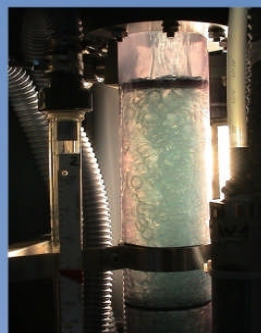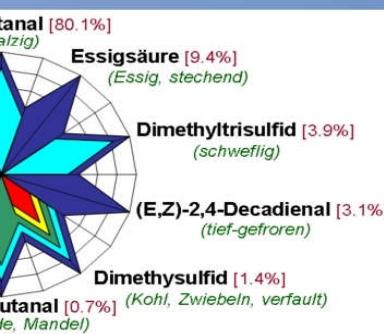Kai Freudenthal

Odour Control By Selective Absorption Using Solubility Agents And Washing Oils

TUHH
Technische Universität Hamburg-Harburg

aww
Institut für Abwasserwirtschaft
und Gewässerschutz

Odour Control By Selective Absorption

Using Solubility Agents And

Washing Oils

Vom Promotionsausschuss der
Technischen Universität Hamburg-Harburg
zur Erlangung des akademischen Grades

Doktor-Ingenieur (Dr.-Ing.)

genehmigte Dissertation

von

Kai Freudenthal

aus
Hamburg

2009

I

Gutachter

    Prof. Dr. Ing. Gerhard Matz   (Prüfungsausschussvorsitzender)

    Prof. Dr. Ing. Ralf Otterpohl   (1. Gutachter)

    Prof. Dr. Dr. h.c. Frerich Keil   (2. Gutachter)

Tag der mündlichen Prüfung: 4. September 2009

Meinen Eltern gewidmet

als Dank für

Ihre Liebe und Fürsorge

Prolog

Ja, mach nur einen Plan
Sei nur ein großes Licht!
Und mach dann noch 'nen zweiten Plan
Geh' n tun sie beide nicht.

Denn für dieses Leben
Ist der Mensch nicht schlau genug.
Doch sein höh' res Streben
Ist ein schöner Zug.

(Bertolt Brecht, 1928)

Danksagung

Ich möchte mich bei Prof. Ralf Otterpohl, meinem Doktorvater, bedanken für seine Unterstützung dieser Arbeit und die große Freiheit die er mir gab bei der Nutzung der Einrichtungen des Institutes. Joachim Behrendt bin ich für die Betreuung und für die vielen fachlichen Diskussionen zutiefst dankbar. Seine Idee der Nutzung von Löslichkeitsvermittlern zur Geruchsstoffabscheidung war die Grundlage für diese Arbeit.

Prof. Ivan Sekoulov bin ich sehr dankbar, dafür, dass er mich mit meinem ersten kleinen Forschungsprojekt beauftragte und damit und mit seinen vielen Anregungen meinen Spaß an der Forschung geweckt hat.

Der Kollegin und den Kollegen vom Institut für AbfallRessourcenWirtschaft Dr. Kim Kleeberg, Dr. Jan Streese und Dr. Mirko Schlegelmilch möchte ich hiermit herzlich danken für die vielen fachlichen Diskussionen und Hilfestellungen und für die Durchführung Gasanalysen mit dem Olfaktometer und dem SPME/GC/MS System. Auch bei allen anderen Hochschul-Kollegen vom Verbundprojekt bedanke ich mich für die gute und kreative Zusammenarbeit. Mein Dank gilt auch allen Projekt-Partnern von den Lebensmittelbetrieben, die durch ihre Unterstützung entscheidend zum Nachweis der Umsetzbarkeit vor Ort beigetragen haben.

Mein besonderer Dank gilt dem Bundesministerium für Bildung und Forschung (BMBF) für die Förderung des Forschungsverbundprojekts und der Hamburger Behörde für Stadtentwicklung und Umwelt für die wohlwollende Unterstützung dieses Projekts.

