Membrane inlet mass spectrometry (MIMS) as a tool for evaluating biological air filters in agriculture

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ABSTRACT

Membrane inlet mass spectrometry (MIMS) is presented as a new tool for monitoring the removal efficiency of biofilters with respect to odour compounds. The MIMS technique is based on the separation of volatile chemicals and gases from an air stream by a thin silicone membrane adjacent to the ion source of a standard quadropole mass spectrometer. The vacuum conditions of the MS forces the separated compounds to diffuse through the membrane and evaporate in the ion source. The compounds are detected by MS by means of specific molecular ions or fragment ions.

It is possible to monitor a number of individual compounds or compound groups contributing to the odour nuisance of livestock facilities. 4-Methylphenol (p-cresol), skatol, indol, 4-ethylphenol, phenol and dimethyltrisulfide give rise to specific signals corresponding to molecular fragments. A variety of carboxylic acids can be detected by signals corresponding to three subgroups of this compound group. The sum of reduced organic sulphur compounds (ROS) are measured by a common signal. The contribution of individual sulphur compounds (mainly methanethiol and dimethyl sulphide) to ROS can be estimated from supplementary MS fragments. MIMS is not suitable for measuring ammonia and hydrogen sulphide for which other methods must be applied.

MIMS is suitable for continuous monitoring on-site and has been applied for evaluation of a number of biofilters in the Danish agricultural sector, primarily for treating ventilated air from pig barns.

1 INTRODUCTION

Odour nuisance is an increasing problem for the local population in many areas due to intensified livestock production. In order to maintain a cost-effective agricultural production in accordance with the local society, there is therefore a need for efficient odour abatement technologies. A number of technologies are proposed, developed and implemented, e.g. biofilters and chemical scrubbers. Testing, evaluating and optimizing such technologies require reliable and accurate methodologies for measuring odour and the efficiencies of odour abatement technologies. Traditionally, the efficiency of odour reduction has been measured by olfactometry based on the odour perception of a trained human panel. Olfactometry is of relevance because it is a direct measure of the actual physiological effect of odour mixtures. However, it is generally accepted that there is substantial uncertainty associated with the measurements. This is particularly a disadvantage in relation to technology optimization where small improvements thus cannot be identified with certainty.

Chemical measurements of odour compounds can in principle be carried out with great accuracy. Provided that the major odour compounds can be identified and the relationship between odour compounds and odour perception can be established with a reasonable statistical certainty, chemical measurements therefore has the potential to supplement and partly replace olfactometry.

Measurements based on gas chromatography with mass spectrometric detection (GC/MS) has been used to detect and identify odour compounds from manure and livestock facilities (Blunden *et al*., 2005; Hobbs *et al*., 1998; Schiffman *et al*., 2001).

Here, we present a related technique, membrane inlet mass spectrometry (MIMS) (Ketola *et al*., 1997; Ketola *et al*., 2002). Compared to GC/MS, MIMS is a direct measurement technique, which allows for on-line measurements of odour compounds. Examples of measurements include monitoring the efficiency of biofilters and the effect of cooling ventilation air.

2 MATERIALS AND METHODS

A mass spectrometer (Balzers, QMG 420) equipped with a membrane inlet consisting of a temperature controlled membrane (50 µm polydimethyl siloxane) and a stainless steel air intake was used for the measurements presented in this paper. An air pump was used to pass unfiltered air by the membrane at a flow rate of ~200 ml/min providing turbulent conditions near the membrane surface, which gives the most efficient uptake of volatile compounds. Odour compounds are sampled from the air by absorption into the membrane, and because of the low pressure inside the mass spectrometer compounds diffuse through the membrane and evaporate into the ion source of the mass spectrometer.

In order to monitor the efficiency of odour abatement technologies, a multiposition valve was used to multiplex between air influenced by the technology, reference air and background (clean) air. In case of a biofilter, for example, a measurement cycle consists of 1) clean air, 2) air sampled before the filter and 3) air sampled after the filter. The efficiency with respect to a certain compound is estimated from the background-subtracted signals before and after the filter, respectively.

3 RESULTS AND DISCUSSION

3.1 Basic studies of MIMS response to odour compounds

In Figure 1, a mass spectrum obtained by sampling the headspace of manure from a Danish pig farm is presented. The sample represents a concentrated odour sample compared to typical emission levels from pig farms and is useful for evaluating which compounds contribute to the main MIMS-signals.

