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Method of gas mixtures discrimination based on sensor array, temporal response and data driven approach

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ABSTRACT

This work presents a method of gas mixtures discrimination. The principal concept of the method is to apply measurement data provided by a combination of sensors at single time point of their temporal response as input of the discrimination models. The pattern data combinations are selected for classes of target gases based on the criterion of 100% efficient discrimination. Combinations of sensors and time points, which provide pattern data combinations in course or repeated measurements, are encoded in the form of addresses. The designer of sensor system is responsible for their selection and they are included in the software of the final instrument. The study of the method involved the discrimination of gas mixtures composed of air and single chemical: hexane, ethanol, acetone, ethyl acetate and toluene. Two sensor arrays were utilized. Each consisted of six TGS sensors of the same type. The dynamic operation of sensors was employed. As an example the stop-flow mode was chosen. The work provides the evidence of the existence of sensor combinations and time points, which are successful in discrimination of studied classes of target gases. The persistence of addresses was discussed considering the ability of sensor array to recognize analytes, variability of repeated measurement results, number of repeated measurements and a twin sets of sensors. Altogether, the validity of the method was demonstrated.

1. Introduction

In the last twenty years, considerable efforts have been devoted to applied sensor arrays as a source of multivariate information in measuring systems, which are called electronic noses. Their optimization is a key issue for identification and quantification abilities of electronic noses. The performance characteristics of these devices are affected by a few factors. The attention of designers is mainly focused on the selection of individual sensing elements, the optimization of configuration and dimension of array, the choice of suitable operating mode.

The ideal sensors to be integrated in a matrix should fulfill several criteria. First of all, there is required high sensitivity towards target gas and low sensitivity towards humidity and temperature, medium selectivity (they must respond to different constituents of a tested sample), short response and recovery time, small weight and dimensions. Additionally, sensors have to be reliable, stable, repeatable, reversible, robust and durable. It should be noted, that it is difficult to meet all of these requirements in practice [1].

An analysis of particular chemical compounds or mixtures of these species with electronic noses is based on chemical fingerprints produced by the sensor array. Patterns are built of outputs of individual sensors. Therefore, a suitable combination of these devices plays a crucial role in designing electronic noses [2,3].

The measuring properties of arrays are also influenced by their dimension, i.e. the number of applied sensor elements [4,5]. For example, a large array may improve discrimination abilities of the electronic nose. However, a calibration effort and time demand for data processing increase considerably in this case. Additionally, multidimensional arrays may include sensors which are not sensitive to target gases and do not contribute to recognition task. A variance (noise) is increased in this situation. Therefore, arrays with less number of sensing elements, but with various response parameters are preferred in practice. By eliminating unimportant sensors, the cost and time of collecting and analyzing data may be reduced. This is crucial for many applications.

Performance of sensing elements in electronic nose can be based on stationary and/or dynamic mode of operation. In commercial instruments, the first strategy is preferred, because the data analysis is easier in this case. However, with the second approach it is possible to utilize transient responses. They may be a source of multivariate information which enhances the identification and quantification ability of the electronic nose [6,7]. For that reason, this mode of operation has received much attention in recent years. A characteristic feature of transient responses is large number of collected variables from each measurement. In practice, some of them contain no valuable information or are strongly correlated with other variables. Additionally, the analysis of large set of data

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Table 1
Concentrations of volatile organic compounds (VOCs) in tested gas mixtures containing single VOC.

Concentration of VOC/ppm				
Hexane	Ethanol	Acetone	Ethyl acetate	Toluene
49	18	75	30	9
99	36	149	60	18
197	71	299	120	36
395	143	598	239	72
790	286	1196	479	143

may cause serious calculation problems. Thus, it is necessary to reduce the number of variables which are analyzed. This operation relies on a compression of sensor array response down to a few single parameters (descriptors). Unfortunately, in the parameter-extraction approach much information about measured chemicals may be lost or inaccessible.

Sensor arrays which are designed in accordance with the presented rules are especially useful in the development of electronic noses dedicated for specific analytical tasks, e.g. identification of well defined odors or other volatile mixtures. Thus, the applicability of these instruments is limited. For this reason, we decided to elaborate a concept which gives an opportunity to expand the scope of applicability of such measuring systems. This concept presents a new approach to dimensionality of sensor array (selection of sensing elements), mode of operation, form of analyte pattern and input of discrimination model. It is discussed in reference to the discrimination of several gaseous mixtures of air and volatile organic compounds.

2. Experimental

2.1. Materials

There were studied gas mixtures composed of air and five organic compounds: hexane, ethanol, acetone, ethyl acetate and toluene, one by one. Chemicals were purchased from Sigma–Aldrich and they were used as received.

In our work a series of five experiments was performed. In course of single experiment there were measured sensor array responses to gas mixtures of all VOCs. Their concentrations are shown in Table 1. Gas mixtures were studied in a randomized order.

