

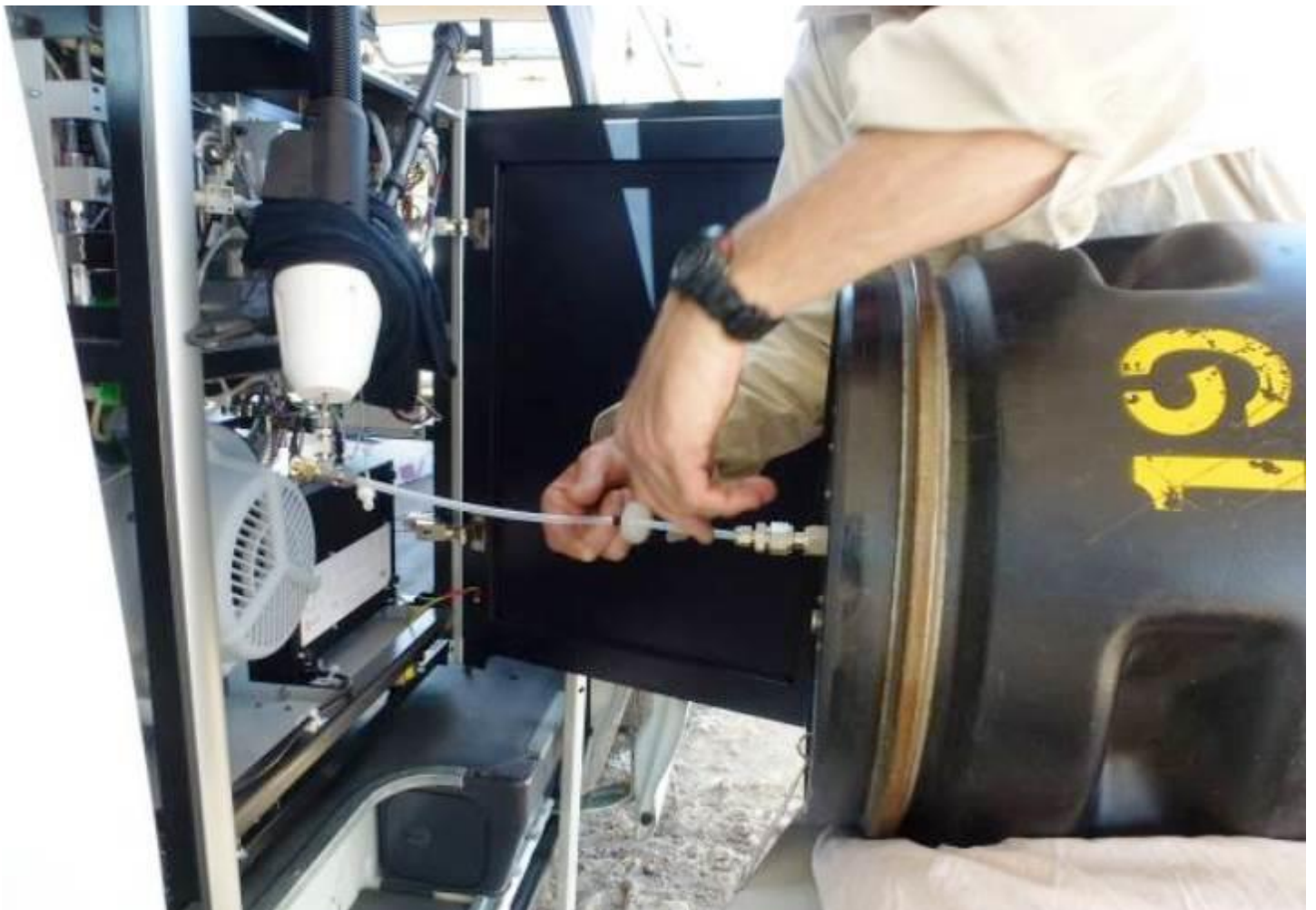


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Rapid continuous chemical analysis of meat chicken shed emissions by SIFT-MS



October 2016

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**Rural Industries Research and
Development Corporation**

Rapid continuous chemical analysis of meat chicken shed emissions by SIFT–MS

by Michael Atzeni, Vaughan Langford, Barry Prince and David Mayer

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Foreword

Understanding the chemistry and behaviour of odour emissions is an ongoing research challenge for Australia's chicken meat industry—and intensive livestock industries in general. This is largely due to the difficulties in determining the dynamics of volatile organic compound (VOC) emissions over time and space, and how these influence poultry odour detection, recognition and nuisance thresholds.

This project trialled a relatively new technology called Selected Ion Flow Tube–Mass Spectrometry (SIFT–MS) to explore its suitability for identification and real time quantification of odorants in meat chicken farm emissions. The research findings will benefit those interested in on-site monitoring of malodours and other complex gaseous mixtures.

This project was funded from industry revenue which is matched by funds provided by the Federal Government. This report is an addition to RIRDC's diverse range of over 2000 research publications and it forms part of our Chicken Meat R&D program, which aims to stimulate and promote R&D that will deliver a productive and sustainable chicken meat industry that provides quality wholesome food to the nation.

Most of RIRDC's publications are available for viewing, free downloading or purchasing online at www.rirdc.gov.au. Purchases can also be made by phoning 1300 634 313.

John Harvey
Managing Director
Rural Industries Research and Development Corporation

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Special thanks to the property owners, managers and staff at the field sites for their cooperation, friendship and hospitality.

Abbreviations

AOS	artificial olfaction system ('electronic nose' designed for odour quantification)
DAFF	Department of Agriculture, Fisheries and Forestry
GC-MS	gas chromatography – mass spectrometry
FSM	full scan mode
LOD	limit of detection
NMVOC	non-methane volatile organic compound
NZ	New Zealand
ou, OU	odour unit. (1 ou = dilution threshold at which 50% of panel can detect an odour.)
pid, PID	photoionisation detector
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PTR-MS	proton transfer reaction with quadrupole mass spectrometry
scm	standard cubic centimetres per minute
SEQ	South-east Queensland
SIFT-MS	selected ion flow tube – mass spectrometry
SIM	selected ion mode
TD-GC-MS	thermal desorption – gas chromatography – mass spectrometry
VIC	volatile inorganic compound
VOC	volatile organic compound

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Executive Summary

What the report is about

Assessing and addressing odour impacts from poultry production is extremely difficult and subjective because the odorants involved and their dynamics over time and space are poorly understood. This knowledge gap is due, in part, to the lack of suitable analytical tools for measuring and monitoring odorants in the field. The emergence of Selected Ion Flow Tube – Mass Spectrometry (SIFT–MS) and similar instruments is changing that. These tools can rapidly quantify targeted odorants in ambient air in real time, even at very low concentrations. Such data is essential for developing better odour abatement strategies, assessment methods and odour dispersion models.

This project trialled a SIFT–MS to determine its suitability for assessing the odorants in meat chicken shed emissions over time and space. This report details evaluations in New Zealand and Australia to determine the potential of SIFT–MS as a tool for the chicken meat industry, including odour measurement (as a proxy for dynamic olfactometry).

Who is the report targeted at?

The report is specifically targeted at those funding and conducting poultry odour research. It will be of interest to those involved with environmental odour monitoring and assessment in general. The high upfront cost of SIFT–MS will lead to potential users wanting compelling evidence that SIFT–MS will meet their needs before they invest in one.

Where are the relevant industries located in Australia?

The Australian chicken meat industry involves around 800 growers and 40 000 employees Australia-wide. Production is concentrated in New South Wales (about a third), Victoria (just under a quarter) and Queensland (about a fifth) according to the Australian Chicken Meat Federation. The projected gross value for 2013-2014 of all Australian poultry production (of which chicken meat comprises about 95 per cent) is \$2.291 billion, according to Australian Bureau of Agricultural and Resource Economics.

Background

Odour characterisation is traditionally performed by lab-based GC–MS. This necessitates collecting, storing and transporting samples appropriately. By contrast, SIFT–MS allows rapid, real time measurement of volatile organic compounds (VOCs) and certain inorganic gases, including ammonia and hydrogen sulphide, to sub-part per billion levels. Since SIFT–MS requires no sample preparation and eliminates sample storage, transport and analysis delays, VOCs contributing to odour could be more readily quantified and monitored over time.

SIFT–MS instruments are expensive and unproven for poultry odour characterisation assessment so should be thoroughly evaluated first. It was therefore proposed that a SIFT–MS instrument be leased and deployed at various meat chicken farms in south-east Queensland to gather a number of relevant datasets for critical evaluation and comparison to other measurements including gas chromatography – mass spectrometry (GC–MS), olfactometry and artificial olfaction system (AOS) (electronic nose) data.

Aims/objectives

The aim was to evaluate the feasibility of using SIFT–MS for poultry odour assessment, based on meat chicken farm evaluations. The evaluation covered VOC identification, odorant quantification, and odorant monitoring in real time. Using SIFT–MS as a proxy for dynamic olfactometry to predict odour concentration was also a consideration.

Methods used

The methodology was as follows:

- A SIFT–MS (Voice200®; Syft Technologies Ltd) was evaluated at four meat chicken farms. A preliminary evaluation was conducted by Syft Technologies Ltd at a meat chicken farm near Christchurch, New Zealand, over three sampling days in June 2013. The instrument was subsequently leased and evaluated at three south-east Queensland farms over a one-month period (starting 16 September 2013).
- The SIFT–MS, mounted in a van, was driven to the relevant site to analyse in-shed, near-shed and downwind odour samples at different stages of the production cycle to ensure a range of bird ages was covered, and also to capture significant odour events (for example, litter harvesting and bird pick-up).
- SIFT–MS analyses were conducted by two methods: Full Scan mode, to scan for all detectable VOCs; and Selected Ion Mode (SIM) to scan for nominated odorants. Both modes were frequently used in succession, for comparing odour concentrations using the two methods. SIFT–MS mass spectra and odour concentration data were reviewed and processed using LabSyft software (Syft Technologies Ltd) supplied with the Voice200.
- For the NZ evaluation, a SIM method was set up and used for scanning 18 specific odorants previously reported to be present in meat chicken odour (but was not calibrated). For the south-east Queensland evaluation, the same method was used, but was first calibrated using a mixture of key poultry odorants generated using permeation tubes in a permeation oven (VICI Metronics).
- A mixture of direct and bag sample analyses were collected depending on the aims for the day. Bag analyses were performed on some samples collected for AOS and olfactometry purposes when time permitted. The SIFT–MS was also used to analyse background odour and odour in empty sheds (before and after litter cleanout; after disinfection).
- Some bagged odour samples collected for AOS analysis and odour quantification by dynamic olfactometry (in a related project) were also analysed by SIFT–MS to investigate its potential as a proxy for dynamic olfactometry.
- Other bagged samples were collected specifically to examine changes in the odour composition over time.
- To confirm that VOCs measured using SIFT–MS were correctly identified, GC–MS odour samples were collected onto Tenax tubes for GC–MS analysis using previously described techniques.
- SIFT–MS in-shed and downwind mass spectra data were critically compared to determine the suitability of SIFT–MS for determining chemical transformations occurring in the odour plume.

Results/key findings

SIFT–MS shows considerable potential for poultry odour applications, particularly for applications measuring targeted odorants for odour assessment/abatement purposes.

Use of SIFT–MS mass spectra data to identify VOCs in poultry emissions is limited by the nominal mass resolution. Compounds with the same integer mass produce overlapping mass spectra which cannot be resolved by SIFT–MS. The presence/absence of overlapping VOCs needs to be confirmed by complementary analyses such as GC–MS.

SIFT–MS’s strength is in quantifying specific odorants in real time using selected ion mode (SIM). It affords the opportunity to verify the effectiveness of odour reduction strategies designed to reduce those odorants. How that odorant contributes to odour perception and detection thresholds can arguably be ascertained with calibrations against odour threshold data using olfactometry.

SIFT–MS provides a vehicle for productive and transparent dialogue about odour impact problems and how to solve them.

Implications for relevant stakeholders

SIFT–MS technology will allow industry to obtain and evaluate comprehensive data for specific odorants of interest. If such data can be subsequently correlated to odour concentrations, then evaluation of odour abatement strategies will be easier and can be implemented with greater confidence.

Due to the high costs involved, the risk in adopting SIFT–MS at this stage would centre round unrealistic expectations about its ability to quantify and monitor odorants causing odour nuisance, which is one of the main areas of interest for odour researchers.

Recommendations

SIFT–MS should be evaluated further to determine its suitability for measuring and monitoring VOCs downwind, but only following development of improved GC–MS methods for poultry odour.

SIFT–MS should be evaluated in conjunction with other potentially useful MS technologies, under controlled experimental conditions, to gauge which combination of analytical instruments will provide the best tools for odour researchers in the foreseeable future. Once this has been established, industry can have confidence in supporting projects that utilise these.

These necessary pre-requisite evaluations must involve personnel with appropriate expertise. Sufficient funding and time needs to be allocated for these evaluation projects with a view to long-term benefits rather than short-term gains.

Introduction

Selected Ion Flow Tube Mass Spectrometry (SIFT–MS) is a relatively new and improving technology capable of measuring certain volatile organic compounds (VOCs) at parts per trillion concentrations in air (Prince *et al.*, 2010). It allows for rapid, economical and convenient quantification of VOCs and certain inorganic gases such as ammonia and hydrogen sulfide, based on full mass scans in the m/z range 15 to 250, using three different precursor ions (H_3O^+ , NO^+ and O_2^+).

SIFT–MS technology has been evolving since the first exploratory work in 1994 (see review by Španěl and Smith, 2011) and has been widely used for food, medical and safety applications but has only been applied to intensive livestock odour assessment in recent years.

Background to the project

Attempts to develop a robust, cost-effective odour measurement tool for poultry odours using AOS technology have been thwarted by the lack of sensitivity and selectivity of the gas sensors they rely on. Current commercial gas sensors are unable to detect most VOCs at the low concentrations they occur (ppb levels or lower) let alone discriminate between them. These sensors are also sensitive to moisture and non-target VOCs and volatile inorganic compounds such as ammonia, making interpretation of non-specific sensor response data very subjective (Atzeni *et al.*, 2014). Furthermore, AOS applications are invariably time- and site-specific—there is no catchall solution. While AOS may be relatively inexpensive technology, their commercial viability will depend on the availability of more specific gas sensors tailored to industry-specific needs (Wilson, 2013).

Given the many factors influencing the composition of poultry odour, it is now evident odour researchers need to determine which odorants are being generated as the basis for predicting odour concentrations over time and space at any given site. The emergence of SIFT–MS technology provides a potential solution in that it can be used to monitor target compounds in real time. SIFT–MS applications include: real-time analysis of exhaled breath; rapid quantification of air components such as toluene and xylene; and real-time atmospheric monitoring (Prince *et al.*, 2010; Smith and Španěl, 2011). The appeal of SIFT–MS for odour researchers is the ability to measure odorant concentrations without the need for sample pre-treatment or pre-concentration—unlike GC–MS. A comparison of features common to both GC–MS and SIFT–MS is given in Appendix A. The operating principles of SIFT–MS are described in detail in Appendix E.

SIFT–MS can be applied to odour assessment in two primary ways: identification of odorants emanating from a particular source; and objective assessment of nuisance odours. SIFT–MS has been used in livestock buildings to measure the odorants in meat chicken and pig odours (Van Huffel *et al.*, 2012). It has also been demonstrated, using ‘similarity coefficients’, that SIFT–MS can be used to link unknown livestock samples to library data sets (Heynderickx *et al.*, 2012).

Using the similar proton transfer reaction–mass spectrometry (PTR–MS) method and olfactometry results, Hansen *et al.* (2012) showed chemical measurement of piggery odorants is an alternative for expressing the odour concentration in grow-out production systems, which could provide increased understanding of different odour types and lead to improved odour abatement technologies.

Poultry industries are also interested in establishing whether there are any compounds that SIFT–MS can measure that can be correlated with dynamic olfactometry results, such that SIFT–MS might provide a useful proxy for dynamic olfactometry under certain circumstances, including one-off assessments of the odour impacts from existing farms, and as a research tool when testing the effects of new technologies.

Objectives

Objectives of the project were to:

- determine the suitability of SIFT–MS for poultry emissions monitoring and odour characterisation
- assemble comprehensive VOC database from SIFT–MS sampling at various meat chicken farms in south-east Queensland (SEQ)
- critically compare in-shed and downwind VOC data to determine key odorants
- critically compare in-shed SIFT–MS data and non-selective sensor array data from an Artificial Olfaction System (AOS).

Methodology

The project was implemented in two stages.

1. A field evaluation conducted over three (non-contiguous) sampling days at a meat chicken farm near Christchurch, New Zealand, by Syft Technologies Ltd (on behalf of DAFF).
2. A one-month evaluation conducted by DAFF in Toowoomba (laboratory analyses) and across three SEQ farms in the Lockyer Valley (on-site analyses).

In addition to the SIFT–MS analyses, GC–MS samples were collected and analysed. In Australia, the SIFT–MS trial was purposely conducted in parallel with a validation trial for an AOS being developed by DAFF so that AOS sensor data was available for comparison. Olfactometry samples were collected and analysed and the results used for both projects.

New Zealand trial

Odour assessments were performed with a Voice200 SIFT–MS on three separate days during a batch. SIFT–MS assessments were conducted directly, and from bagged samples, on in-shed and downwind odour.

Twelve GC–MS samples were also collected to facilitate interpretation of the SIFT–MS results. GC–MS samples were analysed by the University of New South Wales (UNSW).

A report was provided by Syft Technologies (see Chapter 1) detailing the methodologies employed for sample collection and analysis, the measurement results and a discussion of the significance of the results including any interferences, environmental effects or other factors encountered that may have impacted on the observed results.

SEQ trial

Following the New Zealand trial, a Voice200 mounted in a van was delivered 16 September 2013 to DAFF in Toowoomba, by the Australian agent (Thompson Environmental Services) for the one-month lease period. Syft Technologies provided trained personnel who were responsible for the calibration/setup, training and technical support throughout the lease.

The Voice200 was calibrated for several reported poultry odorants using a gas mixture generated from permeation tubes. The instrument was then deployed at three meat chicken farms to conduct strategic sampling. The site details are described in Atzeni *et al.* (2014).

At farm A, the SIFT–MS was used during a trial for the AOS project (RIRDC project; PRJ-002342) thereby value-adding to both projects (Atzeni *et al.*, 2014). A separate study on odour decay (how odorant mixtures change over time in sample bags) was also conducted.

GC–MS samples were collected over the course of the trial to assist with interpretation of the SIFT–MS results. These samples were analysed by the UNSW Odour Laboratory, Sydney.

Olfactometry analysis

Analyses were conducted according to the Australian/New Zealand Standard for Dynamic Olfactometry (AS/NZS 4323.3-2001) (Standards Australia/Standards New Zealand, 2001) using an eight-panellist, forced-choice, dynamic olfactometer.

Olfactometry panels were sourced from a pool of 12 experienced panellists. To improve the accuracy of the measurement, two extra rounds (dilution series) were conducted on each sample.

The panellists were screened using n-butanol to ensure their individual detection threshold was in the range of 20–80 ppb(v/v). The procedures are described in Sohn *et al.* (2008).

TD–GC–MS sampling and analysis

Thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) was used to identify non-methane volatile organic compounds (NMVOCs, otherwise referred to as odorants) in the odour samples collected for this purpose.

Sample collection

Tenax sorbent tubes were used to trap odorants for TD–GC–MS analysis. Samples were collected in duplicate via a common manifold connected to the sample line. A vacuum pump was used to draw samples through the tubes at 100 mL/min (at standard conditions 0 °C, 101.325 kPa). The sample period was 30 minutes unless otherwise indicated in the results. The detailed methodology is described in Dunlop *et al.* (2011).

At the end of each sample period, the pump was turned off and the tubes were immediately capped at both ends. They were then stored in a cool area. Details of the samples were recorded on field sheets.

Analysis of NMVOCs

The following desorption and analysis program was used:

- Thermal desorption: tube desorbed for five minutes at 275 °C, held by a cold trap at -10 °C before the trap was heated at a rate of 40 °C per minute to a final temperature of 290 °C. It was then held for five minutes.
- Gas chromatograph (GC): oven program started by holding the sample for two minutes at 50 °C before increasing the temperature by 10 °C per minute until it reached 175 °C. Then the temperature was increased at a rate of 25 °C per minute until 225 °C was reached. The sample was held for two minutes for a total run time of 18.5 minutes. The GC column used was J&W Scientific DB-VRX 30 m x 0.250 mm x 1.4 µm.
- Mass spectrometer: operated using constant scan 35-335 m/z, 1.25 minute solvent delay.

Amount of each analyte was reported as nanograms (ng) on the tube to two significant figures.

1. New Zealand trial

Summary

A three-day trial was conducted at a meat chicken farm 20 km south-west of Christchurch, New Zealand, to evaluate the utility of SIFT–MS for the monitoring of poultry odorants. Syft Technologies' Voice200 was utilised to measure key odour compounds on three separate days during a production cycle spanning May and June 2013.

The results presented here fulfil the key objectives of this study. They demonstrate the ability of the Voice200 to simultaneously quantify a broad range of chemical species both within and outside the meat chicken shed and to monitor the changes in concentration of these species during the course of the production cycle, and in real-time during the course of a day.

The study also raised some interesting questions that warrant further investigation:

- The concentrations of most of the VOCs measured were observed to increase with the growth of the birds between the first and second day of monitoring. However, there were some notable exceptions. For example, the concentration of ammonia, the highest concentration compound dropped significantly in this period and the concentration of methylamine was virtually unchanged.
- Feedback on the GC–MS analyses suggested the concentration of VOCs observed in this study were much lower than observed in previous studies within Australia. This may be a consequence of the modern meat chicken shed sampled in this work, which utilises new technology ventilation systems—a possibility that is supported anecdotally by comments from contractors working in the shed who stated that the odours were much lower than in other meat chicken sheds they work in.

Background

This initial New Zealand trial was commissioned because of the need to be reasonably confident the Voice200 SIFT–MS could be operated on-site at meat chicken farms, and could detect and quantify those ubiquitous odorants identified by other researchers using GC–MS analysis (Dunlop *et al.*, 2011; Murphy *et al.*, 2014). Syft Technologies Ltd who developed the Voice200 was asked to do this so that they could experience firsthand the nature of the field work proposed for the SEQ trial and address any operational problems.

Evaluation of the Voice200 for analysis of odour compounds produced in a meat chicken shed

Aims

This evaluation aimed to:

- evaluate the general utility of the Voice200 for real-time direct analysis of VOCs arising from livestock emissions
- identify the highest concentration VOCs produced in a meat chicken shed
- measure the changes in these VOC concentrations during the growth cycle of the chickens
- test the ability of the Voice200 to monitor changes in the concentrations of these compounds in real time during the course of the day

- evaluate the use of the Voice200 to carry out measurements of these VOCs downwind of the meat chicken shed
- evaluate the use of Tedlar sample bags for transporting samples of these VOCs for later analysis.

Experimental

Sampling location

Sampling was carried out on three separate dates as detailed below on the property located approximately 20 km south-west of Christchurch, New Zealand. Figure 1 shows a schematic of the trial area of the property. Analysis of air from within shed 1, which contained 39,500 chickens, was carried out by sampling from approximately the centre of the shed. Figure 1 also shows the sites at which outside measurements were carried out, labelled A, B and C and detailed below.

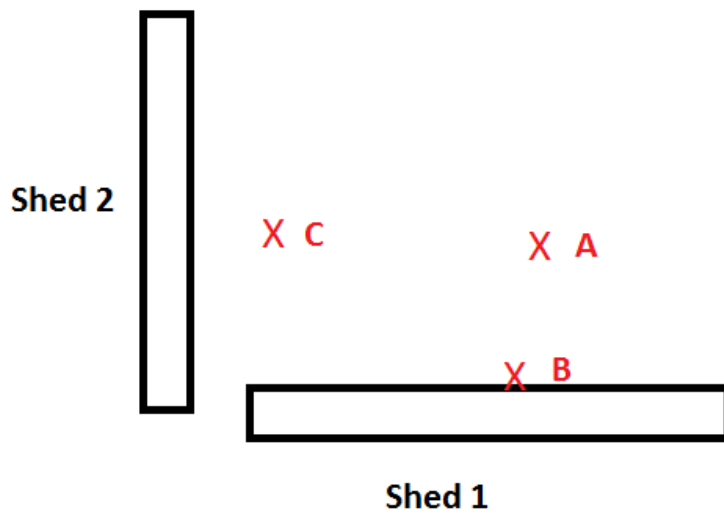


Figure 1. Schematic of the New Zealand SIFT-MS trial site showing relative positions of meat chicken sheds 1 and 2, and external sampling sites A, B and C.

Figure 2 shows a photo of shed 1. Both sheds 1 and 2 were constructed in the two years prior to the trial. They have a ventilation system that involves drawing air in from the sides of the shed and expelling it through fans in the roof.



Figure 2. Meat chicken shed 1.

The outdoor temperature was less than 12 °C on sampling day 1 and less than 10 °C on sampling days 2 and 3. The wind was light and from a southerly direction on all three days of deployment.

- Sampling day 1, 23 May 2013. 16-day-old chickens in shed 1. Outside samples were taken from site A (Figure 1).
- Sampling day 2, 4 June 2013. 28-day-old chickens in shed 1. Outside samples were taken from site B (Figure 1).
- Sampling day 3, 13 June 2013. All chickens were harvested from sheds 1 and 2 by this date. Sampling was carried out solely from site C (Figure 1), while the litter was pushed out from both sheds and trucked away.

Voice200 instrument setup

For the purposes of this study, the Voice200 was housed in a van (Figure 3).



Figure 3. The Voice200 mounted in a van for mobile deployment.



Figure 4. Sample was drawn from the centre of shed 1 to the Voice200 through a transfer line. The section of this transfer line between the Voice200 and the side vent of the shed was heated to ~50 °C to prevent condensation.

When sampling the air within shed 1, the sample was drawn through a 6 mm diameter hose from the centre of the shed through a side vent to the sample inlet of the instrument. To avoid condensation in this transfer line due to the high temperature and humidity in the shed and the low temperature outside the shed, the section of transfer line between the instrument and the shed was heated to ~50 °C (Figure 4).

The Voice200 draws sample at a rate of ~15 mL/min. The volume of sample within the transfer line to the interior of the shed was estimated to be ~500 mL. Thus, to avoid the dead time associated with drawing sample through this transfer line at such a slow rate, a pump was used to pump sample through the transfer line at a rate of ~9000 mL/min. In this way, concentration changes in the shed were visible to the Voice200 with a lag time of only a few seconds.

When sampling outside, the transfer line was removed from the instrument and sampling was performed through the open door of the van. Blank samples were measured on clean air samples known to be free of the target compounds.

At all times during this study, the instrument was powered by an electrical lead running to a mains power outlet in the meat chicken shed or another electrical outlet.

Tedlar bag sampling

On day 2 of sampling, an additional analysis was performed using three Tedlar sample bags, labelled T1–T3. Before sample collection, these sample bags were flushed five times with nitrogen using Syft Technologies' Tedlar bag flushing station. The sample was collected using a Gilian GilAir-3 sampler.

Samples T1 and T3 were filled from the centre of shed 1. Sample T1 was analysed immediately by the Voice200. Sample T3 was left in the shed for three hours (to avoid condensation at the lower outside temperatures) before being analysed by the Voice200. Sample T2 was filled through the transfer line that was used to draw sample from the shed to the Voice200, and analysed immediately using the Voice200.

Thus, a comparison of sample T2 to the 33 Voice200 in-shed measurements assessed the use of Tedlar bags for collecting samples of this type for immediate analysis; a comparison of samples T1 and T2 assessed the transfer line for delivering sample from the inside of the shed to the Voice200 without loss of sample integrity; and a comparison of sample T1 and T3 assessed the use of Tedlar bags for collecting samples of this type for analysis after a delay of three hours.

Tenax tube sampling

In addition to Voice200 analysis, on each day of deployment, samples were also collected by trapping VOCs on Tenax sample tubes. These samples were then sent to UNSW for analysis by TD–GC–MS. Twelve of these Tenax-tube samples were collected over the three sampling days by pumping three litres of air through the tube over a period of 50 minutes using a Gilian GilAir-3 sampler with a flow rate of 60 sccm. The flow rate of sample through the Tenax tube was measured at the beginning and end of each sampling period using a rotameter as shown in Figure 5.

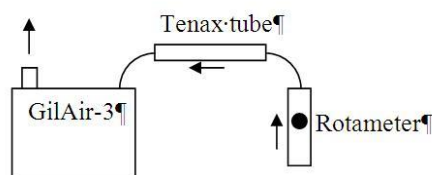


Figure 5. Experimental setup for collecting samples onto Tenax tubes.

The samples collected in this way and their associated Tenax tube IDs are:

- Mi090550 Sampling day 1, sampled from the centre of shed 1, 9.30 am
- Mi090554 Sampling day 1, sampled through transfer line, 10.30 am
- Mi090541 Sampling day 1, blank
- Mi090547 Sampling day 1, sampled from the centre of shed 1, 2 pm
- Mi090543 Sampling day 2, sampled through transfer line, 7.45 am
- Mi090546 Sampling day 2, sampled from the centre of shed 1, 9 am
- Mi090548 Sampling day 2, blank
- Mi090545 Sampling day 2, Site B, 12 pm
- Mi090549 Sampling day 3, Site C, 9 am
- Mi090560 Sampling day 3, Site C, 10 am
- Mi090558 Sampling day 3, Site C, 12 pm
- Mi090557 Sampling day 3, Site C, 1 pm.

Target compounds

The 18 target compounds analysed using the Voice200 in this study are listed in Table 1.

The GC–MS analysis performed on the Tenax-tube samples described above was blind to the amines listed in Table 1 but able to identify all other SIFT–MS target compounds. The limit of detection (LOD) for the target compounds is also listed in Table 1 for the GC–MS and SIFT–MS analyses performed in this study.

Table 1. Limits of detection of the analysis methods used in this study.

<i>Compound</i>	<i>GC-MS LOD (ppb)¹</i>	<i>Voice200 LOD (ppb)²</i>
1-butanol	1.1	0.5
2,3-butanedione	1.0	1.2
3-methylbutanal	1.0	0.4
acetaldehyde	1.9	1.1
acetic acid	1.4	1.4
acetoin	0.9	1.1
acetone	1.4	2.9
ammonia	-	3.5
butanone	1.1	0.4
dimethyl amine	-	0.8
dimethyl disulfide	0.9	0.8
dimethyl sulfide	1.3	0.3
dimethyl trisulfide	0.7	1.5
ethanol	1.8	2.7
hydrogen sulfide	2.4	0.6
methyl amine	-	3.2
methyl mercaptan	1.7	0.3
trimethyl amine	-	1.1

1 Based on 10 ng recovered from Tenax tube from a sample volume of 3 litres

2 Based on a 10 second measurement.

SIFT-MS analysis

SIFT-MS uses chemical ionisation reactions coupled with mass spectrometric detection to rapidly quantify VOCs. VOCs are identified and quantified in real time from whole-gas samples based on the known ion-molecule reaction rate coefficients for reaction of the chemically ionising species (reagent ions) with the target compounds (refer to Appendix E).

