CHEMICAL ENGINEERING TRANSACTIONS
VOL. 30, 2012
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet
Guest Editor: Renato Del Rosso

**ISBN** 978-88-95608-21-1; **ISSN** 1974-9791
DOI: 10.3303/CET1230033

# Odour: Characterisation and Transformation

Gavin Parcsi*, Eric C.Sivret, Xinguang Wang, Richard M.Stuetz

[a]UNSW Water Research Centre, School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW, 2052
corresponding author: g.parcsi@unsw.edu.au

Emissions of odour constitute a variety of chemical compounds that can be odorous or non-odorous. Each odorous chemical (*odorant*) has a particular odorant characteristic and detection threshold, unique and specific to that compound. Within an odour matrix the compounds present will interact to form the overall (*global)* odour; in much the same way as a perfume is composed of many fragrance types. The combination of odorants and non-odorants is complicated by chemical interactions (to form additional species) and the mechanism of combination; it is not simply a matter of addition, for the global odour can be more or less than the sum of the individual components. The management of odorous emissions must first begin with a comprehensive chemical characterisation of the emission in order to identify the key contributors causing the odorous annoyance. This will enable effective odour management to reduce the emission impact; however identification of the nuisance chemicals at the source may differ from those potentially reaching a local receptor; it is therefore imperative that both the source emission be understood and the potential reaction pathways of these chemicals.

## 1. Introduction

Any odorous emission has the potential to interact with receptors, and thus has the potential to cause nuisance to those receptors. Industries; including water and waste water treatment facilities, intensive agriculture practices, food processing plants and waste management operations have an environmental and social obligation to ensure they do not adversely affect the surrounding community during the discharge of their intended function. An odour can be assessed and given a numerical value (OU, odour units) for its odour concentration by dilution olfactometry, however this value does little to describe the character of the odour; be it a pleasant fragrance of roses or the putrid stench of garbage. The character of an odour is partially subjective, and with different people having different sensitivities to specific odorants, the use gas chromatography (GC) substantially increases the understanding of an odour's chemical composition, moreover the use of the human olfaction as a detector on the GC allows for the odorants within a sample to be identified.
The human nose is such a sensitive detector (Breer, 2008) for chemical odorants that it would be ideally suited to the chemical analysis of an odour, in 1964 Fuller et al (Fuller et al., 1964) first reported upon the use of "The Gas Chromatograph with Human Sensor;" although the application was perfume evaluation, olfactory detection has since been applied for the assessment of food flavours and aromas (d'Acampora Zellner et al., 2008), beverages (Plutowska and Wardencki, 2008), malodours (Delahunty et al., 2006), and continues to be used in perfume analysis. Typically coupled with a gas chromatograph to provide chemical separation (GC-O); olfactometry is used extensively for chemosensory analysis; with an additional analytical detector (mass spectrometer, flame ionisation detector, etcetera) providing chemical identification and quantification.

Please cite this article as: Parcsi G., Sivret E., Wang X. and Stuetz R., 2012, Odour: characterisation and transformation, Chemical Engineering Transactions, 30, 193-198 DOI: 10.3303/CET1230033

Significant studies investigating different intensive livestock operations have often focused upon the identification of the volatile organic compound NMVOCs present, only a limited number have expanded the understanding by assessing the chemical emission matrices for odorants. Often the identification of the volatile organic species is performed separate from the odorant identification, however if the effluent from the gas chromatograph can be split between the olfactory detection port and the analytical detector (GC-MS/O, GC-FID/O etcetera), simultaneous chemical identification and quantification and odorant identification and prioritisation can be performed. (Cai et al., 2006; Kleeberg et al., 2005; Rabaud et al., 2003; Schiffman et al., 2001; Trabue et al., 2006). This provides a novel method to efficiently analyse samples for both chemical species present and odorants.

## 2. Methodology

### 2.1 Sample Collection

Field samples from poultry houses and sewer networks were collected using pumped thermal desorption tubes and analysed with thermal desoption-gas chromatography–mass spectrometry/olfactometry (TD-GC-MS/O) analysis. The sorbent tubes used contained Tenax TA sorbent (for n-C7 to n-C30 compounds) (Markes International, UK). Sorbent tubes were chosen for the sample collection method based on proven reliability and robustness, and their intrinsic logistical advantages over other sampling methods such as sampling canisters and odour bags. In addition work presented by Koziel et al. (2005) indicated a greater sample recovery from sorbent tubes over sampling canisters and sampling bags.

