

Use of Chemical Sensor Arrays for the Recognition and Valuation of Odour Emissions from Agriculture

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For a wide variety of reasons, residents who live close to farms are claiming more and more that they are disturbed by odour emissions. Thus far, the human nose has been the only means of assessing the annoyance caused by these emissions. Since this olfactometric method has many disadvantages such as lack of reproducibility, subjectiveness, high personnel expenses, and its dependence upon the daily form of the test persons, a system is being developed which allows odour to be measured by an instrument.

This contribution presents the methods and documents initial quantitative results which prove the suitability of the systems used.

Introduction

Due to the increasing density of the population and the growing demands with regard to air quality, the registration of undesirable odours has become a problem that may no longer be neglected. Even if the concentrations of odour-causing substances are generally so low that they do not pose any danger to health, they often give rise to considerable annoyance. Since authorities must deal with an increasing number of complaints and immission problems in permission procedures, the development of a system for objective odour measurement is necessary.

Even though guidelines [1-3] govern the establishment of odour emissions, no objective measurement method is available at present. Olfactometry is the current state of the art. Human test persons are employed who must decide as of what dilution odour becomes perceptible. This leads to problems with regard to the standardization of this measurement method because the results of different olfactometric groups exhibit a wide range of variation. A ring comparison of different olfactometric groups showed that some measurement results differed by a factor of 10 [4]. The discontinuous measurement method also brings about the question of when and (if immissions are measured) where the samples are taken. The decision about the time and the place of sampling exerts great influence on the result. Moreover, employing a group of test persons results in great personnel requirements and very high costs. Therefore, the development of a system will be attempted that enables „objective odour measure-

ments“ to be taken using the kind of odour, intensity, and the hedonic effect as criteria. The combination of these odour parameters is supposed to lead to the development of an odour measurement figure which enables odour to be assessed objectively (**figure 1**).

The purely analytical examination of the individual components of complex odourant mixtures may be important, but it does not take the mutual influence of single components during odour perception into account. Additionally, not all substances that are present cause an odour stimulus (e.g. carbon dioxide). This allows the conclusion to be drawn that there is no clear correlation between subjective odour perception and an objective chromatogram.

So far different odour measurement methods have been applied (**table 2**). Olfactometry is used to register odorant concentrations. Moreover, humans assess odours under hedonic aspects because only the human nose can decide whether an odour is pleasant or unpleasant. The multi-sensor array provides the advantage of registering the overall odour impression because all substances reach the sen-

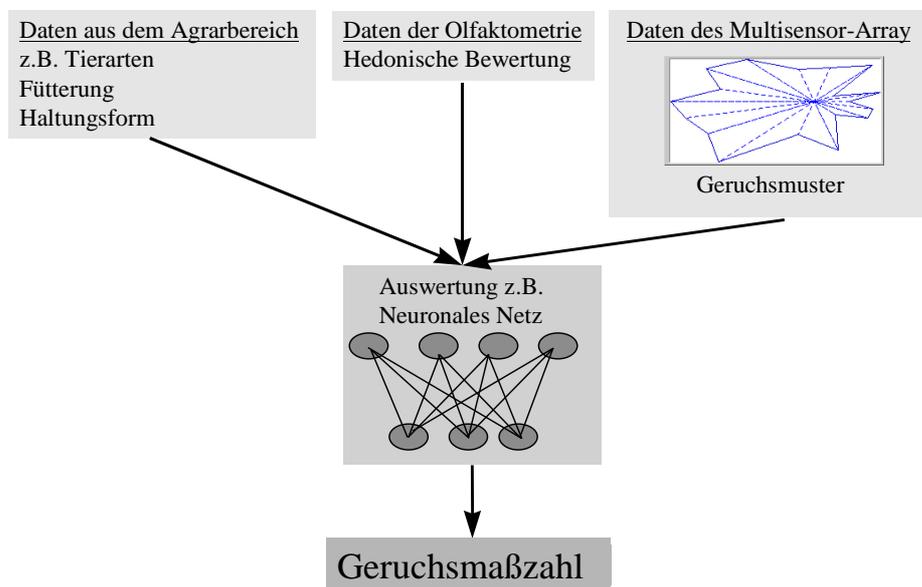


Figure 1: Method of establishing the odour measurement figure

Current Knowledge

Odour from agricultural animal husbandry consists of numerous components. A total of more than 250 different compounds can be registered, of which only approximately 170 have been identified and quantified thus far [5]. There is also a certain variability with regard to the chemical substance class (**table 1**).

sors at the same time. However, these sensors are subject to ageing, which must be taken into account.

