Assessment of Direct Headspace Analysis of Broiler Chicken Litter Odorants

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As population growth has continued in Australia, poultry production has increased to supply high quantities of chicken meat to consumers. Suburbia encroachment on rural landscapes has resulted in increasing odour complaints from local residents. The aim of this study is to develop a reliable and robust methodology to identify and characterise odorant variations from broiler litter material utilising headspace sampling combined with thermal desorption, gas chromatography – mass spectrometry and olfactory detection. This combined sensory/chemical analysis has identified major odorants including reduced sulfurs, ketones, carboxylic acids, terpenes and alcohols. The knowledge gained from this study will assist in developing effective odour abatement and mitigation techniques to reduce odour impact to local receptors.

1 Introduction

In the past 40 years, the Australian meat chicken (broiler) production has expanded extensively to meet the growing consumers' demand. Generally, broiler chickens are grown on thick bedding material spread on the floor of mechanically ventilated tunnel sheds over 7-9 weeks. These intensive livestock practices must ensure minimal nuisance generation to the surrounding population. However, due to emerging urban infringement in the rural environment, intensive livestock facilities have become a target for odour complaints (Powers et al., 2005). Odours are emitting from the chicken sheds due to aerobic and anaerobic microbial activities within the litter and from the animals (Mackie et al., 1998; Lacey et al., 2004; Rappert and Muller 2005). In most cases, the offensive characteristics of odour increase with the accumulation of waste over the chickens growth period, resulting in the local population (i.e. receptors) living near the livestock buffer zone reporting more experience of odour annoyance, reduced quality of life and in some cases indirect health conditions (Schiffman 1998).

In order to mitigate and implement odour guidelines for poultry production facilities, accurate characterisation of odours using reliable and representable techniques are essential to gain a clearer understanding of the emission nature (Schiffman 1998; Lacey et al., 2004; Powers et al., 2005). Similar studies have been conducted in the food, water

and aroma industry using gas chromatography coupled with olfactory. This technique enables the identification of volatiles with low threshold levels and offensive qualities, which are most likely responsible for the occurrence of unpleasant odour. Moreover, this practice has limited application in the assessment of environmental emission from intensive livestock facilities (Rabaud et al., 2003). The objective of this study is to develop a reliable and robust methodologies to identify and characterise variations in odorants composition generated from broiler litter utilising headspace sampling combined with thermal desorption, gas chromatography – mass spectrometry and olfactory detection (TD-GC-MS/O).

2 Materials and Method

Broiler litter samples were collected from a tunnel ventilated broiler shed in Queensland, Australia during winter period (by the Queensland Department of Employment, Economic Development and Innovation) at selected points of the shed in a 2 metre radius. The samples were sealed in clean odour free bags before being transported to the UNSW Atmospheric Emissions and Odour Laboratory for TD-GC-MS/O analysis.

Sampling of volatiles

Closed vessel direct dynamic headspace sampling was used to study volatiles from broiler litter. To ensure minimum occurrences of contamination, sampling vessels utilised for direct dynamic study were screened prior to use. Total ion chromatogram of empty vessels exhibited no background contamination other than carbon dioxide and ethylene dioxide, traced at retention time 1.5-2 minutes. Approximately 100 ml of broiler litter was purged through with helium (He) gas for a minute and the volatiles were concentrated on a general purpose graphitised carbon cold trap held at -10 °C for 3.5 min at a flow rate of 50 ml/min using a dynamic headspace sampler with 2 inlets attached directly to a thermal desorption unit (TDU) (Markes Unity, Markes International, UK). Following sampling the cold trap was rapidly heated to 290°C for 5 min at a rate of 20°C/s to desorb the retrained volatiles on a gas chromatography column using a transfer line held at 140°C.

In order to compare the application of direct dynamic headspace sampling to the commonly used sorbent tubes, litter emissions were captured on conditioned Tenax, TA sorbent tubes. A flux chamber covering litter sample was purged with high purity nitrogen gas at a flow rate of 5 L/min during sampling of litter odour on Tenax TA sorbent tubes. Volatiles were concentrated on sorbent tube at a flow rate of 100 ml/min for 30 min by an AirChek2000 air sampling pump (SKC). Tubes containing litter volatiles were thermally desorbed at 275°C for 5 min retraining volatiles on a general purpose graphitised carbon cold trap held at -10 °C in the TDU. This cold trap was later subjected to a second stage thermal desorption at 290°C for 5 min at a rate of 20°C/s injecting volatiles on the gas chromatography column using a transfer line held at 140°C.