### 2.2 Sample Analysis, Data Acquisition and Analysis

The analytes were thermally desorbed from the sorbent tubes and refocused within the cold trap of the thermal desorber (Markes Unity, Markes International, UK), this allowed for the formation of an analyte ‘slug’ to be injected into the gas chromatograph for subsequent separation and identification. The cold trap of the thermal desorber is a general-purpose graphitised carbon type (U-T11 GPC, Markes International, UK).

Chemical speciation was performed using GC-MS, where the compounds were identified using gas chromatographic separation and mass selective detection (Agilent 6890N GC, 5973N MSD, Agilent Technologies) with an HP-INNOWax capillary column (30m x 0.25mm x 0.25µm film thickness, Agilent Technologies). The flow rate of the gas chromatograph was maintained at a constant flow (1.6mL/min) with helium as the carrier gas. The oven was temperature programmed for a total run time of 26.50min, (50 °C for 2 min, 5.00 °C/min to 125 °C, then 10.00 C to 200 °C, hold at 200 °C for 2 min) this provided adequate separation of the eluting compounds.

The mass selective detector was operating in continuous scan mode (35 – 285 m/z). The mass spectra were recorded using the Agilent ChemStation software and analysed offline using the Enhanced Data Analysis package (Agilent Technologies). Initial identification of the volatile organic compounds relied upon the matching of the acquired mass spectra with the ChemStation data bases (NIST02): selected compounds of interest where purchased as neat standards for subsequent quantification and the retention times were matched to ensure the library matches were accurate.

Odorant speciation was performed using an Olfactory Detection Port (ODP2 Gerstel GmbH & Co., Germany) by splitting the gas-chromatograph effluent between the mass selective detector and the olfactory detection port. The split ratio was calculated to be 2:3 (MSD:ODP), these split ratios were calculated using the Gerstel Column Calculator (Gerstel GmbH & Co., Germany.) The odour chromatograms were recorded using the Gerstel ODP Recorder software. Analysis was performed offline using the Agilent ChemStation Data Analysis software.

## 3. Results

The use of the ODP allowed for the odorous compounds within the matrix to be identified from the large number of compounds that were present. Of the numerous compounds that appear in the mass spectra, only a few have been detected from the olfactory detection port. There are two principle reasons from this; either the compound does not have a notable odour, or that the amount present

within the emission is below the olfactory detectable limit for the average human nose. The selected spectra illustrate the chemical speciation and odorant prioritization of Non-methane volatile organic compound (NMVOC) samples collected at different sites. Figure 1A and Figure 1B shows a typical total ion chromatogram (blue, upper trace) with the olfactory stimulus chromatogram (red, lower trace) obtained from two different wastewater odour emission sources.

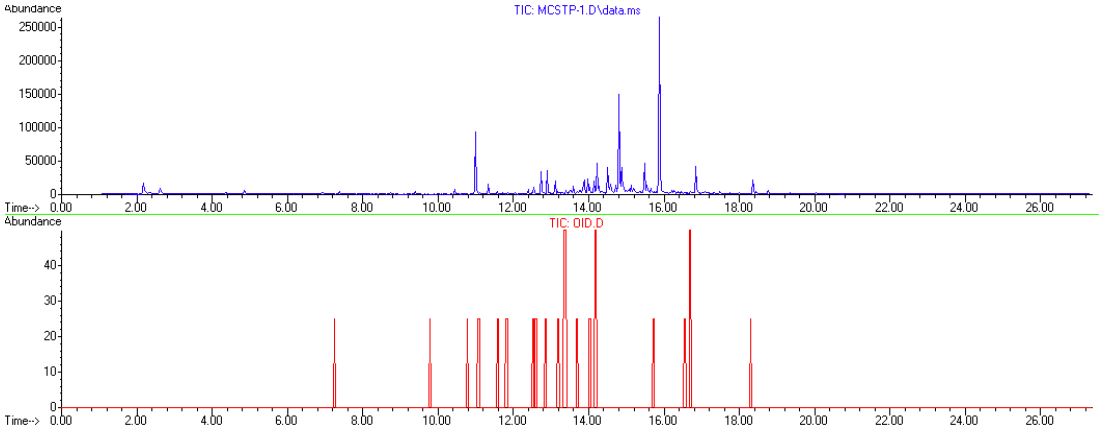


*Figure 1A: Total Ion Chromatogram (blue, upper trace) and Olfactory Stimulus Chromatogram (red, lower trace) from the inlet of a waste water treatment plant.*

