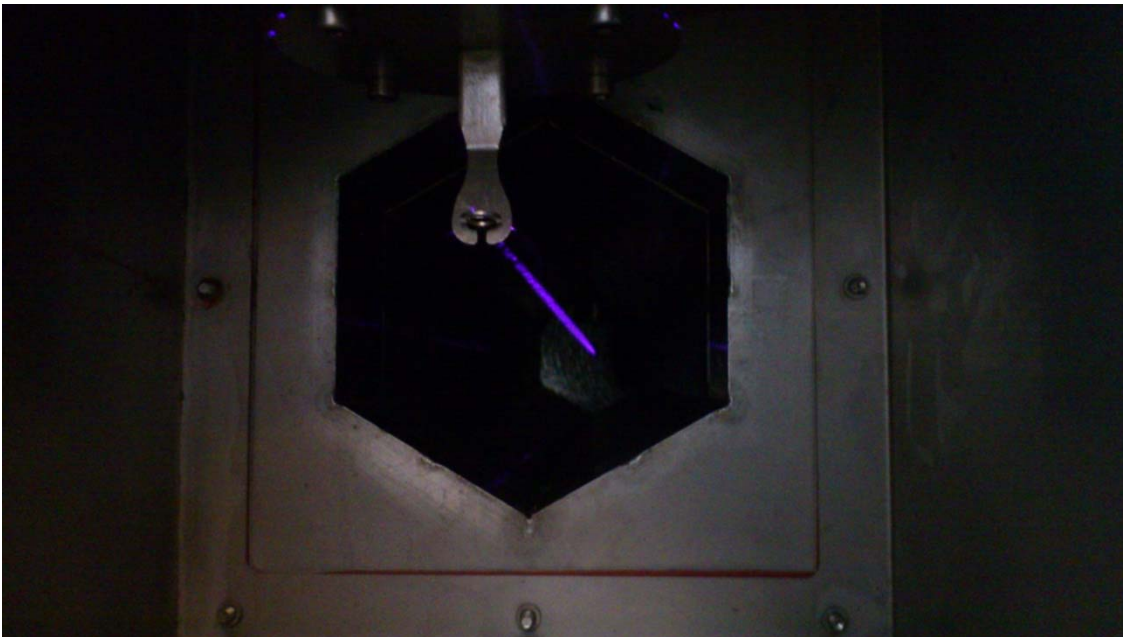




CHEMICAL ASSESSMENT OF NON-THERMAL PLASMA FOR REDUCTION OF ODOUR EMISSIONS FROM PIG HOUSES

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Gas/particle partitioning of odorants in a pig house was also investigated and a method for measuring odorants in particles by filters and TD-GC-MS was developed and evaluated. Only low concentrations and low fractions of odorants were found in the particle phase, thus the contribution to odour from particles was evaluated to be limited.

Keywords: Emission, Environmental engineering, Gas chromatography, Mass spectrometry, Non-thermal plasma, Odour and air quality, Particles, PTR-MS

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Abstract

Methanethiol is an important odorant from pig houses, but it can be difficult to measure due to low concentrations, high volatility and because it easily reacts to form dimethyl disulphide.

A method was developed for sampling and measuring methanethiol with minimum artefact formation using sorbent materials and thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). As odour from pig production can be a nuisance to neighbours, a non-thermal plasma system for odour removal was tested on emissions from pig houses.

The experiments showed good removal for some odorants, especially indole and 3-methyl-1H-indole, and a high degree of particle removal. Gas/particle partitioning of odorants in a pig house was also investigated and a method for measuring odorants in particles by filters and TD-GC-MS was developed and evaluated.

Only low concentrations and low fractions of odorants were found in the particle phase, thus the contribution to odour from particles was evaluated to be limited.

Preface

This thesis is submitted as a requirement for the completion of my Doctor of Philosophy (PhD) degree at Department of Engineering, Faculty of Science and Technology, Aarhus University. The thesis consists of the PhD research that has been conducted in the period from January 2010 to December 2012.

The PhD thesis is based on the following papers:

- Paper I Andersen, K.B., Hansen, M.J., Feilberg, A. (2012) Minimisation of artefact formation of dimethyl disulphide during sampling and analysis of methanethiol in air using solid sorbent materials. *Journal of Chromatography A*, 1245, 24–31.
- Paper II Andersen, K.B., Beukes, J.A., Feilberg, A. (2012) Non-thermal plasma for odour reduction from pig houses -a pilot scale investigation. Accepted in *Chemical Engineering Journal*.
- Paper III Andersen, K.B., Glasius, M., Feilberg, A. (2012) Gas/particle partitioning of odorants in a pig house measured by thermal desorption GC/MS. Submitted to *Atmospheric Environment*.

Additional work that were conducted during this PhD project:

- Andersen K.B., Feilberg A., Beukes J.A. (2010) Abating odour nuisance from pig production units by the use of a non-thermal plasma system. *Chemical Engineering Transactions*, 23, 351-356.
- Andersen, K.B., Feilberg, A., Beukes, J.A. (2012) Use of non-thermal plasma and UV-light for removal of odour from sludge treatment. *Water Science and Technology*, 66(8), 1656-1662.
- A short study of the effect on sorbent tubes exposed to ozone.

The work has been conducted as an industrial PhD project partly funded by Nordforsk as part of their Private Public Partnership (PPP) PhD program. The work was performed in collaboration between Aarhus University and Applied Plasma Physics AS. Half the work was conducted at Aarhus University, at the research centre in Foulum, and half the work was done at Applied Plasma Physic AS' location in Sandnes, Norway.

During the PhD study oral presentations were given in two international conferences, Nose2010 (Florence, Italy) and the 4th IWA Conference on Odours and VOCs (Vitoria, Brazil). In the Norwegian conference, Norwegian Society for Mass Spectrometry Winter meeting 2011 (Hafjell, Norway), an oral presentation and a poster presentation were given. The Nose2012 conference (Palermo, Italy) was attended without any presentation. I participated in the Norwegian competition "Research Grand Prix 2011" for PhD students, which resulted in a shared 2nd place in the national final.

Foulum, Denmark, December 2012

Kristin Barkve Andersen

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Abstract

Odour emissions from livestock buildings are a major problem in many areas. The odorous ventilation air from large pig production facilities can cause negative effects on surrounding neighbourhoods. Good and reliable measurement techniques are necessary to be able to find solutions to the emission problem, but measurements of odorants can be difficult as they are often found in low concentrations and as part of complex mixtures.

Methanethiol (MT) is an important odorant found in emissions from pig houses. It is a compound that can be difficult to measure due to its high volatility and reactivity; it easily reacts to form dimethyl disulphide (DMDS) during sampling and/or analysis. A study was conducted to find an optimal method for sampling and measuring MT with minimum artefact formation using sorbent materials and a thermal desorption-gas chromatography-mass spectrometry method (TD-GC-MS). Sorbent materials and tubes for analysis were tested and evaluated. Investigations of breakthrough, the effects of storage and desorption temperatures were included in the study. Different drying methods were established with respect to quantitative sampling and formation of DMDS. Proton-transfer-reaction mass spectrometry (PTR-MS) was used in the development of the method and was an especially useful tool for determination of breakthrough.

Glass tubes packed with silica gel turned out to be the best choice for pre-concentration of MT before analysis with TD-GC-MS. A combination of Tenax TA and carbonised molecular sieve or Tenax TA can be used, but the tubes should be cooled to $\leq 0^{\circ}\text{C}$ to give acceptable results. 80°C was found to be the optimal desorption temperature. Storage conditions for the tubes were shown to be very critical for transformation of MT. Tubes should be kept at 0°C or lower during storage, room temperature storage should be limited to only a few minutes. Different drying methods for drying air prior to sampling in humid environments were tested. A Nafion dryer, CaCl_2 in a polypropylene tube and a Teflon tube placed on dry ice in a thermo box can all be used as they had no effect on recovery of H_2S , MT and DMS, but the Teflon tube on dry ice gave the lowest relative humidity.

There is a need for a solution that can treat large air volumes at a low cost for abatement of odour nuisance from pig production. Non-thermal plasma (NTP) systems can be used for abatement of different kinds of odour nuisances and a study was therefore conducted to evaluate the efficiency of a low energy NTP system towards emissions from pig houses. A pilot NTP system for odour removal was installed on a slip stream of ventilation air from a pig house and both negative and positive corona discharge modes were utilised. A PTR-MS was used to measure the concentration of selected odorants. Indole and 3-methyl-1H-indole showed the highest removal efficiencies at both positive and negative modes. Significant removal was also observed for methanol, 4-methylphenol, and 4-ethylphenol. Ethanol, 2,3-butanedione and dimethyl trisulphide were produced in the system. Negative voltage gave slightly better chemical transformation than positive voltage, but it also gave a higher ozone production which is not desirable. A principal component analysis (PCA) was used to analyse the results and to evaluate possible degradation mechanisms for the odorous compounds. Particle removal in the NTP

system was measured and showed that particles were easily removed, above 90 % removal for all experiments at a flow of 135 m³/h and voltages from 15 to 45 kV. This is due to the electrostatic effect.

