Characterization and Quantification of Livestock Odorants using Sorbent Tube Sampling and Thermal Desorption coupled with Multidimensional Gas Chromatography–Mass Spectrometry–Olfactometry

A.S. Leaflet R2438

Shicheng Zhang, postdoctoral research associate of ABE;
Lingshuang Cai, assistant scientist of ABE;
Jacek A. Koziel, associate professor of ABE, CCEE

Summary and Implications

Characterization and quantification of livestock odorants is one of the most challenging analytical tasks because odor-causing gases are very reactive, polar and often present at very low concentrations in a complex matrix of less important or irrelevant gases. The objectives of this research is to develop a novel analytical method for characterization of the livestock odorants including their odor character, odor intensity, and hedonic tone and further quantitative analysis of the key odorants responsible for livestock odor emissions. Sorbent tubes packed with Tenax TA were employed for sampling. The automated one-step thermal desorption coupled with multidimensional gas chromatography-mass spectrometry-olfactometry system was developed for simultaneous chemical and odor analysis. Fifteen odorants identified from different livestock species operations are quantified. In addition, odor character, odor intensity and hedonic tone associated with each of the target compounds are also analyzed. The method developed in this research is being used on a multistate, multispecies project focused on quantifying odor and chemical analysis of odor.

Introduction

Odor emissions from livestock facilities affect air quality in surrounding communities. Many volatile organic compounds (VOCs) have been identified, including acids, alcohols, aldehydes, amines, volatile fatty acids (VFAs), hydrocarbons, ketones, indoles, phenols, nitrogen-containing compounds, sulfur-containing compounds, and others (Lo et al, 2008; Schiffman et al, 2001). Compounds contributing to the livestock odor have been identified, such as VFAs, *p*-cresol, phenol, 4-ethylphenol, indole, skatole, and sulfur-containing compounds (Koziel et al, 2006; Bulliner et al, 2006; Cai et al, 2006; Keener et al, 2002; Oehrl et al, 2001).

Livestock odor can be measured using dynamic forced-choice olfactometry, which relies on air sample collection in bags for subsequent evaluation with panelists. This method allows for quantification of the overall odor. However, it does not allow for identification of individual odorous compounds that might be significant to the overall odor controlling. Gas chromatography (GC)-mass spectrometry (MS)-olfactometry offers the advantages of combining sensory assessment with the identification and quantification of compounds. Some researchers have reported using this method for identification of odorous compounds from swine facilities (Koziel et al, 2006; Bulliner et al, 2006; Cai et al, 2006; Keener et al, 2002). Rabaud et al (2002) used thermal desorption-GC-olfactometry/MS to identify and quantify odor compounds from a dairy. However, relatively few references exist on the relationship between livestock VOC concentrations and the odor character (Zahn et al, 2001a and 2001b; Greenman et al, 2005).

The focus of this research is to develop an odor characterization method for specific livestock odorants including their odor character, odor intensity, and hedonic tone and develop quantitative analysis method for the key odorous compounds responsible for livestock odor emissions using TD-MDGC-MS-O system.

Materials and Methods

Simultaneous chemical and sensory analyses of livestock odorants were completed using the thermal desorption- multidimensional GC–MS-olfactometry (TD-MDGC–MS–O) system. The thermal desorption (TD) system is using a Model 3200 automated thermal desorption inlet for Agilent 6890 GC developed by Microanalytics based on a PAL® autosampler. The unique design of the Model 3200 system allows it to utilize a single-step desorption and sample introduction method that eliminates cryotrapping. This design allows the Model 3200 to desorb samples directly into the column interface, eliminating many of the problems associated with dual or two-step desorption such as those associated with the presence of trapped water in sorbent tubes. Multidimensional GC–MS–O (from Microanalytics, Round Rock, TX, USA) was used for all air samples analysed. The system integrates GC–O with conventional GC–MS (Agilent 6890N GC/5973 MS from Agilent, Wilmington, DE, USA) as the base platform with the addition of an olfactory port and flame ionization detector (FID). The system was equipped with two columns in series connected by a Dean's switch. The non-polar pre-column was 12 m, 0.53 mm i.d.; film thickness, 1 μm with 5% phenyl methylpolysiloxane stationary phase (SGE BP5) and operated with constant pressure mode at 8.5 psi. The polar analytical column was a 25 m×0.53 mm fused silica capillary column coated with poly (ethylene glycol) (WAX;

SGE BP20) at a film thickness of 1 μm. The column pressure was constant at 5.8 psi. Both columns were connected in series.

System automation and data acquisition software were MultiTraxTM V. 6.00 and AromaTraxTM V. 7.02 (Microanalytics, Round Rock, TX, USA) and ChemStationTM (Agilent, Santa Clara, CA, USA). The general run parameters used were as follows: injector, 260 °C; FID, 280 °C; column, 40 °C initial, 3 min hold 7 °C min−1, 220 °C final, 10 min hold; carrier gas, GC-grade helium. The GC was operated in a constant pressure mode where the mid-point pressure, i.e., pressure between pre-column and column, was always at 5.8 psi and the heart-cut sweep pressure was 5.0 psi. The MS scan range was 33-280 amu. Spectra were collected at 6 scans s−1 using scan and selected ion monitoring (SIM) simultaneously. Electron multiplier voltage was set to 1000 V. MS tuning was performed using the default autotune setting using perfluorotributylamine (PFTBA) weekly.