2.2. Experimental setup

The experimental setup which was used in our study is shown schematically in Fig. 1. This system was dedicated to preparation of standard samples, which were gaseous mixtures of air and single VOC, and to measuring responses of sensors operated in stop-flow mode. The experimental setup consisted of several functional blocks.

(1) Pure and dry air was produced using zero air generator manufactured by Horiba. The degree of purification met requirements of our studies. It means that sensors applied in arrays did not respond to water vapor and VOCs in purified air, which was used as a reference or the carrier gas. (2) The installation for standard gas preparation included vaporizer in the form of heated glass coil with injection port, Tedlar bag (12 l) and chromatography syringe (Hamilton). (3) The module for delivering and control of gas flow was equipped with diaphragm pump, mass flow controllers, valves and Teflon gas line. (4) Two sensing arrays were equipped with a set of the same gas sensors. Six commercially available Taguchi Gas Sensors made by Figaro Engineering Japan were applied: TGS2620, TGS821, TGS825, TGS826, TGS2104, TGS2602. Each of the sensors was mounted inside its own, specially designed, airtight, flow-type test chamber. Chambers were made of aluminum. We decided to use this type of compartment since chemical reactions of organic compounds and oxygen on the surface of sensing material produce intermediate products which can affect responses of neighboring sensors. The chambers were provided with gas inlet and outlet and they were connected parallel using a Teflon-tubing. Such configuration allowed for the simultaneous exposure of sensors to the same gas. The sensor arrays were attached to module for delivering and control of gas flow. The chambers were also equipped with electrical connections. (5) Each sensor was connected to a voltage supplier and electronic circuit. (6) The output signals were measured in the form of voltage variations on the load resistance with time resolution of 1 s. The ADC (Maxim 1231) was used for analog to digital signal conversion. Signals were recorded by the application developed in LabView. (7) A personal computer with a suitable software was used for data storage, processing and analysis.

2.3. Measuring procedure

The studies reported in this paper consisted of a series of experiments carried out according to the procedure based on two assumptions: (1) the evaporation method was employed for the preparation of standard gas samples, (2) sensors were operated in a stop-flow mode.

In order to prepare a mixture of air with known concentration of organic species, the desired amount of liquid VOC was injected with a chromatography syringe into the heated glass coil. The injected liquid vaporized in the stream of pure, dry air delivered by the Horiba generator. It was essential to ensure constant, known flow of gas through the glass coil, which was connected with the Tedlar bag. The flow rate of 1 l/min lasted for 10 min in our experiments. This time was sufficient to evaporate all amount of organic liquid. Since the volume flow of the carrier gas was precisely adjusted, the dosage of VOC was known, volatile substance was fully converted into vapor and collected into a Tedlar bag, it was possible to determine the quantitative composition of the prepared gaseous mixture.

The stop-flow mode of operation was based on changes of gaseous atmosphere around sensors in a controlled way. In our work, a factor which determined operating conditions (the element of operating conditions, which was varied on purpose in course of measurement procedure) was the flow and the chemical composition of gas in the sensor system. The alterations were introduced according to an algorithm, which is schematically shown in Fig. 2.

The measuring procedure consisted of three, sequentially performed operations. The first one was the dynamic exposition of sensors to a stream of air and volatile organic compound of interest. The sample was allowed to continuously flow through chambers with sensors inside. The gas flow through the experimental setup was set to 1 l/min and it was kept constant. The dynamic exposition ran for 300 s. This time was sufficient to attain the gas equilibrium in the atmosphere surrounding sensors. After this time, the second step followed. During this phase of operation, the gas flow was stopped, the sample remained in sensors chambers. Static exposition to the test gas lasted for 420 s. The third stage functioned both as a recovery process and as a source of analytical information. It was continued for 420 s. Sensors were again in dynamic conditions. However, the chemical composition of gas stream was changed, because the gas line and chambers were cleaned with a stream of pure, dry air. The air flow through the system was 1 l/min. The regeneration of sensors continued afterwards, until readouts from these devices reached the level as before the dynamic exposition to test gas. In all cases, the reversible change in the resistance of sensors was observed. The extensive description of sensors responses in the stop flow mode was presented in our earlier paper [8].