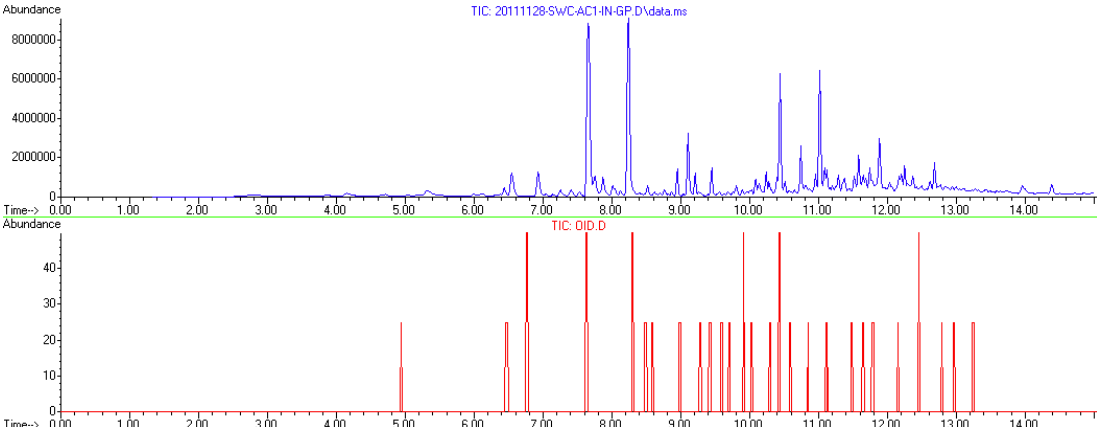


*Figure 1B: Total Ion Chromatogram (blue, upper trace) and Olfactory Stimulus Chromatogram (red, lower trace) from a sewerage pumping station.*

Figure 2 shows another example a typical total ion chromatogram (blue, upper trace) with the olfactory stimulus chromatogram (red, lower trace) obtained from two different poultry odour emission sources. It can be observed that there are instances where a response from the olfactory detector (nose) does not correspond to a mass spectral response; this is explained by the extremely low odour detection thresholds of some compounds (particularly VOSCs).

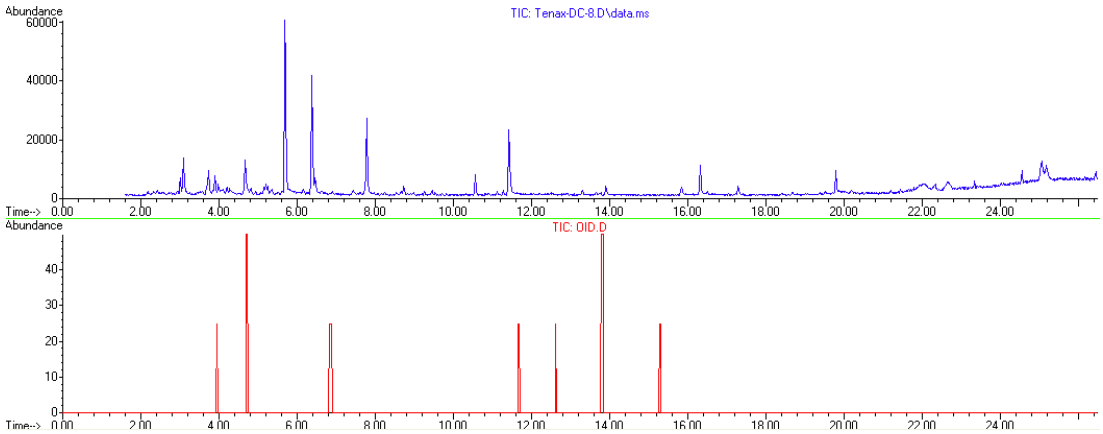


*Figure 2: Total Ion Chromatogram (blue, upper trace) and Olfactory Stimulus Chromatogram (red, lower trace) from another broiler (meat chicken) shed.*

