H₂S, VOC, TOC, electronic noses and odour concentration: use and comparison of different parameters for emission measurement on air treatment systems

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ABSTRACT

Odour measurement via olfactometry is expensive and has a low accuracy compared with chemical or physical methods. In addition, olfactometry is not suited for online monitoring. Hence, an accurate online method for emission measurement would be an enormous improvement. There are several options to more or less replace the offline olfactometry by online measurement available today. Most common are H₂S-concentration as a single gas parameter and VOC and TOC as composite parameters. A fairly new development are multi sensor arrays, usually referred to as "electronic noses" which carry out non-specific gas measurement and deliver measurement data that can visualized as a fingerprint diagram. This paper outlines the use of these different parameters and compares the results to those gained via olfactometry of several case studies.

Key words | air treatment, electronic nose, H₂S, odour, olfactometry, TOC, VOC

INTRODUCTION

Odour concentration c_od is measured according to DIN EN 13725 in Germany. The measurement result is independent of humans’ knowledge about the substances since the human nose as a sensor reacts to every odorous gas above detection limit. However, this kind of detection is expensive and only applicable off line. Looking for an on-line solution that is easy to operate, single gas sensors, carbon-measurement and multi sensor measurement—the so called “electronic noses” –are possible.

The use of surrogate parameters has some disadvantages, as mentioned in the general principles of monitoring given by IPPC (2003). Especially it is necessary to calibrate the measurement device, and it is necessary to demonstrate that the new parameter covers the characteristic features of the original parameter on a high level. In this paper the results of measurement of surrogate parameters are compared with the results of olfactometric measurement.

METHODS

Odour concentration measurement

Odour concentration c_od is a parameter based on human capabilities with the disadvantage that long-term on-line measurement is not possible and that precision is relatively low. The basis of this measurement method is that odour can be detected by a person if the individual odour threshold is exceeded. For example, if the mixture of an odorous air, diluted 2^n times with odourless air, is not detected, whereas the mixture diluted only n times is detected, the odour concentration is the geometrical mean of n and 2^n, which is 1.41 n. In order
to assure a required level of accuracy, at least eight single measurement results are needed to calculate the dilution number. A larger number improves accuracy and because of panel members selection more than eight individual results were measured. Although the dilution number has no unit by physical definition, the odour concentration \( c_{\text{od}} \) is expressed with the unit of European odour units per cubic metre (ouE/m\(^3\)).

It must be kept in mind that the odour concentration is the only measurement that provides information on odour, whereas all other surrogate measurement methods discussed hereafter measure odorants, thus substances that cause an odour impression but do not deal with the phenomenon directly.

**H\(_2\)S measurement**

One of the most important and best described odorant regarding wastewater is hydrogen sulphide H\(_2\)S, as described for example in ATV-DVWK-M 154 (2003). H\(_2\)S is produced under anaerobic conditions and can be found in many sewer systems. H\(_2\)S is member of the group of inorganic gases.

Gas monitors, like the OdaLog by AppTek, are used worldwide in sewer systems. Since a couple of years OdaLogs were used by DESEE. Theses devices offer measurement ranges of 0 ppm H\(_2\)S to 200 ppm H\(_2\)S or up to 1.000 ppm H\(_2\)S, with an accuracy of 1 ppm. Similar devices are available for example by VTA Engineering und Umwelttechnik/Austria.

**TOC and VOC measurement**

Total organic carbon (TOC) and volatile organic compounds (VOC) are sum parameters. Inorganic gases are not detected, hence H\(_2\)S is not monitored with TOC or VOC. Both parameters have a different background and thus describe different characteristics of a gas.

TOC can be measured by a flame ionization detector (FID). VDI guideline 3481 part 6 (1994) recommends the FID measurement without a preceding adsorption/desorption step. FID measurement works continuously and is carried out for example according to DIN EN 12619:1999 and DIN EN 15526:2001. TOC indicates the amount of carbon ions. As there is no information on odour, odour might only be quantifiable with an FID if the respective odour is exclusively due to organic compounds. An identification of individual substances is not possible.

In addition, a photo ionization detector (PID) can be used where ionization energy is delivered via UV light which improves sensitivity on aromatic compounds.