Little is known about the partitioning of odorants between particle and gas phase. The concentrations of 17 known odorants in a pig house were measured in the gas and in the particle phase by using TD-GC-MS. The sampling of particles was done on PTFE coated glass fibre (GF) filters. The gas phase compounds were sampled on Tenax TA and Carbograph 5TD sorption tubes downstream the filters. The method was evaluated for different desorption temperatures and for adsorption from gas phase to the filters. 290 °C was found to be the optimal desorption temperature. Adsorption of propanoic acid, butanoic acid and 4-methylphenol to GF filters and PTFE coated GF filters were specially investigated in laboratory experiments by the use of PTR-MS. High adsorption was seen for both type of filters. To account for adsorption of gas-phase compounds to the filters, backup filters were placed behind the front particle sampling filter during sampling in the pig house. Carboxylic acids (C4-C6) were the most abundant in the particle phase of the odorants investigated in this study. By plotting the logarithm of the subcooled liquid vapour pressures, $\log p_L^\circ$, against the logarithm of the equilibrium gas-particle coefficients, $\log K_p$, the compounds were divided in two groups, dissociating (acids) and not dissociating compounds. These showed linear trends with m_r -values of -0.94 and -0.83 respectively, which are according to expected theoretically values.

During the project a method for sampling and analysing MT on sorption tubes and TD-GC-MS was developed. The importance of taking the right precautions when measuring this compound to minimise the formation of DMDS was shown. Experiments on a low energy NTP system showed good removal for some odorants found in a pig house, especially indole and 3-methyl-1H-indole, and a high degree of particle removal. Gas/particle partitioning of odorants in a pig house was further investigated and a method for measuring odorants in particles by filters and TD-GC-MS was developed and evaluated. Only low concentrations and low fractions of odorants were found in the particle phase, and the contribution to odour from particles was evaluated to be very limited.

Résumé på dansk

Emissioner af lugtstoffer fra husdyrproduktion er et stigende problem i mange områder. Ildelugtende ventilationsluft fra stor svineproduktioner kan medføre en negativ påvirkning af de omgivende nabolag. Pålidelige målemetoder er nødvendige for at identificere og udvikle teknologier, der kan løse dette problem, men målinger af lugtstoffer er en udfordring fordi de ofte er til stede i lave koncentrationer og fordi lugten består af en kompleks blanding af stoffer.

Methanthiol (MT) er et vigtigt lugtstof, der findes i emissioner fra svinestalde. Stoffet er vanskeligt at måle på grund af dets flygtighed og reaktivitet. Under opsamling og analyse dimeriserer stoffet let til dimethyldisulfid (DMDS). En undersøgelse blev gennemført med henblik på at finde den mest optimale metode til opsamling og måling af MT med lavest mulig omdannelse til DMDS. Metoden var baseret på termisk desorption af adsorptionsrør koblet til gas chromatografi og masse spektrometri (TD-GC-MS). Sorbent-materialer såvel som desorptionsrør blev undersøgt med hensyn til gennembrud, lagring og desorptionstemperatur. Endvidere blev forskellige metoder til tørring af luft testet i forhold til genfindning og dannelse af DMDS. PTR-MS (proton-transfer-reaction mass spectrometry) blev anvendt til udvikling af metoden og var særlig velegnet til hurtig bestemmelse af gennembrudsvolumener.

Glasrør pakket med silica gel viste sig at være det bedste valg til opkoncentrering af MT forud for analyse med TD-GC/MS. En kombination af Tenax TA og karboniseret molekyllær si eller Tenax TA alene kan også bruges, men rørene skal køles til $\leq 0^\circ\text{C}$ for at kunne give acceptable resultater. 80°C viste sig at være den optimale desorptionstemperatur. Lagringsbetingelser for adsorptionsrørene efter opsamling viste sig at være kritiske for omdannelsen af MT til DMDS. Rørene skal lagres ved 0°C eller lavere og lagring ved stuetemperatur skal minimeres til få minutters varighed. Tørring af opsamlingsluften ved fugtig luft er nødvendig for at undgå for meget vand i det analytiske system. Forskellige tørremetoder blev testet og en Nafion-kassette, CaCl_2 i et polypropylen-rør samt en Teflonslange placeret i tøris kan alle bruges og har ingen effekt på genfindingen af H_2S , MT and DMS.

For at minimere lugtgener fra Svineproduktion er der behov for renseteknologier, der kan håndtere stor mængde luft med lave omkostninger. Ikke-termisk plasma (NTP)-teknologi kan bruges til at reducere forskellige typer af lugtemissioner fra industri og der blev derfor gennemført en undersøgelse med henblik på at evaluere lav-energi NTP-teknologi som metode til rensning af luft fra svinestalde. Et NTP pilotsystem blev installeret til at behandle en delstrøm af ventilationsluften fra en svinestald og systemet blev kørt med såvel positiv som negativ corona-udladning.

Et PTR-MS instrument blev brugt til at måle koncentrationen af udvalgte lugtstoffer. De højeste rensningsgrader blev set for indol og 3-methyl-1H-indol (skatol) ved både negativ og positiv udladning. Signifikant fjernelse af methanol, 4-methylphenol, og 4-ethylphenol blev også observeret. Ethanol, 2,3-butanedion og dimethyltrisulfid viste sig at blive produceret i systemet. Negativ spænding gav lidt højere kemisk omdannelse i reaktoren, men gav også en højere production af uønsket ozon. En principal-komponent-analyse (PCA) blev brugt til at analysere resultaterne og evaluere hvilke mulige nedbrydningsmekanismer, der kan forekomme. Endvidere blev fjernelse af partikler undersøgt og det

viste sig, at mere end 90% blev fjernet i alle forsøg ved et flow på 135 m³/h og spændinger fra 15 to 45 kV. Dette tilskrives den elektrostatisk effekt.

Der har hidtil været begrænset viden om gas-partikelfordelingen af lugtstoffer. Da gas-partikelfordelingen har betydning for fjernelsen af lugtstofferne i et NTP-system, blev koncentrationer af 17 kendte lugtstoffer målt i en svinestald i såvel gas- som partikel-fasen ved anvendelse af TD-GC/MS. Partiklerne blev opsamlet på PTFE-coatede glasfiberfiltre. Gas-fase komponenterne blev opsamlet på Tenax/Carbograph sorptionsrør placeret efter filtrene.

Metoden blev evalueret med hensyn til desorptionstemperatur samt adsorption af gas-fase-komponenter til partikel-filtrene. 290 °C blev vurderet til at være den optimale temperatur. Adsorption af propansyre, smørsyre og 4-methylphenol til glasfiberfiltre og Teflon-coatede glasfiberfiltre blev undersøgt i speciel laboratorieforsøg ved at måle gennembruddet online med PTR-MS. En høj grad af adsorption blev observeret for begge typer filtre. For at kunne korrigere for adsorption af gasser, blev back-up filtre placeret efter det egentlige partikelfilter under opsamling og koncentrationen af stoffer målt på disse filtre blev brugt til at estimere adsorptionen på det forreste filter. Carboxylsyrer blev fundet i højeste koncentrationer i partikel-fasen. Ved at udtrykke logaritmen til det underafkølede damptryk af stofferne ($\log p_L^\circ$) som funktion af logaritmen til gas-partikel foredlingskoefficienten ($\log K_p$), kunne det vises at stofferne kunne opdeles i to grupper, dissocierende (syrer) og ikke-dissocierende stoffer. Der kunne observeres omtrentligt lineære sammenhænge med hældninger på hhv. -0.94 og -0.83, hvilket er i overensstemmelse med de teoretisk forventede.

Gennem dette PhD-projekt er der udviklet en metode til måling af MT ved hjælp af sorbent-rør og TD-GC/MS. Vigtigheden af at tage nødvendige forholdsregler for at undgå omdannelse af MT til DMDS blev tydeligt understreget. Eksperimenter med lav-energi NTP-teknologi viste god renseseffekt for visse stoffer, især indol og skatol, samt en høj grad af partikel -fjernelse. Gas-partikel-fordelingen af lugtstoffer blev yderligere undersøgt og en metode til måling af lugtstoffer bundet til partikler ved hjælp af TD-GC/MS blev evalueret. Kun lave fraktioner af lugtstoffer blev fundet i partiklerne, og det vurderes at partiklers bidrag til lugt er meget begrænset.

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1. Introduction

1.1.Odour

1.1.1. Odour emissions from livestock production

Odour emissions from livestock production are a problem in many areas and can cause negative effects for the surrounding neighbours. In order to remain commercially competitive, modern livestock production is becoming increasingly intensified and mechanised. Farms are built larger and at the same time, the surrounding communities are growing closer.

The release of odour from pig houses effect both the farmers and the people living in close vicinity to the farms. Exposure to odour from livestock production has been shown to cause many negative health effects such as tension, depression, anger, fatigue and confusion and less vigour (Nimmermark 2004; Schiffman et al. 1995).

