

# The Power of Online Proton Transfer Reaction - Mass Spectrometry (PTR-MS) Measurement of Odorous Emissions from a Pig House

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Online monitoring of odorous compounds in the ventilation air was applied in an experimental pig house in Denmark. The measurements were executed by proton-transfer-reaction – mass spectrometry (PTR-MS) while grab samples are used to confirm the identity of the compounds. Sorbent tubes samples were analysed by gas chromatography – mass spectrometry analysis (GC-MS) and Tedlar bags samples by gas chromatography – sulfur chemiluminescence detector (GC-SCD). For three target odorants, dimethyl sulfide, propanoic acid and p-cresol, the reproducibility after averaging over 1 hour was in the same order of magnitude for both grab and continuous sampling (<16 %). However, the detailed information on the concentration variations during the day provided by online measurements, can never be obtained by any analytic method requiring sample collection. The results emphasize the importance of a suitable strategy when taking grab samples for odour evaluation, for example for olfactometric measurements. Concentrations of odorants can easily differ by a factor of two within one week with similar weather circumstances and identical pigs.

## 1. Introduction

Recently, online measurement techniques were introduced in the field of odour analysis, and have been proven to offer some valuable advantages in comparison to grab samples, collected in sampling bags or on sorbent materials. First of all, a large number of data points can be easily acquired in a short time frame to verify the precision of the measured value. The main limitation of GC-MS, which is widely used for the chemical analysis of odorous air, is the temporal resolution due to the preconcentration and separation steps prior to analysis (Van Huffel et al., 2012). Secondly, the absence of sample collection and storage minimizes the risk of biased concentrations by sample loss. Feilberg et al. (2010b) points out the reactivity of methanethiol, a strong odorant, in some sampling procedures, while it can be quantified directly by PTR-MS, an online analysis method based on chemical ionisation with protonated water ( $\text{H}_3\text{O}^+$ ). Several authors showed limitations related to recovery of odorants on sorbent materials (Koziel et al., 2005) and in sampling bags, both with olfactometric measurements (Zarra et al., 2012) and with chemical analysis (Guillot and Beghi, 2008, Laor et al, 2010). According to Guillot et al (2012), sampling is still the limiting step in odour and odorants analysis, due to the number of samples, the variability of the source or the sample transportation and storage before analysis. Therefore, the direct analysis of PTR-MS combined with the broad range of volatile organic compounds that can be measured, including highly odorous sulphur compounds (Hansen et al., 2012), makes it a valuable alternative method for odour analysis. Finally, online air analysis enables continuous data gathering over a long time span, which reveals emission variation and trends. In practice, mean concentration values are often used, for example in dispersion modelling, where it causes significant uncertainty in the outcome of the models (Romain et al.,

2013). Extreme concentrations and the probability of different concentration levels to occur could be useful in such cases.

PTR-MS has previously been used as a tool for livestock odour analysis for both pig houses (Feilberg et al., 2010b) and cattle buildings (Ngwabie et al., 2008 and Shaw et al., 2007). In this paper, the results of continuous PTR-MS measurements in pig house ventilation air will be displayed, together with results for grab sampling with subsequent GC separation and MS or SCD detection. For the sake of conciseness, one week of measurements, covered by more than 19 000 PTR-MS measurement cycles, will be presented for a selection of three target compounds belonging to diverse chemical groups: dimethyl sulfide, propanoic acid and p-cresol.

## 2. Material and methods

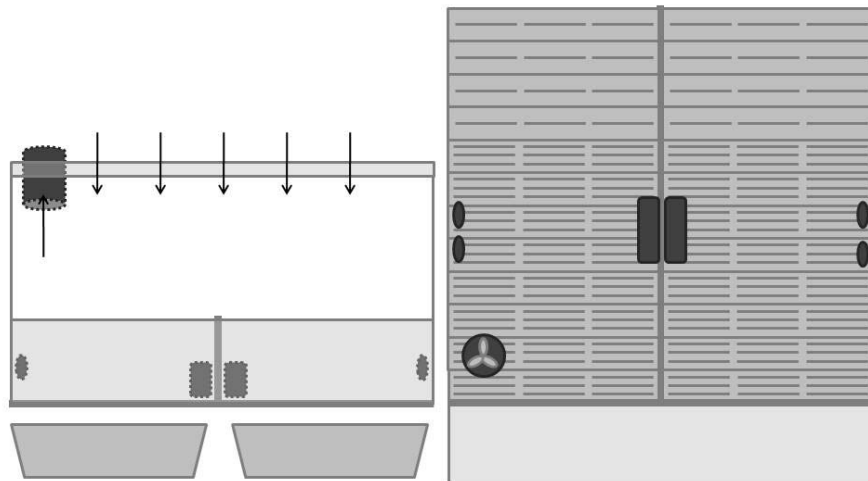


Figure 1: Scheme of the pig room in front view (left) and top view (right).