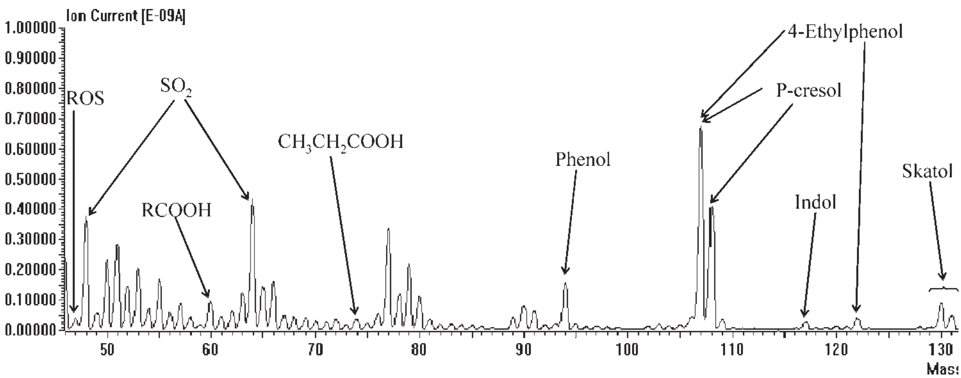

Figure 1. Assignment of MIMS-signals to odour compounds or groups of odour compounds. The x-axis is the mass/charge ratio (m/z) of the ions formed.

It can be seen from Figure 1, that several of the major MIMS-signals can be assigned to important odour compounds or structurally related groups of compounds. Some signals, e.g. from m/z 50 – 58 and from m/z 77 – 80 are less specific and therefore less useful for monitoring odour compounds. The composition of the sample was confirmed by GC/MS.

There are a number of carboxylic acids present in typical samples from pig facilities. These give rise to overlapping MIMS-signals at m/z 60, 73 and 74. Therefore carboxylic acids are mainly measured as groups of compounds according to these signals. Likewise, reduced organic sulphur compounds are detected by a common signal at m/z 47 corresponding to compounds containing the CH_3S- moiety, which mainly comprise methyl mercaptan, dimethyl sulphide and dimethyl disulphide. These sulphur compounds give rise to other MS-fragments which can be used to estimate the contributions of individual sulphur compounds to m/z 47. Other odour compounds, like skatol and indol, possess more specific MS signals.

The sensitivity of MIMS is compound specific and is related to the volatility and polarity of the compound and hence its ability to be absorbed into the non-polar membrane. Carboxylic acids, for example, are highly abundant (as quantified by GC/MS) but do not give rise to the largest MIMS signals due to their high polarity.

An important feature of MIMS is the linearity of the response as a function of concentration. In Figure 2, examples of calibration curves for carboxylic acids (RCOOH; the sum of carboxylic acids containing the mass spectrometric fragment with m/z 60) and p-cresol (4-methylphenol) are shown. The data in Figure 2 was obtained by injecting various amounts of a synthetic mixture of 10 important odour compounds into a Tedlar sampling bag and analyzing by MIMS. The concentration levels were selected in order to cover real-world concentration levels.

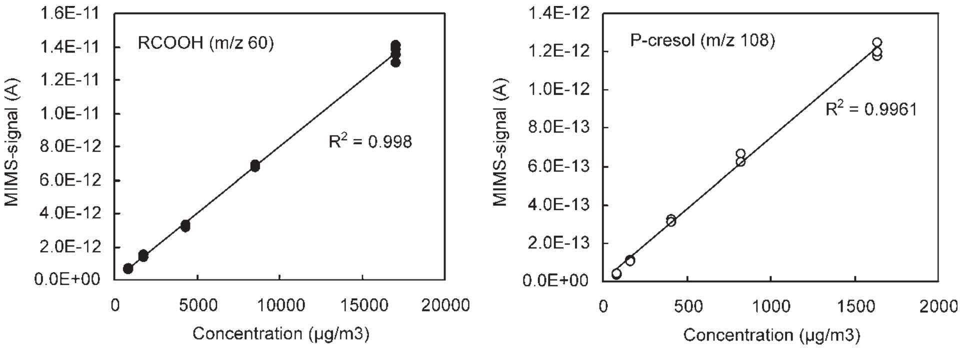

Figure 2. Calibration curves of RCOOH (carboxylic acids) and p-cresol. The straight curves are linear regression data.

