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Measurement of Odorants in Livestock Buildings: SIFT-MS and TD-GC-MS

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Air samples from animal farming are analysed in parallel using traditional TD-GC-MS (thermal desorption gas chromatography mass spectrometry) and SIFT-MS (selected ion flow tube mass spectrometry). In samples from 4 different livestock buildings, 23 odorous compounds are detected and quantified based on TD-GC-MS, including organic acids, sulphur compounds and phenols. Significant concentration differences are found between pig stables and poultry houses. SIFT-MS spectra show similar differences in product ion intensities, suggesting SIFT-MS as a promising fast technique for evaluation of odorous emissions from livestock buildings.

1. Introduction

Odour nuisance related to intensive livestock breeding is an emerging concern (Ubeda et al., 2010), especially in areas with a high population density (Van Langenhove and De Bruyn, 2001). Volatile organic compounds (VOC) are generated by microbial conversions in the gastrointestinal tract of farm animals, in the excretions and in the litter (Pillai et al., 2010). Some of these compounds like phenols, indoles, organic acids, sulphur compounds and amines have an offensive odour and low odour thresholds, and are suggested as being the key VOC emitted from swine houses (Yao et al., 2011), poultry excretions (Cai et al., 2007) and cattle feedlots (Trabue et al., 2011). Next to annoyance, livestock emissions have been associated with physical complaints like eye irritation and respiratory symptoms (Schinasi et al., 2011). Recently, research was performed on different emission-related topics including type and equipment of livestock building (Wang et al., 2011), use or treatment of animal waste (Brandt et al., 2011), type of animal (Zhang et al., 2010) and composition of feed (Hernandez et al., 2011).
For a reliable assessment of the level of odorous emissions, two different strategies are currently used: sensory methods and analysis of the odorous VOC (Defoer et al., 2002). Sensorial analysis like dynamic olfactometry delivers overall odour concentration levels, but are costly and time consuming (Hobbs et al., 1995; Sohn et al., 2010). Moreover, identification and quantification of the various offensive odorants is necessary for treatment and prevention of odorous emissions (Lehtinen and Veijanen, 2011). However, until present no general method exists to provide an evaluation of odorant production, although a great number of indirect measurement methods has been developed (Hansen et al., 2011). In most of the research concerning odorants, GC-MS is used for generating a quantitative list of components (Brattoli et al., 2011). This separation and identification method is usually combined with a sorptive technique for sampling and concentrating (Feilberg et al., 2010b), such as sorbent tubes (Zhang et al., 2010) and solid-phase microextraction, SPME (Koziel et al., 2010). The main limitation of

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GC-MS is the temporal resolution, because preconcentration and separation of the compounds in the air samples requires a relative long period of time, which emphasizes the need for a more convenient and faster technique (Blake et al., 2009). SPME coupled to a mass spectrometer without prior chromatographic separation (SPME-MS) was tested as an alternative method to yield a spectral signature of animal sheds in a short analysis time (Begnaud et al., 2004). Likewise, Feilberg et al. (2010a) employs membrane inlet mass spectrometry (MIMS) to make an online evaluation of a livestock air biofilter. In recent research, proton transfer reaction mass spectrometry (PTR-MS) was applied on pig and dairy cow facilities, achieving real-time measurement of the odorous emissions (Liu et al., 2011; Ngwabie et al., 2008). SIFT-MS uses a similar chemical ionization method, with the advantage of several precursor ions which enables differentiation between isobaric compounds (Wang et al., 2004). This method has had numerous applications (Spanel and Smith, 2011), including one study on livestock waste samples (Smith et al., 2000).
In the present study, full scan SIFT-MS measurements will be used to characterize several livestock house atmospheres, combined with TD-GC-MS analyses to provide more selective quantitative results and facilitate SIFT-MS spectra interpretation. The livestock buildings include both pig and poultry houses and the resulting analytical data will be subjected to statistical analysis to identify the differences between the studied livestock odours. This can be valuable for source appointment of odour nuisance and for comparison to olfactometric data.

2. Material and methods

2.1 Field sampling

Samples are taken at a test facility of the ILVO (the institute for agriculture and fisheries research) in Merelbeke. Animal houses with different species are studied: laying hens, broiler chickens, fattening pigs and piglets. In each livestock building, above the animals at 1.5 m height, 5 air samples are collected within 30 min in 2 L Nalophane® bags. The average temperature in the buildings was 21 °C.

