Gas Sensor Arrays for Monitoring Gases in the Environment of Municipal Sewage Plants

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Introduction

The combination of sampling technique, gas sensor array and a software for recognizing the pattern of the sensor signals is also know as an electronic nose. The basic idea is relatively simple: the array of gas sensors is used to measure a specific gas or a mixture of gases, the response of the sensors is compared to the sensors signals measured before and classified using pattern recognition techniques. With this technology a very fast identification of gases or complex mixtures of gases is possible without the need of time exhaustive laboratory work. The analysis and classification is done on the spot.

Analytical systems based on this technology are being used successfully in different applications. Using this technology it is necessary to keep in mind that an array of gas sensors is used and that a detection and identification of chemicals is possible, but it is not possible to "smell" compounds like a human nose. Similar to other analytical systems an appropriate sampling technique is very important and is often the key for a successful application.

Different sampling methods and their applications for monitoring the environment are shown in the next chapters. A special focus will be the environment of municipal sewage plants and the question if the system is also capable to detect the smell.

The electronic nose PEN2

The electronic nose from Airsense consists of an array of 10 metal oxide gas sensors positioned in a small chamber with a dead volume of only 1.8ml. Thick film gas sensors of different oxides and dopands are used. The temperature for each sensor can be adjusted individually.

By improvements in sensor technology and by optimization of sampling procedures it is possible to achieve working conditions for the sensors allowing also their use in harsh environments. The electronic nose PEN2 (see fig.1) is equipped with a patented sampling system. An automatic supervision of the sensor signals and a controlled addition of clean zero gas ("autoranging") provides different improvements:

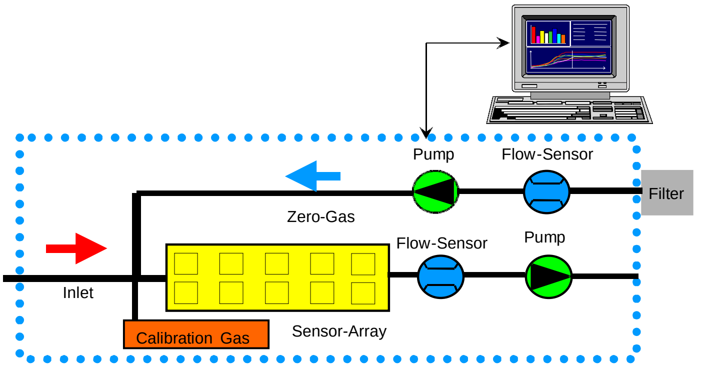

Fig. 1: Gas flow diagram of the gas sensor array system

- Changes in the concentrations of the analytes in the sample can be compensated with the "autoranging" option leading to constant concentrations of the analytes in the sensor chamber. Due to the non-linearity of the sensors a concentration dependency of the pattern is possible, especially when a wide range of concentrations is measured. This can be a reason for false classifications. With the automatic control of the concentration in the sensor chamber there is no or nearly no dependency of the pattern due to fluctuations of the concentration in the sample. With this technology, better qualitative results are obtained. The signals from the gas flow sensors can be used for achieving quantitative or semi quantitative results.
- The continuous supervision of the concentration of the gases in the sensor array chamber enables a safe operation of the sensors. With the fast reacting control

an overloading of the sensors in prevented which increases the lifetime of the sensors and also minimizes drift effects.

- The limitation of the concentration in the sensor array chamber is also useful for improving the cycle rates for the analysis. The recovery time of the sensors is reduced, when high concentrations at the sensors are avoided.

Trap and thermal desorption

Sampling preparation techniques, like an automatic enrichment with a following thermal desorption, are sometimes necessary for a better performance of the electronic noses. The combination of a trap with a sensor array system is displayed in fig. 2. The advantage of using a preconcentrator is not only the improvement of the detection limit by one or more orders of magnitude, it is also the possibility to increase the selectivity of the system.

Gaseous samples are pumped through the solid adsorbent material. Organic compounds will react with the surface of the adsorbent and will only be released by applying heat. The selectivity of the system can be manipulated by using the trap as a preseparation device. For example by using hydrophobic sampling materials, like Tenax®, the cross sensitivity to humidity or even solvents like ethanol can be excluded. If compounds with higher volatility are of interest, charcoal based sampling materials can be used. By changing the sampling material, the temperature during sampling and the sampling time, the selectivity of the measurement system can be changed considerably.

