Impact of Saturation Effects during Dynamic Olfactometry on Low-Concentration Environmental Odour Samples

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Environmental odour samples are often comprised of complex mixtures of compounds with diverse chemical properties and key odorants can be present at concentration levels in the low ppb range. This complicates accurate odour evaluations as adsorption to the inner walls of sampling equipment may significantly alter the chemical composition of the sample, even when the adsorption capacity is low. In the present study, the significance of saturation effects in dynamic Olfactometry on the recovery of single compounds in the low ppb range and the impact on the chemical composition of odour samples typical for livestock houses is evaluated. The results are based on extensive measurements of three olfactometers obtained from accredited odour laboratories, i.e. a TO8, a glass-tube olfactometer and a dilution system based on a mass flow controller. The odorants include hydrogen sulphide, methanethiol, dimethyl sulphide, acetic acid, butanoic acid, propanoic acid, 3-methylbutanoic acid, 4-methylphenol, and trimethylamine. Furthermore, n-butanol, the reference gas according to the European standard, was included. All measurements were performed in real time with high sensitivity Proton Transfer Reaction Mass Spectrometry (PTR-MS). The results show that several key odorants, including 4-methylphenol, trimethylamine and some carboxylic acids, were affected by surface adsorption to an extent, which could likely alter the outcome of odour measurements. Hence, it is recommended to carefully consider olfactometer configuration and compound recovery for this type of odour samples.

1. Introduction

Odour from animal houses is a major environmental issue in the agricultural industry, which may limit the expansion and prosperity of existing and new business developments, while also causing significant nuisance for neighbouring populations. Hence, qualitative odour measurements are needed, and accurate and representative odour measurements essential.

In Europe, dynamic Olfactometry, according to the European standard. EN 13725 (CEN, 2003) is the most recognised and commonly used method for odour quantification. However, accuracy and reproducibility in relation to complex environmental sample matrices has been questioned (Jonassen, 2012, Hansen, 2011). A major issue is variation caused by panellists and panellist selection (Hove et al., 2016, Laor et al., 2014) but diffusion and sorption processes on the walls of measuring equipment can also cause inaccuracy (Koziel et al., 2005, Parker et al., 2010, Hansen et al., 2013, Hansen et al., 2010, Sironi et al., 2014). This is especially an issue, when sample matrices are comprised of complex mixtures of low-concentration compounds with different physicochemical properties. This is often the case when dealing with environmental samples. This means that even a low adsorption capacity of the sampling equipment may alter the chemical composition of the sample to a significant extent and some compounds may be more affected, possibly changing both concentration, intensity and hedonic tone.

In pig production, the key odorants have been identified within the chemical classes: volatile fatty acids, reduced sulphur compounds, ammonia, amines, phenols and indoles (Wright et al., 2005, Feilberg et al., 2010). Several studies have documented loss of these compounds due to adsorption and diffusion processes during storage in sample bags (Koziel et al., 2005, Parker et al., 2010, Hansen et al., 2011, Kasper et al., 2018) and dilution in olfactometers (Hansen et al., 2010, Beauchamp et al., 2010, Hansen et al., 2013, Kasper et al., 2017). The general trend is that sulphur compounds are relatively well preserved, while carboxylic acids,

phenols and indoles undergo varying degrees of compound loss. However, previous experiments on olfactometers have been largely carried out with sample concentrations, which far exceed those present in real odour samples from livestock houses. This is due to the difficulty of accurately measuring exceedingly low concentration levels. The present study seeks to evaluate the effect of dynamic Olfactometry on compounds, which are present in low concentrations similar to original odour samples by examining saturation effects of high dilution samples in olfactometers.

1. Materials and Methods

1.1 Odorants

The study included nine key odorants from pig production including hydrogen sulphide, methanethiol, dimethyl sulphide, acetic acid, butanoic acid, propanoic acid, 3-methylbutanoic acid, 4-methylphenol (p-cresol), trimethylamine and n-butanol. Hydrogen sulphide, methanethiol, dimethyl sulphide and n-butanol were introduced from certified gas cylinders (AGA Liquide, Horsens, Denmark) while the remaining compounds were supplied from permeation tubes (VICI Metronics, Inc. Houston, TX, USA) using a permeation oven (Dynacalibrator model 150, VICI Metronics Inc.). All compounds were introduced in the ppm_v range, as indicated in Table 1.

