

# Modular Sensor Systems for Gas Sensing and Odor Monitoring: The MOSES Concept

JAN MITROVICS, HEIKO ULMER,  
UDO WEIMAR, AND WOLFGANG GÖPEL\*

*Center of Interface Analysis and Sensors,  
Institute of Physical and Theoretical Chemistry,  
University of Tübingen, Auf der Morgenstelle 8,  
D-72076 Tübingen, Germany*

Received August 20, 1997

## 1. Introduction

Widespread application areas of chemical and biochemical sensors include environmental monitoring, process control, medical and food quality analysis, etc.<sup>1–3</sup> Several commercial instruments (usually known as “electronic noses”) are available now,<sup>4</sup> which typically make use of several sensors operating with one of the various possible signal transduction principles. However, for most applications these instruments still have insufficient performances if compared with the established instruments of analytical chemistry (e.g., arrays of gas sensors compared with GC/MS). Usually the individual sensors show drifts and are not sensitive enough.<sup>5</sup> This causes serious problems in the calibration and control of the reproduc-

ibility of sensor arrays as it is required for solving specific analytical tasks.

The required performance in most applications can only be achieved by increasing the amount of chemically “orthogonal” information deduced from a sensor system, i.e., by increasing the number of independent sensor features. This can be accomplished by (1) increasing the number of sensors with different sensitive materials in an array, whereby the array uses the same signal transduction principle (the same “transducer”), (2) recording several independent physical properties of each individual sensor material with different transducers, and (3) modulating the operation conditions of each individual sensor.

These concepts are illustrated by examples in section 2. In section 3 examples of a sensor system equipped with two different sensing principles used in typical applications from the packaging and food industry are given.

Modularity is the key to realize all these concepts efficiently in one instrument. This leads to new flexible designs of a next generation of electronic noses based on modular sensor systems for general gas and odor analysis which at best should include all options for extending the feature space of chemical sensors. For each application this concept makes it possible to choose a sufficient number of modular components which lead to a sufficiently large number of orthogonal chemically (odor, toxicity) relevant parameters as they are determined in the final feature extraction and pattern recognition. In the future these systems will complement and extend the kind of information traditionally obtained in analytical chemistry, e.g., by characterizing human odor sensation or by monitoring toxicity.

Considering the broad spectrum of transducers and of chemically sensitive materials which may be used in principle in such electronic noses (see Tables 1 and 2 as a brief overview) two classes of materials appear to be most promising for future chemical sensor elements: (1) metal oxides with electron, ion, or mixed conduction,<sup>6,7</sup> and (2) polymers or supramolecular structures with systematically varied recognition sites.<sup>8,10,11</sup>

Many research groups develop new materials and transducers with particular emphasis on optimizing interface properties among the gas phase, the sensitive material, and the transducer. By comparing performances of their prototype devices with those of existing sensors or transducers on the market, they optimize new materials and transducer designs for new applications. The necessary quantitative comparison with performances of components in existing sensor systems requires standardized tests. This includes standardized sampling, feature extraction, and pattern recognition procedures. The need for standardization led to the design of a new modular sensor system (MOSES) with an open architecture to be introduced in section 2.4.

Jan Mitrovics received his Diploma in physics in 1995 from the University of Tübingen. He is currently working on his Ph.D. in the group of Professor Göpel at the Institute of Physical and Theoretical Chemistry at the University of Tübingen. His research interests are hybrid arrays of chemical gas sensors and the subsequent pattern recognition and multicomponent analysis.

Heiko Ulmer received his Diploma in chemistry in 1995 from the University of Tübingen, working on olfactory measurements using an electronic nose in the group of Professor Göpel in the Physical Chemistry Department. Since 1996 he has been working on his Ph.D. thesis in the field of quartz microbalance sensors and electronic noses.

Udo Weimar received his diploma in physics in 1989 and his Ph.D. in chemistry in 1993 from the University of Tübingen. During his Ph.D. studies he worked in the field of thin film metal oxide sensors using different kinds of electrical and spectroscopic tools. He is currently a senior member of the Centre of Interface Analysis and Sensors at the University of Tübingen. The research interest of Udo Weimar focuses on chemical sensors as well as on multicomponent analysis and pattern recognition.

Wolfgang Göpel received his Ph.D. from the University of Hannover (Germany) in 1971. After visiting scientist positions at the Xerox Palo Alto (California), Xerox Webster (New York), and IBM Watson (New York) Research Centers he was appointed as Full Professor of Physics at the Center of Surface and Submicron Analysis, Bozeman, MT. Since 1983 he has been the Director of the Institute of Physical and Theoretical Chemistry at the University of Tübingen (Germany), the Steinbeis Technology Transfer Center, and the Center of Interface Analysis and Sensors with research interests in sensors and analytical chemistry, in interface properties of new materials for (bio)chemical sensors, catalysts, molecular electronic and bioelectronic devices, and sensor systems. He has published more than 400 original papers and several textbooks and is editor of the Wiley/VCH series *Sensors*.

\* To whom correspondence should be addressed. Fax: ++49 7071 29-5490. E-mail: wg@ipc.uni-tuebingen.de.

**Table 1. Typical Physical Properties and Corresponding Transducers for Chemical Sensors**

changed physical property	transducers	chemical sensor
resistance, $\Delta R$ , or impedance, $\Delta Z$	two-, three-, and four-electrode arrangements	metal oxide gas sensor, conducting polymer sensor
current, $\Delta I$	two- and three-electrode arrangements	electrochemical cell
capacitance, $\Delta C$	interdigitated capacitors	humidity sensor
work function, $\Delta\phi$	Kelvin probes, field effect devices	gas FET
mass, $\Delta m$	bulk and surface acoustic wave transducers	polymer coated microbalance sensor
temperature, $\Delta T$	thermopiles, ntc or ptc resistors	calorimetric sensor, pellistor
optical absorption, $\Delta\epsilon$	optical waveguides, fibers	absorption or decay-time sensor
optical layer thickness, $\Delta(nd)$	layer structures	interference or surface plasmon sensor

