Sampling and Analysis Methodology Concerns for Volatile Organo-Sulfur Compounds (VOSCs)

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ABSTRACT

A wide range of volatile organo-sulfur compounds (VOSCs) can be produced and emitted by chemical, waste treatment and livestock industries. VOSCs are typically malodorous resulting in odour nuisance for local receptors. While reliable sampling and analysis methods currently exist for volatile organic compounds (VOCs), the transformation and degradation of the labile VOSCs is poorly understood. The development of appropriate VOSC sampling and analysis methodologies is a fundamental step towards developing this understanding. Recent work conducted in Australia identifies several areas of concern and opportunities to improve upon existing analysis techniques for VOSCs, in particular the application of sulfur chemiluminescence detectors, low polarity separation columns, and conducting thorough investigations of sorbent options. Concerns were raised with regards to thermal degradation of VOSCs during sorbent tube thermal desorption, an area requiring further investigation.

INTRODUCTION

The impact of odour emissions from intensive livestock, waste management, and wastewater treatment facilities on nearby communities have become a major concern to facility managers, particularly with the ongoing erosion of existing buffer zones by residential encroachment. While a wide range of odorants have been reported for these facilities, including hydrogen sulfide (H\textsubscript{2}S), methyl mercaptan (CH\textsubscript{3}SH), dimethyl sulfide (CH\textsubscript{3})\textsubscript{2}S and dimethyl disulfide (CH\textsubscript{3})\textsubscript{2}S\textsubscript{2}, organic and inorganic nitrogen derivates such as ammonia (NH\textsubscript{3}), amines, indole and volatile organic compounds such as aromatic, aliphatic and chlorinated hydrocarbons, fatty acids, aldehydes, terpenes and ketones\textsuperscript{2,3,4}, traditionally there has been a focus on H\textsubscript{2}S (and in some cases reduced sulfur and volatile organic carbon compounds) for odour abatement design purposes. Volatile organic sulfur compounds (VOSCs) such as methyl mercaptan, dimethyl sulfide, and dimethyl disulfide are malodorous and can, in many cases, be the dominant odorants emitted from these sources. However, these compounds are also highly labile and subject to transformation and/or degradation during sample handling, transport, storage, and analysis.

Odour concentration measurement (olfactometry) is the dominant tool for odour impact regulation in most jurisdictions, and the analysis of specific odorants is not normally required. But, given the labile nature of VOSCs, and their dominance as odorants for many emission sources, the transformation and/or degradation of these compounds could have a strong impact on odour concentration measurements. While significant effort has been devoted to the standardisation of the specific methodologies for olfactometry (in particular the European...
standard EN 13725:2003 and the Australian/New Zealand standard AS/NZ 4323 part 3: 2001), there is a lack of standardised sampling protocols, and very little understanding of the transformation/degradation and losses of odorants during the sample handling, transportation and storage components of the analysis chain. Some studies have been conducted with regard to the permeation of odorants and water vapour through odour bags, although this work has been restricted to a single sulfur compound (H$_2$S) and does not assess VOSCs or mixtures of odorants. To date, sample handling procedures are primarily based upon rules of thumb with regards to storage times and conditions. Sample storage times are particularly an issue when odour sources are located at significant distances from the population centres where olfactometry laboratories are typically located. This is often the case in many regions of Australia and in certain areas of Canada, where transport times can often be greater than 24 hours up to 48 hours. This is well in excess of the 12 hour timeframe recommended by van Harreveld et al., who noted that it was likely for odour concentrations to reach half their original concentration within 30 hours. However, since the existing work focused on tobacco odours, knowledge gaps remain with regards to odorant transformation and/or degradation for VOSC dominated samples over long timeframes (up to 48 hours).

