

## Stability of volatile reduced sulphur compounds in the dilution system of an olfactometer

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The aim of the present experiment was to investigate the stability of volatile reduced sulphur compounds during dilution in an olfactometer. Two types of olfactometers were used. In the first olfactometer the parts in contact with the samples were made by glass and in the second olfactometer stainless steel and PTFE (polytetrafluoroethylene, Teflon). The olfactometers were tested with a sulphur gas mixture containing hydrogen sulphide, methanethiol and dimethyl sulphide at ca. 5 ppmv. A PTR-MS (Proton-Transfer-Reaction Mass Spectrometer) was used to follow the fate of sulphur compounds in the olfactometers. The samples were diluted as normal samples for olfactometry, and the PTR-MS was used to measure the concentration in the nose mask, where panellists normally assess the diluted samples. The concentration in the samples was analysed prior to dilution in the olfactometers and the expected concentration in the nose mask was estimated using the dilution factor. The concentration measured in the nose mask as a function of the estimated concentration was linear for both olfactometers. This shows that dilution of the samples was working properly. In both olfactometers a part of the sulphur compounds were lost during dilution and the degree of loss correlated with the volatility of the sulphur compounds. The average loss of hydrogen sulphide was 60% for the glass olfactometer and 55% for the olfactometer with stainless steel and PTFE. The average loss of methanethiol was 35% in the olfactometer with glass and 27% in the olfactometer with stainless steel and PTFE. Dimethyl sulphide was only slightly affected by the dilution system in the olfactometer with glass with an average loss at 9.3%, whereas 21% was lost in the olfactometer with stainless steel and PTFE. It can be concluded that panellists assessing samples with reactive volatile reduced sulphur compound in these two types of olfactometers will underestimate the original concentrations.

### 1. Introduction

Odour from animal production and in particular from pig production has gained increased attention during the last years. Odour reduction technologies such as chemical and biological air cleaning have been developed to reduce the odour nuisance from pig production (Melse and Ogink, 2005). The process of developing an odour reduction technology involves evaluation and certification of the odour removal efficiency. In Europe odour is usually measured according to the European standard for olfactometry

where the procedures for collection and analysis of samples are described (CEN, 2003). This method involves a collection of odour samples in sampling bags and storage up to 30 hours before analysis in an olfactometer with panellists. The chemical compounds in an odour sample are usual volatile and reactive, and the chemical composition and the odour perception of the sample could be changed from the time of collection until the time for analysis. The introduction of the odour sample into the sample bag is the first point, where a loss could take place. It was demonstrated that PVC (polyvinyl chloride) and silicone (Sulyok et al., 2002) and stainless steel (Kim et al., 2006) was less suitable for sample introduction of volatile sulphur compounds compared to PTFE (polytetrafluoroethylene, Teflon). The second point where the chemical composition could be changed is during storage in sample bags. Some work has been done to investigate how the chemical composition is changing over time, when odour samples are stored in sample bags (Koziel et al., 2005; Mochalski et al., 2009; Trabue et al., 2006). In general, it seems that the concentration of compounds such as carboxylic acids, sulphur compounds, indoles and phenols will decrease over time in sample bags. For some compounds only minor parts of the original samples are present after one day of storage. The third point, where the chemical composition could be changed, is during dilution in the olfactometer. To our knowledge this has not been investigated yet. The aim of the present experiment was to investigate the stability of volatile reduced sulphur compounds when a sample is diluted in two types of olfactometers with glass or stainless steel and PTFE in contact with the odour sample. Volatile reduced sulphur compounds were chosen because they are believed to have a significant impact on odour nuisances from pig production due to their low solubility in animal slurry and their very low odour threshold values (O'Neill and Phillips, 1992). In addition, sulphur compounds are considered to be difficult to collect and analyse due to their high volatility and chemical reactivity.

## **2. Materials and methods**

### **2.1 Olfactometers**

Two types of olfactometers located at the Danish Meat Research Institute, Roskilde, Denmark, were used in the experiment. The first olfactometer was a homemade olfactometer designed by the Danish Meat Research Institute in accordance with the European standard for olfactometry (CEN, 2003). The parts of the olfactometer in contact with the sample during dilution and the nose masks were made by glass. The olfactometer was designed for three panellists on the principle of forced choice. The flow for each nose mask was ca. 15 l/min. A sulphur gas mixture was diluted with charcoal filtered air in ten steps between 3233 to 417 dilutions. For each dilution step the flow of dilution air was kept constant at 93.9 l/min and the flow of sulphur gas mixture was adjusted. The flow of sulphur gas mixture was controlled by a mass flow controller with a range between 0-200 ml/min (Sierra Instruments Inc., Monterey, USA).