Odour is defined as detection and interpretation of stimuli with the sense of olfaction, the sense of smell. The chemical component that causes the odour is called an odorant. Different volatile chemical compounds can cause odours, but the linkage between odorant properties and odour perception is not clear (Gostelow et al. 2001). Some inorganic substances such as hydrogen sulphide and ammonia are odorants, but a reasonable assumption is that most compounds that cause odours are volatile organic compounds (VOC). VOCs are defined as organic liquids or solids that have a room temperature vapour pressure greater than about 0.01 psi (0.52 mmHg) and atmospheric boiling points up to 260 °C (Cai et al. 2006). This includes compounds with less than 12 carbon atoms (Cai et al. 2006). Many VOCs from livestock production have been identified and measured. These include volatile fatty acids (VFAs), alcohols, aldehydes, amines, hydrocarbons, ketones, indoles, phenols, nitrogen-containing compounds and sulphur-containing compounds (Blanes-Vidal et al. 2009; Feilberg et al. 2010; Yao et al. 2011; Zhang et al. 2010a). The odorants are often present a very low concentration but they also have low perception detection limits. Some important odorants from pig production reported in the literature (Blanes-Vidal et al. 2009; Feilberg et al. 2010) and their odour threshold values (OTV) are listed in Table 1.

Table 1. Common odorants found in pig production and their odour threshold values.

Cas#	Odorants	OTV (ppb)
7783-06-4	Hydrogen sulphide	6.5 ^b
74-93-1	Metanethiol	0.07 ^a
75-50-3	Trimethylamine	2.1 ^a
64-19-7	Acetic acid	236 ^a
75-18-3	Dimethyl sulphide	13.0 ^b
513-86-0	3-hydroxy-2-butanone	25 ^a
79-09-4	Propanoic acid	69 ^b
79-31-2	2-methyl propanoic acid	10.5 ^b
431-03-8	2,3-butanedione	0.6 ^a
107-92-6	Butanoic acid	4.19 ^b
503-74-2	3-methyl butanoic acid	0.7 ^b
109-52-4	Pentanoic acid	7.9 ^b
142-62-1	Hexanoic acid	15.2 ^b
111-14-8	Heptanoic acid	14.3 ^b
624-92-0	Dimethyl disulphide	13.0
108-95-2	Phenol	38.1 ^b
106-44-5	4-methylphenol	0.3 ^b
123-07-9	4-ethylphenol	1.3 ^a
120-72-9	Indole	0.06 ^b
83-34-1	3-methyl-1H-indole	0.09 ^a

^aReported in Feilberg et al. (2010).

^bGeometrical average based on values in Van Gemert (2003).

Odorants may also be trapped in particles as well as in the gas phase (Cai et al. 2006). Particles are tiny pieces of solids or liquids suspended in the air. The air inside a pig house contains high concentrations of particles, often 10-100 times higher than the concentration in other indoor environments (Cambra-López et al. 2010) and the particulate matter (PM) mainly originates from feed and dried faecal material from the animals but also from hair and skin, moulds, pollen grains, mites, insect parts and mineral ash (Bottcher 2001; Carpenter 1986; Dawson 1990).

Cai et al. (2006) reported methanethiol, isovaleric acid, 4-methyl-phenol, indole and 3-methyl-1H-indole as key odorants associated with swine barn PM. In total they measured 50 different compounds in the particulate matter from a swine barn. Hammond et al. (1981) compared their results from particles with previous work on non-particulate gas and found 4-5 times higher concentration of the odorants in the gas phase than in the particle phase, but the particles might be responsible for a considerable amount of the odour emission from the pig house as the odorants may be concentrated in the particles which might result in a more intense perception of the odorants compared to odorants in the gas phase (Bottcher 2001; Hammond et al. 1981).

1.1.2. Measurement methods

Sensory measurements

Odours can be measured in two ways, either sensory by human noses or analytical by measuring odorant concentrations. A major challenge in odour measurements is that a person's response to an odour is highly subjective. Odour detection is affected by age and health (Larsson et al. 2000; Ship and Weiffenbach 1993). The sensitivity to different odours varies from person to person and this is further complicated by the complexity of many odorous emissions (Gostelow et al. 2001). Presence of other compounds can lower odour threshold values synergistically (Miyazawa et al. 2008a) or additively (Miyazawa et al. 2008b). It is therefore difficult to predict the overall odour of complex mixtures.

Four dimensions of odours are generally accepted: (1) concentration, (2) intensity, (3) character and (4) hedonic tone (Gostelow et al. 2001). Odour intensity is the magnitude of the perceived sensation while the odour character is the characteristic properties distinguishing the odours from each other. In a hedonic assessment, odours are scaled from extremely unpleasant to extremely pleasant. Odour concentration is the most frequently measured parameter (Gostelow et al. 2001).

Odour concentration is typically measured by dilution-to-threshold with an olfactometer using human panellists (CEN 2003). The olfactometer dilutes the odour samples with odour-free air. The number of dilutions required to reduce an odour to its threshold concentration determines the odour concentration. European odour units per cubic meter, ouE/m³, is used as the unit of measure for odour and the odour concentration at the detection threshold is 1 ouE. The odour concentration is then expressed in terms of multiples of the detection threshold. Odour panels should be calibrated with n-butanol (123 mg n-butanol in 1 m³ (40 ppb) is the accepted reference value of the European odour unit).

The detection thresholds reported for a chemical compound varies by many orders of magnitude in the literature (Van Gemert 2003). Odour threshold values obtained are dependent on the method used, differences in how the olfactometer is operated, how the odour is presented and on the panellist selection (Dravnieks and Jarke 1980; Trabue et al. 2011). It has been shown that the concentration of odorants can decrease in the olfactometer (Hansen et al. 2010).

Dilution may be static or dynamic but dynamic methods are considered to be better as effects of sample adsorption to internal surfaces of the instrument are minimised (Dravnieks and Jarke 1980). A forced-choice method where the panellists smell several stimuli including blanks and then have to decide which one is different offers advantages over methods where only one stimulus is judged at the time (Dravnieks and Jarke 1980).

The materials used for the presentation of odour samples and how the samples are presented can affect the results from an olfactometry analysis. Choice of sample bags or containers and tubes and connections used for sampling are important. The materials used should be odour free, impermeable and not subject to sample loss through adsorption to surfaces. Stainless steel, glass, Teflon, Tedlar and Nalophan are common materials used. Storage of odour samples can reduce the concentration and should therefore be minimised (Hansen et al. 2011; Koziel et al. 2005; Monks et al. 2009).

The air is often filtered before sampling of odour samples (Bottcher 2001; Cambra-López et al. 2010). It is therefore important to understand the effect particles have on the overall odour. Odour from particles is eliminated from the measurements by filtration of the air, and the odour might be underestimated.

Analytical methods

The concentration of specific odorants can be measured analytically. Analytical methods do not tell anything about the interactions between the different odorants, but measuring individual odorants and comparing them with known threshold values can provide useful information. There are many different ways to measure odorants analytically. Which method to use depends on available instruments and the nature of the compounds to be measured.

A challenge is that the odorant concentrations in the emissions are often very low and part of complex mixtures. Compounds with high volatility and reactivity can be complicated to measure. As it is the concentration of odorants that are measured by analytical methods and not odour, it is difficult to predict the overall odour. The concentrations measured can be compared to threshold values, but these can vary with a factor of several tens. Also, this method does not include synergy effects. But as sensory odour measurements have a high uncertainty, analytical measurement of specific compounds can be very useful, e.g. by measuring inlet and outlet values of known odorants as part of an evaluation process when considering different odour abatement technologies. Hansen et al. (2012a) investigated the use of odorant measurements for predicting odour concentration in facilities with growing-finishing pigs and concluded that chemical measurements of odorants by proton-transfer-reaction mass spectrometry (PTR-MS) can be an alternative for expressing the odour concentration in these types of facilities.

The use of different types of instruments for measuring odorants has been reported in the literature. Solid-phase microextraction (SPME) and gas chromatography-mass spectrometry (GC-MS) have been used for measuring phenolic and indolic compounds, sulfides and VFAs (Kim-Yang et al. 2005; Yao et al. 2011). Indoles, VFAs and methanethiol (MT) from pig odour have been measured by the use of a solid sorption technique based on cartridges and quantification by reversed-phase high-performance liquid chromatography (RP-HPLC) with fluorescence detection and GC combined with flame ionisation detection (FID) (Willig et al. 2004). PTR-MS has been used to measure odorants from pig houses (Feilberg et al. 2010; Hansen et al. 2012a; Hansen et al. 2012b). Odorants and VOCs have also been measured by thermal desorption (TD) GC-MS (Blanes-Vidal et al. 2009; Hobbs et al. 1999; Ras et al. 2008; Schiffman et al. 2001). Reduced sulfur compounds in air can be measured by GC-sulfur chemiluminescence detector (SCD) (Khan et al. 2012).

Several different methods have been used to collect and measure odorants in particles; TD-GC-MS (Rossignol et al. 2012; Waterman et al. 2000; Waterman et al. 2001), headspace SPME coupled with GC-MS and olfactometry (Cai et al. 2006), electrostatic precipitation for particle collection (Hammond et al. 1981). Bulliner et al. (2006) used steel plates, SPME and multidimensional GC-MS-olfactometry to characterise livestock odours from particles and gas phase. Several potential artefacts can be present in

determination of gas/particle (G/P) partitioning. Sampling particles from pig houses on filters was tested by Hammond et al. (1981), but high adsorption from the gas phase to the filters was observed; in general the concentration of the odorous compounds (various acids, phenols and carbonyls) was measured on the backup filter to be around 50 % compared to what was measured on the front filter. G/P partition measurements can easily be biased if particles are erroneously measured as gas phase or fractions of the gas phase mistaken for particles, or if losses occur during sampling (Volckens and Leith 2003). Denuders are sometimes used in determination of G/P partitioning but evaporation of compounds from the particles can cause bias in this method.

