## **Gas Sensor Array with Broad Applicability**

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### 1. Introduction

In recent years, effort has been made to develop instruments for rapid, inexpensive analysis of volatile chemical species that do not require trained personnel. This demand has been mainly driven by a variety of real life applications. Indeed, the problem of classifying and further quantifying chemical substances on a real-time basis is very critical for a broad range of activities in various fields, like: industrial (Garrigues *et al.*, 2004), agricultural (Berna, 2010), medical (Byun *et al.*, 2010), domestic (Zampolli *et al.*, 2004) and environmental (Bourgeois *et al.*, 2003).

Rapid detection and quantification of chemical species are important in control and optimisation of industrial processes and bioreactors. Optimisation of combustion processes can lead to significant energy savings, as well as to minimization of emissions across power, chemical, steel, paper, food and other manufacturing industries. The ability to monitor and precisely measure leakages of combustible and explosive gases is crucial in preventing the occurrence of accidental explosions. Nowadays, a lot of attention is paid to safety monitoring, surveillance and homeland security. Quality control of different products, e.g. food, drinks and agricultural products, are also on the rise.

New demand has recently emerged in the area of medical diagnosis and continuous monitoring of chemical parameters during intensive care. Medical appliances are related mainly to the breath analysis and detection of infections, diseases and bacteria. Environmental applications include e.g. monitoring of air quality (indoor and outdoor), potentially polluting industrial installations, plants and soil contaminations, landfill sites, wastewater treatment plants.

Rapid advancements in sensing technology result in a variety of devices which are able to detect indoor pollutants. They have found widespread commercial application in gas monitoring and alarm applications. New trends in building engineering cause that a distributed control of ventilation is required. Three factors are considered in this kind of monitoring: comfort, productivity, security (agents, pollutants, explosives).

In the past decade there has been a growing interest in the development of olfactory machines and electronic nose systems. Odour monitoring in ambient air is a serious challenge for the measurement technology. There is no technique available for continuous measurement of odour nuisances and the current standard methods of odour measurements cannot be applied to on-line monitoring.

In the applications mentioned above, devices based on gas sensors are especially applicable. They have several advantages over conventional analysers, because of possible miniaturization, low price and maintenance costs, short response time, easy manufacturing and small size. Currently, gas sensors play important, commercial role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere.

Gas sensors are one kind of chemical sensors. According to the current IUPAC's definition, a chemical sensor is a *device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal.* The chemical information may originate from a chemical reaction of the analyte or from a physical property of the system investigated. All chemical sensors consist of a chemically sensitive material (a receptor) that is interfaced to a transducer. In the first unit the chemical information is transformed into a form of energy, which may be measured by the transducer. The receptor is responsible for selectivity of measurements. The transducer part is a device capable of transforming the energy which carries the chemical information about the sample into a useful analytical signal. The transducer as such does not show chemical selectivity. The interaction between an analyte molecule and the receptor can be either reversible (measurand dissociates from the layer when the external concentration is removed) or irreversible (measurand undergoes a chemical reaction and the sensitive material layer is consumed).

The receptor and transducer parts of chemical sensors may be based on various principles. Therefore, these devices have different application ranges. They can be used for:

- detection of some of chemical conditions, e.g. the presence or existence of strictly defined chemical, harmful hazards;
- specific determination of one substance;
- classification of complex gases (determination of classes);
- qualitative and quantitative chemical analysis of multi-component gaseous mixtures.

The application range of gas sensors is defined by their measurement characteristics. The traditional strategy in the sensor techniques is based on a single sensor to convert chemical information to an electric signal. A principle of "lock-and-key" is applied in the design of this device. Selectivity is achieved through recognition of the analyte molecules at the receptor site. In this approach, specific receptor has to be synthesized to bind the analyte of interest strongly and highly selectively. Therefore, the traditional strategy requires highly selective sensor for each analyte under test. This approach is not particularly useful for at least two reasons. Firstly, the synthesis of the separate, specific receptor is not easy to realize. It is a challenge both from chemical and technological point of view. Often, this requirement cannot be achieved due to the working mechanism of the sensor, especially its receptor and transducer functions. Secondly, this approach is impractical for analysing complex vapour mixtures qualitatively and quantitatively. In practice, receptors do not ensure very good selectivity. However, in certain circumstances, under carefully controlled operating conditions, the output signal may provide selective information about individual component, without any major preliminary treatment of the sample. Therefore, conventional sensors are normally designed to operate under well defined conditions, for specified analytes, in certain sample types. They offer rapid and inexpensive detection of many individual volatile substances with simple interpretation of measurement results.

The ideal gas sensor should exhibit reliability, robustness, sensitivity, selectivity and reversibility. These requirements are difficult to attain in practice. For example, often sensing elements cannot achieve the required selectivity. It is a serious problem, because the key function of the analytical equipment is to realize a kind of selectivity for the quantity to be measured. One of the main objectives of current research in the gas sensor technology is the qualitative and quantitative multi-component analysis of chemical environment characterized by the simultaneous occurrence of different volatile species in air. Sensitivity limitation originates from fundamental principles of the sensing mechanism, which is different from "lock-and-key" principle. This disadvantage cannot be eliminated completely because of sensing mechanism of gas sensors. However, there are methods to reduce the influence of interfering chemicals. Recently, there has appeared a strategy that is complementary to traditional chemical sensing. It involves using systems based on:

- sensor array;
- signal processing;
- data analysis.

The advantage of this strategy consists in application of unspecific but satisfactorily reproducible sensors for multi-component analysis of gases.

## 2. Sensor array

Generally speaking, a sensor array is a set of sensors used for gathering information about the object under test. In chemical applications, it consists of several different sensors with broad and partially overlapping sensitivity to various gases. The gas sensor array is used to convert chemical information regarding multi-component gaseous mixtures into a set of measurable signals. Sensors are exploited independently and simultaneously in this device. Therefore, they can be treated as the independent sensing elements in the operation procedure. The multivariate response of a sensor array is created by all sensing elements. This collection of sensors should be characterised by as much chemical diversity as possible. In this case, the array responds to the largest possible range of analytes.

The first report of the sensor array was presented by Persaud and Dodd in the early 1980s (Persaud & Dodd, 1982). The utilization of these devices is inspired by the performance of biological olfactory systems. The sensor array is established on an assumption that a cross-sensitivity of gas sensors is unavoidable. The cross sensitivity means that some chemicals may interact to give a different signal from the component in a mixture compared to the single component. For that reason, instead of trying to eliminate this feature, gas sensors are linked as independent sensing elements in an array configuration. Of course, the principle of "lock-and-key" is abandoned in this approach. Sensing elements are not highly selective toward any given analyte. However, they should be satisfactory reproducible and they should have significantly different gas sensing properties. The selectivity of each sensing element is admittedly low. However, the combination of the responses of different sensors presents a characteristic pattern that can be treated as a unique 'signature' ("electronic fingerprint") of individual chemical species. Subsequent signal processing and data analysis are required to extract information about gas under examination.

A sensor array can provide both qualitative and quantitative information. It shows the ability to classify different complex samples and to quantify components concentrations

when the mixture consists of several constituents. In other words, the array of sensors performs integration to yield a unique signal for complex but distinctive gaseous samples. It is realised without requiring that the mixture is broken down into its individual components prior to, or during, the analysis. This is a disadvantage when the precise qualitative and quantitative information about a complex mixture is necessary, but it is advantageous when only classification of the sample is required. Another potential shortcoming to an array system is the possibility that other unknowns may give the same "unique" signal as a specific analyte of interest. Qualitative and quantitative analysis can be performed only in case the sample consists of several components.

## 3. Design of gas sensor array

A gas sensor array never functions as an independent analytical instrument. It is one of the few essential components of a detector, an analyser, a monitor (the analyser working according to a sampling plan as a function of time) or an automated system for continuous measurements, in real time. For that reason, the sensor array must cooperate with other elements of the analytical equipment. Usually, the following functions are performed by external settings:

- 1. sampling,
- 2. transport and handling of the sample,
- 3. signal acquisition and processing,
- 4. data analysis,
- 5. reporting and visualization of measurement results,
- 6. automatic control of the whole system,
- 7. calibration.

The sensor array construction is particularly dependent on the first four functions. Therefore, the following issues are significant for sensor array design:

- method of sampling, pre-treatment and target gas delivery equipment;
- measurement characteristics of a sensor array;
- working parameters;
- operation mode;
- signal processing;
- data analysis.

Additionally, usability, service and cost of sensor array should be taken into account at the design stage. Improvement in any of these areas will lead to a significantly better performance of the analytical equipment.