Meinen Kolleginnen und Kollegen vom Institut für Abwasserwirtschaft und Gewässerschutz danke ich für die schöne gemeinsame Zeit am Institut und für die tapfere Unterstützung als Probanden bei zahlreichen Geruchsmessungen. Bei Andreas Wiebusch möchte ich besonders bedanken für die vielen kleinen und großen Hilfestellungen, wie z.B. dem Programmieren des Steuer- und Kontrollsystems für die Elektronische Nase.

Den Studentinnen und Studenten, die ich bei ihren Diplom- oder Studienarbeiten betreuen durfte und die mit ihren Ergebnissen direkt oder indirekt meine Arbeit unterstützt haben, möchte ich mich herzlich bedanken. Dies sind Bernd Klingner,

Abstract

Absorption is one of the most widely applied techniques of odour control carried out with gas scrubbers. Odorous substances, called odorants, typically have moderate solubility in water. So effectiveness of scrubbers using water as absorbent is limited.

Aim of this work is to identify alternative absorbents and solubility agents in aqueous solutions, which improve absorption of odour substances from waste air. In experiments Henry coefficients of chosen odorants in alternative washing liquids were determined. Some oils and aqueous solutions with humic substances were found to have much higher solubility of many gases than water has. Applicability of humic substances as solubility agents in bioscrubbers were proofed and verified in several series of measurements. Results from laboratory tests are presented using synthetic waste gases. Good reduction rates of dimethyl sulphide were measured. Reduction rates of the bioscrubber with humic substances were between 34 and 50% in average higher than those of conventional bioscrubbers. As a second step a pilot plant with two bioscrubbers was built-up for testing humic substances for treatment of concentrated waste air from product dryers on site a starch factory. Here conventional bioscrubber achieved reduction rates above 90% during times with high raw gas concentrations (>250,000 OU/m³) in a single step modus. Improvement by humic substance was only between 7% and 10%. Then a test was done in a series modus of two bioscrubbers. While the reduction rate of the second step was about 35% by a conventional bioscrubber it could be increased to 80% by usage of humic substances. A permanent cleaning performance between 94 and 99% was achieved with this combination. Within on site experiments the benefits of an electronic nose for online monitoring of scrubber performance could be demonstrated.

A laboratory air scrubber using oils as absorbents has been assembled to examine cleaning performance with synthetic and real exhaust air streams. Results with the absorbents HC10, an alcane fraction, and tetraethylene glycol dimethyl ether (TEGDE) are presented. Kinetic constants were determined and used for scale-up

calculations to compare required scrubber sizes of a conventional bioscrubber, a bioscrubber with humic substances and an oils scrubber with oil regeneration by steam stripping.

Additionally a screening test is developed as a tool of low expense for testing washing liquids on industrial waste gases. A new parameter named the "relative odour ratio $OR\%_i$", is introduced, which describes the potential contribution of a single odorant to the cumulative odour impression of a gas sample. This parameter is used to identify key compounds of odorous waste air emission and to explain separation effects and selectivity of absorbents. The screening test is verified by experiments at a chocolate factory, a fat and oil refinery and a starch factory.

Content

1

3

Table 1: Parameters

a	volumetric surface a of a column packing	[m²/m³]
A_C	cross sectional area	[m²]
c	constant	[-]
c_M	mean logarithmic gas concentration	[mg/m³] or [OU/m³]
c_1	raw gas concentration	[mg/m³] or [OU/m³]
c_2	purified gas concentration	[mg/m³] or [OU/m³]
D_C	diameter of absorption columns	[m]
F	gas load factor	[Pa$^{0.5}$]
f	concentration factor	[-]
G	Gas mol flow	[kmol/h]
$H_{i,j}$	Henry Coefficient	[bar]
H_C	height of absorption columns	[m]
HETS	height of a theoretical separation stage	[m]
HTU_{OG}	height of transfer units based on overall gas concentration calculation	[m]
I	intensity	[-]
k_1	kinetic constant	[h^{-1}]
K_H	air / water distribution coefficient	[(g/l$_{air}$)/(g/l$_{water}$)]
K_{OW}	octanol / water distribution coefficient	[-]
k_G	overall mass transfer coefficient	[kmol/(h*m³]
$k_G a$	overall gas-phase mass-transfer coefficient	[kmol/(h*m³]
K_H	distribution coefficient	[(g/l$_{air}$)/(g/l$_{water}$)]
L	liquid flow, absorbent mole flow	[kmol/h]
m	slope of the equilibrium line	[-]
M	mass flow	[kg/h]
NTU_{OG}	number of transfer units based on overall gas concentration calculation	[-]
NB	"Nussbeize", trade name of humic acids sodium salt humic substances	[-]
N_t	number of theoretical separation units of absorption	[-]
$N_{t,reg}$	number of theoretical separation units of stripping	[-]
P	operating pressure	[bar]
p_i	vapour pressure/ partial pressure of component i	[bar]
p_i^{sat}	vapour pressure of the pure component i	[bar]
POW	trade name of humic acids potassium salt	[-]
$Q_{g,max}$	maximum volumetric gas flow	[m³/h]
Q_G	volumetric gas flow	[m³/h]