Material and methods

Olfactometry

Olfactometry is current state-of-the-art technology for the measurement of air pollution in odour- and effect-related units.

Table 1: Examples of some identified odour components in pig slurry [5]:

| Name | Formula | Odour threshold (mg/m ³) |
|-----------------------------------|--------------------------------------------------------------------|--------------------------------------|
| Ethanoic acid | CH ₃ COOH | 0.025-10 |
| Propanoic acid | C ₂ H ₅ COOH | 0.003-0.89 |
| 2-methyl-propanoic acid | (CH ₃) ₂ CHCOOH | 0.005-0.33 |
| Butanoic acid | C ₃ H ₇ COOH | 0.0004-42 |
| 3-methyl butanoic acid | (CH ₃) ₂ C ₂ H ₃ COOH | 0.0002-0.0069 |
| Valeric acid | C ₄ H ₉ COOH | 0.0008-0.12 |
| Phenol | PhOH | 0.022-4 |
| 4-methyl-phenol (p-cresylic acid) | CH ₃ PhOH | 0.00005-0.0024 |
| Indole | C ₈ H ₆ N | 0.0006-0.0071 |
| 3-methyl-indole (scatole) | C ₉ H ₈ N | 0.00035-0.00078 |

Table 2: Common methods of odour measurement

| Methods | Use | Deficits |
|-----------------------------|------------------------------------------------------------|-------------------------------------------------|
| Human nose and olfactometry | Hedonic assessment | Odour perception |
| Subjective GC-MS | Odour identification and definition of standard substances | No registration of the overall odour impression |
| Multisensor arrays | Registration of the overall odour impression | Consequences of sensor ageing |

It covers the following range of applications [6-9]:

- Registration of odorant concentration in emissions and immissions
- Establishment of odour thresholds of individual and mixed substances

The method chosen for this purpose includes the dilution of odorant samples. These diluted samples are examined by a group of test persons. They determine as of what dilution odour in the air becomes perceptible. This threshold is defined as an odour unit (OU) for the individual odour:

odour threshold: 1 OU
recognition threshold: 3-5 OU

When setting the guidelines [6-9], it was agreed that the smelling ability of the entire group should be examined. For this purpose, the test persons are exposed to different concentrations of n-butanol and/or hydrogen sulphide.

According to the VDI 3881 guidelines [6-9], the value which causes a group of test persons to perceive odour in 50% of all cases should be within the following limits:

0.60 g/m³ (=0.43 ppb) < measurement value < 15 g/m³ (=11 ppb) for hydrogen sulphide
110 g/m³ (=35 ppb) < measurement value < 2,800 g/m³ (=896 ppb) for n-butanol

Already at this point, it becomes clear how enormously wide the range of values is. The odour immission guideline [1] provides a narrower range:

1.5 g/m³ (=1.1 ppb) < measurement value < 6 g/m³ (=4.3 ppb) for hydrogen sulphide
250 g/m³ (=80 ppb) < measurement value < 1,000 g/m³ (=320 ppb) for n-butanol

A CEN standard [10], which has so far only been available as a draft and is supposed to replace the existing national guidelines, again uses other values. According to this standard, only n-butanol will be used to examine the groups.

Multisensor Array

Structure

The most important part of the instrument used consists of three sensor chambers with six metal oxide sensors each, one temperature sensor each, and one humidity sensor each. In order to control the volume flow through these sensor chambers precisely, the chambers are topped by a mass-flow controller and a pump.

