Research Paper

Evaluation of the performance of field olfactometers by selected ion flow tube mass spectrometry

CrossMark

Christophe Walgraeve[*], *Katrijn Van Huffel, Joren Bruneel, Herman Van Langenhove*

Research Group EnVOC (Environmental Organic Chemistry and Technology), Department of Sustainable Organic Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium

Odour quantification is generally performed by olfactometry, a technique which determines to what extent an odorous air sample should be diluted with odour-free air to be just distinguishable from odour-free air. In this study, the performance of two field olfactometers (Nasal Ranger and Scentroid 110c) was evaluated with respect to their ability to generate accurate dilutions. Therefore, an air stream with known concentrations (500 ppb$_v$ –5 ppm$_v$) of odorous compounds (acetic acid, propanoic acid, n-butanol, dimethyl sulphide, dimethyl disulphide) was diluted by the olfactometers at their different set points after which the concentrations of the target compounds in the diluted air stream were measured by selected ion flow tube mass spectrometry (SIFT-MS). This enabled to determine the observed dilution ratios (DR_{obs}) and relate them to the set point values (DR_{set}). The Nasal Ranger showed good performance in the interval between DR_{set} 3 and 31. Only at the highest set dilution ratio ($DR_{set} = 61$) breakthrough of the compounds through the activated carbon filter was observed. This breakthrough resulted in lower observed dilution ratios (up to a factor of 2 for dimethyl sulphide) when compared to the DR_{set}. For the Scentroid a good linearity between DR_{set} and DR_{obs} was observed but dilution ratios were much higher (up to a factor of 2) than what could be theoretically expected on the basis of air flows. This behaviour could be explained by sorption effects of the target compounds onto the metal parts and into the rubber seal of the Scentroid.

1. Introduction

Emissions of odorous pollutants by industry and agriculture can lead to odour nuisance complaints from nearby residents. This is of increasing importance, since residential homes are now more frequently located in what were traditional rural and farming areas (Gutierrez, Chica, Martin, & Romain, 2014; Melse, Ogink, & Rulkens, 2009). The odour perception is a

* Corresponding author. Tel.: +32 (0)9 264 59 54.
E-mail addresses: Christophe.Walgraeve@UGent.be, Christophe.Walgraeve@gmail.com (C. Walgraeve).

Nomenclature

BP	Boiling point (°C)
BR	Branching ratio (%)
C_{blank}	Concentration in the blank (ppb_v)
C_{ds}	Concentration in the diluted gas stream (ppb_v)
C_{mc}	Concentration in the measuring chamber (ppb_v)
D/T	Dilution-to-threshold (−)
D/T_{obs}	Observed D/T (−)
D/T_{set}	Set point D/T (−)
DMDS	Dimethyl disulphide
DMS	Dimethyl sulphide
DR	Dilution ratio (−)
DR_{obs}	Observed dilution ratio (−)
DR_{real}	Real dilution ratio (−)
DR_{set}	Dilution ratio set point (−)
ECD	Electron capture detection
FEP	Tetrafluoroethylene hexafluoropropylene
FID	Flame ionisation detection
FPD	Photometric detection
H	Henry Coefficient (−)
HS	Headspace
K_{ow}	Octanol-to-water partitioning coefficient (−)
MW	Molecular weight (g mol^{-1})
OAV	Odour activity value
ODT	Odour detection threshold (ppb_v)
P	Pressure measuring point
PET	Polyethylene terepthalate
PID	Photoionisation detection
PMMA	Polymethylmethacrylate
PTR-MS	Proton transfer reaction mass spectrometry
PVF	Polyvinyl fluoride
RSD	Relative standard deviation (%)
SCD	Sulphur chemiluminescence detection
$SIFT_i$	Measuring point for the SIFT-MS, were i can be 1 to 4
SIFT-MS	Selected ion flow tube mass spectrometry
V	Regulatory valve
VOC	Volatile organic compound
VP	Vapour pressure (Pa)
W_s	Water solubility (mg l^{-1})

complex phenomenon and is caused by the interaction of odorous compounds (odorants) with the olfactory cells in the nasal cavity. Very often, a complex mixture of compounds (e.g. emission from landfills, composting facilities, municipal waste incineration plants, waste water treatment plants) is responsible for the odour, rather than a single compound (e.g. the release of tert-butylthiol or tetrahydrothiophene which are used as trace molecules in natural gas) (Behbod et al., 2014; Dincer & Muezzinoglu, 2007). In order to develop effective odour regulation and evaluate abatement technologies for odorous emissions, it is of paramount importance that odours can be quantitatively measured (Akdeniz et al., 2012a, 2012b; Capelli, Sironi, Del Rosso, Centola, & Il Grande, 2008; Laor, Parker, & Page, 2014; Munoz et al., 2010). Basically there are

two main odour measurement strategies: the human nose is used as sensor (olfactometry); or the odorant molecules are analysed by chemical analytical methods. The latter method includes the identification and quantification of the individual compounds as a first step. This is a challenging task since both inorganic gasses and organic compounds are present at variable concentration levels (ppt_v to ppm_v) (Akdeniz et al., 2012a, 2012b). The measurement cannot be conducted by a single analytical technique, and often sensitive and/or advanced techniques are required to detect and quantify the compounds. Inorganic odorants such as H_2S, NH_3 are measured by spectroscopic techniques (Fourier transform infrared spectroscopy, laser spectroscopy, differential optical absorption spectroscopy), gas chromatography or solid state sensors (Hu, Babcock, Bialkowski, Jones, & Tuller, 2014). Volatile organic compounds are generally analysed using gas chromatography combined with a suitable detection technique such as mass spectrometry (MS), flame ionisation detection (FID), photoionisation detection (PID), electron capture detection (ECD), sulphur chemiluminescence detection (SCD) or photometric detection (FPD) (Hayes, Stevenson, & Stuetz, 2014). Analytical procedures are often laborious (sampling, peak identification and quantification) and costly, but recent developments have led to the application of proton transfer reaction mass spectrometry (PTR-MS) and selected ion flow tube mass spectrometry (SIFT-MS) to measure real time concentrations of odorants (Hansen, Adamsen, et al., 2012; Hansen, Liu, et al., 2012; Liu, Lokke, Riis, Mortensen, & Feilberg, 2014; Saha, Feilberg, Zhang, & Adamsen, 2011; Van Huffel, Heynderickx, Dewulf, & Van Langenhove, 2012). The next step in the process, extracting sensorial information (odour concentration, odour character and hedonic tone) from the chemical data, is the bottleneck of this approach. Odour concentration is defined as the dilution factor necessary to reach the detection threshold, i.e the point at which the odour is detectable by 50% of the test panel. Defoer and co-workers (Defoer, De Bo, Van Langenhove, Dewulf, & Van Elst, 2002) showed that the relationship between chemical composition and odour concentration is specific for each type of odour and cannot be generalised. Whereas the authors found a good linear relationship ($r^2 = 0.97$) between odour concentration and total VOCs concentration for biofilter emissions in fruit and garden waste composting plants, a poor relationship was obtained for biofilter emissions in an animal rendering plant (Defoer et al., 2002). Hansen and co-workers used PTR-MS to determine the concentration of 15 odorous compounds in a pig production facility and defined a partial least square regression model to predict the odour concentration (Hansen, Adamsen, et al., 2012; Hansen, Liu, et al., 2012). They have found a correlation (r^2) of 0.53 and a slope of 0.9 between the predicted and measured odour concentrations.