Q_L	volumetric liquid flow	[m³/h]
R	Universal Gas Constant (R = 8.314 J / (mol * K)	[J/(mol*K)]
r	degradation rate	[mg/(m³*h)]
S_i	stimulus	[-]
S	stripping factor	[-]
T	temperature	[K] or [°C]
V_R	reactor volume	[m³]
w_g	gas flow velocity	[m/s]
y_1	raw gas concentration	[ppm]
y_2	purified gas concentration	[ppm]
x_1	absorbent effluent concentration	[ppm]
x_2	absorbent feed concentration	[ppm]
x_i	molar fraction of component i in liquid phase	[ppm]
X_1	molar loading of absorbent effluent	[mol/mol]
X_2	molar loading of absorbent feed	[mol/mol]
y_{reg1}	pure stripping gas concentration	[ppm]
y_{reg2}	loaded stripping gas concentration	[ppm]
Y_1	molar raw gas loading	[mol/mol]
Y_2	molar purified gas loading	[mol/mol]
y_i	molar fraction in gas phase	[ppm]
y_{stripp}	stripping gas concentration	[ppm]
y^*	theoretical gas concentration in equilibrium with the liquid concentration at position	[ppm]
$(\Delta y)_m$	logarithmic mean gas concentration	[ppm]
η_{abs}	separation efficiency of absorption	[%]
η_{reg}	regeneration efficiency	[%]
η_a	area efficiency factor	[m²/m²]
ρ_g	gas density	[kg/m³]
ν_v	volumetric solvent ratio	[(m³/h)/m³/h]
ν_m	molar solvent ratio	[mol/mol]
abs	Index of absorption process / unit	
c	Index of column	
reg	Index of regeneration process / unit	

1 Introduction

Odour control is one of the latest fields in the area of environment protection. In Western Europe the impacts of emissions and noise from industrial and domestic sources and from traffic have been reduced within the last decades significantly by extensive work in the area of environment protectio. Technical progress and legislation worked hand in hand to achieve this. Due to the decrease of emissions and a decreasing acceptance of annoyances at the same time, industrial odour emissions became a subject of public awareness and of political concerns. Additionally new odour problems arose when residential areas were built-up or expanded in areas directly adjoining to industrial sites which emit odorous exhaust gases. This development increased the number of people sensing odours and therefore it increased the frequency of annoyances and complaints. In Germany as a result of a high population density the distance between residential areas and industrial sites is usually less than 1000 m. Therefore, in some areas, there are a lot of complaints about odour annoyances (Both, 1995).

Another factor is the psychological perception of odours. In the past employees of factories or producing companies often lived in its direct neighbourhood. Generally these people had a more positive relation to the plant and therefore they were more likely to accept specific odour emissions. Due to urban development residential areas have been increased and the percentage of employees in the direct neighbourhood of an industrial plant has been decreased. This lead to a lessened acceptance of odour annoyances by the population and odour could become part of the political agenda.

