Chemosensor Systems and Odour Measurement

Current Developments in Electronic Olfactometry

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Chemosensor measuring systems termed "electronic noses" have been introduced which, very generally speaking, imitate the biological sense of smell. Even though these systems cannot primarily analyze odour characteristics, but rather compositions of gas mixtures, they are also used for "electronic olfactometry".
In this contribution, the background and the problems of their use and application for odour measurement are discussed. The methods which have been employed so far do not provide meaningful results.
In addition, perspectives and research goals for future development are described.

Keywords
Electronic nose, chemosensor array, electronic olfactometry

Introduction

The promise contained in the term "electronic nose" could not be kept. The analogy to the biological sense of smell is restricted to the first step of the development of the odour impression in the form of numerous sensors whose response characteristics are unspecific. Therefore, these systems could not imitate the functionality of the sense of smell, whose many functions have only been rudimentarily understood so far.
For this reason, the name "electronic nose" has generally been given up and replaced by the more neutral and more precise term "chemosensor array" [1]. Therefore, the typical range of application of the commercially available systems is actually not odour measurement, but rather the detection of chemical characteristics contained in the gaseous components of samples. The term "chemical imaging" [2] fits this kind of examination.
The application of chemosensor arrays for odour measurement, however, which is expected to provide greater objectivity and the possibility of continuous long-term observation, continues to meet with great interest [3].

Fundamentals of the Measuring Method

Chemosensor arrays are groups of gas-sensitive sensors which are coupled with different methods of data processing. From the viewpoint of selective and quantitative measurement, the individual sensors have very poor characteristics. For chemosensor arrays, sensors are preferred which do not respond to individual gases, but rather to groups of substances, certain chemical functionalities, or form parameters. Therefore, the sensor reactions in their entirety represent different aspects of the substances to be examined. The sensor array thus gains measurement-technological universality, which, in combination with intelligent data processing, enables it to provide information about mixtures of gaseous substances and, above all, to distinguish them from each other. **Figure 1** shows the diagram.

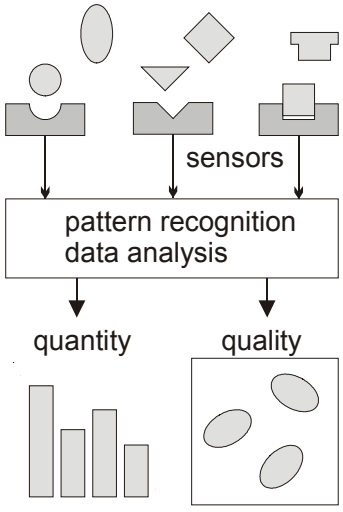

Figure 1: Diagram of the sensor array and the data evaluations

The sensors react to different aspects of the gaseous substances (here symbolized as geometric differences). The sensor data are evaluated by means of pattern recognition or data analysis under two possible aspects. Back calculation allows quantitative values to be determined. Qualitative evaluation, however, analyzes the composition of the mixture of substances.

Behaviour of an Ideal Sensor Array

Below, "ideal" sensor behaviour is assumed in order to discuss effects which occur during odour measurement, independent of the specific characteristics of the sensors. According to equation 1, the sensor reaction of this ideal sensor S_1 of n sensors is linear in relation to the concentrations c_i. Furthermore, the sensor thus defined does not exhibit any ageing- and drift effects.

$$S_1 = a_{1,0} + a_{1,1}c_1 + a_{1,2}c_2 + ... + a_{1,m}c_m \quad (1)$$

The real sensors exhibit non-linear characteristic lines and are subject to numerous influences which lead to changes in the characteristic lines and shifting of the operating points. Therefore, the interpretation of measurements is fraught with additional imponderables, which will not be discussed here.

Odorants

Odorants are a subset of all gaseous substances in the air. The signal character of odorants for living organisms has led to only those substances being filtered out for perception which carry information. Information related to the search for food (ripeness odours) or enemies and competitors, for example, requires sensitive perception. From a chemical viewpoint, this causes irritating differences in the odour thresholds of chemically similar substances due to this highly efficient selection and filtering.
Chemosensors evaluate chemical differences. Generally, chemically similar sub-

stances will lead to similar sensor reactions. Especially the sensors of chemosensor arrays, which are designed so that their selectivity is low, exhibit this behaviour.
Even if a similarly large bandwidth is found at the level of the biological odour receptors [4], the olfactory system in connection with the formation of odour perception in the brain shows high selectivity, which is opposed to the system behaviour of a chemosensor array.