Among odorants, considerable differences exist with respect to their odour detection thresholds (ODT), defined as the lowest compound concentration which can be distinguished from pure odour-free air by 50% of the panel, even comparing compounds of a homologous group (Cometto-Muniz & Abraham, 2010). When the individual ODTs are known, the relative importance of an odorant in a mixture can be described by its odour activity value (OAV), which is defined as the ratio of the compound concentration and the ODT value

(Capelli, Sironi, Del Rosso, & Guillot, 2013). Although the calculation of the sum of the individual OAV values ($\sum$OAV) seems a straightforward approach to characterise an odorous sample, it is often not a good predictor of the odour concentration determined by olfactometry. For example, Parker and co-workers found correlation coefficients (r^2) between 0.16 and 0.52 and found that $\sum$OAV underestimated the odour concentration by a factor of 3 (Parker et al., 2012). A possible explanation for the discrepancies can be found in the synergistic and antagonistic effects between the odorants. Although, the OAV can be useful for the relative assessment of odour abatement technologies as described in the article of Hansen and co-workers (Hansen, Jonassen, & Feilberg, 2014). It becomes clear that characterising an odorous sample is complex and chemical analysis alone is often not sufficient, therefore olfactometry is often employed. In olfactometry, the odorous sample is diluted (with odour free air), in successive increasingly smaller dilutions using an olfactometer. The diluted air is subsequently presented to the assessor who has to indicate whether he can distinguish the diluted odorous air from odour-free air. The final result is an odour concentration, which is a measure of the dilution threshold. It has to be noted that the odour concentration gives no information about the intensity or offensiveness of the undiluted sample that is perceived by the receptor. In Europe and at several research institutes in the USA and South East Asia the international standard EN13725:2003 is used for the determination of the odour concentration (CEN, 2003). In this standard, quality criteria (precision and trueness) are described to assess the overall performance of the sensory measurement method, together with a procedure to select suitable panel members on the basis of their sensitivity towards the reference odorant n-butanol. The olfactory sensitivity of the selected panelists will fall in a much narrower bandwidth than the variability within the general population (CEN, 2003). This laborious panel selection has a direct effect on the costs of an analysis. However, it should be acknowledged that the introduction of the CEN norm has had a positive effect on the standardisation of olfactory measurements. When employing olfactometry, some points deserve special attention. First, sampling artefacts might occur. The odorous gas is typically collected, employing the lung principal, in tetrafluoroethylene hexafluoropropylene (FEP), polyvinyl fluoride (PVF, Tedlar) or polyethylene terepthalate (PET, Nalophan) sampling bags (Trabue, Kerr, Bearson, & Ziemer, 2011; Zhang et al., 2010). Odorous compounds may adsorb on the sampling bag surface or diffuse through the bag during storage or transport (Hansen, Adamsen, Feilberg, & Jonassen, 2011). This results in a sample that might be different in chemical composition when compared to the sample from which the odour had to be evaluated (van Harreveld, 2003). Therefore it is recommended that the sample should be analysed within 30 h (CEN, 2003). Secondly, sampling bags may have significant background odour levels which can disturb the measurement of the odour concentration; careful flushing of the sampling bags is recommended (Brattoli et al., 2011). This background level effect is more important for samples with relative low odour concentration (such as samples taken further downwind from the source) when compared to samples with high odour concentrations (near the source). To evaluate low odour

concentrations, field olfactometers are used. The latter are able to make lower dilutions (when compared to laboratory olfactometers) at the site where the odour nuisance occurs and therefore eliminate the use of sampling bags (Laor et al., 2011; Sheffield, Chahine, Dye, & Thompson, 2007). Their application is particularly popular in the USA and Canada, were several states and provinces set limits at the receptor sites or along the perimeter of odour emitting plants (Benzo, Mantovani, & Pittarello, 2012; Bokowa, 2010; Laor et al., 2014). In Europe however, field olfactometers are not regulated. Field olfactometers make dilutions of the odorous air using odour-free air, which is provided from a portable gas cylinder or made on-site by forcing ambient (odorous) air through a carbon adsorption bed. The ability of (field)-olfactometers, to dilute odorous samples in an accurate way has scarcely been investigated; although this is the key performance criterion (Beauchamp et al., 2010; Hansen, Feilberg, & Adamsen, 2010, 2013). For example, Henry and colleagues have found significant differences between the observed odour concentrations when the same pig manure sample was analysed with different (field) olfactometers (Henry, Schulte, Hoff, Jacobson, & Parkhurst, 2011). These instruments were however designed for the same purpose, i.e diluting the odorous sample. It is therefore very important that the possible reasons for these differences are investigated, in order to standardise their usage. Therefore, the aim of this research is to investigate the performance of two commercially available field olfactometers; (a) the Nasal Ranger by St Croix Sensory (Stillwater, MN, USA) and (b) the Scentroid Model SM110C by Ides Canada Inc. (Markham, ON, Canada) with respect to their ability to generate accurate dilutions. The olfactometers were exposed to an environment with known odorant concentration levels after which different dilutions were made by the olfactometers. The concentrations of the odorants in the diluted air stream were measured by SIFT-MS. From these measurements, the dilution ratio was calculated and compared to the theoretical set point value. The experiments also investigated if discrimination between odorants during the dilution process occurs.

2. Materials and methods

Five compounds were selected as target compounds on the basis of their (a) OTV values (Nagata, 2003), (b) their ubiquitous presence in malodours (pig stable air, air from waste water treatment plant or composting facilities) and (c) their different physical and chemical properties (Howard & Meylan, 1997). The selected compounds belong to three different organic classes: organic acids (acetic acid and propanoic acid), sulphur compounds (dimethyl sulphide (DMS), dimethyl disulphide (DMDS)) and alcohols (n-butanol). n-butanol was chosen since it is used as a reference compound in olfactometry. An overview of the physical and chemical properties of the compounds is given in Table 1 together with their OTV values (Howard & Meylan, 1997; Nagata, 2003). It is clear that the selected compounds have different physical and chemical properties. These different properties might cause a different behaviour of the compounds in the field olfactometers. The water solubility ranges from 3.74×10^3 (DMDS) to as high as

Table 1 — Physical and chemical properties of the target compounds. CAS: CAS number; MW: molecular weight; BP: boiling point; VP: vapour pressure; WS: water solubility; H: dimensionless Henry coefficient; Log(K_{ow}): Logarithm of the octanol—water partitioning coefficient; dim: dimensionless; OTV: odour threshold value (Howard & Meylan, 1997; Nagata, 2003).

	CAS	Formula	MW g mol^{-1}	BP °C	WS (25 °C) mg l^{-1}	Log K_{ow} (−)	VP (25 °C) Pa	H (25 °C) (−)	ODT ppb$_v$
Acetic acid	64-19-7	$C_2H_4O_2$	60.1	118	1.00×10^6	−0.17	2.09×10^3	4.09×10^{-6}	6.0
DMS	75-18-3	C_2H_6S	62.1	36	2.20×10^4	0.92	6.69×10^4	6.59×10^{-2}	3.0
Propanoic acid	79-09-4	$C_3H_6O_2$	74.1	141	1.00×10^6	0.33	4.71×10^2	1.82×10^{-5}	5.7
1-butanol	71-36-3	$C_4H_{10}O$	74.1	118	6.32×10^4	0.88	8.93×10^2	3.60×10^{-4}	38
DMDS	624-92-0	$C_2H_6S_2$	94.2	110	3.74×10^3	1.77	3.83×10^3	4.95×10^{-2}	2.2

1×10^6 mg l^{-1} (acetic acid), the Log(K_{ow}) ranged from −0.17 (acetic acid) to 1.77 (DMDS) and the vapour pressure from 4.71×10^2 (propanoic acid) to 6.69×10^4 Pa (DMS). Also compounds were chosen for which stable concentrations could be obtained (thus photo liable compounds were not considered).