The Syft Technologies Voice200[®] SIFT-MS can be operated in two modes:

- Full Scan Mode (FSM) may aid identification of non-target compounds, but also allows concentrations to be derived.
- Selected Ion Mode (SIM) targets specific compounds for highly sensitive quantitative analysis, providing significantly lower limits of quantitation and better precision than FSM.

In this work, we used SIM for analysis of the targeted VOCs. Quantitative measurements were carried out using the chemical information on the target compounds taken from Syft's compound library. The absolute accuracy of measurements quantified in this way is typically better than $\pm 50\%$. To meet the primary objectives of this study, (that is, the identification of key VOCs and monitoring their changes with respect to time and location) a high level of absolute accuracy is not necessary. The key instrument performance requirements to achieve these objectives are the measurement precision and day-to-day measurement stability. For the Voice200 these measurement parameters are typically much better than $\pm 5\%$.

Results and discussion

Compounds observed in the meat chicken shed and how concentration of these change during the grow-out period

Figure 6 to 9 show the concentration of target compounds measured in shed 1 at approximately 4 pm on sampling days 1 and 2. This corresponds to the time at which ammonia concentrations were the highest observed on each sampling day. The error bars show the measurement precision (a 99 % confidence interval for the true sample mean of measured points). The blank gives a measure of the Voice200 instrument background concentration for each of the target compounds.

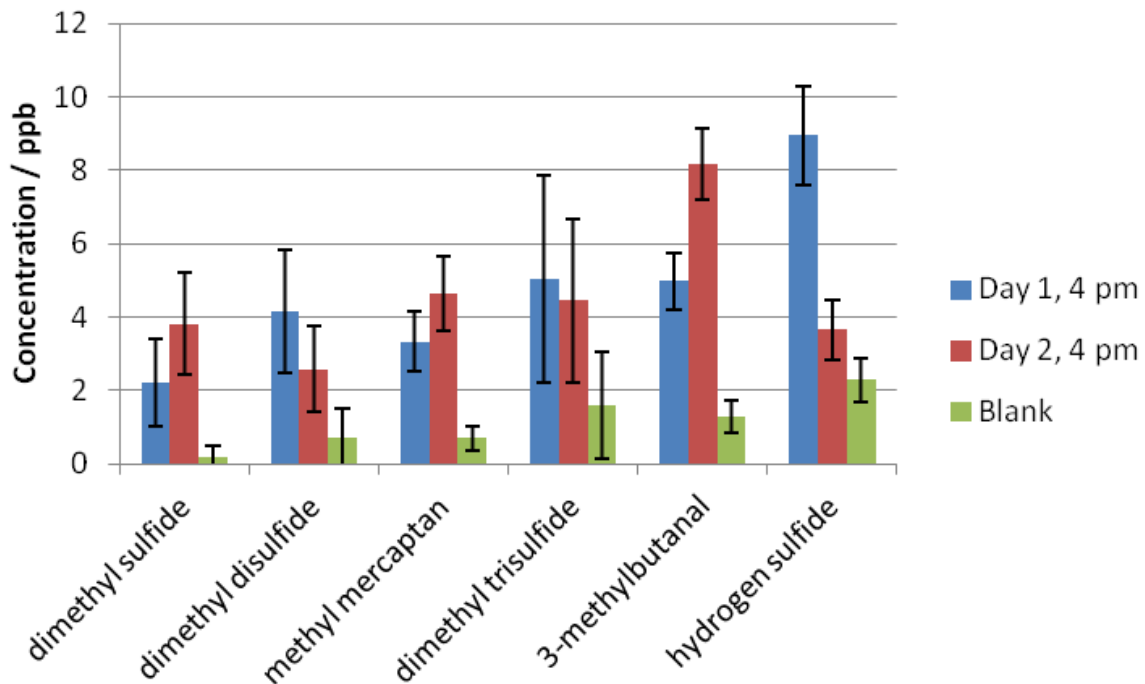


Figure 6. Target compounds with observed concentrations less than 12 ppb in shed 1.

All of the target compounds were observed in shed 1 with the exception of dimethyl trisulfide, which was not detected with notable significance above the instrument background concentration of ~1.5 ppb. The highest VOC concentration observed was ammonia at 5 ppm on sampling day 1. The other VOCs ranged in concentration from 2 ppb up to 1 ppm.

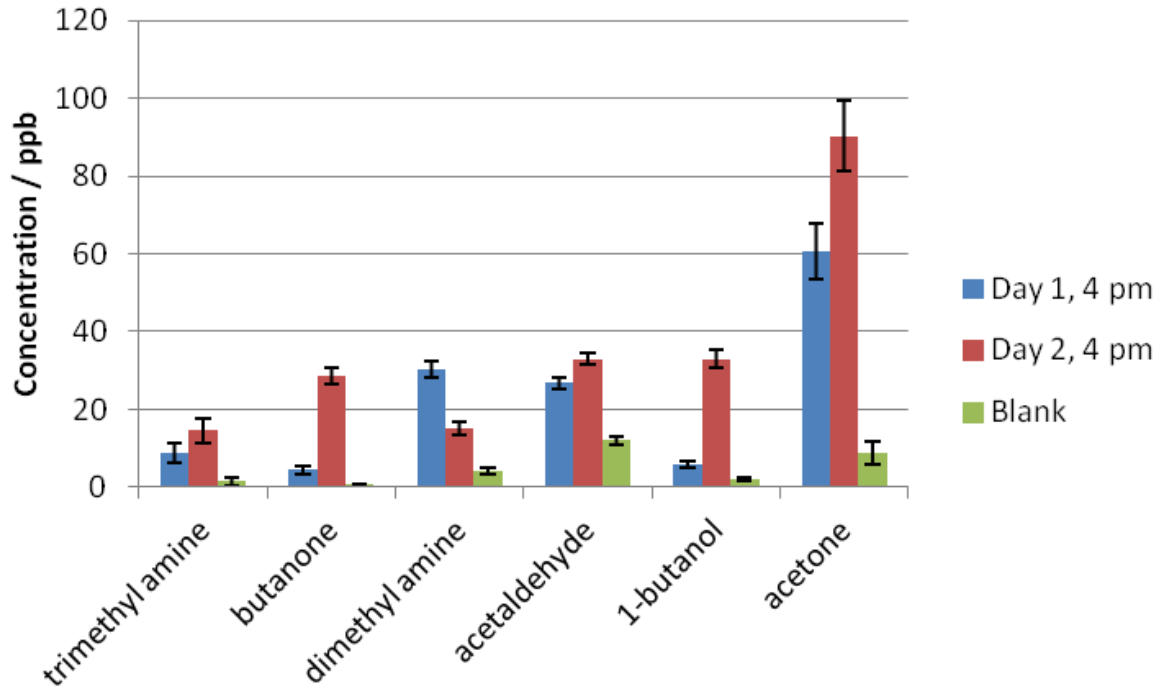


Figure 7. Target compounds with observed concentrations between 12 ppb and 120 ppb in shed 1.

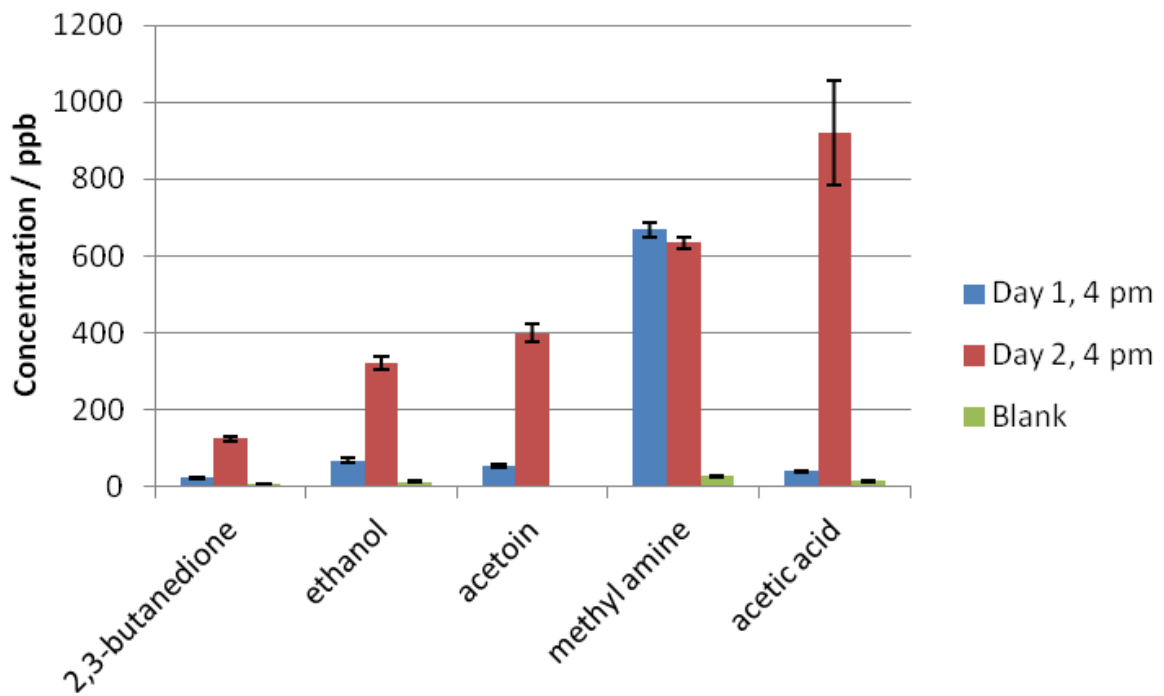


Figure 8. Target compounds with observed concentrations between 120 ppb and 1200 ppb in shed 1.

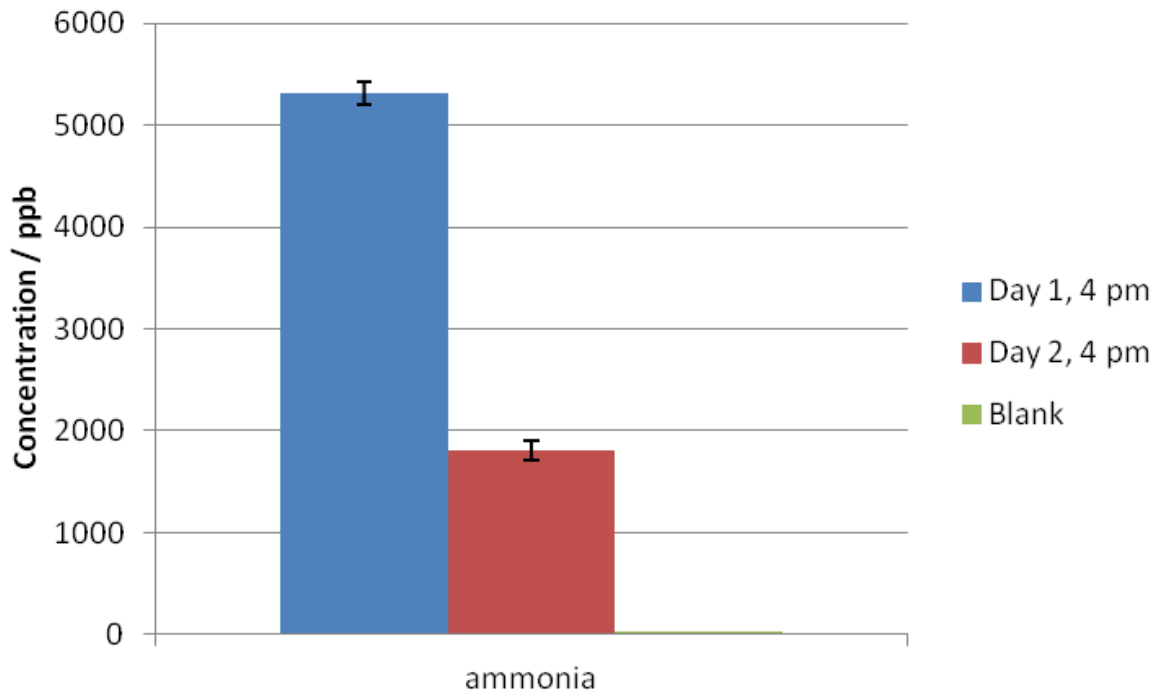


Figure 9. Observed ammonia concentrations in shed 1.

Real-time monitoring of meat chicken shed VOCs during the course of a day

The utility of the Voice200 for real-time monitoring of meat chicken shed VOC concentrations is demonstrated in Figures 10 to 13, which show the concentration 17 of the 18 target compounds for a two-and-a-half hour period during the afternoon of sampling day 1. Dimethyl trisulfide is not displayed since the concentration of this compound was never observed at a level above the instrument background. The inside temperature of the meat chicken shed during these measurements is plotted on Figure 12 and Figure 13 (plotted on the right-hand-side axis). Figure 13 also shows the CO₂ level (in ppm).

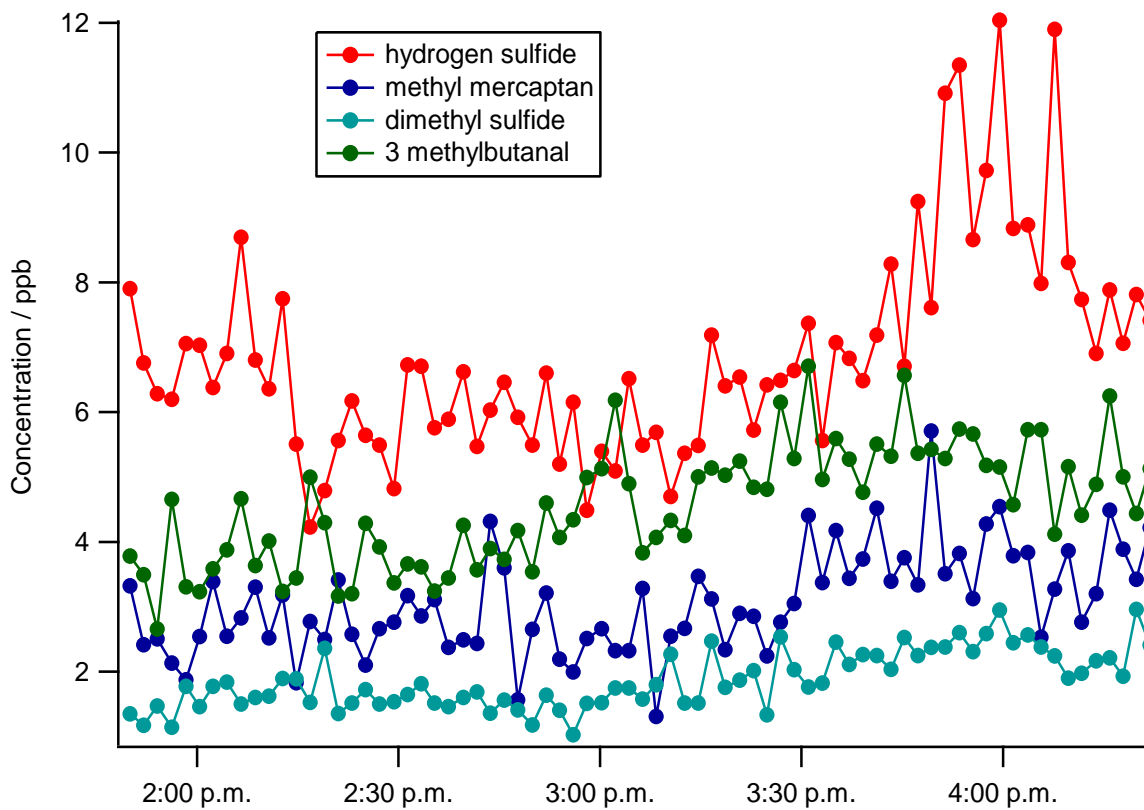


Figure 10. Real-time monitoring of target compounds with concentrations less than 12 ppb.

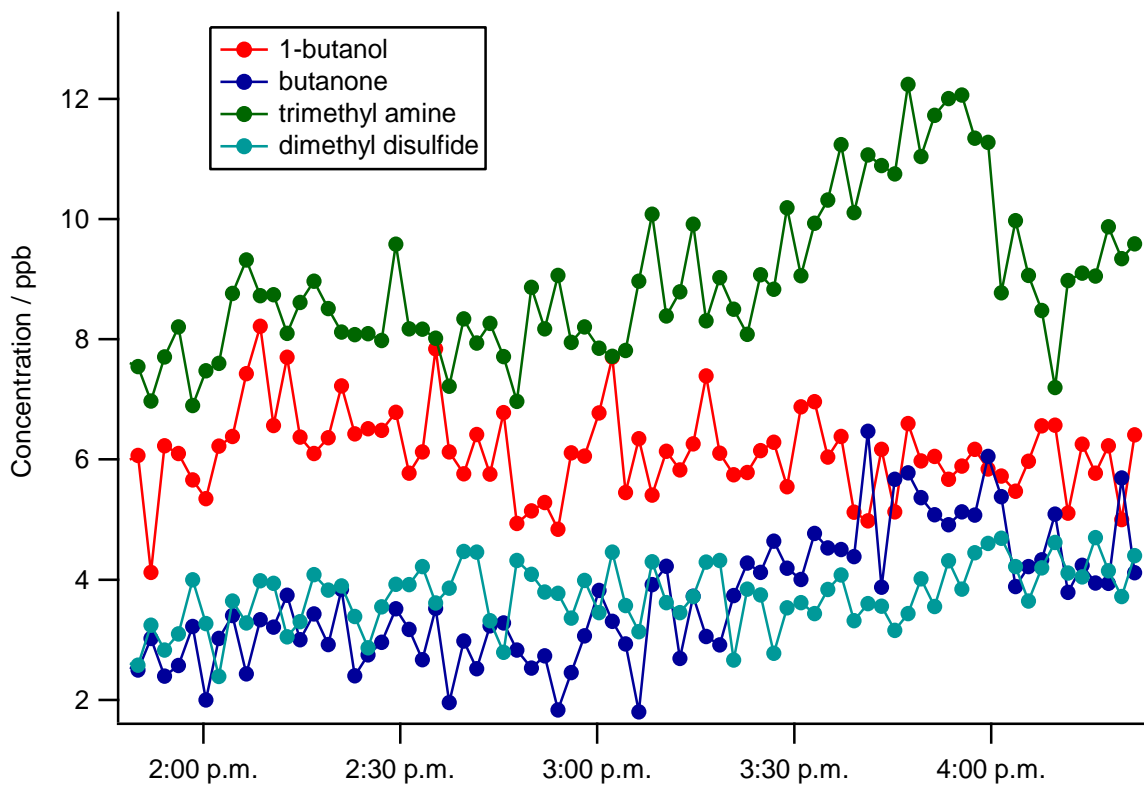


Figure 11. Real-time monitoring of target compounds with concentrations less than 12 ppb.

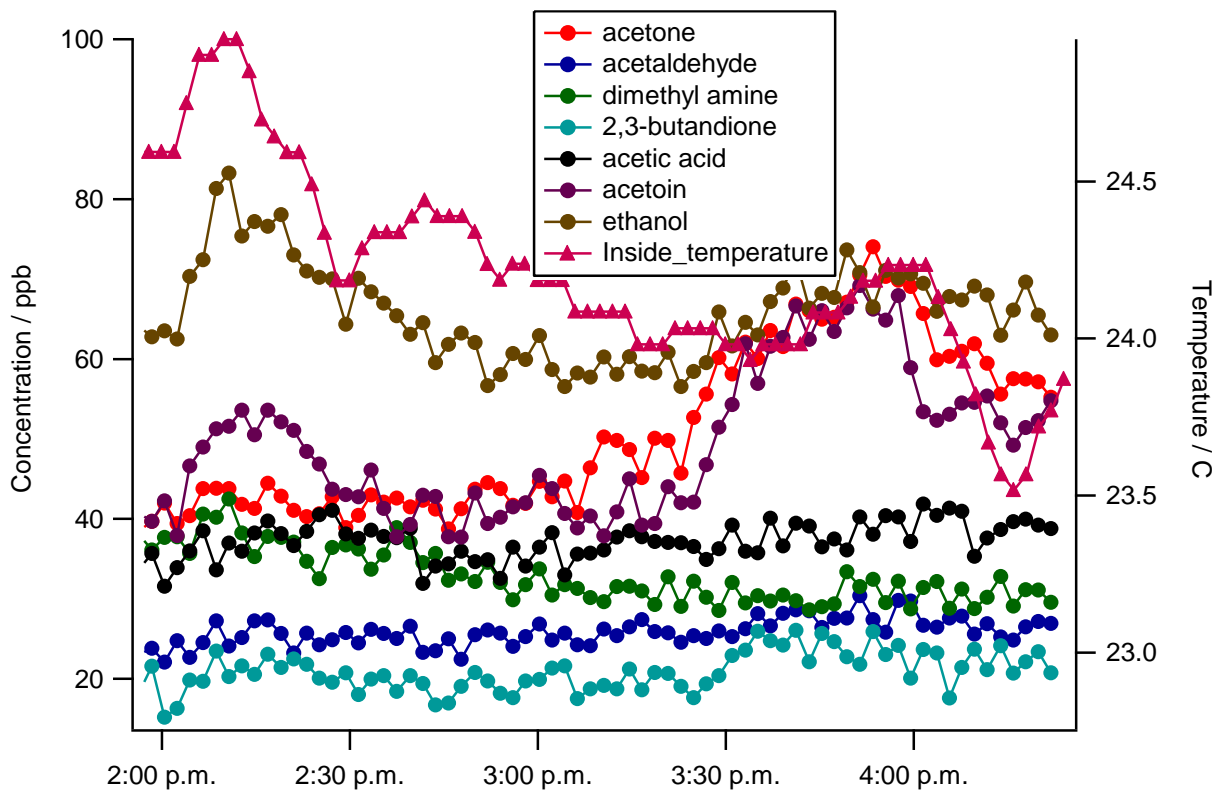


Figure 12. Real-time monitoring of target compounds with concentrations less than 80 ppb. Also shown is the inside temperature, plotted on the right-hand side axis.

The compounds ammonia, methyl amine, acetone, acetoin, and trimethyl amine show a strong correlation with the concentration of CO₂. On the other hand, the concentration of ethanol appears more closely correlated with the internal temperature of the shed.

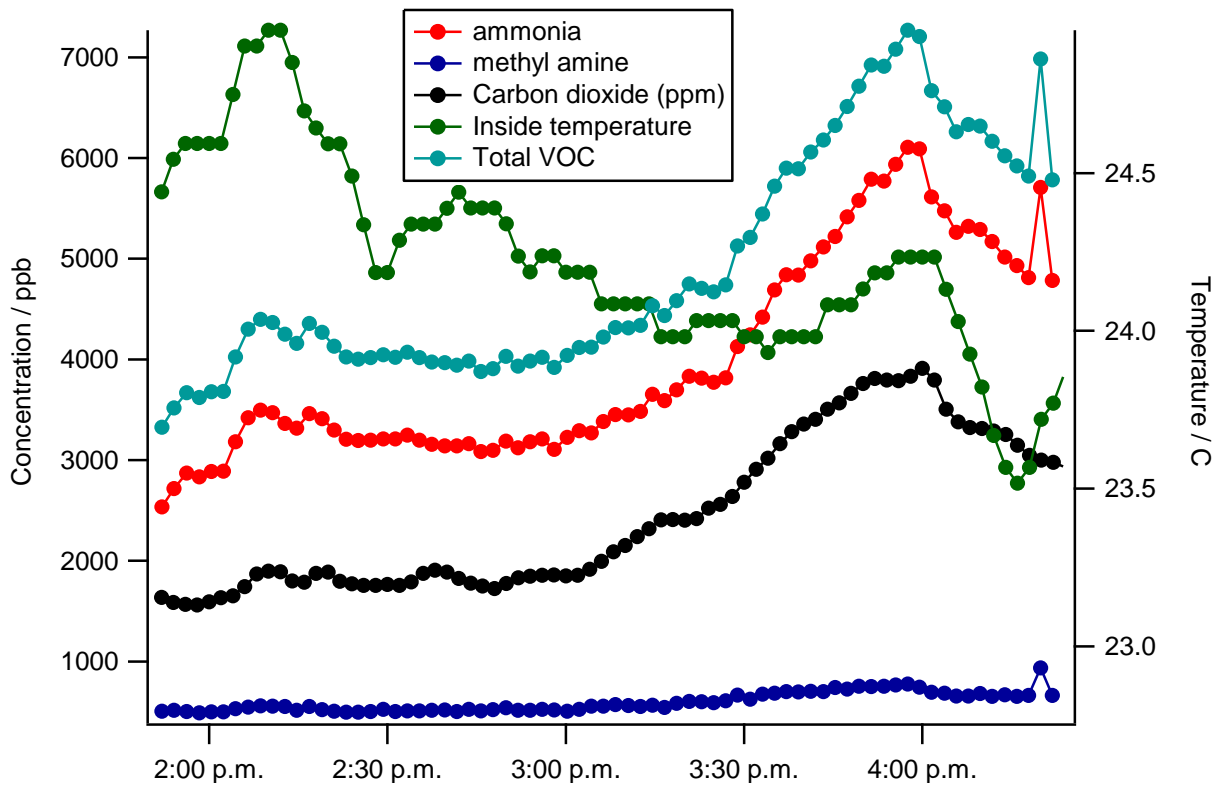


Figure 13. Real-time monitoring of target compounds with concentrations greater than 100 ppb, and the total concentration of all measured compounds. Also shown is the concentration of CO₂ and the inside temperature in the meat chicken shed. CO₂ concentrations can be read off the left-hand axis by substituting ppm for ppb. The temperature is plotted on the right-hand side axis.

Compounds observed downwind of meat chicken shed

The low outdoor temperatures during the three sampling days of measurement made it unlikely that the target compounds would be observed at high levels outside the meat chicken sheds since there was minimal ventilation of the sheds. Nevertheless, of the 18 compounds monitored by the Voice200 in this study, eight were observed above background downwind of the meat chicken shed on at least one of the three days of monitoring. These eight compounds are presented in

Figure 14 and Figure 15.

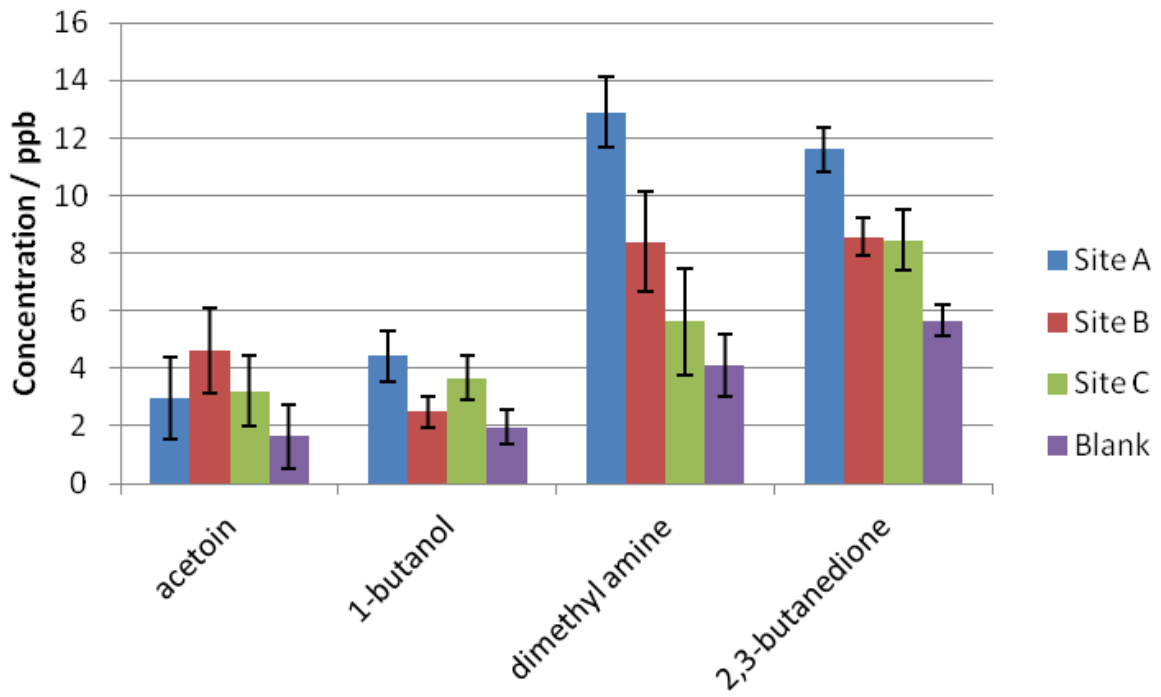


Figure 14. Target compounds with observed concentrations less than 15 ppb downwind of boiler sheds.

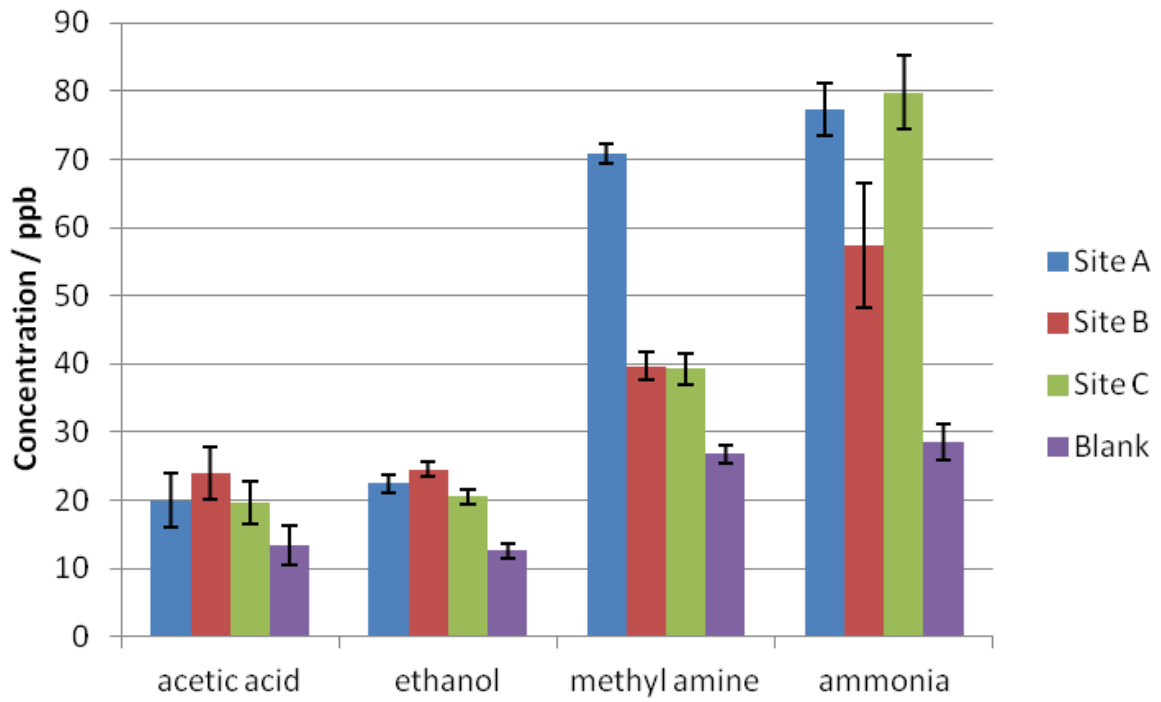


Figure 15. Target compounds with observed concentrations greater than 15 ppb downwind of boiler sheds.