Odour Control has recently established as a new field of environmental engineering and is developing slowly so far due to several reasons. Firstly, impacts of odour emissions are generally not taken as seriously as other environmental topics like emissions of waste water treatment plants or from waste deposits. Harms due to odour emissions are not easily measurable and may only effect indirectly. Odour annoyance can hardly be proofed to be a reason of health problems. That leads to an impression that odour control is a luxury, only affordable for rich industrial nations. This view is not shared by

people being concerned. Odour annoyances may have no or only little physiological impact, but they have psychological impact and thus can lead to discomfort and illnesses.

Secondly, odour control suffers from the lack of a technical odour measurement. Odours are quantified by olfactometry, when gas samples are evaluated by a collective of people smelling these samples. This means the human nose is the only sensor for odour intensity. Samples cannot be measured directly at the source, but have to be collected on site and transported to a laboratory for analysis and handling of gaseous samples is a known source of measuring failures. In the last years olfactometry has been standardised (DIN EN 13725, 2003) which lead to improved measurements and improved comparability. Odour measurement requires many trained people effort still remains and it can only be carried out by few institutions. Still a certain number of measurements are necessary to describe odour conditions with significant statistical relevance. On the one hand it is difficult for the authorities to control odour emissions from industrial plants due to the described characteristics of olfactory measurement and on the other hand the originator cannot quantify his emissions and therefore he cannot control and optimize the performance of his waste gas treatment unit.

The third handicap of odour control is a broad variety in composition of odorous waste airs and variety in treatment opportunities. Especially treatment of exhaust air from food processing plants is a challenge, due to the variety over time in composition and concentration. In food and beverage industry many production and conditioning processes are associated with a development of odorous substances, called odorants. If these are emitted from premises due to ventilation, odour emissions occur. Mechanical treatments like stirring, mixing and crushing improve the mass transfer into the gas phase but thermal treatment processes are the main cause of odour emissions. These are heating, cooking, roasting, distillation and stripping or drying of products. For example in chocolate production a long-term heating of raw chocolate in open vessels, called conching, is done to remove unwanted odours, bitter components and flavours. After refining edible oils run through a stripping process, where bitter substances are removed and have to be discharged afterwards. On the one hand temperature increase

7

raises the vapour pressure of the volatile components and on the other hand new odour intensive components are formed, e.g. by the Maillard reaction. A high variance of production processes leads to an infinite number of odorants with a broad range of chemical and physical properties. Food production is mostly done in batch processes. Exhaust air changes in concentration and composition during process changes and start-ups and shut-downs. Additionally processing steps of a product vary with different producers and food production plants often produce different products at different times. This leads to unique and varying waste air compositions.

Especially manufacturers and providers of waste air treatment plants are faced with this opportunity, which leads to uncertainties in planning and selling plants and ensuring their cleaning capabilities. This leads to a need for good analytical data, which are not available in most cases. Hence these data are required, the choice of an adapted treatment technique and a proper design become a complex task. Due to the unique composition of the waste air from an individual plant, references from similar production plants can only be used for orientation in the planning process. On-site pre-tests with the individual waste air are necessary to gain a more representative data base. Those tests are also necessary to enable a proper estimate of operational costs. These tests are time consuming and cost intensive, which has a negative impact on this line of business.

Purpose of this work is to contribute to the enhancements of odour control technology, to decrease the effort of monitoring plants operation and the effort of preliminary testing for planning and establishing exhaust air treatment plants. Results of this work were gained within the cooperation research project "Innovative methods of determination and reduction of environment polluting odour emissions of agriculture and food production industry" (Niemeyer et al., 2006), which was kindly financed by the Federal Ministry for Education and Research of Germany (BMBF). For this project university departments in the fields of waste treatment and waste water treatment, food chemistry, measurement technology, thermodynamics and biotechnology joined forces with manufacturers of waste gas treatment plants, manufacturers of process components and of measurement technologies, representatives of food production plants and of the

authorities. Project aims were investigations and improvements in measurement and treatment of odours emissions by merging of different disciplines.