**Table 2. Typical Chemically Sensitive Materials (See Also Examples in Section 2)**

class of materials	examples
ionic compounds	electronic conductors (SnO <sub>2</sub> , TiO <sub>2</sub> , Ta <sub>2</sub> O <sub>5</sub> , IrO <sub>x</sub> , In <sub>2</sub> O <sub>3</sub> , ...) mixed conductors (Ga <sub>2</sub> O <sub>3</sub> , SrTiO <sub>3</sub> , La <sub>1-x</sub> Sr <sub>x</sub> Co <sub>1-y</sub> Ni <sub>y</sub> O <sub>3</sub> , more general: perovskites, ...) ionic conductors (ZrO <sub>2</sub> , LaF <sub>3</sub> , CeO <sub>2</sub> , CaF <sub>2</sub> , Na <sub>2</sub> CO <sub>3</sub> , $\beta$ -alumina, nasicon, ...)
molecular crystals	phthalocyanines (PbPc, LuPc <sub>2</sub> , ...), porphyrines
self-assembled monolayers	alkanethiols, dialkylsulfides, (alkoxy)silanes, carboxylic acids
Langmuir–Blodgett films	phthalocyanines, porphyrines, cyclohexapeptides
supramolecular structures	zeolites, calixarenes, resorcinarenes, cyclodextrines, crown ethers, cyclophanes, cyclopeptides
polymers	polyethers, polyurethanes, polysiloxanes, polypyrroles, polythiophenes, polyfluorocarbons, polyolefines, nafion
components of biomolecular functional systems (for liquid sensing)	<i>synthetic</i> : phospholipids, FMD- and AIDS-virus-epitopes <i>natural</i> : glucose oxidase, lactose permease, bacterial cellulose, <i>E. coli</i> cell membranes more general: enzymes, receptors, transport proteins, membranes, cells, tissue

## 2. Extending the Feature Space in Chemical Sensing: Concepts and Typical Examples

The traditional use of chemical sensors focuses on the output of one individual chemical sensor with only one sensor signal (“feature”). The sensor with its chemically sensitive layer and transducer is exposed to the analyte molecule. The chemical information concerning the analyte concentration is converted by the transducer with its chemically sensitive layer into an electrical signal. For example, the diffusion-controlled current of an electrochemical cell is monitored at a fixed potential, or the resistance change of the metal oxide sensor is recorded at a certain voltage and frequency and hence yields a specific feature. The desired chemical information is then obtained in a comparison with calibration data.

Obviously this setup delivers only one value, i.e., one concentration. Whenever more information is desired, a more complex setup including several sensors or different modes of sensor operation is required. This increases the number of independent features for a more complex gas analysis. In this context, the term feature is defined as one quasi-independent variable determined from the measuring setup. The most important reason for increasing the dimensions of the feature space is the fact that no gas sensor is totally selective. If species other than the analyte to be detected are present, cross sensitivities influence the reading of the instrument. Determining a feature space with sufficient dimension and evaluating its data by means of pattern recognition allows in principle the elimination of cross sensitivities, the automatic recalibration, and the adjustment of output information to different tasks. The latter can be optimized in many ways. Examples include the determination of a certain VOC content, an odor, or certain toxicity.

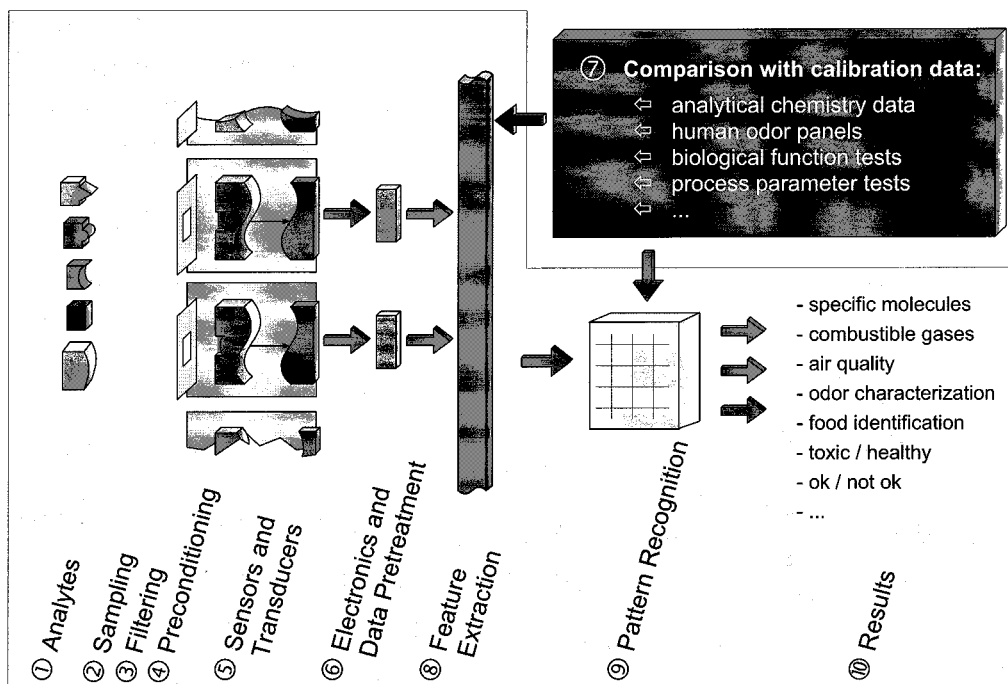
**2.1. Several Sensor Materials/One Transducer Approach.** To achieve a discrimination between different

analytes, several gas sensors are combined to form an array (Figure 1). By modifying the properties of each sensitive layer, these sensors with their partly overlapping sensitivities generate independent features with the same type of transducer. The signals of these sensors are recorded simultaneously. Instead of a simple calibration function, a multicomponent analysis or pattern recognition is used to obtain the desired analytical information.<sup>12–14</sup>

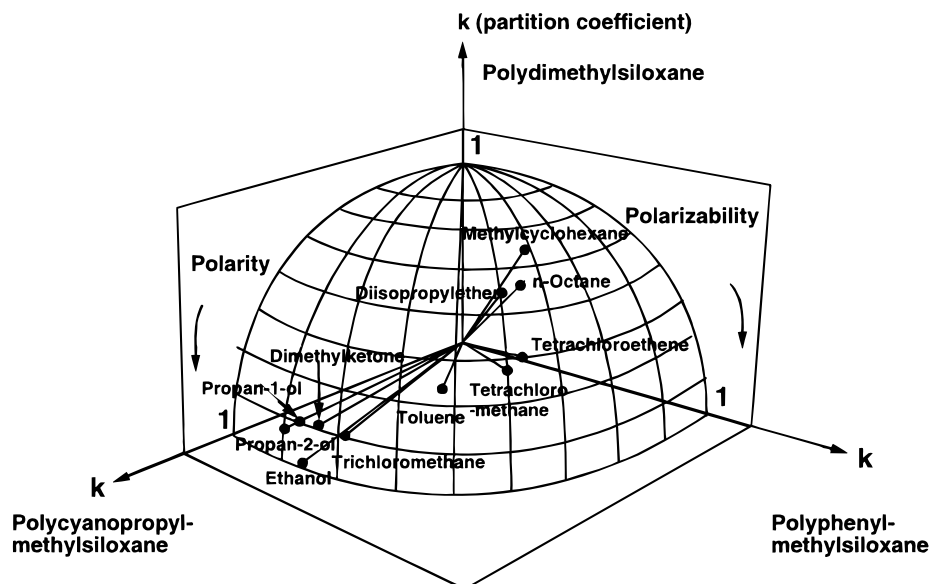
Modified metal oxides are often used as sensor materials in transducer arrays based on conductivity. For details see section 2.3 or ref 15.