#### 3.1 Method of sampling, pre-treatment and gas delivery equipment

A sensor array may be adjusted for dynamic (active) or passive (diffusion) sampling. In the first case, the sample is mechanically drawn into the sensor array, where it is analysed, and then exhausted to the atmosphere or the vent line. This type of sampling is performed by a suitable pneumatic system. This assembly consists of a sample probe and a delivery system, which is designed to transfer the gas from the source to the sensor array. Usually, the delivery system includes a gas line, an electro-valves, an electronic flow meter (a mass flow

controller), a gas mover (e.g. a pump or a fan). The intrinsically safe or explosion-proof pump has to be employed in some applications. The sampling system must be designed to draw continually a fresh sample of the target gas. To ensure the unaltered state of the sample:

- the sampling probe and the gas line must be made of inert materials such as: polytetrafluoroethylene (PTFE), tetrafluoroethylene hexafluoropropylene copolymer (FEP), polyethylene terephalate (PET), glass, stainless steel;
- the transport line should be short;
- particulate matter and moisture cannot accumulate inside the sampling line.

A sample probe and gas line has to be cleaned between successive exposures until all contaminations are removed. Usually, a stream of pure air is used for this operation. Thus, a sensor array has to be connected with a source of this gas. In the dynamic sampling, a sample can be taken directly from a surrounding atmosphere, an industrial installation as well as from a headspace sampler, a bubbler or a pre-concentrator.

A passive (diffusion) sampling operates by allowing gas or vapour molecules to diffuse until they reach sensor surface. Fick's First Law describes the movement of gas. As the diffusion coefficient varies in a known manner with temperature and pressure, these parameters must be taken into account while designing the sensor array. In this kind of sampling, sensor array is often enclosed in explosion-proof housings (if it is required by the conditions in the place of installation), and signals are delivered back to the control panel. The enclosure is described as a "sensor head". The shape and construction of this package affect the measurement characteristics of the sensor array.

In diffusion sampling, the delivery system is not exploited. This is an important advantage in certain applications. For example, as a pump is not used to move the sample, the analytical equipment is completely quiet. Sampling based on diffusion relies on air movement rather than on actively pulling a sample. Therefore, the response time of an array is usually slower in this case. When diffusion sampling is applied calibration of the sensors is often complicated. There are required special accessories to convert a diffusion operation mode to flow-through for calibration purposes. Moreover, the implied equivalence between calibrating via flow-through and monitoring under diffusion is not always well-documented. Furthermore, all gas sensors measure partial pressure, and a sample actively brought to the sensor is at a slightly elevated pressure, while a diffusion sensor operates at ambient pressure. As such, the output sensitivity of sample draw sensors is usually higher than diffusion sensors. This can be important for many toxic gases with low regulatory levels.

In many applications, it may be necessary to pre-treat sample before it reaches a chemical sensitive layer of a sensor. For example, filtration, moisture removal or chemical modification may be required. Different modifications of a delivery system are discussed in the literature (Stetter *et al.*, 2000). For example, the system may be equipped with molecular filters (like charcoal) or a heated filament. If air is used as a carrier gas, the filament performs catalytic oxidation. In case the volatile compounds are in an inert gas (without oxygen), the term pyrolyzer is more appropriate for the filament. A temperature- variable filament is particularly interesting because it provides additional selectivity at the expense of time. As it was mentioned, sensors demonstrate poor selectivity in real analytical

applications. Chromatographic columns can be used to separate constituents of the complex mixtures on the basis of their molecular size or other physical properties prior to analysis. A sensor array can also be connected to a membrane unit. Its material is usually used for separation, purification, and chemical enrichment of the sample. These functions are very well performed by Nafion. This material is a flouropolymer with ion exchange capacity. It belongs to the class of solid polymer electrolytes. Nafion has a hydrophobic  $-CF_2 - CF_2 -$  and hydrophilic  $-SO_3H$  regions in its polymeric structure. Due to these properties Nafion has high permeability for water. Thus this material can be used as a membrane drier. Nafion also removes other compounds from the sample stream e.g. volatile alcohols (methanol, ethanol), acetone and some other polar solvents. This material is really a separator and it fractionates the sample in a predictable and repeatable manner prior to analysis by the chemical sensor array. Therefore, Nafion is capable of enriching or depleting the gas stream with any number of analytes, to which it is permeable.

## 3.2 Measurement characteristics of gas sensor array

Usually, the responses of individual sensors (especially commercial ones) to various substances are only slightly different. Therefore, various methods have to be used to achieve satisfied measurement characteristics of the sensor array. They are based on:

- dimension and composition of a sensor array;
- construction of this device;
- properties of the individual sensors.

## 3.2.1 Dimension and composition of gas sensor array

Dimension of a sensor array is defined by the number of sensors. This factor strongly affects measurement characteristics of the sensor array (Gardner et al., 2005; Gualdr'on et al., 2006). Large number of sensors may in some situations improve discrimination abilities of the sensor array. However, a calibration effort and time demand for data processing increase considerably in this case. Additionally, multi-dimensional arrays may include sensors, which are not sensitive to target gases and do not contribute to the recognition task. Sensors with no responses to the subgroup of analytes increase noise and degrade the ability to make analytical comparisons. Besides irrelevant devices, an array can consist of sensing elements which have very similar sensitivities to tested volatile compounds. The redundant sensors, which are exactly the same, lead to improvements in sensitivity. Perfectly redundant sensors increase the signal-to-noise ratio (SNR) and produce a better low detection limit (LDL). However, these devices provide redundant information which is not useful for the discrimination process. The removal of redundant sensors offers many advantages, e.g. level of drift/noise introduced by these devices can be greatly reduced. Moreover, the description of sensor array response is easier. Thus, simpler classifiers (working on small number of dimensions) can be applied and more qualitative information is obtained. Therefore, arrays with smaller number of sensing elements, but with different response parameters are preferred in practice. By eliminating unimportant sensors, the cost and time of collecting and analysing data may be reduced. This is crucial for many applications. Of course, the range of applications of the sensor arrays with the small number of sensing elements is decreased.

It is important to select sensors not only from the perspective of sensor array dimension. This device may include sensors of different classes, which have different properties. Therefore, sensor arrays are divided to two groups: homogeneous and heterogeneous (Tomchenko *et al.*, 2003). For example, the earliest reported electronic nose was based on a heterogeneous array of combustible and electro-chemical sensors. It was reported in (Stetter *et al.*, 2000) that sensors with chemically independent responses are valuable and make the array more versatile and able to distinguish more analyte differences. Sensors of various classes generally provide more chemically different or chemically independent responses than sensors of the same class with small variations in their formula or structure. Sensors, whose chemical principles are different, give data that are more effective when comparing samples than the same number of sensors of a single class. Moreover, in large arrays of different sensors of one class, sensors that may not contribute with information will always contribute with noise. There is an optimum array composition for any given set of analytes in qualitative detection applications.

There are two possible approaches to design sensor arrays. The first one is commonly applied in commercial instruments e.g., in electronic noses. This strategy is based on an assumption that sensor array should be dedicated to a limited number of chemical species emitted by e.g. food or other goods, human organisms, industrial or agricultural installations. To realize this goal, the set of suitable gas sensors is chosen. The selection process is related to the particular applications and it is performed at the stage of instrument design. The inadequate choice of sensors can potentially result in insufficient information or redundancy. Therefore, the optimisation procedure has to be applied. The considerable efforts have been made in this sector of sensor technique recently. However, the scope of application of sensor arrays constructed in this way is rather limited.

The alternative approach concerns sensor arrays of more universal applicability. These devices require using a broad spectrum of sensing elements, so that a large number of gases could be measured by one analyser or analytical system. Due to progress in the sensor technology the construction of relatively cheap arrays consisting of many sensing elements is already possible. Of course, the problem of sensor selection exists in this strategy too. However, it is solved in another way. We propose to use in the analytical equipment an array with a large number of sensors. They are not selected with a particular application in mind. However, they shall cover as broad range of substances as possible in a partially selective manner. For particular applications from this pool of the sensing elements there are chosen various sensor combinations with conscious intent towards the analytical goal. These sensor subsets have lower dimension than the original sensor array. Additionally, they have optimal measurement characteristics.

## 3.2.2 Construction of sensor array

Many contributions can be found in literature devoted to the characterization of individual gas sensors. However, little attention has been paid to the construction of a sensor array. This approach is inadequate because construction of this device decides about:

- chemical environment of the sensors;
- space distribution of the examined gaseous species inside measurement chamber and its evolution in time;
- thermal, electromagnetic or electrical conditions of measurements.

Gas sensors in an array can be contained in one compartment or in many measurement chambers. It depends on working mechanism of these devices. A sensor array with a set of separated chambers is preferred when individual sensors produce intermediate products during the sensing process which can affect responses of neighbouring sensors. In this case, the chambers have to be connected in parallel using a Teflon-tubing so that all sensors are simultaneously exposed to the gas mixture of the same composition. The compartment has to be airtight and made of chemically resistive material. The measurement chamber is provided with gas inlet and outlet. Geometrical parameters of this compartment such as volume, shape, and the inlet-outlet position influence the development of the fluid flow and the gas concentration distribution inside the chamber. Therefore, they must be considered. To avoid effects due to non-uniform gas concentration in the measurement chamber, it appears reasonable to place the sensor in the gas stream, very close to the point of injection. Similarly, the concentration transient may be reduced to a value substantially smaller than the response time upon reducing the chamber volume and increasing the volume flow rate through the chamber. That is based on hypothesis that the concentration transient is not much longer than the ratio between chamber volume and volume flow rate.