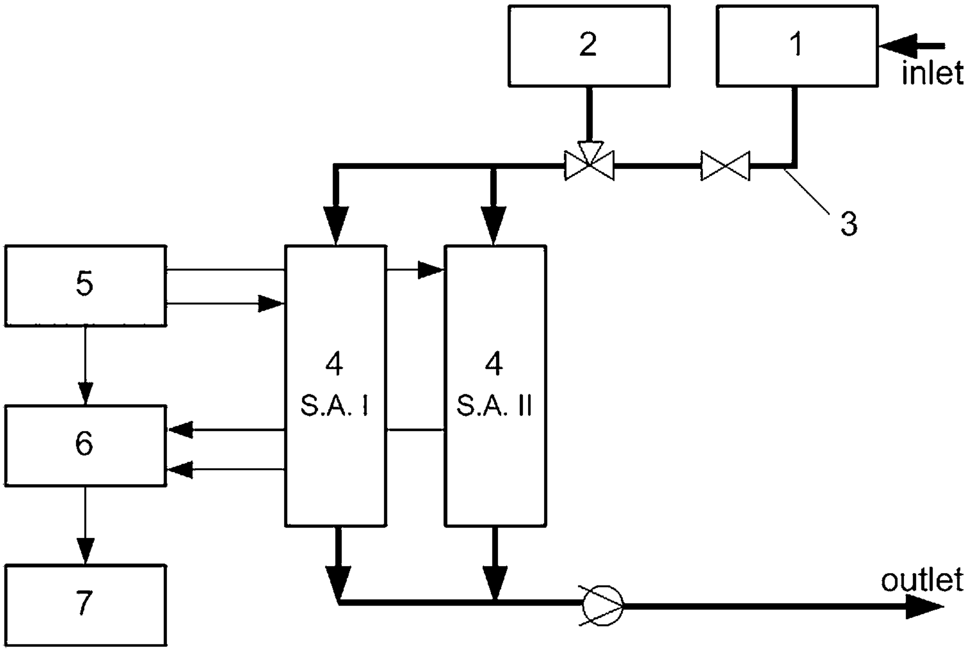

Fig. 1. The schema of the experimental setup. (1) Device for the preparation of pure and dry air, (2) installation for standard gas preparation, (3) apparatus for delivering and control of gas flow, (4) two independent sensor arrays, (5) voltage supplier, (6) interface circuits containing load resistors for measuring output signals, and (7) personal computer.

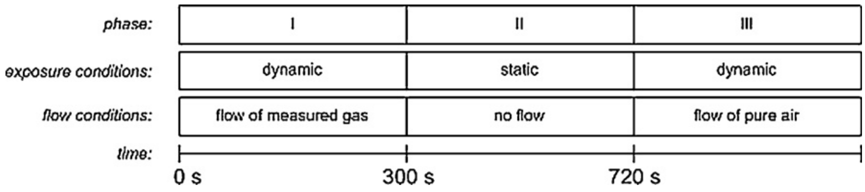

Fig. 2. Phases of the stop-flow mode of sensor array operation.

2.4. Data combinations classification procedure

The main objective of classification was to find pattern data combinations which are best for the discrimination of volatile organic compounds. Based on them, the subsets of sensors and time points were identified which indicate pattern data combinations. They were called addresses. The selection of addresses which results from classification may be considered as the first stage of reduction of data redundancy.

A two-class, one-against-all discrimination approach was employed in this study. The class formed by gas mixtures consisting of air and a selected organic compound (*class 1*) was discriminated from the class formed by gas mixtures composed of air and all the other organic compounds considered individually (*class 2*).

In this work, the discrimination aimed at selection of pattern data combinations was performed using measurement data collected in course of five experiments. Each of them was considered separately.

The linear discriminant analysis (LDA) was used for classification. It is a well known statistical method which allows for solving task of supervised classification. The method calculates a posteriori probability of hitting a particular class with a given test data vector. The class with highest probability assigned to it is considered as the vector's home class. Beforehand, a priori probabilities referring to classes are calculated using the pool of training vectors, which represent these classes [9,10]. The principal advantage of the method is its simplicity. In particular, a simple algebraic form of discriminant function is beneficial, which is easy to parameterize and implement in software application.

The solution of each discrimination problem was evaluated by cross-validation and using leave-one-out procedure. The discrimination performance was jointly assessed for the group of M models, which utilized a fixed set of sensors and a fixed time point of their response as a source of input data. Let M_1 be the number of samples which belong to *class 1*, related to the selected single analyte and M_2 be the number of samples which belong to *class 2*, associated with other analytes. The following was true: $M_1 + M_2 = M$, $M_2 = 4M_1$. A single model in the group was parameterized using measurements of $M - 1$ samples together, as inputs and labels which indicated their class assignment, as outputs. The membership of the remaining sample was calculated with the resulting discriminant function. The following criterion of successful discrimination was set: M_1 samples of a selected analyte were classified correctly as members of *class 1*, and M_2 samples of the other analytes were classified as members of *class 2*. The errorless classification of all samples measured in a single experiment was required to fulfill the criterion. Neither false positive nor false negative classifications were allowed.

After completing data combinations classification procedure, there are found addresses which are common for repeated measurements of the studied compounds. This is the second stage of reduction of data redundancy. While using the instrument the addresses are utilized for pointing at pattern data combinations. They are expected to guarantee successful recognition of measured compounds. Altogether the proposed procedure results in substantial reduction of computational effort at the level of the measuring instrument user.