*Table 1 Chemical species identified as potential contributors to the odour at the emission source and potentially reaching and causing annoyance to a local receptor.*

| Descriptor | Chemical | OTV (mg/m$^3$) |
|---|---|---|
| Butter, rancid, fat | 2,3-butanedione | 0.01 |
| Mushroom, earth | 3-hydroxy-2-butanone | 3 |
| Smoke, burning, rubber | Dimethyl disulphide | 35 |
| Solvent | 1-butanol | 3 |
| Malt, rancid | 3-methyl-butanal | 0.002 |
| Green, citrus | Octanal | 0.015 |
| Sweet, solvent | Toluene | 25 |
| Metallic, sulphur, pungent | Dimethyl trisulphide | 0.05 |
| Pine | α-pinene | 0.005 |
| Earth, mushroom | β-pinene | 65 |

It was observed that there are instances where a response from the olfactory detector (nose) does not correspond to a mass spectral response; this is explained by the extremely low odour detection thresholds of some compounds (particularly VOSCs). Identification of the compounds present within the matrix yielded a large number of different classes of compounds including aromatics, sulphur containing organic species, aldehydes, ketones, alcohols, terpenes and other general hydrocarbons, with only a limited number of the chemicals identified being also identified as potential contributors to a nuisance odour.

Whilst a number of chemicals were detected at the various locations, the emphasis is to understand the chemical profile of specific site a system is being designed for, variation between sites of similar empirical character may yield vastly different odour emissions. Table 1 lists several of the chemical compounds identified within the emission matrices analysed that have also been prioritised as being potential contributors to the odour.

## 4. Discussion

The intrinsic volatility of the chemical species that were collected during the odour analysis should be acknowledged to influence the analytes being capture and detected from the different detectors. The

fate of chemicals in the environment is subject to the environmental conditions (temperature, humidity and sunlight) that may impact the stability of these chemicals; consequently there exists a potential for differences in chemical species at the source to those that could potentially reach a receptor. These species could have a different olfactory impact to those of the source (parent) compound. NMVOCs identified from the chemical characterisation of odorous emissions include several alcohol, aldehydes, ketones and carboxylic acids, which can be related to each other through known oxidation pathways.
The oxidation of a primary (1°) alcohol (1-butanol) to a carboxylic acid (butanoic acid) though an aldehyde (butanal) intermediate is an example of such a reaction pathway. All three of these chemicals were detected in NMVOC samples collected from the different emission sources.
In observing the oxidation of the alcohol to the carboxylic acid, there is also a change in odorant character and an increase in odour threshold value. It has been noted that there is typically an increase in the potency of a compound as it oxides; that is to say the carboxylic acid will have a lower odorant threshold than the alcohol from which it has transformed, however there is a difficulty in substantiating this claim as there is limited data available that has been obtained through identical methods; hence the wide variety of odour threshold values presented in the literature. The odour threshold values listed in Table 2 are from a single source (Cometto-Muniz et al., 1998) to ensure their comparability.

*Table 2 Odour characteristics and odour threshold values of the oxidation series 1-butanol to butanoic acid.*

| **Chemical** | **Odorant Descriptor** | **OTV (mg/m$^3$)** |
|---|---|---|
| 1-butanol | sweet, characteristic | 1.7-3.8 |
| butanal | pungent/green | 8.8 |
| butanoic acid | putrid/vomit | 0.013 |

Within the ODP analysis of the different samples dimethyl disulphide is frequently identified as one of the significant odorants; however it should be carefully considered that the presence of DMDS in the results may strongly indicate the presence of methyl mercaptan at the source. Mercaptans readily dimerise to form the disulphide species; this will alter the character of the odour and also the strength. Methyl mercaptan (0.00016 mg/m$^3$ pungent rotting cabbage) to dimethyl disulphide (0.046 mg/m$^3$ sulphourous vegetable), also the concentration of the disulphide species is half of the original thiol species if 100 % conversion occurs (2r-SH ⇌ R-S-S-R). Therefore it is plausible to conclude that the presence of dimethyl disulphide as a significant odorant within the analysed matrix may correspond to an even greater significance and contribution to the nuisance odour of methyl mercaptan at the source.