A sensor array may consist of many, closely placed sensors. In that configuration, neighbouring sensing elements can interact and interfere with each other. This phenomenon is often described as "cross-talk", and the response of the individual sensor depends not only on the gas under test, but also on its neighbours. From signal processing perspective, cross-talk can be considered either as random noise or as noise which has a certain pattern. The sources of the cross-talk can be different e.g. thermal, electrical, electromagnetic and architectural. This effect is considered as a local one and hence it may be removed by a suitable sensor array design.

The chemical and physical conditions directly around the sensor are also very influential. The sensor response may depend on the temperature of gas under test and the surrounding's. Thus, thermal conditions around the sensing elements should be controlled. This requirement can be realised e.g. by the installation of the sensors into a thermostatic chamber that keeps the temperature of gas at a constant level. Additionally, some of the sensors suffer from the relatively large power dissipation. Therefore, thermal isolation of sensor array is a key issue. In this way, the power consumption by the measurement device may be lowered.

The sensor array construction is strongly determined by the applied technology. Different sensor technologies are used in today's commercially available sensor systems. Recently, considerable interest has arisen in micro-electro-mechanical systems (MEMS). They are fabricated by the thin film and micromachining techniques (Faglia *et al.*, 1999; Vergara *et al.*, 2006). This technology meets the main requirements for gas sensor devices such as: small size, high sensitivity in detecting low concentrations, good selectivity, short response time, long term stability. The additional advantages such as low power consumption, possibility of on-line operation, temperature controllability, small size, low cost, easy realization of sensor array and possibility of on-chip integration with micro-electronics and low-cost fabrication make them attractive for consumer applications. Sensitive layers deposited on micro-machined substrates are the most promising structures.

## 3.2.3 Properties of individual sensors

The measurement abilities of the sensor array are strongly dependent on the measurement characteristics of the individual sensors, which are determined by their operating principles. The sensing elements in the array are not dedicated to any given analyte. They are chosen to respond to a number of different substances or classes of chemicals. With regard to the requirements imposed on the individual sensors that make up the arrays, the ideal sensing element integrated in the array should fulfil several criteria: good accuracy, resolution, precision and repeatability, high sensitivity towards target gas, medium selectivity (they must respond to different constituents of a tested sample), low sensitivity towards humidity and temperature, short response and recovery time, low detection limit, wide span and dynamic range, linearity, low drift and noise, robustness, durability, stability and sensitivity in hostile environment. Additionally, weight, dimension, power consumption, thermal capacity and thermal isolation, design and housing of the sensors are used to evaluate performance of these devices. It is difficult to achieve all of these requirements in practice.

Sensor arrays can include sensing elements based on different operating principles. Usually, they belong to one of the following classes of gas sensors:

- optical (absorbance, reflectance, fluorescence or opto-thermal effect are used for the measurement);
- electro-chemical (These devices are divided to potentiometric and voltammetric sensors. The last group includes amperometric devices);
- electrical (chemically sensitized resistors, diodes and field effect transistors);
- mass sensitive (piezoelectric sensors);
- magnetic for oxygen measurement;
- thermometric and calorimetric (thermal conductivity sensors, catalytic sensors).

Among different kinds of sensors that may be used in sensor arrays electro-chemical devices, mass sensitive sensors, metal-oxide-semiconductor field-effect transistors and chemi-resistors (semiconductor sensors) are especially interesting.

Electro-chemical sensors are the largest group of sensing devices. The important advantage of the first group of sensors is a linear range of the response. Usually, it is greater than 104. These devices are almost insensitive to changes in relative humidity (RH). They also respond to quite different chemical species than chemi-resistors or mass-sensitive sensors. The electro-chemical sensors respond only to gas that has electro-active properties. Therefore, they are not sensitive to some common classes of compounds, such as saturated hydrocarbons. These sensors will only increase the noise of the array during analysis of a sample containing these compounds. The sensing mechanism of these devices is controlled by the nature of the electrode and electrolyte as well as the thermodynamic potential of the sensing electrode, the rate of diffusion, solubility in the electrolyte, and the number of electrons produced per molecule. In general, the active Pt catalyst will record a signal for any electro-oxidizable gas or vapour (CO, SO<sub>2</sub>, H<sub>2</sub>S, NO<sub>x</sub>, and EtOH). The NO<sub>2</sub> sensor is operated with an Au electro-catalyst at more cathodic potentials such that only electroreduceable gases interact such as NO<sub>2</sub>, Cl<sub>2</sub>, and few others. Usually, electro-chemical sensors are optimized for a single analyte like: CO, H<sub>2</sub>S, NO, NO<sub>2</sub>, SO<sub>2</sub>, Cl<sub>2</sub>, O<sub>3</sub> or hydrazine. In this form, they are used in a sensor array. The measurement characteristics of electro-chemical sensors may provide complementary capabilities to sensor array.

Mass sensitive sensors (piezoelectric devices) transform the mass change at a specially modified surface into an alteration of a property (the resonant frequency) of the support material. The mass change is caused by an accumulation of the analyte on the adsorbent layer which is composed of stationary phases used in gas chromatography or by an accumulation in supramolecular host molecules. This group of sensors is split up into:

- quartz crystal microbalance (QCM) based on measuring the frequency change of the quartz oscillator plate caused by adsorption of a mass of the analyte at the oscillator;
- surface acoustic wave (SAW) devices depend on the modification of the propagation velocity of a generated acoustical wave affected by the deposition of a definite mass of the analyte.

Mass sensitive sensors present very good low detection limit. However, their selectivity is low. The sensitivity of the QCM and SAW devices to a particular compound depends on the type of sensitive membrane. These sensors can detect a broad spectrum of chemical species due to the wide range of gas sensitive coatings available. However, these devices suffer from poor SNR. It is caused by the high frequencies, at which SAW sensors are operated or surface interferences in the case of QCM sensors. The circuitry required to operate mass sensitive devices is complex and expensive.

The metal-oxide-semiconductor field-effect transistor (MOSFET) is a transducer device, which transform a physical/chemical change into an electrical signal. The sensing mechanism of MOSFET sensors is based on the principle that the threshold voltage of this device changes upon interaction of the gate material, usually catalytic metal, with certain gases due to the corresponding changes in the work functions of the metal and the oxide layers. These changes are caused by the polarization of the surface and interface of the catalytically active surface. Gas sensing MOSFETs are produced by standard micro-fabrication technique or in the micro-machining technology. In the last case, a hybrid suspended gate FET (HSGFET) sensors are fabricated. Gas sensing MOSFETs have a number of advantages, which result from the CMOS technology. The reproducibility of these devices is quite good. They are small and cheap. Gas sensing MOSFETs also have disadvantages. For example, they suffer from baseline drift and instabilities depending on the sensing material used. Additionally, the properties of these devices are dependent on the gas flow and operating temperature. Therefore, control of the surrounding environment is required.

Chemi-resistors are very often described as the semiconductor sensors, due to the working principle of these devices, which is based on the variation of the sensing material conductivity in presence of oxidizing and reducing gases. Different organic materials e.g. conducting polymers or metal oxides e.g. ZnO, TiO<sub>2</sub>, WO<sub>3</sub> and SnO<sub>2</sub> are used in this sensor technology. Conducting polymers offer many advantages over other sensing materials. An array equipped with polymeric sensors can obtain high discrimination ability because different polymers generate various levels of response to a given gaseous sample. A wide range of polymeric materials is available on the market. They are relatively inexpensive and easy to prepare. Sensors fabricated from polymeric materials can be used in conditions of high relative humidity. They show highly linear responses to many gases. These devices are operated at room temperature. Therefore, power consumption is very low. It means that polymeric sensors can be applied in portable, battery powered equipment. Signal conditioning circuitry required for these sensors is relatively simple as only a change in resistance is measured. The main disadvantage of this type of sensors is aging, which causes drift.

Semiconductor metal oxide gas sensors are considered as one of the basic technologies for the array applications. It results from the advantages of these devices e.g. high sensitivity, short response and recovery time, durability, small weight and dimensions, a real simplicity in function, large number of detectable gases (possible application fields are wide), low cost, flexibility in production. Although semiconductor gas sensors are widely used as invaluable safety devices for the detection of methane, propane or carbon monoxide gas, it is known that these devices suffer from a number of shortcomings such as: lack of selectivity, nonlinearities of sensor's response, long-term drift, variations in the initial resistance, sensing material poisoning and aging, relatively high operating temperature (> 300°C), hysteresis, sensitivity towards humidity and temperature. Therefore, the important goal in the development of chemiresistors is to improve the measurement characteristics.