Another group of sensor materials concerns polymers and supramolecular compounds often used in sensor arrays based on mass sensitive transducers. For details, see the extensive literature.<sup>8,9</sup> These materials offer many options for chemical modifications and hence a huge flexibility in tailoring molecular recognition sites by controlled organic synthesis through supramolecular chemistry, combinatorial chemistry, or matrix-embedding of biomimetic and biomolecular function units.<sup>10,16,17</sup>

By attaching, for example, specific functional groups with different chemical properties to the backbone of a polymer, the sensitivity for the detection of certain analyte molecules is well-known to be enhanced. Just to give typical examples, the cyano group of poly(cyanopropyl)-methylsiloxane introduces a higher polarity to the polymer, and higher polarizability is introduced by adding phenyl groups (in poly(phenyl)methylsiloxane). In Figure 2 the results from these different polymers and polydimethylsiloxane (the pure backbone) span a three-dimensional vector space. The relative frequency variations obtained from quartz crystal microbalance (QCM) measurements determine a vector which increases in length proportional to the gas concentration and which



**FIGURE 1.** Schematic setup of components in a sensor system for gas and odor analysis. Analytes are led to the sensing elements via sampling, filtering, and preconditioning. The sensing elements consist of a chemical sensitive layer (sensor) and a transducer, which transforms the chemical information into an electrical one. This electrical response is recorded, and after some data pretreatment several features are extracted from the response curve. The final result is achieved by comparing these feature values by means of pattern recognition to the calibration data.



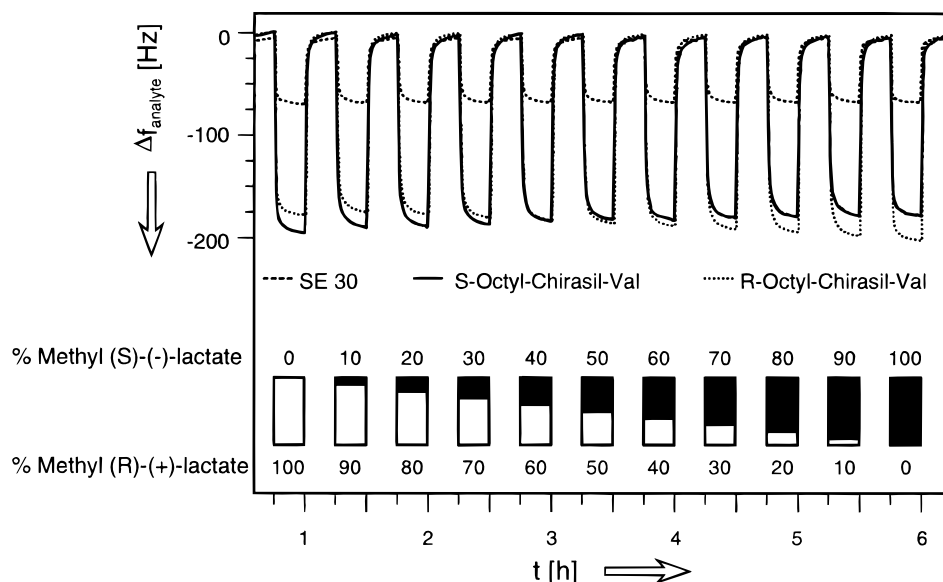
**FIGURE 2.** Different analyte molecules monitored with three different polymer-coated QCMs. Reprinted with permission from ref 18. Copyright 1995 Elsevier. For details, see the text.

after normalization to a unit length of 1 determines a substance-specific direction.

Beneath selectivity these coatings offer other advantages because of their achievable long-term stability. QCM results of an array with six different polymer coatings exposed to different concentrations of toluene and *n*-octane have been reported by Hierlemann et al.<sup>18</sup> On the first day, the calibration data set was determined. Even after 210 days the concentrations of the test mixtures

could be predicted with low errors by a partial least squares or artificial neural net approach using the same calibration data set without any recalibration.

The high selectivity of specific interaction sites in modified polymers becomes of increasing interest in current sensor work. As an example the quantitative chiral discrimination became possible (Figure 3). Chiral groups in the side chain of this polymer provide enantioselective coatings. By using an array of (*R*)- and (*S*)-



**FIGURE 3.** Chiral discrimination with enantioselective polymer coatings: QCM signals (frequency shifts in hertz) of two chiral sensors ((*S*)-sensor, solid line, (*R*)-sensor, dotted line) and an additional nonchiral SE-30-sensor (SE-30 = poly(dimethylsiloxane)) upon exposure to mixtures of different enantiomer contents (%) of methyl lactate. Reprinted with permission from ref 19. Copyright 1997 Nature.

polymer and nonchiral polymer phase coatings, it was possible to discriminate between the (*R*)- and the (*S*)-analyte and to even determine the composition of racemic mixtures to within a few percent of error.<sup>19</sup> This result is of particular interest since our human nose is known to differentiate between certain enantiomers (like spearmint and caraway resulting from (*R*)- and (*S*)-carvone).

**2.2. Several Parameters/One Sensor Material Approach.** An alternative approach is the recording of several independent parameters of the same sensor coating. The simplest option is to use separate transducers for the recording of several independent physical properties of one sensitive layer.

For example, Haug et al.<sup>20</sup> used four different transducers to measure changes in the optical thickness  $\Delta d$ , mass  $\Delta m$ , temperature  $\Delta T$ , and capacity  $\Delta C$  of a polymer layer upon the incorporation of various organic volatiles such as  $C_2Cl_4$ ; Josowicz and Topart measured changes in mass, work function, and optical absorbance of conducting polymers.<sup>21</sup>

In the next degree of sophistication, the different transducer principles may be integrated in one design. As an example, mass changes and changes in the conductance of a conducting polymer have been monitored with a special electrode arrangement on a quartz resonator.<sup>22</sup>

**2.3. Parameter Modulation Approach.** An often applied method to increase the feature space of chemical information is the use of a specific modulation. This concerns either the (internal) operation conditions of the sensor<sup>23–30</sup> or the (external) gas composition.<sup>31,32</sup>

Modulation of the gas composition may be achieved by switching between a reference gas and the gas to be analyzed, or by using filters or catalysts to change the gas composition. The dynamic response of the sensor due to these changes can then be evaluated; see e.g., ref 33.