2.2 Laboratory analysis

For GC-MS analysis, sampling tubes are loaded from the Nalophane® bags within 6 hours after the bags are filled. The sorbent tubes (Markes) contain a 50/50 volume ratio of Tenax TA and Carbotrap, with a total sorbent mass of 200 mg. Before sampling, the tubes are conditioned for 1 hour at 300 °C and loaded with deuterated toluene as an internal standard. Each tube is loaded with 300 mL sample using a Flec air pump at a flow of 100 mL min^{-1}.
Analysis is performed by TD-GC-MS (Markes/Interscience). Tubes are desorbed in a Unity Series 2 Thermal Desorption system (Markes, Llantrisant, UK) at 260 °C for 10 min with a He flow of 20 mL min^{-1}. After desorption, the analytes are refocused on a coldtrap filled with Tenax TA which is flash-heated from −10°C to 280°C. Separation is accomplished on a FactorFour VF-1ms column (Varian, Sint–Katelijne–Waver, Belgium; 100 % dimethylpolysiloxane, 30 m x 0.25 mm x 1 µm) with He as a carrier gas and a constant column head pressure of 70 kPa was applied. The GC (Focus GC, Interscience) oven temperature was initially set at 35°C for 3 min, and increased from 35°C to 150°C at 8°C min^{-1} and from 150 to 240°C at 12°C min^{-1}, which was maintained for 10 min.
A DSQ II Single Quadrupole MS (Thermo Scientific, Austin, TX, USA) hyphenated to the GC was operated in full scan mode (140 ms per scan). Data were processed in XCalibur software based on retention time, mass spectrum and selected ions. External standard calibration for TD-GC-MS was performed by means of a standard solution containing the target compounds in methanol. Selection of these compounds is based on different criteria including the frequency of appearance in similar studies, reported odour detection thresholds (ODT) and earlier demonstration of contribution to livestock odour.
In the SIFT-MS instrument (Voice 200®, SYFT Technologies Ltd.) precursor ions H_3O^+, NO^+ and O_2^+ are generated in a discharge ion source, a specific mass is selected by a quadrupole mass filter and then injected as selected ionic species into fast-flowing He carrier gas in a flow tube, where the sample to be analyzed is introduced. Determination of the counts per second (CPS) of the precursor ions and the resulting product ions is performed by a downstream quadrupole mass spectrometer in the m/z range 15 to 250. In order to prevent condensation of water vapour, the sample inlet lines are heated to

~ 373 K. The He carrier gas pressure is 20 Pa at room temperature. Each livestock sample is analysed 3 times, resulting in 15 SIFT mass spectra for each animal house.

2.3 Data analysis

The aim of statistical analysis on the concentration levels measured by TD-GC-MS is to investigate a possible distinction in chemical composition between the emissions of different species. A Kolmogorov-Smirnov test on 5 % significance level was used to verify if the compounds represented a normal distribution in each stable, which is the case for 90 % of the concentration levels. Compound concentrations are compared between the different livestock buildings by analysis of variances (ANOVA).

For the SIFT-MS data, Pearson correlation analysis was performed on product ion intensities to confirm the identity of unknown compounds.

3. Results and discussion

In Table 1 the concentration levels in the different buildings are given, together with their standard deviation. From the selected target compounds, heptanoic acid, 3-methylbutanal, 1-butanol, 4-ethylphenol and indole were not detected in any of the samples and therefore are omitted from all resulting tables and figures. Since conditions in livestock buildings cannot be considered as constant in time and space, the relatively large deviation on some data points is not unexpected.

Table 1: Average concentration levels and standard deviation (µg m^{-3}), n = 5.