2.1. Nasal Ranger

The Nasal Ranger generates a series of discrete dilutions by mixing odorous air with odour-free air. The Nasal Ranger makes use of the breathing rate of the assessor to aspirate and mix the odorous air with odour-free air. The latter is obtained by carbon filtration of the odorous air. The performance of the Nasal Ranger was checked by exposing it to known pollutant concentrations. The different dilution-to-threshold (D/T) positions (D/T: 60, 30, 15, 7, 4, 2) — D/T is defined as the ratio of the flow of carbon filtered air to the flow of odorous air-were selected and the concentration in both the concentrated and the diluted air stream was measured by SIFT-MS. This enabled the dilution ratio (DR), defined as the ratio of the concentration in the concentrated stream and the concentration in the diluted stream, to be determined. If no interferences occur, the dilution ratio should be equal to D/T+1.

For the evaluation, the Nasal Ranger was fitted into a homemade exposure chamber made of a rigid tube-shaped element (diameter: 0.24 m, length 0.5 m) made of polymethylmethacrylate (PMMA) attached to a shrinkable Nalophan bag (diameter: 0.47 m; length: 2—4 m; volume: 0.35—0.69 m^3). The nose-piece of the Nasal Ranger was attached by means of Teflon tubing to a custom made glass bulb, which is used as a measuring point for the SIFT-MS. A scheme and photos of the experimental setup are given in respectively Fig. 1A and Supplementary Fig. S1. The measuring bulb was further connected to the suction side of a pump (to simulate the inhalation of the assessor). The flow rate through the Nasal Ranger was adjusted by a regulating valve v, positioned upstream of the pump (No35 1.2 AN 18, Neuberger, Freiburg), to ascertain that the flow rate is in accordance with the operating conditions set by the manufacturer (0.016—0.020 m^3 min^{-1}). Working at the optimal flow rate was also assured by checking the indicator LEDs (green: optimal flow; red −: flow to low; red +: flow to high) on top of the Nasal Ranger during the measurements. The dilution to threshold D/T dial from the Nasal Ranger could be easily adjusted to the different D/T set points and blank positions while the Nasal Ranger remained in the exposure chamber. The concentration in the exposure chamber could be measured directly by SIFT-MS via a disposable needle pierced through a septum in the wall of the exposure chamber.

Before the experiment took place, the Nalophan bag was inflated with a dry air supply from the laboratory and contaminated with the selected compounds. This was done by injecting a volume (depending on the vapour pressure of the compound, see Table 1) of saturated headspace (HS) in the exposure chamber via a needle (BD Microlance 3, Franklin Lakes, NJ, USA) mounted on a disposable polyethylene syringe (BD Plastipak Luer tip, 1, 10 or 60 ml). The air was thoroughly mixed by a fan installed in the exposure chamber to assure a homogeneous concentration. The stability of the concentration inside the chamber was checked by SIFT-MS measurements. Therefore, the concentration inside the exposure chamber was measured before, during and after the measurements of the dilution series. The sampling scheme is as follows: chamber, blank 1, D/T 60, D/T 30, D/T 15, blank 2, chamber, blank 3, D/T 7, D/T 4, D/T 2, blank 4 and chamber. The used Nasal Ranger was brand new and was regularly maintained by changing the carbon filters on both sides of the Nasal Ranger.

2.2. Scentroid SM110C

The Scentroid SM110C uses compressed (odour free) air from a gas cylinder (is additionally filtered over an active carbon bed) to dilute the odorous air. The odorous air is drawn using the vacuum created by a flow of compressed diluting air (552 kPa), through a venturi pump. The dilution-to-threshold ratio is controlled via a regulatory valve which changes the number and size of the openings through which the odorous air is sucked. The range of the D/T ratios can be changed by replacing the restrictor plate (i.e. a metal plates with a number of holes of different diameters) on the venturi pump. Restrictor plate "H" (Ides, Canada) was used during the experiments and has 15 D/T set points (101, 60, 45, 35, 28, 24, 19, 13, 11, 9, 7, 6, 5, 4, 3). The diluted stream was than directed via Teflon tubing to a face mask, which, under field conditions, was placed over the assessor's nose and mouth.

Concentrations of the selected pollutants were made by injecting saturated headspace (volume depending on the vapour pressure of the compound) in a Nalophan bag via a disposable polyethylene syringe. The air inside the bag was homogenised and the stability of the concentration was verified by SIFT-MS. The Nalophan bag was connected to the venturi pump of the Scentroid via Teflon tubing. A schematic overview and photos of the experimental setup are given in Fig. 1B and supplementary figure, Fig. S2, respectively. A glass
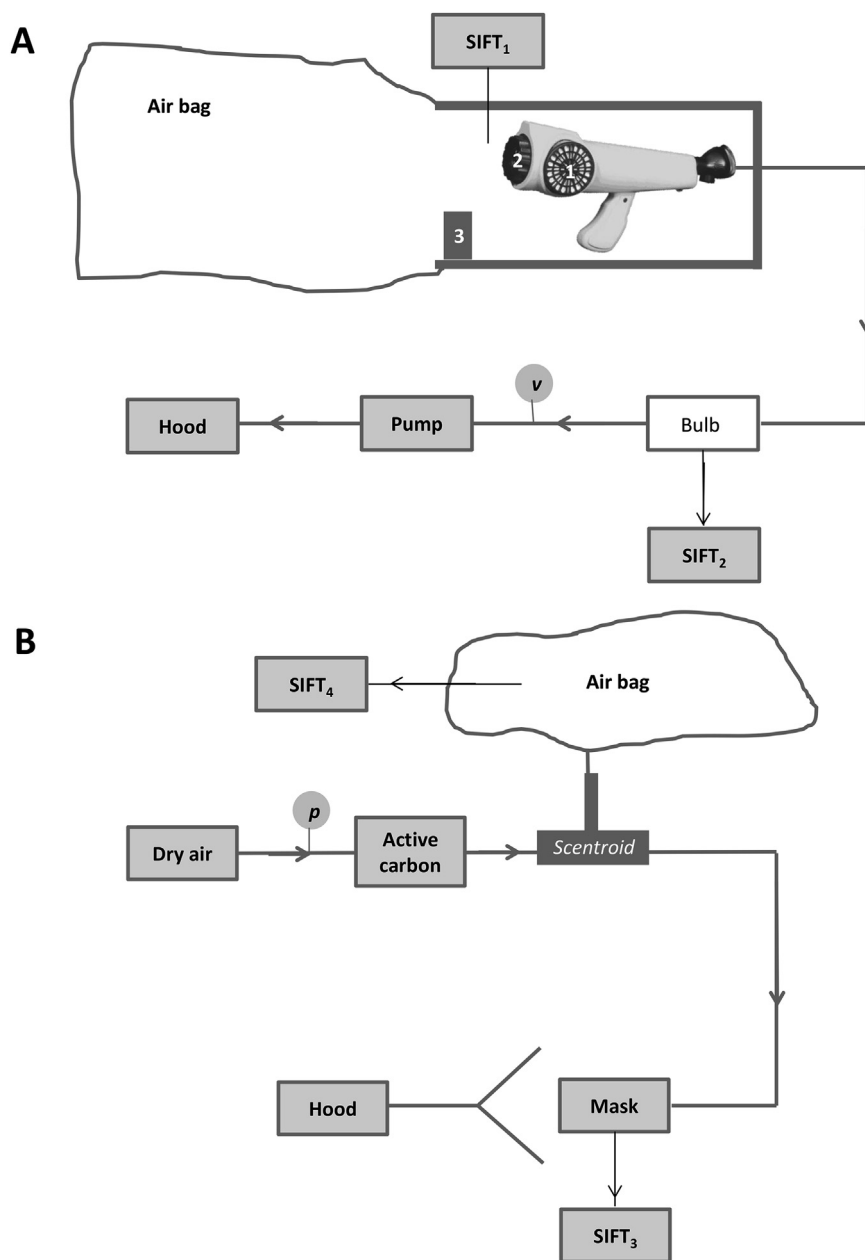
Fig. 1 — Schematic overview of the experimental setup for A) the Nasal Ranger and B) the Scentroid. $SIFT_{1-4}$: measuring point; 1: carbon filters (one on each side); 2: dilution-to-threshold dial; 3: fan; v: valve to regulate the gas flow; p: manometer.