*Fig. 2: Combination of **e**nrichment and **d**esorption **u**nit EDU (upper instrument) with the **p**ortable **e**lectronic **n**ose PEN*

By sampling through Tenax® as adsorbent material at a sampling temperature of T= 35°C a discrimination between very volatile gases and semi-volatile gases is possible, because the very volatile gases are not trapped on Tenax®. This improvement in selectivity is important for example during the analysis of environmental samples, where permanent gases such as methane are present in higher concentrations. Other compounds in much lower concentrations might be responsible for the odor. Methane is not trapped on Tenax and can be excluded from the analysis. The cross sensitivity to humidity and non interesting compounds like methane or other non smelling gases like CO or H2 can be avoided with this sampling method.

Enrichment factors of the trapping systems are well known and depend on the breakthrough volumes of the analytes. The detection limit can be increased typically by a factor of 10 to 1000. Sampling parameters like sampling temperature, time and flow-rate have to be taken also into consideration.

Cycle times for the analysis depend very much from the application and range from some seconds to minutes. When working with the trap the cycle time expands to typically 7 to 10 minutes.

Air monitoring at sewage plants

Many different applications for monitoring the air quality can be found in literature using gas sensor arrays. Some examples regarding sewage will be presented in this paper.

Detection of odorous events

If odor sources are responsible for complains, it is important to have a device to register the odorous compounds. For registration of sporadic odorous events, the sensor system monitored a small biofilter used to clean gases from a sewage duct. The sewage duct with the biofilter is located under a parking lot of a shopping mall and it was supposed to be the source of annoying fecal odors.

With the electronic nose, it was possible to monitor the sporadic release of the odor. Fig.3 displays the sensor signals obtained during a period of 30 minutes. Gaseous compounds released from the cars can be distinguished from the "smelling" events, becuase different compounds are released from the biofilter. The system was installed over a longer period of time. The electronic nose is capable to detect the smell from the duct breaking through the biofilter.

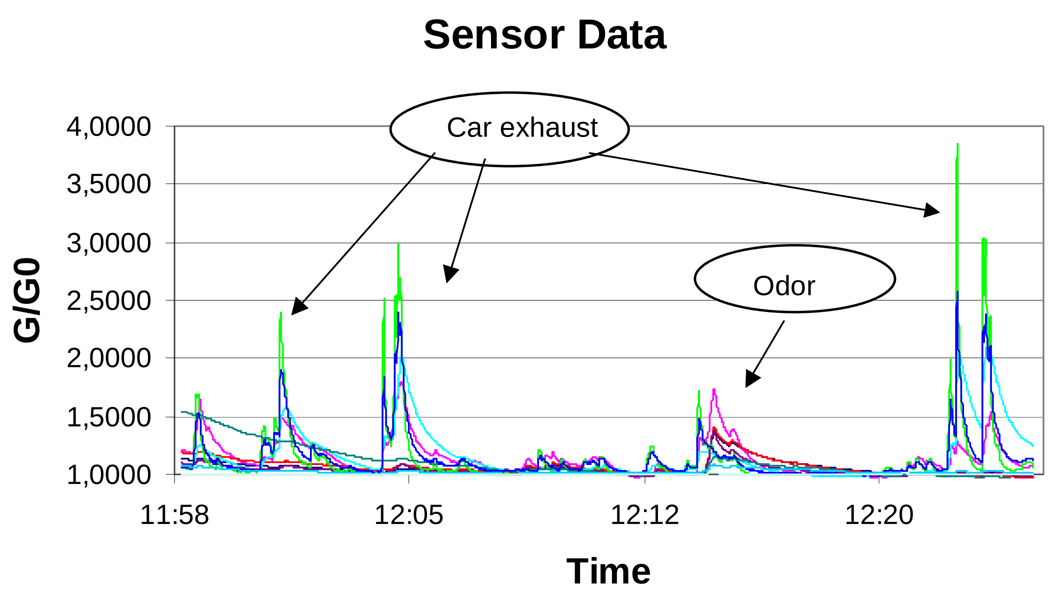

Fig. 3: Sensor signals during a 30min measurement

<u>Detection of the odor source</u>

Monitoring immission is possible with the sensor array. Often a trap is needed, because of the low concentrations of the chemicals. If there are not too many different sources of diffusive emissions, the localization of the source is possible.

In fig. 4 the results from an analysis of the environment of a sewage plant are shown.

