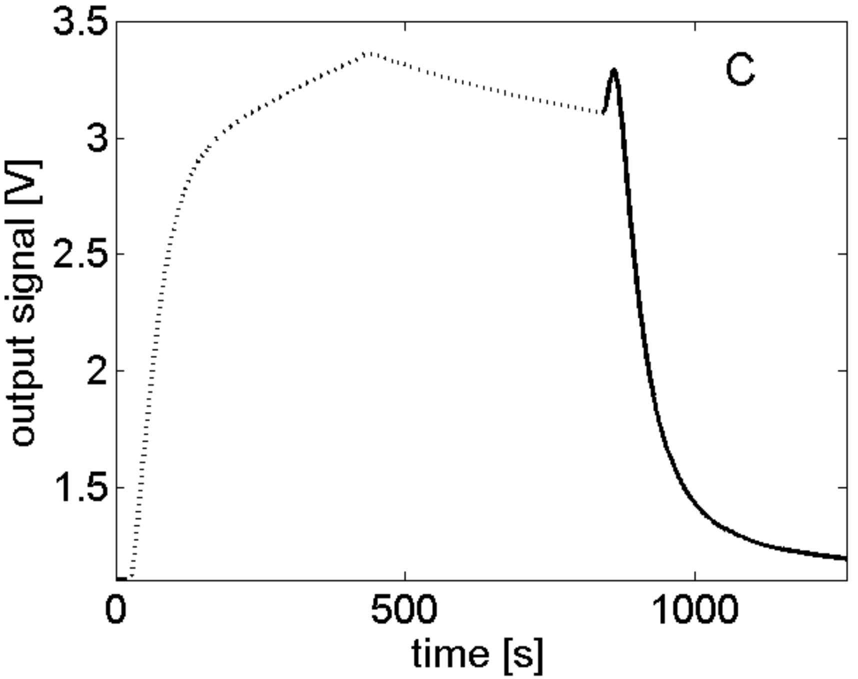
Second type of exposure

- Second type of exposure was realized in static conditions.
- The gas flow was stopped, but the sample remained in sensor chambers.



Third type of exposure

- The third type of exposure functioned both as the recovery process and the source of analytical information.
- Sensors were again in dynamic conditions.
- However, the chemical composition of the gas around sensors was changed.
- The gas line and chambers were cleaned with a stream of pure, dry air.

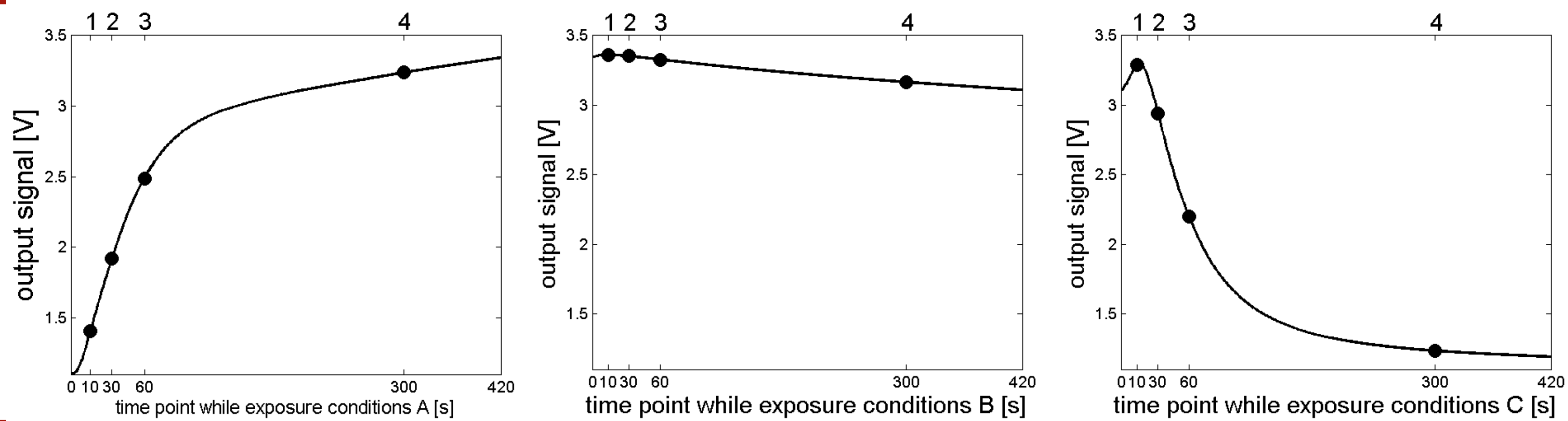


Features

The feature was defined as the value of sensor signal associated with a single time point, upon applying a defined exposure type.