The second olfactometer was a commercial olfactometer (Olfactometer TO8, Ecoma GmbH, Kiel, Germany). This olfactometer was also designed in accordance with the European standard for olfactometry (CEN, 2003). The parts of the instrument in contact with the sample during dilution were made by stainless steel and PTFE and the nose

masks were made by glass. The olfactometer was designed for four panellists based on the yes/no method. The flow for each nose mask was ca. 20 l/min. A sulphur gas mixture was diluted with dry and charcoal filtered air in nine steps from 4096 to 16 dilutions. A PVF (polyvinyl fluoride, Tedlar) bag containing ca. 30 l of the sulphur gas mixture was placed in the sample nozzle and the instrument performed the dilution of the sample. The PVF bag was filled right before the measurements.

## 2.2 Analytical instrument

A PTR-MS (Proton-Transfer-Reaction Mass Spectrometer, Ionicon Analytik, Innsbruck, Austria) was applied for measuring volatile sulphur compounds prior to and after dilution in the olfactometers. The PTR-MS technique has recently been reviewed by de Gouw and Warneke (2007). The PTR-MS was operated under standard ion drift tube conditions applying a total voltage of 600 V and maintaining the pressure in the range of 2.1-2.2 mbar. The temperature of the drift tube was controlled at 60 °C.

## 2.3 Sulphur gas mixture

A certified sulphur gas mixture containing hydrogen sulphide, methanethiol and dimethyl sulphide in dinitrogen (Air Liquid, Horsens, Denmark) was used, see table 1. The undiluted sulphur gas mixture for the glass olfactometer was measured in the outlet from the mass flow controller, and for the olfactometer with stainless steel and PTFE it was measured in the PVF bag. Diluted samples were measured directly in the nose mask and the expected concentration was estimated using the dilution factor. For all three sulphur compounds the measured concentrations were adjusted with a factor based on the specified concentration and a measurement in the outlet from the regulator on the sulphur gas mixture. Accordingly the measured concentration of hydrogen sulphide, methanethiol and dimethyl sulphide was adjusted with a factor 13.1, 1.2 and 1.1 respectively.

*Table 1: Specified concentration  $\pm$  standard deviation in the certified sulphur gas mixture.*

Compound	Hydrogen sulphide	Methanethiol	Dimethyl sulphide
Concentration , ppmv	5.43 $\pm$ 0.16	5.17 $\pm$ 0.26	5.33 $\pm$ 0.27

## 3. Results and discussion

The measured concentrations of the sulphur gas mixture in the outlet from the mass flow controller and in the PVF bag is presented in table 2. The measured concentrations of methanethiol and dimethyl sulphide were close to the specified concentrations presented in table 1, whereas hydrogen sulphide was ca. 10 to 15 per cent higher than specified. Table 2 also shows that there was only a small difference between the sulphur gas mixture coming from the mass flow controller and the PVF bag. This implies that even though the sulphur gas mixture was introduced differently to the two olfactometers, the results are comparable.

Table 2: Measured concentration  $\pm$  standard deviation in the sulphur gas mixture used for dilution in two types of olfactometers.

Compound	Hydrogen sulphide	Methanethiol	Dimethyl sulphide
Measured at mass flow controller, ppmv (n=9)	6.23 $\pm$ 0.09	5.11 $\pm$ 0.06	5.16 $\pm$ 0.07
Measured in PVF bag, ppmv (n=6)	5.99 $\pm$ 0.05	5.13 $\pm$ 0.04	5.17 $\pm$ 0.04

In figure 1 and 2 the measured concentration of hydrogen sulphide, methanethiol and dimethyl sulphide as a function of the estimated concentration after dilution are shown for the olfactometer with glass and stainless steel and PTFE respectively. For both olfactometers the  $R^2$  value for the linear regression line was above 0.99 for all three sulphur compounds, which indicates a linear relation between the estimated and measured concentrations. This shows that dilution of the samples was working properly. The slopes for the three curves are below one for both olfactometers which indicates some loss during dilution. The average loss for the olfactometer with glass expressed in percentages  $\pm$  standard deviation was 60  $\pm$  10 (hydrogen sulphide), 35  $\pm$  11 (methanethiol) and 9.3  $\pm$  2.5 (dimethyl sulphide). For the olfactometer with stainless steel and PTFE, the loss were 55  $\pm$  7.9 (hydrogen sulphide), 27  $\pm$  6.8 (methanethiol) and 21  $\pm$  5.6 (dimethyl sulphide). It seems that the loss increases with the volatility of the sulphur compounds, with hydrogen sulphide being the most volatile and dimethyl sulphide the least volatile. The loss of sulphur compounds in the olfactometers could be due to adsorption to the surfaces in the dilution system, or perhaps more likely a reaction with other gases or particles within the dilution system. Even though the gas mixture should only contain the mentioned sulphur compounds, dimethyl disulphide was also measured in the undiluted samples. In contrast to the other sulphur compounds, dimethyl disulphide increased after dilution in both olfactometers. This indicates that reactions takes place within the dilution system and a part of the sulphur compounds is presumably oxidized to dimethyl disulphide. The shown loss of sulphur compounds within the dilution system of an olfactometer underlines that precaution has to be taken when olfactometry is used for measuring odour from a source emitting sulphur compounds. The sulphur gas mixture used in the present experiment was dry and clean which excludes the possible interference from other compounds and particles normally present in field samples. Further work is needed to demonstrate the effect on field samples. However, it seems that besides the possible loss during sample introduction (Kim et al., 2006; Sulyok et al., 2002) and storage (Koziel et al., 2005; Mochalski et al., 2009; Trabue et al., 2006) sulphur compounds can also be lost in the olfactometer. The loss during sample introduction and storage could be minimized if the olfactometer was situated in proximity of the odour source, however this might induce background odour. Besides, it is very impractical. Neither glass nor stainless steel is known to be inert materials for sulphur compounds and a possible way to reduce the loss in the olfactometer could be to use more inert materials.