2 Task

Task of this work is the investigation of absorbents and solubility agents in water, to quantify their ability to dissolve typical odorants and to test their applicability in physical scrubbers or bioscrubbers to industrial waste air on site. Developed methods with alternative liquids should be compared to the technology of conventional bioscrubbers, which represents the state of the art in odour control.

3 Method

In this work solubility agents will be tested for usage in bioscrubbers. Agents should be selected which improve the solubility and selectivity to odorants and which allow a biodegradation at the same time. Substances will be investigated which are reported in other contexts as having solubility improving effects like humic substances, which have been investigated in the field of water treatment (Bollag and Myers, 1992) or dimethyl sulfoxid (DMSO), which was used to enable a biological treatment of mineral oil emulsions and polycyclic hydrocarbons (Cuno et al., 1995).

Another approach of this work will be the investigation of washing oils which offer high solubility to organic gas pollutants and which enable a separation and disposal of the separated compounds at the same time. Here liquids should be chosen which have been used in gas scrubbers in the field of solvents recovery. These absorbents are HC10, a high boiling alcane fraction (Kalina, 1997); tetraethylene glycol dimethyl ether (TEGDE), propylene carbonate (PLC) and bis(2-ethyl hexyl) adipate (BEHA) (Weisweiler et al., 1992; Schmitter, 1993; Winterbauer, 1994; Kalina, 1997). Silicone oil will be investigated as a reference since it has been investigated for usage in bioscrubbers (Hekmat and Vortmeyer, 1999; Schippert, 1994).

9

Promising washing liquids will be tested within this work in three steps. Firstly, their ability to solute odorants should be quantified by determination of Henry coefficients in combination with chosen odorants. Secondly, solubility agents will be tested for usage in bioscrubbers within laboratory experiments using synthetic waste air with a single odorant. Experiments will be carried out to test washing oils in physical scrubbers. Here the method of regeneration should be investigated additionally. The method of steam stripping is chosen for an experimental set-up of laboratory experiments.

Thirdly, the most capable liquids should be tested in on site experiments for treatment of industrial waste gases. Thus, kinetic parameters for separation of odorants by bioscrubbers and by oil scrubbers should be determined. These parameters should be used for scale-up calculations and comparisons of methods. Additionally the applicability of a sensor array or electronic nose, respectively for process monitoring of bioscrubbers should be tested. Results will be compared based on olfactometric measurements. Finally a new set-up will be described for testing absorbents on real exhaust gas samples for capability of separating odorants.

4 Theoretical Basics

4.1 Odours and odorants

Psychologists define odour as a sensation caused by an environmental influence. The perception of an odour can be summed up according to Hangartner (1987) with the following simplification [eq. 1]:

Odour perception = odour sensation + odour interpretation **eq. 1**

Odour sensation is the result of a direct interaction of chemical components with the peripheral receptor systems of the nose. It can evoke both positive and negative

feelings (Ohlof 1990). Perception of an odour sensation results from combination of the physiological detection of the stimulus and its psychological procession (Bockreis und Steinberg, 2004). The olfactory sense can detect an unlimited number of chemical compounds at very low concentrations, contrary to the sense of taste, which is limited in differing in sweet, sour, salty and bitter (Ohlof 1990). Humans can distinguish between about 10.000 different odour qualities (DIN EN 13725, 2003). Connection of odour perception and the stimulus caused by a certain odour concentration in air can be described with the Weber-Fechner law or the psycho-physical measure formula, respectively (eq. 2). It states that the perceived intensity I is proportional to the logarithm of the intensity of the stimulus S_i. This law is valid for medium stimulus intensities and cannot be transferred to extremely high or low stimulus intensities.