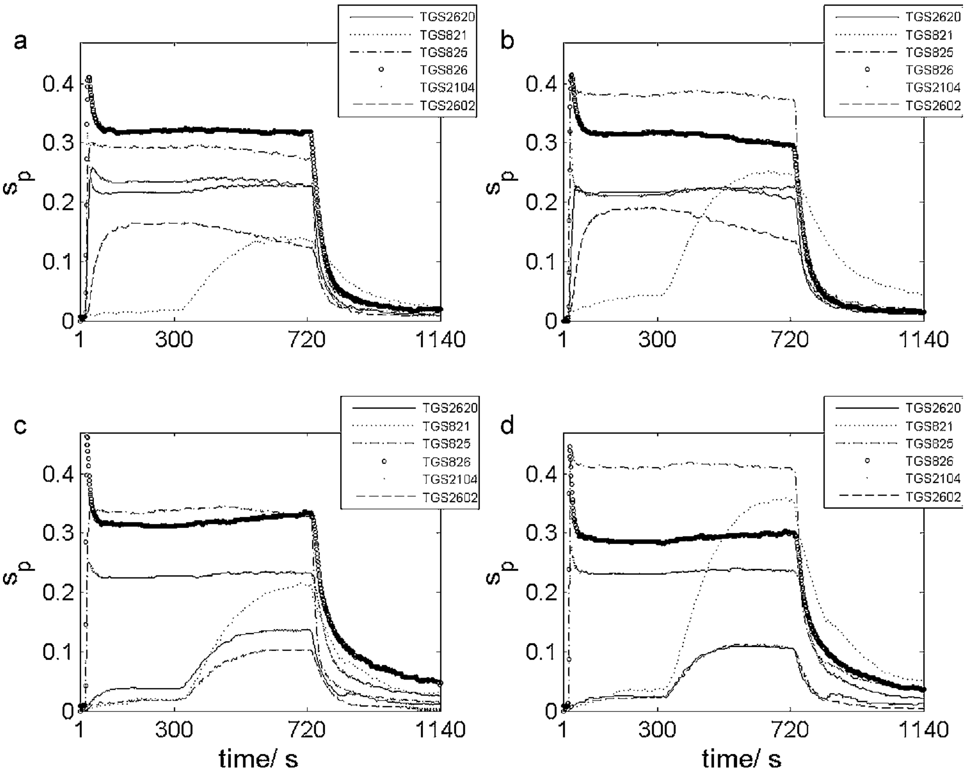

Fig. 3. The pooled standard deviation of sensor response to analyte versus time. (a) Ethanol in air measured by S.A.I, (b) ethanol in air measured by S.A.II, (c) ethyl acetate in air measured by S.A.I, (d) ethyl acetate in air measured by S.A.II.

3. Results and discussion

The concept shown in this paper is based on several assumptions. (1) The sensor array may consist of many various sensors of the same type. The high selectivity of these devices is not required. Sensors should have different sensitivities to various gases. (2) The operation of sensing element should be based on a stop-flow mode, because combination of transient and steady-state sensor responses enlarges a source of available information about analytes. (3) The procedure of response value compression is not used since extracted parameters convey less information than standardized/normalized results of measurements. (4) The discrimination task is performed by using linear discriminant analysis (LDA). (5) An essential issue in our concept is a form and content of input data which is used for: parameterising discrimination models which are used in sensor system; discriminating target gases by the instrument and calibration of the measurement system. In our strategy these processes utilize sets of data, which are called pattern data combinations. The fundamental unit of this collection is a combination of sensors responses to the analyzed gases, which are recorded at the same time-point. The primary problem in this approach is the selection of combinations which are best suitable for the discrimination of analyzed gases. The rules of the selection are developed by the designer of the sensor system. They are in the form of addresses which refer to single combination of sensors associated with single time point. Each class of gases is assigned its own set of addresses. The addresses are determined using sensors responses to standard gases representing all the classes. The criterion of 100% effective discrimination is employed for their selection. In order to improve the reliability of the addresses, multiple measurements of all standard gases are considered. The addresses indicate combinations of sensors and time points which granted satisfactory discrimination in a number of repeated experiments. In this way, it is possible to incorporate the information about combinations of sensors and time points which are best suitable for discrimination tasks in data analysis module of the instrument.

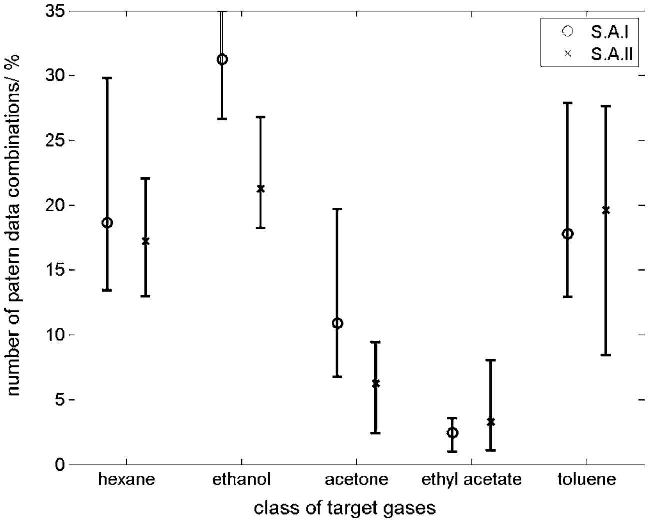

Fig. 4. Number of pattern data combinations for various classes of gas mixtures. They were found for all repeated measurements.