1.1.3. Odour removal technology

Different odour removal technologies exist and are in use in livestock production today. Biofiltration is a technique using microorganisms to capture and degrade pollutants. The microorganisms are immobilized on an adsorptive filter substrate in the form of a biofilm (Togna and Singh 1994). This can consist of a mixture of compost and wood chips, peat or soil (Iranpour et al. 2005; Togna and Singh 1994). Odorous air is forced through this material so the microbes can degrade the compounds if the air-water mass transfer is sufficient. Compaction of the media over time and high pressure drop can cause operational problems. Biofilters exist both as open and closed beds. Open beds are typically build outdoor and are larger than the closed ones. Biofilters for pig farms have been developed at a commercial scale. They have been shown to be able to reduce both odour and ammonia (Chen and Hoff 2009; Iranpour et al. 2005).

Biotrickling filters are similar to biofilters. The main difference in biotrickling filters is a continuous circulation of water (Melse and Ogink 2005; Togna and Singh 1994). The liquid recirculation helps to avoid dryness of the packing material. It also allows for removal of the metabolites produced. Biotrickling filters may show a greater performance compared to biofilters at high contaminant loadings, which might be due to higher internal biomass concentrations (Togna and Singh 1994). However, biotrickling filters have been observed to give average NH₃ removal efficiencies from 35 % to over 90 % and odour removal efficiencies from 20 to 80 %, which indicates that process control is important (Jensen et al. 2005; Jensen and Hansen 2006; Melse and Ogink 2005; Riis and Jensen 2007; Sørensen and Riis 2008).

Increase in pressure drop and obtainment of sufficient air distribution limit the odour removal. At high inlet concentrations (7 - 1000 mg/m³) and/or high empty bed gas residence time (11 - 180 s), removal efficiencies >90 % for hydrogen sulphide (H₂S) and odour by biofilters and biotrickling filters have been shown (Gabriel and Deshusses 2003). Biological treatment has especially good potential for emissions where the concentrations of the specific compounds are high which allows for growth of specific microorganisms. However, this is not the situation when treating emissions from livestock production.

The effect of chemical acid scrubbers on emissions from farms has been investigated. They have shown to be very efficient towards ammonia, but have little or no effect on the odour (Melse and Ogink 2005).

Experiments on direct ozonation treatment of the air inside a pig house have been conducted but the results showed that it is not practical because of the high ozone concentrations needed to achieve the desired odour reduction (Kim-Yang et al. 2005). The effects of ozonation of pig slurry have been investigated and a potential for odour removal has been shown (Bildsoe et al. 2012; Liu et al. 2011; Watkins et al. 1997; Wu and Masten 2002; Wu et al. 1999). Reduction of H₂S (~77 %) by ozonation was shown by Liu et al. (2011). Experiments by Bildsoe et al. (2012) showed that short-term reduction of H₂S is possible by low-dose ozonation. Watkins et al. (1997) showed reduction of 4-methylphenol, 4-ethylphenol, indole and 3-methyl-1H-indole. Emissions of volatile fatty acids have shown no effect by ozonation (Watkins et al. 1997; Wu et al. 1999). More research is needed as ozone production is expensive, toxic to humans and as ozonation might result in an increase of NH₃ emissions (Bildsoe et al. 2012).

Reducing odour by spraying various additives inside the confinement pig building is in use in some facilities. Spraying additives were evaluated by Kim et al. (2008). They measured some odour reduction after spraying artificial spice and essential oil while others, like tap and salt water and soybean oil sustained or increased odour intensity and offensiveness until 24 h after spraying. Reduction of odour by spraying additives might be a good solution in some cases, but the long-term effect and amount of additive necessary must be considered.

The effects of dietary manipulation on the emissions from livestock buildings have been investigated, but the results are inconclusive. Eriksen et al. (2010) investigated acidification via diet manipulation and found effective reduction of ammonia emissions but the results indicated that odour control related to VSC will be difficult to achieve. Experiments by Hayes et al. (2004) showed that lower levels of crude proteins in finishing pig diets could reduce the odour and ammonia emissions. Low dietary crude protein levels might appear as a low cost alternative to end of pipe solutions for odour removal from pig houses, but the cost of adding synthetic amino acids instead of conventional protein sources must be considered (Hayes et al. 2004)

Treatment of emissions of VOCs by non-thermal plasma technology has shown promising results (Chang 2003; Jarrige and Vervisch 2007; Oda 2003; Zhang et al. 1996). This kind of technology is described in detail in Chapter 1.2.

1.2. Non-thermal plasma

1.2.1. Plasma and non-thermal plasma

Plasma is the fourth state of matter (solid, liquid, gas and plasma) and is created when energy is added to a gas. The plasma consists of ions, electrons, charge-neutral gas molecules and other species in varying degrees of excitation. The free electrical charges, the electrons and ions, make the plasma electrically conductive, internally interactive and strongly responsive to electromagnetic fields (Fridman 2008).

Plasma can be divided into thermal plasma and non-thermal plasma (NTP). Thermal plasma has electrons and bulk gas at the same temperature. In NTP there is no thermal equilibrium between the electrons and the bulk gas. Energy is added to electrons and these will typically have temperatures ranging from 10,000 K to 250,000 K (1-20 eV) while the background gas stays at ambient temperature (Vandenbroucke et al. 2011; Jarrige and Vervisch 2007).

NTP processing is a promising technology for air cleaning (Chang 2003; Jarrige and Vervisch 2007; Oda 2003; Zhang et al. 1996). The NTP has a very strong chemical reactivity and is therefore expected to reduce or decompose VOCs in the gas phase (Oda 2003). The NTP can be created by high voltage. Certain NTP systems also have a great potential for particle removal due to the electrostatic effects.

1.2.2. Removal mechanisms

In NTP systems, high-speed electrons are bombarding the bulk gas molecules. This results in production of excited gas molecules such as (N_2^* , O_2^*). The excited molecules lose their excess energy by emitting photons or heat. Ionisation, dissociation, electron attachment and other processes will also occur in the discharge zone (Jarrige and Vervisch 2007; Vandenbroucke et al. 2011). This gives formations of unstable reactive species like ions and free radicals (Vandenbroucke et al. 2011). The free radicals are highly reactive and therefore ideal for conversion of environmental pollutants to CO_2 , H_2O and other degradation products (Vandenbroucke et al. 2011). The OH radical is considered to be one of the most important ones in the NTP system (Fridman 2008). Formation of OH radicals in air plasma can happen through different channels and air humidity is an important parameter (Fridman 2008).

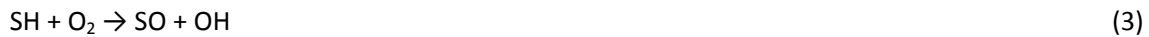
Many of the mechanisms occurring in a NTP reaction chamber are still unknown but mechanisms for some odorants have been proposed in the literature. Tsai et al. (2001) investigated decomposition of MT and Jarrige and Vervisch (2007) presented high removal efficiencies for dimethyl sulphide (DMS) and H_2S at high power inputs (Specific input energies (SIE) from 12 J/L to 95 J/L depending on concentration and compound). The reaction mechanisms for these compounds are discussed in the literature (Fridman 2008; Jarrige and Vervisch 2007; Sørensen et al. 1996; Tsai et al. 2001). Proposed mechanisms for H_2S , DMS and hydrocarbons are shown in the following section.

Hydrogen sulphide (H₂S)

Jarrige and Vervisch (2007) investigated the degradation of H₂S in pulsed corona discharge and measured reaction products. They proposed a reaction mechanism for removal of H₂S. A general assumption is that atomic oxygen O(³P) is the main oxidising agent produced by an electrical discharge in air so the first step is assumed to be dehydrogenation by atomic oxygen (Jarrige and Vervisch 2007). Secondary hydroxyl radicals (OH) are also produced and can react with H₂S.



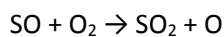
SH radicals are produced and can react with O or O₂ (Jarrige and Vervisch 2007):



It can also react by self-reaction producing atomic sulfur and regeneration of H₂S (Jarrige and Vervisch 2007):



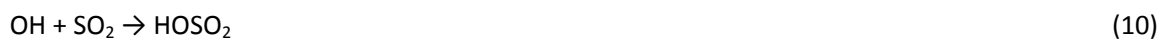
Experiments done by Jarrige and Vervisch (2007) showed that SO₂ was the predominant final stable by-product:



Formation of SO₃ and regeneration of SO₂ might also occur.



Presence of water is supposed to improve removal efficiencies as it leads to formation of OH which is much more reactive than O(³P), but experiments performed by Jarrige and Vervisch (2007) did not show a great extent of variation with humidity in the destruction rate of H₂S. The humidity seemed to promote the production of SO₂ for low SIE but it decreases at higher SIEs because of formation of sulfuric acid (H₂SO₄) (Jarrige and Vervisch 2007):



Dimethyl sulphide (DMS)

DMS in air can be removed by plasma generated oxidisers, especially OH radicals (Barone et al. 1996; Sun et al. 1997; Turnipseed et al. 1996):



The CH_3S radical is an intermediate molecule that is formed either directly in an elementary reaction or through the transformation of the CH_3SCH_2 radicals produced. The CH_3SCH_2 radicals can attach molecular oxygen and form a peroxide radical (Fridman 2008; Turnipseed et al. 1996):



The peroxide radical $\text{CH}_3\text{SCH}_2\text{OO}$ can transform into the radical $\text{CH}_3\text{SCH}_2\text{O}$. This happens through reactions with different active species but especially through reactions with NO (even when the concentration of NO is relatively low) (Fridman 2008):



Decomposition of the $\text{CH}_3\text{SCH}_2\text{O}$ forms the major intermediate molecule of the DMS oxidation (Fridman 2008). Formaldehyde molecules are also formed as a by-product:



CO_2 , H_2O and SO_2 are the final products after further oxidation of the major intermediate active CH_3S (Fridman 2008).