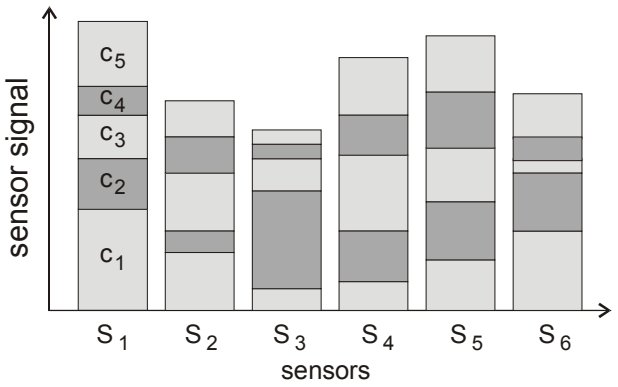

Figure 2: Sensor signals caused by different components of a mixture

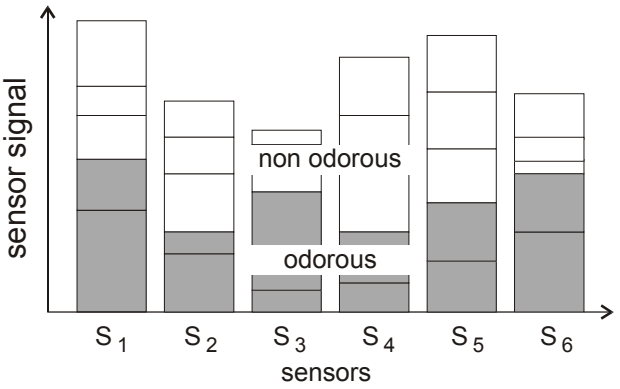

Figure 3: Percentage of the odour-active and odour-neutral components of the sensor signal

Reaction of the Array to Odour-Carrying Air Mixtures

In the assumed ideal case, the reaction of an array to mixtures of substances is a superposition of the individual reactions. **Figure 2** shows the reaction of 6 sensors to a mixture of 5 substances. Each sensor shows a differently strong signal, which is composed of the sensor reactions to the individual substances. The sensor does not make a distinction between odour-active and odour-neutral substances.
Equation 1 provides a general description of the individual sensor reaction. When considering the odour activity of the gas components, equation 1 can be broken up into two parts:

$$S_1 = a_{1,0} + a_{1,1}c_1 + a_{1,2}c_2 + ... + a_{1,n}c_n + \\ + a_{1,n+1}c_{n+1} + ... + a_{1,m}c_m \qquad (2)$$

The concentrations c_1 to c_n include the odour-active components, while c_{n+1} to c_m comprise the odour-neutral components. Under this aspect, the sensor signal (cf. **figure 3**) is formally caused by two components, i.e. the odour-active and the odour-neutral components.
The physiological-olfactory reaction to a substance mixture is only caused by the odour-active components. If this causation is summarized using the olfactory activity G as an auxiliary term, it is a function of the odour-active components c_1 to c_n with:

$$G = f\left(c_1, c_2, ..., c_n\right) \qquad (3)$$

A comparison of the equations 1 and 3 clearly shows the discrepancy between the formation of the sensor signals (by the components 1 through m) and the generation of the odour impression (by the subset of the components 1 to n).
For metal-oxide sensors, it was possible to show the relation of the odour-active to the odour-neutral components of the sensor signal in an experiment [18]. With the aid of special active coal, the high-molecular and sulphur-containing gaseous components were removed from the exhaust air of a stall for fattening pigs (which had been washed with sulphuric acid). After filtration, the exhaust air was free of odours. The sensor sum signal of a metal oxide sensor array changed from an average of 7.14 V for unfiltered exhaust air to 6.91 V for filtered exhaust air, i.e. by 3.2%. This very small percentage of 3.2% of the sensor sum signal represents the odour-active gas components. 97% of the signal, however, is caused by odour-neutral components, such as methane.
This result does not apply to other sensor types because metal oxide sensors specially respond to oxidizable gases, while conducting polymer sensors and mass-sensitive sensors react to polar and high-molecular compounds respectively. Unsolved problems concerning the two last-mentioned sensor types comprise the high water cross-sensitivity of polymer sensors, which plays a particular role in the case of biological sources, and the lower degree of sensitivity towards low-molecular odorants exhibited by mass-sensitive sensors. It remains to be examined which of the three measuring principles is best suitable for electronic olfactometry.