Separation and identification of volatiles

Volatiles introduced on the gas chromatography column employing both sampling techniques were analysed using a gas chromatography-mass spectrometry coupled to an olfactory detection port (GC-MS/O) (Agilent Technologies, USA and Gestrel, Germany) for chemical and sensory characterisation. Separations of volatiles collected were conducted using a polar HP-INNOWax column with dimension of 0.25 mm x 30 m x 0.25 μm (Agilent Technologies, USA) with He flowing at 1.6 ml/min. The initial oven temperature was set and held at 50°C for 2 min before being ramped at 5°C/min til 125°C for 10 min and finally at 10°C/min til 200°C for 2 min. The total run time of this program was 26.50 min. As the eluted compounds exited the GC column, a splitter separated the vapour at a ratio of 2:3 to a mass selective detector (MSD) (MSD 5975, Agilent Technologies, USA) and an olfactory detection port (ODP) (Gerstel, Germany). The MSD functioned under electron impact mode at 70 eV, scanning m/z ranged from 35 to 500. Instrumental identification of separated compounds was performed by comparing the mass spectra to the NIST02 library available in the GC-MS system.

As no scientific instrument has the capability of interpreting perceived odorants in the way a human nose does, two screened human detectors with different sensitivities (i.e. butanol detection thresholds) were used for olfactory detection of the volatiles, recording the odour description and intensity of the compounds as low, mild, high and very high using scale system 1-4 on the ODP recorder software (Gerstel, Germany). The odorants were identified by matching total ion chromatogram obtained from the GC-MS with peaks obtained on the aromagram from the ODP to establish the key odorants being emitted from the litter.

3 Results and Discussion

The comparison of direct dynamic headspace against sorbent tubes sampling revealed reliable results reflecting on the simplicity in the preparatory and sampling procedure. Solvent free condition has minimised the interference and formation of artefacts. Limited physical and chemical changes made to the sample matrix enabled the sampling conditions to resemble the litter environment of a broiler shed at ambient temperature. A range of volatiles varying in chemical functionality were obtained from broiler litter odour using both sampling techniques, demonstrating the complexity of the litter odour emissions. Major odorants observed from broiler litter were labelled on the total ion chromatograms in Figure 1. Fewer odorants were obtained from odour sampled on Tenax sorbent tubes compared to the direct dynamic headspace technique. Table 1 shows volatiles trapped using both techniques, displayed large differences in relative abundance.

Direct dynamic headspace sampling analysis showed an increased sensitivity and detectability of odorants. This is most likely because of volatiles being analysed as a whole headspace extract rather than targeting at a single or specific compound. Sealed vessel and a short period of inert gas purge prevented the continuous dilution and loss of volatiles into the atmosphere. Purging of inert gas through the litter samples increased

volatilisation and concentration of odorants from the condensed phase to the gas phase above the sample matrix, resulting in greater detection of odorants. In contrast to this, loss and dilution of concentrations of analytes due to long period of inert gas purging above litter sample in an unsealed flux hood caused many odorants to be not detected or traced at low detection level using sorbent material. These findings were also reflected in the odorgram obtained from both sampling techniques using human detectors with different odour sensitivity levels (Figure 2). Human detectors recorded more odorants with higher odour intensity levels from direct dynamic headspace technique than the use of sorbent tubes (Table 2). However, compounds with higher relative abundance do not necessarily have an offensive character. This primarily depends on the odour characteristic and threshold limits of a compound. Identification of a greater number of odour peaks on the odorgram than total ion chromatogram confirms the greater sensitivity of a human receptor at low detection limits compared to chemical analysis via the mass selective detector.
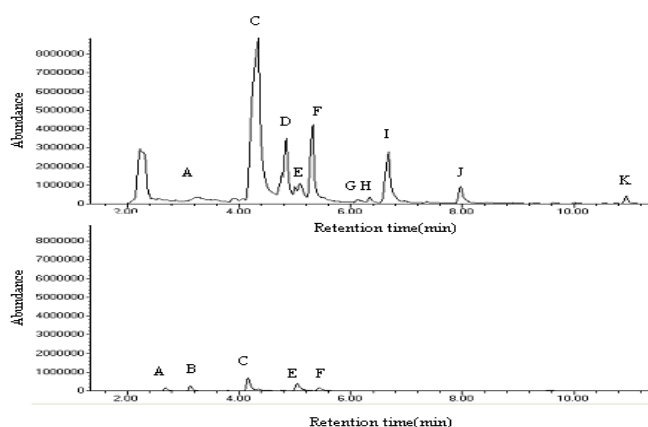

Figure1 Total ion chromatogram for dry litter using direct headspace (top) and sorbent material sampling (below)