Table 1: Odorants

	m/z value	Detection limit (ppb)	Inlet concentration (ppm)	Odor Threshold value* (OTV, ppb)	Typical concentration range* (ppm)
Hydrogen sulphide	35	2.6	5.55 ± 0.55	0.8	100-1500
Methanethiol	49	0.06	5.15 ± 0.51	0.03	1-20
Dimethyl sulphide	63	0.19	6.03 ± 0.30	2.3	1-15
Acetic acid	61+43	1.0	4.4 ± 0.1	8.3	50-400
Butanoic acid	89+71	0.41	3.2 ± 0.2	0.23	10-100
Propanoic acid	75+57	0.20	3.2 ± 0.4	5.7	20-150
3-methylbutanoic acid	103+85	0.29	5.3 ± 0.7	0.09	1-5
4-methylphenol	109	0.50	3.6 ± 0.2	0.02	1-10
Trimethylamine	60	0.55	2.7 ± 0.1	0.08	1-20
N-butanol	57	0.37	20 ± 1.0	39.0	-

* Based on (Feilberg et al., 2010), (Hansen et al., 2011), (Nagata and Takeuchi, 2003) and (Hansen et al., 2018)

1.2 Olfactometers

Three olfactometers were obtained from accredited odour laboratories in Europe. They consisted of 1: A glass olfactometer made entirely of glass tubes (i.d. 428 mm), 2: An ECOMA TO8 olfactometer consisting of stainless steel and PTFE (polytetrafluoroethylene) tubing, and 3: A dilution system based on a mass flow controller (MFC) (Bronkhorst, Ruurlo, The Netherlands) consisting of stainless steel and PTFE tubing. Samples were introduced to the olfactometers with descending dilution factors as single compounds and a blank sample between each. All dilution rows were repeated three times.

1.3 Measuring Method

Dilution air for the permeation oven was supplied from a HiQ zero air station (Linde AG, Germany) while dilution air for olfactometers was supplied through a charcoal/silica gel filter. All flows were supplied through Teflon tubes and controlled by mass flow controllers (Bronkhorst, Ruurlo, The Netherlands), which were flushed with sample air for at least 1 hour.

All measurements were obtained with high-sensitivity Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) (Ionicon Analytic, Innsbruck, Austria). The instrument was operated at an E/N of 135-150 Td (1Td=10^{-17} V cm^2) applying a total drift tube voltage of 600 V, maintaining a pressure of 2.1-2.2 mbar and the temperature at 90 ℃. A PEEK (polyether ketone) tube of dimensions 1.6 mm OD and 0.064 mm ID was used for the inlet. For hydrogen sulphide the correction method described by Feilberg et al (2010) was applied (R^2>98%). For compounds showing strong adsorption tendencies, a delay in the PTR-MS system was observed. To eliminate this effect the odorant breakthrough curves of the PTR-MS system alone was modelled and the effect eliminated in the subsequent data treatment (Kasper et al., 2017).

The method and materials used are described in more detail in Kasper et al., 2017 and Kasper et al., 2018.

2. Results and Discussion

The results of the study showed that olfactometers played a significant role in the recovery of odorous compounds, even at the longest pulse of 15 s as recommended by the European standard. All compounds, except dimethyl sulphide, showed a delayed response and only sulphur compounds were found to reach their maximum recovery within 2.2 s and showed little to no adsorptive behaviour in the olfactometers, though a reactive loss was observed for hydrogen sulphide (data not shown). Conversely, the remaining compounds were found to adsorb to the walls of the olfactometers to varying degrees, which could be correlated to their volatility (Kasper 2017). Trimethylamine was found exceedingly adsorptive and was excluded from further testing, as the concentration of this compound could not be confidently determined.