$$I = c \cdot \log(S_i)$$ **eq. 2**

Olfaction is the result of a cascade of physiological events that are initiated by the first contact of an odorant with the nasal epithelium and end-up with the conscious perception and fine discrimination of smell (Daniels 2002). First of all, odorants have to be carried by inhaled air into the nasal cavity, where they reach the nasal epithelium. This region contains nerve endings of the fifth cranial or trigeminal nerve. About 70 % of odours are said to stimulate the trigeminal nerve although, in general, they may be less sensitive than the olfactory receptors of the Regio olfactoria. With humans, the olfactory epithelium is located in the roof of the nasal cavity, just below and between the eyes (Figure 1). The olfactory region of each of the two nasal passages in humans is a small area of about 2.5 cm². The olfactory epithelium is developed in order to allow the olfactory transduction upon the contact with an odorant. The olfactory epithelium is made up of three kinds of cells: supporting cells, basal cells, and receptor cells (Figure 2). The supporting cells produce the mucus which covers the olfactory epithelium. The basal cells are stem cells. They divide regularly producing fresh receptor cells to replace those that die. The receptor cells are ciliated sensory neurons embedded into the layer of supporting cells. The cilia of the sensory neurons are immersed in a layer of mucus.
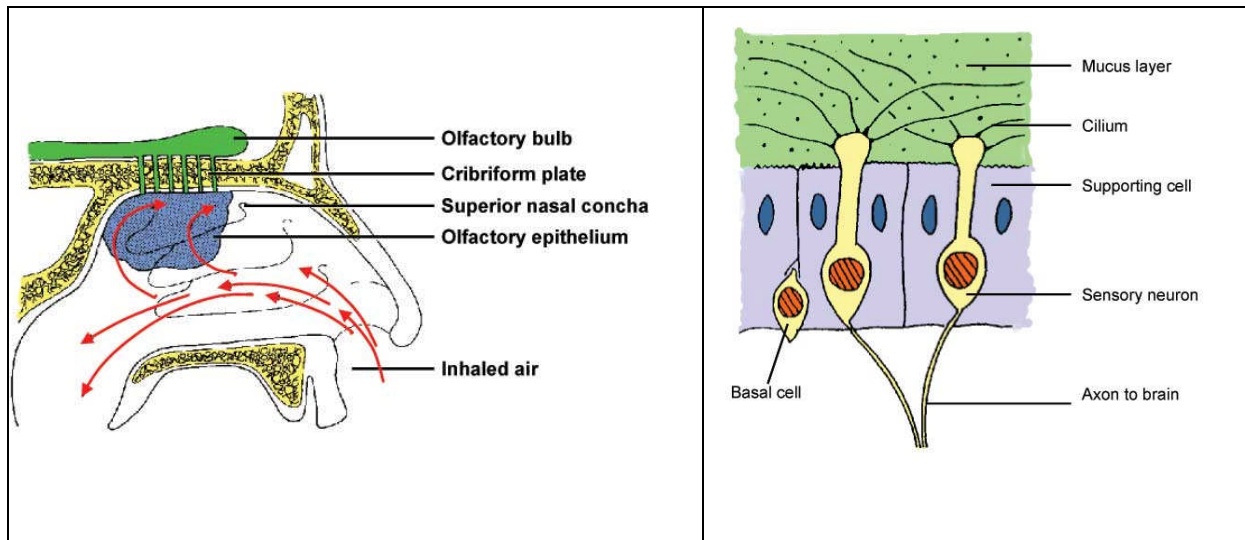
Figure 1: Functional anatomy and structure of the human olfactory system

Figure 2: Structure of the olfactory epithelium (both Fig. in Daniels, 2002)

At the opposite side the neuronal cells form axons that send their signal to the brain via glomeruli in the olfactory bulb, mitral cells, and the olfactory nerve tract. Humans possess approximately 50 million primary sensory receptor cells each having 8 - 20 cilia. Interestingly, the sensory neurons of dogs which have a more developed sense of smell than humans have about 100 cilia. The odorant receptors are located in the cilial membrane. They contain 7 helical trans-membrane regions and are linked to a G-protein. However, before reaching the receptor, an odorant molecule has to dissolve in the mucus layer around the cilia and diffuse to the site of action. Diffusion of odorants through the mucus layer depends on their physical and chemical properties. So far it is not fully understood how the enormous repertoire of odours is detected. However, in the light of current research it is obvious that odour perception requires a combinatorial strategy. Most odour molecules are recognized by more than one receptor and most receptors recognize several odours, probably related by chemical property (Daniels 2002).