This requirement can be achieved in different ways since semiconductor sensor response to target gas depends on many factors. For example, the improvement of sensitivity, selectivity and response time of theses devices can be reached by:

- the selection of a semiconductor with the suitable intrinsic properties (metal oxides e.g. SnO<sub>2</sub>, ZnO, TiO<sub>2</sub> or organic materials e.g. phthalocyanines, conducting polymers);
- the addition of catalysts and promoters or more specific surface additives;
- bulk/surface dopings;
- the choice of a suitable physical parameters of sensing layer (thickness of the gassensing entity, internal porosity, layer microstructure, crystallinity and crystalline structure, grain size, grain-grain contacts, surface morphology);
- the application of different technologies of the sensing material deposition and formation on the substrate;
- the aging and the preconditioning procedures;
- the modification of sensing layer, especially its surface; application surface coatings e.g. membranes and a diffusion filter layer such as SiO<sub>2</sub> on top of the semiconductor;
- the selection of a suitable material and geometry of the substrate;
- the appropriate choice of material and setup of the electrodes;
- the choice of the sensor structure and enclosure.

#### 3.3 Working parameters

The measurement characteristics of sensor array can be controlled to some extent by working parameters. Mechanism of gas sensing causes that operating conditions of chemiresistors are primarily determined by the temperature, flow rate of sample, gases partial pressures or potential (bias). These parameters may be constant or time-varying in course of the measurement. The alteration may be predetermined (programmed), controlled by the sample and the sensor or accidental.

#### 3.4 Operation mode

In principle, the term operation mode means a manner or a way employed to operate a device. In practice, it is a description of conditions under which analytical equipment works. Usually, the operation mode is characterized by an applied procedure, sensor environment, method of sensor response (output signal) measurement and working parameters.

Operation mode may affect the performance characteristics of semiconductor sensors since it determines the state of these devices during measurements. Generally speaking, a gas sensor can be in a steady or unsteady state. The first case is obtained in stable conditions that do not change over time. The sensing material is in equilibrium with a surrounding gas. In commercial instruments, the sensor responses in this state are preferred up to now, because the output signals are easily measurable and time-independent. The steady-state of sensor's signal as input for discriminators are easier and less complicated for processing and data analysis. Additionally, problems with unstable flow, pressure and temperature of gas sample, which are encountered at the beginning of exposure are minimised. However, when a sensor is in the steady state a lot of information about tested gases is lost. First of all, there is inaccessible information originating from the kinetics of processes that cause sensor response. In many applications of chemical sensors, information can be gained not only from a steady-state value of the sensor signal, but also from the kinetics of the response. Hence, an alternative approach has received much attention in recent years. It is based on sensor responses, which are recorded when the device is in an unsteady state. In this case, the sensor is not in the equilibrium with a chemical environment. The sensor response in the unsteady state is a time-dependent (temporal or transient). It conveys information, which is particularly useful to an enhancement in the discriminating ability of chemiresistors. For that reason, the semiconductor sensors in this state have received much attention in recent years.

The operating mode is often classified as a static or dynamic. Static mode means that any quantity acting on the sensor is constant with time. In other words, the device is exposed to the gas under test in stationary conditions. The dynamic mode is based on alteration of working parameters or operating conditions with time. A special variant of this operation technique is based on signal modulation. In this mode, the alteration of the quantity acting on the sensor or sample is characterized by frequency and amplitude. The dynamic mode operation techniques can be grouped into four categories:

- modulation of measurement parameters such as potential (bias) or frequency (impedance spectroscopy) - AC operation mode (Amrani et al., 1992; Gutierrez et al., 1991, 1992);
- modulation of the working temperature of the sensors (Gouws & Gouws, 2003; Gutierrez-Osuna et al., 2003; Llobet et al., 1997; Vergara et al., 2007);
- modulation of the gas flow (Barbri et al., 2008);
- modulation of the gas concentration (Gouws & Gouws, 2003; Llobet et al., 1997).

In the AC operation mode, a periodic waveform (e.g. a sinusoidal) is applied to the sensor input as a reference voltage instead of a fixed DC power supply. The voltage in the sensor heater is kept constant. Gas discrimination is enhanced in AC operation mode, by taking measurements of different electrical parameters (such as sensor capacitance, conductance or dissipation factor) at different frequency values of the reference voltage generator. This offers several advantages. For example, SNR is usually better, because narrow band amplification (either by filters or lock-in techniques) can be implemented and the 1/f noise component is less significant. Thus lower detection limits can be achieved.

In the past few years, modulating the working temperature of metal oxide sensors has been one of the most used methods to enhance sensor selectivity (Gutierrez-Osuna *et al.*, 2003).

This mode consists in altering the kinetics of the sensor response through changes in the operational temperature of the device. It is well known that when the working temperature of a gas sensor is modulated, the kinetics of the gas-sensor interaction is altered and this leads to characteristic response patterns. Temperature modulation can be grouped into two broad categories:

- thermal transients;
- temperature cycling (oscillation).

In the thermal transient approach, the heater voltage of the sensors heater is driven by a discontinuous step function (e.g. a heater supply is switched from a high voltage to a low voltage) or a pulse signal that is used to drive the heater voltage. The discrimination is performed in the transient response induced by the fast change in temperature. In the temperature cycling, the sensor heater is driven by a continuous function. Different modulating waveforms (e.g. ramp, sinusoidal, triangular, saw-tooth and asymmetrical square waves) can be used for temperature oscillation. The semiconductor ceramic sensors deposited on a substrate with high thermal inertia (e.g. TGS sensors) do not seem the best candidate sensors for an effective temperature cycling. Under these conditions extremely low modulating frequencies are used, which results in long, impractical, measurement times. With the development of the micro-system technology, the availability of micro-machined substrates for metal oxide gas sensors implied that sensors could have their operating temperature modulated in a more efficient way.

The effect of flow modulation can be analysed from two points of view. Firstly, the concentration of analytes at the surface of sensors is modulated. Secondly, fast periodical flow changes result in periodical cooling and heating of sensors' surface. Therefore, specific response patterns, which are characteristic of the analytes present, develop. The method can be easily adapted to both static and dynamic headspace sampling strategies. A wide range of concentrations and contaminants have been tested which confirms that flow modulation allows for a reliable identification of different vapour species.

Concentration modulation produces an output signal that contains information on the dynamic adsorption and desorption processes. The transient signals in this mode are generated while the controlled modulation of a sensor input parameter is performed. The concentration modulation may be achieved by means of fast-switching valves. The frequency spectrum of these transient signals should be a source of information containing details on the dynamics of the interaction process and have the potential for analyte identification.

Usually, transient characteristics are obtained by operating sensors at different temperatures. In particular, modulation of this working parameter is used to reduce long time drift effects and diminish cross-sensitivities. Unfortunately, this method requires a temperature control and additional equipment. The operation based on altering the target gas partial pressure to get unsteady state of the sensor is relatively rarely tested and applied in practice.

#### 3.4.1 Stop-flow operation mode

In the last years, considerable efforts have been made to use sensor dynamics as a source of multivariate information aimed at an enhancement in the discriminating ability of poorly-

selective metal oxide gas sensor arrays. The detection of reducing gaseous substances, e.g. volatile organic compounds by chemiresistors like Taguchi gas sensors (TGS) is caused by a change in conductivity of semiconductor. This effect is induced by the interactions between gaseous molecules and sensing material. The mechanism of chemiresistor operation is complex. It is controlled by several surface phenomena such as: diffusion of target gases into the sensing layer through pores, adsorption/desorption, catalytic reactions and followed by a charge transfer between the adsorbate and surface of sensing material leading to a measurable change in electrical resistance of semiconductor. These phenomena are directly or indirectly affected by factors, which function as working parameters of sensors.

Usually, this group of parameters includes temperature, potential (bias), sample flow rate and partial pressure or concentration of target gas. The output signal of gas sensor depends not only on an absolute value of working parameters, but also on measurement conditions. It results from a nature of the mentioned phenomena. Measurements in stationary conditions reflect mainly the thermodynamics of interactions between target gas and sensing material, whilst results obtained in dynamic conditions contain information about kinetics of adsorption/desorption, chemical reactions and charge transfer. Each of these processes has its own characteristic time constant, which is dependent on properties of sensing material and gas molecules, especially their molecular weight and shape, electron affinity, ionization potential, diffusion coefficient. Hence, the informative contents of sensor response measured in dynamic and static conditions, in steady or unsteady state are quite different. In our research work, it is assumed that the diversification of working parameters and operating conditions may cause increase in sensor ability to distinguish particular substances. Hence, an operation mode is proposed, which offers a significant alteration of the listed factors during measurements. The mode is called stop-flow. This approach consists of a few predetermined and controlled steps. The main factor, which defines each of these stages, is the alteration of exposure conditions, e.g. the sample flow rate. Other working parameters may also be changed during particular steps. During measurements sensors are either in steady or in unsteady state, and both dynamic or static conditions of operation are encountered. The stop-flow operation mode was characterized with regard to its application for measuring system based on the sensor array (Maciejewska et. al, 2009, 2010; Szczurek et al., 2010).