Field experiments were carried out at an experimental pig production facility of the Department of Engineering in Foulum, Denmark (scheme in **Figure 1**). A pig section with fully slatted floor consisting of two pens (each 11.5 m<sup>2</sup>), housed 30 fattening pigs from 22th of October to 3th of December. The ceiling duct ventilation rate was automatically controlled by the room temperature, which was constant at 19.9±0.6 °C. Outside air (8.3±1.6 °C) entered the room through a diffusive ceiling inlet, resulting in a ventilation rate of 1474±201 m<sup>3</sup>/h (*Figure 2*).

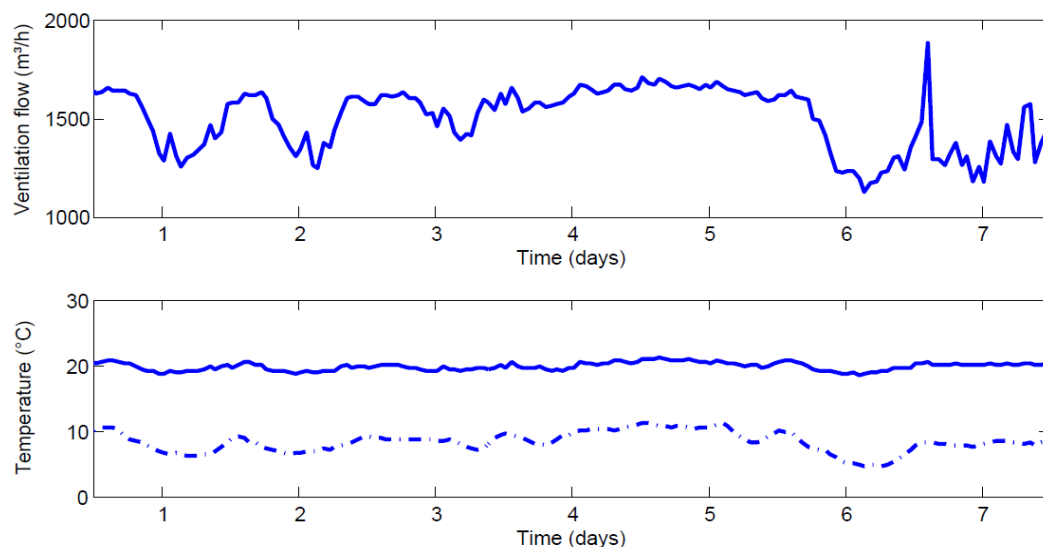


Figure 2: Ventilation flow (m<sup>3</sup>/h) and temperature (°C) in the pig room (solid line) and in the outdoor air (dashed line) during

From the 4th week of the fattening period, the ventilation air was continuously analysed for odorants. This was done by means of a PTR-MS instrument (Ionicon Analytic, Innsbruck, Austria) operated under standard ion drift tube conditions at a voltage of 600 V and a pressure of 2.1-2.2 mbar. The drift tube temperature was controlled at 60 °C and the inlet flow was 111±2 mL/min. The sensitivity of the instrument was calculated based on the rate constants of proton transfer (Feilberg et al., 2010c). Measurements were conducted in selected ion monitoring (SIM) mode using a dwell time of 500 ms per mass, with a complete measurement cycle accounting for 15 s. Dimethyl sulfide was measured at m/z 63, propanoic acid at m/z 57 and 75, and p-cresol at m/z 109.

A heated switch valve box was employed to measure through different sampling lines. The concentration in the room ventilation duct and the background air concentration were examined alternately every 12 minutes.

The set-up consisted further of a heated sampling line (Teflon, FEP, length 6 m, internal diameter 1.6 mm) connecting the inlet line of the PTR-MS (PEEK, 1 m, 1mm) to the exhaust duct, where a 5 µm PTFE filter (Millipore Millex-LS) excludes larger particles.