The time points were arbitrarily selected for each type of exposure. These were 10th, 30th, 60th and 300th second since the beginning of exposure.

Features



Typical output signal of TGS sensor obtained in course of three exposure types: A, B and C. Dots indicate features associated with fixed time points.

Features

The feature vector was indicated by the set of sensors and the time point of exposure.

For pattern recognition there were considered two kinds of feature vectors.

The first ones were composed of signal values of all sensors in the array (15 elements).

The second ones included selected features (5 elements out of 15). The selection was done using wrapper approach. The feature space was searched by means of simulated annealing.

Qualitative assessment of VOCs Classification problem

The classification problem was defined as the nine-class problem.

Single class contained patterns representing one VOC or water vapour.

k-nearest neighbor (KNN, k=1) method was used for pattern classification.

The classifiers were iteratively trained and validated using bootstrapping technique (30 fold).

Qualitative assessment of VOCs
Classification problem

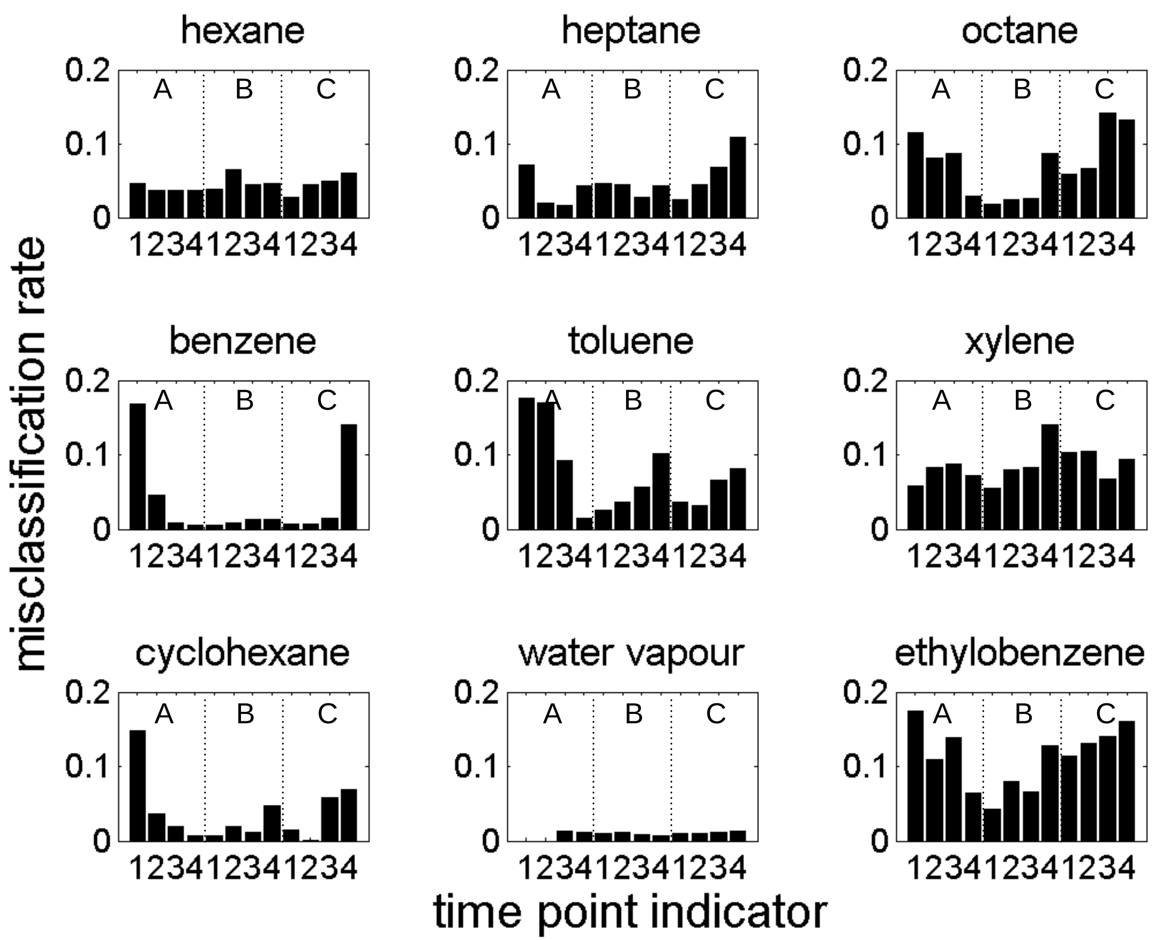
The misclassification rate (*MR*) was applied to estimate the classification performance.

