SIFT-MS for livestock emission characterization: application of similarity coefficients

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SIFT-MS (selected ion flow tube mass spectrometry) is used to construct libraries for emissions from pig and broiler farming activities. Libraries are based on full mass scans in m/z range 15 to 250 using H_3O^+, NO^+ and O_2^+ precursor ions. The so-called 'Yule coefficient', which represents one algebraic number as singular descriptor for similarity between samples, is chosen as the best tool to identify similarities between a given sample and library data. The proposed methodology, which is simple and straightforward, is successfully applied on data from different experimental sampling campaigns. From an engineering point of view, it is considered to be a promising technique to evaluate whether a sample corresponds to one of the catalogued library data sets.

1. Introduction

Odour nuisance related to intensive livestock breeding is an emerging concern in areas with a high population density (Melse et al., 2009). Volatile organic compounds, VOC, are generated by microbial conversions in the gastrointestinal tract of farm animals, e.g., in the litter, and in their excretions (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 the key VOC emitted from swine houses (Trabue et al. 2011) and poultry excretions (Trabue et al., 2010). Identification and quantification of offensive odorants is necessary for treatment and prevention of odorous emissions (Capelli et al., 2008; Kim and Park, 2008; Bianchi et al., 2010; Boeker et al., 2010; Koziel et al., 2010).

However, until present no general method exists to provide a fast evaluation of livestock VOC production. In most of the research conducted so far TD-GC-MS (thermal desorption gas chromatography mass spectrometry) is used, which involves sorptive sampling and possible loss of unstable and highly volatile compounds.

In this paper, selected ion flow tube mass spectrometry (SIFT-MS) is used as a fast and convenient method to analyse gas phase samples, based on full mass scans in the m/z range 15 to 250, using H_3O^+, NO^+ and O_2^+ as precursor ions, rather than the comparison of calculated concentrations. The SIFT-MS technique has a myriad of applications, such as real-time analysis of exhaled breath analysis (Španěl P. and Smith, 2011), rapid quantification of components in air such as xylene and toluene (Ross and Vermeulen, 2007) and real-time monitoring of the atmosphere (Prince et al., 2010).

The concept of the so-called 'similarity coefficient' is introduced. This coefficient represents one algebraic number as singular descriptor for similarity between samples, i.e., the outcome of the comparison can be condensed into one value. The samples are constituted from SIFT-MS full mass scans.

2. Material and methods

2.1 Field sampling
Gas samples were taken at a test facility of the Institute for Agricultural and Fisheries Research, in Merelbeke, Belgium. The emissions from broiler chicken and pig houses were recorded during two sampling campaigns on March 4th and June 7th 2011. In each livestock building, respectively two and five air samples were collected above the animals at 1.5 m height within 1.8 ks in 2 L Nalophane[®] bags during the campaign in March and June. The average temperature in the buildings was 21 ± 4 °C. Analysis with the SIFT-MS of the Nalophane[®] bags, see section 2.2, was performed within three hours after taking the samples.

2.2 SIFT-MS analysis
Gas samples were analyzed by the so-called SIFT-MS technique. This technique has been described in numerous publications (Smith and Španěl, 2005; Španěl et al., 2006), so only a brief summary is given. In a Voice 200[®] apparatus precursor ions H_3O^+, NO^+ and O_2^+ are generated in a microwave discharge ion source. A specific precursor ion mass is selected by an upstream quadrupole mass filter and then injected as selected ion species into fast-flowing He carrier gas in a flow tube. The sample is continuously injected in the flow tube and ion reactions of the selected precursor ion and the admitted gas phase molecules take place.

Determination of the counts per second, CPS, of the precursor ions and the product ions, resulting from the reaction of the former with gas phase molecules, 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 gas pressure in the flow tube is 20 Pa at room temperature.

Each of the samples per livestock is analyzed three times by SIFT-MS, giving rise to six and fifteen data sets per livestock for the campaigns in March and June respectively. The data from the sampling campaign in June were averaged, see Eq. (1), and the corresponding standard deviations, σ, were calculated via Eq. (2), in which $F_{i,j,k}$ represents the CPS of the individual product ion i for data set j, j = 1…15, corresponding to precursor ion k, k = 1…3. Hence, each averaged data set has three subsets, corresponding to the product ions, generated by the three precursor ions H_3O^+, NO^+ and O_2^+.

$$\mu_{i,k} = \frac{1}{15} \cdot \sum_{j=1}^{15} F_{i,j,k} \tag{1}$$

$$\sigma_{i,k}^2 = \frac{1}{14} \cdot \sum_{j=1}^{15} \left(F_{i,j,k} - \mu_{i,k} \right)^2 \tag{2}$$

With respect to the followed procedure in this paper, the data treatment, as presented in this section, results in two 'library' data sets originating from the sampling campaign in June, which are considered as characteristic for the broiler chicken and pig livestock emissions. On the other hand, the data from the sampling campaign in March are considered as individual measurements, which are used to be compared to the constructed libraries, see section 3.