This paper discusses experiments conducted to elucidate concerns and identify potential sources of improvement with regards to the sampling and analysis of samples containing VOSCs. A focus has been placed on the impact of detectors and separation column selection, chemical capture limitations associated with specific sorbents used in sorbent tubes, and VOSC degradation and/or transformation associated with sorbent tube desorption. Addressing existing knowledge gaps with regards to VOSC analytical and sampling methodologies is an important step in providing a foundation on which to build robust and scientifically defensible sampling and analysis guidelines for odorous emissions dominated by these compounds.

EXPERIMENTAL METHODS

A range of odorous samples (collected from poultry sheds in Queensland and Victoria, Australia, and from the headworks of a wastewater treatment plant in Cairns, Australia) were collected and analysed to identify sources of concern in existing VOSC sampling and analysis techniques with regards to VOSC degradation and/or transformation. Samples were collected using two types of sorbent tubes (Markes International, UK):

- Tenax TA – a widely used, inert, hydrophobic, weak sorbent. Targets volatile organic compounds in the n-C$_7$ to n-C$_{30}$ range; and
- Carbotrap 300 - multi-bed sorbent tube containing three different sorbents. In increasing sorbent strength and packing order within the tube, the sorbents are Carbopack C (hydrophobic), Carbopack B (hydrophobic) and Carbosieve SIII (mildly hydrophilic). Provides an approximate analyte capture range of ethane (C$_2$) to n-C$_{20}$.

Analytes were thermally desorbed from the sorbents in accordance with manufacturer specifications, and refocused within the thermal desorber cold trap (Markes Unity, Markes International, UK). A U-T11PGC cold trap (Markes International, UK) was used for general work, while a special sulphur cold trap (U-T6SUL, Markes International, UK) was used for sulfur specific work. Samples were analysed using a gas chromatograph (GC) equipped with
mass selective (MS) and sulfur chemiluminescence (SCD) detectors (Agilent 6890N GC, 5973NMSD, 355 Sulfur Chemiluminescence Detector, Agilent Technologies, USA) coupled to an Olfactory Detection Port (ODP2 Gerstel GmbH & Co., Germany). Three chromatographic separation columns were tested in the system (Agilent Technologies, USA):

- **HP-5MS** - non-polar stationary phase, 30m x 0.25mm x 0.25µm film thickness;
- **HP-INNOWax** - polar stationary phase, 30m x 0.25mm x 0.25µm film thickness; and
- **DB-VRX** - low polarity stationary phase, 30m x 0.25mm x 1.4µm film thickness.

A constant flow rate through the gas chromatograph was maintained using helium as the carrier gas. Specific oven temperature programs and run times are presented alongside each analysis presented in the results. The mass selective detector was operating in continuous scan mode (35 – 500 m/z) and mass spectra were recorded using the Agilent ChemStation software and analysed offline using the Enhanced Data Analysis package (Agilent Technologies, USA). Individual compounds were identified through matching the acquired mass spectra with ChemStation data bases (NIST04 and Wiley275).

To optimise the use of the panellist as an odour detector the split between the MSD and ODP was initially set at 1:1, before being refined to 2:3 (MSD:ODP). Split ratios were calculated using the Gerstel Column Calculator (Gerstel GmbH & Co., Germany). All odour chromatograms were recorded using the Gerstel ODP Recorder software (Gerstel GmbH & Co., Germany).

**RESULTS AND DISCUSSION**

Four key areas of concern were identified while analysing a range of odorant samples: (i) detector selection, (ii) the type of separation column employed, (iii) sorbent properties, and (iv) VOSC degradation and/or transformation during sample storage and analysis.