Table 1 Comparison of relative abundance of major odorants

| Peak label	Odorant	Relative abundance with sorbent material	Relative abundance with direct dynamic headspace
A	Acetone	4.08E+05	3.00E+07
B	2-butanone	5.83E+05	not detected
C	α pinene	1.75E+06	1.00E+09
D	Camphene	not detected	3.00E+08
E	Dimethyl disulfide	1.17E+06	1.00E+08
F	β pinene	trace	2.00E+08
G	α phellandrene	not detected	2.00E+07
H	1-methyl-4-(1-methylethyl)- 1,3-cyclohexadiene	not detected	2.00E+07
I	D-limonene	not detected	2.00E+08
J	1-methyl-2-(1-methylethyl)- benzene	not detected	6.00E+07
K	1-methyl-4-(1-methylethenyl)- benzene	not detected	2.00E+07
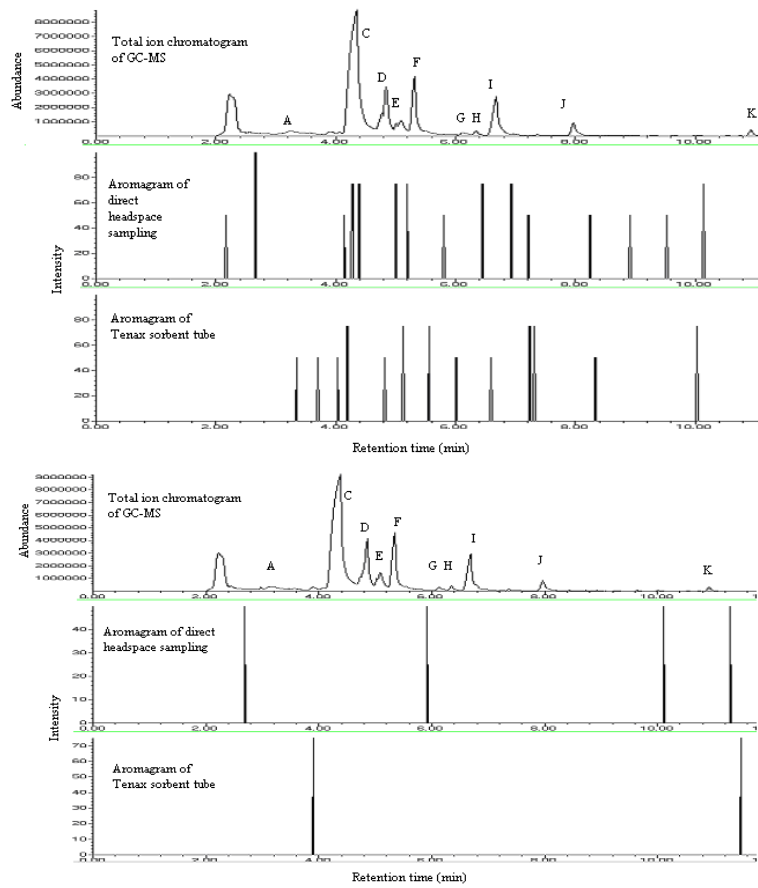
Figure 2 Comparison of odorants identified by highly sensitive (top) and averagely sensitive (bottom) human detectors based on total ion chromatogram and aromagram for both direct headspace and sorbent tube sampling.

Table 2 Litter odorants identified by human detectors

Peak label	Highly sensitive human detector				Averagely sensitive human detector			
	O_D	I_D	O_T	I_T	O_D	I_D	O_T	I_T
A	trace	2	ash	2	none	0	none	0
B	trace	2	solvent	2	none	0	solvent	3
C	pine	3	pine	3	none	0	none	0
D	chemical	3	trace	3	none	0	none	0
E	manure		manure	3	none	0	none	0
F	resin	3	resin	3	chemical	2	none	0
G	none	0	none	0	none	0	none	0
H	foul	3	none	0	none	0	none	0
I	citrus	3	trace	3	citrus	3	none	0
J	smoke	2	trace	2	smoke	2	none	0
K	foul	2	trace	2	foul	2	none	0

O_D = odour description with direct sampling; I_D = perceived odour intensity with direct sampling; O_T = odour description with Tenax tube; I_T = perceived odour intensity with Tenax tube

4 Conclusions

Direct dynamic headspace sampling coupled to gas chromatography-mass spectrometry /olfactory (GC-MS/O) was successfully employed to analyse odorants from broiler litter. This method demonstrated a number of advantages compared to sampling of volatiles using sorbent tubes. It offered simplicity in preparation, constant repeatability and sensitivity of both human and instrumental parameters in detecting odorants in small quantity in a short analysis period. Elimination of solvent and minimal physical and chemical changes may reduce sample and analyte degradations, interference of contaminants and the formation of artefacts. The accurate characterisation of odorants using human and chemical detectors coupled with direct dynamic headspace sampling will aid in selecting and implementing effective odour abatement and mitigation techniques to reduce odour impacts on local receptors.

5 Acknowledgements

6 References

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