4.2 Odorants

Classifying a substance as an odorant is determined empirically. Odour is not a physical or chemical property of the substance and is not deducible from its physical or chemical properties. It depends on the detector and his odour perception if a substance causes an odour or not. The most important parameter of odour perception is the odour threshold, which is the concentration of an odorant at which it can be detected by 50% of human beings. Since this value is determined by individuals, odour thresholds found in literature can vary widely for the same substance. Olfactory thresholds used in this work are taken from Gemert (1977), Devos (1990) and Rychlik (1998).

According to Frechen (1988) the following statements on odorants can be derived from the physiology of odour sensation. Firstly, odorants should be volatile (molecular weight up to 350 g/mole), so that they can be transported in the gas phase and reach the olfactory epithelium as the main area of odour sensation in the human nose. Secondly, odorants should be hydrophilic and lipophilic at the same time, so they can make their way through mucus and adipose tissue to reach the olfactory epithelium. Consequently the solving behaviour of odorants in water and organic liquids has a direct influence on their detectability.

Shape and size of the molecular structure determine the odour quality. According to the "stereo chemical theory of olfaction" (Amoore, 1970) an odour is only detected if the stimulus meets the complementary detector site of the receptor system, which is described by the lock and key principle. So the molecule's shape has an important influence on the odour sensations in a way that even isomeric substances can cause different odour sensations (Schön, 1996). According to Ohloff (1990) chemical reactivity of a molecule is not required for its odorous properties. The presence of a functional group is not necessary for stimulating a receptor cell, but many odorants possess those groups. These functional groups are residues of carbonyl groups, esters, hydroxyl groups, alcoxy groups and hetero-atomar analogues. Odorants are mostly organic compounds. There are only limited numbers of inorganic substances that cause odours.

The most important are hydrogen sulphide and ammonia. In Table 2 examples of industrial and agricultural emittents and typical odorous components of these industries are listed.

Table 2: Typical odorous components and their sources (Sattler and Feindt, 1995; Cheremisinoff, 1993)

Odour emitter	typical odorants
livestock farming	ammonia, hydrogen sulphide, amines, aldehydes, thioles, disulphides, esters, alcohols
rendering	ammonia, hydrogen sulphide, amines, aldehydes, thioles, disulphides, esters, alcohols
coffee / cacao roasters	acetaldehyde, diacetyl, amines, fats , thioles, ammonia, furan, furfurol, methyl ethyl carbinol, hydrogen sulphide
laminated paper dryers	acetone, formaldehyde, cresols, methanol, phenol
latex lamination machines	formaldehyde, thioles, ammonia, amines, styrol, hydrogen sulphide
foundries	amines, methylene chloride, formaldehyde, ammonia, phenol, acetone, methanol, cracking products
biological wastewater treatment plants	amines, ammonia, formaldehyde, thioles, hydrogen sulphide
mineral oil refineries	SO_2, H_2S, NH_3, HC, organic acids, aldehydes, thioles,
inorganic chemical industries (e.g. fertilizer)	NH_3, aldehydes, SO_2, H_2S
organic chemical industries (e.g. organic chemicals, plastics, textiles, soap, detergents, paints etc.)	NH_3, aldehydes, SO_2, thioles, organic acids, hydrocarbons

4.3   Odour measurement and analysis of odorants

Since odour is a sensory perception, it is impossible to measure odour by technical means. Per definition odour can only be sensed with the human nose, so it can only be quantified via the olfactometer, where the sensors is the human nose. An olfactometer is a dilution apparatus which mixes samples of odorous air in specific ratios with odour free air for the presentation to panel members. With the dynamic olfactometer the dilution is continuously produced. This method, which is widely used in Europe and other countries, was standardized in 2003 after extensive examinations (DIN EN 13725). With this method the dilution ratio is permanently reduced during measurement until the panellists sense an odour impression. Result of olfactometric measurement is the odour concentration given as a multiple of one odour unit, which represents the amount of odorants present in one cubic meter of odorous gas under standard conditions at the 50% detection threshold of the panel. This measurement technique requires a lot of manpower and has a low sample throughput only. Additionally, the accuracy of this method is limited by the influence of individual sensitivity, although panellists are trained and calibrated for an olfactometric measurement. This is shown by several round robin tests. Consequently, this technique is unsuitable for frequent measurements or monitoring.