Human panelists were used to sniff separated compounds simultaneously with chemical analyses. Odor caused by separated VOCs was evaluated with a 64-descriptor panel, intensity scale, and hedonic tone scale in Aromatrax software.

Results and Discussion

Using TD-GC-MS-O system, quantification of odorants concentration and odor intensity could be performed simultaneously. After the compounds were separated via GC column, the isolated compounds were split into the mass detector and sniff port with the split ratio of 1:2. The concentration of the compounds could be quantified through the mass detector, and the odor character, intensity, duration time, and hedonic tone could be identified and quantified via the sniff port by the panelist. The standard sample included 15 typical odorous VOCs. With the increase of the retention time, the start time of an odor event delayed much longer, up to 2.85 min. And the duration time also increased with the increase of retention time, which was called “lingering” of odor event. As a result, some odor events overlaid each other, especially for the compounds with retention times longer than 18 min. In order to quantify the odor event accurately, it is important to separate each odor event correctly.

For compounds with longer retention times, especially 2-aminoacetophenone, indole and skatole, the GC-MS-O analysis of single compound was performed. It could be found that the odor events for indole and skatole overlaid together, and the odor events for 4-ethylphenol and 2-aminoacetophenone overlaid together. The odor events for other compounds were separated pretty well. The duration time and start time of odor events for indole and skatole are separately of 30.60 min and 3.33 min, and of 31.66 min and 3.47 min. In order to keep the comparability of different experiments, during the analysis of mixed compounds or the real sample, the odor event for indole would be stopped and the odor event for skatole would be started at 32 min. The same thing for 4-ethylphenol and 2-aminoacetophenone, the duration time and start time of the odor events for 4-ethylphenol and 2-aminoacetophenone skatole are separately of 25.17 min and 2.48 min, and of 26.30 min and 1.51 min. So, the odor event for 4-ethylphenol was stopped and the odor event for 2-aminoacetophenone was started at 26.50 min. The peaks of indole and 4-ethylphenol were a little bit slim and the duration times were also shorter. If this analysis method keeps constant for all the experiments, the data should be comparable.

Based on above methods, sorbent tubes adsorbed of the standard solution with different concentration including 15 VOCs were analyzed using the TD-GC-MS-O system. We investigated the correlation of odor intensities to odorants mass in one tube. For the TD-GC-MS-O system used in this work, the make-up air flow rate is constant, so the correlation of odor intensities to odorants mass should be similar with that of odor intensities to odorants concentration. For many odorants used in the food and fragrance industry, there is a linear relationship between log olfactory intensity reported by the individual and the air concentration of the odorant present in air (Turk and Hyman, 1991). Zahn et al. (2001) also reported the total air concentration of VOCs emitted from swine manure correlate well with the log stimulus intensity. This relationship between perceived olfactory stimuli and intensity of sensation is referred to as the fundamental psychophysical law (Stevens, 1957). We found that the mass of each VOCs correlate well with the log stimulus intensity. All of the correlation coefficients (R^2) are greater than 0.74, and 10 correlation coefficients are greater than 0.90. Therefore, this confirmed with the fundamental psychophysical law.

Acknowledgements

The authors would like to thank the U.S. Department of Agriculture for funding this research.

Table 1 Typical odorous compounds quantified in this study, linear range and method detection limits (MDL).

	Compounds	MW	Retention time (min)	MS Ion(1)	Linear range (ng)	MDL (ng)
1	Acetic Acid	60.05	12.78	45, ***60***, 15	0.2183~1944.3	0.2183
2	Propanoic Acid	74.08	14.4	***74***, 28, 48	0.2350~2092.6	0.235
3	Isobutanoic Acid	88.11	14.91	***43***, 27, 73	0.2847~2535.5	0.2847
4	Butanoic Acid	88.11	16.00	***60***, 27, 73	0.2009~1788.9	0.2009
5	Isopentanoic Acid	102.13	16.73	***60***, 43, 87	0.1956~1741.8	0.1956
6	Pentanoic Acid	102.13	17.88	***60***, 73, 27	0.2878~2563.3	0.2878
7	Hexanoic Acid	116.16	19.68	***60***, 73, 27	0.3066~2730.3	0.3066
8	Guaiacol	124.14	20.06	***109***, 124, 81	0.3462~3083.3	0.3462
9	Heptanoic Acid	130.19	21.38	***60***, 73, 41	0.0871~775.52	0.0871
10	Phenol	94.11	22.13	***94***, 66, 39	0.1951~1737.5	0.1951
11	*p*-cresol	108.14	23.28	***107***, 77, 90	0.1004~894.6	0.1004
12	4-Ethylphenol	122.17	24.61	***107***, 122, 77	0.0816~726.84	0.0816
13	2-Aminoacetophenone	135.16	25.41	***120***, 135, 92	0.1296~1154.5	0.1296
14	Indole	117.15	28.23	***117***, 90, 63	0.0621~552.97	0.0621
15	Skatole	131.18	28.88	***130***, 77, 103	0.0498~443.27	0.0498

Note: (1) The ions shown in bold italic type were used for quantification.

Figure 1 Thermal desorption system and multidimensional GC-MS.