Jarrige and Vervisch (2007) proposed a reaction mechanism with atomic oxygen via formation of a $\text{CH}_3\text{S(O)CH}_3$ adduct:



The possible reactions between the CH_3SO and active species generated in the discharge are mostly unknown, but measurements of by-products performed by Jarrige and Vervisch (2007) showed that cleavage of C-S bonds most likely occurs early in the degradation mechanism.

Hydrocarbons

Different plasma generated active oxidisers are involved in oxidation of hydrocarbons; OH radical, atomic oxygen, electronically excited oxygen, ozone etc (Fridman 2008). The OH radical is considered to be especially important. The following reactions show one way of reaction for the oxidation process as

proposed in Fridman (2008). The oxidation of the hydrocarbon starts with dehydrogenisation which results in the formation of an R radical:



The R radical almost immediately reacts with oxygen to form an organic peroxide radical:



RO_2 is able to react with another saturated hydrocarbon, RH. Saturated organic peroxide is then formed and this propagates the chain mechanism of RH oxidation in air.



The peroxides RO_2 and RO_2H can further oxidise to CO_2 and H_2O . This can happen with or without additional consumption of OH and other plasma-generated oxidizers (Fridman 2008).

1.2.3. Non-thermal plasma technology for air treatment

The literature reports on different designs and types of NTP reactors. Some are only tested in small scale while others are in use in full scale applications. NTP systems for air treatment are being used for odour removal, removal of VOCs and dust collection.

One type of NTP system for collecting particles, VOC decomposition and odour removal is the packed bed reactors. This is a reactor packed with a ferroelectric material such as BaTiO_3 (most widely used), Mg_2TiO_4 , CaTiO_3 and SrTiO_3 (Ogata et al. 1999). A spontaneous polarisation occurs in the direction of the electric field when the ferroelectric material is exposed to an external electrical field. This results in a high electric field at the contact points of the pellets. In the vicinity of the pellets' contact points, electrical discharges occur. These are sometimes referred to as a partial discharge. A disadvantage with these systems is high pressure drop (Kim 2004). Catalysts like cordierite, zeolite, titanium-dioxide, vanadium oxide or tungsten oxide can easily be incorporated in the packed bed reactors (Oda 2003). Zhang et al. (1996) obtained high removal of ammonia and odours from animal houses by the use of packed bed ferroelectric plasma (up to 95 % for ammonia, SIE $>30 \text{ Wh/m}^3$).

In a dielectric barrier discharge (DBD) reactor a dielectrical layer is covering one or two of the electrodes in the discharge gap. Glass or silica glass are preferred materials for the dielectric barrier, ceramic materials, thin enamel or polymer layers can be used in special cases (Kogelschatz 2003). The discharge starts in the gas volume at a sufficiently high voltage between the electrodes. The discharge then spreads out until it reaches the electrodes. At the dielectric it builds up a space charge. This cancels the applied electric field and at that moment the discharge stops. Operating conditions of voltage and frequency, gas composition and type of material are all important for the discharge characteristics in a

DBD reactor (Falkenstein and Coogan 1997). The DBD reactors are popular because the insulating barriers between the electrodes prevents flashover discharge (Oda 2003).

A corona discharge is a weak luminous discharge. It can appear at atmospheric pressure near sharp points, edges or thin wires where the electrical field is sufficiently large (Fridman 2008). A strong electric field, ionisation and luminosity are located in the vicinity of one electrode, which always makes the corona discharge non-uniform (Fridman 2008). The weak electric field drag charged particles from one electrode to the other to close the electric circuit. An asymmetric electrode pair is used in corona discharge reactors; point-to-plane or wire-in-cylinder geometries are the most common methods (Fridman 2008). A DC wire-cylinder reactor is more promising for practical applications than dielectric barrier discharge because of the ability to remove aerosols and gaseous pollutant at the same time and the low cost connected to a DC power supply (Wang et al. 2011).

Reactors using a pulsed power supply are sometimes applied (Jarrige and Vervisch 2007; Kim 2004; Oda 2003). A fast voltage rising time of several tens of nanoseconds results in a pulsed corona discharge. By using pulsed voltage, it is possible to increase corona power to a higher level than by the use of DC voltage without transition to sparks (Fridman 2008). Pulsed corona discharge sets high requirements to the power supply and to the electrical properties of the plasma chamber, which makes it an expensive solution.

1.3. Background and objective

Odour emissions from livestock buildings are an increasing problem. It can cause negative health effects for both the farmer and the surrounding community (Nimmermark 2004; Schiffman et al. 1995). Today biological air treatment is the only solution for treatment of odour from this sector because of price and efficiency, but this solution has limitations when it comes to operation, cost and cleaning efficiency. There is a need for further development of existing technology or development of new technology to treat odour emissions from pig houses.

Applied Plasma Physics AS (APP) has since 1993 developed and produced NTP systems for odour removal. Their systems are installed and in operation for treatment of emissions from pet food production, fish feed production and emissions from tobacco factories (Vetthus 2008). Studies on NTP technology have shown promising results for odour removal (Chang 2003; Jarrige and Vervisch 2007; Oda 2003) but usually at high energy inputs which result in too high costs for pig production. It was therefore of interest to investigate the performance of the APP NTP system which operates on low energies on odour emissions from pig houses. Further knowledge of the mechanisms involved in this type of NTP system is also needed to be able to better predict the effect of the system and to be able to optimise it.

The main important odorants from pig production are well described in the literature (Blanes-Vidal et al. 2009; Feilberg et al. 2010; Hansen et al. 2012a; Schiffman et al. 2001). Sensory measurements are both expensive and have a high degree of uncertainty. Analytical methods measuring individual odorants were therefore evaluated as the preferred method for characterisation of the NTP system.

A TD-GC-MS is a common instrument found in many labs. It is also an instrument that was available both in the lab at Aarhus University, Foulum and in the APP lab. Some odorants, like carboxylic acids, are easily measured by the TD-GC-MS but it can be difficult to measure more volatile compounds like the sulphur compounds. MT is an important odorant in pig house emissions (Feilberg et al. 2010), but it is difficult to measure as it is highly volatile and reacts easily to form dimethyl disulphide (DMDS) (Lestremau et al. 2004; Trabue et al. 2008). The compound is difficult to measure by GC-SCD as the concentration is very low. Pre-concentration on sorption tubes before analysis with TD-GC-MS is complicated because of the high volatility and reactivity. The first part of the PhD study was therefore an investigation of the possibility of sampling and analysing MT with sorption tubes and TD-GC-MS. The results from this work are published in Paper I and included in this thesis, Chapter 3.1.

Some ozone is produced in the NTP system (often 1-2 ppm). This creates a challenge for sampling and analysis of outlet samples from the system by the use of sorbent tubes and TD-GC-MS as the ozone might affect the samples. Experiments were conducted to investigate these effects, both formation of compounds on sorption tubes and the effect on measured concentration from odour samples when the tubes were exposed to ozone after sampling. A method to remove ozone by using a copper tube coated with potassium iodide (KI) prior to the sampling tube was tested. The data from these experiments are not published in any scientific journal but are presented in this thesis, Chapter 6.3.

The method involving the use of a KI coated copper tube did not give desired results but due to limited time in the PhD project, it was decided not to continue working on a solution to the ozone problem. In the second part of the PhD project a thorough pilot test of the NTP system was performed on pig house emissions. The ozone problem was avoided by using a PTR-MS for measurements of odorant.

A pilot scale NTP system based on the full scale system of the APP NTP air cleaner was used. Both positive and negative discharge modes were tested and evaluated. The system was tested both by varying the flow and by changing the SIE. Experiments based on a few individual compounds were conducted in order to test differences in removal efficiency in the absence of dust and co-contaminants. Ozone production and particle removal were also measured during the study. The results from this study are presented in Paper II which is included in this thesis in Chapter 3.2.

The NTP system showed high removal efficiencies for particles. Odorants have been found in particles by other researchers and particles are expected to play an important role for odour perception (Bulliner et al. 2006; Cai et al. 2006; Hammond et al. 1981), but knowledge on the partitioning of odorants between the particle phase and the gas phase in a pig house was still missing. As the last part of this PhD study odorants in the particle phase and in the gas phase were therefore measured and the results are presented in Paper III which is included in this thesis in Chapter 3.3.

Two additional studies on the NTP system were performed. The NTP system was tested on odour from a pig house. The system was evaluated by the use of TD-GC-MS/olfactometry and by sensory measurements performed on bag samples analysed by a NasalRanger™. This study was presented at the Nose2010 conference in Florence, Italy and is published in Chemical Engineering Transactions. The NTP system was also tested in combination with a UV treatment step on emissions from a sludge treatment plant. The study was presented at the 4th IWA Conference on Odours and VOCs in Vitoria, Brazil in 2011 and is also published in Water Science and Technology. The results from these studies are included in this thesis in Chapter 6.1 and 6.2.