The responses of sensors in the stop-flow operation mode are obtained using the procedure consisting of three successive stages. The first step is the dynamic exposition. The gas sample is allowed to continuously flow through sensor chambers. The gas flow rate through the experimental setup is set to a defined value and it is kept constant. The dynamic exposition takes place. After this step, the gas flow is stopped and static exposition to the test gas is performed. The third stage could be described as a recovery process. The gas line and chambers are cleaned with a stream of pure air. The air flow rate through the system is again constant. The duration of each step is defined. They usually last for several minutes each and these times add up to the length of entire measurement. The regeneration of sensors is continued afterwards, until readouts from these devices reached the level as before the dynamic exposition. In our studies, a reversible change in the resistance of sensors was observed in all cases.

The typical output signals of TGS sensors obtained in stop-flow operation mode are presented in Fig. 1.

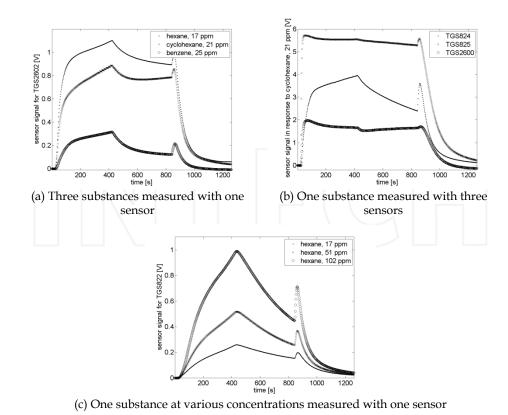


Fig. 1. Typical output signals of TGS sensors obtained in stop-flow operation mode.

Each of the output signals shown in Fig. 1 can be split into three main parts. They correspond to different conditions of operation during particular stages of the stop-flow operation mode. One can characterize the signal in respect of this partition.

As a consequence of the applied measurement procedure, after sample injection into the apparatus, some time is needed to exchange the atmosphere in the chambers. During this time interval the gas concentration is continuously changed, until it reaches the maximum value. As a result, the sensor signal changes, first rapidly than at lower rate until quasiconstant value is reached. It is observed that single minutes were sufficient to attain the gas equilibrium in the atmosphere surrounding sensors. The transient output signal upon exposure of sensor to a stream of gas sample was caused by the change in analyte concentration and the diffusion-limited processes which take place in the porous structure of the sensing material. It is known that the conductivity changes in semiconductor sensors depend on: the transport of the reactive species into the sensor, the diffusion of the gas molecules inside pores of the sensing material, adsorption and desorption, the catalysed redox reactions on the surface of the sensing layer (mainly their kinetics) and the electrical/electronic effects in the semiconductor. The sensor response resulting from those

processes is strongly related to the concentration and chemical properties of VOCs. For that reason, the transient output contains information about the tested gases.

The second part of sensor response starts when the gas flow is stopped. At this moment, the static exposure begins. The sensor response depends mainly on desorption and diffusion processes. Also the change in sensor temperature has its influence on it. The oxidation of organic compounds at the semiconductor surface and the lack of gas sample flow inside chambers cause the concentration of analyte to diminish. It results in the decreasing output signal. It is shown in Fig. 1 that the second phase, just like the first one is featured by versatile sensor response patterns.

In the third phase, upon the recovery process due to the removal of organic compounds from sensor chambers, the drop of measured output signal is observed. The rate of decrease is sensor-dependent. It is also influenced by the analyte and its concentration. The initial surge of signal in this phase may be observed with its magnitude and duration depending on the dead volume of the gas line.

The examination of sensor signal shown in Fig. 1 reveals that coupling flow and no-flow conditions in one operation mode of sensor system shaped the response pattern of sensor array. Each, dynamic and static exposure yielded transient responses with characteristic shapes and time constants which are affected by the composition of the atmosphere surrounding sensors. Therefore, the chemical information contained in measurement could be useful for distinguishing different gases.

## 3.5 Signal processing

The response of the sensor array is measured and converted into an electrical signal (e.g., a voltage). This function is realised by means of interface circuits. In sensor techniques, the term "signal" can be understood as a sequence of measurements that are related by some ordinal variable such as time. In the beginning, the raw measurements are converted from analogue readings to a digital signal that can be interpreted by a computer. The digitised signal is processed online or stored for future analysis. The signal pre-processing stage operates on the gas sensor outputs in a way that improves the overall pattern analysis performance. It can be achieved by extracting parameters that are descriptive of the sensor array responses. Thus, the raw data are transformed into a characteristic feature vector. Although signal pre-processing will depend on the application, a series of steps are commonly carried out. Signal pre-processing serves various purposes and consists of the following operations:

- baseline manipulation;
- · compression;
- normalization.

The final effect all of these operations is a set of features arranged in a form of an initial feature vector.

Baseline manipulation procedures transform the sensor response relative to its baseline to minimise the effects of temperature, humidity and short term drift. Three baseline methods are commonly used: difference, relative and fractional. The selection of a proper baseline manipulation technique is highly dependent on the sensor technology and the particular application.

Sensor array signals are represented by a set of data. While taking a measurement with the multi-element sensor array operating in dynamic conditions a lot of data is acquired. The number of collected data depends on the size of sensor array, the duration of time response and sampling rate. Usually, not all data are necessary to form a distinct pattern of measured gas. In practice, some of them contain no valuable information or are strongly correlated with other variables. Additionally, an analysis of a large set of data may cause serious calculation problems. The elimination of data, which contain no valuable information in the specific application or which show large correlation to another data within data set, may be advantageous. Thus, it is necessary to reduce the number of variables, which are analysed, resulting in reduced acquisition time, improved selectivity and recognition accuracy. This is aimed at using only relevant data in feature vectors for pattern recognition purpose.

Various compression algorithms are employed in the sensor technique. The standard procedure is to select the steady-state response of a sensor. To extract additional information from the transient response, a few methods have been proposed e.g.:

- model fitting;
- ad-hoc parameter extraction;
- sub-sampling.

A signal can be defined as an information-conveying function of one or more independent variables. Sometimes, this function can be described in an analytical form. For example, the transient response may be modelled as the sum of exponential functions, also using polynomials, autoregressive and state space models and their estimated parameters form the initial feature vector. Exponential curve-fitting methods can result in nearly lossless compression of the sensor transients but are computationally intensive. For these reasons ad-hoc parameter extraction and sub-sampling methods are more commonly employed.

The ad-hoc parameter extraction approach relies on a compression of sensor array response down to a few single parameters without fitting sensor signal with any kind of function. They are usually easy to calculate. Each of them should contain information about gases which are in the multi-component mixture. Different descriptors may be extracted from the transient response curves e.g. response value of initial saturation or in steady-state, final or maximum response (deep saturation), average of several points or of the whole signal, the response rate of sensor to tested gas (transient slope), pulse heights, derivatives, integrals and time constants (e.g. time-to-threshold) They are used as coordinates of feature vectors or elements of fingerprints for pattern recognition purpose. Unfortunately, in the model fitting and ad-hoc parameter extraction approach much information about chemicals may be lost or inaccessible. This refers in particular to the information, which is locally present in the signal and therefore any representation, which refers to longer parts of signal shadows it. Conceptually, it fits considering sensor signals as a set of discrete and separate information sources. Solutions employing model fitting or parameter extraction technique may require complicated analysis of the whole dataset. Thus sub-sampling has received much attention recently. In this method parameters describing signal are exchanged by a set of signal subsamples. This term means samples drawn from a large sample. The set of sub-samples is a compact representation of the all sampled data. The complicated form of the sensor signal causes that sub-sampling is an attractive method of data compression in the stop-flow operation mode.

#### 3.6 Data analysis

In principle, a sensor array with broad applicability has to face numerous tasks of gas assessment. In general, they are of qualitative or quantitative kind. At the level of sensor array data analysis these tasks are addressed as pattern recognition problems. Classification and regression tasks are considered respectively. Data analysis involves defining pattern recognition problems, which correspond to gas assessment problems, and finding best ways to solve them. The main elements in this process are: patterns, feature space and pattern recognition.