Evaluation of Chemosensor Measurements

Chemosensor measurements can be evaluated under the aspects of quantitative analysis and qualitative classification. **Figure 4** shows the two possibilities. For clarity´s sake, the n-dimensional sensor space is shown in only three dimensions. The three sensor reactions S_1, S_2, and S_3 form a vector of a certain length. If the composition of the mixture is identical, the length is a measure for the concentration of the mixture of substances to be examined (figure 4, left side). The spatial di-

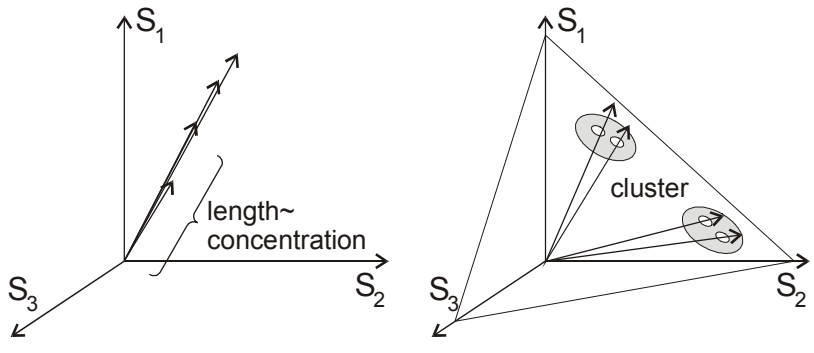

Figure 4: Possibilities of evaluating sensor array data

rection of the vector differentiates mixtures according to their composition. Mixtures with a similar composition feature the same direction in space. Using the method of principal component analysis (PCA), this image is reduced to two dimensions. The right side of Figure 4 shows the (discriminance) level with the clusters of the measurement values.

The Use of Chemosensor Arrays for Odour Measurements

The area of application of chemosensor measuring systems is the quality control of samples which are compared with standards. It is not the explicit goal of the measurement to determine the odour value, but to characterize the mixture of all gaseous components emitted by a sample. The determination of the odour similarity of the samples is a result of the similarity of the gas mixture, which also includes the measurement of the odour-neutral components.

The term "electronic noses" for chemosensor measuring systems suggests that they can also be used for "real" odour measurement. Several work groups have examined the technology of the chemosensor arrays for this application.

In the scientific literature, a number of applications of chemosensor arrays for odour measurement are documented. The authors used different sensor technologies and instruments. Electrically conducting polymer sensors [6, 13, 14, 15] and metal oxide semiconductor sensors [3, 5, 7, 8, 9, 10, 11, 12, 16, 17] were employed.

The qualitative classification of odours is examined in [3, 7, 10, 11, 12]. The use of arrays for the quantitative measurement of odour intensity is discussed in [3, 5, 8, 9, 11, 12, 15, 16].

A commercial instrument [8] is offered for the on-line monitoring of odour emissions.

Measurement of Odour Intensity

The continuous monitoring of odour sources requires the determination of odour intensity. The reference value of odour intensity is the odour unit per volume (OU/m^3), a value which is measured at the olfactometer through the stepwise dilution of samples. It represents the physiological effect of the odorant mixture. When calculating the spreading of odorants, the odour unit is treated like a concentration.

Two substances (or mixtures of substances) with the same odour intensity in OU/m^3 generally have different real concentrations due to their different odour thresholds.

The resulting odour impression of several substances is not the sum of the individual impressions. A large number of phenomena, such as mutual masking and reinforcement, does not allow any conclusion about odour impression to be drawn based on chemical composition.