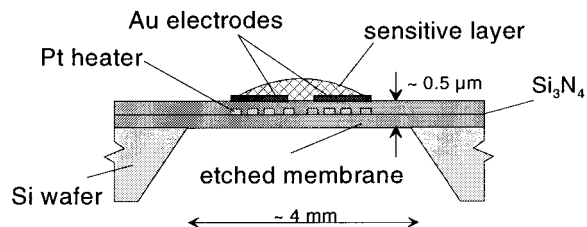
Modulation of the operation conditions of the sensor

itself can be achieved in many ways which are often determined by the transducer design. Metal oxide gas sensors, for example, may be used at varied operation temperature or potential of the measuring electrodes.

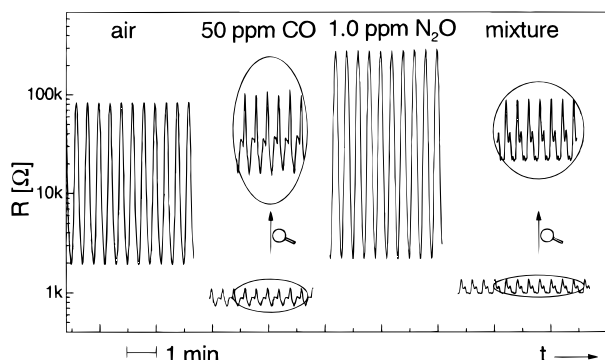
Two examples will illustrate the concept. Frequency modulation is of particular interest in this context (“complex impedance spectroscopy”). The overall electrical characteristics of the sensor consist of contributions from the surface, volume, contact, and grain boundaries, all of which are affected by chemical reactions of the sensor with the analyte. By using an ac-modulated working potential of the sensor, it is possible to enhance the performance of the sensor, if the operating frequency is chosen carefully to enhance a specific contribution to the complex impedance. Measuring at different frequencies can lead to detailed features for the subsequent pattern recognition.<sup>23</sup> Other options for extending the feature space concern systematic modifications of the transducers, with their contact arrangements, the selection of the base material, like  $SnO_2$ , and systematic modifications of its nanocrystallinity, added catalysts, dopants, etc.<sup>34</sup>

Temperature modulation offers alternative opportunities. It is well-known that the chemistry and hence the sensitivity of a metal oxide sensor depend critically on its working temperature. By modulating the temperature, it is therefore possible to discriminate between different analytes. To allow for fast changes in the temperature, microstructured transducers have to be chosen with their low thermal inertia. Figure 4 shows a cross section of a micromachined sensor which was used recently by Heilig et al. for temperature modulation measurements (Figure 5).<sup>28</sup>

Using fast Fourier transformation (FFT; Figure 6) and subsequent neural network analysis of the resulting changes in the resistance of the metal oxide, it was



**FIGURE 4.** Schematic cross section of a silicon micromachined sensor for temperature modulation. Reprinted with permission from ref 28. Copyright 1998 Elsevier.

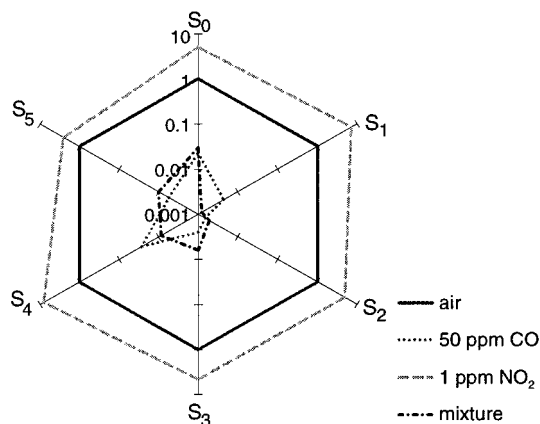


**FIGURE 5.** Time-dependent changes of the resistance  $R$  of a micromachined  $\text{SnO}_2$  sensor in synthetic air (50% rh) and during additional exposure to 50 ppm CO, 1.0 ppm  $\text{NO}_2$ , and a mixture of 50 ppm CO and 1.0 ppm  $\text{NO}_2$  due to sinusoidal temperature modulation with peak-to-peak amplitudes of 200 and 420 °C at a frequency of 50 mHz.

possible to determine concentrations of mixtures of  $\text{NO}_2$  and CO in air with only one sensor.

**2.4. Modular Sensor System Approaches.** The examples described above indicate that the feature space of general sensor systems may easily be extended by monitoring a huge number of independent features. The latter are generated by varying the sensor materials, transducer principles, and mode of operation for each sensor/transducer combination. This leads to a theoretical dimensionality of the “hyperspace of chemical sensor features” in the order of  $10^{21}$  (Figure 7). Because of the large number of possible variations in a complete sensor system, all of which determine the overall system’s performance, a modular setup offers the best flexibility for optimizing the choice of these features by optimizing each individual component of the system for specific applications.

Several commercial electronic nose instruments are currently modified toward their use as modular sensor systems. Companies such as AlphaMOS, Neotronics, and Nordic-Sensors offer additional options to add other transducer modules to their original version which started from exclusively metal oxide, conducting polymer, or MOSFET devices. This trend and details have been described comparatively in ref 4. The market-oriented optimization of these modular sensor systems has to focus on optimizing a limited number of components in order to provide the end-user with a “reliable” instrument which at best should be handled by nonexperts without too sophisticated instructions.



**FIGURE 6.** Logarithmic polar plot for the different gas compositions with the normalized amplitudes  $S_0$ – $S_5$  as a ratio of the amplitudes of the base frequency and the higher harmonic overtone amplitudes ( $a(f)_{\text{gas}}$ ,  $i = 0$ – $5$ ) to the corresponding amplitudes of measurements in pure air ( $a(f)_{\text{air}}$ ,  $i = 0$ – $5$ ). Reprinted with permission from ref 28. Copyright 1998 Elsevier.