2.3 Data analysis
Two data sets can be compared based on a singular descriptor, i.e., the outcome of the comparison can be condensed into one value, indicating the similarity or the dissimilarity between the two given data sets. This descriptor is a so-called 'similarity coefficient and in this work, the Yule coefficient (Yule, 1912), see Eq. (3), is chosen to compare data sets:

$$S_Y = \frac{a\,d - b\,c}{a\,d + b\,c} \qquad\qquad (3)$$

A test sample, say A, can be compared to a library set, say B, constituted from average values for each product ion mass i, B_i, and corresponding standard deviation, σ_i, see section 2.2. If both CPS are zero for product ion i, they are considered as 'no match' and subsequently the decision variable d_i is set unity, see Table 1. If the CPS for product ion i in sample A is zero then either $A_i \in [B_i - \sigma_i, B_i + \sigma_i]$ and a_i is set unity, or $A_i \notin [B_i - \sigma_i, B_i + \sigma_i]$ and a_i is zero and c_i is unity, see Table 1. If the CPS for product ion i in sample A is nonnegative and the corresponding CPS in B is zero, then b_i is set unity. If both CPS are nonnegative for product ion i, the decision variable a_i is set unity in the case $A_i \in [B_i - \sigma_i, B_i + \sigma_i]$. If $A_i \notin [B_i - \sigma_i, B_i + \sigma_i]$, b_i and c_i are set unity, whereas a_i and d_i are zero.

For the calculation of the Yule similarity coefficient the number of twofold matches, a, the singular matches, b and c, and no matches, d, are calculated out of the number of total possibilities, i.e., the total number of product ions, n = 236. For a, b, c and d, see Eq. (3), hold $a = \sum_{i=1}^{n} \delta(a_i, 1)$,

$b = \sum_{i=1}^{n} \delta(b_i, 1)$, $c = \sum_{i=1}^{n} \delta(c_i, 1)$ and $d = \sum_{i=1}^{n} \delta(d_i, 1)$ in which $\delta(y_i, 1)$ is the Krönecker symbol, which

is set to unity if $y_i = 1$ and equals zero otherwise.

It has to be stressed that the calculation of similarity coefficients serves one purpose: revealing similarity between two given sets by means of one and only one algebraic outcome, based on full mass scan SIFT-MS data. No specific attention has been paid to the detailed statistical interpretation of these coefficients.

Table 1: Decision values for a_i, b_i, c_i and d_i. A_i = (A)$_i$, B_i = (B)$_i$ and σ_i is the standard deviation on B_i, in this application based on fifteen replicate measurements from the sampling campaign in June, see sections 2.1 and 2.2.

Condition	a_i	b_i	c_i	d_i	Remark
$A_i = B_i = 0$	0	0	0	1	
$A_i = 0$ and $B_i > 0$	1	0	0	0	$A_i \in [B_i - \sigma_i, B_i + \sigma_i]$
	0	0	1	0	$A_i \notin [B_i - \sigma_i, B_i + \sigma_i]$
$A_i > 0$ and $B_i = 0$	0	1	0	0	
$A_i > 0$ and $B_i > 0$	1	0	0	0	$A_i \in [B_i - \sigma_i, B_i + \sigma_i]$
	0	1	1	0	$A_i \notin [B_i - \sigma_i, B_i + \sigma_i]$