The aim of the project was to do a chemical assessment of the NTP system for odour removal in pig house emissions and to improve the analytical measurement methods. It was hypothesised that a low energy NTP system could be a good solution for odour removal from pig houses, and it was desirable to investigate if a TD-GC-MS could be used for the evaluations of the system.

The work done in the PhD study was divided into three parts which each resulted in a paper manuscript. The first part was done on analytical measurement techniques with focus on MT as this is the only compound of the main odorants found in a pig house that is difficult to measure with both TD-GC-MS and GC-SCD. The aim was to find a method that minimises the formation of DMDS when MT is sampled on sorption tubes and analysed by TD-GC-MS. The second part was an investigation of odour reduction from pig house emissions by the use of a NTP system. The third part was a study on G/P partitioning of odorants inside a pig house as particles were well removed in the NTP system.

2. General overview of the main measurement techniques

In this PhD project, a thermal desorption unit coupled with a gas chromatograph and a mass spectrometer (TD-GC-MS) and a proton-transfer-reaction mass spectrometer (PTR-MS) were the analytical instruments used to measure odorants.

The use of TD-GC-MS:

Paper I The aim was to find a method for measuring MT by TD-GC-MS with minimum formation of DMDS. PTR-MS was used as a tool in process of finding a method but TD-GC-MS was used to further investigate and to validate the method.

Paper III TD-GC-MS was used to measure odorants in the particle and gas phase.

The use of PTR-MS:

Paper I PTR-MS was used to find a method for sampling MT on sorption tubes with minimal formation of DMDS. It was used to evaluate the suitability of different tube materials and packing materials. The PTR-MS was an especially useful tool in investigations of breakthrough of MT.

Paper II PTR-MS was used to measure inlet and outlet concentrations of odorants from a NTP pilot system.

Paper III PTR-MS was used to investigate adsorption of odorants to particle filters.

The TD-GC-MS and the PTR-MS are described in the following sections.

2.1.1. Thermal Desorption Gas Chromatography and Mass Spectrometry (TD-GC-MS)

A TD-GC-MS is a common instrument used in many laboratories for different types of analysis. Sampling on sorption tubes before thermal desorption gives an advantage that allows for analysis of low concentrations. There are many different sorption materials that can be used for the sampling, e.g. Tenax TA, Carbograph, molecular sieve and silica gel. They have different properties and the sorption material should be chosen based on the properties of the compounds that are to be sampled. Type of material for the sample tubes should be considered, e.g. stainless steel, inert coated tubes or glass.

A disadvantage of the method is that some compounds can be difficult to sample due to high reactivity and volatility. Breakthrough of volatile compounds might be a problem when sampling on sorption tubes and analysis might be biased if the tubes are exposed to ozone.

The GC utilises a capillary column to separate the different chemical compounds in a mixture. The difference in the chemical properties between the different compounds results in separation of these as the sample travels through the column and they are eluted from the column at different times. Different dimensions and properties of different columns can be used depending on what compounds it is desirable to separate.

An MS downstream the GC is used to detect the molecules by breaking the molecules into ionised fragments and detecting them by using their mass to charge ratio. Different types of detectors exist. The most common type used in combination with GC is the quadrupole MS. In the MS the molecules are ionised. The ions formed are then detected typically by an electron multiplier which turns the ions into an electrical signal that can be detected. The most common form of ionisation is electron impact ionisation. The molecules are bombarded with free electrons emitted from a filament causing the molecules to fragment in a characteristic and reproducible way. The fragmentation pattern is dependent on the electron energy applied, typically 70 eV is used. The data from the MS can then be analysed by comparing the fragmentation patterns to a library such as NIST.

GC-MS is used for a large variety of different applications. Among others it is applied for detection of narcotics, in forensics science, analysis of food, measuring VOCs and odorants from waste treatment and livestock production (Gueissaz and Massonnet 2012; Statheropoulos et al. 2011; Cappellin et al. 2012; Rodriguez-Navas et al. 2012; Zhang et al. 2010b; Lee et al. 2012; Uhl 1997).

The combination of GC and MS has several advantages. One benefit is that the identification of compounds is based on both retention time and on mass spectrum. The GC provides a good separation of the compounds while the MS is a sensitive detector. The fragmentation patterns produced in the MS are reproducible by the fixed electron voltage and make it possible to create and share databases between users. A traditional detector like a flame ionisation detector cannot differentiate between co-eluting molecules which usually can be done through the different fragmentation patterns provided in the MS.

In this project, a thermal desorption gas chromatograph with a mass spectrometer (TD-GC-MS) (TD: Turbomatrix ATD; PerkinElmer, Waltham, USA; GC: Agilent technologies 6890 N, USA; MS: Agilent Technologies 5973, USA) was used.

2.1.2. Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

A high sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) was used for measuring odorants in several experiments in this PhD project. The PTR-MS was developed as a technique to detect gaseous organic compounds in air and was first introduced in the mid-1990s (Blake et al. 2009). It has previously been used and reported as a good tool for measuring odorants from pig production (Feilberg et al. 2010; Hansen et al. 2012b). A great advantage of a PTR-MS is that it takes online measurements with fast response (1-10 sec) and provides adequate detection limit and sensitivity (10-100 pptv) (de Gouw and Warneke 2007).

The PTR-MS works by chemical ionisation of the gas sample by proton transfer. The proton source is normally H_3O^+ . An ion source in the instrument produces H_3O^+ ions from water vapour in a hollow cathode discharge. These are led into a drift tube where the H_3O^+ reacts with the VOC trace gasses in the

sample air. A proton transfer occurs as long as the VOCs have a higher proton affinity than water. The protonated VOCs are then analysed in a mass spectrometer.

The main reaction in the PTR-MS instrument can be described as:



R is a trace gas that interacts with the protonated water (H_3O^+). A proton is transferred from the hydronium to the trace gas molecule. This gives a protonated and ionised molecule (RH^+) and neutral water (H_2O). This reaction is energetically possible for VOCs with higher proton affinity than water (166.5 kcal/mol (de Gouw and Warneke 2007)). Calibration can be done based on proton transfer rate constants or by using authentic standards as described in Feilberg et al. (2010).

An advantage of using PTR-MS is that it is a soft ionisation method that usually does not lead to fragmentation of the product ions (de Gouw and Warneke 2007). The mass of the product ion will therefore be equal to the VOC mass plus one. It is desirable to avoid fragmentation in the PTR-MS to not complicate the analysis but fragmentation patterns can also help identify and separate compounds. Carboxylic acids will typically fragment and lose one water molecule (Feilberg et al. 2010). This is dependent on the humidity but the sum of the protonated parent molecule and the fragments is constant ($\pm 5\%$) (Feilberg et al. 2010).

In addition to the reaction in eq. (22), the RH^+ and H_3O^+ can form ion clusters with H_2O molecules in the sample (de Gouw and Warneke 2007). This is not desirable as it complicates the interpretation of the mass spectra. The $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ cluster ions can still react with VOCs if the proton affinities of the VOCs are higher than that of the $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ cluster ions, depending on the electric field and pressure in the drift tube. The sensitivity of the PTR-MS will therefore depend on the humidity of the sample.

Variation in sample humidity can cause problems when measuring compounds with proton affinity only marginally above that of water. The proton transfer reactions are reversible and VOCs can also be deprotonated by reaction with water as is the case for H_2S (proton affinity 170.2 kcal/mol (Hansel et al. 1995)). Therefore, it is important to consider humidity dependence when calculating concentrations of H_2S and similar compounds with proton affinity close to that of water. Humidity dependence can be measured as described by Feilberg et al. (2010).

O_2^+ and NO^+ can also be used to ionise molecules instead of protonated water. By using O_2^+ it is possible to ionise molecules with too low proton affinity to be ionised by H_3O^+ , but there is a higher chance of fragmentation of most compounds due to high ionisation energy. Ionisation by NO^+ makes it possible to separate several isomeric molecules.

PTR-MS is a direct method and no sample collection is required. This gives the method an advantage as sampling and pre-concentration can cause problems and bias the results in some cases (Andersen et al. 2012).

3. Studies conducted during the PhD project

- Paper I Andersen, K.B., Hansen, M.J., Feilberg, A. (2012) Minimisation of artefact formation of dimethyl disulphide during sampling and analysis of methanethiol in air using solid sorbent materials. *Journal of Chromatography A*, 1245, 24–31.
- Paper II Andersen, K.B., Beukes, J.A., Feilberg, A. (2012) Non-thermal plasma for odour reduction from pig houses -a pilot scale investigation. Accepted in *Chemical Engineering Journal*.
- Paper III Andersen, K.B., Glasius, M., Feilberg, A. (2012) Gas/particle partitioning of odorants in a pig house measured by thermal desorption GC/MS. Submitted to *Atmospheric Environment*.

3.1.Minimisation of artefact formation of dimethyl disulphide during sampling and analysis of methanethiol in air using solid sorbent materials.

Andersen, K. B., Hansen, M. J., Feilberg, A.

Published in Journal of Chromatography A

3.2. Non-thermal plasma for odour reduction from pig houses -a pilot scale investigation.

Andersen, K. B., Beukes, J. A., Feilberg, A.