VOC measurement can be done with a GC-MS-device. With a standard library, some 60 different VOCs are detected and quantified. These, according to 2004/42/EG (2004), share the property of having a boiling point of 250°C or lower. The VOC value is the sum of the concentrations of quantified compounds. If a substance is not listed in the library, its contribution to the total amount of VOC is disregarded.

In this paper, VOC measurement results were obtained with a GC-MS (3rd party laboratory, device GC Agilent 6,890, MS Agilent 5,973, column J&W DB 624). TOC is measured by using a FID (Thermo Scientific TVA 1,000 B). This device also includes a PID unit.

**Electronic Noses**

Multi sensor array devices—also called “electronic noses”—carry out a non-specific measurement on gas samples. There are different techniques of measurement (i.e. quartz micro balance sensors QMB, metal oxide sensors MOS etc); therefore, the results may differ in span and accuracy. In this paper, measurement results using an AirSense PEN2 (MOS) are shown. The device delivers raw data (resistance values of the semiconductor sensors), but there is no knowledge on how to convert this data set into one odour concentration value.

In order to develop a mathematical model that might be able to convert the raw sensor data into a proxy for odour concentration, it is necessary to perform a reasonable number of parallel measurements with the electronic nose and via olfactometry. Then mathematical models are necessary, and even those which are capable of a good explanation within the calibration—for example neural networks—might have problems with prediction of the values of the proxy for odour concentration from new or unknown raw data.
In this paper, results are presented by means of a graphical display of the metric sensor profiles and as numeric results of the method of frequency analysis. The latter differentiates measurement results into classes by using only some of all available sensors, selected in a learning process.

RESULTS AND DISCUSSION

Odour concentration and H$_2$S

The correlation between H$_2$S and odour concentration measurements on a biofilter is presented in Figure 1. The results shown were obtained in a research project carried out by DESEE and financed by the city of Frankfurt a.M. from 2006 to 2008. Detailed results are given in Frechen et al. (2007) and Franke et al. (2007).

In this case, a biofilter was used to treat the air from sludge tanks. This air contained H$_2$S, dimethyl sulphide and mercaptan; therefore, H$_2$S was not the only sulphur compound present, but the only one for which an analytical measurement device was available. The results in Figure 1 show clearly that there is no correlation between H$_2$S and odour concentration up to 10,000 ou$/$m$^3$, and no significant correlation between H$_2$S and odour concentration in the range above. Therefore measuring H$_2$S in this case is not a satisfactory surrogate parameter for odour monitoring, although sulphur is a major compound in the monitored polluted air.

Odour concentration and carbon related parameters

Two measurement methods are available, as explained above, namely VOC and TOC. In addition to TOC measured with an FID, a similar technique is carried out with a PID. In Figure 2, results from a three day deodorization device performance measurement are shown. Samples No. 1, 3 and 5 are raw gas and No. 2, 4 and 6 are from the clean gas.

Basically, two conclusions can be derived from this data:

- odour concentration in the sample air polluted with aromatic and aliphatic compounds is not correlated to VOC or TOC (neither FID nor PID results),
- VOC increases during treatment. This is attributed to the fact that this kind of air treatment—using photoionization and activated carbon—changes the compound matrix. It is assumed that VOC producing as well as VOC reducing processes occur.

Electronic noses

The data from the PEN2 were evaluated in two ways. One is to visualize the metric profile of the different sensor signals. The second result is derived from maximum values of sensor signals, telling us about odour intensity.

Visualization of the raw data in the form of metric profiles allows to distinguish between different odour sources. As an example, Figure 3 shows metric profiles of 7 samples from one sewer as well as the resulting typical medium profile.

In Figure 4, metric profiles of different odorous explosives are shown. As can be seen, different types of explosives produce different, very specific profiles.
In fact, this way of visualizing the results gives no information on the odour concentration of the respective samples. However, we can conclude from the results that identification of an odour quality via electronic nose seems to be possible.

In order to extract more information from the raw data, a mathematical procedure called Profile Frequency Analysis (PFA) was developed. This procedure transforms the metric profile into an ordinal profile. PFA consists of five steps:

1. Definition of limits of categories concerning odour concentration, for example 1.000 ouE/m³, 5.000 ouE/m³ etc.
2. Data-splitting, selecting about 50% of the data set as training cases.
3. Combination of categories to profiles.
4. Applying the relevant profile on training cases and test cases.
5. By using the Configuration Frequency Analysis it is possible to test the profile on statistical relevance.