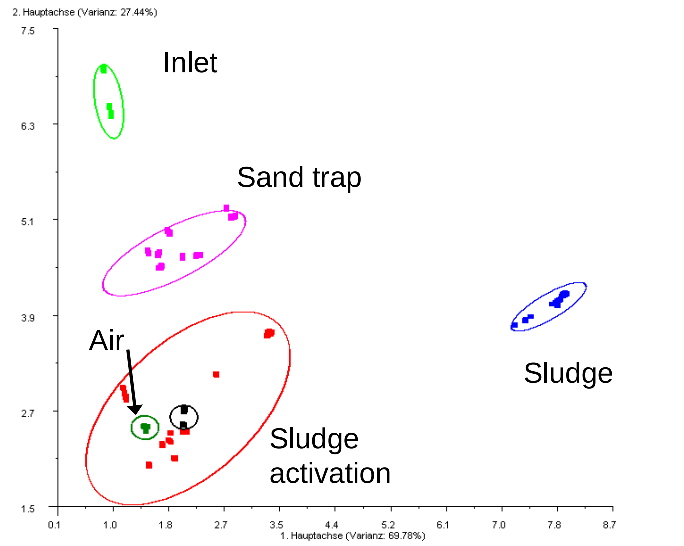

Fig.4: Identification of odor sources at different locations of a municipal sewage plant

Different regions of the complex filtration system were sampled with Tenax® adsorption tubes and afterwards thermally desorbed. It was possible to differentiate between odor sources and also an identification of the source is possible.

Detection of smell

The correlation with the human nose is not always possible, because of the completely different gas detection mechanisms. Some compounds can be detected with the human nose at ppt-levels, which is some orders of magnitude better than even the combination of trap and sensor array system. An electronic nose system with such a low detection limit will also react to other compounds, which the human nose will not smell (chemical noise).