Accepted in Chemical Engineering Journal

3.3. Gas/particle partitioning of odorants in a pig house measured by thermal desorption GC/MS

Andersen, K. B., Glasius, M., Feilberg, A.

Submitted to Atmospheric Environment

4. General discussion and conclusion

Reliable measurement methods are vital for carrying out high quality scientific research. Results need to be reproducible and it is important to be able to trust that what is measured is what is actually there. This is a challenge working with odour as the measurements usually come with high uncertainties. Measuring odorants analytically are more precise than olfactometry but the choice of method must be selected carefully and improvement and optimisation are necessary for many methods.

In this study, a method for measuring MT by sampling on sorption tubes and analysis by TD-GC-MS is presented. The results show how important it is to take the necessary precautions when sampling and analysing MT to avoid formation of DMDS. The study gave good and promising results, but the method still needs to be tested in the field to verify that the same degree of recovery can be obtained in the presence of other VOCs. The study call into question other studies reported in the literature where DMDS are measured without considering if this can be due to conversion of MT. As MT has a much lower odour threshold value compared to DMDS, it is very important to measure the right compound when odour is evaluated.

Emission of odour from pig houses is a problem and there is a need for a solution to treat the emissions at low cost. A study of a low energy NTP system was conducted as NTP systems previously have shown a great potential for removal of odour from other sources. The results from the experiments showed that some compounds had high removal efficiencies, some showed little change and other compounds were produced. Particles showed to be very well removed as was expected due to the electrostatic effect. Based on the results it was suggested that high reactivity towards OH radicals and possibly surface reactions induced by electron capture are important for high removal efficiencies for the compounds evaluated in the study. A deeper knowledge about the chemical removal processes in the system was achieved which can be useful in the evaluation of the technology for other emission sources also.

The NTP systems showed great results for particles removal. It was therefore natural to continue the work with a study of G/P partitioning of odorants. A simple method for measuring odorants in particles by TD-GC-MS was developed and evaluated. It was shown how important it is to use backup filters to account for gas phase adsorption to the filters. The partitioning of odorants between gas phase and particle phase in a pig house was successfully measured by the use of this method.

The following general conclusions can be drawn from this thesis:

- Measurement techniques must be critically evaluated as bias might occur and result in faulty results. TD-GC-MS and PTR-MS are both good and useful instruments for measuring odorants from pig houses. The PTR-MS has the advantage that it is online and provides a fast response. The TD-GC-MS is a good and accurate instrument as long as precautions are taken to minimise bias.
- It was shown that quantitative sampling of MT for TD-GC-MS analysis is possible but a number of precautions must be taken to minimise DMDS formation. Silanised glass tubes packed with silica gel proved to be the best choice of tubes of the ones tested for thermal desorption of MT. The tubes must be analysed right after sampling or stored for as short a time as possible at 0 °C or lower. The thermal desorption temperature should not be higher than 100 °C. A Nafion dryer, CaCl₂ in polypropylene tube and a Teflon tube placed on dry ice in a thermo box can all be used to dry the air prior to sampling in humid air as they had no effect on recovery of H₂S, MT and DMS, but the Teflon tube on dry ice gave the lowest relative humidity. The method requires so many pre-cautions that it is not very suitable for routine analysis but can be used for e.g. confirmation of the presence of MT.
- A low energy NTP system with both negative and positive discharge mode was evaluated and tested on emissions from a pig house. It showed high removal efficiencies for indole and 3-methyl-1H-indole. Production of some compounds were observed, others were little affected by the NTP treatment. Negative corona discharge mode gave a slightly higher conversion than the positive discharge mode but also higher ozone production. Tests with DMS, H₂S and MT showed that the degradation of the compounds was not affected by presence of dust or other contaminants. Particles were well removed in the NTP system; a reduction above 90 % was seen for all particle sizes for most of the experiments.
- Investigations of the G/P partitioning of 17 known odorants showed that only a few odorants and only at low concentrations were found in the particles. The highest particle concentrations were found for the carboxylic acids. Plots of the logarithm of the subcooled liquid vapour pressures, $\log p_L^\circ$, against the logarithm of the equilibrium gas-particle coefficients, $\log K_p$, divided the compounds into two groups, polar and non-polar compounds. Linear trends for the two groups were found and m_r -values were determined to -0.94 and -0.83 respectively. This is according to what has previously been reported in literature. Sampling on filters and analysing directly with a TD-GC-MS was proved to be a good method for analysing compounds in particles in pig houses. High adsorption from gas phase to filters was seen for both glass fibre filters and PTFE coated filters so backup filters must be used during sampling to be able to account for adsorption. A desorption temperature of 290 °C was found to be optimal.

5. Perspectives

Odours are difficult to measure due to high uncertainties. A lot of research is still needed to improve the methods for both sensory and analytical measurements. It is important to be aware of the limitations in the methods and continuously work on improvements.

Analytical methods can measure the concentration of the individual odorants, but mechanisms behind the olfactory sense and synergetic effects between odorants in mixtures are not fully understood so measuring and predicting the overall odour is difficult to do analytically. In the future research should focus on gaining a better understanding of the relationship between the concentrations of the odorants and the overall odour.

In the first part of the thesis a method for MT measurements by TD-GC-MS was developed. Future studies should be conducted to investigate and verify that the same results are obtained from real samples, and to investigate possible effects when other VOCs are present.

A problem with using TD-GC-MS in the process of characterising and optimising the NTP system is the effect of ozone on outlet samples. Experience has shown that ozone can reduce the concentration of some compounds sampled on sorption tubes and it can also result in formation of some compounds due to degradation of the packing material in the sorption tube. A solution to the ozone problem will make the evaluation of the cleaning efficiency on specific odorants more accurate. As a TD-GC-MS is a common instrument found in many labs, a solution for taking samples when ozone is present will be useful to many.

In this PhD study the effect of a NTP system on emissions from pig houses were tested and a better understanding of the removal mechanisms was obtained. In the future, more research should be done to gain more knowledge that will make the reactions in the system more predictable. A better understanding of the system will also make it easier to optimise and to potentially reduce costs.

The NTP system proved to be very good for particle removal, but only few odorants and only low concentrations were found in the particles from a pig house. More research is needed to better understand how the G/P partitioning of odorants affects the perception of the odour.

6. Additional work

- Andersen K.B., Feilberg A., Beukes J.A. (2010) Abating odour nuisance from pig production units by the use of a non-thermal plasma system. *Chemical Engineering Transactions*, 23, 351-356.
- Andersen, K.B., Feilberg, A., Beukes, J.A. (2012) Use of non-thermal plasma and UV-light for removal of odour from sludge treatment. *Water Science and Technology*, 66(8), 1656-1662.
- A short study of the effect on sorbent tubes exposed to ozone.

6.1. Abating odour nuisance from pig production units by the use of a non-thermal plasma

Andersen K.B., Feilberg A., Beukes J.A.

Published in Chemical Engineering Transactions

6.2. Use of non-thermal plasma and UV-light for removal of odour from sludge treatment

Andersen, K.B., Feilberg, A., Beukes, J.A.

Published in Water Science and Technology

6.3.Effect of ozone on sorption tubes

Introduction

Ozone interferences have been observed when sampling on sorption tubes before analysis with TD-GC-MS. Compounds might be formed on sorption tubes when they are exposed to ozone and loss of sample can occur. Different techniques for ozone removal before sampling of VOCs exist. Both effects of ozone and techniques for removal of ozone at low levels (up to ~200 ppb) are well presented in the review by Helmig (1997).

As ozone is produced in the NTP system a study was conducted to investigate what effect ozone has on the sorption tubes and on samples of odorants. The use of potassium iodide (KI) coated copper tubes to remove ozone before sampling was tested.

Methods

Formation of compounds on steel tubes packed with Tenax TA and Carbograph 5TD when exposed to different concentrations of ozone was tested. 1 L of air containing 1.5, 3 or 5 ppm ozone was sucked through the tubes at 100 ml/min. Air without ozone was sucked through tubes to adjust for background. The tubes were analysed by TD-GC MS (TD: Markes International Unity 2™, England; GC: Agilent Technologies 7890 A, USA; MS: Agilent Technologies 5975B VL MSD, USA). The experiments were repeated three times at 1.5 ppm ozone and two times for 3 and 5 ppm.

The differences in production of compounds for different types of sorption tubes were investigated. Steel tubes packed with Tenax TA and Carbograph 5TD, inert coated tubes packed with Tenax TA, steel tubes packed with silica gel and inert coated tubes packed with carbonised molecular sieve were exposed to 1.5-1.8 ppm of ozone by sucking 1 L through the tubes at 100 ml/min. The results were repeated three times for the steel tubes packed with Tenax TA and Carbograph 5TD, one time for the inert coated tubes packed with Tenax TA and two times for the steel tubes packed with silica gel and the inert coated tubes packed with carbonised molecular sieve. The tubes were analysed by TD-GC-MS.

Semi-quantifications of the chemical concentrations were done by comparing integrated signals directly with a standard 1 L 10 ppb toluene reference.