Monitoring changes in compound concentrations outside meat chicken shed

Real-time monitoring of the target compounds outside the meat chicken sheds was carried out on sampling day 3 while the litter was pushed out of sheds 1 and 2 onto the concrete pad that connects the two sheds at the southern end of shed 2 and the western end of shed 1 (Figure 1). The sampling location on this day (Site C) was 50 m directly downwind of this concrete pad, although the wind was very light. The process of pushing out the litter and trucking it away started at approximately 10 am and lasted for five hours.

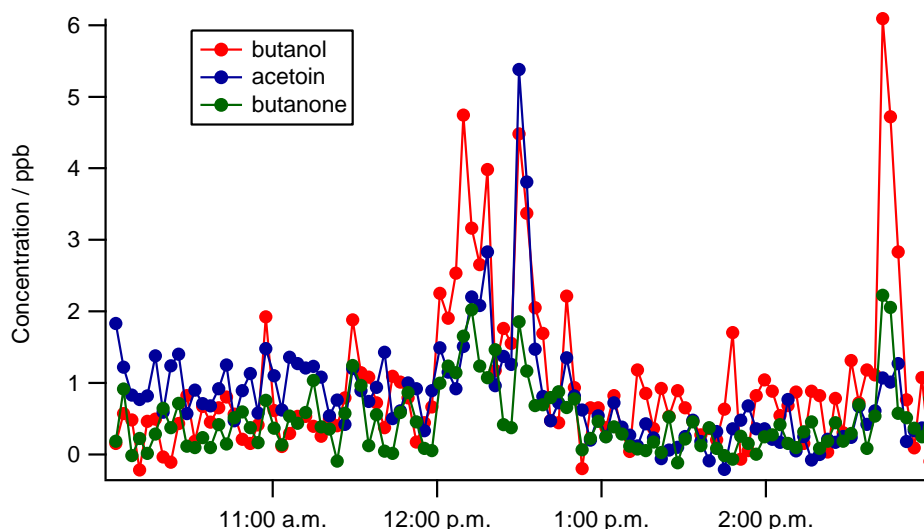


Figure 16. Real-time monitoring of target compounds with concentrations not exceeding 10 ppb. Sampled from Site C (Figure 1) while the litter was pushed out of sheds 1 and 2.

Of the 18 target compounds monitored during this process, seven were observed above the background level at multiple times during the day. These seven compounds are plotted in Figures 16 and 17. There is a strong correlation between all of the observed compounds suggesting they emanate from the same source, which is entirely expected in this case.

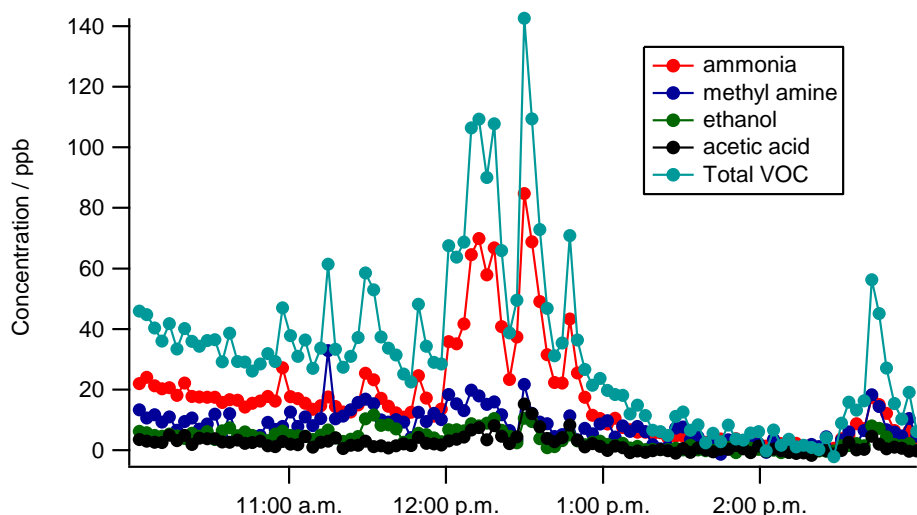


Figure 17. Real-time monitoring of target compounds with concentrations greater than 10 ppb, and the total concentration of all measured compounds. Sampled from Site C (Figure 1) while the litter was pushed out sheds 1 and 2.

Validation of Tedlar bag sampling

The concentration of targeted compounds measured from Tedlar bags is presented in Figure 18 to Figure 21. The most striking conclusion immediately apparent from these results is that Tedlar bags are entirely unsuitable for the collection of ammonia, acetic acid, and to a lesser extent acetoin, in this type of sample matrix, as these compounds are immediately lost from the gas phase (presumably due to adsorption to the walls of the bag). Also evident is that the measured concentration of hydrogen sulfide, methyl mercaptan, 3-methyl butanal, acetaldehyde and methyl amine increase with the time between the collection of the sample into the Tedlar bag and the analysis. This result is difficult to explain, but may be connected with the fact that sample T3 was left in the shed during the three-hour period before the analysis was performed.

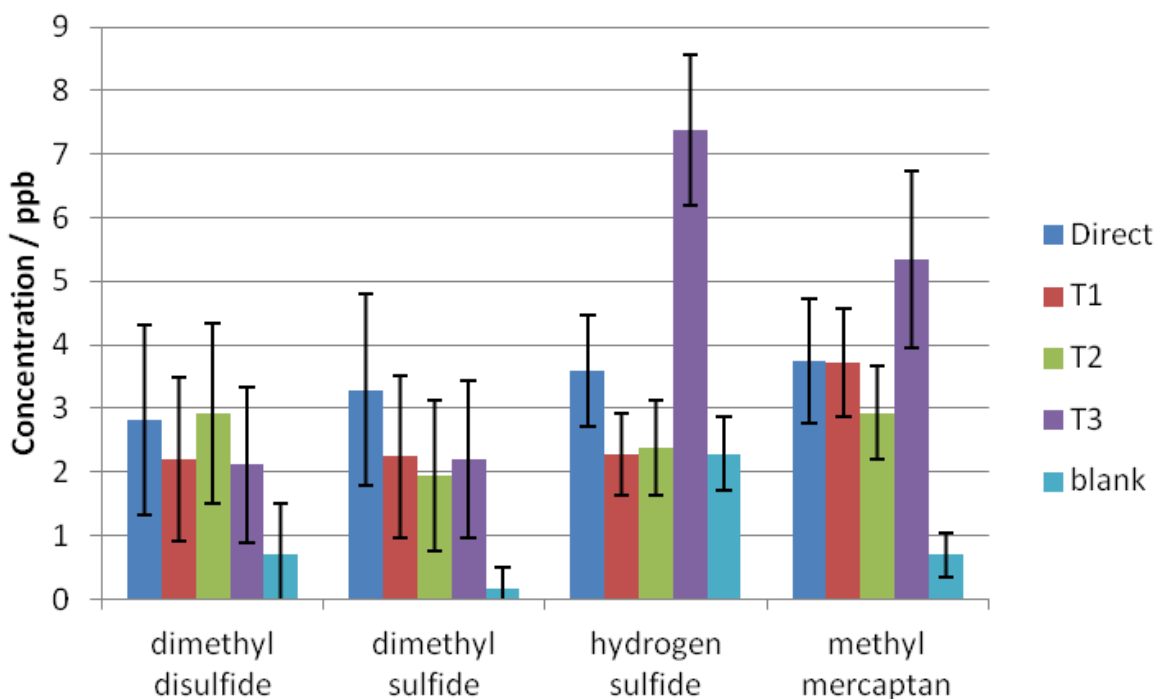


Figure 18. Target compounds measured in Tedlar bags with concentrations less than 10 ppb. The sample labelled Direct was measured immediately prior to the analysis of sample T1 by using the Voice200 to directly analyse the gas from within the shed being drawn through the transfer line.

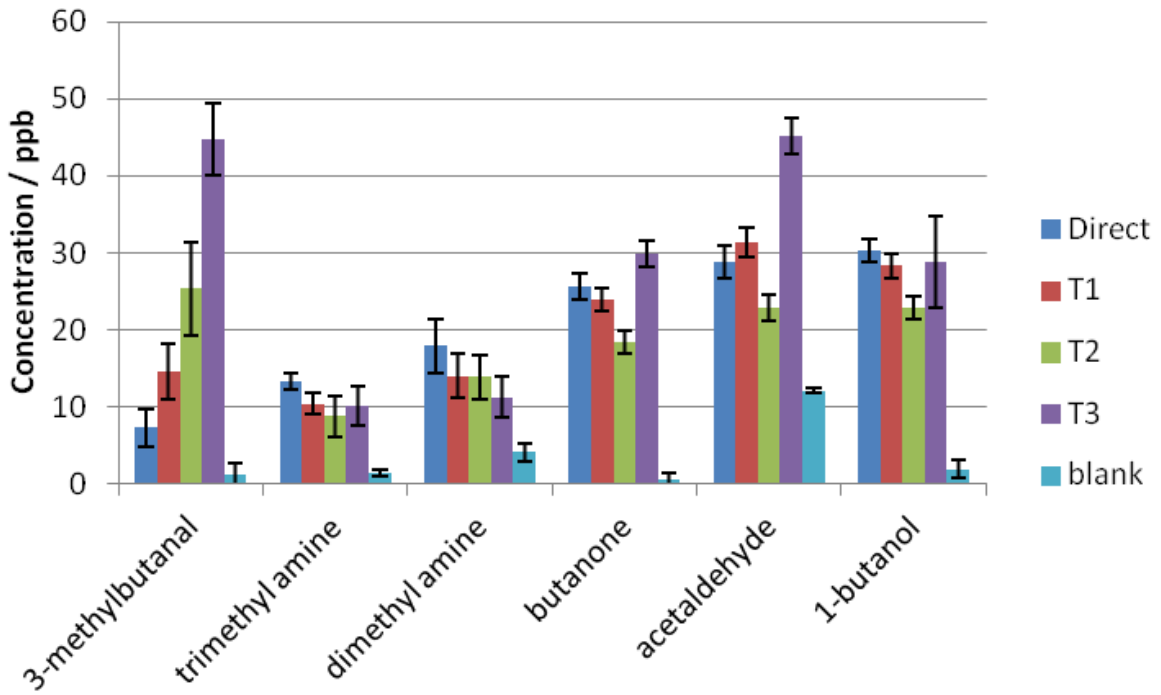


Figure 19. Target compounds measured in Tedlar bags with concentrations between 10 ppb and 50 ppb.

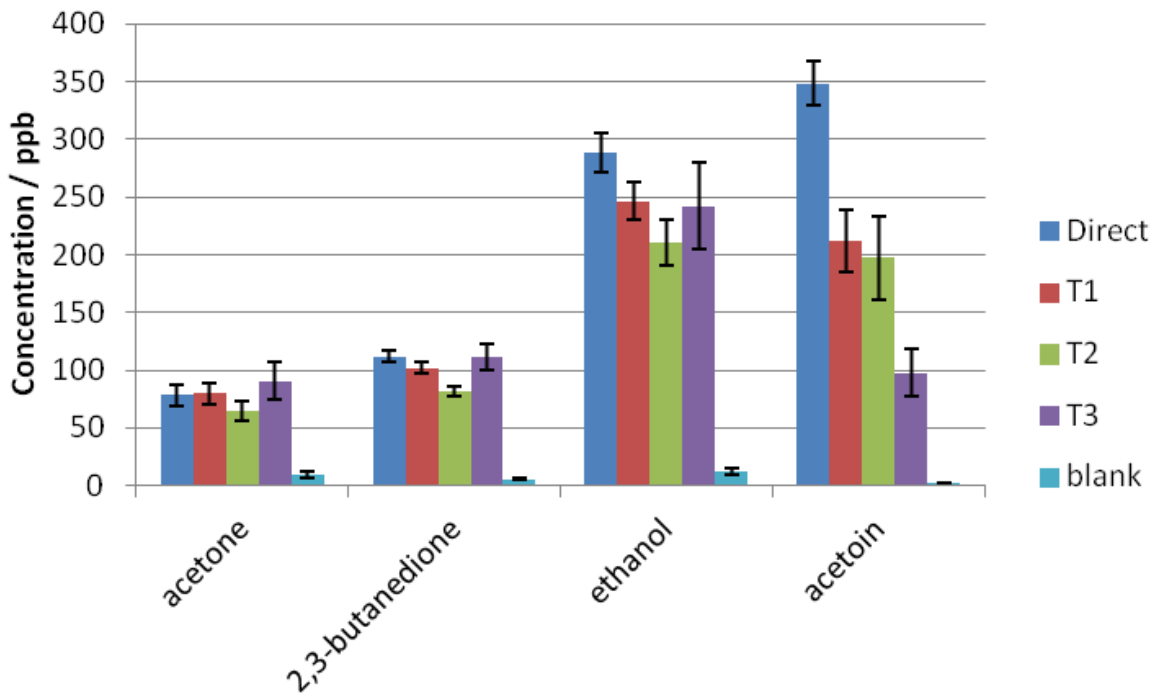


Figure 20. Target compounds measured in Tedlar bags with concentrations between 50 ppb and 400 ppb.

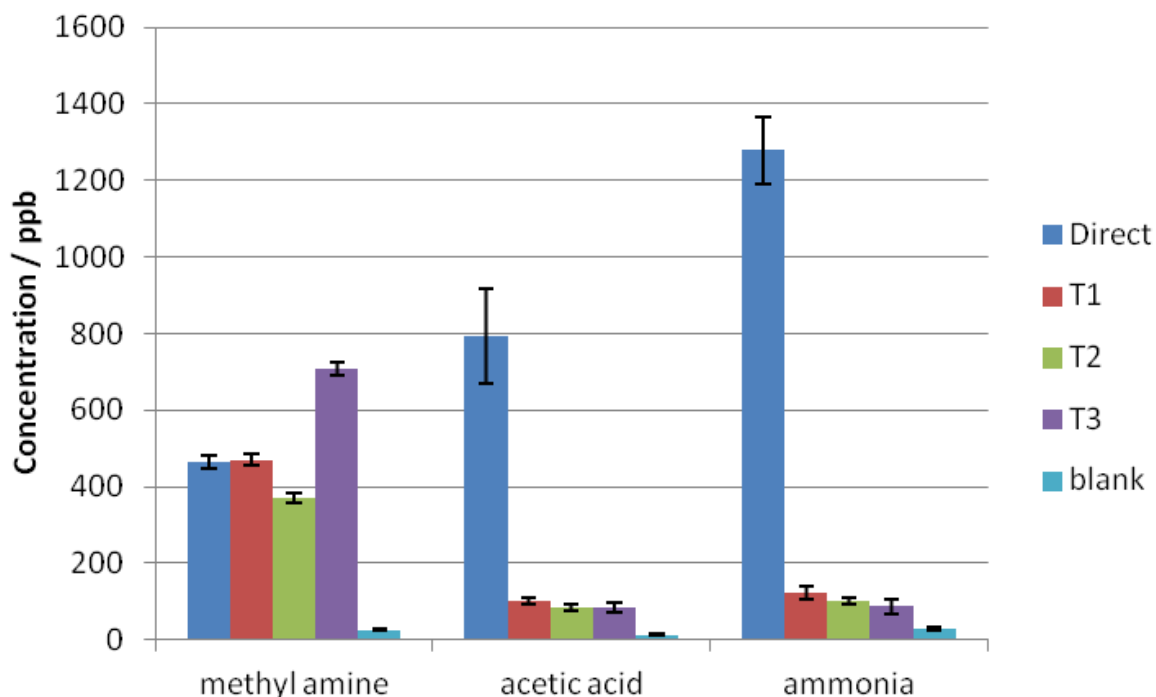


Figure 21. Target compounds measured in Tedlar bags with concentrations greater than 50 ppb.

GC–MS analysis of meat chicken shed compounds

The GC–MS approach employed in this study was unable to measure the amine compounds, which were amongst the most prominent compounds measured in this study. The GC–MS analysis was also unable to identify most of the other target compounds that were analysed by SIFT–MS, despite the fact that the limits of detection of the two techniques are comparable (Table 1). Many of the compounds observed by SIFT–MS were close to the limit of detection, so one explanation for the absence of compounds observed by GC–MS is that there was less than 100 per cent recovery of analyte from the Tenax tubes, thereby dropping the analyte concentration below the limit of detection for the GC–MS method employed.

There were also some anomalies in the GC–MS results (see sample IDs Mi090543, Mi090546, Mi090547, Mi090548) for which the only conceivable explanation seems to be human error associated with either the sample collection at the shed or the sample analysis at the laboratory.

A brief summary of the GC–MS results is:

- Mi090550 Sampling day 1, sampled from centre of shed, 9.30 am
 - 2,3-butanedione: 16 ppb (GC–MS); 23 ppb (SIFT–MS)
- Mi090554 Sampling day 1, sampled through transfer line, 10.30 am
 - 2,3-butanedione: 17 ppb (GC–MS); 18 ppb (SIFT–MS)

- Mi090543 Sampling day 2, sampled through transfer line, 7.45 am
 - 2,3-butanedione: 12 ppb (GC–MS); 140 ppb (SIFT–MS)
 - Acetoin: 70 ppb (GC–MS); 400 ppb (SIFT–MS)
- Mi090541, Blank
 - No VOCs detected by GC–MS or SIFT–MS
- Mi090545 Sampling day 2, Site B
 - GC–MS detected only artefacts. SIFT–MS detected low levels of 2,3-butanedione along with many other odour compounds.
 - The artefacts are thought to have been due to other farm-related emissions in the vicinity of Site B which were not among the target species analysed for by SIFT–MS.
- Mi090557, Mi090549, Mi090558, Mi090560, Sampling day 3, Site C
 - No VOCs detected by GC–MS.
 - 2,3-butanedione not detected by SIFT–MS but other VOCs detected during the period of Mi090558 sample.
- Mi090548, Blank
 - No VOCs detected by SIFT–MS.
 - High levels of VOCs detected by GC–MS.
- Mi090547, Mi090546, Sampled from centre of shed
 - No VOCs detected by GC–MS.
 - High levels of VOCs detected by SIFT–MS.

Conclusion

There are many unforeseeable factors that influence the results of field trials such as this, so it is not without precedent that the outcomes of this study include some surprising results that will require further investigation to better understand. It is unfortunate that the GC–MS measurements planned for this study yielded little in the way of validation of the SIFT–MS results.

Nevertheless, the primary objectives of this study were well met by the results obtained. The Voice200 was shown to be a suitable tool for the measurement of a broad range of odorous compounds with concentrations ranging from ppm down to sub-ppb levels. Samples were analysed directly with no requirement for pre-concentration or sample work-up of any sort so there is no pre-selection or discrimination between the compounds. Furthermore, sample analytes were monitored in real-time allowing dynamic processes to be studied in situ.

SIFT–MS is a technology that shows promise in this field of study. There is no question that the results presented in this report justify the further deployment of this technology to further investigate the factors affecting the release of odorous compounds from meat chicken sheds under different environmental conditions and to endeavour to answer some of the questions raised by this study.

2. South-east Queensland evaluation

Background

Following the New Zealand trial, the project proceeded with an on-site evaluation of SIFT–MS technology at meat chicken farms in south-east Queensland (SEQ) trial. The Christchurch site was convenient, but not representative of Australian operations and conditions. The SEQ trial would capture VOC data at representative Australian farms in a semi-tropical area. This would also provide the unique opportunity to compare SIFT–MS data with artificial olfaction system (AOS) data and olfactometry data being collected in parallel during a related odour project.

The New Zealand trial highlighted the benefits of performing direct in-shed odour analysis over delayed lab analyses of odour samples collected into Tedlar bags. Delaying analyses resulted in significant changes in the odorant concentrations. Hence, the majority of the SIFT–MS sampling in SEQ was done on-site. The NZ trial also raised concerns about the GC–MS methodology which remained unresolved coming into the SEQ trial.

Calibrations

Aim

In the first phase of this study, the ability of SIFT–MS to detect and quantify certain compounds was questioned. This experiment was intended to:

- verify that the compounds were detectable using SIFT–MS
- provide calibration factors that could be applied in subsequent SIFT–MS analyses.

Method

Initially, seven permeation tubes, each containing a different target poultry odorant (Table 2), were equilibrated in a VICI® Dynacalibrator (Model 500) permeation oven (Valco Instruments Co. Inc, Houston, Texas, USA) at 40 °C for several days leading up to the calibration. A flow rate of 200 standard cubic centimetres per minute (sccm) of high-purity air (instrument-grade) was used. Flow rates were set and confirmed periodically using a flow meter.

The output flow of calibration gas from the permeation oven was delivered to the fully automated sample inlet of the Syft Voice200 SIFT–MS instrument. The gas stream was analysed using the same analytical method ('Poultry' SIM method) as that used in the New Zealand trial.

Another two permeation tubes arrived after this calibration and were added to the chambers. These were experimental tubes that could not be certified before the trial began. They were certified, along with the other tubes, after the trial.

Results and discussion

Table 2 shows the results of SIFT–MS analysis of the permeation tube standards. Five replicate SIFT–MS analyses were performed over a period of approximately 70 minutes, with each ion being analysed for 1.7 seconds in each analysis.

Table 2. Results for SIFT–MS analysis of compounds in permeation tubes using several product ions. VICI Metronics concentration data for the tubes are also shown.

<i>Compound</i>	<i>Product ion [m/z]</i>	<i>Reagent ion</i>	<i>Ratio Syft / VICI METRONICS</i>	<i>VICI Metronics Data</i>		<i>Syft Calibration Data</i>		
				<i>Conc. / ppbv</i>	<i>Uncertainty</i>	<i>Mean / ppbv</i>	<i>Standard deviation / ppbv</i>	<i>Std dev. as % of mean</i>
2,3- butanedione	C ₄ H ₆ O ₂ ⁺ [86]	NO ⁺	1.08	996	Est.	1070	21	1.9%
	C ₄ H ₆ O ₂ ⁺ [86]	O ₂ ⁺	0.87			867	21	2.5%
	C ₄ H ₇ O ₂ ⁺ [87]	H ₃ O ⁺	1.86			1860	28	1.5%
acetone	C ₃ H ₇ O ⁺ [59]	H ₃ O ⁺	1.17	784	15%	914	2.1	0.2%
	NO ⁺ .C ₃ H ₆ O [88]	NO ⁺	1.83			1440	21	1.5%
butanone	C ₄ H ₈ O ⁺ [72]	O ₂ ⁺	1.09	250	15%	273	4.7	1.7%
	NO ⁺ .C ₄ H ₈ O [102]	NO ⁺	1.66			415	6.7	1.6%
dimethyl sulfide	(CH ₃) ₂ S ⁺ [62]	NO ⁺	0.79	38.6	25%	31	0.6	1.9%
	(CH ₃) ₂ S ⁺ [62]	O ₂ ⁺	0.75			29	0.8	2.9%
	(CH ₃) ₂ S.H ⁺ [63]	H ₃ O ⁺	1.26			49	2.9	5.9%
dimethyl disulfide	(CH ₃) ₂ S ₂ ⁺ [94]	NO ⁺	1.24	40.3	25%	50	3.4	6.8%
	(CH ₃) ₂ S ₂ ⁺ [94]	O ₂ ⁺	1.18			48	3.1	6.4%
	(CH ₃) ₂ S ₂ .H ⁺ [95]	H ₃ O ⁺	1.39			56	3.2	5.7%
dimethyl trisulfide ¹	C ₂ H ₆ S ₃ ⁺ [126]	NO ⁺	0.16	39.8	Est.	6.4	1.4	22%
	C ₂ H ₆ S ₃ ⁺ [126]	O ₂ ⁺	0.06			2.5	5.5	219%
	C ₂ H ₆ S ₃ H ⁺ [127]	H ₃ O ⁺	0.03			1.3	4.3	333%
acetic acid	CH ₃ COOH ₂ ⁺ [61]	H ₃ O ⁺	0.61	6266	15%	3830	320	8.3%
	NO ⁺ .CH ₃ COOH [90]	NO ⁺	0.46			2870	230	8.1%

¹ Experimental permeation tube appeared defective, or had a much lower permeation rate than predicted by VICI Metronics.

These standards were identified and monitored using their nominal mass (m/z) values. With single pure compounds, this calibration approach is straightforward but as the number of permeation tube standards increases, so does the chance of overlapping mass spectra. This is a weakness in using the SIFT–MS technology for complex gaseous mixtures.

Permeation tube certification

After the SEQ trial was completed, the permeation tubes were returned for certification by the supplier VICI Metronics. The results are shown in Table 3. Two of the tubes (3-methyl butanal and 3-hydroxy-2-butanone) were out by an order of magnitude.

Table 3. Re-certified permeation tube results.

<i>Chemical</i>	<i>ORIGINAL Perm. rate (ng/min)</i>	<i>(RE)-CERTIFIED Perm. rate (ng/min)</i>	<i>True accuracy %</i>	<i>Ratio Original/certified</i>
Acetone	373	351.79	1.35	1.1
2-butanone (methyl ethyl ketone)	148	152.71	1.13	1.0
2,3 -butanedione (diacetyl)	702	624.46	1.17	1.1
Acetic acid	3080	2892.10	0.79	1.1
Dimethyl sulfide	20	26.91	1.91	0.7
Dimethyl disulfide	31	26.91	1.36	1.2
Dimethyl trisulfide	41	45.75	1.88	0.9
3-methyl butanal (isovaleraldehyde)	56	193.60	1.97	0.3
3-hydroxy-2- butanone (acetoin)	2158	652.80	1.87	3.3

The main advantages of permeation tubes are their relatively low cost and their potential to provide a very large volume of calibrated gas. Establishing a flowing gas mix should also overcome adsorption of semi-volatile compounds on the sample delivery line.

Comments on the performance of the Voice200 instrument

- These data were obtained using generic SIFT–MS ion-molecule reaction kinetic data (that is, no calibration was performed prior to this analysis). Many ions lie within Syft’s expectation that these data are within 50 per cent of the true value. The analytical method was subsequently updated to include these calibration factors.
- SIFT–MS data are generally highly repeatable as indicated by the standard deviations. Acetic acid and dimethyl trisulfide are not so repeatable (see comments below)—the uncharacteristic variability of the results for the latter suggest that there is minimal or no delivery to the Voice200 (compare the results for the related dimethyl sulfide and dimethyl disulfide compounds). Based on the good detection of other compounds, the permeation tube could be faulty.

Comments on specific compounds

- The dimethyl trisulfide permeation tube either delivers a much lower flow than estimated by the manufacturer, or the tube is defective. The compound is readily detectable using SIFT–MS (see Wang *et al.*, 2004).
- Acetic acid is a very sticky compound and exhibits a slow rise when the ‘sample’ inlet port of the Voice200 instrument is used. The data for acetic acid were calculated when the signal had plateaued (0.5 seconds of signal per product ion).

Summary and recommendations

- Generally, the results of SIFT–MS analysis of the permeation tube standards demonstrate that SIFT–MS provides reliable, repeatable quantitation of VOCs and organosulfur compounds.
- Use of SIFT–MS library values, rather than specific calibration, will provide sufficiently accurate quantitation for many applications.

- Variability in the measurements of standards when using multiple permeation tubes for calibration has raised questions about this particular calibration. Reactions in the permeation oven, adsorption on the delivery tube (which was quite long), and faulty permeation tubes are possible causes.

Bagged litter samples

Aim

Assess the ability of SIFT-MS to identify volatile, odorous compounds evolved from litters.

Method

Dry litter, wet litter ('cake'), litter from under the 'cake' ('undercake') and a 'shed composite' sample were collected from a meat chicken shed. The 'shed composite' was a litter sample formed from sub-samples of litter collected throughout a shed, comprising litter of various moisture and manure content conditions. The sample was collected, mixed/homogenised, bagged and transported prior to SIFT-MS analysis.

Samples were placed in 'ziplock' style bags and presented to the SIFT-MS instrument for direct headspace analysis. Samples of fresh litter materials (wood shavings and straw) were also analysed in the same way.

Results and discussion

Full mass scans are shown in Figure 22 for all samples that were analysed in this experiment. High concentrations were detected in the 'cake' and 'shed composite', in particular, resulting in additional spectral complexity. This would not happen if samples were more dilute.

By comparison, the fresh litter materials emit much lower levels of VOCs as shown in Figure 23.

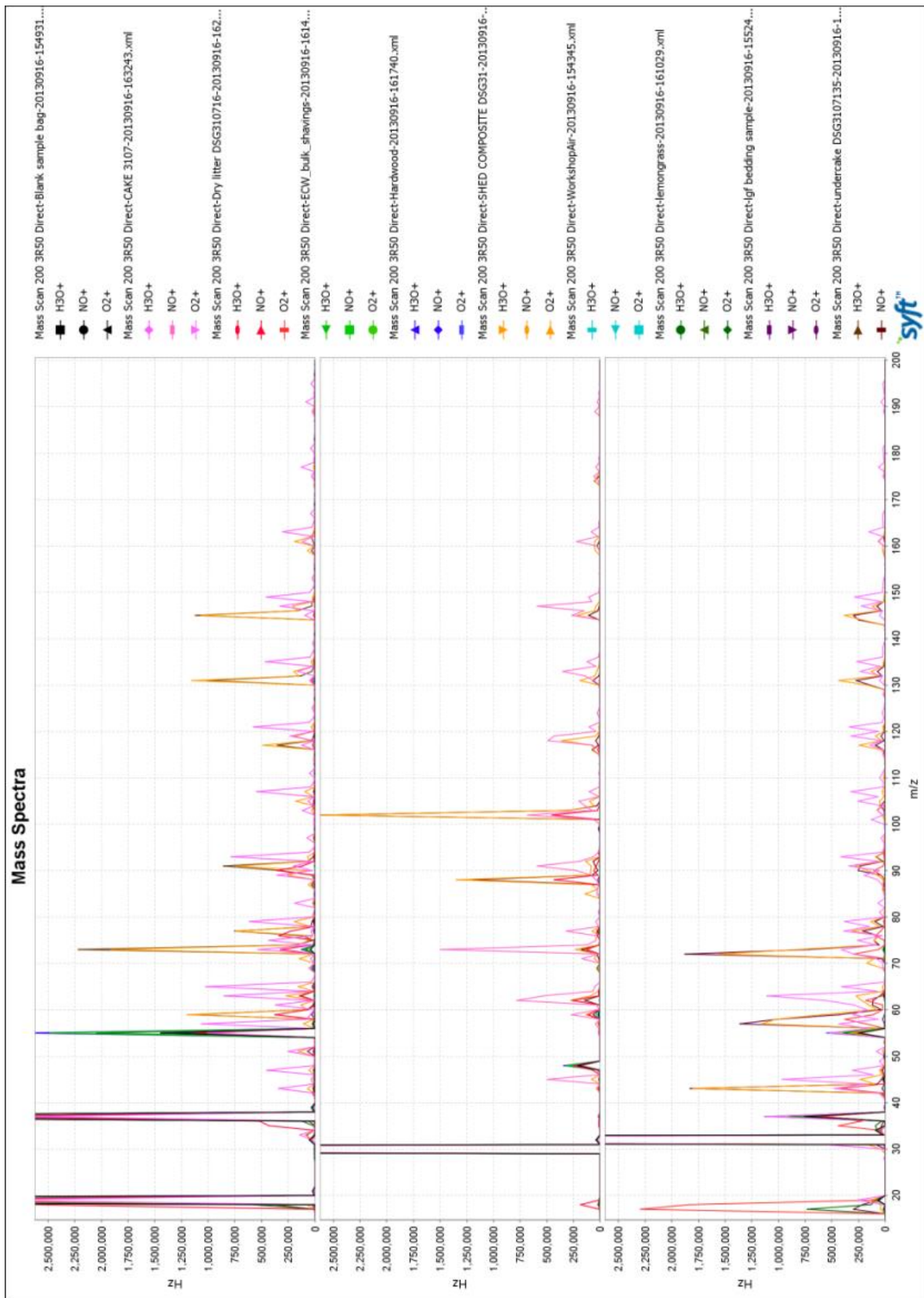


Figure 22. Full mass scan SIFT-MS data for shed litter (and fresh substrate samples). VOC concentrations in the 'cake' and 'shed composite' samples are high leading to significant spectral complication (pink = 'cake', brown = 'undercake', orange = 'shed composite').