Use of Sensor Sum Signals

The standard procedure in such problematic situations is empirical data collection and the search for correlations in order to determine the connection between odour impression and the composition of the mixture. Several examinations [3, 5, 8, 9, 11, 12, 13, 14, 15, 16] have followed this route and established correlations between the sensor signals and odour intensity by means of comparative olfactometric measurements and the concurrent use of chemical sensors.

Except for the sources [13, 14], a common feature of all approaches is the use of a sum signal, which is formed from the signals of the individual sensors. This sum signal is plotted against the measured odour intensities. Thus, the sought relation between the sensor signals and odour intensity is determined through linear regression. The sum signal of n sensors, which behave ideally in the sense defined above, is calculated using the following equations:

$$S_1 = a_{1,0} + a_{1,1}c_1 + a_{1,2}c_2 + \ldots + a_{1,m}c_m$$

$$S_2 = a_{2,0} + a_{2,1}c_1 + a_{2,2}c_2 + \ldots + a_{2,m}c_m$$

$$\ldots$$

$$S_n = a_{n,0} + a_{n,1}c_1 + a_{n,2}c_2 + \ldots + a_{n,m}c_m$$

$$\sum_1^n S_i = \sum_1^n a_{i,0} + \sum_1^n a_{i,1}c_1 + \ldots + \sum_1^n a_{i,m}c_m \qquad (4)$$

As the equations 4 show, *the sum signal behaves like the signal of an individual sensor* with "average" characteristics of all sensors added up. If the sensitivity of the sensors towards different substances varies, the sum signal exhibits wide response behaviour.

The information contained in the pattern of the individual sensor reactions is not exploited when the sum signal is used.

Determination of Correlations between the Odour and the Sensor Signals

The published literature [16] reports that the correlations found only apply to certain odour sources and therefore separate correlations must be used for each source. As an additional complication, the correlations do not prove stable over longer measuring periods [13, 14].

For this reason, it is interesting to consider the origin of such correlations and the data they are based on. Biological odour sources are substrates where odorants are formed and released through biochemical processes. The mixture of the components is dependent upon the biochemical condition. **Figure 5** shows an odour source which is situated in a ventilated building. Such configurations occur in indoor composting facilities, stall buildings, or storage containers. The odorants are emitted in the building and discharged by the air flow. The concentration of the odorants c_i is calculated from the relation of the emission mass flows $\dot{m}_i$ and the volumetric air flow $\dot{V}$

$$c_i = \frac{\dot{m}_i}{\dot{V}} \qquad (5)$$

According to equation 3, the odour intensity G which results at a measuring point is a function of the odorant concentrations c_i and, according to equation 5, it is also dependent upon the volumetric air flow $\dot{V}$ and the release $\dot{m}_i$ of the odorants.

For further argumentation, an assumption is important. In the case of the coupled generation of odorants in biochemical processes, the relative relation of the components and, hence, the composition of the mixture changes with the state of the process (cf. figure 6). In composting facilities, it thus depends on the rotting degree. In stalls, it is dependent upon the age of the animals or feed composition, for example. During slow or changing processes, the odorant mixture therefore also alters slowly.

The release $\dot{m}_i$ of a given odorant mixture may change due to external parameters, such as compost conversion or animal activity, or factors which influence mass

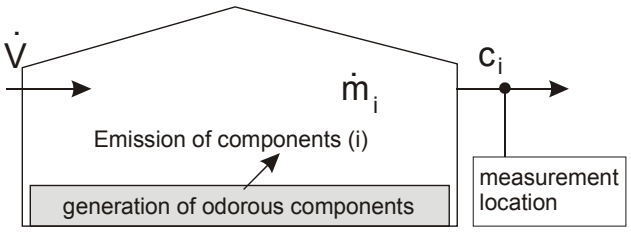

Figure 5: Release and dilution of odorants

transfer, such as temperature or air flow. Additionally, the diluting volumetric air flow is altered by the ventilation system (or the wind conditions in the case of sources which are exposed to free air flows).
Data regarding correlation between odour intensity are collected during a limited period. As a result, different odour intensities are obtained together with the sensor signals measured simultaneously. According to the assumptions made above, the odorant mixtures are similar. However (and this is the important aspect), dilution is different. Both changes in the volume flow and alterations in substance release lead to different dilution and resulting changes in the sensor signals.
For this reason, the indicated correlations are an expression of graduated dilution and, in particular, they do not represent any odour-related characteristics.
Especially the non-odour-active components contribute to the measuring signals, which results in the paradox situation that a correlation between odour intensity and a sensor signal is obtained even if the sensor is entirely insensitive towards the odour-active components.

