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Citation: *AIP Conf. Proc.* **1137**, 231 (2009); doi: 10.1063/1.3156514

View online: <http://dx.doi.org/10.1063/1.3156514>

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Field Air Sampling and Simultaneous Chemical and Sensory Analysis of Livestock Odorants with Sorbent Tube GC-MS/Olfactometry

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Abstract. 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 objective of this research was to develop a novel analytical method for characterization of the livestock odorants including their odor character, odor intensity, and hedonic tone and to apply this method for quantitative analysis of the key odorants responsible for livestock odor. Sorbent tubes packed with Tenax TA were used for field sampling. The automated one-step thermal desorption module coupled with multidimensional gas chromatography-mass spectrometry/olfactometry system was used for simultaneous chemical and odor analysis. Fifteen odorous VOCs and semi-VOCs identified from different livestock species operations were quantified. Method detection limits ranges from 40 pg for skatole to 3590 pg for acetic acid. In addition, odor character, odor intensity and hedonic tone associated with each of the target odorants are also analyzed simultaneously. We found that the mass of each VOCs in the sample correlates well with the log stimulus intensity. All of the correlation coefficients (R^2) are greater than 0.74, and the top 10 correlation coefficients were greater than 0.90.

Keywords: GC-O, livestock, odor, field sampling.

PACS: 01.30.Cc

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^{1, 2}. Compounds contributing to the livestock odor have been identified, such as VFAs, p-cresol, phenol, 4-ethylphenol, indole, skatole, and sulfur-containing compounds³⁻⁷.

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 facilities³⁻⁷. Rabaud et al⁸ 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 character⁹⁻¹¹.

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.

EXPERIMENTAL AND METHODS

2.1 Thermal Desorption- Multidimensional GC–MS/Olfactometry (TD-MDGC–MS/O) system

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 equipped with two columns in series connected by a Dean's switch. The non-polar pre-column was 12m, 0.53mm i.d.; film thickness, 1 μ m with 5% phenyl methylpolysiloxane stationary phase (SGE BP5) and operated with constant pressure mode at 8.5 psi. The polar analytical column was a 25m \times 0.53 mm fused silica capillary column coated with poly (ethylene glycol) (WAX; SGE BP20) at a film thickness of 1 μ m. 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 $^{\circ}$ C; FID, 280 $^{\circ}$ C, column, 40 $^{\circ}$ C initial, 3 min hold, 7 $^{\circ}$ C min⁻¹, 220 $^{\circ}$ 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 Aromatrx software.

2.2 Sampling

Sampling sorbent tubes were constructed of 304 stainless steel and then double passivated with a proprietary process. They were packed with 65 mg Tenax TA. Silanized glass wool plugs and stainless steel screens were placed in the two ends of the tubes to hold the sorbent.

Before the first use, sorbent tubes were conditioned by thermal cleaning (260 $^{\circ}$ C for 5 hrs) under a flow rate of nitrogen of 100 mL min⁻¹. For subsequent uses, pre-conditioning at 260 $^{\circ}$ C for 30 min was applied.

Field air samples were taken using a SKC pump with the set flow rate of 70 mL min⁻¹ for 1hr, were stored at 4 $^{\circ}$ C, and were analyzed within 7 days. The sampling flow rates were detected on-line using a Bios DryCal digital flow meter.

2.3 Standards and Calibration

Fifteen compounds were selected as the target compounds for this work. The selection was based on the previous studies relative to typical odorous volatile organic compounds emitted from livestock facilities (shown in Table 1)^{1, 3-7}. Sulfur VOCs were not quantified due to the limitations of Tenax TA sorbent. Standard solutions were prepared by diluting stock standard solutions in methanol and were stored at 4 $^{\circ}$ C in dark. Stock standard solutions of VFAs and phenolics were prepared by adding certain weights of neat chemicals in a 40 mL pre-cleaned vial, and then filled the vial with a certain weight of methanol. Response factors for odorants were determined by direct injection of 1.0 μ L of standard solution onto the GC column and measuring recovery of each odorant.

For sorbent tube analysis, 5 μ L or 10 μ L of the standard solution was spiked into a sorbent tube using an ATISTM Adsorbent Tube Injector System (Supelco). A nitrogen flow of 50 mL min⁻¹ for 5 min with the block heater temperature of 75 $^{\circ}$ C was needed to transfer the target odorants onto the sorbent tubes.

RESULTS AND DISCUSSION

Using TD-MDGC-MS/O system, quantification of odorants concentration and odor intensity was performed simultaneously. Target compounds were separated in GC column and isolated compounds were split into mass detector and sniff port with the split

ratio of 1:3. The concentration of the compounds was quantified with the mass detector, and the odor character, intensity, duration time, and hedonic tone was identified and quantified via the sniff port by the panelist (Table 2). Figure 1 shows the chromatogram and aromagram of a standard sample with 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.

TABLE 1. Summary of target odorous compounds quantified in this study, with the method linear range, and method detection limits (MDL).