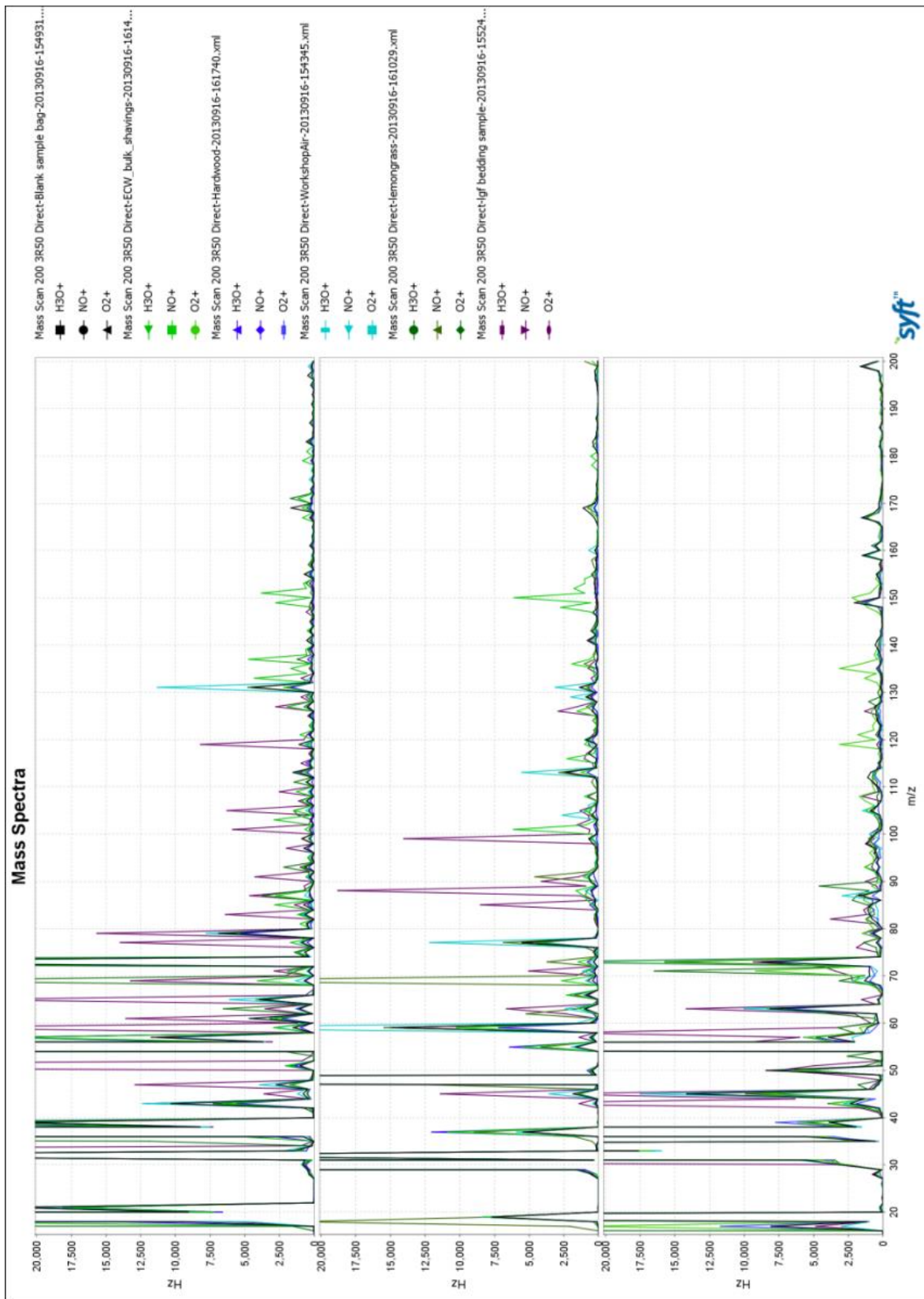


Figure 23. Full mass scan SIFT-MS data for litter samples emitting lower concentrations of VOCs (purple = light, fine straw; dark green = coarse straw; light green = bulk shavings; dark blue = hardwood shavings; light blue = background; black = blank).

Summary and recommendations

- The dominant compounds are those previously identified using GC–MS, though the VOC ‘signature’ is very complex.
- GC–MS analysis in full scan mode is a better option than using SIFT–MS in full scan mode for identifying compounds due to its higher selectivity and larger mass spectral library.
- SIFT–MS is more suited to targeting compounds in dynamic processes that have been identified using GC–MS or related techniques (for example, GC with a sulfur detector).
- Lower level VOCs detected in the headspace of litter samples are unlikely to be detected outside the sheds.

Flux chamber experiments

Aim

Preliminary assessment of SIFT–MS for monitoring dynamic odour processes in laboratory experiments.

Method

A litter sample was evenly spread across a tray and the flux chamber was placed over the top of it (Figure 24). High purity air was passed through the chamber and the SIFT–MS was used to analyse air from the chamber outlet.



Figure 24. Using SIFT–MS to analyse flux hood litter headspace samples.

Results and discussion

Most of the samples exhibited stable concentration readings over the less than 30-minute time scale of the experiment. However, several examples of dynamic behaviour were observed in the shed composite sample using the poultry odour method as shown in Figure 25 and Figure 26. Note:

- a logarithmic scale has been used to enable all compounds to be displayed clearly on a single graph. This tends to exaggerate the noise on the low ppb signals
- calibrations have not yet been retrospectively applied.

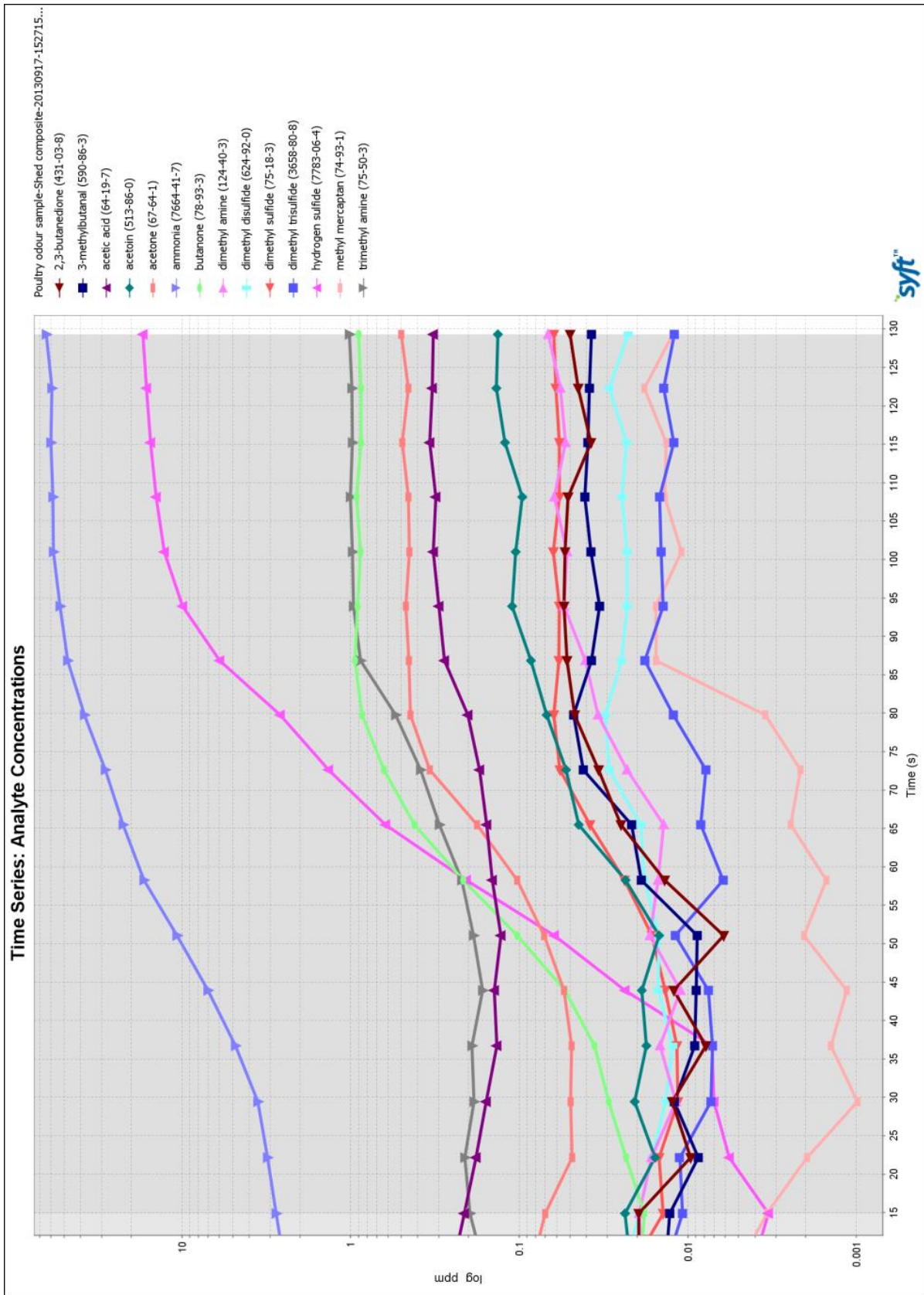


Figure 25. First SIM analysis of the shed composite sample in the flux chamber tests.

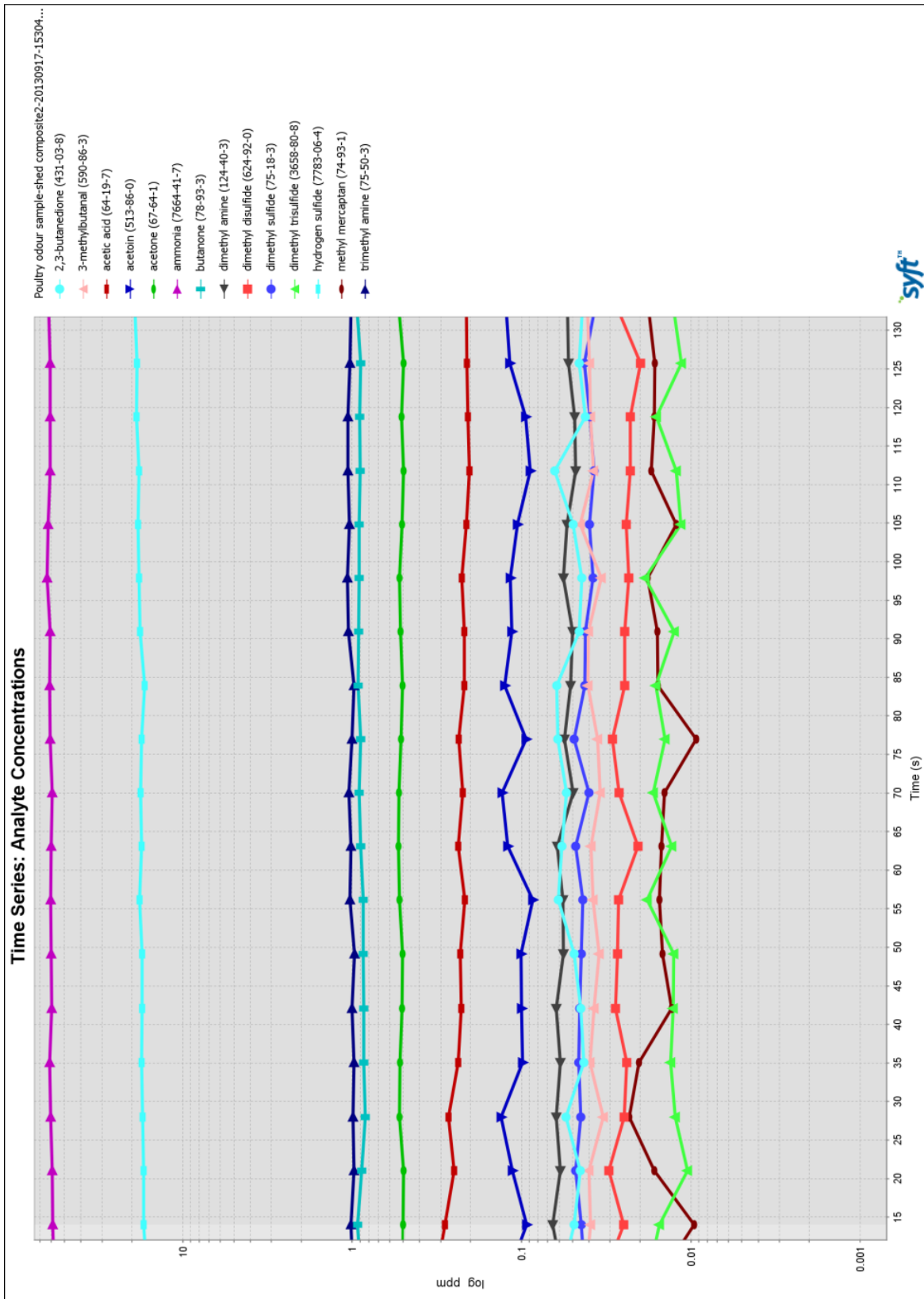


Figure 26. Subsequent SIM analysis of the shed composite sample in the flux chamber tests— concentrations have stabilised (Note that colour coding has changed from Figure 25).

A 30-minute full scan analysis was used for the dry litter sample (Figure 27). This has been reprocessed using the calibrated 'Poultry' method (that is, calibrations were applied to these data). Note that several other compounds have been added (methanol, benzaldehyde, and beta-pinene—the latter representing the 'monoterpenes', which probably arise from plant matter used for litter).

Interestingly, hydrogen sulfide and methyl mercaptan rise somewhat more slowly than ammonia and butanone (MEK). This demonstrates the usefulness of real-time SIFT-MS analysis for monitoring dynamic processes.

Figure 28 shows the full scan data obtained for the various samples.

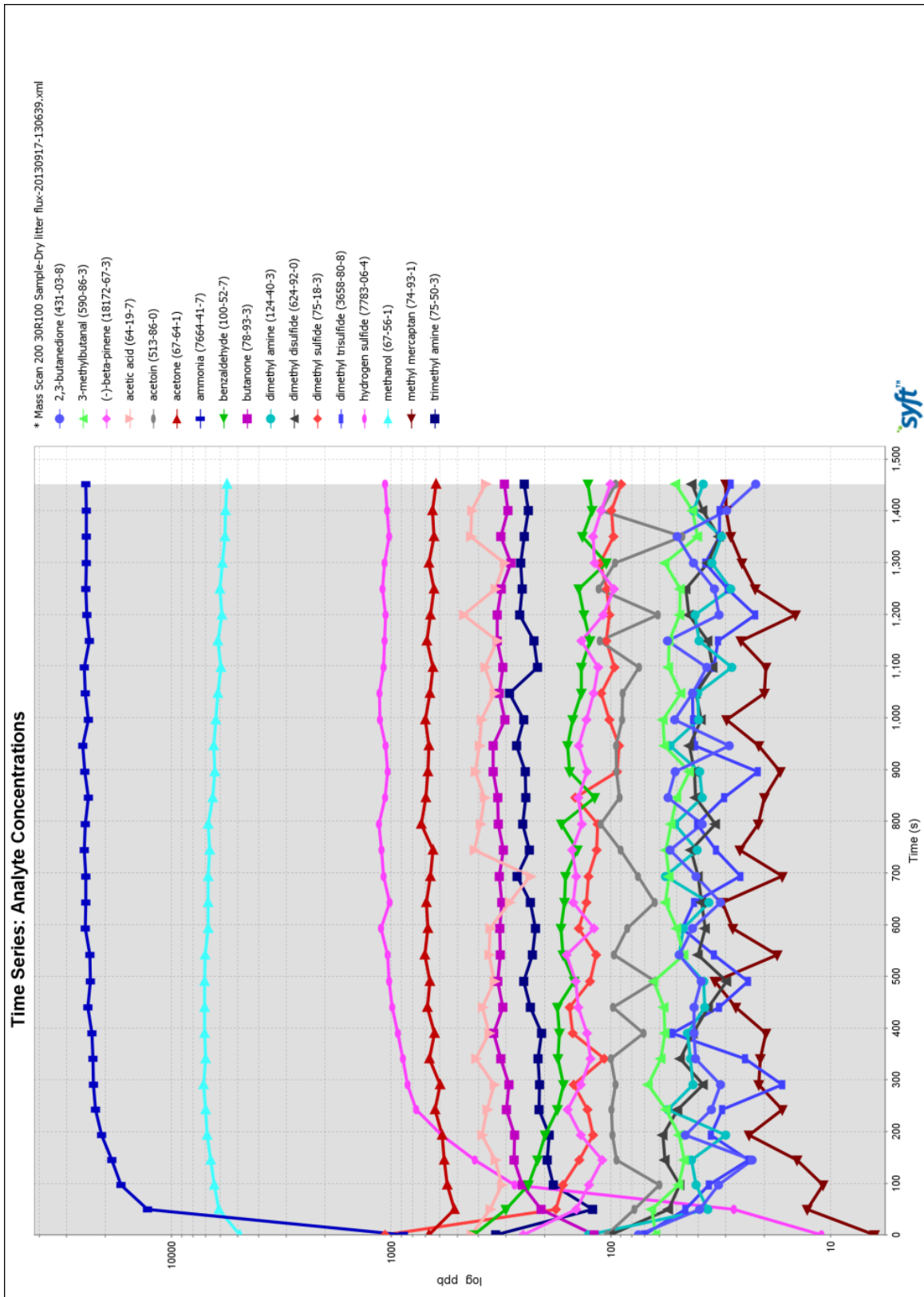


Figure 27. Concentrations calculated from a 30-minute mass scan analysis of dry litter in the flux chamber testing. See the text for more details.

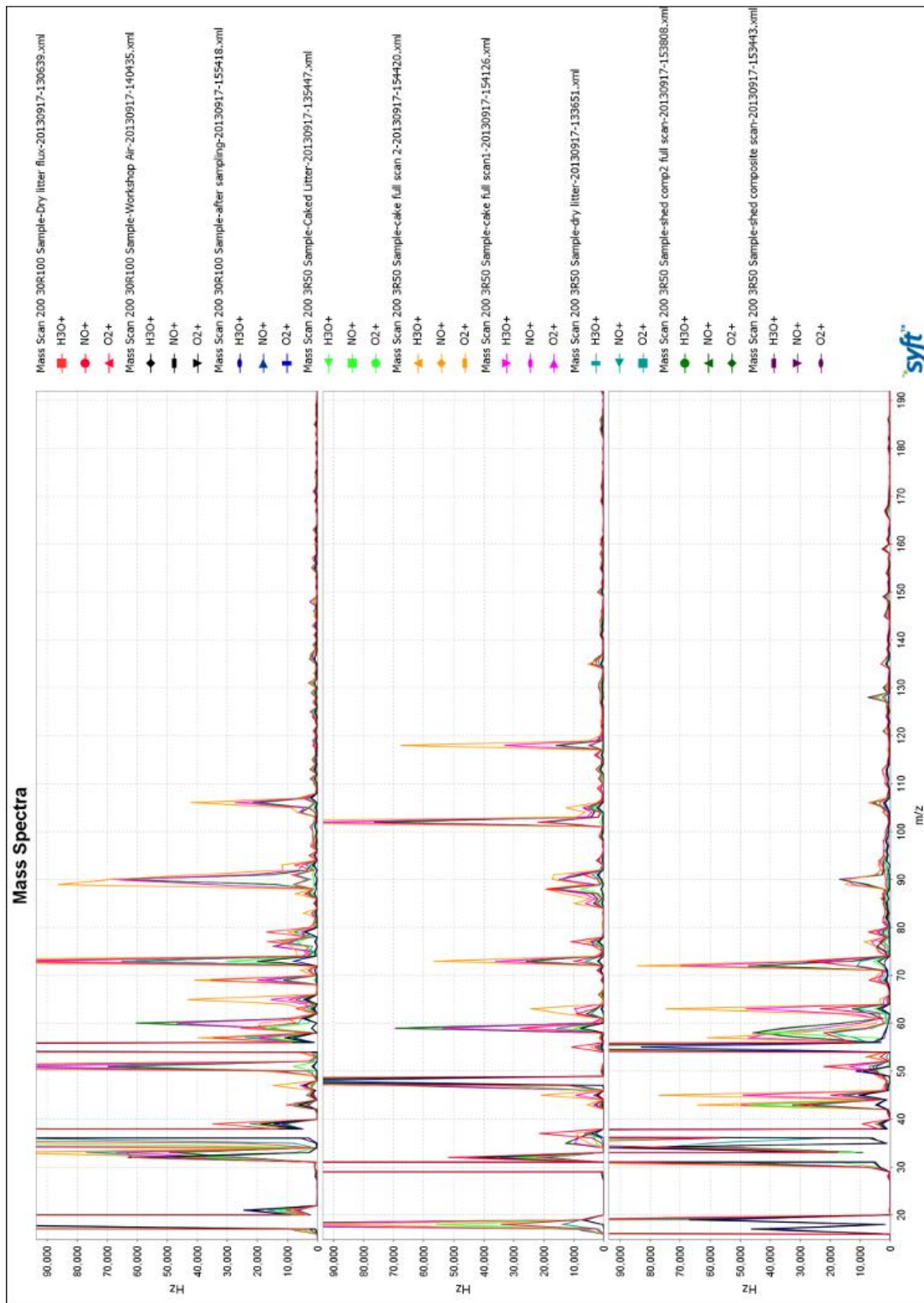


Figure 28. Full scan data for all samples (zoom is at a level where most high-level compounds remain in the view).

Concentrations ($\mu\text{g}/\text{m}^3$) of 18 target odorants emitted from the litter samples are shown in Figure 29, demonstrating the potential use of SIFT-MS for 'odour-printing' different odour sources. Figure 30 shows the estimated odorant emission rates from these litter samples.

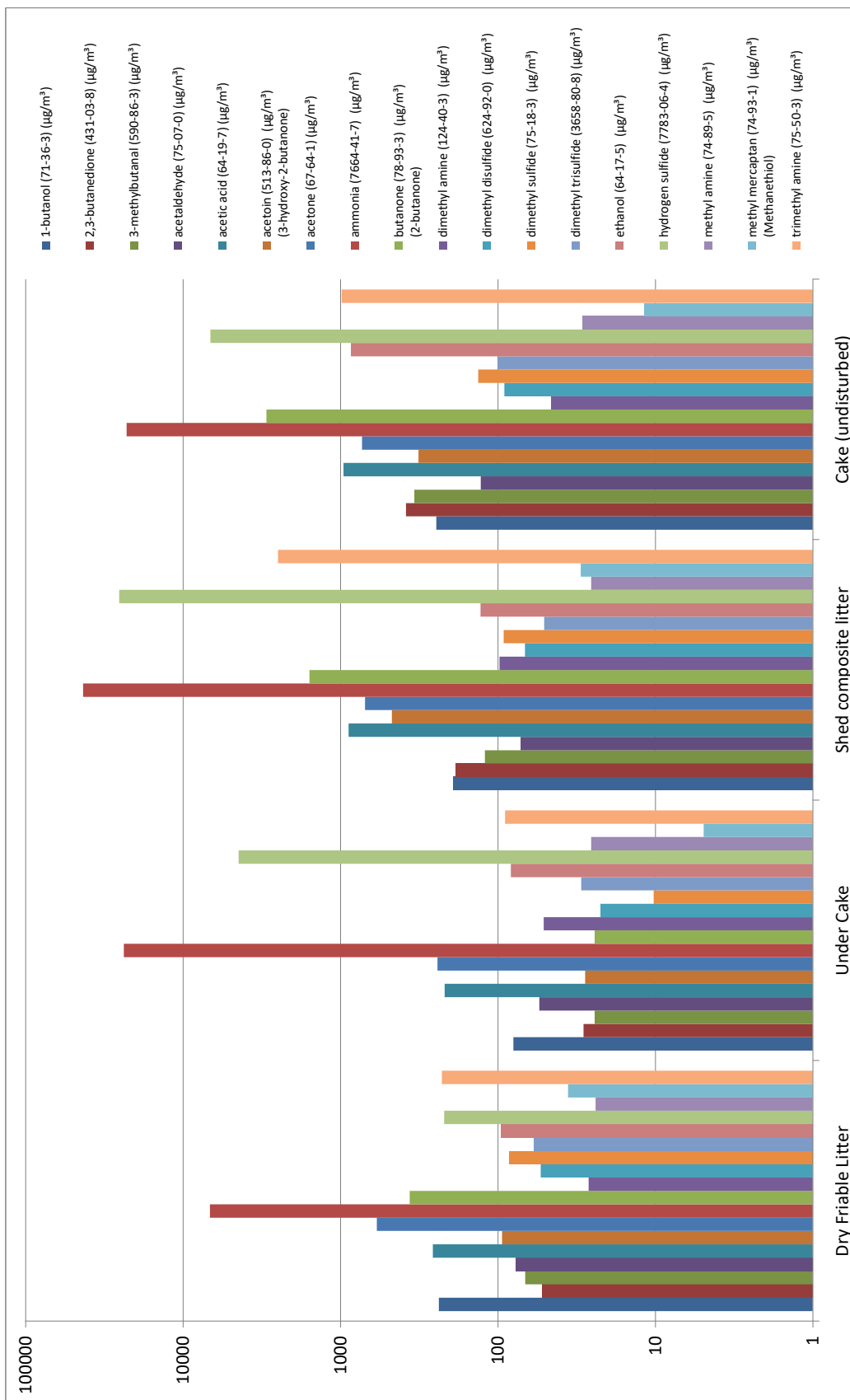


Figure 29. Odorant concentrations from litter headspace samples.

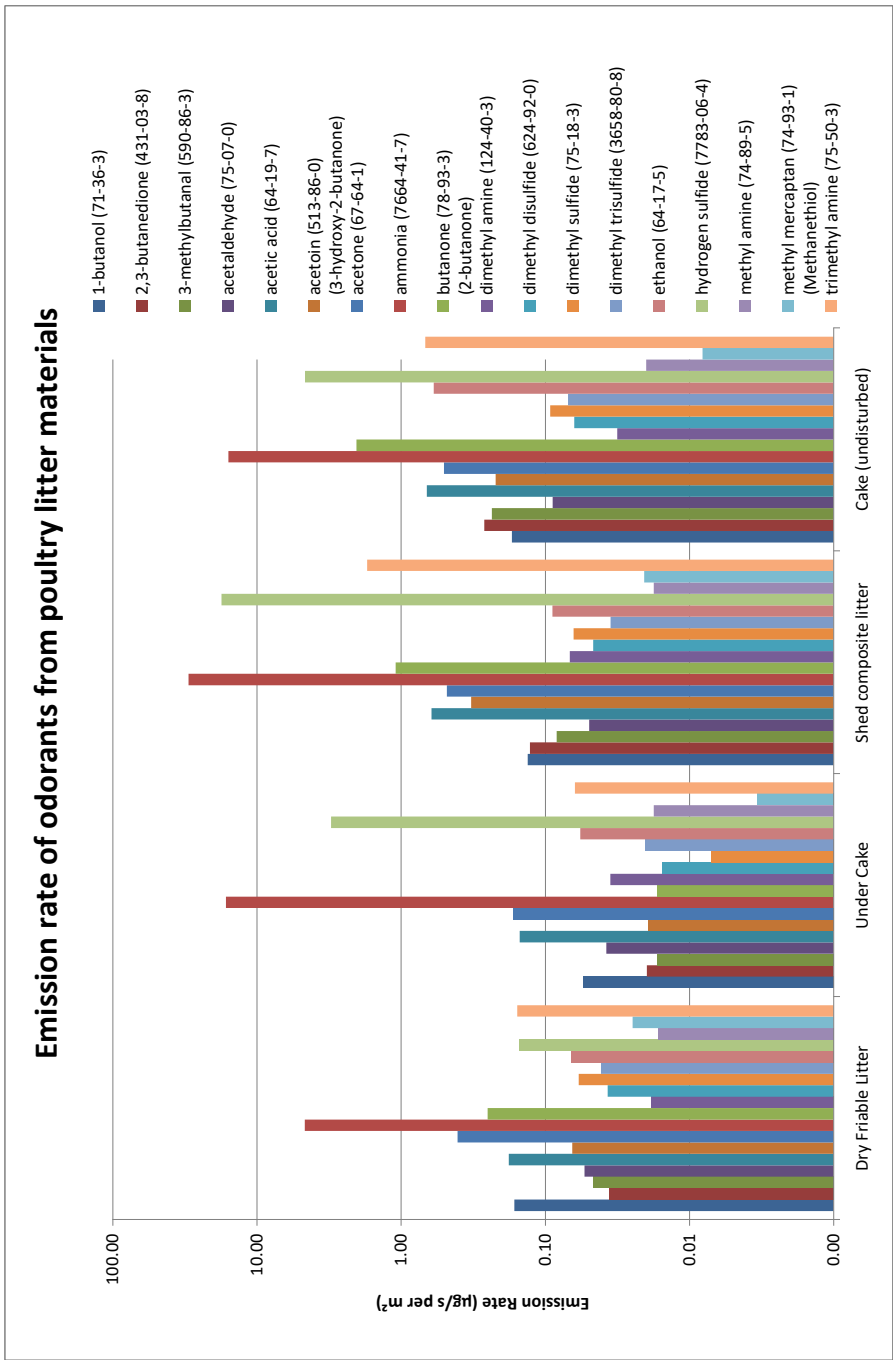


Figure 30. Emission rate of target odorants from poultry litter.