In contrast to this approach, a recently developed modular sensor system (MOSES) has been optimized as a research tool and hence optimized toward determining a maximum number of independent chemical features. After an analysis of the application-driven information content of each feature, their number may subsequently be reduced and optimized for the specific application. This system comprises a variety of different sample input units and transducer principles. The latter determine different types of modules in this “hybrid” modular system. Each sensor module consists of a measurement chamber with a sensor/transducer unit, a printed circuit board for the sensor electronics, and a microcontroller or digital signal processor (DSP).

Since maximum reliability of the modular sensor system is an important goal of MOSES, components and instrumentation well-known from analytical chemistry are included in the total system whenever possible. In this way the advantages of the modular sensor system on one hand and of the know-how from well-established analytical chemistry approaches on the other hand are combined. The following brief description of the different modules in a complete system illustrates this concept (compare also schematic Figure 1 and functions described in sections 2.1–2.3).

**2.4.1. Input Modules.** Sampling is a critical step in any gas and odor analysis. A variety of sampling devices optimized for their use in analytical chemistry hence have been adapted for the modular sensor system. These include headspace autosamplers (often used for comparative studies, e.g., of samples from the food and packaging industry) or purge and trap instruments for analyzing very low concentrations and specifically designed preconcentrators.

For on-line applications, a dedicated “Input Module” has been developed. This module is equipped with a gas pump, mass flow controller, temperature and humidity sensor, and an input valve array. The latter contains three

$$\begin{array}{cccccccc}
 \text{Materials} & + & \text{Transducers} & + & \text{Transducer} & + & \text{Modulation} & + & \text{Parameter} & + & \text{Multiple} & & \text{Hyperspace} \\
 & & & & \text{Geometries} & & \text{Parameters} & & \text{Shapes} & & \text{Modulation} & & \text{of Chemical} \\
 & & & & & & & & & & \text{Parameters} & & \text{Sensors} \\
 & & & & & & & & & & & & \\
 10^8 & * & 10^1 & * & 10^2 & * & 10^2 & * & 10^2 & * & 10^6 & = & 10^{21}
 \end{array}$$

FIGURE 7. "Hyperspace" of  $10^{21}$  chemical sensor features. Reprinted with permission from ref 29. Copyright 1998 Elsevier.

inputs for the selection of the gas sample, e.g., for reference, test, and purge gas.

**2.4.2. Quartz Crystal Microbalance (QCM) and Surface Acoustic Wave (SAW) Module.** In the QCM measurement chamber eight quartz crystals are used as mass-sensitive transducers. The quartzes are operated as thickness shear mode resonators (TSMR) at a fundamental frequency of 30 MHz. A modified version of this module for eight surface acoustic wave (SAW) devices is under development. Their principle advantages concern the use of monolayer thin film coatings.

In the standard configuration of MOSES, a set of eight selected polymers was chosen which shows optimum stability and "chemical orthogonality" for a broad spectrum of common applications. In addition, new materials are continuously synthesized and tested for their use as QCM coatings. This includes in particular the use of polymers known to form stable coatings in gas chromatography, of polymers with incorporated specific adsorption sites (such as enantiomeric selective centers; see Figure 3 above), of supramolecular monolayers, of cyclopeptides prepared by combinatorial chemistry, etc. For details, see section 2.1 and ref 10.

**2.4.3. Metal Oxide Module.** This module is equipped with eight different metal oxide sensors. However, any other sensor-active material or transducer type which monitors resistance changes may also be used in this module.

In the standard configuration eight metal oxide sensors were selected from several commercial suppliers to optimize chemical orthogonality in their responses. Alternatively, our own microstructured oxide sensors may be used, which already in the present test stage show better sensitivities and selectivities than commercial ones.<sup>35</sup> All commercially available or self-made conductivity sensors can be exchanged in this module.

**2.4.4. Calorimetric Module.** Calorimetric transducers measure the temperature change in the sensitive layer due to ad- and absorption, due to desorption, and due to catalytic conversion of analyte molecules. The change of the temperature is related to changes in the concentration of the analyte in the gas phase.

The calorimetric sensor module consists of an array of eight microstructured calorimetric sensors and a complex sampling arrangement. An onboard digital signal processor (DSP) evaluates the sensor responses during gas changes between analyte and inert gas.<sup>37,38</sup>

**2.4.5. Other Modules.** A variety of different modules, including electrochemical and optical transducer modules, are under development.

### 3. Typical Application Areas and Selected Examples for Electronic Nose Analysis

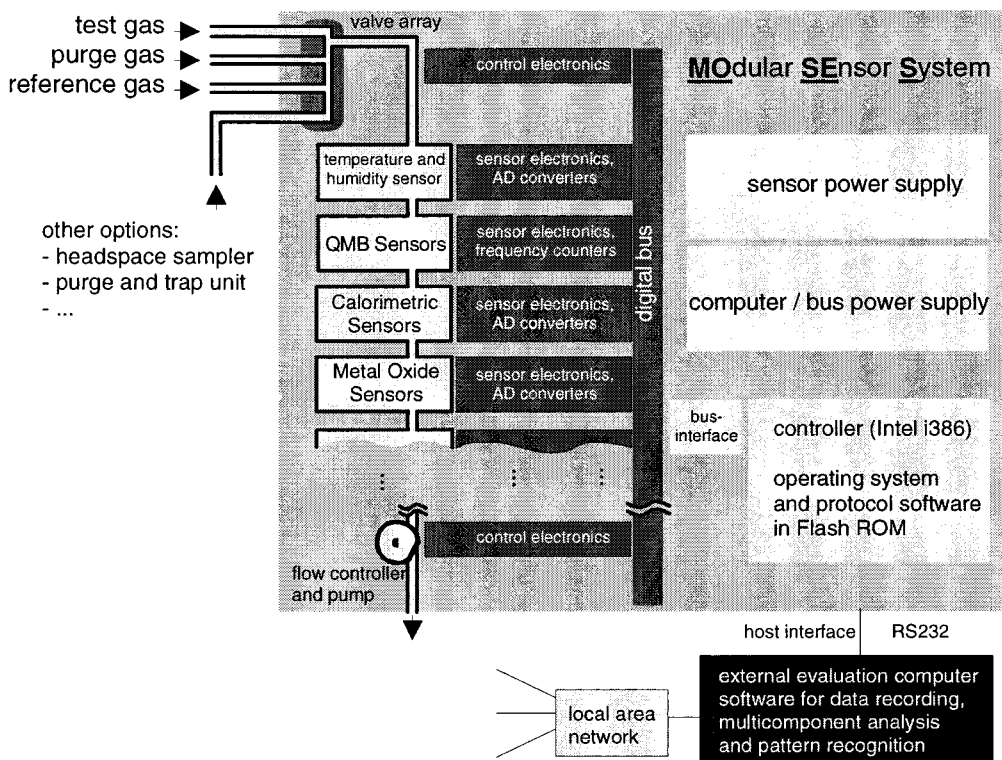
Modular electronic noses have been applied to a variety of qualitative and quantitative analyses of gas mixtures or to odor characterization. The performance of an analysis with modular sensor systems may at best be deduced from results presented in a principal component analysis plot. Measurements of the same kind should show a small spread as compared to the Euclidean distance between measurements from different compounds, different odors, or different kinds of samples (compare differentiation schemes in Figure 1). For details, the reader is referred to a variety of case studies (see refs 39–42 and those published as technical notes of MOSES, AlphaMOS, Nordic Sensors, etc.<sup>4</sup>). The following specific examples from the food and packaging industries may illustrate a few details and hence indicate the present state of the art.