For the compounds showing adsorptive behaviour, a strong dependence on dilution step, i.e. the concentration of the incoming sample, was observed. Especially in the MFC based dilution system and the TO8, where high dilution samples were subjected to a greater loss than samples with low dilution, i.e. higher concentrations. This is illustrated in figure 1. This is consistent with the surfaces of the olfactometers being saturated as the concentration increases. The same effect was not observed to a considerable extent in the glass olfactometer, presumably due to the much smaller surface- area-to-sample-volume ratio in this type of olfactometer (i.d. 42.8 mm compared to 8 mm for the other two systems). The highest loss was observed in the MFC based system. This is expected to be due to a larger exposed stainless steel surface area (Kasper et al., 2017).
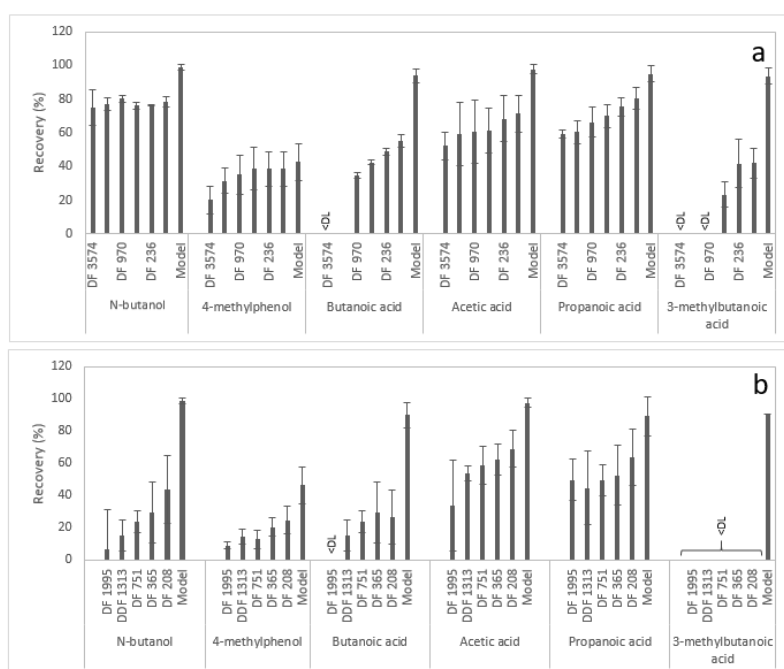

Figure 1: Recovery of compounds in a) TO8 and b) MFC-based dilution system with a 2.2 s pulse. Recoveries are presented as the average of three repetitions. DF=Dilution factor, Model = output predicted by model of PTR-MS signal, i.e. the level at which no adsorption in the olfactometer is taking place, <DL = below detection limit.

A major cause for the impairment of the recovery at the highest dilutions is that these low concentration samples are run on a clean instrument, where the absorption capacity is highest (no adsorption sites are saturated yet). The three replicates performed for each dilution row in these experiments were performed sequentially and uninterruptedly with a blank sample between each dilution step and -row. For highly adsorptive compounds, i.e. trimethylamine, 3-methylbutanoic acid, 4-methylphenol and butanoic acid, this means that the highest dilutions, especially in the first replicate, will undergo significant losses with concentrations approximating zero. As the surfaces become saturated with the compounds, due to the introduction of lower dilution steps and as the experiments proceed, this effect decreases, and the recovery of all diluted samples approaches the expected value (or at least a maximum plateau) when reaching the low dilutions of the last replicates.

Figure 2 shows the first three replicates of the three highest dilutions for 4-methylphenol in the MFC system and for butanoic acid in the TO8. It should be noted that between the three dilution-steps shown in the figure, lower dilution steps are introduced (i.e. 5-6 dilution steps in total). Again, the severity of these effects were found to correlate to the volatility of compounds and the effect was greater in the MFC system than in the TO8.
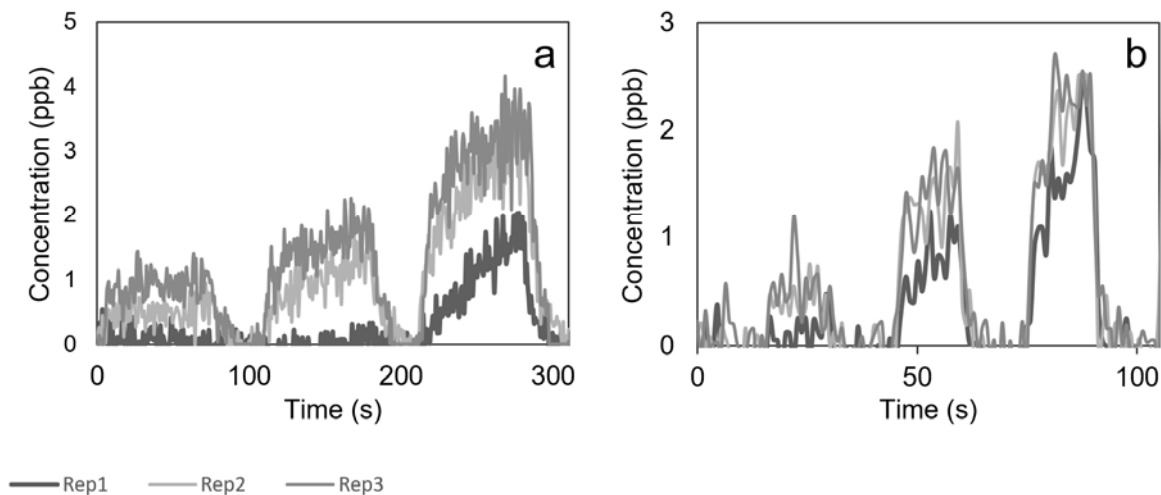