Summary and recommendations

- SIFT–MS is suited to monitoring dynamic processes. For two samples, several compounds show different behaviours. (Other samples appear more stable, though this has not been investigated in detail, and different scan types were run on each in different orders.)
- The full mass scan is the best option for this type of sample because it best facilitates recalculation when additional compounds are discovered.
- For such samples, the SIM method will need fine-tuning due to high ammonia concentrations.

Field evaluation of SIFT–MS

Aims

- Collect, evaluate and compare odour data from various sources.
- Identify best practices for on-site work through lease period.
- Conduct continuous monitoring during odorous events.

Method

The Syft Voice200 instrument was used to analyse:

- ambient air directly (that is, using no sampling lines or pre-concentration)
- air sampled into odour bags in drums as used for dynamic olfactometry odour and GC–MS assessments (Figure 31 to Figure 33).

A variety of analyses in full mass scan and SIM modes were undertaken at the site and at the DAFF facility in Toowoomba after the return early in the afternoon (to conduct olfactometry).

For continuous monitoring, at farm B, the Voice200 instrument was used to analyse ambient air directly downwind from a shed (that is, using no sample medium). At farm A, in-shed air was analysed via a sampling probe inserted through the shed wall during bird pickup and the bulk of the litter removal. GC–MS samples were collected from the shed on the last day of the batch.



Figure 31. Sampling from bag sample in drum.



Figure 32. Collecting ambient sample for analysis by SIFT-MS, GC-MS, AOS and olfactometry.



Figure 33. Sampling from drum for odour decay study. Providing shade for the sample was important as the black drums absorbed heat quickly in direct sunlight.

Results and discussion

Figure 34 shows ammonia and methylamine are the most concentrated odorants during bird pickup preliminary example is shown in Figure 35 to Figure 37, where concentrations of compounds in the calibrated 'Poultry' method have been calculated using the LabSyft software from the long full mass scan. Rising and falling behaviours correlate between the compounds that have been plotted here, which is encouraging. Though unable to confirm the reasons, these peaks and troughs should correspond with the periods of activity and inactivity in the pickup process.

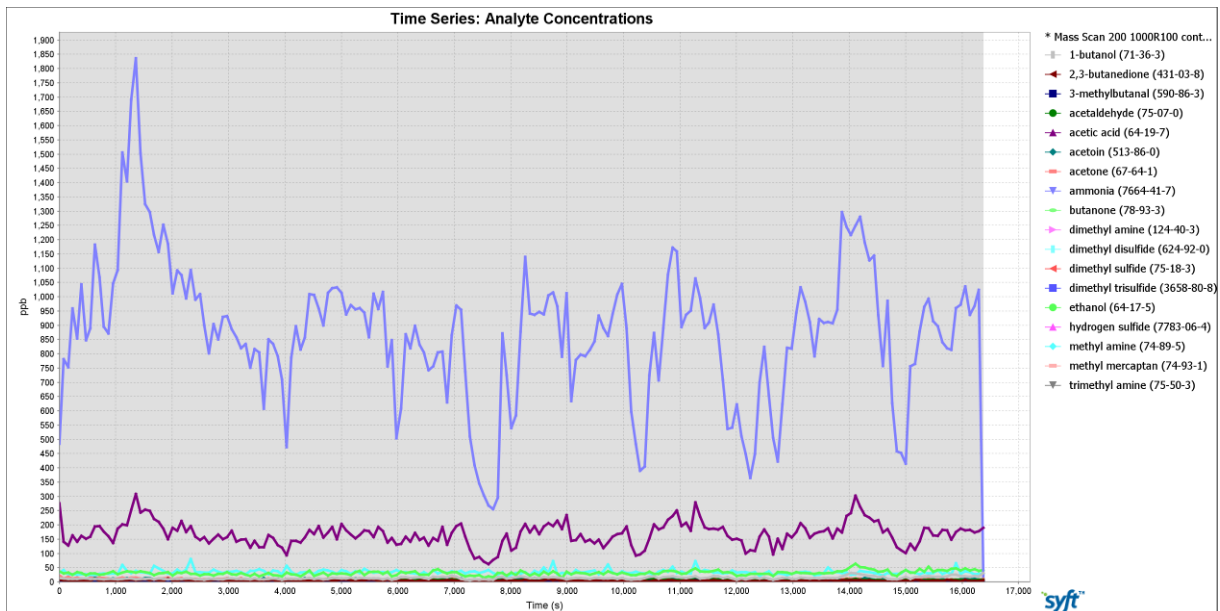


Figure 34. SIFT-MS concentrations calculated from the long full mass scan obtained on 23 and 24 September 2013.

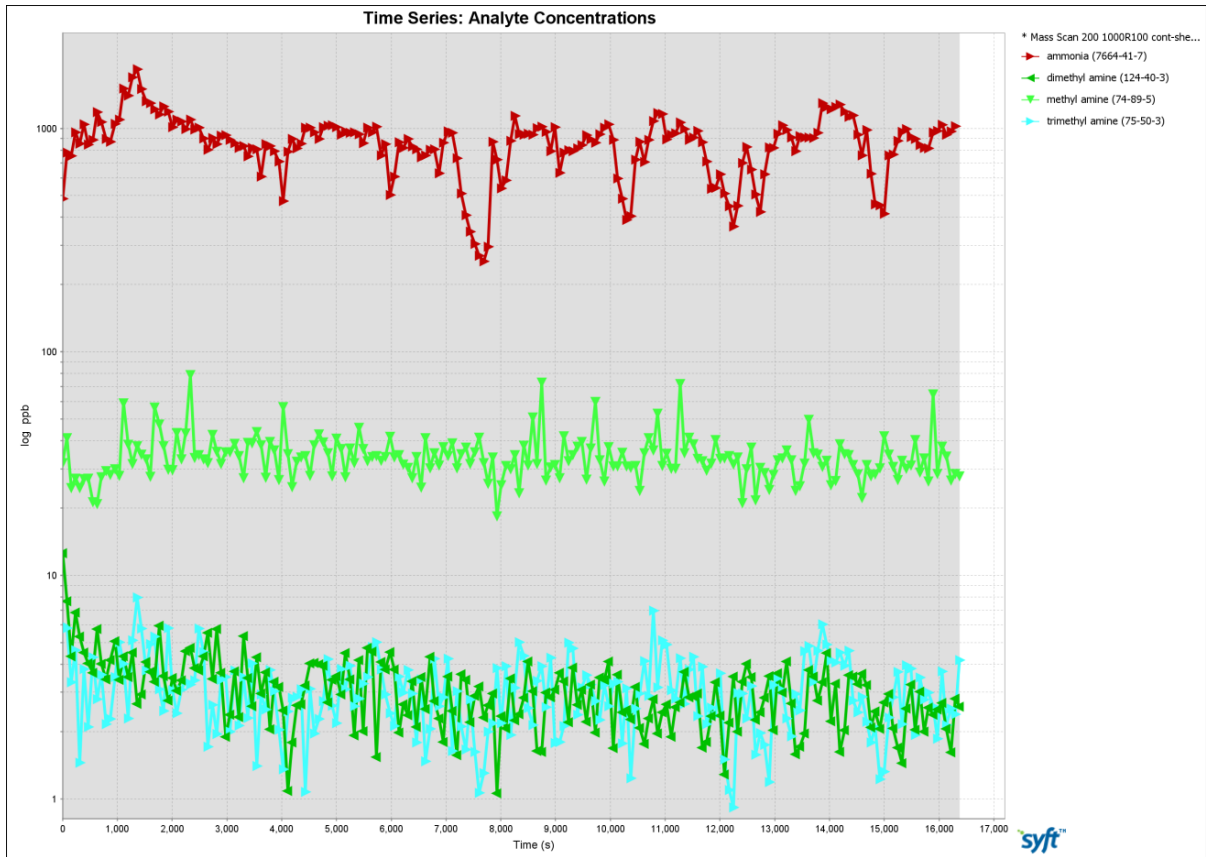


Figure 35. SIFT-MS ammonia and amine concentrations calculated from the long full mass scan obtained on 23 and 24 September 2013. There appears to be a significant background signal for methylamine, which has not been subtracted from these data.

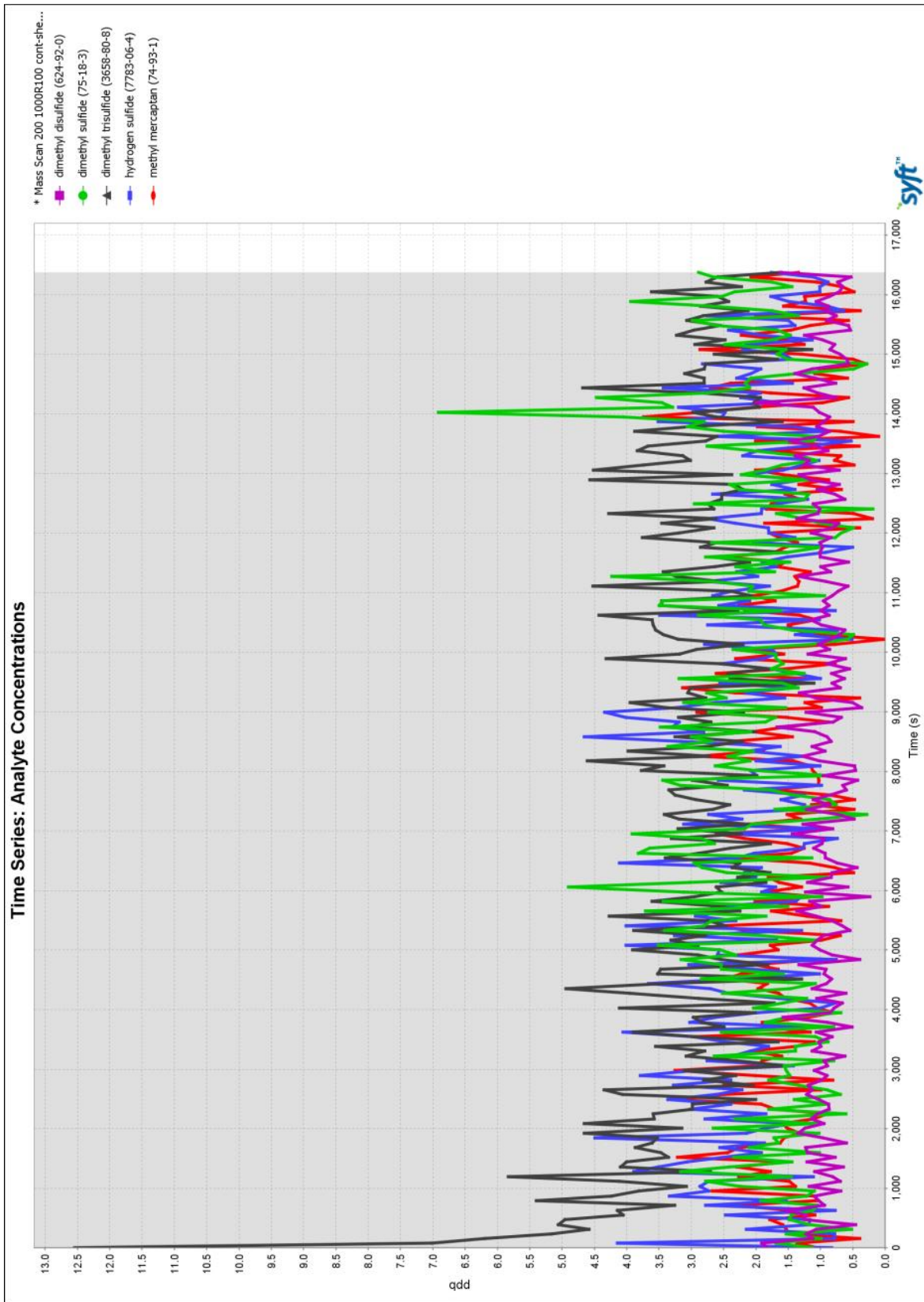


Figure 36. SIFT-MS hydrogen sulfide and organosulfur concentrations calculated from the long full mass scan obtained on 23 and 24 September 2013. Note the linear scale in this figure.

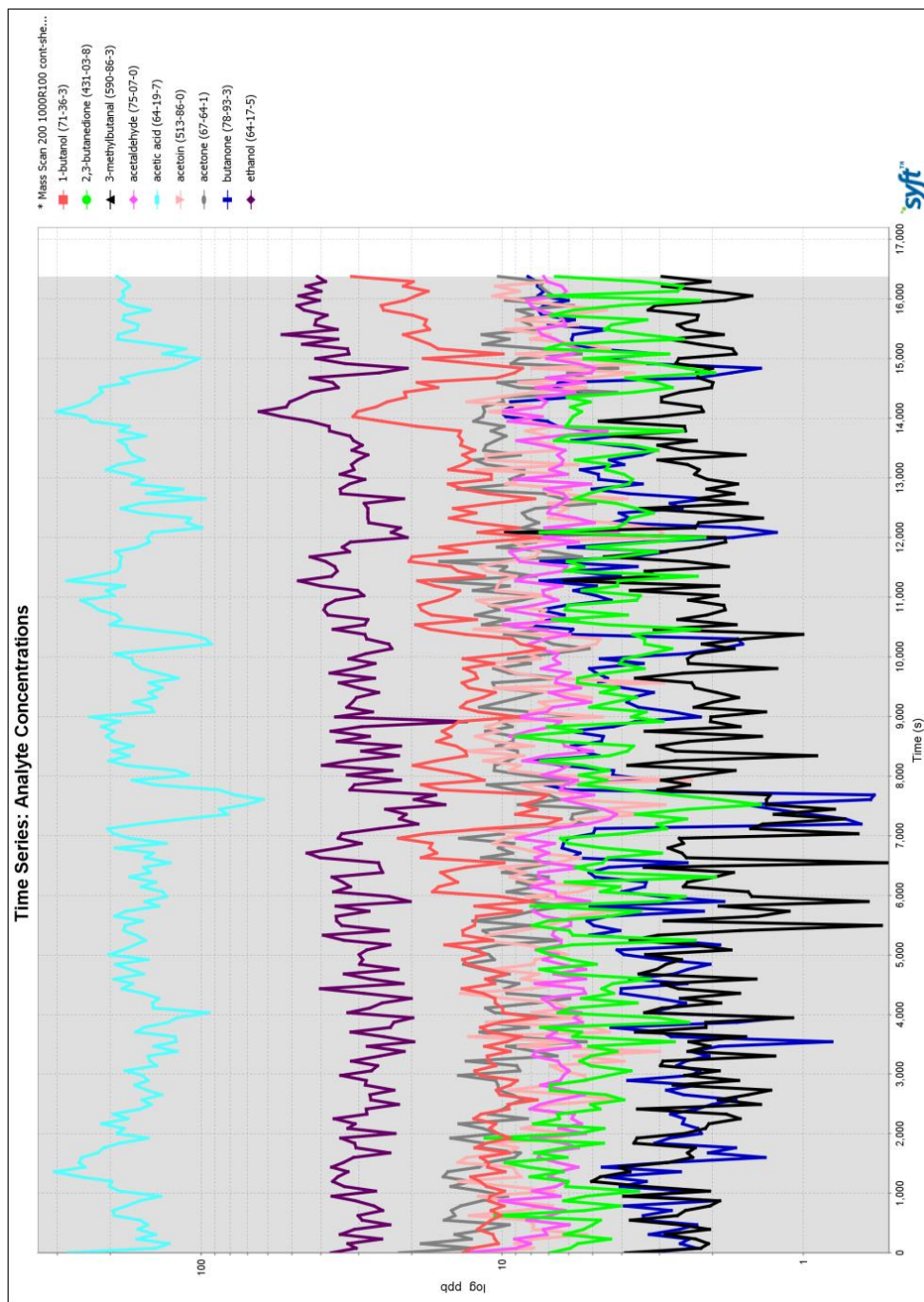


Figure 37. SIFT-MS oxygenate concentrations calculated from the long full mass scan obtained on 23 and 24 September 2013. Note the logarithmic scale in this figure.

Figure 38 to Figure 42 show the results of continuous monitoring for a bird pickup overnight followed later by a litter harvesting event starting at 5 am. Intermittent disturbance of the birds is marked by proportional fluctuations in the odorants. Once litter harvesting began, ammonia and hydrogen sulfide levels rose sharply. At 11 am the sampling probe was moved from inside the shed to a position outside and away from the shed to sample the ambient air while the last of the litter cleanout was loaded on to the trucks. The spikes at that time correspond to the breeze blowing dust (and odour) in the direction of the probe. Of interest is the marked increase in methyl amine and dimethyl amine during the litter harvest.

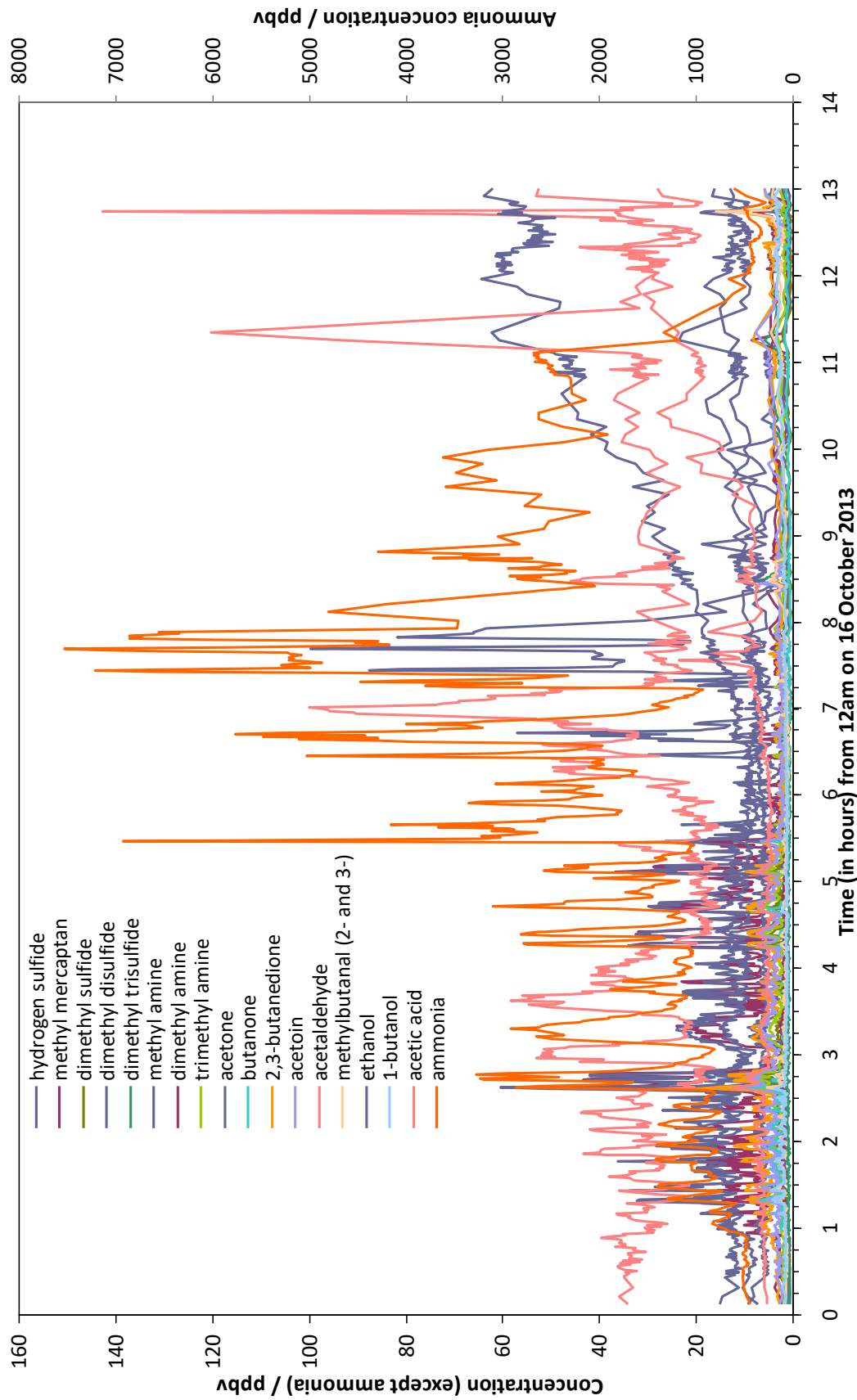


Figure 38. Continuous monitoring of target odorants during bird harvest and litter collection. For a breakdown of this graph, see Figure 39 to Figure 42.

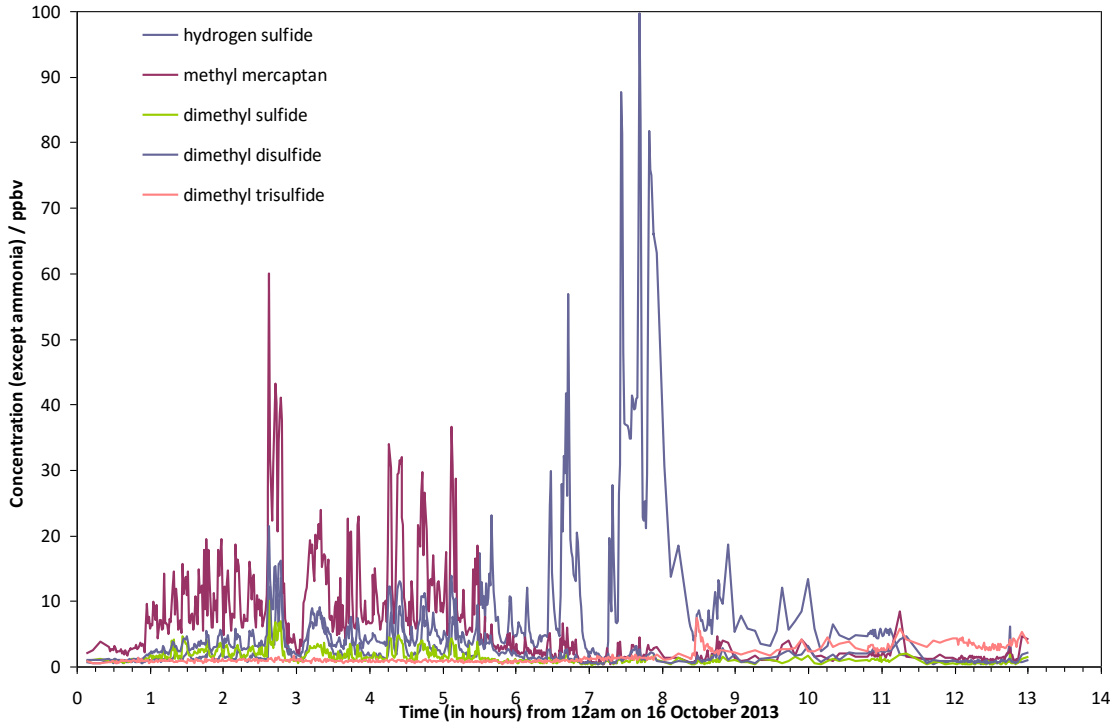


Figure 39. Continuous monitoring of sulfides during bird harvest and litter collection

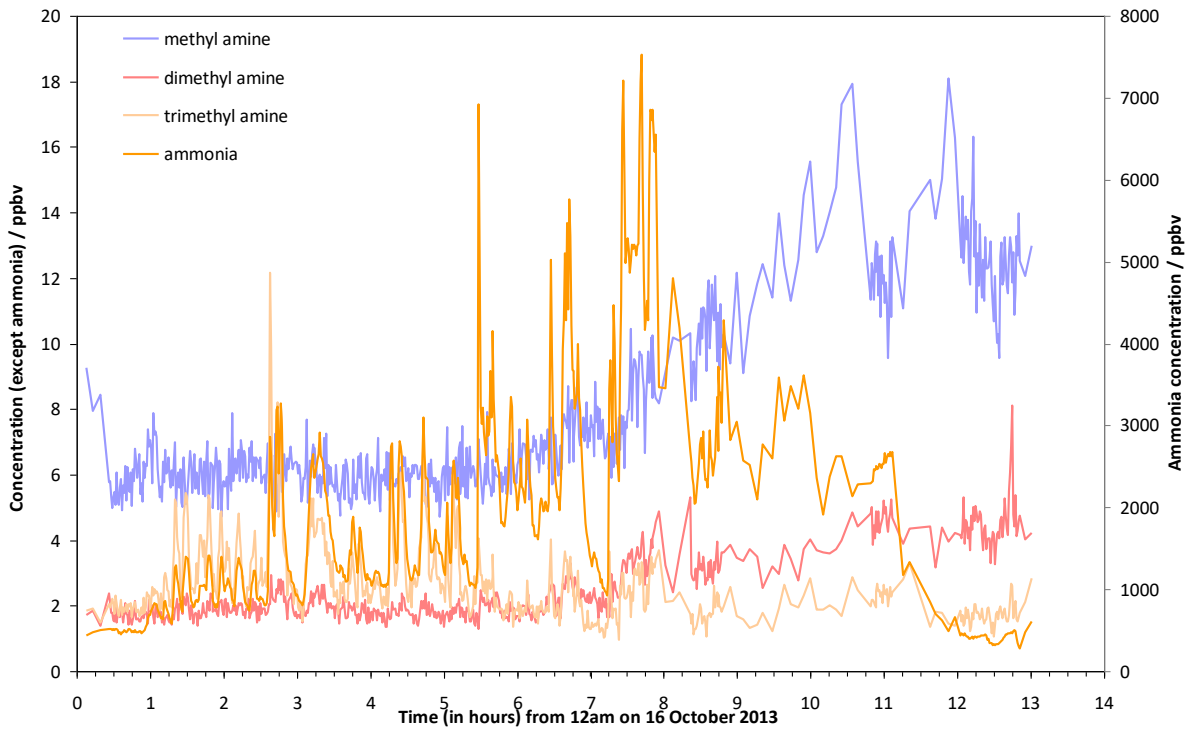


Figure 40. Continuous monitoring of ammonia and amines during bird harvest and litter collection.

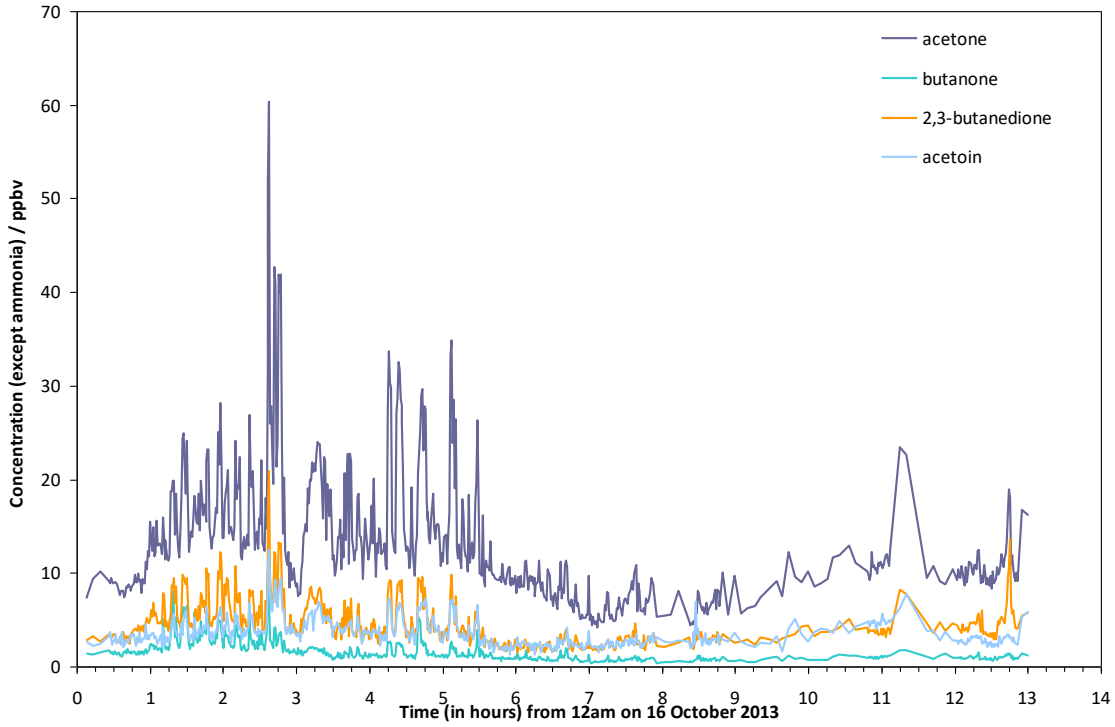


Figure 41. Continuous monitoring of ketones and related compounds during bird harvest and litter collection.

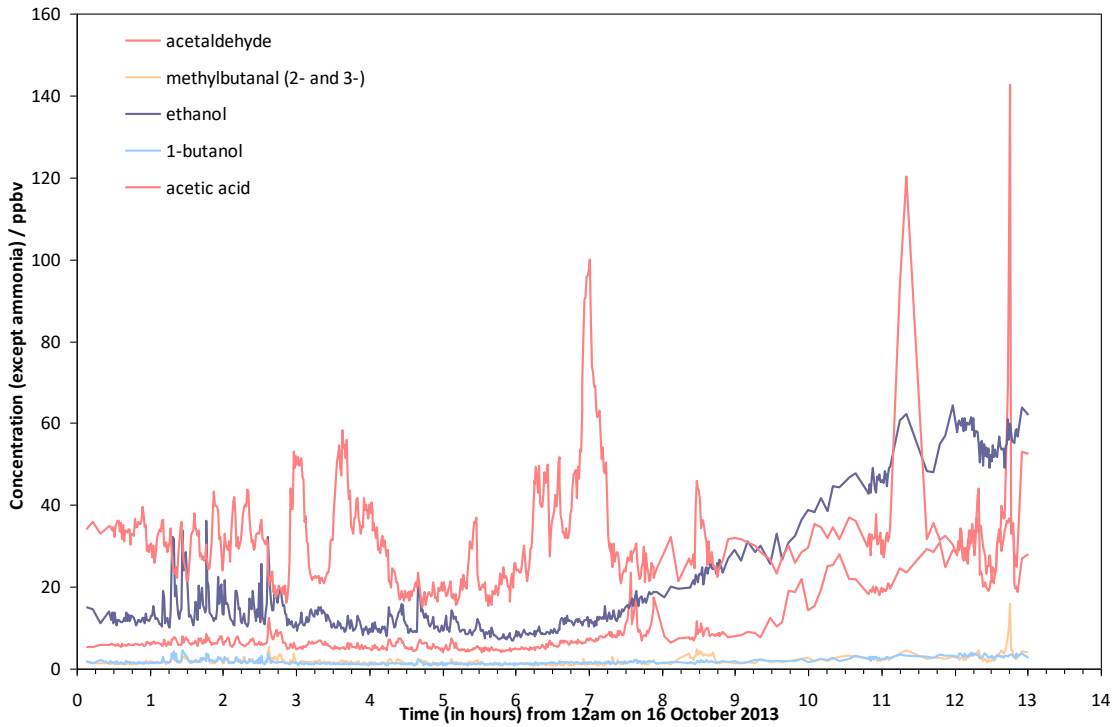


Figure 42. Continuous monitoring of aldehydes, alcohols and acetic acid during bird harvest and litter collection.