3. Results

Figure 1 shows averaged experimental SIFT-MS spectra, using the experimental data from the campaign in June, see section 2.1, for pig (hatched bars) and broiler chicken (black bars) livestocks. Averages and error bars are obtained via Eqs. (1) and (2). Only product ions with CPS > 1 kHz are included. If the m/z value only appears in one data set an additional '*' is added. It can be observed from Figure 1 that thirty-one m/z values, are significantly different and that seventeen m/z values are statistically not distinguishable. Moreover, m/z 17, 30, 35, 43, 64, 74, 83, 85, 95, 97, 117 and 121 are only significantly present in the spectrum of pig sample, reacting with precursor ion H_3O^+, whereas m/z 90 is only significantly present in the spectrum of broiler chicken. Similar results for the NO^+ and O_2^+ precursor ions are acquired (not shown for conciseness). These observations, as given in Figure 1, and the corresponding interpretation with respect to the decision values, see Table 1, are taken along the calculation of the Yule similarity coefficient, see section 2.3.
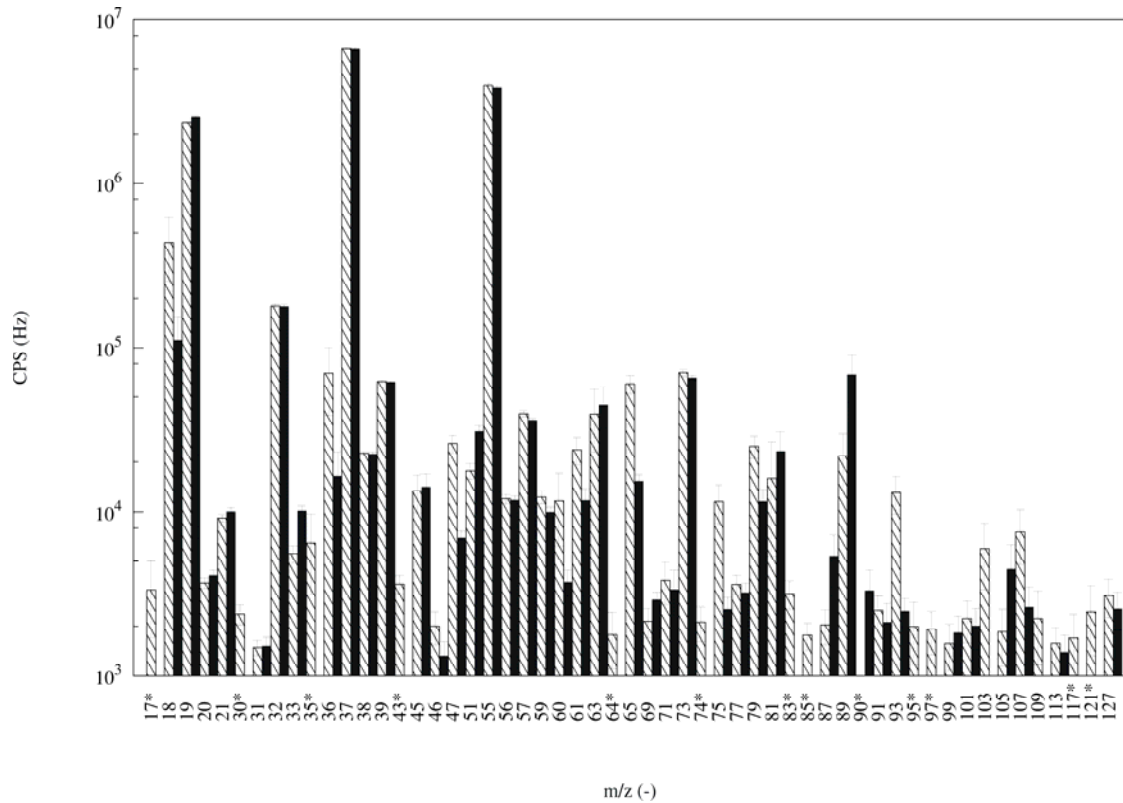
Figure 1: Averaged mass spectra obtained by SIFT-MS for pig ( ) and broiler chicken ( ) livestocks using precursor ions (a) H_3O^+; (b) NO^+; (c) O_2^+. Averages and corresponding standard deviations are calculated by Eqs. (1) and (2), using the data from the sampling campaign in June, see section 2.1.
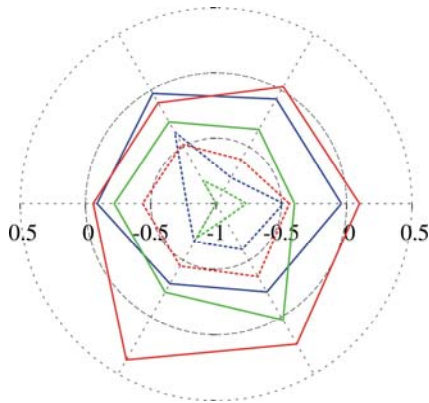

Figure 2: Yule similarity coefficient, calculated by Eq. (3), when six broiler chicken livestock data sets from the sampling campaign in March are compared to the constructed libraries of broiler chicken (full line) and pig livestock (dashed line), see section 2.1, for the precursor ions H_3O^+ (blue), NO^+ (red) and O_2^+ (green). Each of the six radii corresponds to one of the six individual broiler chicken data sets of the March sampling campaign.

The proposed methodology was checked by experimental data, obtained from the sampling campaign in March, see section 2.1. Figure 2 gives the calculated Yule similarity coefficient when broiler chicken livestock data are compared to the libraries of broiler chicken (full line) and pig livestock (dashed lines) for the precursor ions H_3O^+, (blue), NO^+ (red) and O_2^+ (green). It is observed that the dashed line polygon lies fully within the full line polygon, indicating that the given calculation method points out the preference in similarity of the given sample with respect to an applied library data set. Based on the specific construction of the given example, this result is not surprising, but it shows that the presented methodology works properly.

4. Conclusions

SIFT-MS is used as a fast and convenient apparatus to link an unknown sample to a set of library data samples, based on full mass scans in m/z range 15 to 250 using H_3O^+, NO^+ and O_2^+ precursor ions. Library samples were based on pig and chicken livestock emissions. The Yule coefficient was chosen as the best tool to identify similarities between a given sample and a library data set. The proposed methodology, which is simple and straightforward, is successfully applied on data from different experimental sampling campaigns, showing good prediction properties. From an engineering point of view, it is considered to be a promising tool to evaluate whether a sample corresponds to one of the catalogued library data sets.

Acknowledgements

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