#### 3.6.1 Patterns

The feature vector is the basis for building a pattern which represents a measured gas. Pattern is obtained by assigning values to features, which are elements of feature vector. As features are parameters of sensors signals, their values are taken from sensor array measurement data. For developing a targeted sensor array, calibration patterns are used. Calibration patterns come from measurement data, which are collected while exposing sensor array to known gases. Therefore, it is straightforward to assign a calibration pattern with a discrete label, which indicates its membership in a particular class, respectively to the category of the measured gas. The calibration pattern may also be assigned with a value of continuous variable, which refers to a quantitative parameter of calibration gas, e.g. its concentration. The set of calibration patterns which refer to various gases and the associated label vector/concentration vector is the multivariate calibration data. Using this data, supervised classifiers are trained to define decision boundaries between patterns, which belong to different classes. Also regression methods are employed for setting the transformation between the matrix of patterns and the corresponding concentration vector. This process is called a supervised learning. The obtained pattern recognition models are further used for prediction purposes, regarding patterns associated with unknown gases. In our research on sensor arrays, it is favoured to work with many patterns representing the same test gas and many pattern recognition models respectively.

#### 3.6.2 Feature space

Pattern recognition proceeds in feature space, which is defined by the selection of sensor signal parameters to become features. Many feature spaces are usually available for solving pattern recognition tasks based on sensor array data. The accessible spectrum of features depends on the pool of sensor signal parameters to select from. Particularly extensive sources of features are signals obtained when using techniques to increase their information content e.g. the stop-flow operation mode. The effectiveness of solving pattern recognition task is related to the feature space, where it is performed. Actually, it is determined by the mutual distance of sensor array response patterns, which represent various gases in that space. Pattern coordinates are set by features. Therefore, the selection of features decides about the pattern layout, and makes it different in different feature spaces. It is imaginable that there exist a feature space(s), which offers the best solution of gas assessment task in terms of the corresponding pattern recognition task, as compared to other spaces, due to the most favourable layout of patterns in this space.

In our work the idea of solving each gas assessment task is to use the feature space(s) where the associated pattern recognition problem is solved best (Szczurek et al., 2011). For realisation of this approach it is good to propose a way for defining many significantly different feature spaces. There are a number of factors, associated with construction and operation of sensor arrays, which cause the differences among features. Looking at the measurement data from a sensor array, they are most readily represented by the sensor dimension and the time dimension accordingly (see Fig. 2). The variability associated with the sensor dimension is commonly exploited for pattern recognition in sensor arrays. It actually is a part of the sensor array concept. The realisation is performed using the parameters of signals of many sensors as features. Recently, attention is paid to the utilisation of time dimension. In general, there are two ways to include factors revealed in time domain for shaping feature space. The direct way consists in using parameters, which synthetically represent entire sensor signal or its substantial part, as features. The best candidates are parameters of mathematical models used for fitting sensor signals. The other approach uses results of single measurements, which the sensor signal is composed of, as features. Here the time domain enters the feature space indirectly, as a set of variables associated with different time moments of the sensor signal. As mentioned before, the second strategy is called sub-sampling. In principle, the concept of sub-sampling refers to a single sensor signal. We proposed its extension to the collection of signals from the sensor array. In this way a uniform framework is proposed, which allows to build versatile feature spaces. They may account for all different sorts of factors, which are associated with sensor array construction as well as operation and which cause differences among features. Considering the kind of feature used, it actually is a data driven approach.

In our strategy, the output signal of sensor array operating in the dynamic conditions, was a result of a sequence of discrete measurements. The data obtained in course of exposure may be arranged in the following matrix form:

Fig. 2. Sensor array data arrangement. Sensor and time dimension are associated with main groups of factors, which cause variability in feature space.

The matrix dimension is mxn where, m is the number of measurements during single exposure to gas mixture, and n is the number of sensors in the array. In this notation k, k=1,...,m corresponds to different time points of the exposure time interval, while j, j=1,...,n indicates sensors in the array. A single matrix element is  $\mathbf{r}_{kj} = \mathbf{r}_{kj} \mathbf{g}^{as} - \mathbf{r}_{0,j}$  where  $\mathbf{r}_{kj} \mathbf{g}^{as}$  is the output signal of  $j^{th}$  sensor to gas mixture, measured in  $k^{th}$  time point of exposure, and  $\mathbf{r}_{0,j}$  is the baseline signal. This data arrangement may be fixed. In that form, it corresponds to a strictly defined sensor array setup and measurement procedure and may be considered as a template of the response of sensor array to a gas mixture.

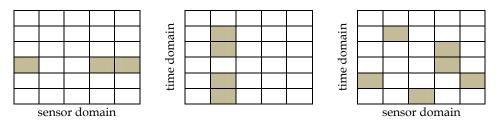


Fig. 3. Location of feature vector elements in sensor array data matrix. The following sources of features variability are represented in the feature vector: (a) sensor kind, (b) factors acting in time domain, (c) both, sensor kind and factors acting in time domain.

In our work the element  $r_{kj}$  of data matrix **R** is considered a feature. Within the framework of extended sub-sampling, in the feature vector there may be represented:

- 1. variability associated with the senor kind,
- 2. variability exhibited in time domain,
- 3. both kinds of variability jointly. These three cases are illustrated in Fig. 3.

The approach allows for generating different feature spaces. Additionally, the number of feature spaces is substantial. Considering an array composed of n sensors and sensor signal composed of m discrete measurement results, the number of feature spaces is:

$$N_{fs} = \sum_{k=1}^{n \cdot m} \frac{(n \cdot m)!}{k!(n \cdot m - k)!} \tag{1}$$

where i is the number of variables in the feature vector.

In our recent works, the feasibility of the approach regarding feature vectors is shown where the differences among features are caused by the sensor kind. It is indicated that the contribution of this factor for pattern recognition is variable upon varied conditions of sensor array operation and the resulting sensor states (Maciejewska *et al.*, 2009; Szczurek *et al.* 2010, 2011). The steady state, which is commonly favoured in commercial devices based on a sensor array is shown to provide equally or less valuable feature spaces, as compared to other sensor states. This gives a reason for further investigation of factors, which act upon a sensor array in time domain. Moreover the interaction of these factors and sensor variability builds another perspective. These can all be exploited for extending the applicability of a sensor array.

#### 3.6.3 Selection of best feature space

With the emphasis on solving gas assessment task using the feature space(s) where the corresponding pattern recognition problem is solved best, attention is paid to the search for an appropriate feature space. In principle, it can proceed in two ways, via feature extraction or feature selection. Feature extraction is achieved by transforming entire initial feature space into a new one. The main advantage of this transformation consists in compressing valuable information into new features, which are fewer than the original ones. Often, new features also have other advantageous properties. For example, when using principal component analysis (PCA) as a method of extraction, new features are orthogonal. Furthermore, features resulting from independent component analysis (ICA) are statistically

independent. The independence or at least orthogonality is beneficial when applying regression analysis. However, the extracted features lack the direct physical interpretation, which is available for the original ones. Also, the number of transformations of the original feature space is limited.

In our work the search for an appropriate feature space is done by means of feature selection. The goal is to find a set of original features, which maximises the information content or the predictive accuracy criterion. This is synonymous with finding best space(s) of original features. The selection involves two aspects:

- 1. search through feature sets,
- assessment of feature sets. In classical perspective the sets are actually subsets of one, original feature set.

Although substantial workload and time may be required at this stage, in this way we avoid one additional transformation of feature space before proceeding to pattern recognition stage. Additionally, much bigger flexibility when dealing with feature vector composition is retained.

Considering search strategies, the one which guarantees arriving at globally optimal solution is the exhaustive search. However, the number of possible subsets grows exponentially with the number of features. The approach is impractical for spaces composed of more than 20 features. To obtain a solution in a reasonable time, the search strategies are used which examine the feature space in a more efficient way. They may be grouped into: heuristic, deterministic and stochastic. The heuristic approach is attractive as a means of initial reduction of feature space, and ultimately shortening the search time. It utilises the expertise of the researcher, especially regarding information value of single features. Deterministic search strategies are mostly algorithms of local optimization, except for the branch and bound technique. Therefore, they are claimed suboptimal. However, many of them are attractive due to fast convergence. This group is dominated by variants of sequential search. Search strategies, which are considered nearly optimal, belong to the last category. Among the stochastic methods, genetic algorithms and simulated annealing are the most acknowledged ones. In these algorithms the random element is involved in the selection of feature sets. For that reason they are less prone to stucking in a local minimum. However, the algorithms are also computationally more demanding and time consuming than deterministic approaches.

The assessment of feature space is usually carried out using one of three following approaches: filter, wrapper or embedded. The first approach is free from the context of pattern recognition method. It utilises the assessment criteria like e.g.: the distance between object categories, interclass vs. intraclass pattern variability, information content measures. Due to using so general criteria it has high cognitive value, in particular as a means of assessing individual features. Filtering is willingly employed for sensor array optimisation on a feature by feature, univariate basis. Regarding multivariate feature assessment and pattern recognition context, filters have smaller practical value than other approaches. The wrapper approach allows for the assessment of joint performance of pattern recognition method and feature space in the context of particular pattern recognition task. The result is less general. However, the method is well suited for finding best feature spaces for solving gas assessment task represented as a pattern recognition one. The approach favours simple

classifiers like linear discriminant analysis (LDA), k-nearest neighbours method (k-NN), because the time required for model learning is the limiting factor just like the number of feature spaces to search through. In case of using more time consuming methods e.g. ANN, SVM, feature spaces pre-selection is usually done in a simpler manner. In recent years the embedded approach is slowly gaining interest in the sensor array community. The name comes from embedding the strategy of feature selection in the process of classifier development. The most serious candidates in this group of methods are random forests.