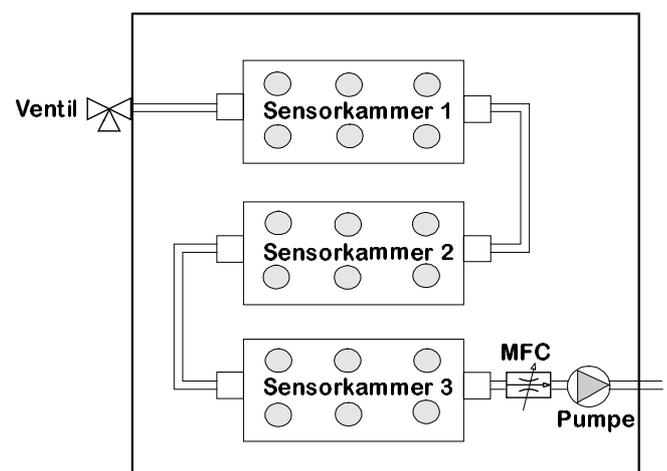


Figure 2: Structure of the multisensor array

This guarantees precise apportioning of the samples and the reproducibility of the measurements. A preceding valve controls whether a sample is fed into the chamber or whether the sensors are rinsed with clean air (figure 2).

The metal oxide sensors consist of two layers. The selective layer, which interacts with the sample gas, is at the surface. This layer is formed by doping the material with foreign atoms from the semiconductor. The lower part consists of pure semiconductor material (figure 3).

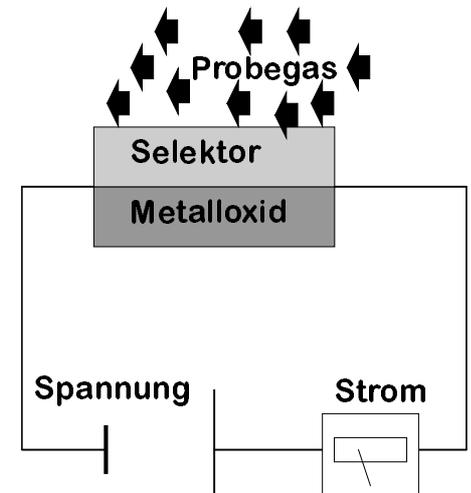


Figure 3: Working principle of the MOS sensor

The surface of the sensor loads itself with oxygen from the carrier gas. The formation of negatively charged oxygen molecules causes electrons to be drawn from the conduction band of the semiconductor. Therefore, its resistance changes (steady state value).

If a sample that contains reducing substances is conducted over the sensors, they react with the chemisorbed oxygen and give electrons back to the conduction band of the semiconductor. This causes its resistance to change. This alteration of resistance is registered as a measurement

signal. Mainly tin oxide doped with different substances is used as sensor material.

Valuation Algorithms

If oxidable substances are present, the sensors change their conductivity. For valuation, the pure resistance value is not used; instead, the values are scaled to initial resistance (represented value: $\Delta R/R_0$). This value best represents the alteration compared with zero air. As a result, 18 sensor responses to an odour sample or a graph with 18 lines are obtained. For better illustration, only the sensor deflections in one sensor chamber (sensor chamber 2) are shown in the next diagram (figure 4).