The validity of the proposed concept of discrimination method was examined by addressing the following issues:

- variability of response of individual sensors operated in stop-flow mode,
- selection and characterization of data combinations which are patterns of classes of target gases,
- persistence of addresses regarding repeated measurements,
- overlap of addresses between two identical sensor arrays.

Much attention was devoted to the issue of persistence of combinations of sensors and time points, which is crucial for the successful functioning of the proposed method of gas mixtures discrimination.

3.1. *Variability of sensor response values*

The variability of sensor response values was defined as the variation among independent results of measurements, which were obtained: (1) upon repeated exposures of sensor array to test samples which had identical qualitative and varied quantitative composition, (2) by the same operator of the measuring system, (3) under the same conditions including location, procedure and repetition over a short period of time, (4) by individual sensors, (5) at the defined time point of sensor response. The variation of measurement results was represented by the pooled standard deviation, as indicated by the following formula:

$$s_p = \sqrt{\frac{\sum_{i=1}^{k}(n_i - 1)s_i^2}{\sum_{i=1}^{k} n_i - 1}}$$

where s_i^2 is the variance of sensor response to the ith concentration of measured compound (There were considered $k = 5$ concentrations of each compounds.); $n_i = 5$ is the number of repeated measurements at a fixed concentration.

The pooled standard deviation was calculated for all classes of gas mixtures, sensors and time points of their temporal response. As an example, the time plots of pooled standard deviation for two selected classes: *ethanol* and *ethyl acetate*, are shown in Fig. 3.

Based on the calculated pooled standard deviation there were no substantial differences between the variability of measurement results of various VOCs in air. The variability was lowest for toluene and hexane. In those cases the values of s_p was in general smaller than 0.35 V. The variability was higher for acetone, ethanol and ethyl acetate. In those cases the values of s_p was in general smaller than 0.40 V.

Considering phases of sensor array operation in the stop-flow mode, the variability of measurement results was usually lower in *phase I* (flow of the measured gas) than in *phase II* (stopped flow of the measured gas). The decreasing variability in *phase III* (purging sensor chambers with pure air) was most probably a side-effect of rapid decrease of sensor signals due to removing measured compound from sensors chambers.

Clearly there were differences between sensors regarding pooled standard deviation (Fig. 3) of measurement results. However, the corresponding sensors in sensor arrays: S.A. I and S. A II showed similar variability of measurements of the same analyte, as illustrated by the example presented in Fig. 3.

It shall be mentioned that the variability of sensors responses is by no means indicative for the existence of combinations of sensors and time points, which are suitable for the discrimination tasks. However, the measurement variability is potentially indicative for the persistence of such combinations across repeated measurements.

3.2. *Persistence of suitable combination of sensors and time points*

Although majority of data combinations carried nonselective information, there were found pattern data combinations for every studied class of target gases. As shown in Fig. 4, pattern data combinations were between 1% and 35% of all available data combinations, depending on target gas, repetition of the experiment and sensor array.

It was shown by the analysis of variance, that the number of pattern data combinations was significantly dependent on the analyte and it was not significantly influenced by the repetition of measurement or the exchange of sensor array to the identical one.

The two-way ANOVA was employed to consider simultaneously the influence of the analyte and the repetition of experiment on the number of pattern data combinations. The p-values calculated for the factor: analyte were $p = 6.22\mathrm{E}{-07}$ and $p = 1.87\mathrm{E}{-05}$, in case of S.A. I and S.A.II, respectively. They confirmed the statistically significant influence of this factor. Regarding repetitions of experiment, the obtained p-values were $p = 0.102$ and $p = 0.0229$ in case of S.A. I and S.A.II, respectively. Therefore, taking as an arbitrary reference the significance level $\alpha = 0.05$, the number of pattern data combinations did not change in a statistically significant manner in subsequent experiments.

The two-way ANOVA with replicates was used to study simultaneously the influence of the analyte and sensor array on the number of pattern data combinations. Five performed experiments were considered as replicates. The p-value calculated for the factor: sensor array was $p = 0.063$. Therefore, taking as an arbitrary reference the significance level $\alpha = 0.05$, the number of pattern data combinations was not significantly affected by changing between the measurement data provided by S.A. I and S.A. II. The significance of analyte as a factor influencing the number of pattern data sets was confirmed in this analysis as the associated critical significance level was $p = 2.34\mathrm{E}{-12}$.

In our study the highest number of pattern data combinations was found for ethanol (on average 31% for S.A. I and 21% for S.A. II). Smaller number of data combinations was successful in discrimination of toluene (on average 18% for S.A. I and 20% for S.A. II) and hexane (on average 19% for S.A. I and 17% for S.A. II). Still less data combinations were available for effective discrimination of acetone (on average 11% for S.A. I and 6% for S.A. II). The smallest number of pattern data combinations was indicative for ethyl acetate (on average 2% for S.A. I and 3% for S.A. II).