3.2 Application of MIMS for monitoring odour reduction

An example of results from the application of MIMS for monitoring the efficiency of a biofilter is presented in Figure 3. The biofilter tested is a vertical cellulose pad biofilter with a relatively short residence time (< 1 second). Recirculated water is applied on top of the filter matrix and flows down mainly on the inlet side of the filter. It appears that the efficiency of the filter towards different compounds is quite stable, whereas there is more variation regarding the efficiency towards different types of compounds. P-cresol and carboxylic acids are efficiently removed, whereas organic sulphur compounds are less reduced and with much more variability in the results. These results are not surprising since it is a prerequisite for efficient removal that the odour compounds are absorbed into the aqueous phase of the biofilter. Organic sulphur compounds, such as dimethyl sulphide, are much less water soluble than carboxylic acids or p-cresol.

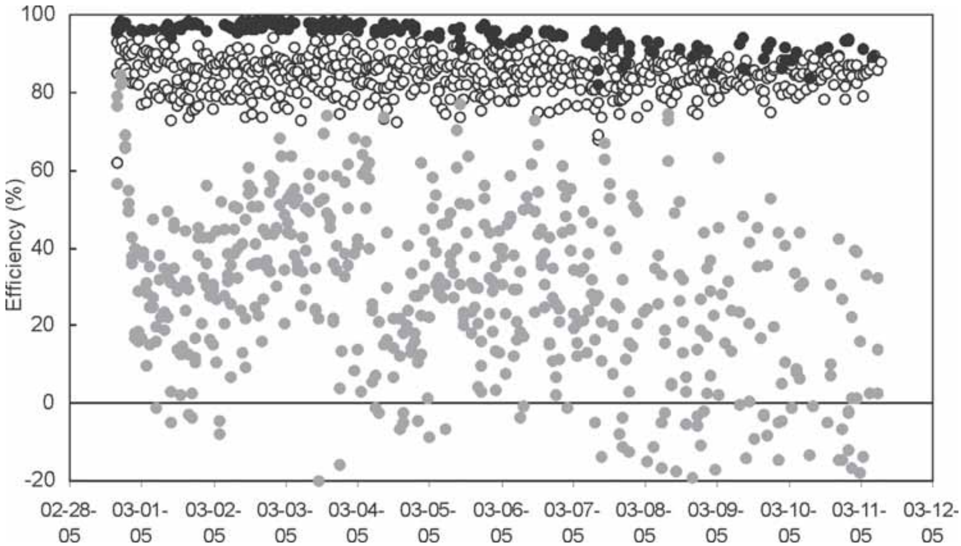

Figure 3. Biofilter efficiencies towards p-cresol (black circles), RCOOH (open circles) and reduced organic sulphur compounds (ROS; grey circles). Data from March 2005. The efficiency is estimated from the MIMS signals before and after the filter.

Another example is shown in Figure 4 and 5. In this case a vertical filter consisting of two filter walls placed inside a large bin (2.5x10m) was tested. The filtermaterial was light expanded clay aggregates (LECA©) with a filter thickness of 15 cm and a residence time of approximately 5 seconds. Air is added between the two filter walls and is humidified with spray nozzles. Water is normally recirculated but during the measurements presented here, water was frequently changed and clean water added to the system.