structure was attached to the face mask to simulate the shape of the human face. The diluted air was sampled in the mask and introduced in the SIFT (0.035×10^{-3} m^3 min^{-1}) via a disposable needle (BD Microlance 3, Franklin Lakes, NJ, USA) mounted on the SIFT-MS inlet. The different D/T were set and the concentrations of the odorants in the diluted air stream were measured by SIFT-MS in the face mask. The sampling scheme is as follows: blank 1, Bag 1, D/T 101, 60, 45, 35, 28, 24, 19, 13, 11, 9, 7, 6, 5, 4, 3, Bag 2.

For each D/T setting, the flow that was drawn by the venturi pump was also measured in triplicate by a liquid film metre, together with the gas stream that passed through the main duct. This enabled the real dilution (DR_{real}) ratios for each D/T set point to be calculated.

2.3. Selected ion flow tube mass spectrometry

The concentration of the pollutants was measured by SIFT-MS (Voice 200 by Syft technologies, Interscience, Louvain-La-Neuve, Belgium). SIFT-MS is a relatively new analytical technique for the real time measurement of VOC concentrations in air matrices. It is based on the chemical ionisation of the VOC by reagent ions (NO^+, O_2^+ and H_3O^+) produced in the microwave plasma of moist air. A specific reagent ion is selected by a first quadrupole mass filter and an ion current of this reagent ion is injected into the flow tube where it is transported along the flow tube by means of a fast flowing helium carrier gas. The sample to be analysed is introduced into the flow tube by a calibrated capillary leak (0.035×10^{-3} m^3 min^{-1}) and the VOC

reacts with the selected precursor ion by a known reaction rate constant. The sample inlet line of the SIFT-MS is heated to 373 K. The product ions and the remaining reagent ions are then analysed by a second quadrupole mass spectrometer. The concentration of the target compound is proportional to the ratio of the count rate of the product ion and the count rate of the remaining reagent ions. The SIFT-MS provides a continuous concentration measurement for a selected time. In Table S1 an overview is given of the product ions of the target compounds.

3. Results and discussion

3.1. Nasal Ranger

The performance of the Nasal Ranger was evaluated by verifying its ability to make accurate dilutions from an odorous air sample with known odorant concentrations. Therefore the air in the measuring chamber was contaminated with a selected set of well-known odorants (concentration in the chamber depends on the experiment (n = 3): acetic acid (711—1267 ppb$_v$), propanoic acid (512—605 ppb$_v$), dimethyl sulphide (564—1382 ppb$_v$), dimethyl disulphide (535—1385 ppb$_v$), n-butanol (846—2139 ppb$_v$) as described in Section 2.1). The target compounds concentration was measured in both the measuring chamber (2.3—2.9 min; 43—125 data points per ion) and in the diluted air flows (0.6—0.9 min; 18—25 data points per ion) by the continuous monitoring of the target compounds' characteristic product ions using SIFT-MS. Only product ions for which the branching ratio is at least 50% and for which the signal showed the least fluctuations (i.e relative standard deviation (RSD) <15% on the continuous measurement) on the highest concentration (measuring chamber) and lowest concentrations (diluted gas streams) were withheld for further calculations. The final selected product ions are given in Table 2. Three dilution series were measured, representing the six D/T set point values of the Nasal Ranger. The concentration in the measuring chamber should remain stable throughout the experiment and was evaluated by calculating the RSD on the average product ion signals (within experiment stability) obtained from continuous measurements (2.3—2.9 min; 43—125 data points per ion) before, in the middle (between D/T: 15 and D/L: 7) and at the end of the measurement period for the dilution series. The results are given in Table 2 and the within experimental stability was between 1 and 7% (n = 3), indicating that the concentration levels remained stable during the measurements.

The results of the dilution experiment are given in Fig. 2 as the set dilution ratio (DR$_{set}$) versus the observed dilution ratio (DR$_{obs}$). If the Nasal Ranger is working perfectly the measuring points should lie on the first bisector. The measurement of the dilution series for n-butanol was performed in a separate experiment, given the interference from the product ions (for example the product ion 75$^+$ (precursor ion H_3O^+, $C_4H_{11}O^+$) with the product ion 75$^+$ (precursor ion H_3O^+, $C_2H_5COOH_2^+$) from propanoic acid (See Table S1)).

It can be seen that the DR$_{obs}$ dilution ratios for the Nasal Ranger correspond well with the set DR$_{set}$ in the interval

Table 2 — Overview of the mass and structure of the selected product ions monitored by SIFT-MS. They are sorted according to their precursor ion (H_3O^+, NO^+, O_2^+). The branching ratio (BR) reflects the percentage of the target product that reacts with a specific precursor ion (H_3O^+ or NO^+ or O_2^+) towards a specific product. For both the Nasal Ranger and Scentroid experiment the stabilities (RSD) of the concentrations are given for the concentrated (measuring chamber and bag) and diluted air streams. The within experiment stability represents the RSD on the average signal in the concentrated stream over the dilution experiment.