Numbers of best suitable combinations of sensors and time points are given in Table 2 for each considered class of target gas.

There were found many combinations of sensors and time points which were suitable for the discrimination of gas mixtures containing hexane, ethanol, acetone and toluene in air, in all five experiments. There was none such combination found for gas mixtures containing ethyl acetate in air. In the considered example, the discrimination of ethyl acetate may be solved indirectly, by eliminating other possible identities of test samples.

There are shown in Fig. 5 the addresses of pattern data combinations, which were common for five experiments. The indicators of sensor combinations are deciphered in Table 3. Based on the layout of points in Fig. 5 the successful discrimination of the investigated gas mixtures was driven by a particular combination of sensors rather than by a particular time points. Usually, single combination of sensors provided pattern data combination located at many neighboring time points of sensor array response. Those time points were nearly exclusively associated with *phase I* and *phase II* of exposure, with the special emphasis on the stop-phase. Also the very beginning of the regeneration process – *phase III* delivered pattern data combinations. This explicitly shows the advantage of

Table 2
Number of addresses for different classes of target gases/%.

Class of target gases	S.A. I	S.A. II	S.A. I and S.A. II
Hexane	9.2	8.9	7.6
Ethanol	17.3	8.6	7.3
Acetone	3.5	0.8	0.7
Ethyl acetate	0	0	0
Toluene	6.0	5.3	2.8

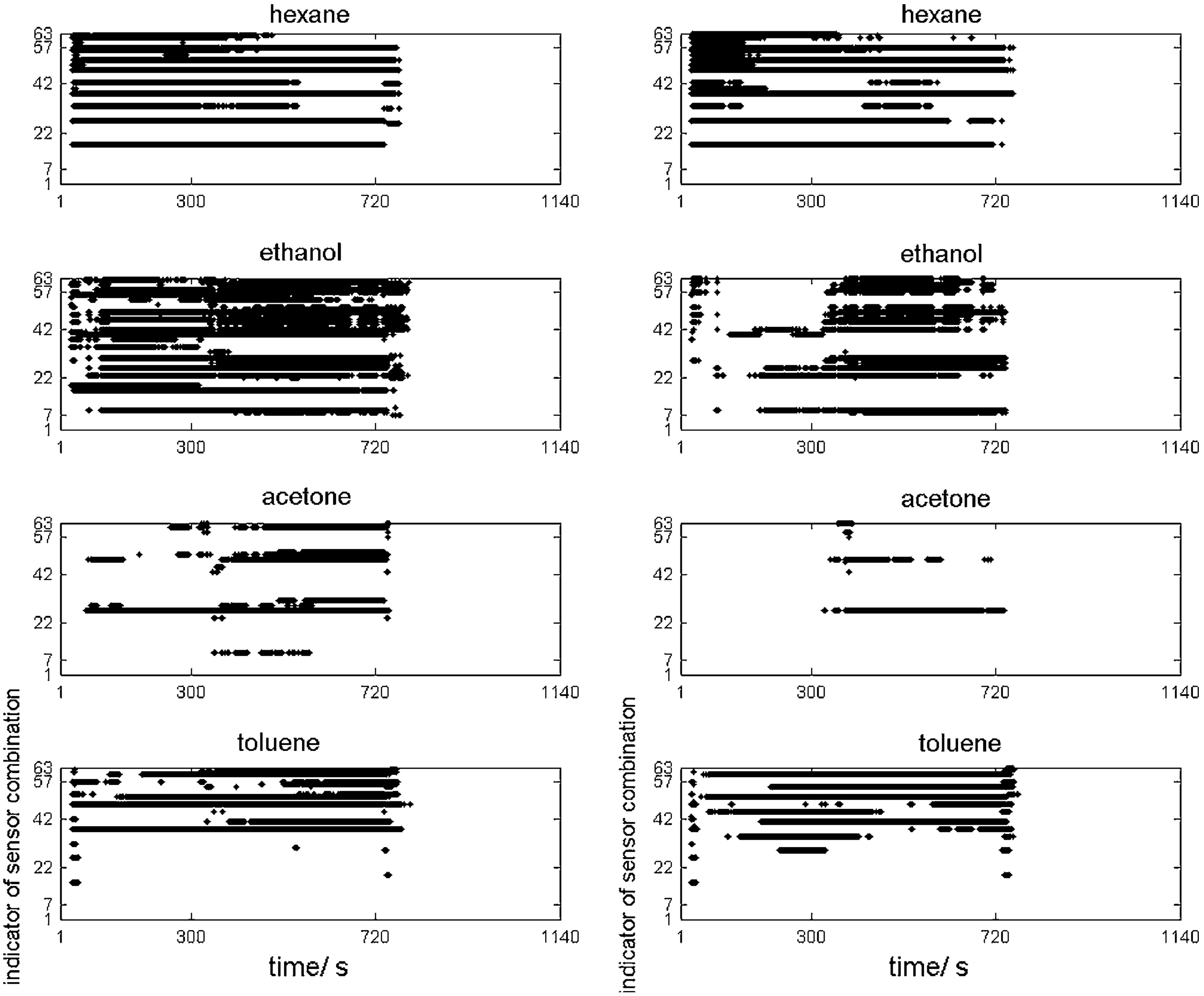

Fig. 5. Addresses of pattern data combinations. Sensor combinations represented by their indicators are given in Table 3. Plots in the left column refer to measurements done with S.A. I, and plots in the right column refer to measurements done with S.A. II.