Considering the concept of finding best feature space for each kind of gas assessment task, which is realised with a sensor array, the wrapper and embedded approaches are favoured for feature space evaluation. So far in our works the first one was examined in combination with the heuristic pre-selection. Using heuristics, the feature spaces were preselected in which the differences among features came from the differences among the sensors at the particular moment of their exposure to the test gas. The rule was applied to the data provided by the sensor array composed of 15 sensors, which was operated in the stop-flow operation mode. As a result, over a thousand of 15-dimensional feature spaces were obtained. It was demonstrated that the complete search of those feature space could be performed in an acceptable time. To a large extent it was achieved due to employing fast learning pattern recognition methods. Regarding feature set assessment criteria, the classification success rate was used in the case of qualitative problems and the error of concentration prediction (RMSE and/or MRE) was applied for quantitative problems. The feature space was considered best for solving a particular qualitative problem of gas assessment if the corresponding pattern classification task was solved with null classification error rate. The feature space was considered best for solving a particular quantitative problem of gas assessment if the projection of feature set into corresponding quantitative variable resulted in a concentration estimation error, which was lower than the threshold of several percent. In our research a number of gas mixtures were considered to investigate the assessment problems (Maciejewska et al., 2010; Szczurek et al., 2011). The results show that many best feature spaces are available for each of them. Usually, there are more than several hundred ones in single case. It is meaningful that numerous low dimensional spaces (3 and even 2 dimensional) were found to fulfil the criteria of best feature space.

## 3.6.4 Pattern recognition

In the research work on sensor arrays we retract from looking for the pattern recognition method, which performs best in an imposed feature space in favour of searching for the feature space(s) where the particular pattern recognition method performs best. The first approach is the conventional one. In general, it allows for highly multi-dimensional feature spaces and it favours nonlinear pattern recognition methods. The most popular ones are artificial neural networks (ANN) and support vector machines (SVM). ANN are available in many kinds: multi-layer perceptrons (MLP), radial basis function neural networks (RBFNN), probabilistic neural networks (PNN), Kohonen maps, just to mention the most frequently used ones. They are suitable for solving linear as well as nonlinear problems. Additionally, classification as well as regression tasks may be approached with ANN. One of their drawbacks results from the fact that models have many parameters to be adjusted and this requires substantial calibration data sets. SVMs in turn offer very good classification results in the cases when data sets are small and the classification problems are highly nonlinear.

They are competitive as compared to ANN regarding the classification success rate, the number of user defined parameters and the time required for learning. However, they are not used for mapping features into continuous variables.

It is most frequently assumed that sensor array pattern recognition problems are nonlinear and therefore the above listed methods are preferred. However, there are many examples of successful pattern recognition using simpler, in particular linear methods, even if the feature space is not selected with using them in mind (Arnold et al., 2002; Pardo et al., 2006). In our approach simple classifiers and simple regression models are used. It is assumed that the probability of finding a feature space where patterns are linearly or at least nearly linearly separable is nonzero. Similarly, an assumption is made concerning the existence of feature set, which can be linearly transformable into the gas concentration. So far, linear and fast to train pattern recognition methods have been used in our research on senor arrays with broad applicability. These are: DFA for classification tasks and multiple liner regressions (MLR) for quantitative problems. They performed very well as feature space assessment methods in the framework of wrapper approach (Maciejewska et al., 2010; Szczurek et al., 2011). The exhaustive search of 15 dimensional feature spaces is relatively fast and it allows for arriving at solutions in an acceptable time. It was shown by the results of our research that there were available numerous feature spaces where qualitative gas assessment could be solved as linear pattern recognition task. The same was found regarding quantitative gas assessment. In both cases simple pattern recognition methods were sufficient.

## 3.6.5 Data analysis arrangement for test gas assessment

While designing sensor array with broad applicability it is particularly important to propose reliable and functional solutions regarding measurement data analysis. Our proposal is grounded on the ability to achieve best results of pattern recognition in low dimensional spaces, by means of simple classifiers and regression models. The key elements of this concept are:

- A sensor array is prepared for solving defined problems of qualitative and quantitative
  gas assessment. However, the list of tasks is not a closed one. It can be extended any
  time by the producer of sensor array. The aim of this possibility is to increase the
  universality of measurements.
- The problem of qualitative gas assessment is considered as the corresponding classification problem (prediction) and the problem of quantitative gas assessment is approached as the corresponding regression problem (prediction). They are solved in an earlier defined feature spaces. These are best feature spaces in a sense, which was discussed earlier.
- There is assigned one, parameterised classifier for solving a particular classification problem in one, feature space and there is assigned one parameterised regression model for solving a particular regression problem in one feature space.
- A structure called data record is used for keeping the information about one feature space and the associated classifier/regression model, both assigned for a particular qualitative/quantitative problems. A data record is composed of two parts. The first part defines the feature space by means of feature vector. In our approach features are elements of matrix R (see Fig. 2). The coordinates of feature vector are indicated using

the position (k, j) of elements in data matrix R. The second part of data record contains parameters of the associated classifier/regression model in a predefined order. The parameters of pattern recognition models are obtained in course of supervised learning, using calibration patterns.

- A number of data records are available for each qualitative gas assessment problem and
  it is so for each quantitative gas assessment problem. We propose that the set of data
  records addressed to a particular gas assessment problem contains between several and
  several dozen data records.
- Data records are defined by the producer of a sensor array and they are held in the library of the device. In our strategy, this operation is realised at a level of sensor array design, on the basis of calibration measurements. Responses of different sensors to standard gaseous mixtures (in accordance with a procedure applicable in the stop-flow mode) are considered. Data records may be updated in course of periodic calibrations.
- The qualitative gas assessment is provided as the result of majority vote of the committee of classifiers. Member classifiers operate on different patterns, which represent the same gas in different feature spaces, following the reference provided by the respective data records.
- The quantitative gas assessment is given as the median of predictions provided by the set of regression models. Models operate on different patterns, which refer to the same gas in different feature spaces, following the reference provided by the respective data records. Quantitative gas assessment, is preceded by the qualitative assessment unless the identity of gas is known.

Due to low dimensionality of best feature spaces and the simplicity (small number of parameters) of pattern recognition models, the memory requirements are very modest in the proposed arrangement. Also, the computational requirements are low, which offers that gas assessment is performed quickly, once the measurement is complete. The user interaction with the data analysis is very limited and restricted to the selection of gas assessment problem, which needs to be solved, from the library of the device.

#### 4. Conclusions

Gas sensors already have a considerable share in detecting and monitoring the presence of hazardous gases in various atmospheres. However, for achieving their broad application, the ability to perform qualitative and quantitative assessment of chemical substances is required. Despite numerous positives like fast response time, small size and low price, gas sensors have some limitations, in particular regarding sensitivity and selectivity. The recognised way to overcome them and to achieve the requested functionalities is to use a sensor array. It is based on the idea that selectivity may be achieved by using a set of partially, but differently selective sensors. It was actually shown that the responses of such a set provides data patterns, which represent the measured gas in a nearly unique manner. The gas assessment is achieved by analysing the pattern with pattern recognition methods.

Sensor array design involves a number of aspects. The major ones are:

- 1. method of sampling and sample pre-treatment,
- 2. measurement characteristics of sensor array,

- 3. working parameters,
- 4. operation mode,
- 5. signal processing,
- 6. data analysis.

The improvement on any of these elements contributes to the overall performance of sensor device. Their careful consideration is especially important regarding design of sensor array with broad applicability.

Sampling is necessary for presenting samples to sensors. Two main kinds are active and passive sampling. While diffusion sampling is practically effortless, dynamic sampling requires more complex measuring setup. At that cost, the gas delivery is under control, lower gas concentrations can be measured and instrument calibration is easier. Therefore, the dynamic sampling is our choice for sensor array addressed to wide range of applications.

Performance of a sensor array is directly influenced by the selection of sensors and the construction of sensor array. Selection of sensors refers to the kind of sensors and the number of sensors in the array. Many kinds of sensors are applied in sensor arrays. The most popular ones are: electro-chemical sensors, mass sensitive devices, MOSFETs and chemi-resistors. Due to utilizing different sensing mechanisms, heterogeneous sensor arrays are more versatile. More popular, homogeneous arrays are easier to construct and operate. The measurement characteristics of sensor array are not proportional to the number of sensing elements because the sensors' usability is different regarding various applications. Currently, sensor array designers often perform application-oriented sensor selection. It is in principle against the idea of broad applicability. We propose another approach. It consists in that sensor selection does not refer to the physical presence of a sensor in an array but to the use of sensor output signal in gas assessment tasks, associated with particular application. The sensor array is composed of very many sensors. They all perform measurements. However, only selected combinations are involved in providing data for various pattern recognition tasks. In this way, a great flexibility regarding adjustment to numerous applications is reached.