In Figure 5, an example is given for a data set of 108 samples that were measured via olfactometry as well as via the PEN2.

A data set for training was selected and with this a model for assigning 4 ordinal profile numbers (0 ... 3) was calculated. The limit values between the 4 profiles were chosen to 500 ouE/m³, 5,000 ouE/m³ and 15,000 ouE/m³, respectively.

The left part of Figure 5 shows the result of application of the model on the training data set, revealing that 65% of the profile numbers assigned to the respective electronic nose measurement received the same profile number that was set according to the result of the olfactometric measurement, and 35% of the profile assignments received an adjacent profile number.

The right part of Figure 5 shows with the predictive capabilities using the test data set. As could be expected, the
hit rate decreased. However, still two-thirds of the cases were hits or one profile number away.

Hence a prediction with this relatively simple procedure is possible though not too accurate. Neural networks or other complex mathematical procedures also have problems with assignment, according to Giebel & Frechen (2007a, b).

These results were obtained within an ongoing R&D-project carried out by DESEE which is financed by Emschergenossenschaft, Essen, Germany.

CONCLUSION

Data presented in this paper show that H₂S measurement does not provide a valid surrogate measurement for odour concentration. Even though absence of odour definitely means absence of H₂S, the contrary assumption, that if H₂S is not present, there is no odour, is not true. Nevertheless sulphur compounds are a very important and widespread odour in sewage systems.

VOC and TOC do not seem to be the best choice to measure odour, either. VOC does not seem to be suited because of the non-balanceable character of this parameter. TOC is problematic, as well, as no correlation could be found between odour concentration and TOC value.

In contrast, a multisensory array system (“electronic noses”) seems to be a helpful tool for odour measurement. With an electronic nose, different odour qualities can be distinguished. Moreover, an estimation of odour quantity is possible though not very accurate. Therefore, to implement electronic noses – and multi sensory array measurement in general – seems to be a promising track for the measurement of odour though still a lot of work has to be done. Problems to be solved include the development of a combined procedure using profile analysis and intensity values for describing and predicting the values of odour concentration.

REFERENCES

ATVDWKM 154 2003 Geruchsemissionen aus
Entwässerungssystemen – Vermeidung oder Verminderung –

DIN EN 12619 1999 Stationary Sources Emissions – Determination
of the Mass Concentration of Total Gaseous Organic Carbon
at Low Concentration in Flue Gases – Continuous Flame

DIN EN 13526 2001 Stationary source emissions – Determination of
the mass concentration of total gaseous organic carbon in flue
gases from solvent using processes – Continuous flame
ionisation detector method; German Version.

DIN EN 13725 2003 Air quality. Determination of odour
concentration by dynamic olfactometry; German version EN

IPPC 2003 Integrated Pollution Prevention and Control (IPPC) –
jrc.es/pub/english.cgi/0/733169 (Oct. 5th, 2008).

Franke, W., Frechen, F.-B. & Scholl, B. 2007 Einsatz
mineralischer Filtermaterialien in der biologischen
Abluftbehandlung zur Minderung von Geruchsstoffen und
Schwefelwasserstoff. Posterbeitrag und Buchbeitrag. VDI
Tagung Gerüche in der Umwelt, Bad Kissingen,

Frechen, F.-B., Franke, W. & Scholl, B. 2007 Odour and H2S
degradation in a full scale biofilter with a mineral based
organic coated filter media. Presentation and Proceedings of
the 2nd international congress of Biotechniques for air
pollution control, La Coruna, 3 – 5 October, 2007. ISBN:
987-84-9749-258-4.

Giebel, S. & Frechen, F. B. 2007a Ermittlung von Geruchsprofilen
durch Sensorarrays: Anwendung in der Kanalisation. VDI
Tagung Gerüche in der Umwelt, Bad Kissingen,
978-3-18-01995-9.

Giebel, S. & Frechen, F. B. 2007b Schätzung der
Geruchstoffkonzentration anhand von Sensorarrays:
Vergleich zwischen Logistischer Regression und Neuronalen
Netzen. VDI Tagung Gerüche in der Umwelt, Bad Kissingen,