$$MR = \frac{1}{K}\sum_{k=1}^{K}\frac{n_{mk}}{n_k}$$

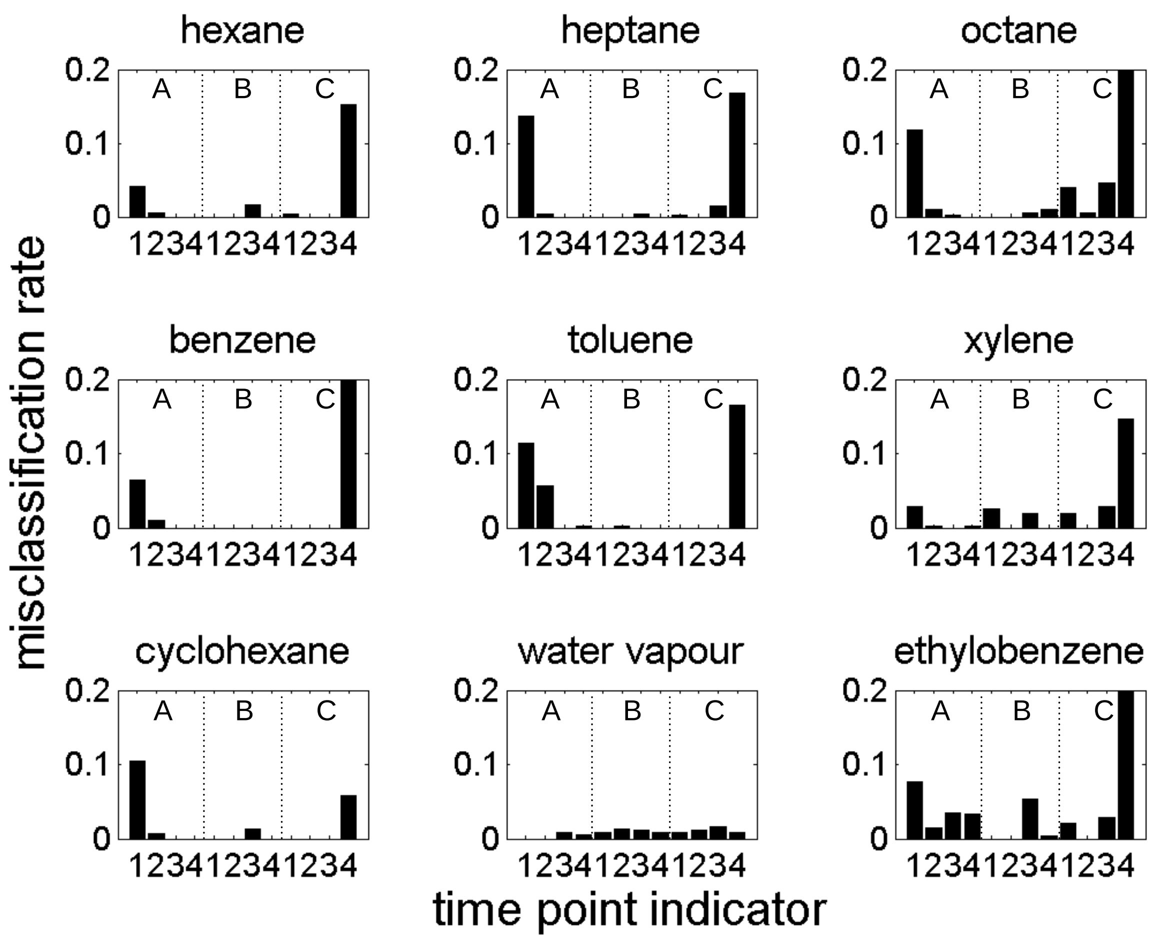
where: K is the number of classes, n_k is the number of patterns in *k-th* class, n_{mk} is the number of misclassified patterns in *k-th* class.

Misclassification rates were calculated for eight VOCs and water vapour.