employing stop-flow mode of operation as a source of information for discrimination tasks.

There were needed at least two sensors for the realization of discrimination task and bigger sensor sets were preferred, as shown in Fig. 5. However, the composition of sensor set was important and their size was not so decisive. Among combinations of the same size, some were considered suitable for gas mixtures discrimination while others did not carry useful information.

As shown in Table 2 the numbers of addresses obtained in our work for different classes of target gases were between 0% and 17.3% of all possible combinations of sensors and time points. Although not so impressive these numbers are orders of magnitude higher than the probability that a randomly selected data combination was successful in the discrimination of a particular analyte in all five repetitions of the experiment.

Numbers of addresses of different classes of target gases were dependent on several factors.

Decisive was the inherent ability of sensor array to recognize a particular compound. In our work, this ability was represented by the number of pattern data combinations selected based on measurement data recorded in course of one experiment involving complete set of measurements of standard gases. If the number of pattern data combinations was high, it was more likely to find a common set of sensors and time points combinations for a number of repeated measurements. In this work, big set of pattern data combinations and subsequently, high number of addresses was found for the class *ethanol*. Contrarily, low number of pattern data combinations indicated difficulties in finding the addresses of the class of target gas. In our work such was the case of ethyl acetate. No common addresses were found for this class.

The number of addresses of the class of target gases was dependent on the number of experiments, which were repeated for finding most reliable addresses. In our work common combinations of sensor and time points were calculated for 2, 3, 4 and 5 experiments. An example of the relationship between the number of addresses and the number of repeated measurements is shown in Fig. 6, using the example of target gas class: *acetone*. While developing sensor array the designer has to choose how many repetitions of measurements shall be executed in order to identify best suitable combinations of sensors and time points. The increasing number of experiments is cost and time consuming. It also causes decreasing numbers of analytes addresses (Fig. 6). For example, the common addresses of the class *ethyl acetate* were found for two repetitions at most. However, the higher number of repeated measurements the more reliable addresses.

The significance of variability of sensor response to analyte for the number of addresses of the class of target gases was equivocal. For example, the lowest variability of measurement was observed

Table 3
Sensor combinations and their indicators, as used in Fig. 5.

1	2	3	4	5	6	7	8	9	10	11	12	13
TGS2620	TGS821	TGS825	TGS826	TGS2104	TGS2602	TGS2620 TGS821	TGS2620 TGS825	TGS2620 TGS826	TGS2620 TGS2104	TGS2620 TGS2602	TGS821 TGS825	TGS821 TGS826
14	15	16	17	18	19	20	21	22	23	24	25	26
TGS821 TGS2104	TGS821 TGS2602	TGS825 TGS826	TGS825 TGS2104	TGS825 TGS2602	TGS826 TGS2104	TGS826 TGS2602	TGS2104 TGS2602	TGS2620 TGS821 TGS825	TGS2620 TGS821 TGS826	TGS2620 TGS821 TGS2104	TGS2620 TGS821 TGS2602	TGS2620 TGS825 TGS826
27	28	29	30	31	32	33	34	35	36	37	38	39
TGS2620 TGS825 TGS2104	TGS2620 TGS825 TGS2602	TGS2620 TGS826 TGS2104	TGS2620 TGS826 TGS2602	TGS2620 TGS2104 TGS2602	TGS821 TGS825 TGS826	TGS821 TGS825 TGS2104	TGS821 TGS825 TGS2602	TGS821 TGS826 TGS2104	TGS821 TGS826 TGS2602	TGS821 TGS2104 TGS2602	TGS825 TGS826 TGS2104	TGS825 TGS826 TGS2602
40	41	42	43	44	45	46	47	48	49	50	51	52
TGS825 TGS2104 TGS2602	TGS826 TGS2104 TGS2602	TGS2620 TGS821 TGS825 TGS826	TGS2620 TGS821 TGS825 TGS2104	TGS2620 TGS821 TGS825 TGS2602	TGS2620 TGS821 TGS826 TGS2104	TGS2620 TGS821 TGS826 TGS2602	TGS2620 TGS821 TGS2104 TGS2602	TGS2620 TGS825 TGS826 TGS2104	TGS2620 TGS825 TGS826 TGS2602	TGS2620 TGS825 TGS2104 TGS2602	TGS2620 TGS826 TGS2104 TGS2602	TGS821 TGS825 TGS826 TGS2104
53	54	55	56	57	58	59	60	61	62	63		
TGS821 TGS825 TGS826 TGS2602	TGS821 TGS825 TGS2104 TGS2602	TGS821 TGS826 TGS2104 TGS2602	TGS825 TGS826 TGS2104 TGS2602	TGS2620 TGS821 TGS825 TGS826 TGS2104	TGS2620 TGS821 TGS825 TGS826 TGS2602	TGS2620 TGS821 TGS825 TGS2104 TGS2602	TGS2620 TGS821 TGS826 TGS2104 TGS2602	TGS2620 TGS825 TGS826 TGS2104 TGS2602	TGS821 TGS825 TGS826 TGS2104 TGS2602	TGS2620 TGS821 TGS825 TGS826 TGS2104 TGS2602		