Alteration of the Odour Patterns in Biological Processes

In the n-dimensional sensor space, alterations of the odorant mixtures appear as the covering of a certain distance, a mixture path. The right hand side of **figure 6** shows a three-dimensional sensor space. Three odorant mixtures GM_1, GM_2, and GM_3 are plotted on the mixture path. Left hand side of Figure 6 again refers to the two aspects of qualitative classification and quantitative evaluation. The criticized "odour measurement" approach requires a separate correlation for each mixture GM because only the quantitative information is processed, whereas the information contained in the qualitative classification of the mixtures is ignored.
It is therefore not surprising that a separate "correlation" between odour intensity and averaged sensor signals is obtained for each new mixture GM [18] because these signals only express the underlying dilution of the odorants.

Summary and Future Prospects

The problem of the determination of odour intensity based on chemosensor measurements can be considered unsolved.
The methods described above do not allow the set goal to be met for two reasons:

1 The often used sensor sum signal reduces the chemosensor array to the functionality of a single sensor. Therefore, the potential possibilities of the chemosensor measuring system are not exploited.
2 The connected correlation with odour intensity is the expression of a covered dilution series and does not apply to other odorant mixtures. This kind of correlations can also be obtained with suitable single sensors or the FID (flame ionization detector) technique [10].

The first goal in the development of chemosensor odour measurement should be the development of evaluation methods suited to the problem which are adapted to the characteristics of the interaction of chemosensors with the conditions of odour perception. The method should evaluate all information contained in the sensor signals and assess it using the means of statistical data analysis. Initial approaches in this direction have been attempted with the Canonical Correlation Analysis in references [13, 14].
The sensors used for odour measurement should be specially adjusted for this application. This requires that the odour-active components and their level of concentration should be known. These data allow the sensors to be adjusted, which enables the measuring system to give the odour-active components preference and to suppress existing disturbing components by means of compensation calculation.
An adapted measuring gas processing- and preconcentration technique allows important selected components to be reinforced and the percentage of the odourless components of the measuring signal to be reduced. Thermodesorption in connection with suitable absorber materials also enables the mixtures to be partially separated by choosing the temperature level.
The analytical characterization of the gas atmospheres can be carried out using the methods of analytical chemistry, such as gas chromatography, mass spectroscopy, infrared spectroscopy, and other gas-analytical techniques.

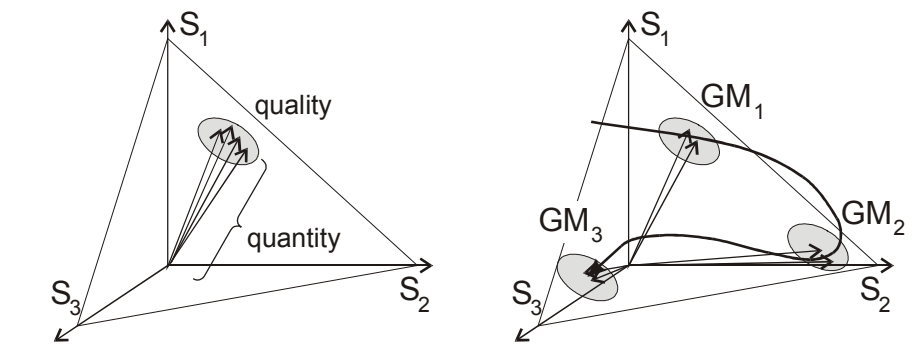

Figure 6: Alteration of odour patterns

Acknowledgements
Special thanks are due to Dr. Gerhard Horner from HKR Sensorsysteme for numerous suggestions and discussions about the methods of chemosensor analysis.

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