Patterns classification using all sensors in the array



Patterns classification using five selected sensors



Quantitative assessment of VOCs

Regression problem

Simple linear regression and nonlinear regression models were used for fitting the relationship between concentrations of VOCs and single features.

$$c = a_{i,t} + b_{i,t} S_{i,t} + \varepsilon$$

$$c = \alpha_{i,t} \beta_{i,t}^{S_{i,t}} + \varepsilon$$

where: S_{it} is the value of *i-th* sensor signal at *t-th* time point of the defined type of exposure to a single VOC; c is the concentraton of VOC; a_{it}, b_{it}, α_{it}, β_{it} are model parameters, ε represents random component.

The regression models were iteratively parameterized and validated using bootstrapping technique (30 fold).

Quantitative assessment of VOCs Regression problem

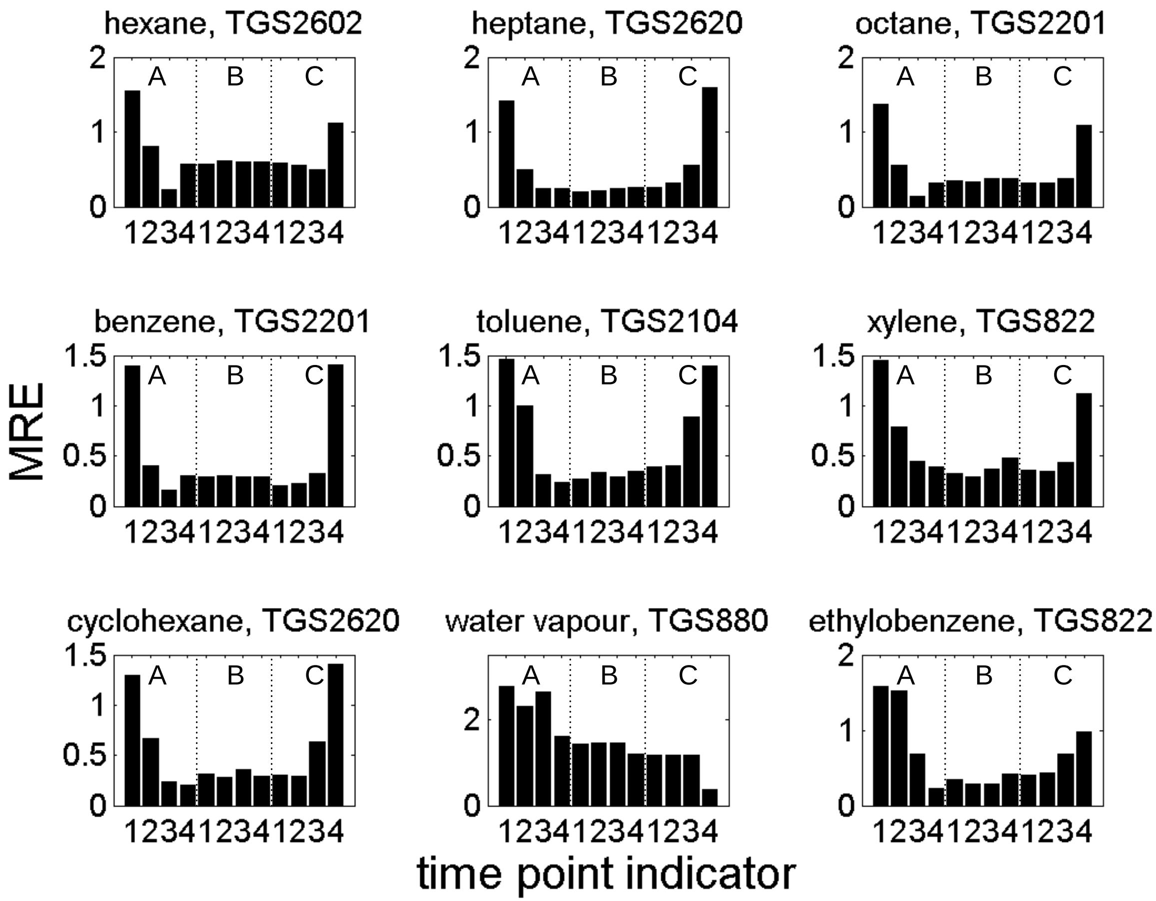
The mean relative error of concentration prediction (MRE) was applied to estimate quantification performance.

$$MRE = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\hat{c}_i - c_i}{c_i}\right|$$