**Detector Selection**

Mass spectrometer detectors are among the most popular detectors and are widely used (particularly for their versatility), and are often used for simultaneous detection of VOCs and VOSCs. Some limitations, however, exist with regards to the sensitivity of these techniques for VOSCs, particularly relative to odour detection thresholds. As seen in a simultaneous analysis of a poultry odour sample via GC-MS and ODP (Figure 1), while there was significant chemical abundance detected for ODP peaks A and B (2,3-butanedione and dimethyl disulfide, respectively), there was relatively low abundance for ODP peaks C and D (dimethyl trisulfide and β-pinene, respectively) and no chemical abundance at all for ODP peak E. GC-MS analysis provides a low level of resolution for the VOSC in the sample. Given the typically low odour thresholds for VOSCs, this poor resolution may indeed result in these compounds not being identified while still having a significant contribution to the overall odour impact of the sample.
Figure 1. Analysis of a poultry odour sample via GC-MS and ODP.
50°C oven temperature for 2 minutes, 5°C/min increase to 125°C, 10°C/min increase to 200°C, hold for 2 minutes. 26.5 minute total run time.

To provide enhanced detection around or below odour thresholds, an SCD was employed for the selective analysis of sulfur compounds. In addition to enhanced sensitivity, the selective targeting of sulfur compounds eliminates the many of the non-odorous VOC spectral peaks observed in Figure 1. As seen in Figure 2, when analysing a similar poultry odour sample, this detector provides highly identifiable spectral peaks and allows the detection of a larger range of VOSCs in the sample.

Figure 2. Analysis of a poultry odour sample via GC-SCD.
40°C oven temperature for 2 minutes, 5°C/min increase to 140°C, hold for 1 minute, 10°C/min increase to 200°C, hold 1 minute, 25°C/min increase to 250°C, hold for 8 minutes. 40 minute total run time.
**Separation Columns**

Three types of columns were tested for the separation of VOCs and VOSCs: (i) an HP-5ms (non-polar stationary phase) column, (ii) an HP-INNOWax (polar stationary phase) column, and (iii) a DB-VRX (low polarity) column. A comparison of duplicate poultry odour samples analysed via GC-MS using the HP-INNOWax and HP-5ms separation columns is presented as Figure 3.

**Figure 3. Increased odorant separation afforded by a polar column.**

50°C oven temperature for 2 minutes, 5°C/min increase to 125°C, 10°C/min increase to 200°C, hold for 2 minutes. 26.5 minute total run time.

The polar column offers significantly better separation than the non-polar column, in which most of the compounds of interest were bunched into the first 4.5 minutes of the elute. The two unlabeled peaks near the start of the non-polar column run (isopropyl alcohol and hexane) were likely a result of contamination and were not observed when the sample was analysed with the polar column. It should also be noted that the use of the polar column allowed the identification of butanal, which was likely obscured by the other peaks in the non-polar test.

While the polar column significantly outperforms the non-polar one for this application, its application is somewhat limited by column bleed. Unlike the non-polar column (which is low bleed and very stable), there is a retention time shift in the polar column change as it ages, increasing the calibration demand and complicating direct comparison of successive chromatograms. A third (low polarity) column (DB-VRX) was tested (on a different sample) as a compromise between these two columns (Figure 4).
Figure 4. Odorant separation using a low polarity (DB-VRX) column.
50°C oven temperature for 2 minutes, 2.5°C/min increase to 50°C, 15°C/min increase to 175°C, 5°C/min increase to 225°C, hold for 3 minutes. 27.33 minute total run time.

The DB-VRX column retains much of the strengths of the polar and non-polar separation columns, providing a good separation and peak identifiably while still having low bleed and stable retention times. This column is currently being used for both GC-MS and GC-SCD analysis.

**Sorbent Tube Types**

Two sorbent tube types were assessed during these studies: (i) Tenax TA (hydrophobic, weak sorbent) and (ii) Carbotrap 300 (multibed sorbent with range of strengths and hydrophobicities). Duplicate samples collected from a wastewater treatment plant headworks using both sorbent tube types and analysed via GC-MS (Figure 5) demonstrate significant differences in compound capture.
Figure 5. Comparison of Tenax TA and Carbotrap 300 sorbent tubes for dry sources.

40°C oven temperature for 2 minutes, 5°C/min increase to 140°C, hold for 1 minute, 10°C/min increase to 200°C, hold 1 minute, 25°C/min increase to 250°C, hold for 8 minutes. 40 minute total run time.