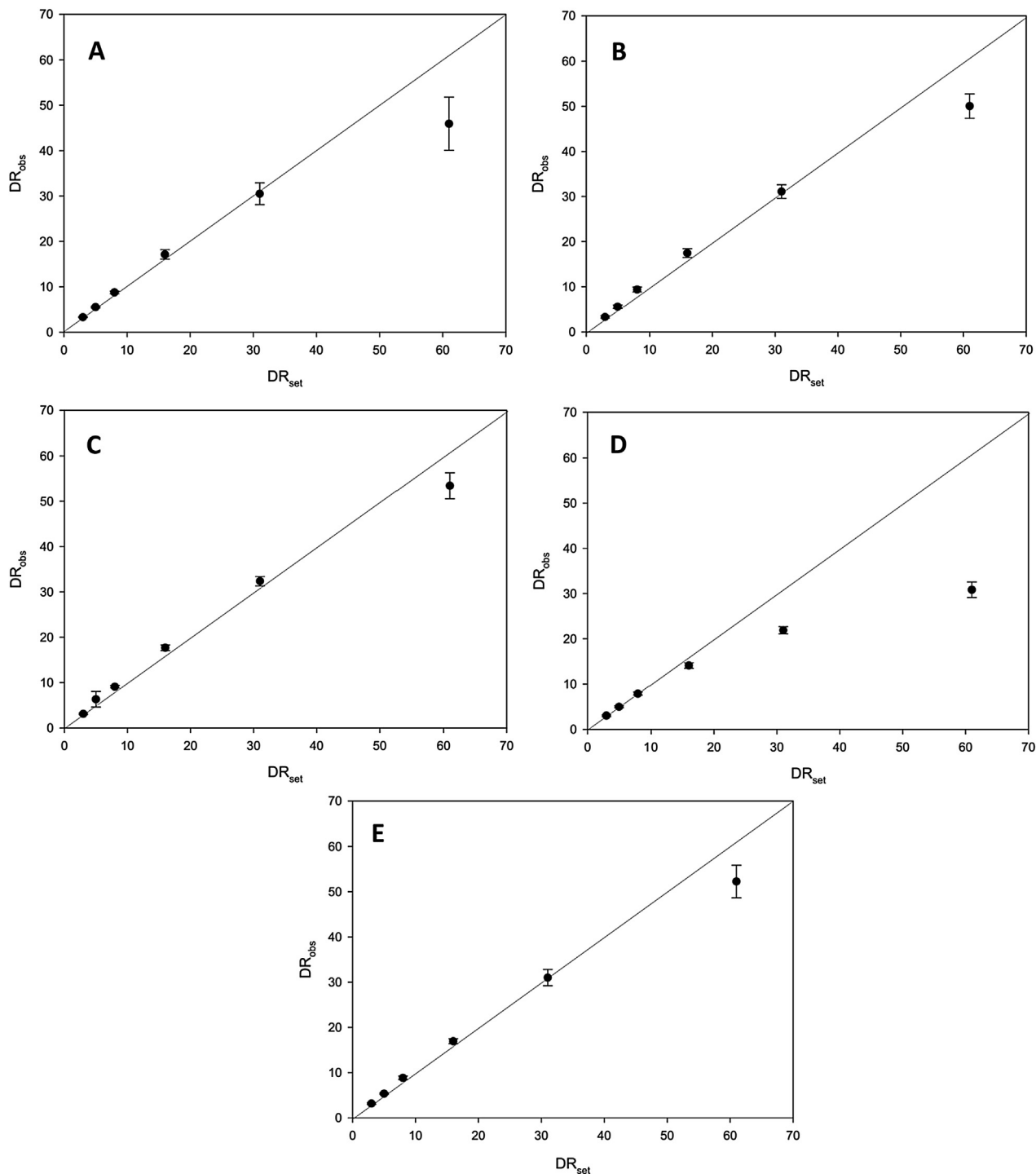| Compound name	Precursor ion	Product ion	BR (%)	Nasal Ranger Concentrated Stream (measuring chamber) RSD (%), n = 9	Nasal Ranger Within experiment stability RSD (%), n = 3	Nasal Ranger Diluted stream RSD (%), n = 18	Scentroid Concentrated stream (bag) RSD (%), n = 6	Scentroid Within experiment stability RSD (%), n = 3	Scentroid Diluted stream RSD (%), n = 45
Acetic acid	H_3O^+ (19$^+$)	$CH_3COOH_2^+$ (61$^+$)	100	2–8	3–7	1–8	–	–	–
	NO^+ (30$^+$)	$NO^+·CH_3COOH$ (90$^+$)	100	1–7	2–4	3–13	2–2	4–4	3–12
DMS	H_3O^+ (19$^+$)	$(CH_3)_2S·H^+$ (63$^+$)	100	–	–	–	1–2	4–4	3–8
	NO^+ (30$^+$)	$(CH_3)_2S^+$ (62$^+$)	100	2–6	2–3	2–10	2–2	4–4	3–9
	O_2^+ (32$^+$)	$(CH_3)_2S^+$ (62$^+$)	60	2–5	2–3	2–11	2–2	5–5	4–12
Propanoic acid	H_3O^+ (19$^+$)	$C_2H_5COOH_2^+$ (75$^+$)	90	1–7	1–3	2–6	1–1	3–3	2–7
	NO^+ (30$^+$)	$NO^+·C_2H_5COOH$ (104$^+$)	70	1–7	2–4	2–9	2–2	4–4	2–12
	O_2^+ (32$^+$)	$C_2H_5COOH^+$ (74$^+$)	80	2–7	2–3	2–11	–	–	–
1-Butanol	NO^+ (30$^+$)	$C_4H_9O^+$ (73$^+$)	95	2–7	2–2	2–7	2–2	9–9	3–11
	O_2^+ (32$^+$)	$C_4H_8^+$ (56$^+$)	80	2–5	2–2	2–6	2–2	11–11	3–9
DMDS	H_3O^+ (19$^+$)	$(CH_3)_2S_2·H^+$ (95$^+$)	100	3–4	2–4	2–12	1–2	2–2	3–10
	NO^+ (30$^+$)	$(CH_3)_2S_2^+$ (94$^+$)	100	3–5	1–4	2–10	2–2	4–4	3–11
	O_2^+ (32$^+$)	$(CH_3)_2S_2^+$ (94$^+$)	80	–	–	–	2–2	4–4	4–14

Fig. 2 – Observed dilution ratio (DR_{obs}) versus set dilution ratio (DR_{set}) for the Nasal Ranger for the different target compounds: A) butanol; B) acetic acid; C) propanoic acid; D) dimethyl sulphide; E) dimethyl disulphide. Solid line represents the 1st bisector.

between 3 and 31. In this interval the relationship was linear. High correlation coefficients were found for acetic acid ($r^2 = 0.997$), propanoic acid ($r^2 = 0.998$), dimethyl sulphide ($r^2 = 0.98$), dimethyl disulphide ($r^2 = 0.998$) and n-butanol ($r^2 = 0.998$). In this interval, the ratio of DR_{obs} to DR_{set} is 100–117%, 104–127%, 71–102%, 100–111%, 98–111% for acetic acid, propanoic acid, dimethyl sulphide, dimethyl disulphide

and n-butanol respectively. This indicates that the Nasal Ranger performed well in generating accurate dilutions. Only at the highest D/T value (60), lower ratios (DR_{obs} to DR_{set}) between 51% (dimethyl sulphide) and 88% (propanoic acid) were observed. It should however be noted that for the majority of the field sampler applications the odour concentration is below D/T = 60, and generally less than D/T = 10.

This observation of the lower DR_{obs} at the $DR_{set} = 61$ can be explained by the adsorption behaviour of compounds on the active carbon beds. Carbon beds are indispensable for the operation of the Nasal Ranger, since they are aimed to remove odorants from the air stream that is used to dilute the odorous air. The effect is the greatest for dimethyl sulphide. Dimethyl sulphide has a low affinity for active carbon and can be regarded as the most difficult sulphur compound to adsorb (Cui & Turn, 2009). Dimethyl sulphide might exhibit a breakthrough on the sorbent bed, which has the consequence that the diluting air contains a certain amount of dimethyl sulphide lowering the DR_{obs}. To provide evidence for this assumption a mass balance over the Nasal Ranger was made. The latter enabled the ratio of the gas flows (i.e D/T_{obs}) to be estimated when the concentration in the measuring chamber (C_{mc}, measured in measuring point SIFT$_1$), the concentration in the diluted air stream (C_{ds}, measured in measuring point SIFT$_2$) and the concentration in the blank (C_{blank}, measured in measuring point SIFT$_2$, dial [2 in Fig. 1] was adjusted and all odorous air is passing through the carbon filters) were known (Equation (1)).

$$D/T_{obs} = \frac{C_{mc} - C_{ds}}{C_{ds} - C_{blank}} \qquad (1)$$

For dimethyl sulphide the deviation between D/T_{obs} and the D/T_{set} was 24% (<51%). This means that the Nasal Ranger was able to blend the air streams according to the specifications, but that breakthrough of odorants caused the observed dilution ratio be lower than what was expected from the respective air streams. A possible solution could be found in replacing the sorbent in the filters by one which has a higher capacity for the target compounds. Another characteristic of the Nasal Ranger is the relative high exposure area (diameter: 0.08 m; bed height: 20 mm; 66 g [activated carbon]) of the carbon filters, which may lead to a high uptake of the odorants through passive sampling (i.e. by molecular diffusion) in a polluted environment. This passive sampling can be reduced by reducing the exposure area (i.e. using a smaller diameter) of the carbon filters. However, for application in the field, this will lead to higher back pressures and resistance while inhaling, if the same amount of activated carbon is used.