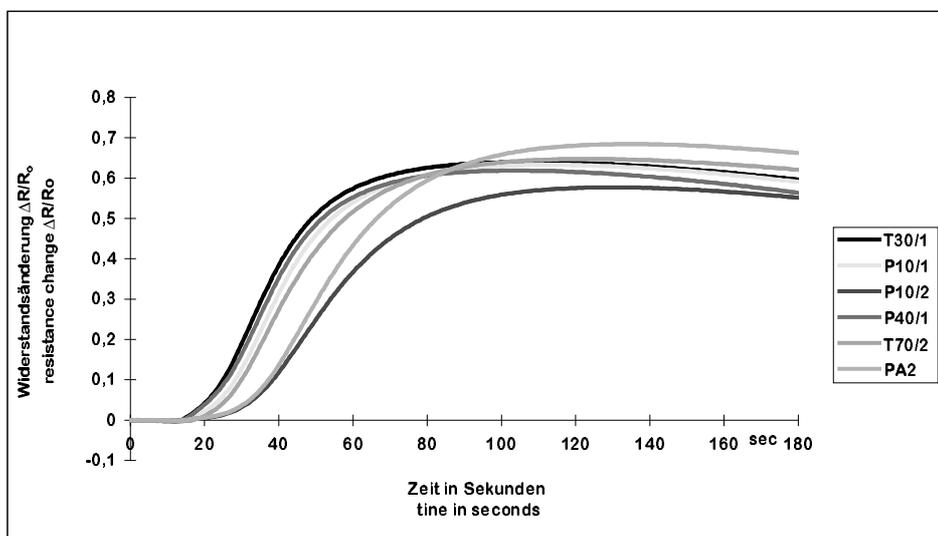


Figure 4: Deflection of the sensors after the injection of a sample

In the example shown in figure 4, a sample was injected for 10 seconds after an operating time of 10 seconds. It becomes clear that the sensors exhibit different behaviour with regard to their reaction and the decay of this reaction. The sensors do not reach maximum deflection at the same time. Only one value per sensor and measurement can be used for valuation. Usually, only the maxima of the sensor deflections are employed. Therefore, each of the 18 sensors provides one measurement value. These measurement values are shown optically in a radial plot (figure 5). The sensor deflections are plotted in 18 directions, starting from a zero point. Such a radial plot is also called an „odour pattern“.

Subsequently, the individual measurements are processed using different valuation algorithms in order to form groups of individual measurements. The valuation algorithms can be grouped according to different criteria. Distinctions are made between model-based and model-free

processes (neural networks) and between monitored and unmonitored processes. The unmonitored processes are used for qualitative examinations. Only the sensor signals are relevant for these models, which try to group the different measurements. The groups can be chosen freely. Among the model-based processes, the PCA model can serve as an example of such a model. The 18 sensor values open up a space with 18 dimensions. However, these sensor signals are not independent of each other since, due to the lack of selectiveness of the individual sensors, two sensors can react to the same substance. Therefore, mathematical transformation enables the signal of one sensor to be

describes the transformation of a substance vector into a main component and, hence, into one axis of the PCA plot:

$$PC_k = \sum_{i=1}^n a_{ik} X_{ij}$$

PC_k = kth main component
 a_{ik} = eigenvector
 X_{ij} = deflection of a sensor for one substance
 n = number of sensors

In neural networks, which constitute the group of model-free processes, the repeated comparison of signal pattern characteristics leads to generalization, as in neural processes in biology. This comparison and its constant checks, together with the fact that the corrections are stored, are called „learning“.

At the beginning of the learning process, the available set of data, which consists of all vectors of all substance classes that are to be differentiated, is divided into two groups of the same size. One group is defined as the learning pattern. These are those vectors where the network knows what class these patterns belong to. The other group is defined as so-called test patterns, i.e. the network only knows the sensor values. This division into groups is done at random in order to achieve optimal mixing of the vectors.

During each learning step (= iteration step), the weighting parameters are optimized. At first, the network is offered all learning patterns. After 10 iteration steps, for example, the capability of the network to correctly classify the test patterns is tested. This process is repeated until either all test patterns are classified correctly or the learning process is broken off because the error rate increases again (overtraining).

converted into the signal of another sensor. The PCA model attempts to do just that, for example by placing a two-dimensional plane into the 18-dimensional space (formation of the PCA plot figure 6) so that this chart retains as much of the original information as possible. The following mathematical equation de-

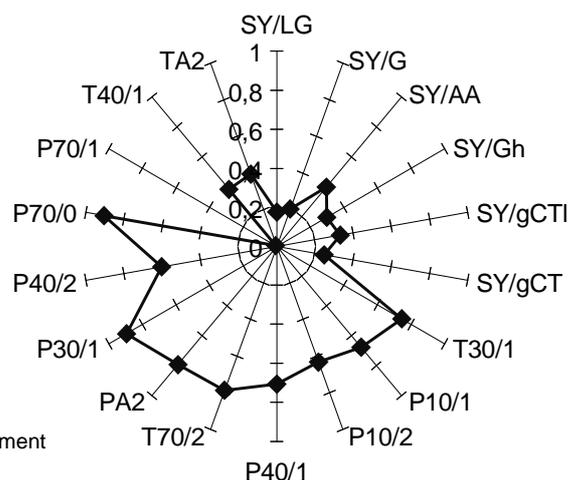


Figure 5: Radial plot of a measurement (example: sample from a piggery)

Results and Discussion

Comparison of the Sensitiveness of Olfactometry and the Multisensor Array for the Measurement of n-Butanol

In the paragraph about olfactometry (p. 20), certain limits were set for the ability of test persons to smell n-butanol, which apply to an olfactometric group. Using a gas-mixing station, similar concentrations were generated and filled into sample bags. The multisensor array was employed to analyze these samples. **Figure 7** shows the PCA plot that resulted from this analysis.