On the second day of the PTR-MS measurements, 3 grab samples (10 min at 150 mL/min) were collected in the ventilation duct on Tenax TA/Carbograph 5TD sampling tubes (Feilberg et al., 2010a) for TD-GC-MS analysis (TD 100, Markes International Ltd., Llantrisant, United Kingdom and GC 6890 N and MSD 5973, Agilent Technologies A/S, Horsholm, Denmark). The GC was equipped with a polyethylene glycol capillary column (HP-INNOWax, Agilent Technologies A/S, Horsholm, Denmark; 30 m length, inner diameter 0.25 mm and stationary phase 0.25 µm). The helium carrier gas flow rate was pressure controlled at 7.6 psi. The GC oven temperature was hold for 4 min at 50 °C, ramped up to 250 °C at 10 °C min<sup>-1</sup> and hold for 5 min at 250 °C, with propanoic acid eluting at 13.6 min and p-cresol at 20.2 min. The GC-MS calibration was done by spiking 1 µL of standard solution on 3 sampling tubes under a He flow of 100 mL/min.

Simultaneously, 3 Tedlar bags (10 L) were filled with ventilation air for GC-SCD analysis (GC 7890 A and SCD 355, Agilent Technologies A/S, Horsholm, Denmark). The gas chromatograph was equipped with a dimethylpolysiloxane capillary column (DB-1, Agilent Technologies A/S, Horsholm, Denmark; 60 m length, 0.53 mm inner diameter and stationary phase 5 µm). The helium carrier gas flow rate was set to 10 mL min<sup>-1</sup>. The GC oven temperature was held for 1 min at 60 °C, ramped up to 200 °C at 20 °C min<sup>-1</sup> and held for 1 min at 200 °C. The GC-SCD instrument was calibrated by means of a calibration gas bottle containing 5 ppmv of H<sub>2</sub>S (retention time 1.7 min), methanethiol (2.2 min) and dimethyl sulfide (2.8 min).

### 3. Results and discussion

#### 3.1 Precision

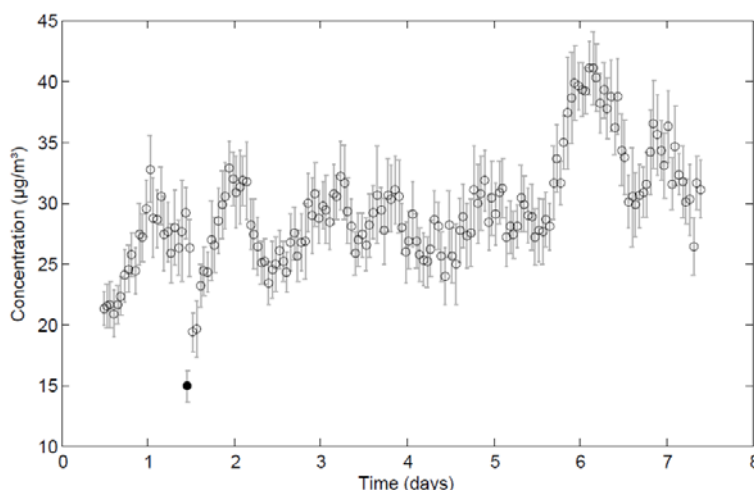


Figure 3: Concentration of dimethyl sulfide in room ventilation air measured by PTR-MS (empty circles) and GC-SCD (full circle) with standard deviation ( $n$  around 40 and  $n=3$ , respectively)

During one week of measurements, the room ventilation air was analysed 415 times for 12 minutes, alternated with background air analysis. Each measurement series of 12 minutes consists of around 47 cycles (individual datapoints for every ion), where the last 15 cycles are used for concentration calculation to ensure a stable concentration level. The measured concentration values were sufficiently reproducible, with relative standard deviations (RSD) over 15 cycles between 1.1 and 12.2 % for propionic acid,

between 3.8 and 12.7 % for dimethyl sulfide and between 3.1 and 16.0 % for p-cresol. The higher RSD range for p-cresol is clearly related to low concentration levels. One hour averages, which provide a clearer overview and cover 2 to 3 measurement series, have a similar RSD. In Figure 3, hourly averages ( $\pm$  one standard deviation) are shown for dimethyl sulfide together with the corresponding GC-SCD samples ( $n=3$ ) collected on the second measurement day, with a value of  $14.9 \pm 1.2 \mu\text{g}/\text{m}^3$  (RSD 8.2 %). Time is expressed in days from midnight of the first measuring day. For propanoic acid and p-cresol, the GC-MS concentrations were respectively  $840 \pm 84 \mu\text{g}/\text{m}^3$  (RSD 9.8 %) and  $46.7 \pm 7.3 \mu\text{g}/\text{m}^3$  (RSD 15.7 %).

### 3.2 Daily variation

In Figure 3, it could be noticed that the dimethyl sulfide concentration varies greatly over time. This applies to other odorants present in pig house air, which can be seen for the target compounds in Figure 4a.