3.2. Scentroid

Dilutions of a known odorous air sample were made by the Scentroid which was equipped with dilution plate "H" (D/T range from 3 to 101). Before use, the dilution plate was cleaned in an ultrasonic bath using methanol. An air sample with known concentrations of acetic acid (3528–5398 ppb$_v$), propanoic acid (3081–4587 ppb$_v$), dimethyl sulphide (4074–5741 ppb$_v$), dimethyl disulphide (4237–5285 ppb$_v$) and n-butanol (1106–1211 ppb$_v$) was made in a Nalophan bag (See Section 2.2) and connected to Scentroid via Teflon tubing. The characteristic ions (that were used for the calculation of the dilution ratios) were selected in similar manner as for the Nasal Ranger. Stability, expressed as the RSD on the continuous measurements, was between 1 and 2% in the Nalophan bag (highest concentration) and between 3 and 14% in the diluted air streams (see Table 2). In order to verify that the concentration remained stable in the Nalophan bag during

the measurement of the dilution series (n = 3), the concentration inside the bag was measured before and after the dilution series. The relative standard deviation on the average concentration (n = 2) ranged between 2 and 11%.

In first instance, the real dilution ratios at the different D/T set points were calculated (DR_{real}) as the ratio of the measured main gas flow rate and the gas flow rate drawn by the venturi effect. These flows were measured in triplicate by a liquid film metre. (This measurement could not be performed with the Nasal Ranger since it was not possible to measure the streams separately). The results are plotted in Fig. 3 as the DR_{set} versus the DR_{real}. It can be seen that the real volumetric dilution ratios correspond well with the DR_{set} values. The ratio of DR_{real} and DR_{set} was between 0.8 and 1.2. Only for the highest dilution (DR_{set}: 102), was a high discrepancy observed with a $DR_{real} = 71$ (not shown in the figure). For all further calculations, this highest dilution was ignored.

In Fig. 4 the relation between the DR_{set} and DR_{obs} is shown. The DR_{obs} of all compounds follow a linear relationship with the DR_{set} (when the highest dilution (S/N: 101) was not taken into account), as exemplified by the high correlation coefficients observed for acetic acid ($r^2 = 0.993$), propanoic acid ($r = 0.990$), dimethyl sulphide ($r^2 = 0.995$), dimethyl disulphide ($r^2 = 0.994$) and n-butanol ($r^2 = 0.98$). However, it can be seen that the DR_{obs} was higher than the theoretically expected DR_{set} (for each set dilution ratio) for acetic acid, propanoic acid, dimethyl sulphide dimethyl disulphide and also butanol (in the lower dilution ratios). The DR_{obs} to DR_{set} ratio for the individual target compounds ranged from 159 to 210%, 143 to 193%, 162 to 213%, 162 to 213%, 81 to 192% for acetic acid, propanoic acid, dimethyl sulphide, dimethyl disulphide and n-butanol respectively. For n-butanol, the average DR_{obs} are up to a factor of 2.6 times lower when compared to the DR_{obs} of the other target compounds, and this effect is more pronounced at the higher dilution ratios. So compound specific behaviour was observed.

From Fig. 3 it is clear that the discrepancy between DR_{set} and DR_{obs} cannot be caused by the flow rates (DR_{real}). However, sorption effects of the target compounds on the Scentroid
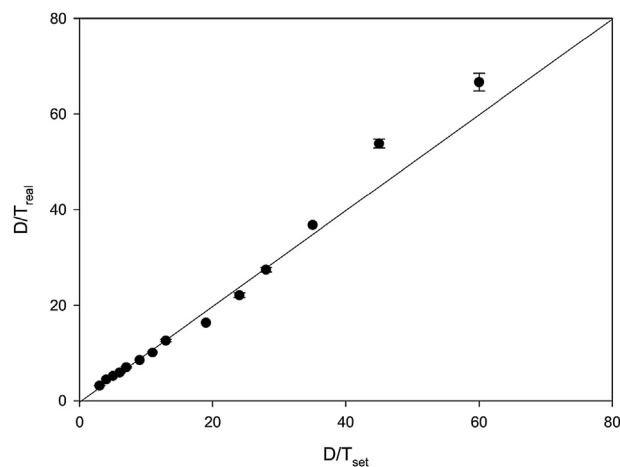
Fig. 3 – **Measured dilution-to-threshold ratio (D/T_{real}) versus dilution-to-threshold set point for the Scentroid (n = 3).**
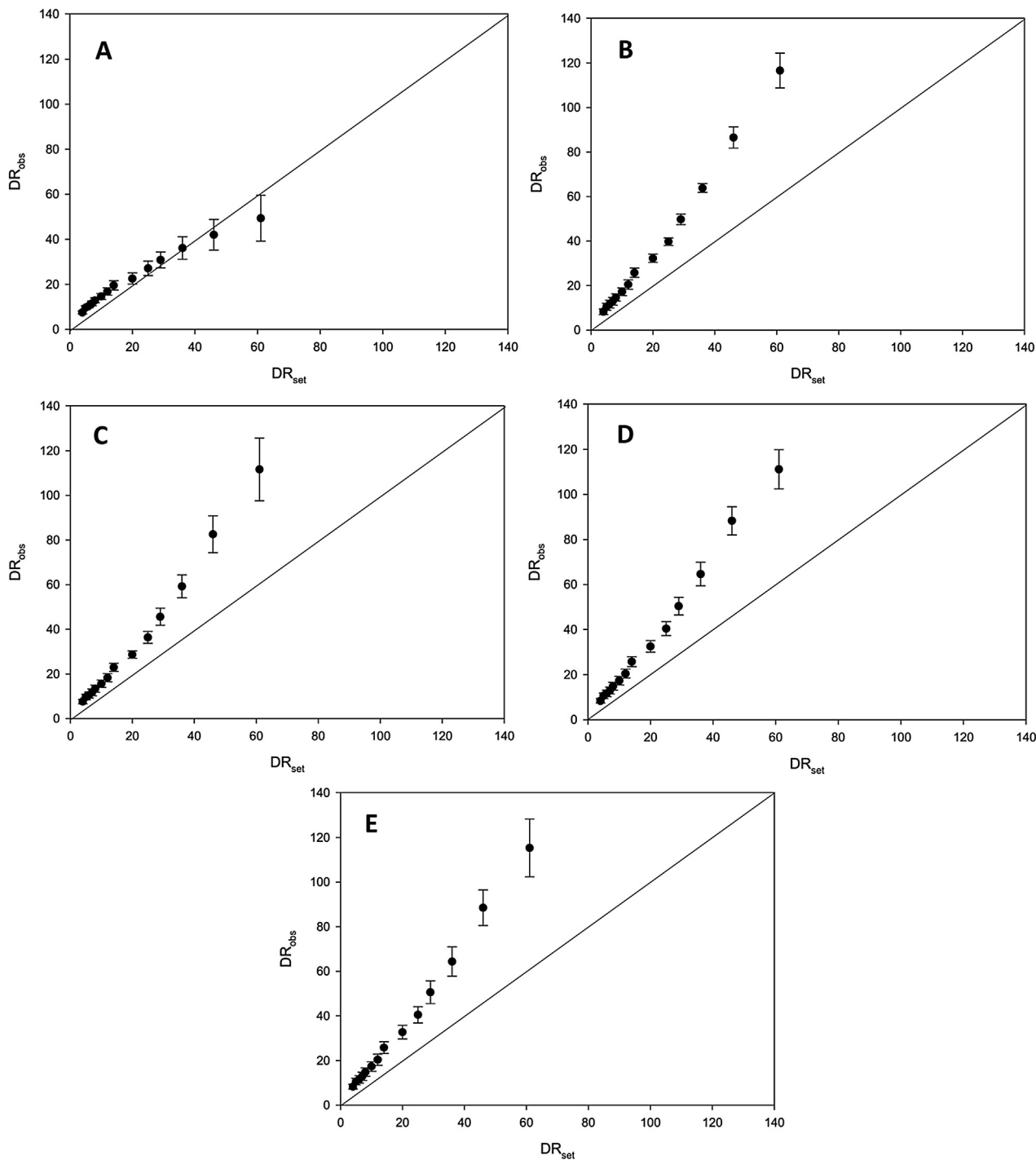
Fig. 4 — Observed dilution ratio (DR_{obs}) versus set dilution ratio (DR_{set}) for the Scentroid for the different target compounds: A) butanol; B) acetic acid; C) propanoic acid; D) dimethyl sulphide; E) dimethyl disulphide. Solid line represents the 1st bisector.