The figures correspond to the concentrations of n-butanol in ppb. PCA analysis is used to divide the different concentrations. However, this division does not follow the order of the concentration. As discussed in the previous chapter, this can be explained as a result of the fact that this chart is generated by transforming a higher-dimensional space into two dimensions. If another transformation is used, the chart alters. If this result is compared with the result of the olfactometric group, this means that, with regard to n-butanol, the multisensor array follows the guidelines for an olfactometric group. Sensitiveness (as shown by the gradations of concentration) is significantly higher than in the results that can be achieved with test persons.

Comparison of the Sensitiveness of Olfactometry and the Multisensor Array with Regard to Agricultural Odours

For the multisensor array to be used for the registration of odour emissions, its sensitiveness must be similar to that of the human nose when examining real samples. For this comparison, real odour samples from a piggery were used.

With the aid of a gas-mixing station, an original sample from fattening pig husbandry in an outdoor climate stall was diluted in a 1/10 relation. As shown in **Figure 8**, the olfactometric group was exposed to both the original and the diluted sample. This experiment was repeated three times. When the test persons A, B, C, and D were exposed to the undiluted sample, a relatively uniform odorant concentration of 167 OU/m³ was established. Test person E found a concentration of only 54 OU/m³. The entire group thus established an average value of 144 OU/m³ for the original samples. Subsequently, the test persons were exposed to the diluted sample. Test person A established an odorant concentration of 31 OU/m³. This result (31 OU/m³ : 170 OU/m³ = 0.18) was closest to the dilution of 0.1. Even though the concentrations

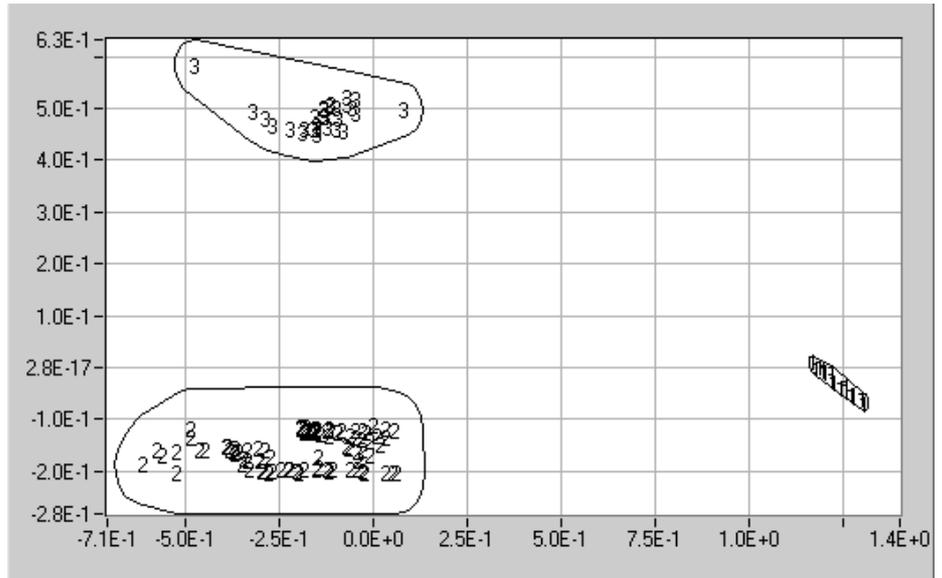


Figure 6: PCA plot for three samples (1, 2, and 3)