**3.1. Quality Control of Packaging Materials in the Food Industry.** Figure 9 shows a principal component analysis of three different packaging materials used in the food industry. From each type of polyethylene foil 10 samples have been prepared by cutting the material into small pieces. The samples were then added to 20 mL vials. The numbers in the diagram represent the number of the vial. The measurements were performed using the head-space sampler HP 7694. Here eight quartz microbalance sensors and eight metal oxide sensors were applied.

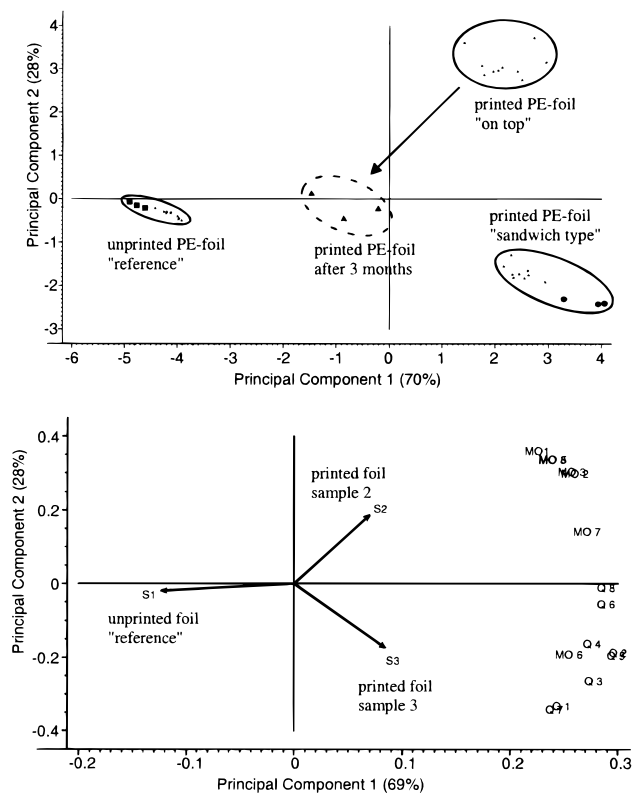
The sample marked "reference" contains an unprinted foil. As can be seen in Figure 9a the principal component 1 (PC1, *x*-axis) discriminates clearly between the unprinted and the printed materials. The two printed foil samples (samples 2 and 3) are discriminated by the second principal component. Another piece of information to be deduced from the graph is that the difference between printed and unprinted materials is larger than between different printed materials.

The different amounts of scattering within one sample (size of the clusters) basically result from the sample preparation. The unprinted material is the most homogeneous and exhibits the smallest scattering. The larger deviations in the measurements of the printed samples (especially sample 2) result from the inhomogeneity of the printing on the foil with areas of different colors. By cutting the sample into small pieces, a certain amount of error was shown to be introduced in the measurement, because changing amounts of the different colors are present in the individual samples.

After a period of three months three additional vials (marked with symbols in the scores plot) were prepared from the same samples. In the meantime the samples



**FIGURE 8.** General system layout: Independent modules communicate via a digital bus with the system controller. Several alternative input units may be chosen. The number of different transducer modules is constantly increasing.<sup>36</sup>



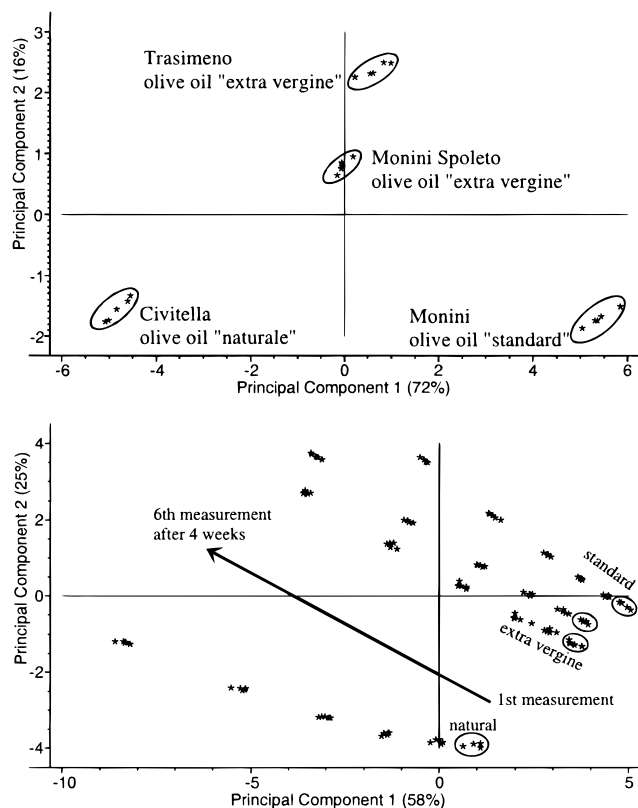
**FIGURE 9.** (a, top) Discrimination of different plastic foils used as packaging materials. (b, bottom) loadings plot of different plastic foils.

had been stored in the refrigerator at  $-20\text{ }^{\circ}\text{C}$  to avoid losing volatile compounds. For the unprinted reference there is almost no shift. The new results are very close to

the old ones: For the "sandwich type" printed material there is a small shift only. The sandwich structure (PE film/print ink/PE film) does not lose volatile compounds. Therefore, the headspace composition remains almost the same. However, for the "on top" printed material the headspace composition changes dramatically. Results from the new samples are now represented in a totally different area, which is closer to the unprinted reference sample. Evidently this type of sample lost a large amount of its volatile compounds even though it was stored in the refrigerator.