No.	Compounds	MW	Retention time (min)	MS Ion ⁽¹⁾	Linear range (ng)	MDL (ng)
1	Acetic Acid	60.05	12.78	45, 60 , 15	1.31-1135.54	3.59
2	Propanoic Acid	74.08	14.4	74 , 28, 48	1.39-1202.28	0.57
3	Isobutyric Acid	88.11	14.91	43 , 27, 73	1.28-1108.45	0.30
4	Butanoic Acid	88.11	16.00	60 , 27, 73	1.26-1089.11	0.38
5	Isopentanoic Acid	102.13	16.73	60 , 43, 87	0.99-860.84	0.40
6	Pentanoic Acid	102.13	17.88	60 , 73, 27	1.97-1710.08	0.82
7	Hexanoic Acid	116.16	19.68	60 , 73, 27	2.08-1802.93	0.87
8	Guaiacol	124.14	20.06	109 , 124, 81	0.74-637.90	0.03
9	Heptanoic Acid	130.19	21.38	60 , 73, 41	2.28-1976.07	1.08
10	Phenol	94.11	22.13	94 , 66, 39	1.35-1175.45	0.14
11	<i>p</i> -cresol	108.14	23.28	107 , 77, 90	0.73-640.52	0.05
12	4-Ethylphenol	122.17	24.61	107 , 122, 77	0.69-601.50	0.06
13	2-Aminoacetophenone	135.16	25.41	120 , 135, 92	0.88-764.64	0.08
14	Indole	117.15	28.23	117 , 90, 63	0.71-619.87	0.03
15	Skatole	131.18	28.88	130 , 77, 103	0.71-615.09	0.04

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

TABLE 2. Sensory analysis of typical standard solution

No.	Compound	Mass (ng)	Odor Character	Odor Intensity (%)	Hedonic Tone	RSD (%)
1	Acetic Acid	149.7	Acidic	30	-2	2.16
2	Propanoic Acid	161.1	Fatty acid, Body odor	30	-2	5.72
3	Isobutyric Acid	195.2	Body odor, Fatty acid	30	-2	3.03
4	Butyric Acid	137.7	Body odor, Fatty acid	50	-2	1.84
5	Isovaleric Acid	134.1	Body odor, Fatty acid	50	-2	4.25
6	Valeric Acid	197.4	Body odor, Acidic, Spicy	30	-2	9.55
7	Hexanoic	210.2	Acidic, Spicy	50	-3	9.79
8	Guaiacol	59.7	Burnt, Medicinal, Phenolic	30	-2	3.70
9	Heptanoic	237.4	Acidic, Spicy	50	-3	7.35
10	Phenol	133.8	Burnt, Phenolic	10	-1	0.57
11	<i>p</i> -cresol	68.9	Barnyard, Medicinal, Phenolic	30	-2	3.67
12	4-Ethylphenol	56.0	Burnt, Phenolic	30	-2	3.68
13	2-Aminoacetophenone	88.9	Taco Shell, Medicinal, Phenolic, Sweet	30	-1	2.05
14	Indole	42.6	Medicinal, Taco Shell, Barnyard, Sweet	30	-2	3.89
15	Skatole	34.1	Taco Shell, Medicinal, Sweet, Barnyard	30	-2	2.81

Method detect limit (MDL) was determined applying the U.S. EPA methodology¹². The MDLs were defined as the minimum concentration of a substance that can be measured and reported with 99% confidence when the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The MDLs for our method were listed in Table 1, which were

generally lower than those reported in other similar studies^{13, 14}.

Precision study was conducted by consecutive analysis of 3 tubes spiked with the same amount of a standard work solution. Values of repeatability (% relative standard deviation values) are reported in Table 2. All of the odorants showed repeatabilities <20% that accomplished US EPA performance criteria¹⁵. To examine odorants breakthrough, two

tubes were connected in series into the standards spiking system. Individual analysis of each tube showed that no significant breakthrough (measured as % odorant in the back tube) was observed for most of the standard odorants. Only some percentages of breakthrough were observed for low molecular compounds: acetic acid, propionic acid, and isobutanoic acid. This is due to the weak adsorbability of Tanx TA to low molecular compounds.

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 air¹⁶. Zahn et al^{9,10} 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 law¹⁷. 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 the top 10 correlation coefficients were greater than 0.90. Therefore, this confirmed with the fundamental psychophysical law.

CONCLUSIONS

The TD-MDGC-MS/O system could be used to estimate concentrations of VFAs and phenolic compounds associated with CAFOs odorous issue. Odor character, odor intensity, and odor hedonic tone can be assessed for separated target compounds simultaneously with chemical analyses. Concentrations of odorous compounds correlated well with the log stimulus intensity.

ACKNOWLEDGMENTS

The authors would like to thank the USDA for supporting this work via following grants: USDA-CSREES grant # 2005-35112-15336 "Odor emission and chemical analysis of odorous compounds from animal buildings" and USDA-CSREES grant # 2005-35112-15368 "Mass transfer modeling validation for gas and odor emissions from manure storages and lagoons".

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