in case of toluene and hexane, but the number of common addresses in those cases was second and third best (Fig. 5). The highest number of addresses was found for ethanol (Table 2) but, the variability of measurements of this compound was relatively higher and similar with ethyl acetate. There were none common address found for ethyl acetate (Table 2).

The addresses of classes of target gases were found using measurement data provided by two sensor arrays in parallel. As shown in Table 2, S.A. II shared ~85% addresses of ethanol, hexane and acetone with S.A. I. In case of toluene 44% addresses were common. It is thus well pronounced that two sensor arrays, composed of sensor of the same types and operated in the same manner exhibited a considerable overlap concerning location to analyte-indicative information in their responses.

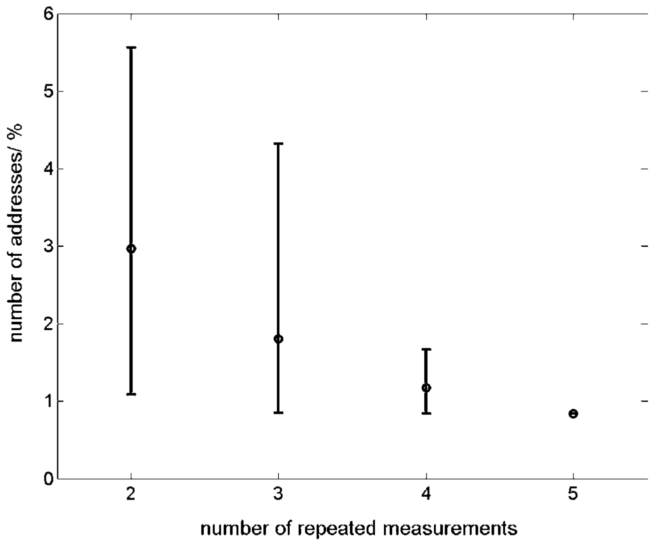

Fig. 6. The number of addresses of the class *acetone*, which were common for different numbers of repeated measurements. Measurements were done with S.A. II.

4. Conclusions

The concept of gas mixtures discrimination method was presented in this work. The method is based on sensor array, temporal response and data driven approach. The study of the method was carried out by investigating the discrimination of gas mixtures composed of air and single organic compounds: hexane, ethanol, acetone, ethyl acetate and toluene. The sensor array was composed of 6 TGS sensors and it was operated in the stop-flow mode. The measurement data was recorded with time resolution of 1 s.

Principal for the method was the use of measurements data provided by a selected combination of sensors at single time points of sensor array response, as the input of discrimination model. The data collection was considered a pattern of a class of test gases if they allowed for solving the discrimination tasks with 100% efficiency.

The combinations of sensors and time points, best suitable for discrimination tasks were shown to exist. They were mainly associated with the ‘flow’ and ‘stop’ phases of sensor array exposure. It emphasizes the advantage of employing stop-flow mode of operation as a means of increasing the amount of classification-useful information in sensor array response.

The best suitable combinations of sensors and time points were persistent regarding repeated measurements of standard gases. The number of best suitable combinations was dependent on the inherent ability of sensor array to recognize a particular class of gases, repeatability of measurements of a particular analyte and it was influenced by the number of experiments utilized for finding common combinations. Many pattern data combinations and low variability of measurements were indicative for a high number of addresses of a class of gas mixtures. Numerous, repeated experiments promoted selection of fewer but most reliable combinations.

Best suitable combinations of sensor sets and time points were also shown persistent regarding sensor array. This finding provided a strong argument for the possibility of sensor replacement without immediate impairing sensor array performance.

The rules of accessing pattern data combinations, expressed in the form of their addresses are easy to incorporate in the data analysis software of the sensor system.

The proof that there exists persistent combinations of sensor sets and time points which provide the data for successful discrimination of target gases is principal for our concept of discrimination method. It confirms that there is a reliable source of information about test gases in the form of sensor measurement data as directly recorded. This source is easy to access, simple to exploit and highly reliable at the same time. We have shown it feasible to ground the discrimination method directly on sensor array measurement data recorded by sensor array operated in stop-flow mode.

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