The concentration fluctuations are generally triggered by the changing intensity of animal activity during a day (Blanes-Vidal et al., 2008, Romain et al., 2013), but are also influenced by the ventilation flow rate. Both propanoic acid and p-cresol show a maximum concentration in the late afternoon, and a minimal concentration during the night, with elevated concentration levels corresponding to higher animal activity. Due to the temperature-driven ventilation system, the ventilation flow rate will be higher at daytime, with higher heat production inside the pig room and with increasing outside air temperature. In Figure 4b, the effect of changing ventilation flow rate is included by calculating the hourly emission of the target odorants. For propanoic acid and p-cresol, this conversion emphasizes the extreme values even more, for instance in the nights following day 1, 2 and 6, where the outside temperature dropped to  $5^\circ\text{C}$  and rises to  $10^\circ\text{C}$  at noon of the following day, resulting in very low and quite elevated, respectively, ventilation flow rates and emissions.

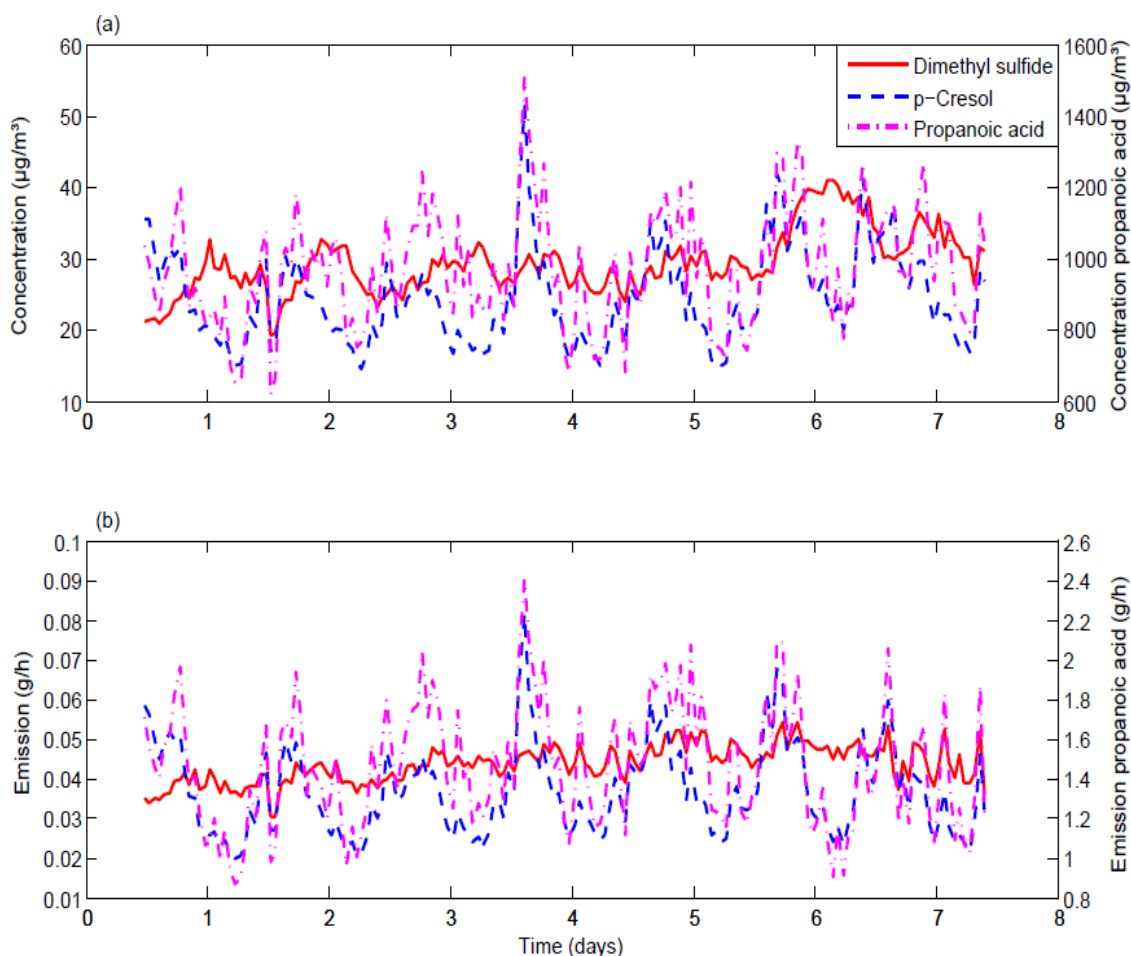


Figure 4: Concentration in room ventilation air ( $\mu\text{g}/\text{m}^3$ ) (a) and emission ( $\text{g}/\text{h}$ ) (b) of dimethyl sulfide, p-cresol and propanoic acid over one week of measurements.