Comparing the loadings of the features reveals detailed information about the input from each individual sensor to the total measurement task. In Figure 9b the loadings of the feature are shown for the measurements of Figure 9. For simplification only the measurements from the first run are included in this evaluation. The corresponding positions of the samples (chosen as centers of the measurements of the three types of samples) are indicated here by S1 (unprinted foil), S2 (sample 2), and S3 (sample 3). For each sensor one feature has been extracted from the sensor response. This represents the maximum change in frequency or conductivity, respectively, upon exposition of the sensors to the headspace of the sample. The labels for the features indicate the sensor by MO (metal oxide sensors, MO1–MO8) and Q (quartz microbalance sensors, Q1–Q8).

Metal oxide and quartz sensors are represented in different regions of the loadings space. Evidently both of the two transducer principles provide different but essential information: As all features are far away from the



**FIGURE 10.** (a, top) Discrimination of different olive oils. (b, bottom) Change of headspace composition due to autoxidation of olive oils over a period of four weeks.

axis intercept, all sensors contribute to the discrimination between the samples, and the use of a hybrid system (metal oxide sensors plus QCM sensors) is a real advantage in this analysis.

**3.2. Discrimination of Olive Oils.** As a next example, the discrimination of different types of olive oil by headspace analysis is illustrated in Figure 10. These olive oils from different manufacturers are prepared in three different ways and labeled "extra virgin", "natural", and "standard". Here five samples of each type of oil have been measured with the same sensor setup as described above. The numbers in the diagram again represent the individual vial.

All types of oils are clearly separated. The two extra virgin oils are represented in the same region, indicating higher similarity of equally produced oils from different manufacturers. Clusters of repeated measurements are well separated from each other.

Olive oils spoil very fast due to an autoxidation of unsaturated compounds in the presence of oxygen and light. Therefore, it is necessary to control the quality of olive oils over time. In this context, five additional measurements were performed each with five vials for each sample over a period of four weeks. Between measurements, the different olive oils were stored in the refrigerator at 5 °C. For each sample a shift over time is observed with the same trend for all samples. In a recent study, the aging of rapeseed oil was studied and correlated with the content of peroxide as determined independently.<sup>42</sup> Other examples from food and related indus-

tries, including samples of coffee, tobacco, and alcoholic beverages, can be found in ref 39.

The next step is to correlate parameters from human panels with the location of these results in the principal component space. The goal is to determine similarities to human odor sensation by a training of an artificial neural net with sensor data.

## 4. Conclusion

General problems of electronic noses so far have concerned drift, calibration, little basic understanding of sensing elements, too high expectations of the users with too little success to solve their practical problems, high prices of commercially available instruments, and the requirement to have trained experts in-house.

To overcome these problems, research and development is directed nowadays toward the use and optimization of modular sensor systems. Modularity provides the necessary flexibility to adapt these systems to a broad range of applications and allows new technologies and new concepts for extending the "feature space" of chemical sensing to be installed.

Modular sensor systems may also be used as benchmark tools for basic research to understand the thermodynamics, kinetics, and molecular-scale aspects of molecular recognition for well-defined key-lock systems, of odor perception, or of toxicity. In these studies different calibration strategies must be chosen. The adaptation of the system for a specific application is achieved by varying just a few critical parameters which have to be optimized for constant parameters of the rest of the total sensor system. For many cases, the sample uptake and the pattern recognition procedure have to be kept constant. The atomistic understanding of sensing mechanisms is then obtained from subsequent interface analysis.<sup>15</sup> This leads to new design strategies for improved sensor materials.

Due to the increased complexity of a modular system if compared with a standard off-the-shelf instrument, application development will mainly be carried out by specialists in close collaboration with the end-user of a modular setup to be optimized jointly. Once an application has been solved, a specific, cheaper, easier-to-use instrument may be developed with higher volume markets. This will finally lead to a situation in which the electronic nose technology really fulfills the high expectations which many people had in the past.

*We gratefully acknowledge Lennartz Electronics (Tübingen, Germany) for the cooperation in developing the now commercially available MOSES II<sup>36</sup> and Hewlett-Packard (Little Falls, DE) for providing us with the HP 7694 headspace sampler and HP 7695 Purge and Trap. The Calorimetric Sensor Module was developed in collaboration with J. Lerchner, D. Caspary, and G. Wolf from TU Bergakademie Freiberg and M. Krügel and M. Nitzsch from Eurotronics, Leipzig, and we gratefully acknowledge the cooperation with these groups.*

## References

- (1) Göpel, W. *Sens. Actuators, B* **1994**, *18–19*, 1–21.