Some hexanoic acid, o-cresol, m-cresol, indole and 3-methyl-1H-Indole were put in the bottom of a glass flask. The flask was heated to increase the concentration in the headspace. The odorants were sucked on to steel tubes packed with Tenax TA and Carbograph 5TD tubes from the headspace, 1 L at 100 ml/min. The suction to the tubes was done in parallel for two tubes at the time. Afterwards 1 L of air containing 1.6-2 ppm ozone was sucked through one of the tubes. The experiments were repeated four times but hexanoic acid was first included in the two last repetitions. The tubes were analysed by TD-GC-MS.

Experiments were conducted to investigate if sucking the odour samples through a copper tube coated with KI would result in loss of the compounds. A 750 mm long copper tube with an inner diameter of 4 mm was cleaned by flushing with 2 M H₂SO₄ 5 times and then 5 times with water. The tube was then filled with a saturated KI solution for 15 min before it was dried by flushing with air. 1 L of air from the heated flask containing hexanoic acid, o-cresol, m-cresol, indole and 3-methyl-1H-Indole was sucked through sorption tubes at 100 ml/min. Two parallel tubes were used and the air was sucked through the copper tube before it reached one of the tubes. Three sample sets were prepared; one where no air had been sucked through the copper tube before sampling, one where 6 L of the air were sucked through the tube before sampling and one with 7 L sucked through for saturation of the tube. Steel tubes packed with Tenax TA and Carbograph 5TD were used. The tubes were analysed by TD-GC-MS.

Quantifications of hexanoic acid, o-cresol, m-cresol, indole and 3-methyl-1H-Indole were done by comparison with standards for all compounds (a p-cresol standard was used for o-cresol and m-cresol).

Results and discussion

The compounds formed on a steel tube packed with Tenax TA and Carbograph 5TD are shown in Figure 1. It is clear for all compounds that the concentrations increase with higher ozone concentrations.

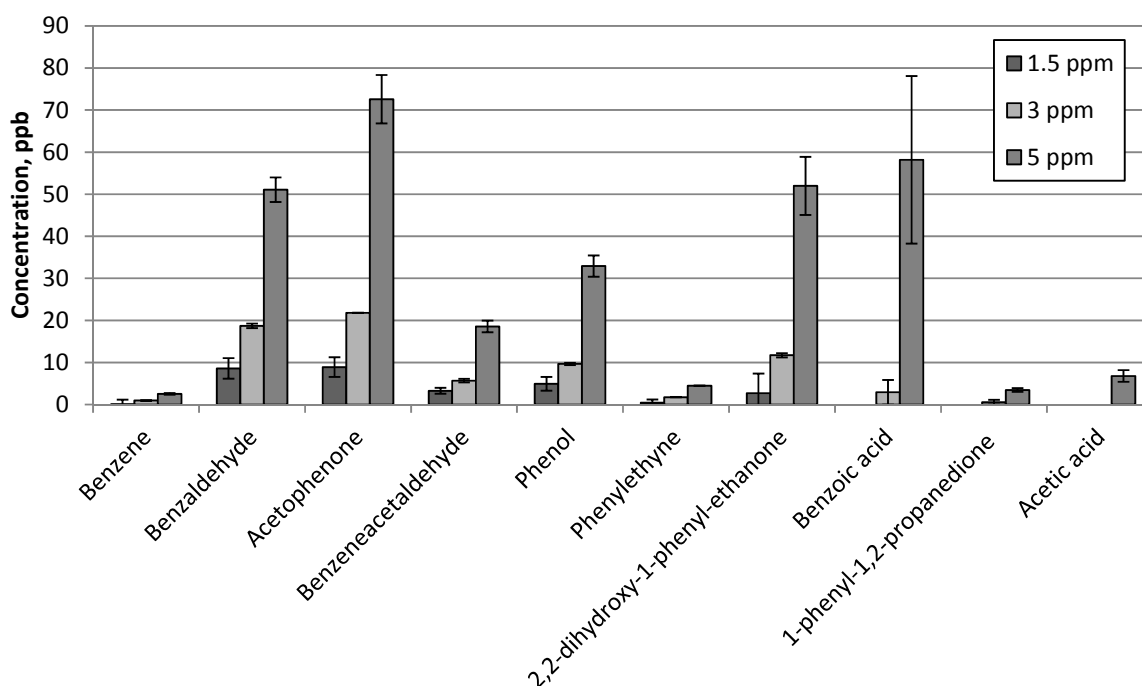


Figure 1. Compounds formed on steel tubes packed with Tenax TA and Carbograph 5TD after exposure to different ozone concentrations.

The formation of compounds when different tubes and packing materials were exposed to ozone was tested. The result of this is shown in Figure 2.

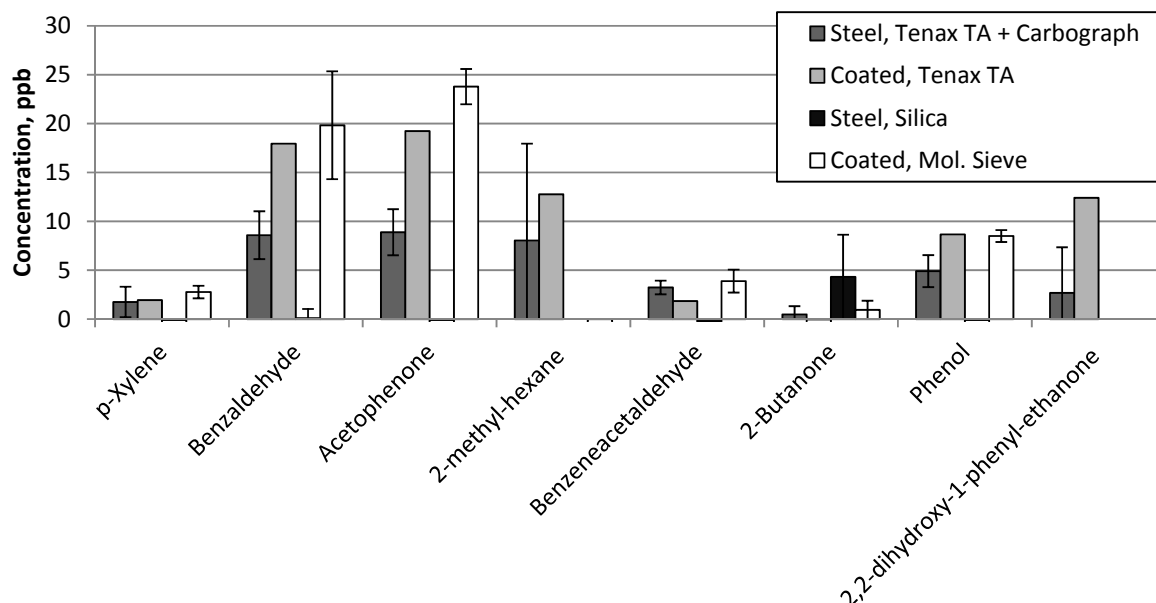


Figure 2. Comparison of compounds produced when different types of sorption tubes are exposed to 1.5-1.8 ppm ozone.

The formation of compounds is not a major problem for the analysis of odour samples as the compounds formed are not important odorants. The effect on samples on the tubes when they are exposed to ozone is of higher importance. Hexanoic acid, o-cresol, m-cresol, indole and 3-methyl-1H-indole were sampled on a steel tube packed with Tenax TA and Carbograph 5TD and exposed to 1 L air containing 1.6-2 ppm ozone after sampling. The recovery of the compounds is presented in Table 1. Hexanoic acid shows high recovery (87 %) while very little indole and 3-methyl-1H-indole (2%) can be detected after ozone exposure. The low recovery of indole can be explained by the high rate constant for reactions with ozone, k_{O_3} of $4.9 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al. 1995), and the same is expected for 3-methyl-1H-indole.

Table 1. Recovery of odorants on a steel tube packed with Tenax TA and Carbograph 5TD after exposure to 1 L air containing 1.6-2 ppm ozone after sampling.

	Recovery (%)	Standard deviation (%)	Average amount on tube (ng)	Standard deviation (ng)
Hexanoic acid**	87	1	275	77
o-Cresol*	67	7	58	56
m-Cresol*	61	12	89	82
indole	2	3	17	16
3-methyl-1H-Indole	2	3	14	17

* Quantification done by the use of p-cresol

** Range used instead of standard deviation due to n=2

The results from the test using a KI coated copper tube upstream the sorption tube during sampling are shown in Table 2. These tubes are not exposed to ozone. This method was shown not to be satisfactory as there is a major reduction in the concentration for all compounds. Sucking 6-7 L of odorous air through the tube before sampling increased the recovery but not to acceptable levels.

Table 2. Recovery of odorants when a copper tube coated with KI is used upstream the sorption tube (tubes are not exposed to ozone).

	No saturation before sampling	Saturated with 6 L before sampling	Saturated with 7 L before sampling
	Recovery (%)	Recovery (%)	Recovery (%)
Hexanoic acid	14.1	19.6	51.8
o-Cresol	11.4	16.8	62.0
m-Cresol	21.5	39.8	45.0
Indole	50.9	58.8	64.6
3-methyl-1H-Indole	75.1	80.3	90.3

Leading air containing ozone through the KI coated copper tube and measuring breakthrough of ozone was tested (data not shown), but ozone was rapidly measured in the outlet which also shows that this method is not suitable for removal of ozone before sampling.

Other methods for removal of ozone, e.g. addition of ethylene as O₃ scavenger, should be tested to improve the method of sampling on sorbent tubes in the outlet of the NTP system.

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