Compound	Fattening pig	Piglet	Broiler chicken	Laying hen
Ethanoic acid	432.6 ± 139.9	155.2 ± 45.1	146.3 ± 65.1	248.2 ± 167.0
Propanoic acid	73.8 ± 16.9	40.0 ± 14.1	5.9 ± 1.8	7.6 ± 2.1
Butanoic acid	23.6 ± 7.3	25.5 ± 10.3	7.5 ± 3.0	5.1 ± 1.9
2-Methylpropanoic acid	22.1 ± 9.4	7.9 ± 3.4	n.q.[a]	n.q.
2-Methylbutanoic acid	10.6 ± 5.4	5.2 ± 2.5	n.d.[b]	n.d.
3-Methylbutanoic acid	10.1 ± 4.5	6.4 ± 2.4	n.d.	n.d.
Pentanoic acid	12.8 ± 5.7	11.5 ± 3.9	5.8 ± 2.5	7.5 ± 4.2
Hexanoic acid	7.1 ± 3.4	8.5 ± 4.5	4.1 ± 1.4	8.3 ± 5.2
Dimethyl sulfide	7.2 ± 1.0	11.7 ± 2.2	0.8 ± 0.1	16.0 ± 5.5
Dimethyl disulfide	2.9 ± 0.2	9.8 ± 3.1	0.7 ± 0.3	14.2 ± 3.4
Dimethyl trisulfide	2.0 ± 1.0	9.0 ± 5.7	n.d.	0.7 ± 0.3
Carbon disulfide	1.2 ± 0.1	1.9 ± 0.2	0.7 ± 0.1	1.2 ± 0.2
Skatole	0.3 ± 0.1	0.3 ± 0.1	n.d.	n.d.
Phenol	3.7 ± 1.7	7.7 ± 5.7	8.0 ± 4.1	4.9 ± 4.6
4-Methylphenol	6.6 ± 4.7	2.5 ± 1.4	0.5 ± 0.2	0.6 ± 0.3
Butanal	5.1 ± 2.4	3.1 ± 1.6	5.1 ± 1.2	3.6 ± 0.5
Hexanal	4.0 ± 1.0	3.5 ± 0.7	4.1 ± 0.3	2.6 ± 1.6
Heptanal	2.6 ± 0.6	2.2 ± 0.5	2.3 ± 0.3	1.4 ± 1.1
Benzaldehyde	9.4 ± 1.7	7.4 ± 1.0	7.9 ± 2.2	6.6 ± 2.2
2-Butanone	10.7 ± 2.0	17.3 ± 3.0	11.7 ± 2.0	7.7 ± 1.6
Ethylacetate	8.3 ± 1.7	5.0 ± 1.2	4.6 ± 0.6	6.1 ± 1.7
Toluene	4.6 ± 1.3	3.0 ± 0.3	2.0 ± 0.8	1.5 ± 0.2
1-Phenylethanone	7.3 ± 2.7	4.2 ± 0.5	4.7 ± 1.0	6.0 ± 1.7

[a] Not quantified, [b] not detected.

The most abundant compound in all samples is ethanoic acid (EA), reaching more than 40 % on mass basis of the total concentration. Other dominant compounds are propanoic acid (PA) and butanoic acid (BA) for both pig stables, 2-butanone and phenol for the broiler chickens and dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) for the laying hens.

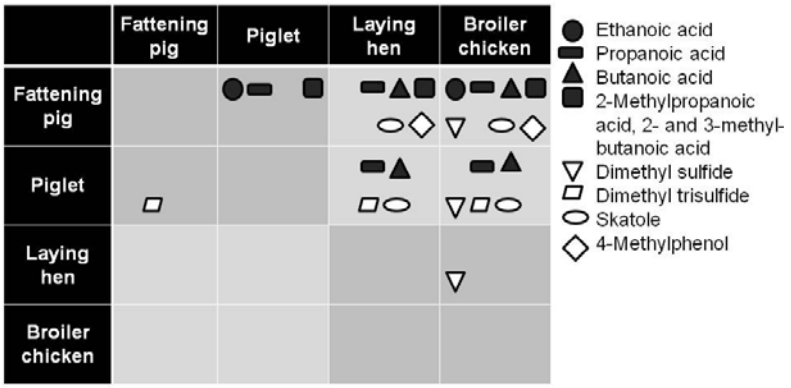

Figure 1: ANOVA analysis: significant differences between livestock samples. Symbols indicate a higher concentration in the sample shown left in the table compared to the sample on top.