While using commercial sensors as measuring elements in sensor array, the way to enhance the information content of sensor array response is to vary sensor operating conditions in course of exposure to a measured gas. In this respect, our original proposal is a stop-flow operation mode. It involves measurements in static and dynamic conditions, including both steady states of sensors and transients. The mode is simple in execution and it was shown to provide for a considerable increase in the number of best domains for pattern recognition.

A sensor array with broad applicability has to face numerous gas assessment problems of qualitative and quantitative kind. Any gas assessment performed by the sensor array is addressed at the data analysis level as pattern recognition problem. In currently offered arrays, different pattern recognition tasks are usually solved in one feature space and nonlinear pattern recognition methods are favoured. In our work we promote the idea of solving each gas assessment task using the feature space(s) where the associated pattern recognition problems are solved best. The best feature spaces are found in course of feature

selection process using wrapper approach. The concept of extended sub-sampling is introduced as a means of generating numerous feature spaces where various factors associated with sensor array construction and operation are exploited to cause differences among features. Considering pattern recognition methods we retract from using complex ones in favour of fast learning classifiers and simple regression methods, preferably linear ones. Feature selection is to provide feature space(s) where these particular pattern recognition methods perform best. To improve the reliability of our results, many patterns which represent the same test gas are considered while performing test gas assessment. For that reason low dimensional feature spaces are favoured. Calibration of pattern recognition models, which operate in such spaces, may be satisfied using calibration data sets of modest size.

It is believed that the presented approach is original ant it will gain interest in the community of sensor array designers.

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## 6. References

- Amrani M.E.H., Payne P.A., Persaud K.C. (1992). Multi-frequency measurements of organic conducting polymers for sensing of gases and vapours. *Sens. Actuators B: Chem.*, Vol. 8, pp. 137-141
- Arnold Ch., Harms M., Goschnick J. (2002). Air quality monitoring and fire detection with the Karlsruhe electronic micronose KAMINA. *IEEE Sensors Journal*, Vol. 2, No. 3, pp.179-188
- Barbri N.E., Duran C., Brezmes J., Cañellas N., Ramírez J.L., Bouchikhi B., Llobet E. (2008).

  Selectivity Enhancement in Multisensor Systems Using Flow Modulation
  Techniques, *Sensors*, Vol. 8, pp. 7369-7379
- Berna A. (2010). Metal Oxide Sensors for Electronic Noses and Their Application to Food Analysis. *Sensors*, Vol. 10, pp. 3882-3910
- Bourgeois W., Romain A.C., Nicolas J., Stuetz R. M. (2003). The use of sensor arrays for environmental monitoring: interests and limitations. *J. Environ. Monit.*, vol. 5, pp. 852–860
- Byun H.G., Persaud K. C., Pisanelli A.M. (2010). Wound-State Monitoring for Burn Patients Using E-Nose/SPME System. *ETRI Journal*. Vol. 32, No. 3 pp. 440-446
- Faglia F., Comini E., Cristalli A., Sberveglieri G., Dori L. (1999). Very low power consumption micromachined CO sensors. Sens. Actuators B: Chem., Vol. 55, pp. 140– 146
- Gardner J.W., Boilot P., Hines E.L. (2005). Enhancing electronic nose performance by sensor selection using a new integer-based genetic algorithm approach, *Sens. Actuators B: Chem.*, Vol. 106, pp. 114–121
- Gouws G.J., Gouws D.J. (2003). Analyte identification using concentration modulation and wavelet analysis of QCM sensors. *Sens. Actuators B: Chem.*, Vol. 91, pp. 326–332.

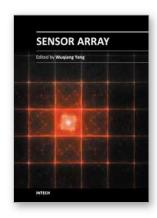
- Gualdr´on O., Llobet E., Brezmes J., Vilanova X., Correig X. (2006). Coupling fast variable selection methods to neural network-based classifiers: Application to multisensor systems. *Sens. Actuators B: Chem.*, Vol. 114, pp. 522–529
- Gutierrez F.C., Ares L., Horrillo M.C., Sayago I., Agapito J.A., Lopez L. (1991). Use of complex impedance spectroscopy in chemical sensor characterization. *Sens. Actuators B: Chem.*, Vol. 4, pp. 359-363
- Gutierrez F.C., Ares L., Robla J.I., Horrillo M.C., Sayago I., Agapito J.A. (1992). Properties of policrystalinne gas sensor based on d.c. and a.c. measurements. *Sens. Actuators B: Chem.*, Vol. 8, pp. 231-235
- Gutierrez-Osuna R., Gutierrez-Galvez A., Powar N. (2003). Transient response analysis for temperature-modulated chemoresistors. *Sens. Actuators B: Chem.*, Vol. 93, pp. 57–66
- Llobet E., Brezmes J., Vilanova X., Sueiras J., Correig X. (1997). Qualitative and quantitative analysis of volatile organic compounds using transient and steady-state responses of a thick-film tin oxide gas sensor array. *Sens. Actuators B: Chem.*, Vol. 41, pp. 13–22
- Maciejewska M., Szczurek A., Ochromowicz Ł. (2009). The characteristics of a "stop-flow" mode of sensor array operation using data with the best classification performance. *Sens. Actuators B: Chem.*, Vol. 141, pp. 417–423
- Maciejewska M., Szczurek A., Bodzoj L., Flisowska-Wiercik B. (2010). Sensor array and stopflow mode applied to discrimination and quantification of gas mixtures. *Sens. Actuators B: Chem.*, Vol. 150, pp. 93–98
- Pardo M., Sisk B.C., Sberveglieri G., Lewis N.S. (2006). Comparison of Fisher's linear discriminant to multilayer perceptron networks in the classification of vapors using sensors array data, *Sens. Actuators B: Chem.*, Vol. 115, pp. 647-655
- Persaud K., Dodd G.H. (1982). Analysis of discrimination mechanisms of the mammalian olfactory system using a model nose. *Nature*, Vol. 299, pp. 352–355
- Stetter J.R., Strathmann S., McEntegart C., Decastro M., Penrose W.R. (2000). New sensor arrays and sampling systems for a modular electronic nose. *Sens. Actuators B: Chem.*, Vol. 69, pp. 410–419
- Szczurek A., Maciejewska M., Flisowska-Wiercik B., Bodzoj L. (2010). The stop-flow mode of operation applied to a single chemiresistor, *Sens. Actuators B: Chem.*, Vol. 148, pp. 522–530
- Szczurek A., Maciejewska M., Flisowska-Wiercik B. (2011). Method of gas mixtures discrimination based on sensor array, temporal response and data driven approach. *Talanta*, Vol. 83, pp. 916–923
- Tomchenko A.A., Harmer G.P., Marquis B.T., Allen J.W. (2003). Semiconducting metal oxide sensor array for the selective detection of combustion gases. Sens. Actuators B: Chem., Vol. 93, pp. 126–134
- Vergara A., Martinelli E., Llobet E., Giannini F., D'Amico A., Di Natale C. (2006). An alternative global feature extraction of temperature modulated micro-hotplate gas sensors array using an energy vector approach. *Sens. Actuators B: Chem.*, Vol. 124, pp. 352–359
- Vergara A., Llobet E., Martinelli E., Di Natale C., D'Amico A., Correig X. (2007). Feature extraction of metal oxide gas sensors using dynamic moments. *Sens. Actuators B: Chem.*, Vol. 122, pp. 219–226

Garrigues S., Talou T., Nesa D. (2004). Comparative study between gas sensors arrays device, sensory evaluation and GC/MS analysis for QC in automotive industry. *Sens. Actuators B: Chem.*, Vol.103, pp. 55–68

Zampolli S., Elmi I., Ahmed F., Passini M., Cardinali G.C., Nicoletti S., Dori L. (2004). An electronic nose based on solid state sensor arrays for low-cost indoor air quality monitoring applications. *Sens. Actuators B: Chem.*, Vol. 101, pp. 39–46







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Sensor arrays are used to overcome the limitation of simple and/or individual conventional sensors. Obviously, it is more complicated to deal with some issues related to sensor arrays, e.g. signal processing, than those conventional sensors. Some of the issues are addressed in this book, with emphasis on signal processing, calibration and some advanced applications, e.g. how to place sensors as an array for accurate measurement, how to calibrate a sensor array by experiment, how to use a sensor array to track non-stationary targets efficiently and effectively, how to use an ultrasonic sensor array for shape recognition and position measurement, how to use sensor arrays to detect chemical agents, and applications of gas sensor arrays, including e-nose. This book should be useful for those who would like to learn the recent developments in sensor arrays, in particular for engineers, academics and postgraduate students studying instrumentation and measurement.

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