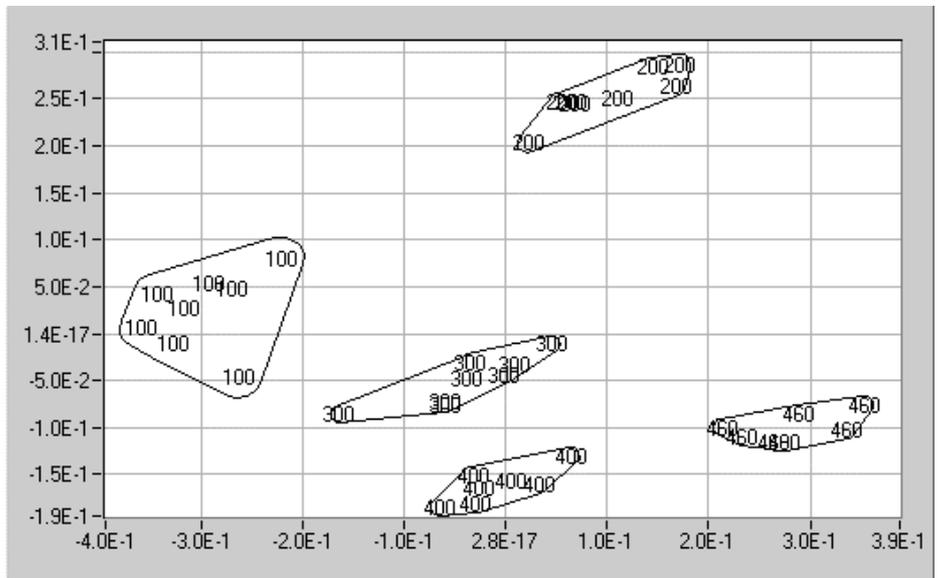


Figure 7: PCA plot for samples with different concentrations of n-butanol (100 ppb, 200 ppb, 300 ppb, 400 ppb, 460 ppb)

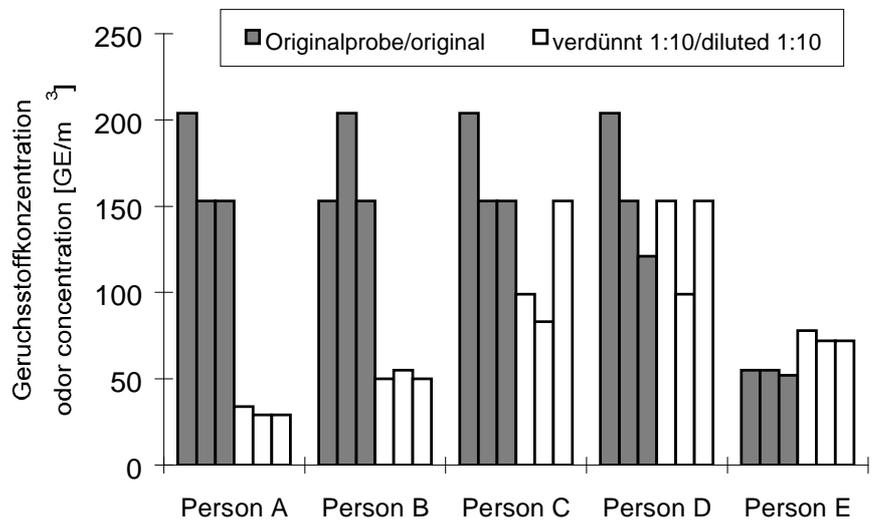


Figure 8: Results of the olfactometric measurements of different concentrations of piggery air

found by test persons B, C, and D still allow the trend towards a lower average concentration of the diluted samples to be recognized, the values of 0.3, 0.6, and 0.8 are ever farther away from the actual dilution. The odorant concentration established by test person E (74 OU/m^3) was even higher than the concentration found by this person when evaluating the original sample (54 OU/m^3).

According to the VDI guideline 3881 (page 1-4) [6-9], only the result of the entire olfactometric group is used for actual valuation. Consequently, the dilution relation established in this case was $80 \text{ OU/m}^3 : 144 \text{ OU/m}^3 = 0.55$. When considering the entire group, it was possible to recognize the trend towards a lower concentration in the diluted sample. However, precise establishment of the concentration difference was impossible.

The olfactometer used may provide a possible explanation. Its lowest indicated measurement value is 15 OU/m^3 if the method required by the VDI guideline is applied [6-9]. If one assumes that the concentration of the original sample was established correctly, the concentration of the diluted sample should have been measured to be 14 OU/m^3 . This is one OU/m^3 below the stated limit of the olfactometer's measurement range.

The multisensor array examined the same original and diluted samples that were used for the above-described olfactometer measurements. Each measurement was repeated seven times. The sensor sum signal was used to measure the relative concentration. For this purpose, the maximum deflections of the sensors were added. Additionally, the sum signal with clean air is shown (figure 9).

The measurement values established for the original sample ranged between $4.1 \Delta R/R_0$ and $3.5 \Delta R/R_0$, which leads to an average value of $3.8 \Delta R/R_0$ in the sensor sum signal. The sample diluted to 1/10 caused significantly smaller deflections. The measurement results obtained from the original and the diluted samples did not overlap, as did the olfactometric results. The average value was measured to be $2.1 \Delta R/R_0$. As compared with olfactometry, the main advantage of the measurements with the multisensor array resides in the high reproducibility and the resulting reliability of the individual measurements.