Figure 2: Time resolved output of PTR-MS showing the first 3 dilution steps of each of 3 consecutive dilution rows. a) 4-methylphenol in MFC based dilution system and b) butanoic acid in TO8

The results illustrated in Figure 1 and 2 raise a serious concern that when real odour samples with much lower concentration levels are introduced, the recovery will be more severely impaired, as the system is not saturated to the same extent as the dilution row proceeds. Considering this, it is imperative to keep in mind that the concentration level for these experiments are a factor 58 and 655 higher than those found in real odour samples from pig houses for butanoic acid and 4-methylphenol, respectively (Table 1). It is thus highly conceivable that key odorants such as 4-methylphenol and butanoic acid will not reach the nose cones of the olfactometers to a representative or even perceivable level. Especially, when also considering the significant losses these compounds can be subjected to during storage (Kasper et al., 2018).

The effects shown in Figure 2 are difficult to project directly onto samples of lower concentration as this may be exacerbated as the concentration is lowered. However, simply assuming that the average percentagewise loss of compound (given in Figure 1) is the same for low concentration samples as for higher concentration samples, it is possible to evaluate the effect on real samples tentatively (as a best-case scenario). Using 4-methylphenol, 3-methylbutanoic acid and butanoic acid as examples, the concentration of these compounds in a real sample (using the average concentration of those given in Table 1) and after the TO8 and MFC olfactometers are estimated and shown in Figure 3. The same results for the glass olfactometer are not shown, as odour threshold values would not have been reached for low concentration samples, with the dilution steps included in this study. However, it should be noted that total compound recoveries were similar (with minor compound specific variations) in the glass olfactometer (Kasper et al. 2017).

The sense of smell is logarithmic, which means that perception of a change in smell requires a doubling or halving of the compound concentration.

From Figure 3 it is evident that saturation effect in the olfactometer can effectively halve the concentration of adsorptive compounds and displace the dilution factor at which odour threshold is exceeded by more than one.