building materials (adsorption on metal venturi pump, valve system, flow regulator valve, dilution plate; absorption into the rubber seal) might explain this observation. Several authors have investigated the behaviour of compounds on construction materials. For example (Kim et al., 2006), investigated the sorptive and chemical transformation losses caused by the construction materials (Teflon and stainless steel) of valve systems used for sample introduction. They found that stainless steel valve systems reduced the

recoveries for H_2S (48%), DMS (51%) and DMDS (71%) when compared to the recoveries obtained using a Teflon valve system. The sorption effects can therefore result into a diluted air stream concentration which is lower than what can be expected from the gas flows, causing the observed dilution ratios to be higher for all compounds (except for n-butanol at dilution ratios higher than $DR_{set} = 46$). These results are in accordance with the study of Hansen et al. (2010) which investigated the performance of 2 laboratory olfactometers

(internal structures made of glass and stainless steel/Teflon). The authors found that the observed dilution ratios were higher than the set dilution ratios for hydrogen sulphide, methanethiol and to a lesser extend dimethyl sulphide. Losses by the olfactometer were quantified to be 9–21% (DMS), 27–35% (methanethiol) and 55–60% (H_2S). Hansen et al. (2013) investigated the laboratory TO8 olfactometer and found high recoveries for dimethyl sulphide (100%) and n-butanol (90–95%), but for acetic acid, propanoic acid, butanoic acid, methanethiol and trimethylamine recoveries were lower (20%–85%) and also depended on dilution level.

The mask of the Scentroid, which in field observations is put over mouth and chin of the assessor, is not completely airtight. The diluted air flows around the face of the assessor in the field or around the glass structure in the laboratory setup. It is possible that dilution with ambient air occurs and this may partially explain the higher DR_{obs}. However, it should be noted that the concentration of the target compounds in the diluted air stream was measured inside the mask and 2) the flow rate was high compared to the internal volume of the mask. This indicates that this dilution effect might be of only minor importance.

In order to possibly reduce and prevent the problem of the sorption effects, it is suggested that the internal structures of the Scentroid are coated by an inert material (e.g. Teflon) and that the seal of the plunger of the flow regulator valve of the venturi pump (a standard black rubber-like material) is replaced by an inert analogue.

4. Conclusions

Two field olfactometers: the Nasal Ranger and the Scentroid were evaluated with respect to their potential to create dilutions from an odorous air sample with known odorant concentrations. Concentrations in the diluted air stream were measured by SIFT-MS and observed dilution ratios were calculated and compared to the dilution ratios set point values. It was found that the Nasal Ranger performed well in generating dilutions for all compounds. Only at the highest dilution a discrepancy was found between the set and observed dilution ratios. This was explained by the breakthrough of the target compounds through the carbon filters of the Nasal Ranger. A stronger sorbent might solve the problem. The Scentroid on the other hand showed a linear relationship between the set and observed dilution ratios. However, higher observed dilution ratios (up to a factor 2) when compared to the dilution ratio set points were observed. This could be explained by the sorption of the target compounds onto the internal metal structures of the Scentroid or into the rubber ring of the plunger. A coating of the metal surfaces (venturi pump and valve system) and the use of an inert seal might help to improve the control of the dilution ratios. We can state that field olfactometers might have possible advantages when compared to laboratory olfactometers because i) they eliminate the need for the storage of the odour sample and ii) they are able to measure low odour concentrations (downwind from the source). However, knowledge of the (sorption) behaviour of compounds inside olfactometers is of paramount importance to assure their reliability.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biosystemseng.2015.07.007.

REFERENCES

Akdeniz, N., Jacobson, L. D., Hetchler, B. P., Bereznicki, S. D., Heber, A. J., Koziel, J. A., et al. (2012a). Odor and odorous chemical emissions from animal buildings: part 2. Odor emissions. *Transactions of the ASABE, 55,* 2335–2345.

Akdeniz, N., Jacobson, L. D., Hetchler, B. P., Bereznicki, S. D., Heber, A. J., Koziel, J. A., et al. (2012b). Odor and odorous chemical emissions from animal buildings: part 4. Correlations between sensory and chemical measurements. *Transactions of the ASABE, 55,* 2347–2356.

Beauchamp, J., Frasnelli, J., Buettner, A., Scheibe, M., Hansel, A., Hummel, T., et al. (2010). Characterization of an olfactometer by proton-transfer-reaction mass spectrometry. *Measurement Science & Technology, 21.*

Behbod, B., Parker, E. M., Jones, E. A., Bayleyegn, T., Guarisco, J., Morrison, M., et al. (2014). Community health assessment following Mercaptan Spill: eight mile, mobile county, Alabama, September 2012. *Journal of Public Health Management and Practice, 20,* 632–639.

Benzo, M., Mantovani, A., & Pittarello, A. (2012). Measurement of odour concentration of immissions using a new field olfactometer and markers' chemical analysis. In *Nose 2012: 3rd International Conference on Environmental Odour Monitoring and Control* (Vol. 30, pp. 103–108).

Bokowa, A. H. (2010). Review of odour legislation. In *Nose 2010: International Conference on Environmental Odour Monitoring and Control* (Vol. 23, pp. 31–36).

Brattoli, M., de Gennaro, G., de Pinto, V., Loiotile, A. D., Lovascio, S., & Penza, M. (2011). Odour detection methods: olfactometry and chemical sensors. *Sensors, 11,* 5290–5322.