Operational and technical matters

In general, the SIFT–MS was easy to use and the technical support we received during the trial from Syft Technologies was excellent. However, we encountered some problems that prevented a more comprehensive evaluation:

- Inability to move SIFT–MS instrument during analysis hinders spatial measurement, for example, along a transect. This limited the spatial sampling capability on any given day. Start up and shutdown procedures waste valuable field time.
- Does not notify user when scan has failed. Continues to plot real time data ‘on screen’ so the user is unaware of the fault until they attempt to stop the scan and the instrument ‘hangs’.
- Overheating of SIFT–MS at ambient temperatures around 30 °C. This is a problem if air-conditioning is not available as was our case. Providing adequate shade and ventilation to the instrument can be problematic in hot weather, as was experienced on occasions during the trial. We regularly had to leave the side casing off the instrument to prevent it from overheating.
- Failure of the heat exchange sampling column. This is a critical component for controlling the sample’s consistent delivery, particularly in humid environments. This component failed for some unknown reason and had to be replaced during the trial by a Syft technician.
- For our study, the logistics of collecting samples and conducting SIFT–MS and AOS measurements in the field, then returning to Toowoomba, to conduct timely dynamic olfactometry and AOS sample humidity calibrations, limited the number of samples that could be done on any given day.

Summary and recommendations

The results indicate:

- Farm boundary measurements had very low ppb concentrations of odour compounds and other VOCs arising from the meat chicken sheds. Under these conditions, full mass scans do not have the required sensitivity of measurement and short cycle time to make them useful for identifying additional odour compounds.
- It is better to identify odour compounds from the concentrated air in the shed itself, before it is dispersed.
- The SIFT–MS SIM mode is a better option than full scan mode—allowing known odour compounds to be targeted at higher repetition rates and sensitivity.

SIFT–MS monitoring data can:

- capture odorant fluctuations well, which is particularly helpful for analysing those short-term events that may contribute to odour impacts
- provide insight into the odorants that may contribute to odour nuisance and illicit complaints.

Odour decay studies

During the period between collection and analysis of bagged odour samples, the chemical composition and concentrations of odorants can change. Such changes may influence the strength of the odour and hence the odour concentration result from dynamic olfactometry.

Aim

To evaluate use of SIFT–MS to detect variation in target odorants in olfactometry bag samples over time.

Method

An in-shed sample was collected at Farm A and analysed for 1.75 hours immediately following collection. The sample line connecting the sample to the SIFT–MS was minimal length (Figure 43) and was primed with sample using a vacuum pump (Figure 44) to ensure the sample was presented at full strength for the entire SIFT–MS analysis. Priming was conducted at a rate of ~9000 mL/min.

Three additional olfactometry samples (same source; in odour plume) were assessed with SIFT–MS at different times after being collected.



Figure 43. SIFT–MS sample line connection to drum.



Figure 44. Pump to prime SIFT–MS sample line.

Results and discussion

Figure 45 to Figure 47 show the time variation of odorant concentrations in the 1.75 hrs following collection of a bagged in-shed odour sample, typical of those collected for dynamic olfactometry. Whilst most chemicals were relatively stable, ammonia concentration dropped within the first eight minutes by ~30 per cent (probably due to adsorption in the bag) then gradually recovered, doubling in concentration over the next hour (Figure 45). Acetic acid, ethanol and methyl amine also displayed this increasing trend during this period, while acetaldehyde decreased 50 per cent during the first 20 minutes before stabilising.

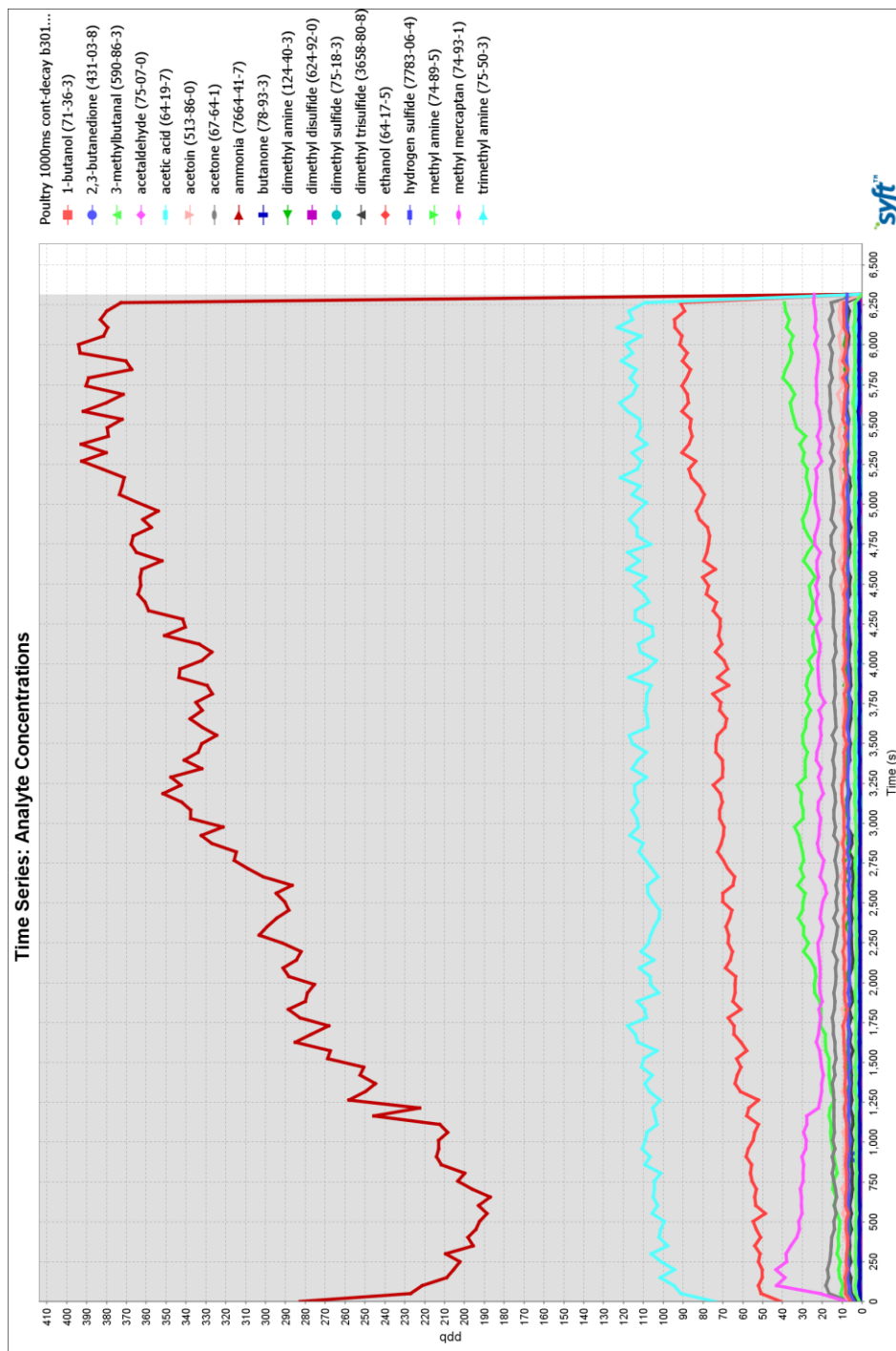


Figure 45. Time variation of all targeted odorants over the first 1.75 hours of storage.

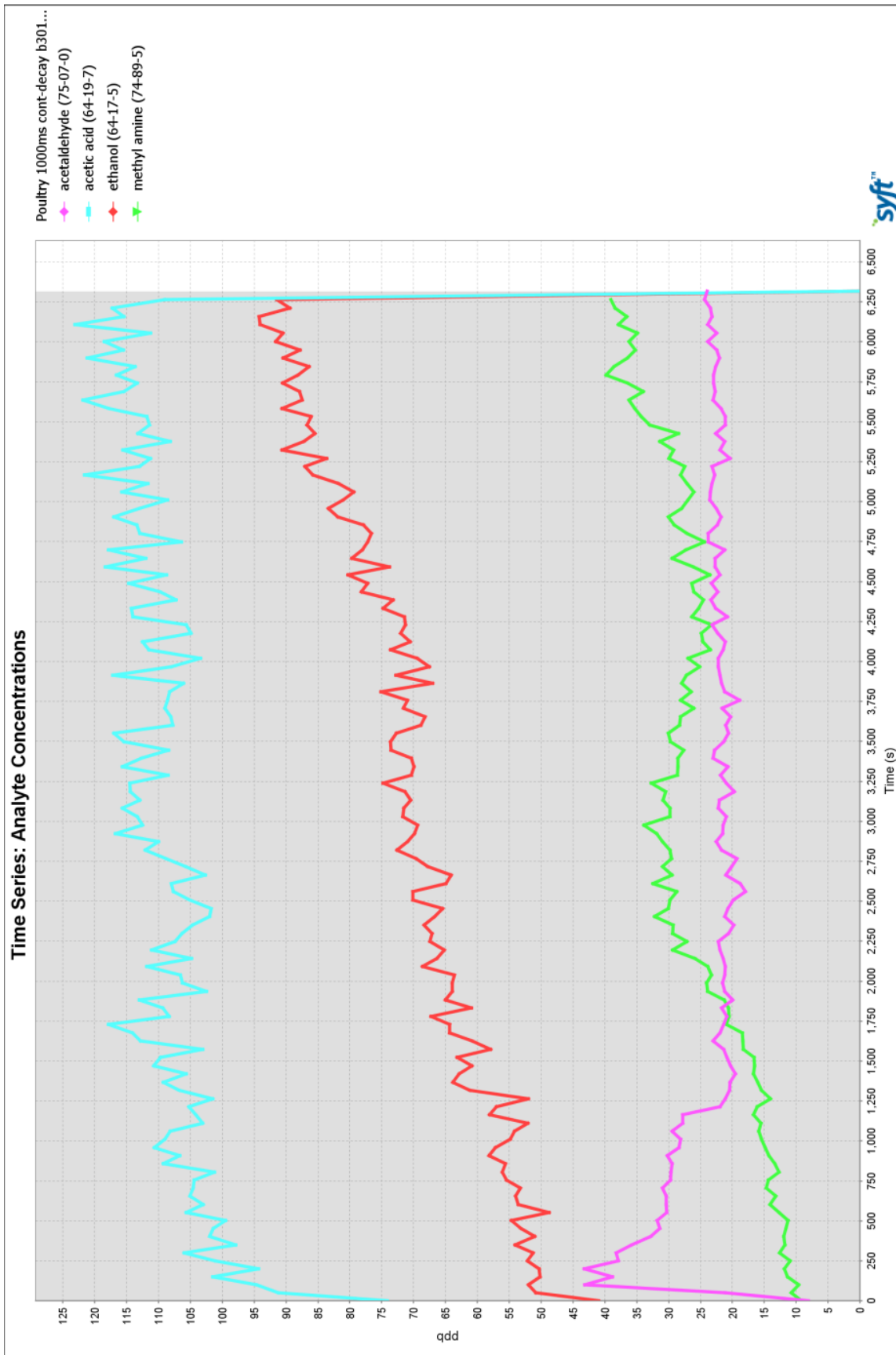


Figure 46. Time variation of VOCs with concentrations < 130ppb over the first 1.75 hours of storage.

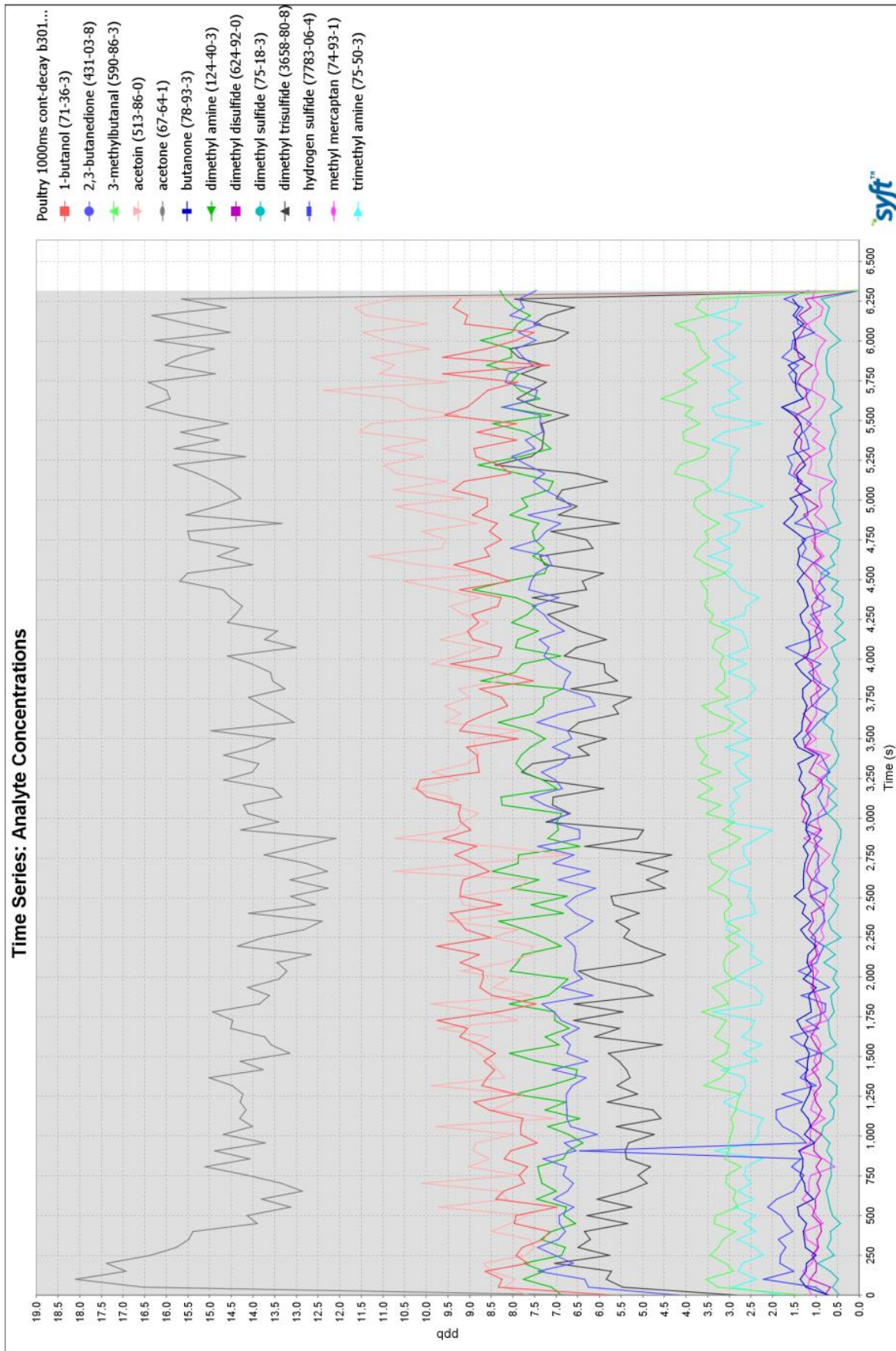


Figure 47. Time variation of VOCs with concentrations < 20ppb over the first 1.75 hours of storage.

These VOC fluctuations are indicative of chemical changes that may be due to various reasons including: drum contaminants permeating into the bag; VOCs permeating out of the bag; VOCs adsorbing to the sides of the bag; and chemical transformations. The stability of the sulfides may have a masking effect on the odour concentration, hence the lack of variation in odour concentration. This analysis was not repeated so the question remains whether these observations are typical or not. In many shorter scans, ammonia was more erratic and trends were not as apparent.

Any chemical changes may influence the odour concentration. However, there were no significant differences in odour concentration for the three decaying samples (collected from the same source) examined as shown in Table 4.

Table 4. Results of olfactometry for three ‘decaying’ samples from Farm C.

<i>Sample</i>	<i>Hours since collection</i>	<i>Odour concentration (ou)</i>
B3073	6	242
B3071	4¼	203
B3071	7¼	211
B3070	4¾	203
B3070	7	192

Figure 48 shows the declining average ammonia concentration in olfactometry sample B3070 over a seven hour period using the SIM method and two different dwell times (the length of time spent analysing each m/z ratio value). Each SIM scan was run for ~10 minutes. Ignoring the 0 hr readings (since adsorption was likely a confounding influence), the dwell time for ammonia had little impact. However, for the sulfides, the 500 ms readings were significantly lower than the 100 ms readings (dimethyl sulfide, by 33 per cent; hydrogen sulfide, by 44 per cent; methyl mercaptan, by 28 per cent).

Figure 49 shows declining concentrations of all monitored odorants, except for H₂S and methyl mercaptan, which were stable.

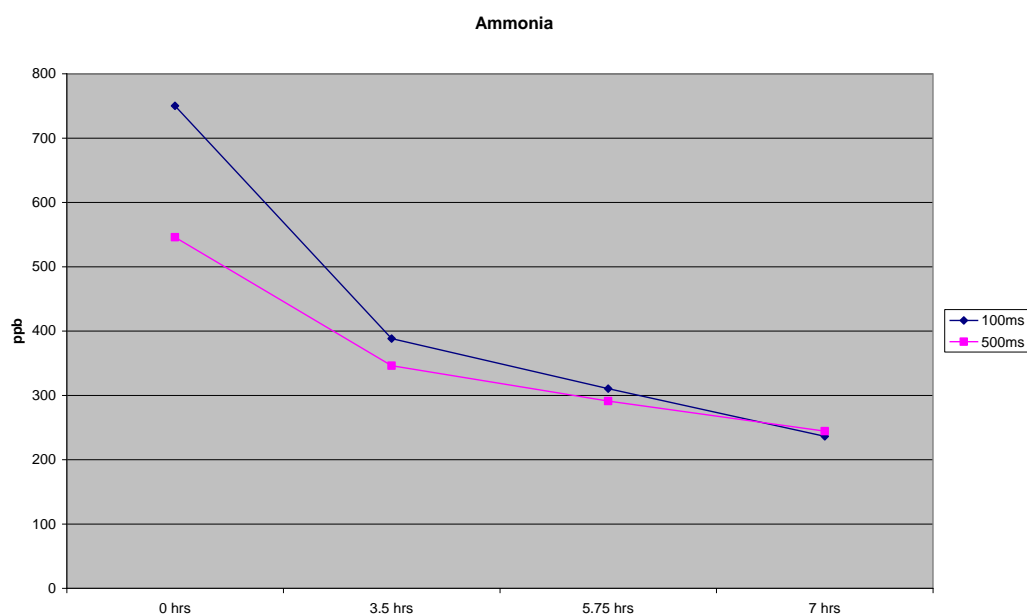


Figure 48. Ammonia concentration using SIM scans with different dwell times.

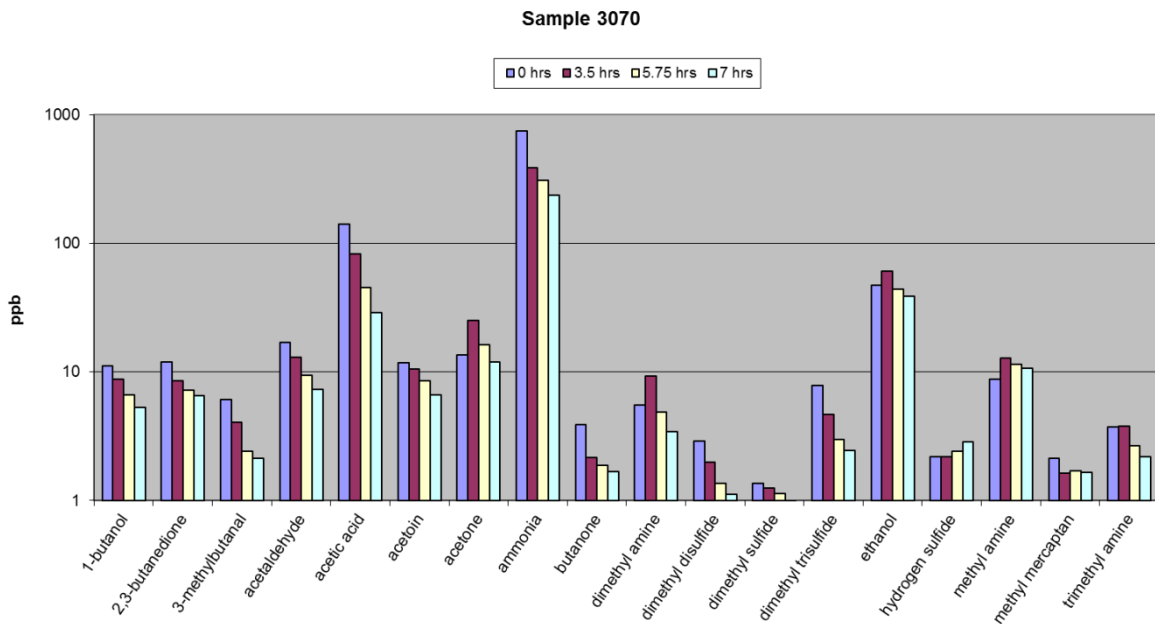


Figure 49. Changes in poultry odorant concentrations in an olfactometry sample.

Key findings

- Ammonia was the most unstable odorant measured.
- Hydrogen sulfide and methyl mercaptan were the most stable.
- Longer dwell times produce significantly lower sulfide concentrations.
- There was generally a gradual decrease in all odorants after 3.5 hours storage indicating chemical changes continue to occur.
- Olfactometry results changed over time but not significantly.

3. Odour prediction using SIFT–MS

Aims

There is interest in tools to measure odour more cost-effectively. The aim here was to explore the potential of using SIFT–MS as a proxy for dynamic olfactometry. An additional aim was to determine whether gas sensor response data from an artificial olfaction system developed for poultry odour could be correlated to the SIFT–MS odorant concentration data.

Methods

Those odour samples collected for dynamic olfactometry analysis were firstly analysed immediately after collection by AOS, then SIFT-MS.

The AOS used is described in Atzeni *et al.* (2014). The AOS's sensor array contained five Figaro TGS metal oxide semiconductors (MOS), two photo-ionisation detectors (PID) and an ammonia sensor (Table 5). The processed sensor array data was used to predict odour concentration (ou). The odour concentration results determined by dynamic olfactometry are included in Appendix D. In the field, the AOS analysis was done immediately after sample collection, followed closely by a SIFT–MS full scan and sometimes a SIM scan. Scans were kept to approximately 10 minutes duration to try and minimise the effects of odour composition changes.

Of the 17 qualifying samples, eight samples had both 'full' and 'SIM' scan data. Though the original intention was to use the full scan data, preliminary inspection showed some marked average concentration differences between the full and SIM scan data for the targeted odorants, particularly for sulfides as shown in Figure 50. This was due to the brevity of these full scans (a maximum of three complete cycles achieved) which yielded poor average results compared with the SIM scans.

Therefore, it was decided to ignore full scan data for this exercise, which left only eight valid samples to work with. Realistically, this is too few to base firm conclusions upon, especially in an over-parameterised situation (where there are more potential predictor variables than observations).

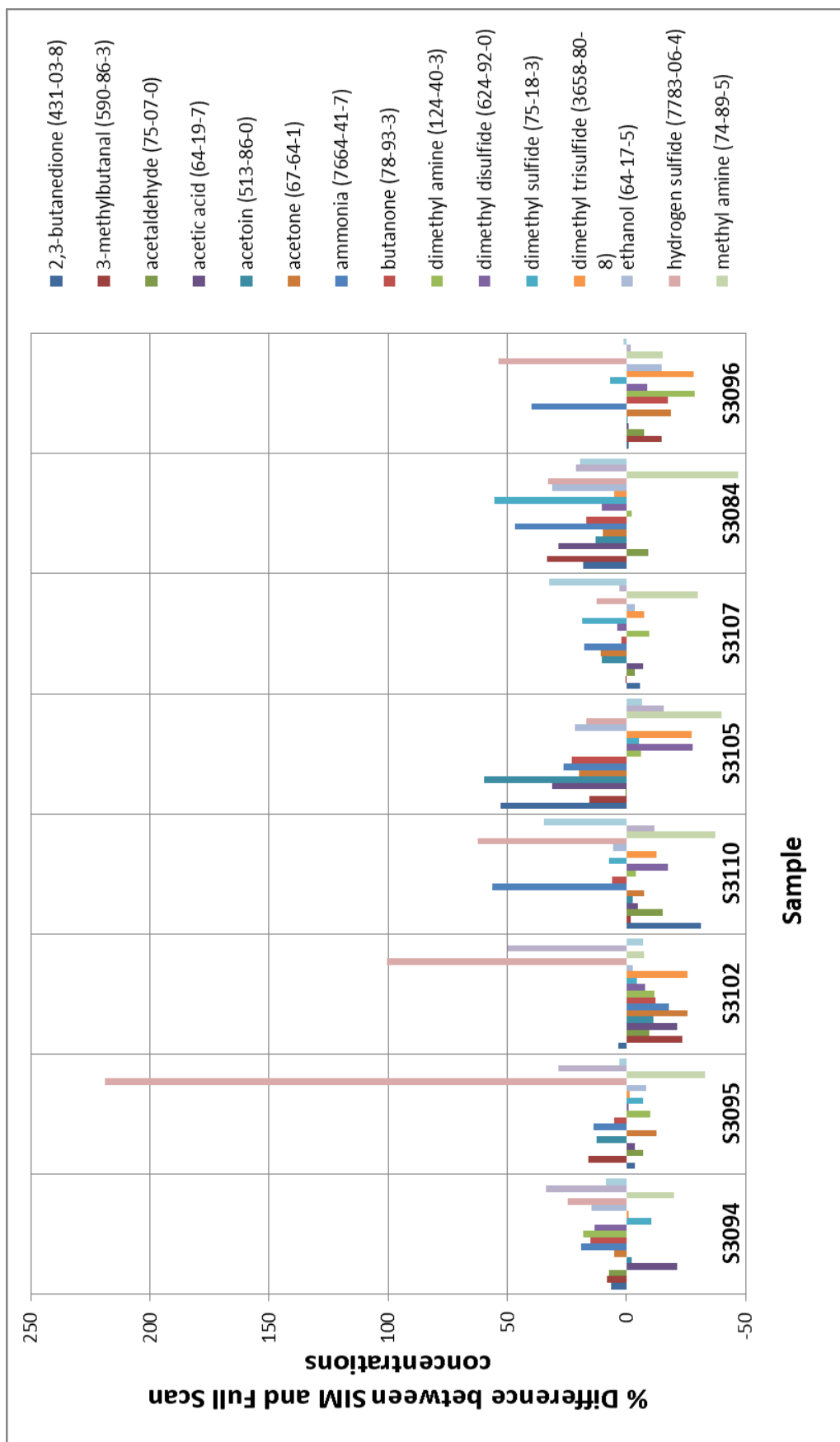


Figure 50. Difference (%) in sample odorant concentrations between SIM and full scans. Results based on ~10-minute, back-to-back scans.

Table 5. Sensors used in DAFF AOS sensor array.

<i>Sensor</i>	<i>Type</i>	<i>Usage</i>
Figaro TGS 2600	MOS	Detection of air contaminants
Figaro TGS 2602	MOS	Detection of air contaminants
Figaro TGS 2610	MOS	Detection of LP gas
Figaro TGS 2611	MOS	Detection of methane
Figaro TGS 2620	MOS	Detection of solvent vapours
Alphasense piD-AH 10.6 eV	PID	Detection of VOCs and other gases with Ionisation Potential < 10.6 eV
Alphasense piD-AH 9.6 eV	PID	Detection of VOCs and other gases with Ionisation Potential < 9.6 eV
Sensoric NH ₃ 3E 100 SE	Chemo-electrical	Ammonia monitoring (0-100 ppm)
Honeywell HIH-4000 series RH sensor	Humidity Sensor	Humidity monitoring
PT100	Temperature sensor	Temperature monitoring

The variable ‘Ammonia’ is as measured by SIFT–MS, whereas ‘NH₃’ is taken from the AOS data. These were highly, but not totally, correlated ($r = 0.94$). Total VOCs were calculated as the summation of the individual VOCs (therefore ammonia, being a volatile inorganic compound (VIC), was not included here).

Again, odour units (OU) were taken as the dependent variable, \log_{10} -transformed due to positive skewness and heterogeneous variance. NH₃ and pid10.6 (were similarly \log_{10} -transformed, to approximately linearise their relationships with $\log(\text{OU})$). For pid10.6, a constant of 1.0 was added to avoid negative numbers prior to this \log -transformation. For VOCs, any models which fitted with a negative coefficient were retained, as in this complex system there remains the possibility that these may be masking or suppressing the effects of other odorants.

Results

As shown in Table 6 to Table 9, there are considerable degrees of correlation amongst the variables.

For $\log(\text{OU})$, the best linear predictor ($R^2 = 77.4\%$) was tgs2602 (an AOS sensor). However, with this limited data set, none of the other sensors (nor $\log\text{NH}_3$) offered a significant improvement to this model.

Within the SIFT–MS data, $\log\text{Ammonia}$ actually had the best fit, closely followed by 2,3-butanedione. Table 10 lists the results of alternate step-forward regression models. Neither sequence gave a significant 4th term.