Calibration Function of the Multisensor Array for Emissions from Piggeries and Cattle Stalls

In order to reach the goal of developing an odour measurement figure, the data of olfactometry and sensor measurements

were joined. The sensor sum signal is used to establish a correlation between the odour units measured by olfactometric means and the sensor signals [12; 13]. The diagram shown in Figure 10 shows initial results of such a correlation for samples from a piggery and a cattle stall. Two provisional calibration functions can be set which differ with regard to their gradient. This difference can be explained as a result of the different composition of the individual samples.

Conclusions

The results reported in this article show that the multisensor array enables different concentrations of both individual substances and gas mixtures from agriculture to be distinguished. With regard to the differentiation of concentrations, a comparison between the performance of

this instrument and the olfactometric method demonstrates that, thanks to the better reproducibility of the measurement results, this instrument is superior to the conventional method.

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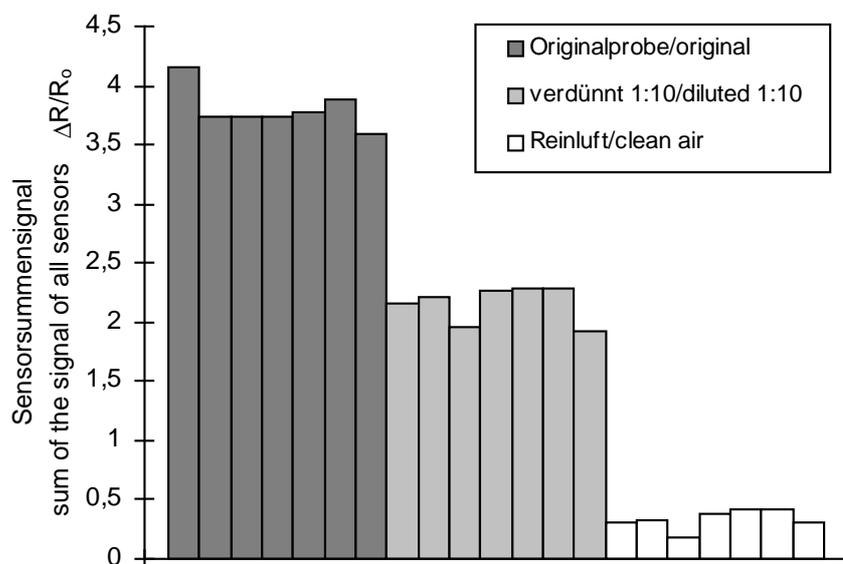


Figure 9: Results of the MSA measurements of different concentrations of piggery air

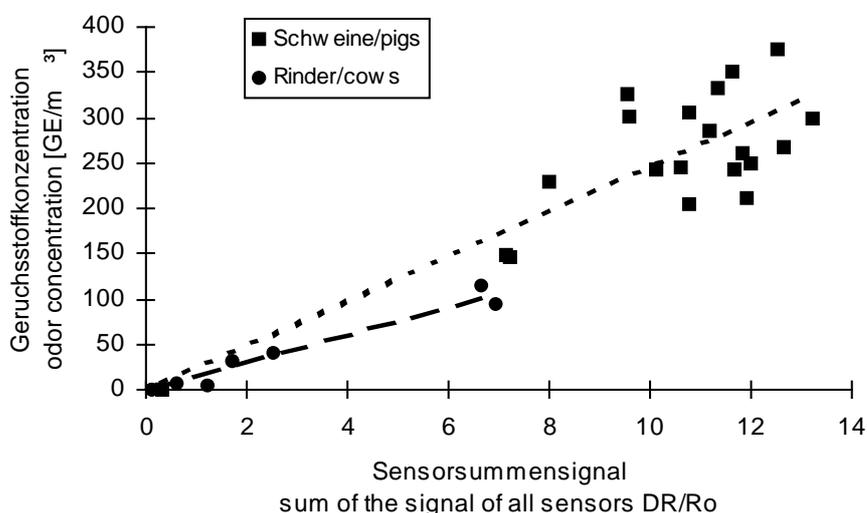


Figure 10: Correlation between the sum of all sensor signals and odour concentration

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