The use of an olfactory detection port to complement the MS detector provided information to enable the elucidation of the odorants from emission sources. The elution of the chemicals from the GC to the two detectors allows for the simultaneous identification of the chemical and its odorant characteristic, however the sequential elution does not allow for the appreciation of the global odour character. The global odour will be composed of all the chemical species interacting in different manners, of which there is three principle interactions that the odorants can undergo; additive, antagonistic and synergistic. The additive mechanism will yield a global odour that is composed of the chemicals in their respective ratios, the antagonistic mechanism will yield a global odour that is less than the total of the components, and the synergistic mechanism will yield a global odour that is greater than the total of the individual components. Through these mechanisms it is plausible that when assessed in isolation a low impact chemical species may not be detected from the ODP, however may constitute a significant impact when combined with other odorants or non-odorous chemical species (Ryan et al., 2008).

## 5. Conclusion

Developing an odour mamagement stratergy requires an understanding of the chemical characteristic of the emission source; both in terms of chemical speciation and odorant and potential odorant composition. Appreciating the fate and transformation of the chemicals in the environment is required

before a conclusive and comprehensive list of the chemical species present and more importantly their respective abundances can be drawn with complete and absolute certainty. To design an efficient system a detailed characterisation of the specific source must be completed as there is significant variability between seemingly identical sources. Simultaneous chemical and odorant characterisation is efficiently achieved through GC-MS/O, however careful interpretation of the acquired data must be performed to ensure accurate understanding of both the odorants present within the matrix, and the chemicals that could potential react in the environment to form odorants.

**Acknowledgements**

This work has been supported by the Poultry CRC (Project 04-45) and the Australian Research Council Discovery Project (DP1096691).

**References**

Breer H., 2008. The Sense of Smell. Annals of the New York Academy of Sciences, 1126, 1-6.

Cai L., Koziel J. A., Lo Y.-C., & Hoff S.J., 2006. Characterization of volatile organic compounds and odorants associated with swine barn particulate matter using solid-phase microextraction and gas chromatography-mass spectrometry-olfactometry. Journal of Chromatography A, 1102, 60-72.

Cometto-Muñiz J.E., Cain W.S., Abraham M.H., 1998. Nasal pungency and odor of homologous aldehydes and carboxylic acids. Experimental Brain Research, 118, 180-188.

D'Acampora Zellner B., Dugo P., Dugo G., Mondello L. 2008. Gas chromatography-olfactometry in food flavour analysis. Journal of Chromatography A, 1186, 123-143.

Delahunty C.M., Eyres, G., Dufour, J.-P., 2006. Gas chromatography-olfactometry. Journal of Separation Science, 29, 2107-2125.

George H., Fuller R.S., Tisserand G.A., 1964. The gas chromatograph with human sensor: perfumer model. Annals of the New York Academy of Sciences, 116, 711-724.

Kleeberg K.K., Liu Y., Jans M., Schlegelmilch M., Streese J., Stegmann R., 2005. Development of a simple and sensitive method for the characterization of odorous waste gas emissions by means of solid-phase microextraction (SPME) and GC-MS/olfactometry. Waste Management, 25, 872-879.

Koziel J.A., Spinhirne J.P., Lloyd J.D., Parker D.B., Wright D. W., Kuhrt F.W., 2005. Evaluation of sample recovery of malodorous livestock gases from air sampling bags, solid-phase microextraction fibers, Tenax TA sorbent tubes, and sampling canisters.(Technical Paper). Journal of the Air & Waste Management Association, 55(11), 1147.

Plutowska B., Wardencki W., 2008. Application of gas chromatography-olfactometry (GC-O) in analysis and quality assessment of alcoholic beverages - A review. Food Chemistry, 107, 449-463.

Rabaud N.E., Ebeler S.E., Ashbaugh L.L., Flocchini R.G., 2003. Characterization and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California. Atmospheric Environment, 37, 933-940.

Ryan D., Prenzler P.D., Saliba A.J., Scollary G.R., 2008. The significance of low impact odorants in global odour perception. Trends in Food Science & Technology, 19, 383-389.

Schiffman S.S., Bennett J.L., Raymer J.H., 2001. Quantification of odors and odorants from swine operations in North Carolina. Agricultural and Forest Meteorology, 108, 213-240.

Trabue S.L., Anhalt J.C., Zahn J.A., 2006. Bias of Tedlar Bags in the Measurement of Agricultural Odorants. Journal of Environmental Quality, 35, 1668-77.