Table 6. Correlation matrix (r-values) for the SIFT-MS and AOS data.

logOU	1.000						
totalVOC	0.782	1.000					
butaned	0.834	0.792	1.000				
methylb	0.847	0.741	0.978	1.000			
acetaldehyde	0.437	0.579	0.232	0.141	1.000		
acetic_acid	0.479	0.689	0.782	0.652	0.202	1.000	
acetoin	0.837	0.775	0.630	0.703	0.471	0.159	1.000
acetone	0.761	0.942	0.675	0.671	0.550	0.445	0.893
logAmmonia	0.829	0.906	0.634	0.645	0.645	0.336	0.944
butanone	0.564	0.894	0.439	0.388	0.711	0.404	0.722
dim_amine	0.532	0.769	0.290	0.301	0.655	0.103	0.812
dim_disulf	0.730	0.760	0.474	0.535	0.569	0.066	0.971
dim_sulf	0.741	0.752	0.477	0.542	0.560	0.059	0.975
dim_trisulf	0.509	0.578	0.698	0.695	0.221	0.420	0.570
ethanol	0.752	0.932	0.625	0.632	0.591	0.384	0.910
hyd_sulf	0.049	0.522	-0.049	-0.170	0.707	0.262	0.174
meth_amine	0.686	0.823	0.454	0.484	0.645	0.159	0.918
meth_merc	0.772	0.783	0.494	0.543	0.609	0.108	0.967
trimeth_amine	0.742	0.844	0.535	0.573	0.559	0.202	0.955
mox_temp	0.813	0.731	0.625	0.658	0.709	0.198	0.897
logPID_10_6	0.898	0.767	0.694	0.764	0.447	0.209	0.990
tgs2600	-0.867	-0.649	-0.842	-0.906	-0.297	-0.367	-0.808
tgs2602	-0.901	-0.848	-0.882	-0.877	-0.574	-0.555	-0.823
tgs2620	-0.860	-0.645	-0.845	-0.906	-0.302	-0.380	-0.792
tgs2611	-0.569	-0.308	-0.665	-0.688	-0.294	-0.306	-0.406
tgs2610	-0.842	-0.595	-0.822	-0.887	-0.295	-0.334	-0.775
rh_%	-0.626	-0.205	-0.480	-0.567	-0.309	0.063	-0.575
logNH3	0.863	0.768	0.644	0.708	0.537	0.168	0.993
	logOU	totalVOC	butaned	methylb	acetald	acetic_acid	acetoin

Abbreviations: butaned=2,3-butanedione; methylb=3-methylbutanal; acetald=acetaldehyde; dim_amine=dimethyl amine; dim_disulf=dimethyl disulfide; dim_sulf=dimethyl sulfide; dim_trisulf=dimethyl trisulfide; ethanol; hyd_sulf=hydrogen sulfide; meth_amine=methyl amine; meth_merc=methyl mercaptan; trimeth_amine=trimethyl amine; mox_temp = MOS temperature

Table 7. Correlation matrix (r-values) for the SIFT-MS and AOS data.

acetone	1.000						
logAmmonia	0.960	1.000					
butanone	0.912	0.896	1.000				
dim_amine	0.882	0.908	0.942	1.000			
dim_disulf	0.901	0.956	0.813	0.919	1.000		
dim_sulf	0.893	0.954	0.800	0.910	0.999	1.000	
dim_trisulf	0.647	0.503	0.379	0.316	0.479	0.467	1.000
ethanol	0.981	0.983	0.933	0.927	0.934	0.929	0.519
hyd_sulf	0.468	0.461	0.785	0.677	0.357	0.338	-0.084
meth_amine	0.921	0.970	0.909	0.972	0.976	0.973	0.401
meth_merc	0.905	0.972	0.830	0.920	0.995	0.995	0.447
trimeth_amine	0.958	0.978	0.882	0.941	0.984	0.981	0.516
mox_temp	0.766	0.881	0.666	0.715	0.872	0.876	0.491
logPID_10_6	0.865	0.923	0.663	0.739	0.933	0.939	0.588
tgs2600	-0.625	-0.705	-0.373	-0.388	-0.667	-0.680	-0.548
tgs2602	-0.782	-0.838	-0.630	-0.564	-0.733	-0.737	-0.600
tgs2620	-0.611	-0.693	-0.364	-0.373	-0.650	-0.662	-0.539
tgs2611	-0.199	-0.305	-0.002	0.029	-0.254	-0.265	-0.408
tgs2610	-0.572	-0.659	-0.313	-0.333	-0.628	-0.641	-0.549
rh_%	-0.233	-0.399	-0.009	-0.119	-0.452	-0.469	-0.331
logNH3	0.871	0.941	0.705	0.788	0.959	0.963	0.570
	acetone	logAmmonia	butanone	dim_amine	dim_disulf	dim_sulf	dim_trisulf

Abbreviations: dim_amine=dimethyl amine; dim_disulf=dimethyl disulphide; dim_sulf=dimethyl sulfide; dim_trisulf=dimethyl trisulphide; ethanol; hyd_sulf=hydrogen sulfide; meth_amine=methyl amine; meth_merc=methyl mercaptan; trimeth_amine=trimethyl amine; mox_temp = MOS temperature

Table 8. Correlation matrix (r-values) for the SIFT-MS and AOS data.

ethanol	1.000						
hyd_sulf	0.519	1.000					
meth_amine	0.968	0.535	1.000				
meth_merc	0.940	0.387	0.979	1.000			
trimeth_amine	0.977	0.432	0.984	0.983	1.000		
mox_temp	0.815	0.240	0.843	0.884	0.828	1.000	
logPID_10_6	0.873	0.091	0.867	0.937	0.915	0.900	1.000
tgs2600	-0.647	0.178	-0.593	-0.674	-0.637	-0.850	-0.858
tgs2602	-0.795	-0.164	-0.722	-0.757	-0.742	-0.912	-0.859
tgs2620	-0.635	0.176	-0.579	-0.658	-0.620	-0.846	-0.843
tgs2611	-0.225	0.320	-0.182	-0.263	-0.190	-0.660	-0.479
tgs2610	-0.592	0.227	-0.545	-0.634	-0.588	-0.842	-0.830
rh_%	-0.274	0.388	-0.325	-0.457	-0.336	-0.750	-0.637
logNH3	0.891	0.170	0.904	0.962	0.934	0.937	0.992
	ethanol	hyd_sulf	meth_amine	meth_merc	trimeth_amine	mox_temp	logPID_10_6

Abbreviations: hyd_sulf=hydrogen sulfide; meth_amine=methyl amine; meth_merc=methyl mercaptan; trimeth_amine=trimethyl amine; mox_temp = MOS temperature

Table 9. Correlation matrix (r-values) for the SIFT-MS and AOS data.

tgs2600	1.000						
tgs2602	0.926	1.000					
tgs2620	0.999	0.928	1.000				
tgs2611	0.826	0.746	0.841	1.000			
tgs2610	0.996	0.910	0.997	0.866	1.000		
rh_%	0.825	0.679	0.827	0.883	0.866	1.000	
logNH3	-0.835	-0.859	-0.821	-0.480	-0.809	-0.643	1.000
	tgs2600	tgs2602	tgs2620	tgs2611	tgs2610	rh_%	logNH3

Table 10. Regression models for logOU.

<i>Terms</i>	<i>R² (%)</i>
<i>SIFT-MS data -</i>	
logAmmonia	62.7
logAmmonia + dimethyl amine [#]	86.9
logAmmonia + dimethyl amine [#] + methyl amine	91.7
2,3-butanedione	60.8
2,3-butanedione + methyl mercaptan	77.8
2,3-butanedione + methyl mercaptan + trimethyl amine [#]	88.9
3-methylbutanal	55.1
3-methylbutanal + methyl amine	71.9
Partial least squares (PLS; one dimension)	66.9
PLS (two dimensions)	81.2
PLS (three dimensions)	87.9
<i>AOS data -</i>	
tgs2602	77.4

[#]note: the coefficient for this term is negative, that is, higher levels of this VOC results in lower OUs

All of the three-parameter models (including the three-dimension PLS) gave similar degrees of fit, with R^2 between 87.9 and 91.7 per cent. Whilst this appears somewhat impressive, recall that there are only eight points, so the R^2 values are likely to be overestimates and should be treated with caution. The best AOS model only had R^2 of 77.4 per cent. The fit for the best general linear model (logAmmonia + dimethyl amine + methyl amine) is shown in Figure 51.

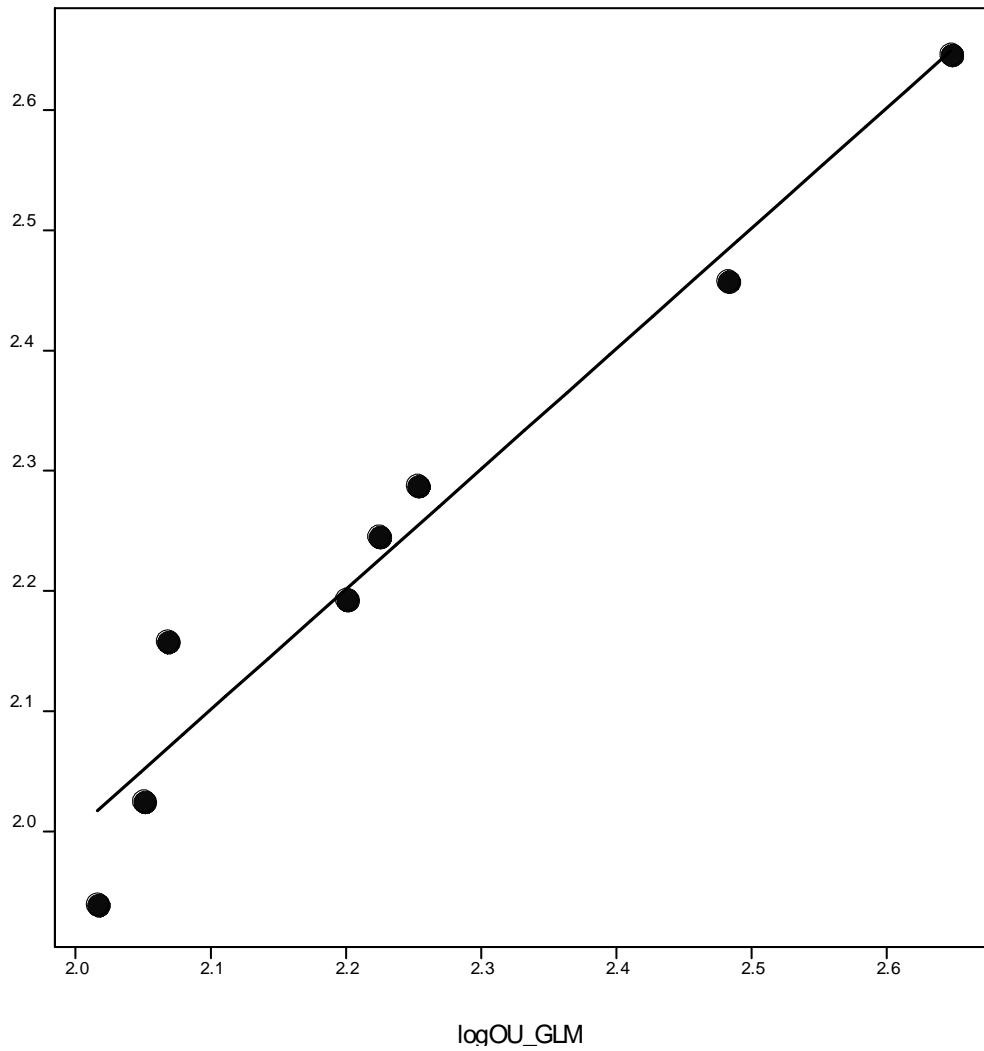


Figure 51. Fitted values from the general linear model (GLM) against observed odour units (OU). Note there are only eight data points. Additional data points are required to establish a statistically valid relationship.

Table 11. Regression models for AOS sensors against SIFT-MS VOC data.

<i>Dependent term (Y)</i>	<i>Independent terms (Xs)</i>	<i>R² (%)</i>
Total VOCs	tgs2602	66.3
	tgs2602 + tgs2611	93.4
2,3-butanedione	tgs2602	73.3
3-methylbutanal	tgs 2600	78.6
	tgs 2600 + rh%	88.6
methyl mercaptan	logNH ₃	91.0
	log pid 10.6	85.3
	logNH ₃ + tgs2600	96.9
trimethyl amine	logNH ₃	84.6
	log pid 10.6	80.5

Discussion and conclusions

For OU, the apparent strong linear relationship may be an aberration due to the low numbers of observations but, assuming the relationship is sound, the key gasses here appear to be ammonia, 2,3-butanedione and 3-methylbutanal (Table 10). Total VOCs (using SIFT-MS data) was not a good indicator of OU; nor were the AOS sensors. Given the complexities of how the gas dynamics contribute to OUs, there appears no simple answer, and realistically we have relatively few observations here.

A further query is whether the AOS sensors could predict either total VOCs (which itself did not correlate well with OUs), or the key odorants (not including ammonia) that combined for the best models for OUs? In other words, could the sensors be used to predict the key SIFT-MS VOC data that could then be used to predict odour concentration? The individual correlations amongst all these measures were previously listed in Table 6 to 9. Overall, as shown in Table 11, these models proved to be rather disappointing. Relatively few multiple models were significant. Given the 'only average' degree of fit between the AOS sensors and the VOCs, and then also between VOCs and OUs, there is little evidence to support this proposed two-stage approximation of odour concentration.

4. GC–MS analyses

Background

Identification and reporting of VOCs detected in poultry odour samples using GC–MS analysis has been a common objective of odour research conducted on behalf of the Australian chicken meat industry in recent years (Jiang and Sands, 2000; Dunlop *et al.*, 2011; Atzeni *et al.*, 2014).

Integral to this objective has been the development of a methodology by UNSW for sampling and analysing poultry odour samples from meat chicken and layer farms and quantification of several ubiquitous odorants (Pillai *et al.*, 2010; Parcsi, 2010). Murphy *et al.* (2014) subsequently used this odorant data to demonstrate time-specific odour concentration prediction in sheds.

The potential of using SIFT–MS VOC data to predict odour, as a proxy for dynamic olfactometry in certain circumstances, has also been raised. To help identify and verify the VOCs measured by SIFT–MS, GC–MS analysis was used.

Aims

- To build a database of VOCs in poultry emissions.
- To compare GC–MS results with SIFT–MS data.

Methods

Sampling and analysis methods are described earlier (See TD–GC–MS sampling and analysis).

Results and discussion

The results of the GC–MS analyses for the New Zealand samples were discussed in Chapter 1. The anomalies were unable to be resolved coming into the Australian trial. Despite following the recommended sampling and analysis procedures the same problems emerged (missing expected odorants, low concentrations, poor duplication) rendering the GC–MS data of little benefit.

The details of the GC–MS samples collected are given in Appendix B. These samples also served a related odour project. The summary of the GC–MS laboratory analyses is provided in Atzeni *et al.* (2014, Appendix B).

Table 12 lists the compounds detected and the maximum concentration recorded. Some of the odorants have been previously identified in Australian meat chicken farms (Jiang & Sands, 2000; Pillai *et al.*, 2010; Murphy *et al.*, 2014). In this study, fewer odorants were detected overall, and in much lower concentrations. The odorant detection threshold has to be taken into account though when considering the most dominant odorants; it is not necessarily those with the highest concentrations. In our samples, 2,3-butanedione and acetoin were the two most abundant odorants. The maximum concentration of 2,3-butanedione was 58 ppb—approximately seven times higher than its detection threshold (Table 12).

The fact that sorbent tube samples are prone to degradation, contamination and producing artefacts, as well as lower recovery rates (Pillai *et al.*, 2010) could help explain some of the anomalous GC–MS results. Also, the GC–MS sampling time of 30 minutes was probably not long enough for the concentration of odorants in the air at the time of sampling. The method is also not suitable for the sulfides, which are key odorants.

Table 12. Summary of TD–GC–MS results obtained from field sampling campaign.

<i>Compound</i>	<i>Chemical formula</i>	<i>Maximum concentration (ppb)</i>	<i>Odour detection threshold (ppm)</i>
Acetoin	C ₄ H ₈ O ₂	64	Unknown
Acetic acid	CH ₃ COOH	64	13.0
2,3-butanedione	C ₄ H ₆ O ₂	58	8.6 ppb
Trichlorofluoromethane	CCl ₃ F	13	45.0
Acetone	C ₃ H ₆ O	13	20.0
Toluene	C ₇ H ₈	5	1.6
2-methyl-butane	C ₅ H ₁₂	3	Unknown
Xylene	C ₈ H ₁₀	2	1.1
Tetramethylbenzene	C ₁₀ H ₁₄	2	0.1
2-butanone	C ₄ H ₈ O	2	5.4
Camphene	C ₁₀ H ₁₆	2	Unknown
Cymene	C ₁₀ H ₁₄	1	Unknown
γ-Terpinene	C ₁₀ H ₁₆	1	Unknown
Benzene	C ₆ H ₆	<1	4.7
Ethylbenzene	C ₈ H ₁₀	<1	2.3
Trimethylbenzene	C ₉ H ₁₂	<1	2.4
Nonanal	C ₉ H ₁₈ O	<1	0.53 ppb

Even for artificial odour samples (generated using permeation tubes), duplicate analyses were disparate in concentrations and peaks. Co-elution of acetic acid and 2,3-butanedione was an additional problem observed. The gas chromatographs and identified compounds are given in Appendix C.

It is evident the current procedures were not ideal and need reviewing. The shortness of the SIFT–MS Australian trial (one month) provided no opportunity to review and re-evaluate the GC–MS procedures in this case. From that perspective alone, short-term leases are impractical for evaluating SIFT–MS or similar analytical instruments.

Had the GC–MS results for the NZ results revealed other poultry VOCs, these compounds could have been added to the SIM analysis used for the SEQ trial. This would have given better detection limits than reprocessing full scan data based on GC–MS findings, which were not that useful for downwind.

Summary and recommendations

SIFT–MS data should be evaluated against GC–MS results ‘on the fly’ to ensure the data are optimal, sensible and ultimately defensible. Short-term leases are impractical for evaluating SIFT–MS and similar technologies on meat chicken farms because of the time required to conduct sufficient GC–MS analyses and compare outputs.

In planning and conducting future projects:

- Sufficient time must be allowed for conducting GC–MS analyses and troubleshooting.
- GC–MS sampling and analysis methodologies need to be checked and revised if necessary before embarking on odour sampling campaigns.
- Ensuring the provision of timely GC–MS analyses (including quality control data) is critical for research projects involving SIFT–MS.

Conclusions

SIFT-MS can provide real-time odorant concentration data for multiple compounds of interest. This capability will be a welcome one for odour researchers who have been seeking better ways to assess odour and appraise odour reduction strategies for the poultry industry and other intensive livestock industries.

The nominal mass resolution (m/z resolution = 1) is a constraint. The possibility of some compounds masking others that have the same nominal mass (that is, overlapping mass spectra that cannot be resolved with SIFT-MS) could lead to data misinterpretation (for example, exaggerated concentrations of some target VOCs, misidentified compounds), particularly if GC-MS also fails to identify these compounds.

That said, SIFT-MS offers detection limits of low parts per billion and parts per trillion levels that are well beyond the capabilities of any commercially available VOC sensors, now and in the foreseeable future. For most odorants, no specific sensors even exist and the situation is unlikely to change because it is not commercially viable to develop such sensors. So the shortcomings of SIFT-MS must be put into perspective when compared to the alternatives.

There is no proven single analytical technique for assessing poultry odours conveniently and confidently. Ideally, SIFT-MS now needs to be trialled more rigorously along with other established and emerging analysis technologies to properly gauge the strengths and weaknesses of these expensive analytical instruments for satisfying research and assessment needs and ultimately achieving the chicken meat industry goals.

SIFT-MS technology opens up the field for well-designed, well-targeted, odour monitoring research. With the AOS technology now proving an unviable long-term prospect, SIFT-MS technology is a prudent investment for the future for predicting odour levels, better understanding poultry odour perception and impacts over time and space, and evaluating the efficacy of abatement measures.

Implications

Poultry emissions assessment

Used appropriately, in conjunction with reliable GC–MS data, SIFT–MS can provide the industry with useful odorant data that will enable more structured, targeted and insightful odour research, leading to more satisfactory outcomes for industry in future.

The processes generating the key odorants that cause odour nuisance are likely to become new areas of research. The result will be more defensible assessments and decision-making in relation to odour impacts and concerns. Nevertheless, GC–MS remains the most important diagnostic tool and is pivotal to any research efforts involving SIFT–MS. Other new analytical technologies should also be evaluated as they become available.

Odour concentration prediction

Using SIFT–MS as a proxy for dynamic olfactometry deserves further investigation. Preliminary results are promising but inconclusive due to insufficient data. SIFT–MS odorant data can potentially be used to approximate odour concentration in a more intuitive and accurate way than will ever be possible with non-specific chemical sensors, that is, AOS technology (Atzeni *et al.*, 2014).

Odour modelling

SIFT–MS data may be a useful tool for odour modelling provided certain key odorants are shown to be good predictors of odour strength and are stable. If that is the case, then arguably odour dispersion models could be based on odorant emission rates and dispersion, and the modelling could be ground-truthed using SIFT–MS and wind data.

Recommendations

GC–MS methods for analysis of poultry VOCs and other odorants need to be revised and improved for both in-shed and downwind sampling. Without reliable GC–MS results, SIFT–MS results cannot be resolved and verified, and much of the data interpretation becomes speculative.

We recommend additional evaluations of SIFT–MS and other gas analysis technologies to identify and measure poultry odorants. Co-analysis of representative odour samples using GC–MS is required. Evaluations should include analyses of controlled headspace samples and samples collected at source, farm boundary and receptor.

Appendix A. SIFT–MS and GC–MS characteristics

SIFT–MS and GC–MS are complementary analytical techniques. The similarities and differences between the two techniques are summarised in Table A1.

Table A1. Comparison of SIFT–MS and GC–MS characteristics in common.

<i>SIFT–MS</i>	<i>Characteristic</i>	<i>GC–MS</i>
VOCs and certain inorganic gases	Compounds analysed	VOCs and semi-volatile VOCs (SVOCs), inorganic gases
Gas (including headspace)	Suitable matrices	Gas (including headspace), liquid
A fraction of a second to minutes, depending on requirements	Speed of analysis	Typically 10 to 45 minutes (determined by elution time for analytes)
Real-time analysis at sub-ppbv concentrations / sub-ng L ⁻¹	Detection limits	Routinely sub-nanogram (ng) level, but dependent on system inertness, sample matrix and ionisation method
Generally preparation free due to analysis of whole air	Sample preparation	Usually requires preparation and/or pre-concentration (for example, solvent extraction, purge and trap, thermal desorption, SPME)
Real time analysis because there is no chromatographic separation of analyte, which also eliminates discrimination. Compounds resolved due to the relatively simple chemical ionisation ‘fingerprints’	Analyte separation	Separation of analytes using appropriate column and temperature program. May require several runs through the GC to separate analytes of differing polarity (discriminatory)
Three standard soft chemical ionisation agents (H ₃ O ⁺ , NO ⁺ , O ₂ ⁺)	Ionisation mechanism(s)	Typically 70 eV electron impact ionisation; sometimes chemical ionisation
Quadrupole mass selection and particle multiplier detection (ion counting)	Ion selection and detection	Typically use quadrupole-based mass selection and measure ion current
Full Scan Mode and Selected Ion Monitoring (SIM) – the latter allows real-time quantitative analysis	Data collection modes	Full Scan Mode and Selected Ion Monitoring (SIM)
High – multiple reagent ions, but no chromatography	Compound identification	Very high due to chromatography
Real-time quantitation from reagent and product ion intensities, reaction rate coefficients and sample flow rate	Quantitation	From full calibration of system for particular analytical method
Calibration is required infrequently; for some applications it is not required at all	Calibration	Calibrated regularly using a set of dilutions of known concentrations
Routine validation using automated on-line analysis of certified gas standard	Validation	Validation involves use of spiked samples and blanks in the analytical sequence
Technical and non-technical operation	Ease-of-Use	Technical operators only
Low – primarily vacuum pumps	Maintenance requirements	High – frequent fouling of column and ion source

1. Typical performance data for the Syft Voice200[®] SIFT–MS instrument (Prince *et al.*, 2010)

Appendix B. GC–MS sample details

Table B1. GC–MS sample details for SEQ trial. Samples are listed in their duplicate pairs.

<i>Sample Tube</i>	<i>Sample Date</i>	<i>Source Reference</i>	<i>Farm</i>	<i>Bird age (days)</i>	<i>Source description</i>
Mi 181813	19/09/2013	A22	A	26	downwind 23m; from bag
204093	19/09/2013	A22	A	26	downwind 23m; from bag
204082	19/09/2013	A22	A	26	downwind 70m; from bag
Mi 181826	19/09/2013	A22	A	26	downwind 70m; from bag
204018	26/09/2013	B4	B	..	downwind 20m
204037	26/09/2013	B4	B	..	downwind 20m
204061	26/09/2013	B4	B	..	at fan; from bag
Mi 181852	26/09/2013	B4	B	..	at fan; from bag
204030	26/09/2013	B4	B	..	in-shed
204010	26/09/2013	B4	B	..	in-shed
Mi 181808	2/10/2013	A4	A	5	in-shed
204091	2/10/2013	A4	A	5	in-shed
204076	2/10/2013	A32	A	9	in-shed
204035	2/10/2013	A32	A	9	in-shed
204038	2/10/2013	AT6	A	na	in-shed; empty; disinfected
204060	2/10/2013	AT6	A	na	in-shed; empty; disinfected
204058	2/10/2013	AT6	A	na	in-shed; near-empty
204033	2/10/2013	AT6	A	na	in-shed; near-empty
204036	3/10/2013	A25	A	14	at fan
204043	3/10/2013	A25	A	14	at fan
204096	3/10/2013	A14	A	27	in-shed
204086	3/10/2013	A14	A	27	in-shed
204013	3/10/2013	A24	A	34	in-shed
204024	3/10/2013	A24	A	34	in-shed
204053	3/10/2013	A21	A	41	in-shed
204072	3/10/2013	A21	A	41	in-shed
M 181816	14/10/2013	A31	A	21	at fan
M 181860	14/10/2013	A31	A	21	at fan
Mi 181836	14/10/2013	A9	A	35	in-shed
Mi 181861	14/10/2013	A9	A	35	in-shed
M 181846	16/10/2013	A20	A	50	in-shed
M 181871	16/10/2013	A20	A	50	in-shed
Mi 181821	16/10/2013	A19	A	48	at fan; from bag
Mi 181811	16/10/2013	A19	A	48	at fan; from bag

Appendix C. GC–MS permeation tube results

The lab analysis results for an ‘artificial poultry’ odour created using permeation tubes of key odorants appear in Figures C1 to C4. Samples 1 and 2 were duplicate samples (30-minute collection time), as were samples 3 and 4 (90-minute collection time).

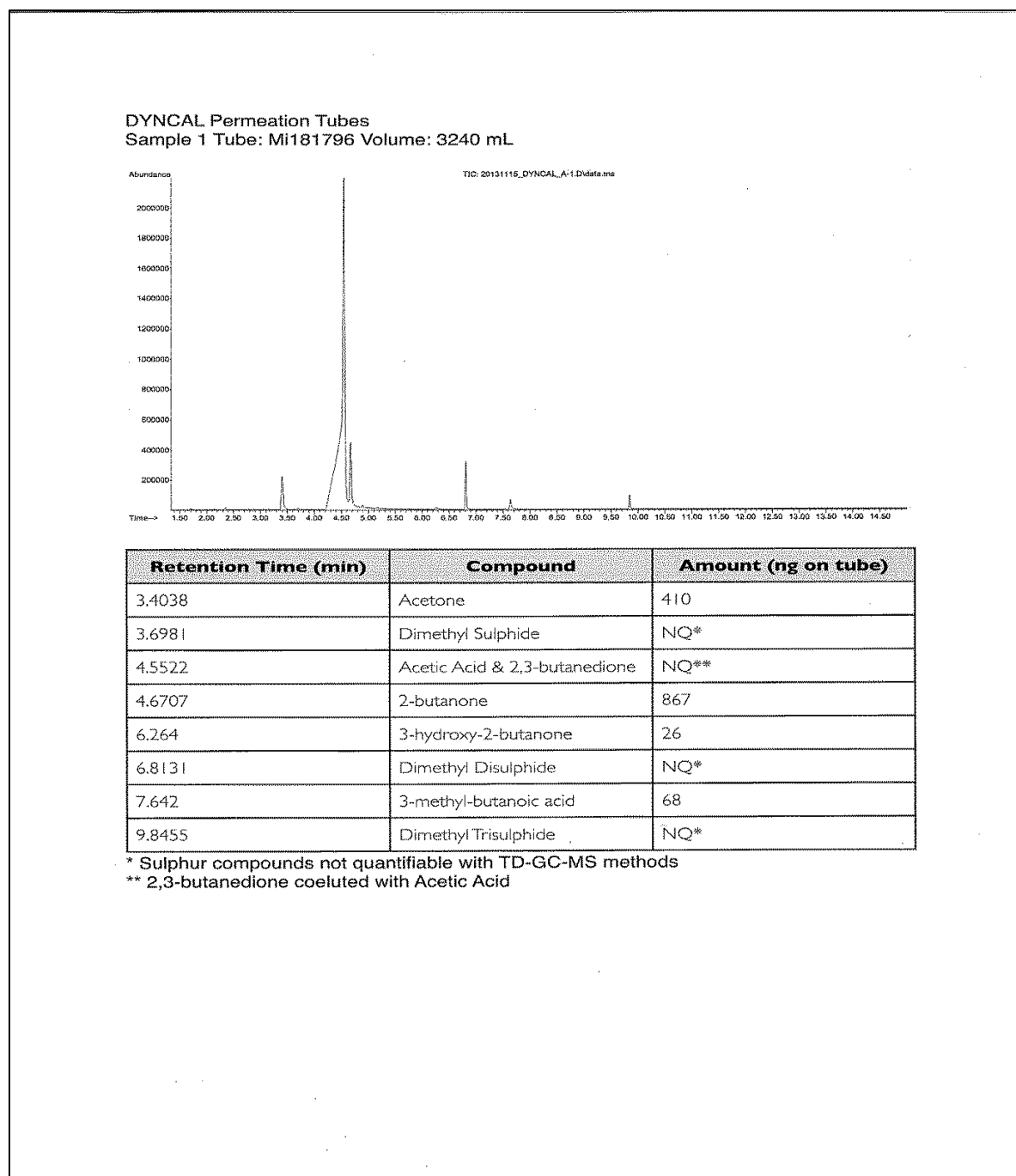
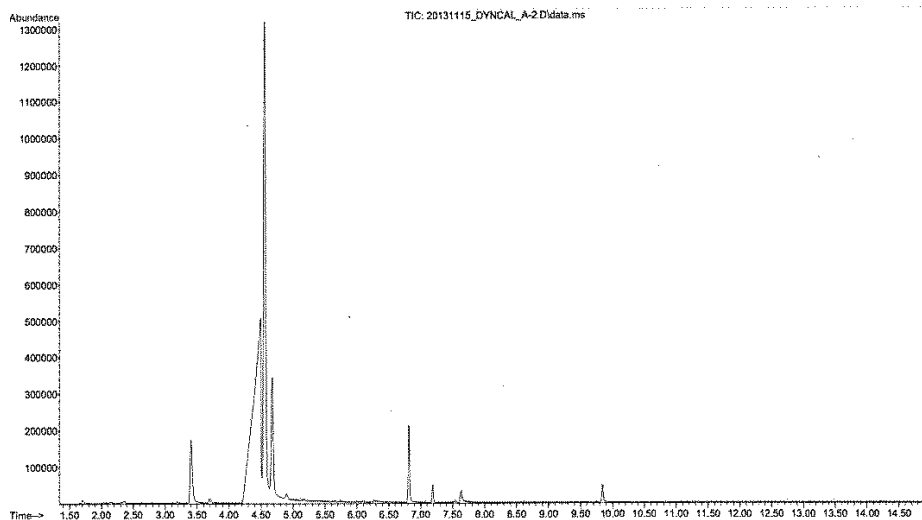


Figure C1. GC–MS analysis of artificial poultry odour (permeation tube mixture). Duplicate to Sample 2 (Figure C2).