- (2) Gardner J. W.; Bartlett P. N. *Sens. Actuators, B* **1994**, 18–19, 211–220.
- (3) Gardner J. W., Bartlett P. N., Eds; *Sensors and Sensory Systems for an Electronic Nose*; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992.
- (4) For a review on concepts including commercially available instruments, see: Hierlemann, A.; Schweizer-Berberich, M.; Weimar, U.; Kraus, G.; Pfau, A. Pattern Recognition and Multicomponent Analysis. In *Sensors Update: Volume 2*; Baltes, H.; Göpel, W.; Hesse, J.; VCH: Weinheim, 1996, pp 121–155. An overview of existing instruments with links to research institutes and companies can also be found at: <http://sch-www.uia.ac.be/struct/review/research@sales.html>.
- (5) Göpel W.; Oehme M. Chemical Sensors and Instrumentation in Analytical Chemistry. In *Sensors: A Comprehensive Survey, Vol. 2: Chemical and Biochemical Sensors*; Göpel, W., Hesse, J., Zemel, J. N., Eds.; VCH: Weinheim, 1991; p 429.
- (6) See e.g. Göpel, W.; Schierbaum, K. D. *Sens. Actuators, B* **1995**, 26, 1.
- (7) Göpel, W. *Philos. Trans. R. Soc. London, A* **1995**, 353, 333.
- (8) Ballantine, D. S.; White, R. M.; Martin, S. J.; Ricco, A. J.; Zellers, E. T.; Frye, G. C.; Wohltjen, H. *Acoustic Wave Sensors*; Academic Press: San Diego, 1997.
- (9) Grate, J. W.; Frye, G. C. Acoustic Wave Sensors. In *Sensors Update: Volume 2*; Baltes, H., Göpel, W., Hesse, J., Eds.; VCH: Weinheim, 1996; pp 38–83.
- (10) Göpel, W. *Sens. Actuators, B* **1995**, 24–25, 1.
- (11) Hierlemann, A.; Weimar, U.; Kraus, G.; Göpel, W. Polymers for Detecting Organic Vapours in the Environment. *Sensors for Domestic Applications*, Proceedings of the European School on Sensors, Castro Marina (I) 9/1994; D'Amico, A., Sberveglieri, G., Eds.; World Scientific: Singapore, 1994; p 49.
- (12) Carey, W. P.; Beebe, K. R.; Kowalski, B. R. *Anal. Chem.* **1986**, 58, 149–153. Carey, W. P.; Kowalski, B. R. *Anal. Chem.* **1986**, 58, 3077–3084.
- (13) Ballantine, D. S.; Rose, S. L.; Grate, J. W.; Wohltjen, H. *Anal. Chem.* **1986**, 58, 149–153. Carey, W. P.; Kowalski, B. R. *Anal. Chem.* **1986**, 58, 3085–3066.
- (14) Holmberg, M.; Winquist, F.; Lundström, I.; Davide, F.; Di Natale, C.; D'Amico, A. *Sens. Actuators, B* **1996**, 35–36, 528–535.
- (15) Göpel, W.; Reinhard, G. Metal Oxide Sensors: New Devices Through Tailoring Interfaces on the Atomic Scale. In *Sensors Update: Volume 2*; Baltes, H., Göpel, W., Hesse, J., Eds.; VCH: Weinheim, 1996, p 49.
- (16) Grate, J. W.; Abraham, M. H. *Sens. Actuators, B* **1991**, 3, 85–111.
- (17) Grate, J. W.; Patrash, S. J.; Abraham, M. H. *Anal. Chem.* **1995**, 67, 2162–2169.
- (18) Hierlemann, A.; Weimar, U.; Kraus, G.; Schweizer-Berberich, M.; Göpel, W. *Sens. Actuators, B* **1995**, 26–27, 126.
- (19) Bodenhöfer, K.; Hierlemann, A.; Seemann, J.; Gauglitz, G.; Koppenhoefer, B.; Göpel, W. *Nature* **1997**, 387, 557–558.
- (20) Haug, M.; Schierbaum, K. D.; Nahm, W.; Gauglitz, G.; Göpel, W. *Sens. Actuators, B* **1993**, 11, 383.
- (21) Topart, P.; Josowicz, M. *J. Phys. Chem.* **1992**, 96, 8662.
- (22) Kunugi, Y.; Nigorikawa, K.; Harima, Y.; Yamashita, K. *J. Chem. Soc., Chem. Commun.* **1994**, 873.
- (23) Weimar, U.; Göpel, W. *Sens. Actuators, B* **1995**, 26–27, 13.
- (24) Amrani, M. E. H.; Persaud, K. C.; Payne, P. A. *Meas. Sci. Technol.* **1995**, 6, 1500.
- (25) Wlodek, S.; Colbow, K.; Consadori, F. *Sens. Actuators, B* **1991**, 3, 63.
- (26) Heilig, A.; Barsan, N.; Weimar, U.; Schweizer-Berberich, M.; Göpel, W. *Conf. Proc. EuroSensors X*, Leuven 1996.
- (27) Nakata, S.; Akakabe, S.; Nakasuji, M.; Yoshikawa, K. *Anal. Chem.* **1996**, 68, 2067.
- (28) Heilig, A.; Barsan, N.; Weimar, U.; Schweizer-Berberich, M.; Gardner, J. W.; Göpel, W. *Sens. Actuators, B*, in press.
- (29) Göpel, W. Chemical Imaging: I. Surfing in the Hyperspace of Chemical Features. *Sens. Actuators, B*, in press. Weimar, U.; Göpel, W. Chemical Imaging: II. Trends in Practical Multiparameter Sensor Systems. *Sens. Actuators, B*, in press. Plenary Talk. *Conf. Proc. EuroSensors XI*, Warsaw, 1997; Vol. 2, pp 527–542.
- (30) Aigner, R.; Dietl, M.; Katterloher, R.; Klee, V. *Conf. Proc. Transducers '95, EuroSensors IX*, Stockholm, 1995, p 839.
- (31) Otagawa, T.; Stetter, J. R.; *Sens. Actuators* **1987**, 11, 251.
- (32) Schweizer-Berberich, M.; Vaihinger, S.; Göpel, W. *Sens. Actuators, B* **1994**, 18–19, 282.
- (33) Dubbe, A.; Wiemhöfer, H. D.; Göpel, W. *J. Electroanal. Soc.* **1995**, 1428, 2757.
- (34) Göpel, W. Sensors and 'Smart' Molecular Nanostructures: Components for Future Information Technologies. In *Sensors: A Comprehensive Survey, Vol. 8: Trends in Sensor Technology/Sensor Markets*; Göpel, W.; Hesse, J.; Zemel, J. N., Eds.; VCH: Weinheim, 1995; p 295.
- (35) Kappler, J.; Barsan, N.; Weimar, U.; Dieguez, A.; Alay, J. L.; Romano-Rodriguez, A.; Morante, J. R.; Göpel, W. *Fresenius J. Anal. Chem.*, submitted for publication.
- (36) <http://www.ipc.uni-tuebingen.de/moses>.
- (37) Lerchner, J.; Seidel, J.; Wolf, G.; Weber, E. *Sens. Actuators, B* **1996**, 32, 71–75.
- (38) Lerchner, J.; Caspary, D.; Wolf, G. *Conf. Proc. Vol. 3, Sensor 97*, Nürnberg, 1997, pp 225–230.
- (39) Ulmer, H.; Mitrovics, J.; Noetzel, G.; Weimar, U.; Göpel, W. *Sens. Actuators, B* **1997**, 43, 24–33.
- (40) Ulmer, H.; Mitrovics, J.; Weimar, U.; Göpel, W. *Conf. Proc., Transducer 97*, Chicago, 1997; p 555.
- (41) Mitrovics, J.; Davide, F.; Lloyd, Spetz, A.; Ringvall, T.; Hamrefors, G.; Sauter, D.; Martensson, P.; DiNatale, C.; Weimar, U.; D'Amico, A.; Lundstroem, I.; Göpel, W. Dynamical Analysis of Process Gases in a PFBC-Plant with a Hybrid Sensor-Array. *Conf. Proc. IMCS*, Gaithersburg, 1996.
- (42) Ulmer, H.; Bodenhöfer, K.; Mitrovics, J.; Weimar, U.; Göpel, W. *Conf. Proc. 3. Dresdner Sensor-Symposium*, Dresden, 1997, Vortrag 18.

AR970064N