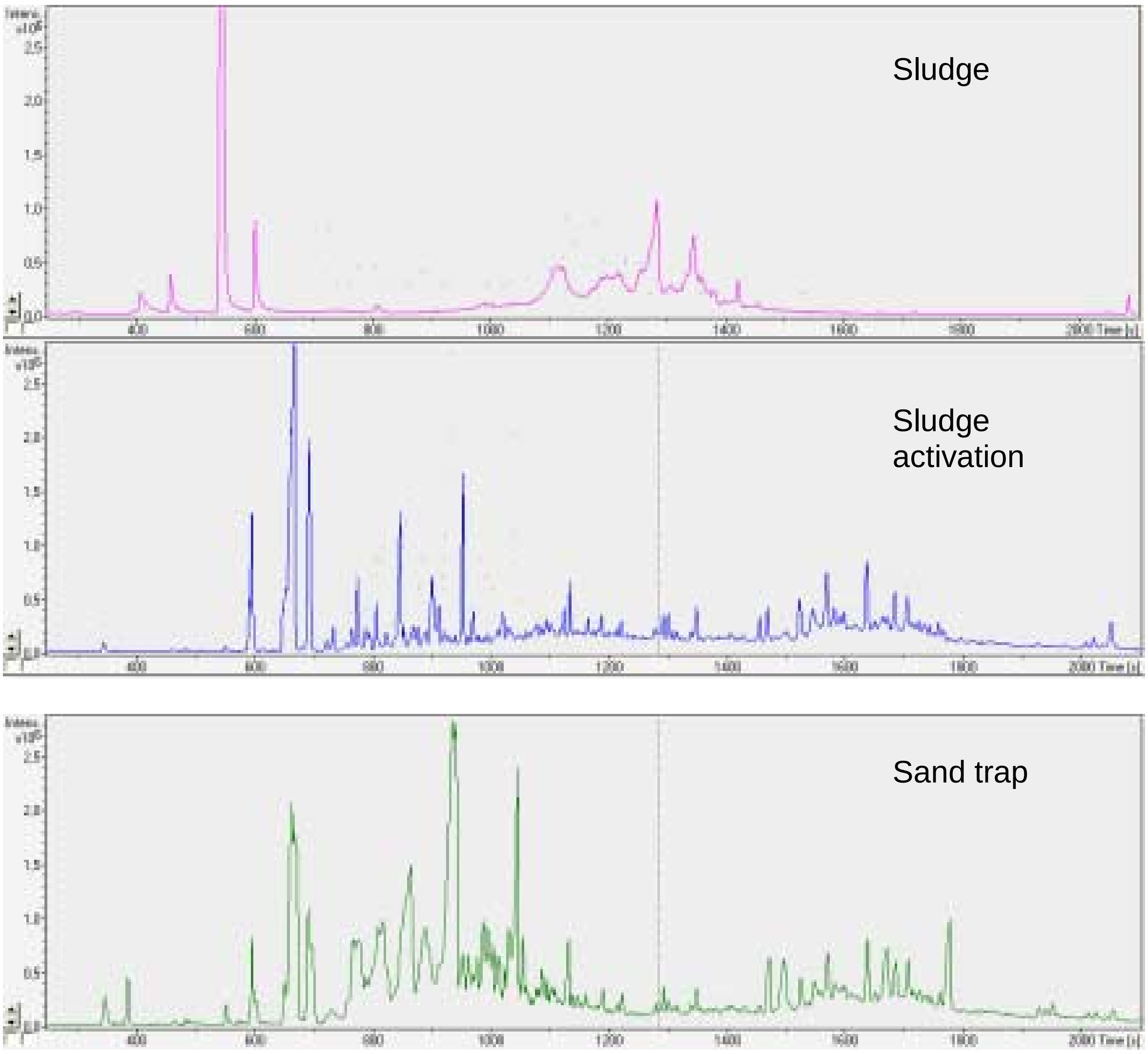

Fig.5: Gaschromatographic runs of three samples from different regions of a municipal sewage plant

Nevertheless a supervision of odors is often possible, especially when the smelling compounds are technical vapors or when complex mixtures, with relative constant compositions, are responsible for the odor.

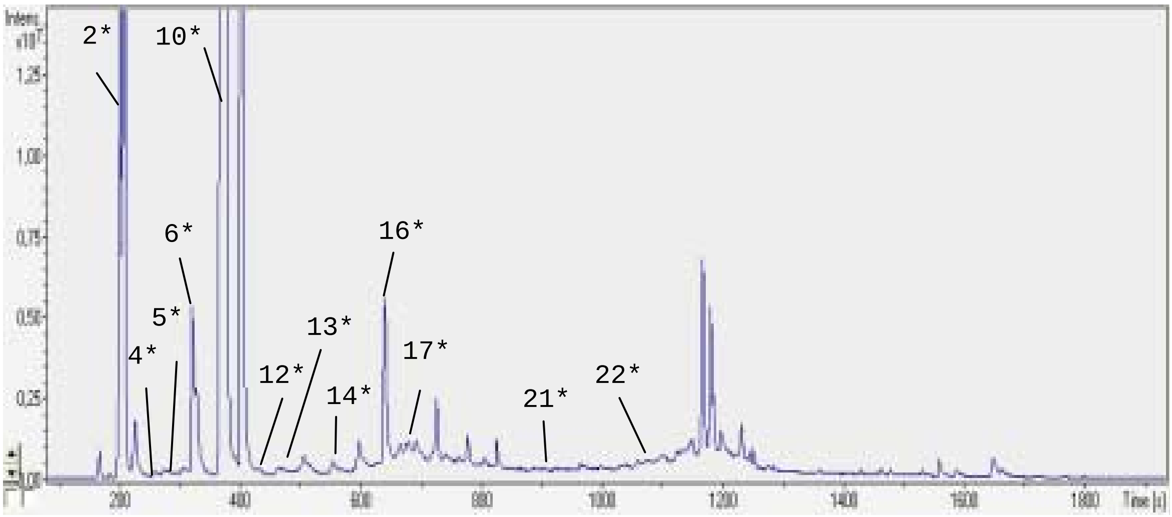

Fig.6: GC analysis of the air measured in the air from the region where the sludge is processed. The numbers indicate regions where the human nose detected odors at the sniffing port. Odor descriptions are displayed in table1.

The figure 5 shows gas chromatograms (GC) obtained with a GC-MS system (GCQ-Finnigan). Sampling was performed with pumping the ambient air on adsorbent tubes (Tenax TA 60/80 mesh, 22 Liter sampled in 2 hours). The tubes were transported to the lab immediately, thermally desorbed (Gerstel-Desorber) and analyzed. The gases eluting from the GC were splitted into the mass spectrometric detector and into a sniffing port (Gerstel). A human nose smells the compounds eluting from the GC column. An odorous event and if possible a description of the odor is then registered. The advantage of this solution is that the odorous compounds in the mixture can be detected and identified.

It can be seen from the chromatograms that the composition of the gaseous compound is different in each location (as previously also measured with the electronic nose, see fig. 4).

Fig. 6 shows a chromatogram were the compounds detected by the human nose are marked. Table 1 shows the corresponding odor description. Most compounds could not be identified by comparison with mass spectral data bases (NIST 98).