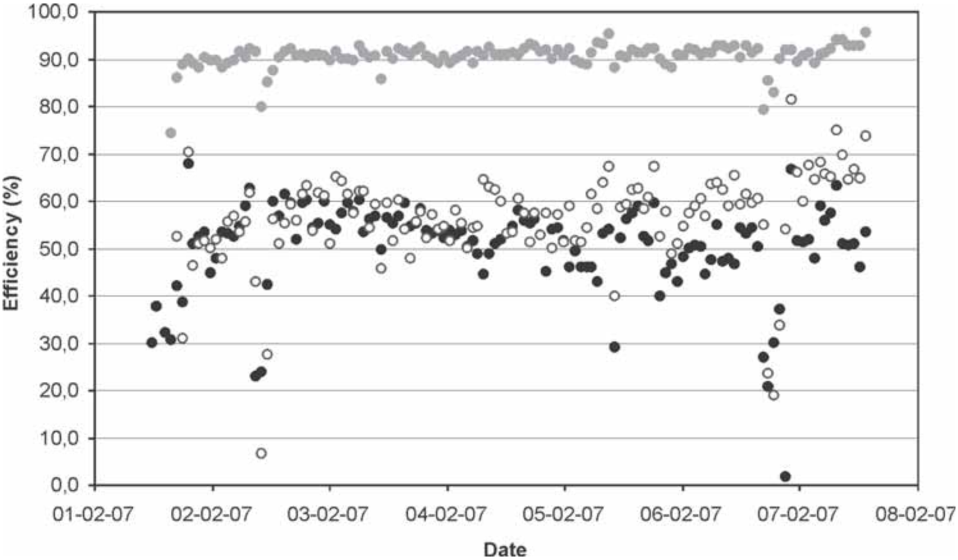

Figure 4. Biofilter efficiencies towards reduced organic sulphur compounds (ROS; black circles), dimethyl sulphide (open circles) and skatol (grey circles). Data from February 2007. The efficiency is estimated from the MIMS signals before and after the filter.

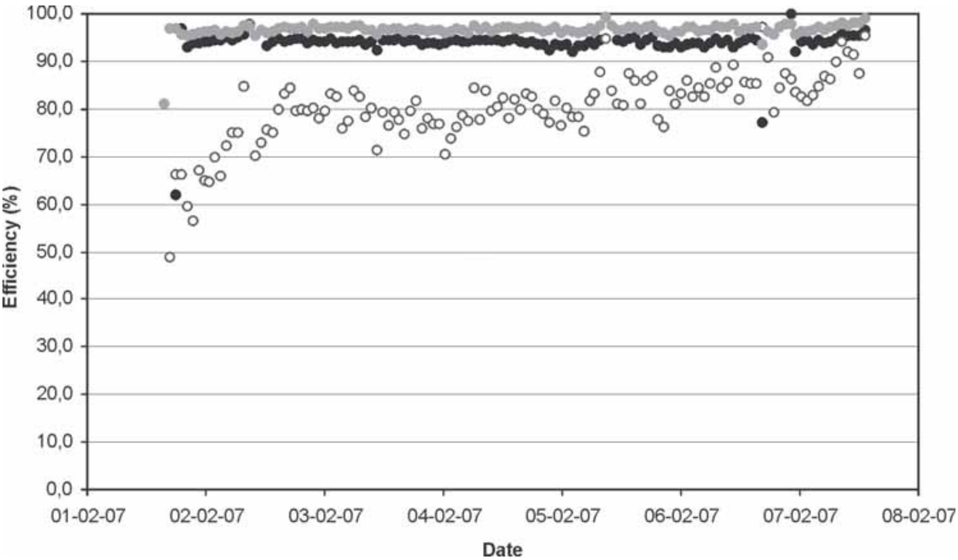

Figure 5. Biofilter efficiencies towards carboxylic acids (black circles), 4-ethylphenol (open circles) and p-cresol (4-methylphenol; grey circles). Data from February 2007. The efficiency is estimated from the MIMS signals before and after the filter.

Similar to other filters tested, water soluble odour compounds such as carboxylic acids and phenols are consistently removed efficiently (80-100 %). In the LECA© filter type, however, it is documented that organic sulphur compounds are also removed with an efficiency of ~40-60 %. This is most likely due to a longer residence time combined with relatively clean water used for wetting the filters.

3.3 Comparison with olfactometry

A dataset consisting of olfactometric measurements and MIMS-measurements were subject to multivariate statistical analysis in order to attempt to elucidate a statistical relationship between odour reduction observed by olfactometry and odour reduction predicted from MIMS-measurements. The analysis was based on 23 data points from 3 different types of odour abatement technologies and resulted in a correlation coefficient (R^2) of 0.56. Although this is statistically significant ($P<0.001$), it is also clear that a more extensive dataset is needed for this purpose. Part of the difficulty with this approach is the inherent uncertainty associated with olfactometry.

4 CONCLUSIONS

Membrane Inlet Mass Spectrometry (MIMS) has been tested as a technique for continuous measurements of odour compounds in or emitted from pig facilities. MIMS is able to detect a range of compounds either as individual compounds or as groups of structurally related compounds. MIMS has been demonstrated to be sufficiently robust to be used on-site and to carry out measurements unattended for extended periods of time. Examples of MIMS-measurements include monitoring of the efficiencies of biofilters installed in pig facilities. A tentative comparison of MIMS with olfactometry indicates a potential for predicting odour reduction from MIMS-measurements, although more data is needed to confirm this.

5 ACKNOWLEDGEMENTS

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