Sample 2 Tube: Mi181818 Volume: 3240 mL

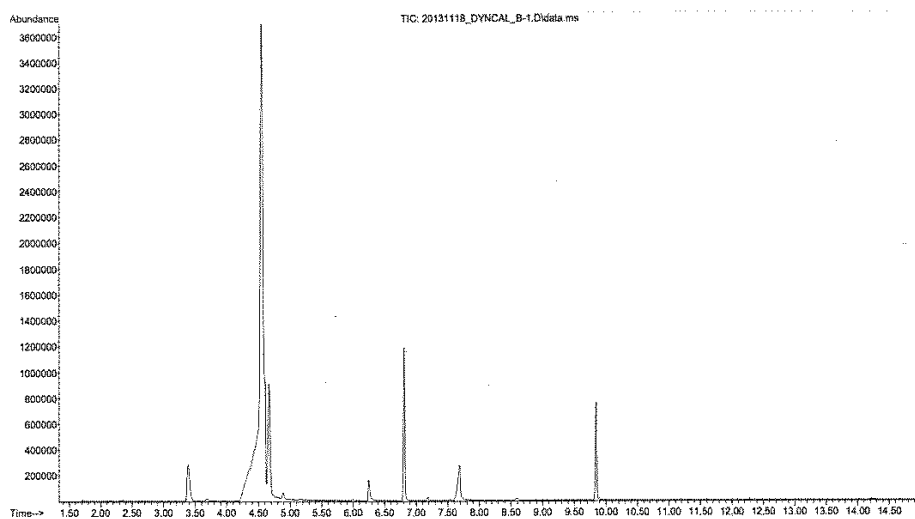


Retention Time (min)	Compound	Amount (ng on tube)
3.4074	Acetone	319
3.6981	Dimethyl Sulphide	NQ*
4.4912	Acetic Acid	2770
4.5522	2,3-butanedione	1504
4.6707	2-butanone	719
6.8131	Dimethyl Disulphide	NQ*
7.1898	Toluene	87
7.642	3-methyl-butanoic acid	45
9.8455	Dimethyl Trisulphide	NQ*

* Sulphur compounds not quantifiable with TD-GC-MS methods

Figure C2. GC-MS analysis of artificial poultry odour (permeation tubes). Duplicate to Sample 1 (Figure C1).

Sample 3 Tube: Mi181844 Volume: 9720 mL



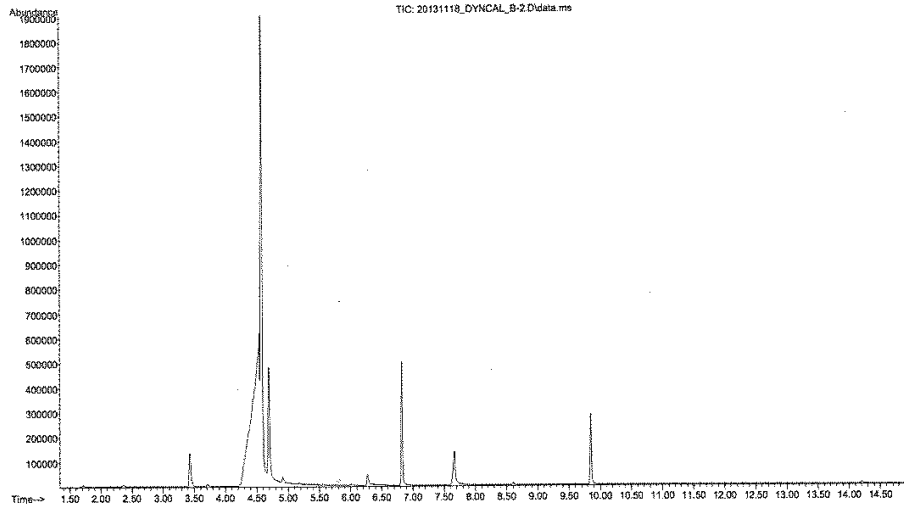
Retention Time (min)	Compound	Amount (ng on tube)
3.3894	Acetone	647
3.6908	Dimethyl Sulphide	NQ*
4.1574	Butanal	8
4.5485	2,3-butanedione & Acetic Acid	NQ**
4.6669	2-butanone	1917
6.2495	3-hydroxy-2-butanone	220
6.8094	Dimethyl Disulphide	NQ*
7.1862	Toluene	17
7.6886	3-methyl-butanoic acid	427
9.8453	Dimethyl Trisulphide	NQ*

* Sulphur compounds not quantifiable with TD-GC-MS methods

** 2,3-butanedione coeluted with Acetic Acid

Figure C3. GC-MS analysis of artificial poultry odour (permeation tubes). Duplicate to Sample 4 (Figure C4).

Sample 4 Tube: Mi181866 Volume: 9720 mL



Retention Time (min)	Compound	Amount (ng on tube)
3.4289	Acetone	2278
3.7196	Dimethyl Sulphide	NQ*
4.5414	Acetic Acid	3337
4.5737	2,3-butanedione	2014
4.6921	2-butanone	955
6.2747	3-hydroxy-2-butanone	74
6.8131	Dimethyl Disulphide	NQ*
7.6671	3-methyl-butanoic acid	180
9.849	Dimethyl Trisulphide	NQ*

* Sulphur compounds not quantifiable with TD-GC-MS methods

Figure C4. GC-MS analysis of artificial poultry odour (permeation tubes). Duplicate to Sample 3 (Figure C3).

Appendix D. Olfactometry results

Table D1. Summary of olfactometry samples and concentration (ou) during SIFT-MS trial.

<i>Date</i>	<i>Time</i>	<i>Farm</i>	<i>Bag</i>	<i>Concentration (ou)</i>	<i>Type</i>	<i>Bird age (days)</i>	<i>Shed</i>	<i>Distance downwind (m)</i>
19/09/13	09:51:00	A	3094	156	..			
19/09/13	..	A	3095	443	in-shed	41	22	0
19/09/13	09:30:00	A	3102	176	downwind	26	22	70
4/10/13	12:44:00	A	3016	192	in-shed	42	21	0
4/10/13	12:00:00	A	3045	197	in-shed	42	21	0
4/10/13	13:01:00	A	3104	181	downwind	42	21	
4/10/13	09:53:00	A	3109	147	downwind	42	21	48
9/10/13	12:05:00	A	3084	194	downwind	47	21 & 22	
9/10/13	13:10:00	A	3096	287	in-shed	47	21	0.5
9/10/13	11:29:00	A	3105	106	downwind	47	21 & 22	10
9/10/13	10:42:00	A	3107	87	downwind	47	21 & 22	12
9/10/13	09:47:00	A	3110	144	downwind	47	21 & 22	27
10/10/13	11:35:00	A	3072	140	downwind	47	21 & 22	
10/10/13	12:30:00	A	3078	108	downwind	47	21 & 22	
10/10/13	10:25:00	A	3111	319	in-shed	47	22	0.5
16/10/13	09:43:00	A	3130	362	in-shed	50	20	0
16/10/13	11:00:00	A	3132	650	in-shed	48	19	0.5
16/10/13	11:40:00	A	3133	650	downwind	48	19 & 20	10

Appendix E. SIFT–MS operating principles

An overview of SIFT–MS

SIFT–MS uses soft chemical ionisation reactions coupled with mass spectrometric detection to rapidly quantify VOCs in real time from whole-gas samples. Three standard chemical ionisation agents (or reagent ions) are used in SIFT–MS: H_3O^+ , NO^+ and O_2^+ . These reagent ions are mass selected (Figure E1) and react with trace VOCs in very well controlled ion-molecule reactions but do not react with the major components of air, allowing SIFT–MS to analyse whole air for trace VOCs to pptv levels.

Soft chemical ionisation yields a smaller number of product ions per compound than electron impact mass spectrometry (as used in standard GC–MS, for example), so gas chromatographic separation is unnecessary. This speeds sample throughput and provides instantaneous quantification of VOCs. Use of multiple reagent ions also greatly reduces interferences, markedly increasing the specificity of SIFT–MS compared with most other direct mass spectrometry technologies.

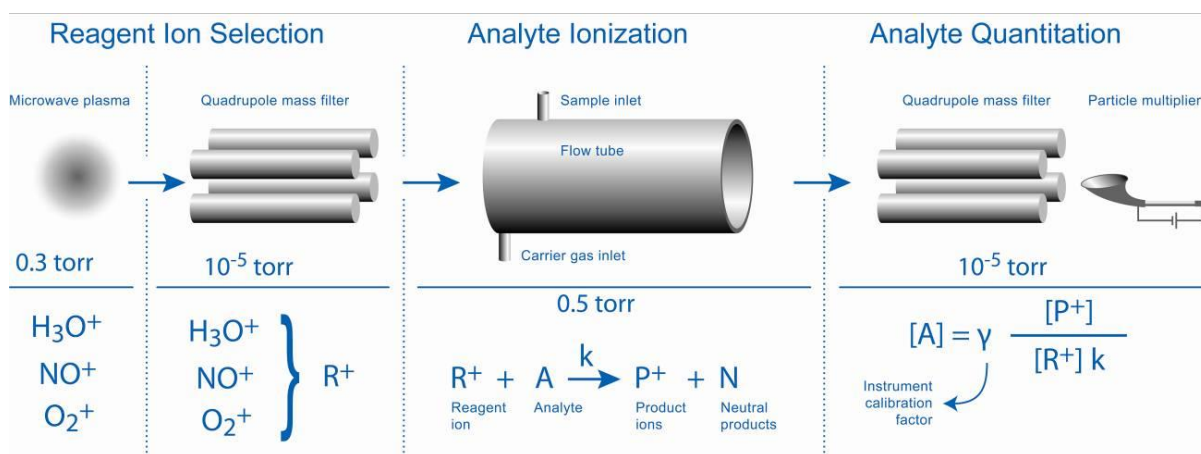


Figure E1. Schematic representation of the SIFT–MS technique.

Principles of SIFT–MS

This section describes the principles of the SIFT–MS technique that are essential to understanding how it complements GC–MS. In particular, it focuses on how soft chemical ionisation is applied very precisely in SIFT–MS, allowing it to provide unparalleled selectivity among direct mass spectrometry techniques, and creating an ideal companion technique for GC–MS.

a. Chemical ionisation in SIFT–MS

Chemical ionisation (CI) uses a molecular ion to transfer charge on to the target compound (analyte). CI is ‘softer’ than many other types of ionisation, so it transfers less energy to the analyte, resulting in less fragmentation. SIFT–MS is a unique CI–MS technique because it precisely controls ion energies to allow repeatable, real-time quantitative analysis. Another benefit is long-term calibration stability.

SIFT–MS uses softer chemical ionisation (CI) agents than GC–MS and terms them ‘reagent ions’ (or ‘precursor ions’). The standard reagent ions used in SIFT–MS are H_3O^+ , NO^+ and O_2^+ . By applying these ions in a soft ionisation process, SIFT–MS encounters significantly reduced fragmentation compared to harsher CI and electron impact (EI) ionisation.

Figure E2 compares ionisation of ethylbenzene using 70-eV EI (as used in GC–MS) and 12.1-eV O₂⁺ CI (as used in SIFT–MS). Reduced fragmentation means chromatography is unnecessary, which allows SIFT–MS to be applied as a real-time technique.

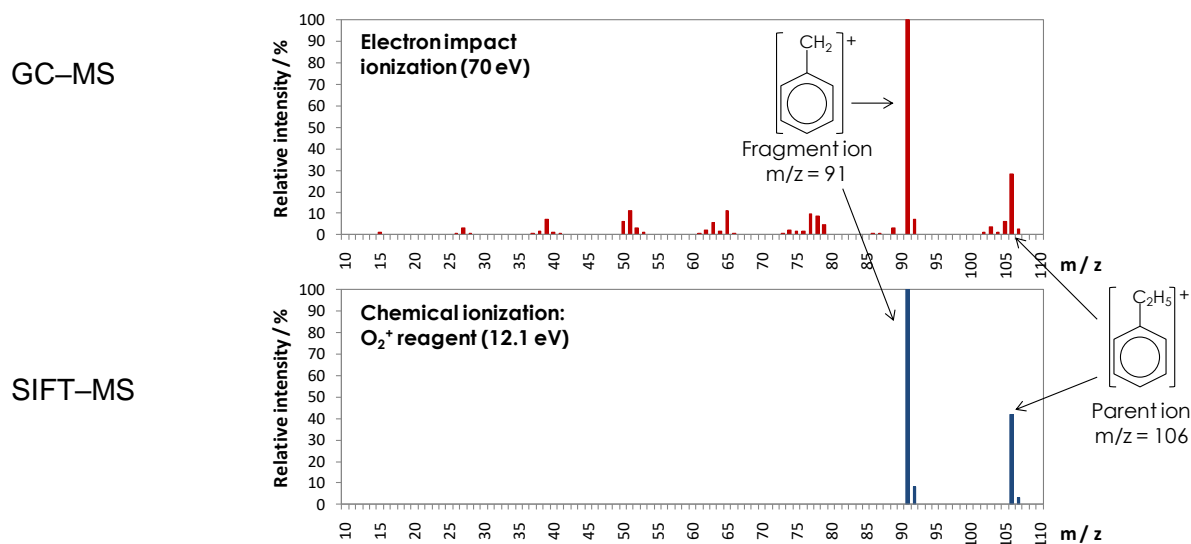


Figure E2. Electron impact and chemical ionisation of ethylbenzene illustrates the much simpler fragmentation observed for SIFT–MS than standard GC–MS.

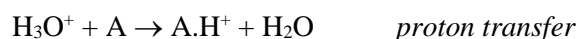
Fragmentation and chromatography mean GC–MS can have higher selectivity than the somewhat cleaner mass spectra produced by SIFT–MS. Therefore, in certain applications involving *complex* mixtures, SIFT–MS is ideal as a rapid screening tool, while GC–MS is ideal for methodical identification and quantitation of every compound. The strength of SIFT–MS is its fast, broad analysis and hence, it is complementary to rather than competitive with GC–MS.

b. Chemistry of the SIFT–MS reagent ions

This section provides a short overview of the gas-phase reaction mechanisms for the three standard SIFT–MS reagent ions: H₃O⁺, NO⁺ and O₂⁺.

The SIFT–MS H₃O⁺ reagent ion

The H₃O⁺ reagent ion almost always reacts with analyte ‘A’ via the proton transfer mechanism:



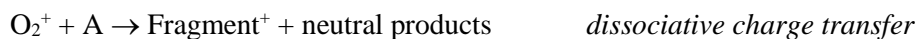
The product is generally detected at one mass unit higher than the neutral mass. For compound ‘A’ to react, it must have a proton affinity (PA) greater than that of water (PA = 691 kJ mol⁻¹). If this condition is fulfilled, then a reaction occurs on every ion-molecule collision (100% efficiency).

The SIFT–MS O₂⁺ reagent ion

Oxygen has an ionisation potential of 12.1 eV and is the strongest SIFT–MS reagent ion. O₂⁺ transfers charge to analytes with lower ionisation potentials by removing an electron:



O_2^+ also often ionises molecules with sufficient excess energy to produce fragment ions (for example, the 91 m/z product of ethylbenzene in Figure E2).



The efficiency of the charge transfer process is often less than 100% (*i.e.* not all collisions between the O_2^+ reagent ion and a molecule lead to a reaction).

The SIFT-MS NO⁺ reagent ion

The ionisation potential of NO is 9.1 eV, so it ionises fewer compounds via the charge transfer mechanism than does O_2^+ .



As for O_2^+ , charge transfer efficiency is often less than 100%. Although dissociative charge transfer is less common for NO^+ than O_2^+ due to the lower ionisation energy, it still occurs for certain compounds.

NO^+ often reacts by two other very useful mechanisms:



Real-time resolution of isomeric and isobaric compounds

The triple reagent ion system of SIFT-MS is able to resolve certain isobaric and isomeric compounds. A simple example is provided in Table E1 for the acetone and propanal isomers of C_3H_6O . The NO^+ reagent ion provides the most effective differentiation because it reacts via a different mechanism for the two compounds and yields a single product ion for each.

Table E1. Product ions formed from reaction of the SIFT-MS H_3O^+ , NO^+ and O_2^+ reagent ions with isomeric compounds acetone and propanal.

Reagent ion	Acetone product ion (m/z)	Propanal product ion (m/z)
H_3O^+	$(CH_3)_2CO.H^+$ (59)	$CH_3CH_2CHO.H^+$ (59)
NO^+	$(CH_3)_2CO.NO^+$ (88)	$CH_3CH_2CO^+$ (57)
O_2^+	$(CH_3)CO^+$ (58); CH_3CO^+ (43)	$CH_3CH_2CHO^+$ (58); $CH_3CH_2CO^+$ (57)

Figures E3 and E4 illustrate how a hypothetical multi-component sample is analysed using electron impact mass spectrometry (using, GC, GC-MS and SIFT-MS), respectively. In Figure E3, the high degree of fragmentation arising from EI ionisation is shown. Without GC, EI-MS is complicated and allows few compounds to be targeted uniquely. However, the same mode of ionisation applied in GC-MS allows compounds to be separated in time through the GC column, while the relatively unique mass spectral ‘fingerprints’ of each compound can be used to identify and quantify the compound.

In Figure E4, the same mixture is analysed using the three standard SIFT-MS reagent ions. All fifteen compounds can be resolved in real-time without using chromatography.

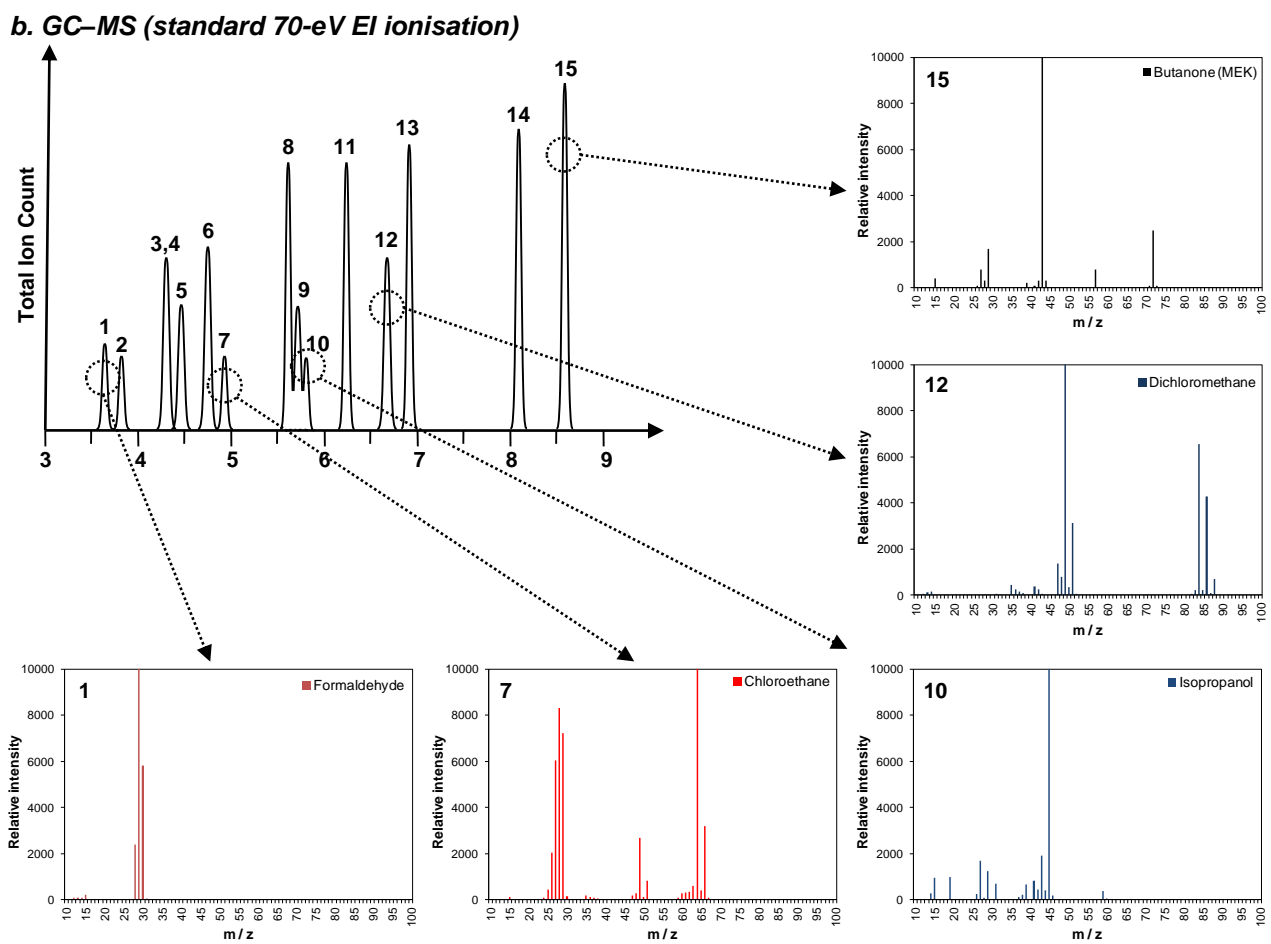
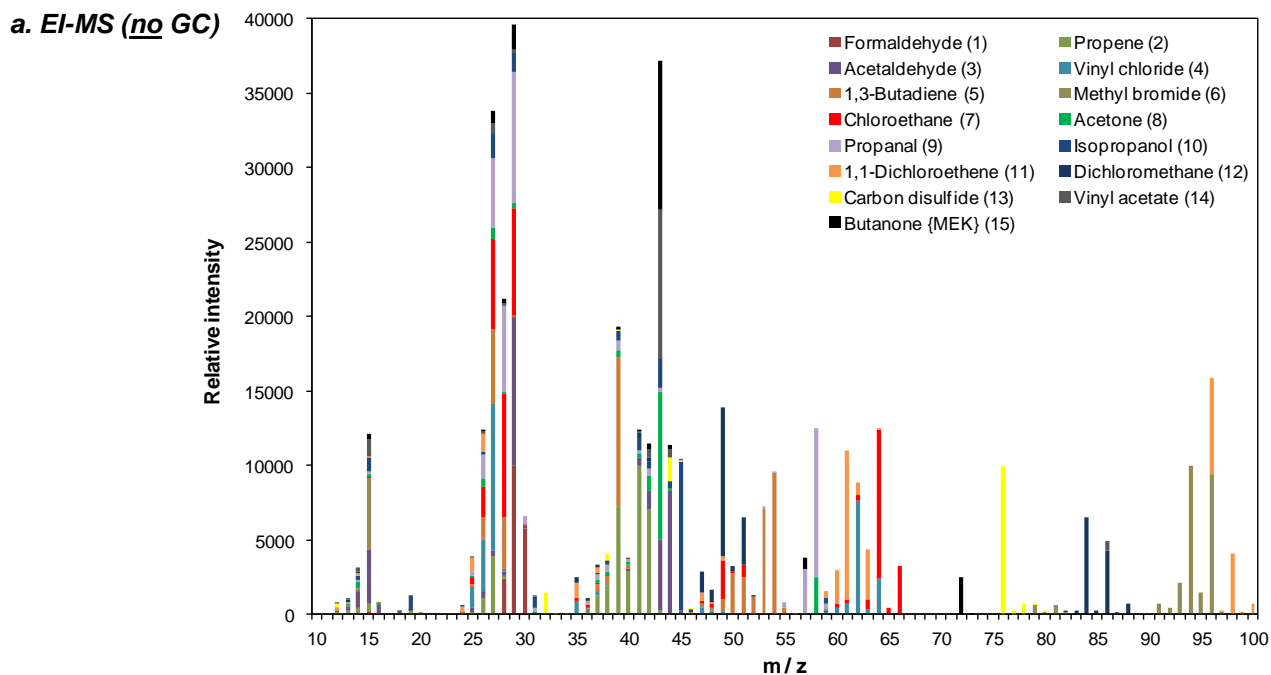


Figure E3. 70-eV electron impact mass spectrometry (a) without and (b) with gas chromatography. The hypothetical 15-component sample is derived from the US EPA Compendium Method TO-15 and generated from mass spectra in the NIST library (<http://webbook.nist.gov/chemistry/>).

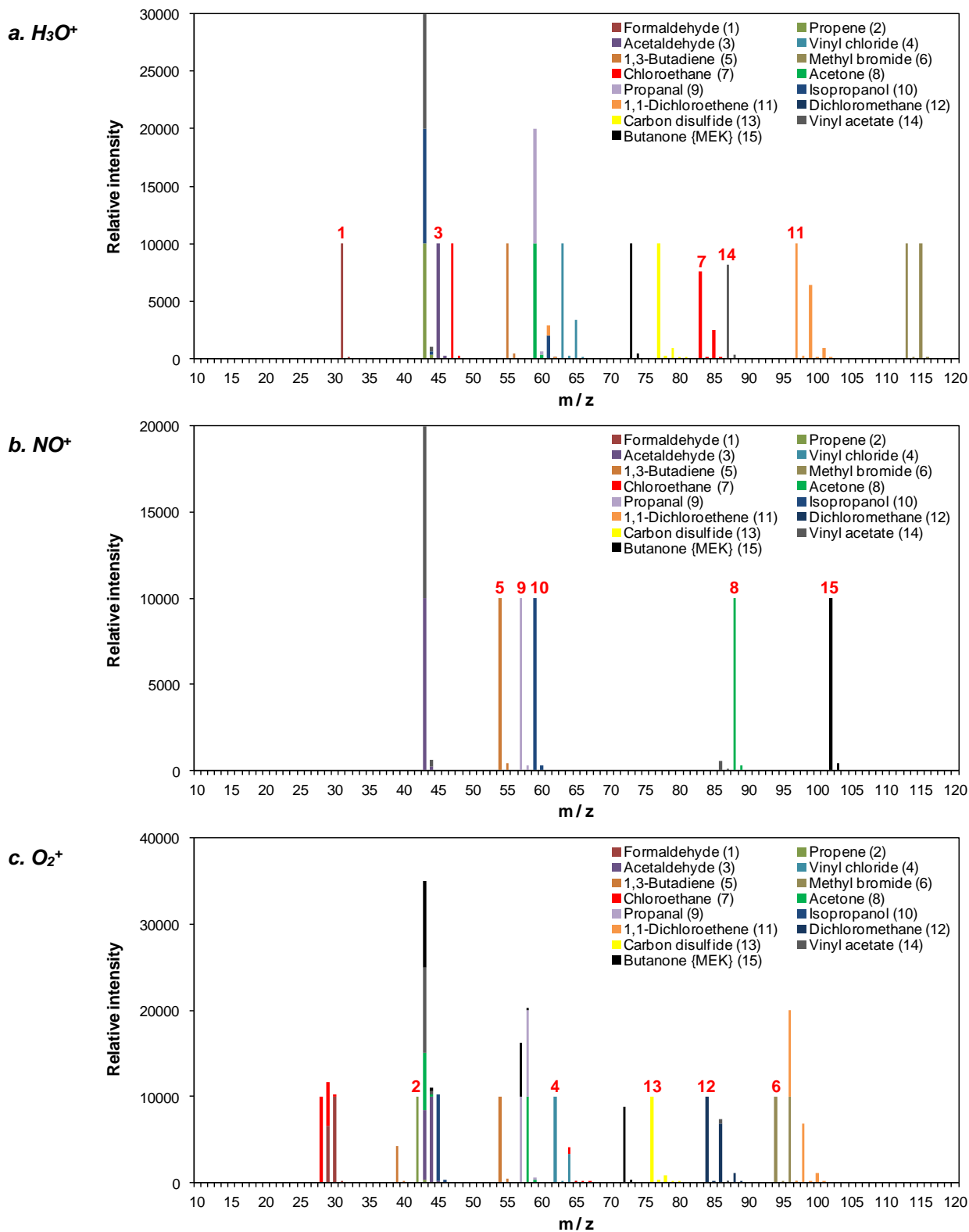


Figure E4. Three standard SIFT-MS reagent ions (a) H_3O^+ , (b) NO^+ and (c) O_2^+ for real-time resolution of the 15-component sample shown in Figure D3. SIFT-MS data were taken from the Syft compound library. Red numbers identify some unique ions useful for quantitation.

c. How does SIFT–MS control the chemistry so precisely?

Consistency of reagent ion energy is one of the most critical factors in controlling analyte ionisation, which in turn provides very consistent product formation and reliable, stable quantitation. In SIFT–MS the use of a carrier gas enables the chemical ionisation process to be controlled very effectively compared to EI ionisation and other forms of CI mass spectrometry. The carrier gas used in SIFT–MS plays two very important roles in controlling ionisation:

- It thermalises the reagent ions prior to introduction of sample, which means that the energies of the reagent ions are as low and consistent as possible, providing predictable, precise, and soft chemical ionisation.
- It transports the product ions and unreacted reagent ions down the flow tube to the detection region without addition of excess energy, such as use of an electric field to accelerate ions toward a detection region. Adding additional energy complicates mass spectra, reducing specificity and ability to uniquely quantify compounds.

d. Quantitation in SIFT–MS

SIFT–MS SIM scans are analogous to GC–MS SIM scans and involve targeting VOCs in a well-characterised sample matrix. In this mode, specific reagent and product ions are selected and their count rates measured repeatedly. Combining this experimental information with the known rate coefficient (k) for reaction of the reagent ion and analyte, and the dilution of the sample gas into the carrier gas, the absolute concentration of an analyte can be calculated and displayed in real time. Simply put, more VOCs in the sample will result in a greater proportion of the reagent ion reacting and hence more of the product ions for that VOC will be observed.

Movement of inert helium or hydrogen carrier gas through the flow tube entrains the reagent ions and analytes and provides a region of known conditions. It is in this region that reaction between the sample VOCs and ions occurs. This means the reaction time (the amount of time they have to react with each other) is a coefficient in any given SIFT–MS instrument.

At a known reaction time (determined by the flow conditions) the amount of reagent ion reacted will be proportional to the concentration of the analyte in the flow tube. Using a little math and the ratio of reagent and product ions along with the rate coefficient, it is possible to deduce the concentration of a VOC in the flow tube from the ratio of the product ion to the reagent ion count. From this point it is possible to relate the VOC concentration in the flow tube to the VOC concentration in the original sample, as the flow ratios of the sample and carrier gases into the flow tube gives the dilution ratio.

As long as the flow of the sample gas is small compared to the carrier gas flow and the total level of volatiles in the sample does not attenuate the reagent ion signal by more than about 10%, the number of VOC product ions is an absolute measure of the VOC in the sample. This gives a typical linear range of approximately from mid-ppt to about 50 ppm. Higher concentration samples can be analysed either by attenuating the sample flow or by diluting the sample.

e. Calibration of SIFT–MS instruments

SIFT–MS enables absolute quantitation of target compounds at high precision based on the compound data contained in the Syft library (namely, the reaction rate coefficient and the product masses together with their branching ratios). However, if high accuracy analysis is required, formal calibration is recommended, rather than simply relying upon the compound library. Once calibrated for a particular compound, the SIFT–MS calibration is usually valid as long as the instrument passes validation using the Syft automated daily validation standard.

SIFT-MS is a dedicated whole gas analyser and cannot analyse liquid samples. Therefore, suitable certified gas standards are used for calibration of SIFT-MS instruments. The two main options for suitable standards are compressed gases and permeation tubes.

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