A noteworthy result from this work is that n-butanol, the reference gas according to the European standard, is also affected by saturation effects. As shown in Figure 1, n-butanol is showing highly adsorptive behaviour in the MFC based dilution system and Figure 4 illustrates how this could shift the dilution factor at which odour threshold is reached for this compound as well. As this is the compound used to select panellist this could influence the odour measurements on a more general basis, contributing to inter-laboratory discrepancies.
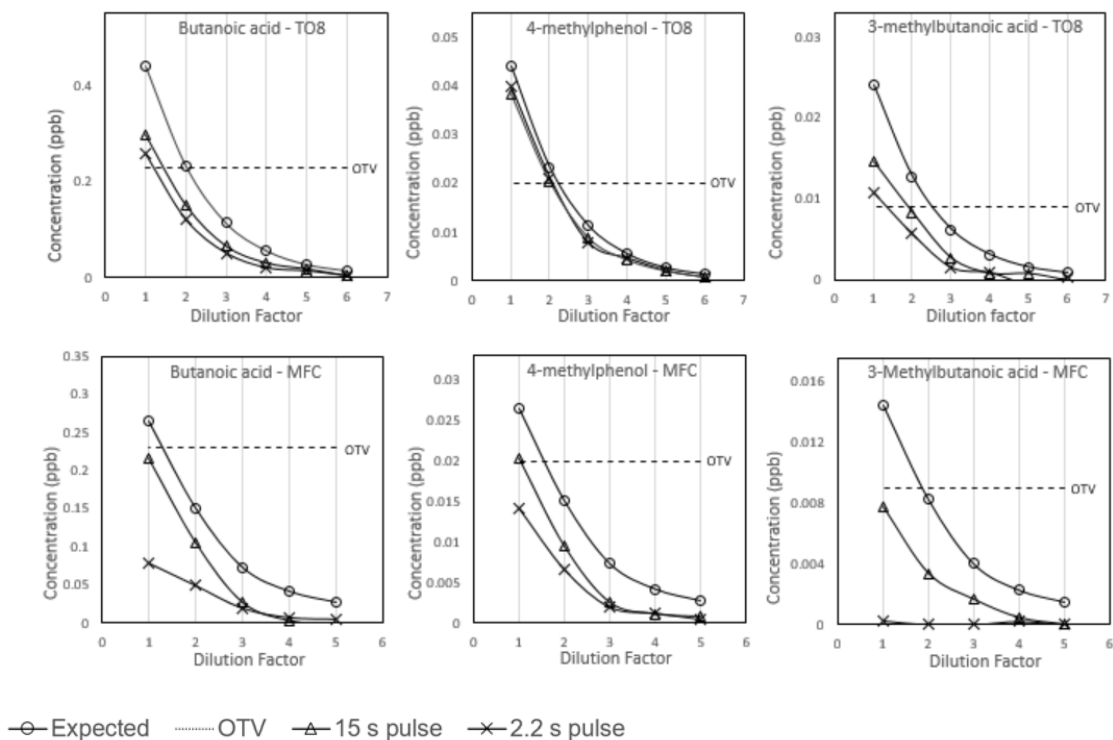
Figure 3: Predicted concentration profiles of Butanoic acid, 4-methylphenol and 3-methylbutanoic acid in TO8 and MFC-based dilution system. OTV= odour threshold value. Dilution factor 1-6 corresponds to dilutions between 3574 to 125 for the TO8 and 1995 to 208 for the MFC-system with a factor 2 between each.
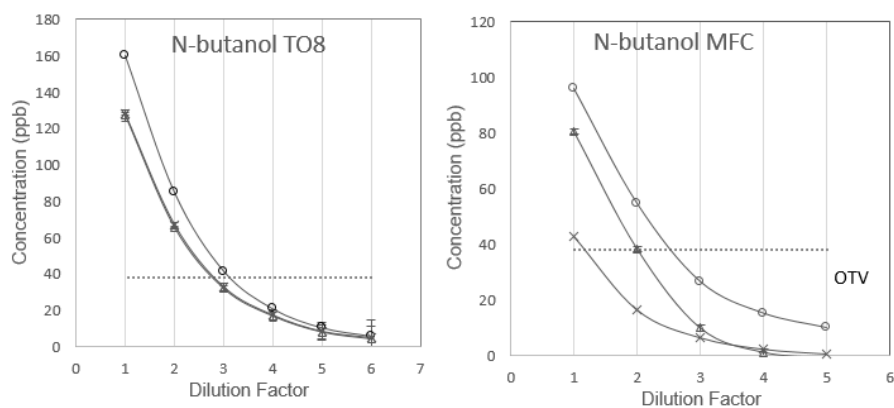

Figure 4: Concentration profiles of n-butanol in a) TO8 and b) MFC-based dilution system

Conclusions

It is evident from the results of this study that low concentration samples are more severely affected by adsorption effects in olfactometers. Compounds such as 4-methylphenol, butanoic acid, trimethylamine and 3-methylbutanoic acid could conceivably be reduced to concentration levels, which would significantly lower their impact on odour evaluations, even though these compounds have been determined as key odorants from this source. It was shown that the dilution factor at which odour threshold is exceeded could be shifted by one or more dilution steps due to these effects, depending on the olfactometer and compound characteristics. Furthermore, these saturation effects were found to affect the concentration of n-butanol considerably and could contribute to inter-laboratory discrepancies.

From the results of this study, it is highly recommendable to consider compound recovery and olfactometer configuration carefully, when dealing with these low concentration samples. Previous studies have shown that

by avoiding stainless steel and glass surfaces and choosing PTFE, PFA or possibly coated steel surfaces for the parts of the olfactometer, which come in direct contact with the sample matrix, these effects can be largely overcome (Kasper et al., 2017).

Acknowledgments

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