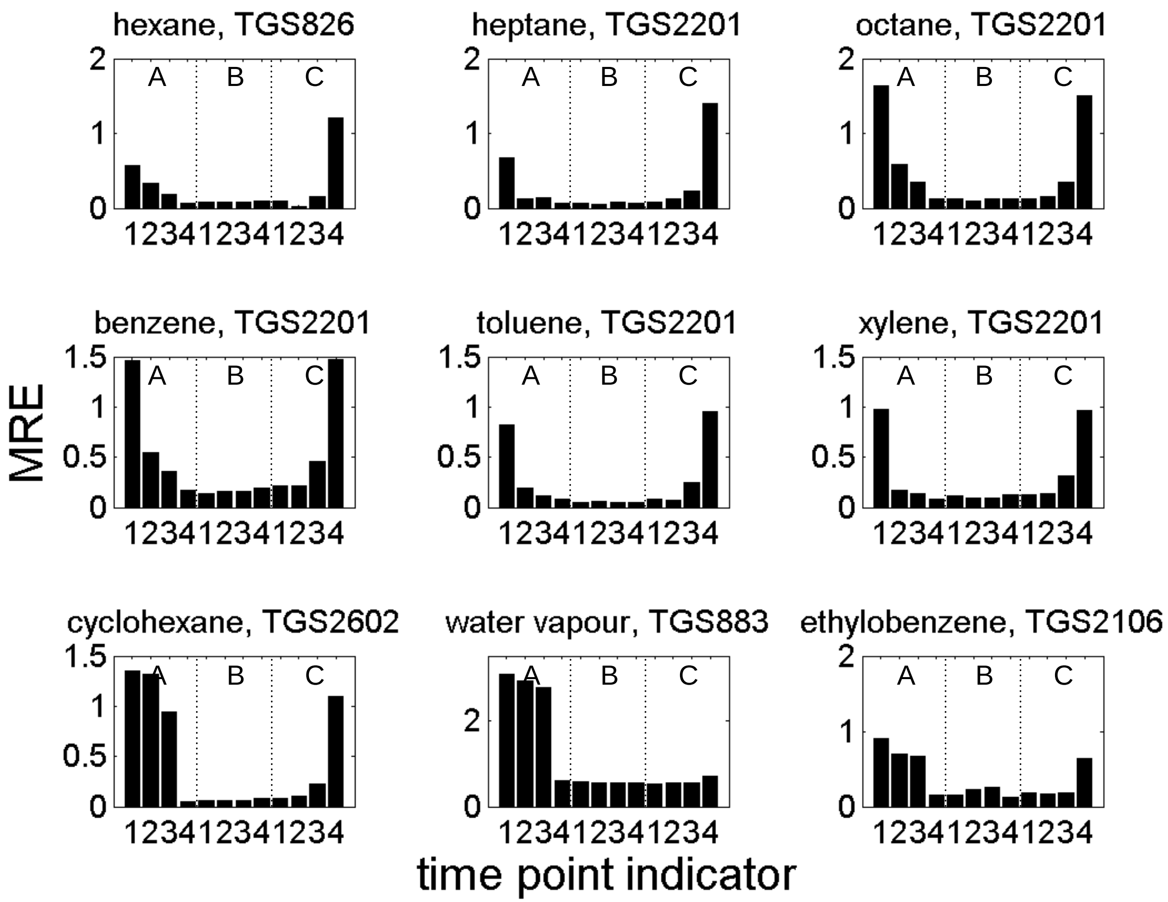
where: *n* is the number of samples used for model validation, c_i is the real concentration of the compound in *i-th* sample, $\hat{c}_i$ is the predicted concentration of VOC in the *i-th* sample.

MRE of VOCs concentration prediction using best features (sensors) are shown for eight VOCs and water vapour.

VOCs concentration prediction using best sensor and linear regression



VOCs concentration prediction using best sensor and nonlinear regression



Conclusions

It was shown that the ability to qualitatively assess VOCs was related to the conditions of sensor array exposure.

They differently affected sensors responses to the gas under test.

Sets of sensors were found which performed best as the basis for classification in particular conditions of exposure.

Using best sets of sensors and most favorable exposure conditions the misclassification rate of VOCs was reduced to zero.

Conclusions

Exposure conditions were also found as influencing sensor array ability to determine target gas concentration.

Single sensors differently performed upon altered exposure conditions.

For each of the examined VOCs a sensor was found which offered lowest error of concentration prediction.

When using nonlinear regression the quantitative analysis was performed with an error of several percent.

Conclusions

The obtained results have large practical significance due to providing information e.g. regarding the most effective mode of operation and the method of sampling.

Acknowledgements

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Thank you for your attention!