On the contrary, dimethyl sulfide tends to show higher concentration levels at lower ventilation flow rates, which suggests this odorant originates from a different source (Feilberg et al., 2010c), which is apparently independent of animal activity. Volatile sulphur compounds are formed by sulfate reduction and metabolism of sulfur containing amino acids (Mackie et al., 1998) and their emissions originate from three excretion pathways: evaporation from faecal material, excretion through flatus and through respiratory gases (Poulsen et al., 2012). When looking at the emission of dimethyl sulfide in Figure 4b, it seems approximately constant in the course of one day, and gradually increasing during one week of measurements.

If the emission of odorants and the related dispersion and possible nuisance of odour should be evaluated, it is of importance to study the emission at a suitable moment. If for instance grab samples are collected in the morning, concentration of both phenols and organic acids will be underestimated compared to weekly average concentrations (Figure 5), and surely compared to the maximum concentration. For the odorants included in this study, differences of a factor 2 between minimum and maximum concentration are no exception. For emission sources which show diurnal variation and evolution over a longer time period, a suitable sampling strategy should be selected to have a realistic estimate of the emission. This was illustrated recently by Daelman et al. (2013) applied on the emission of nitrous oxide from wastewater treatment plants. Short term sampling proved to be inadequate for average emission estimates, while both long-term grab samples and online measurements covered a representative temperature range and gave more accurate estimates. However, online measuring was the only suitable strategy to link daily variation in the emission to changes in process conditions (Daelman et al., 2013). The study of daily dynamics in such highly variable emissions, due to natural changes in animal and microbial activity, is essential to gain information on the origin of the emissions and the possible remediation.

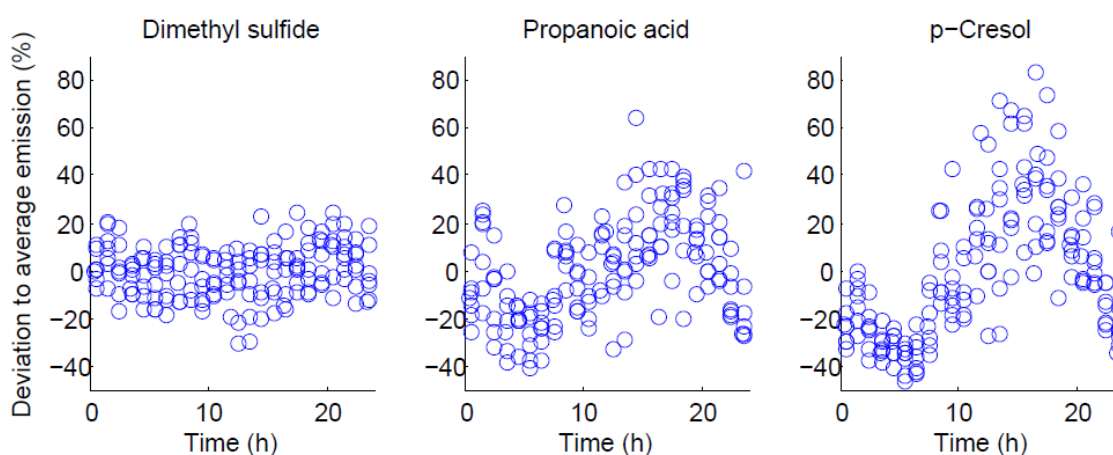


Figure 5: Deviation (%) of the target compound emissions of the whole week (167 hourly averages) compared to the weekly average emission as a function of time during the day, from 00h00 to 24h00.

#### 4. Conclusions

When evaluating odorous air originating from a pig house on a chemical base, both continuous analysis by PTR-MS and grab sampling by sorption or in Tedlar bags, provide reproducible results for the target compounds in this study. However, concentrations of odorants in pig houses can vary greatly over time. For propanoic acid and p-cresol, the daily variation is significantly influenced by animal activity, with a minimum during the night, and a maximum during late afternoon. Dimethyl sulfide concentrations increase when the ventilation flow rate is lower, while propanoic acid and p-cresol concentration extremes coincide with extremes in the ventilation rate, suggesting different formation mechanisms and sources for these odorants. To ensure the collection of a representative and useful grab sample of livestock air, knowledge of the concentration dynamics inside a pig house is essential. In this study, PTR-MS monitoring provided this information in an easy and comprehensible way and proved to be a suitable instrument to enable online measurements on fluctuating emission sources.

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