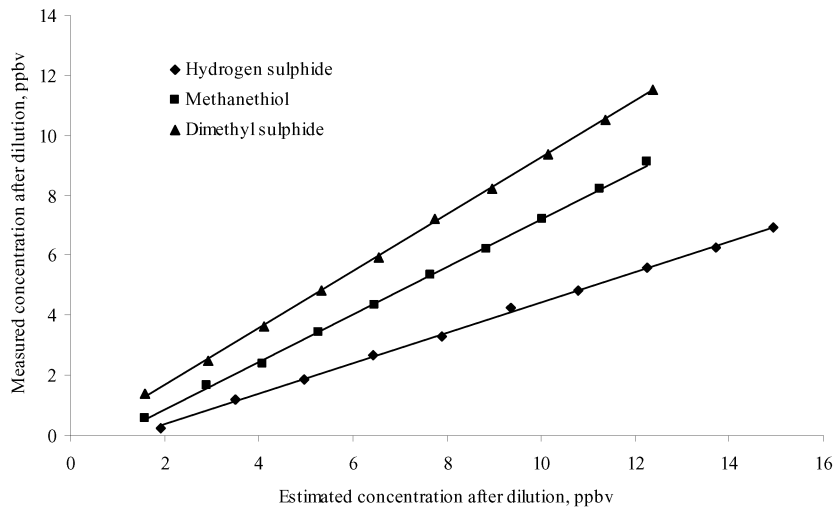


Figure 1: Measured concentrations as a function of estimated concentration of sulphur compounds diluted in an olfactometer made by glass. Regression lines: hydrogen sulphide ( $y=0.51 \cdot x - 0.65$ ,  $R^2=0.9990$ ), Methanethiol ( $y=0.80 \cdot x - 0.74$ ,  $R^2=0.9992$ ) and dimethyl sulphide ( $y=0.94 \cdot x - 0.19$ ,  $R^2=0.9997$ ).

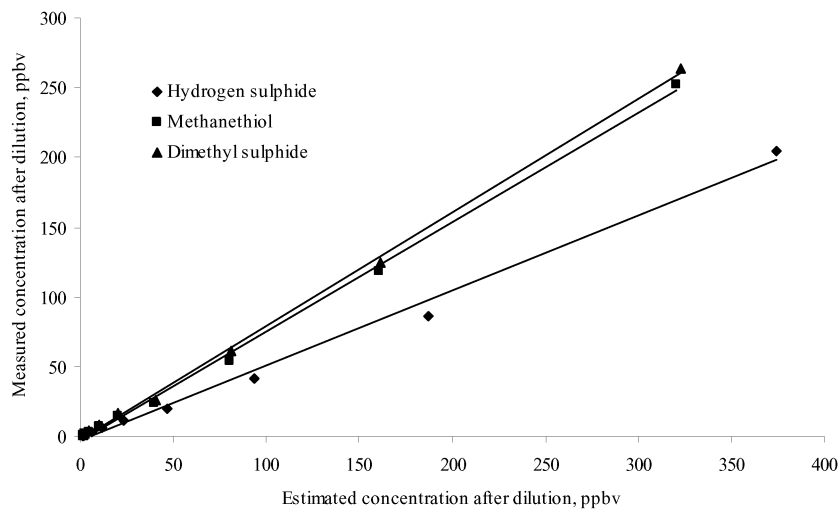


Figure 2: Measured concentrations as a function of estimated concentration of sulphur compounds diluted in an olfactometer made by stainless steel and PTFE. Regression lines: hydrogen sulphide ( $y=0.54 \cdot x - 2.93$ ,  $R^2=0.9931$ ), Methanethiol ( $y=0.78 \cdot x - 2.54$ ,  $R^2=0.9978$ ) and dimethyl sulphide ( $y=0.81 \cdot x - 1.62$ ,  $R^2=0.9988$ ).

#### 4. Conclusion

It can be concluded from the present experiment that volatile reduced sulphur compounds can be lost during dilution in olfactometers where the parts in contact with the sample is made by glass or stainless steel and PTFE. This implies that odour panellists assessing samples from sources containing volatile reduced sulphur compounds will underestimate the original odour concentrations in these olfactometers.

#### References

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