Table 1: Odor description the GC displayed in fig. 6

Peak Nr.	*Retention Time [s]*	*Odor*
2*	207	Sulfur like
4*	246	Smoke
5*	288	Solvent
6*	321	Burnt
8*	342	Solvent
10*	375	Pungent
12*	420	Rancid, butyric acid
13*	468	Aromatic
14*	553	Itching, acid
16*	641	Fruity
17*	678	Sweet
21*	925	Faecal
22*	1086	Faecal

Many of the odorous compounds are not the main compounds in the mixture. On the other side, the analytical approach does not reflect the real situation because not all compounds can be analyzed with this method. Ammonia and hydrogen sulfide are for example important compounds, which can not be detected with the method, but are responsible for many annoyances in biological processes.

From the GC-MS results, it seems that an electronic nose based on simple gas sensors should not be capable to detect the odors. The gas sensors detect the main compounds in a gas mixture and can also detect deviations from the mixture. If there is a correlation between the main compounds and the odorous compounds an electronic nose can be used for monitoring the odors.

In order to investigate if there is such a correlation the same samples were measured by olfactometry (TO7 from ECOMA). The same gases transported in the bags used for olfactometry were measured with the electronic nose PEN2. The response of the sensors was correlated with the odor units obtained from olfactometry. The correlation was performed with a partial least square (PLS) method. The next figure 7 shows the results from the last 18 months. They were obtained by using all results from different municipal sewage plants and different locations in the plants. It shows that there is a significant correlation, encouraging us for further investigations. It is planned to use different PLS calculations depending on the identified pattern.

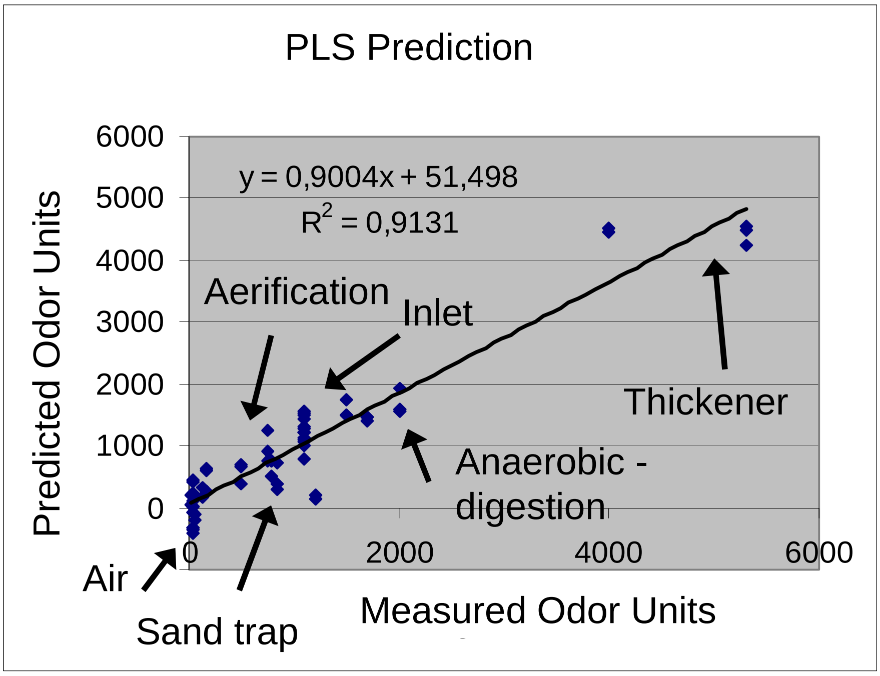

Fig.7: Correlation between the results obtained from olfactometry and the electronic nose. The predicted results obtained by the e-nose are displayed against the results obtained from olfactometry. Partial least square (PLS) algorithms were used.

Conclusion:

Gas sensor array systems can be used for different air monitoring purposes. This cost-effective technology is suited for online monitoring applications such as supervision of filtration systems or industrial effluents.

Due to special sampling methods also some new applications are possible. The combination with the trap and thermal desoption technique enhances the analysis in several ways. The detection limits are lowered and also the discrimination of disturbing compounds is possible, which is very important for some applications. By choosing an optimal adsorbent material and an adequate sampling temperature, the trapping efficiency can be adjusted to the current needs of the actual application.

An electronic nose can be used for monitoring odors, especially if the main compounds are also the odorous compounds. Detection of odors is also possible if the main non-odorous compounds correlate with the odorous compounds. This seems to be the case for municipal sewage plants.

Acknowledgement

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