Based on the ANOVA statistical tests, 17 of the 23 observed compounds show significant differences (on the 0.05 level) between the livestock buildings, of which a selection is presented in Figure 1. The concentration of EA was higher in the fattening pig stable compared to the broiler chicken and the piglet building. For PA and BA, both pig house concentrations are higher than both chicken stable concentrations, and the fattening pigs give rise to higher PA concentrations than the piglets. For the branched organic acids (2-methylpropanoic acid, 2- and 3-methylbutanoic acid), the fattening pigs produce more elevated concentrations than all the other species. However, in the chicken buildings these compounds concentrations are below quantification limits, as is the case for skatole, were fattening pigs and piglets show similar concentrations. DMS shows a lower level in the broiler house than in all other buildings, and in the laying hen house compared to the fattening pig building. For dimethyl trisulfide (DMTS), the piglet stable concentrations exceed all other species emissions. 4-Methylphenol (p-cresol) is more abundant in the fattening pig building compared to both chicken buildings

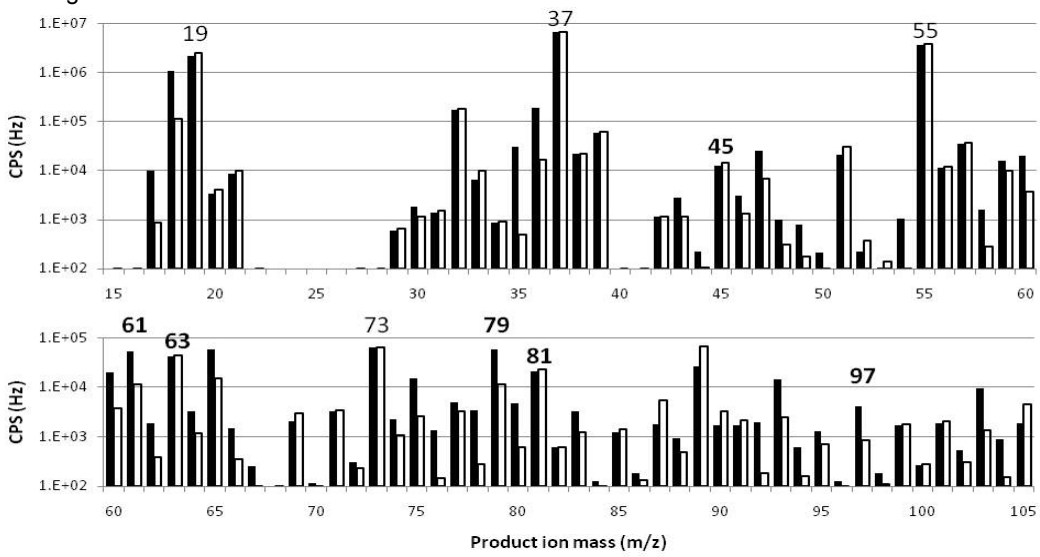

Figure 2: Typical SIFT-MS spectra obtained by the analysis of fattening pig (black bars) and broiler chicken (white bars) atmospheres. m/z 19 is the precursor ion and 37, 55 and 73 are its water clusters. Ethanoic acid is present at m/z 61, 79 and 97 while m/z 45, 63 and 81 are probably related to ethanal.

The SIFT-MS spectra (averaged over 15 measurements) also show differences between the various animal housing atmospheres. In Figure 2, examples are given of mass spectra for fattening pigs and broiler chickens generated with H3O+ (m/z 19) as precursor ion. To improve readability, the m/z range is restricted to the lower regions (<106 m/z) where most of the relevant compounds are detected, and the spectra are spread over two graphs. Most ions are detected in both samples, but have significantly higher intensities in one sample, for example m/z 61, 79 and 97, which are the product ion and water clusters of ethanoic acid. As shown in the TD-GC-MS results, ethanoic acid is more abundant in the fattening pig stable compared to the broiler chicken stable. Other ions show equal intensities in both mass spectra, for example m/z 45, 63 and 81 which are probably related to ethanal. Ethanal is identified in the TD-GC-MS analyses and had equal peak areas in both samples, however it is not quantified because it was not present in the standard solution. Not all product ions in the SIFT-MS spectra could be identified, but similar patterns can be seen for several other compounds and in the mass spectra generated with NO+ and O2+.

4. Conclusions

In this research the established GC-MS technique was used for livestock air measurement in parallel with fast and innovative SIFT-MS. Both methods can distinguish between samples from different livestock buildings, which can be useful for appointing the source of odour nuisance and for comparison to olfactometric data. In the GC-MS chromatograms, 23 compounds were identified and quantified, of which the majority showed higher concentrations in pig stables compared to poultry houses. SIFT-MS shows to be a useful method for fast analysis of air samples from animal farming. A drawback is the possible overlap between compounds resulting in incomplete interpretation of the spectra. In further research, a database of parallel measurements will be built which will improve the knowledge about odorous VOC-levels in and emissions from intensive livestock breeding and will facilitate the interpretation of SIFT-MS spectra.

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