The Tenax TA sorbent tube (n-C$_7$ to n-C$_{30}$ compound range) provided significantly greater compound capture, which is counterintuitive given the dominance of the butyl compounds (n-C$_4$) in the sample (in line with the Carbotrap 300 sorbent tube compound range of C$_2$ to n-C$_{20}$). This result demonstrates the importance of conducting initial scans of samples using a range of sorbents prior to conducting an extensive sampling program.

While not significant for a dry sample (Figure 5), moisture capture in hydrophilic sorbents can have a strong impact on the quality of the results for wet (humid) sources (Figure 6). Sample collected using the hydrophobic Tenax TA sorbent tube show no effect by moisture, whereas moisture is captured in the Carbotrap 300 sorbent tube (most likely in the mildly hydrophilic third sorbent bed). When this tube is desorbed, the water co-elutes with many of the compounds of interest, obscuring their identification. Given the improved capture and lack of impact by source moisture (humid gas conditions are commonly encountered for many sources of interest in the livestock and wastewater industries), Tenax TA sorbent tubes have been used for ongoing sampling work.
Figure 6. Comparison of Tenax TA and Carbotrap 300 sorbent tubes for wet sources.
50°C oven temperature for 2 minutes, 5°C/min increase to 125°C, 10°C/min increase to 200°C, hold for 1.5 minutes. 26 minute total run time.

VOSC Transformation and Degradation

Sulfur compounds are known to be highly labile and subject to transformation and/or degradation, as a result care must be taken in the handling and analysis of VOSC dominated samples (sorbent tubes and bag samples). For odorant samples collected using sorbent tubes, in addition to capture limitations discussed previously, there is significant potential for VOSC transformation and/or degradation during thermal desorption. These thermal effects are apparent in Figure 7, which compares poultry odours that were analysed directly via GC-MS and also sampled using a Tenax TA sorbent tube and subsequently analysed on the same GC-MS. A significant and identifiable methyl mercaptan peak (Peak B) was observed in the sample analysed directly, while it was not detected in the sorbent tube sample. Conversely, a significantly greater dimethyl disulfide peak (Peak C) was obtained from the sorbent tube sample over the one analysed directly. Given that dimethyl disulfide is a decay product of methyl mercaptan (via dimerisation) it is likely that the thermal desorption is responsible for the loss of the methyl mercaptan. The significance of thermal desorption on specific VOSC degradation and/or transformation is an area requiring further investigation.

While not related to VOSCs, it is also interesting to note that trimethylamine was detected in the directly analysed sample but not in the sorbent tube sample. This suggests poor capture of nitrogen compounds by the sorbent.
For bag samples being sampled directly to the GC, storage time, sample humidity, environmental conditions (temperature and exposure to light), and sample bag material are all parameters that can influence odorant transformation and/or degradation. To date there has been limited assessment of these influences on VOSC transformation and degradation (as well as limited guidance on sample handling, transport, and storage), and it is an area demanding future work.

**SUMMARY**

A range of odorous samples containing VOSCs were analysed with the objective of identifying areas of concern and potential improvement for commonly applied analytical techniques.
Analytical results presented in this paper demonstrated the benefits associated with the application of sulfur chemiluminescence detectors over the more traditional mass selective detectors. The use of low polarity columns provided a good compromise between separation and peak identifiability (characteristic of polar columns) and having stable retention times between analyses (characteristic of non-polar columns). Counterintuitive compound capture results when assessing different sorbents highlighted the need for initial scans prior to widespread sampling to identify the most appropriate sorbent for the application. Samples analysed for humid sources demonstrated that there was significant co-elution of water with analytes of interest for sorbent tubes containing hydrophilic sorbents, thus these sorbents are not suitable for humid sources. Finally, concerns were raised with regards to potential thermal degradation of VOSCs during sorbent tube thermal desorption, and further investigation is needed into this area.

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KEYWORDS

odours, odour measurement, GC-MS, sulfur compounds