Capelli, L., Sironi, S., Del Rosso, R., Centola, P., & Il Grande, M. (2008). A comparative and critical evaluation of odour assessment methods on a landfill site. *Atmospheric Environment, 42,* 7050–7058.

Capelli, L., Sironi, S., Del Rosso, R., & Guillot, J.-M. (2013). Measuring odours in the environment vs. dispersion modelling: a review. *Atmospheric Environment, 79,* 731–743.

CEN. (2003). *Air quality. Determination of odour concentration by dynamic olfactometry (EN 13725:2003).* Euopean Committee for standardization.

Cometto-Muñiz, J. E., & Abraham, M. H. (2010). Structure-activity relationships on the odor detectability of homologous carboxylic acids by humans. *Experimental Brain Research, 207,* 75–84.

Cui, H., & Turn, S. Q. (2009). Adsorption/desorption of dimethyl sulfide on activated carbon modified with iron chloride. *Applied Catalysis B − Environmental, 88,* 25–31.

Defoer, N., De Bo, I., Van Langenhove, H., Dewulf, J., & Van Elst, T. (2002). Gas chromatography-mass spectrometry as a tool for estimating odour concentrations of biofilter effluents at aerobic composting and rendering plants. *Journal of Chromatography A, 970,* 259–273.

Dincer, F., & Muezzinoglu, A. (2007). Odor determination at wastewater collection systems: olfactometry versus H_2S analyses. *Clean-Soil Air Water, 35,* 565–570.

Gutierrez, M. C., Chica, A. F., Martin, M. A., & Romain, A. C. (2014). Compost pile monitoring using different Approaches: GC-MS, e-nose and dynamic olfactometry. *Waste and Biomass Valorization, 5,* 469–479.

Hansen, M. J., Adamsen, A. P. S., & Feilberg, A. (2013). Recovery of odorants from an olfactometer measured by proton-transfer-reaction mass spectrometry. *Sensors, 13*, 7860–7871.

Hansen, M. J., Adamsen, A. P. S., Feilberg, A., & Jonassen, K. E. N. (2011). Stability of odorants from pig production in sampling bags for olfactometry. *Journal of Environmental Quality, 40*, 1096–1102.

Hansen, M. J., Adamsen, A. P. S., Pedersen, P., & Feilberg, A. (2012). Prediction of odor from pig production based on chemical odorants. *Journal of Environmental Quality, 41*, 436–443.

Hansen, M. J., Feilberg, A., & Adamsen, A. P. S. (2010). Stability of volatile reduced sulphur compounds in the dilution system of an olfactometer. In R. DelRosso (Ed.), *Nose 2010: International Conference on Environmental Odour Monitoring and Control* (pp. 67–72).

Hansen, M. J., Jonassen, K. E. N., & Feilberg, A. (2014). Evaluation of abatement technologies for pig houses by dynamic olfactometry and on-site mass spectrometry. In R. DelRosso (Ed.), *Nose2014: 4th International Conference on Environmental Odour Monitoring and Control* (pp. 253–258).

Hansen, M. J., Liu, D., Guldberg, L. B., & Feilberg, A. (2012). Application of proton-transfer-reaction mass spectrometry to the assessment of odorant removal in a biological air cleaner for pig production. *Journal of Agricultural and Food Chemistry, 60*, 2599–2606.

van Harreveld, A. P. (2003). Odor concentration decay and stability in gas sampling bags. *Journal of the Air & Waste Management Association, 53*, 51–60.

Hayes, J. E., Stevenson, R. J., & Stuetz, R. M. (2014). The impact of malodour on communities: a review of assessment techniques. *Science of the Total Environment, 500*, 395–407.

Henry, C. G., Schulte, D. D., Hoff, S. J., Jacobson, L. D., & Parkhurst, A. M. (2011). Comparison of ambient odor assessment techniques in a controlled environment. *Transactions of the ASABE, 54*, 1865–1872.

Howard, P. H., & Meylan, W. M. (1997). *Handbook of Physical Properties of Organic Chemicals*. CRC-Press.

Hu, E., Babcock, E. L., Bialkowski, S. E., Jones, S. B., & Tuller, M. (2014). Methods and techniques for measuring gas emissions from agricultural and animal feeding operations. *Critical Reviews in Analytical Chemistry, 44*, 200–219.

Kim, K. H., Choi, G. H., Choi, Y. J., Song, H. N., Yang, H. S., Oh, J. M., et al. (2006). The effects of sampling materials selection in the collection of reduced sulfur compounds in air. *Talanta, 68*, 1713–1719.

Laor, Y., Naor, M., Ravid, U., Fine, P., Halachmi, I., Chen, Y., et al. (2011). Odorants and malodors associated with land application of biosolids stabilized with lime and coal fly ash. *Journal of Environmental Quality, 40*, 1405–1415.

Laor, Y., Parker, D., & Page, T. (2014). Measurement, prediction, and monitoring of odors in the environment: a critical review. *Reviews in Chemical Engineering, 30*, 139–166.

Liu, D., Lokke, M. M., Riis, A. L., Mortensen, K., & Feilberg, A. (2014). Evaluation of clay aggregate biotrickling filters for treatment of gaseous emissions from intensive pig production. *Journal of Environmental Management, 136*, 1–8.

Melse, R. W., Ogink, N. W. M., & Rulkens, W. H. (2009). Overview of European and Netherlands' regulations on airborne emissions from intensive livestock production with a focus on the application of air scrubbers. *Biosystems Engineering, 104*, 289–298.

Munoz, R., Sivret, E. C., Parcsi, G., Lebrero, R., Wang, X., Suffet, I. H., et al. (2010). Monitoring techniques for odour abatement assessment. *Water Research, 44*, 5129–5149.

Nagata, Y. (2003). Measurement of odor threshold by Triangle Odor Bag Method. In *Odor measurement review* (pp. 118–127). Tokyo, Japan: Office of Odor, Noise and Vibration. Government of Japan. Ministry of the Environment.

Parker, D. B., Koziel, J. A., Cai, L., Jacobson, L. D., Akdeniz, N., Bereznicki, S. D., et al. (2012). Odor and odorous chemical emissions from animal buildings: part 6. Odor activity value. *Transactions of the ASABE, 55*, 2357–2368.

Saha, C. K., Feilberg, A., Zhang, G., & Adamsen, A. P. S. (2011). Effects of airflow on odorants' emissions in a model pig house – a laboratory study using Proton-Transfer-Reaction Mass Spectrometry (PTR-MS). *Science of the Total Environment, 410*, 161–171.

Sheffield, R. E., Chahine, M., Dye, B., & Thompson, M. B. (2007). Odor concentrations downwind of Idaho dairies and heifer facilities. *Transactions of the ASABE, 50*, 255–263.

Trabue, S., Kerr, B., Bearson, B., & Ziemer, C. (2011). Swine odor analyzed by odor panels and chemical techniques. *Journal of Environmental Quality, 40*, 1510–1520.

Van Huffel, K., Heynderickx, P. M., Dewulf, J., & Van Langenhove, H. (2012). Measurement of odorants in livestock Buildings: SIFT-MS and TD-GC-MS. In *Nose 2012: 3rd international conference on environmental odour monitoring and control, 30* pp. 67–72).

Zhang, S., Cai, L., Koziel, J. A., Hoff, S. J., Schmidt, D. R., Clanton, C. J., et al. (2010). Field air sampling and simultaneous chemical and sensory analysis of livestock odorants with sorbent tubes and GC-MS/olfactometry. *Sensors and Actuators B – Chemical, 146*, 427–432.