Combined analytical methods consisting of a gas chromatograph (GC) and a flame ionization detector (FID) or a mass spectrometer (MS) as a mass selective sensor are often used for a of exhaust air. With these techniques concentrations of single gas components can be measured but not the odour concentration. Combined with a high-performance enrichment of samples these systems are useful for discrete recording, identification and partly for quantification of single substances. However, no conclusion can be drawn based on identified substances regarding to olfactory sensation, due to the variety of possible interactions of odours. The only analytical possibility to determine correlations of the concentration of single substances with the total odour concentration of a sample is the addition of a sniffing port to these systems (e.g. GC-MS-sniffing port), where the eluate of the GC is evaluated by a human nose in parallel. However, combined methods are reserved to scientific purposes due the high demand on manpower and need for scientific interpretation.

15

Another analytical technique is the so called electronic nose, which is an instrument, consisting of an array of electronic sensors with partial specificity and a pattern-recognition system, capable of recognising simple or complex odours. The sensors, which are mostly semiconductors, get into contact with components of the gaseous sample, which causes a difference in the electronic attributes of the sensors and provides a specific set of measurements. This data pattern is compared with stored patterns for known materials by a pattern-recognition algorithm. This method enables the discrimination of different odours just by a relatively small number of non-selective receptors. By that, an electronic nose uses the same principle as the human olfactory system. So far the application of electronic noses is restricted to the detection of trained odours (Gardner and Bartlett, 1994). With this technique it is impossible to quantify or identify unknown odours or odorants. However, in individual cases the application of electronic noses is proved to be a useful supporting measuring technique (Ungethüm, B. et al., 2003). The still existing lack of a technical odour measurement leads to a hindrance of the branch of waste gas treatment technology (Freudenthal, 2004a), because nuisances cannot be identified and quantified reliably and the effectiveness of treatment facilities can only be monitored and judged inadequately.

4.4 Characterisation of Odour Emissions – Odour Register

Planning of an effective odour control requires a reliable data set of the odour emissions, which can only be gained by repeated measurements and a detailed characterisation of the odour sources. A systematic approach, called the Odour Register („Geruchskataster"), is developed and described by Schlegelmilch et al. (2004b). Based on this method all odour sources of a site or a facility should be

- registered: investigation of all sources based on local conditions like buildings, plants etc.

- characterised: source type (diffuse or particular), flow, concentration, physical properties (e.g. temperature, moisture) etc.

- validated assessing the sources and defining the need and scope of additional measurements

Based on findings of a systematic evaluation like this, treatment concepts can be worked out as a combination of preventive and reactive measures.

4.5 Methods of preventing formation of odorous emissions

The most effective odour control is preventing a formation of odorous waste gases. Generally, preventive measures are less cost-intensive because they are often subject of process management instead of technical solutions. Typical measures are (Cheremisinoff, 1993):

- general cleanliness
- good housekeeping
- proper operations
- spill prevention
- substitution of raw material
- raw material handling and storage
- process changes or modifications
- replacement of compressors with single mechanical seals by double mechanical seals or magnetic drive compressors
- coverage of storage vessels e.g. by floating roofs

4.6 Odour reduction by waste air treatment techniques

4.6.1 Choice of methods

Methods of odour control differ in separation efficiencies, gas flow capacity, size of equipment and costs, in terms of investment and operating costs. Operating costs are mainly caused by energy consumptions of gas blowers, which have to overcome pressure losses, which are caused by the gas stream passing through the equipment. Other operating costs, which can be significant, are caused by energy consumption by additional equipment, e.g. by heating or liquid pumps, depending on the method. In the following chapter, proofed methods of air treatment for odour control are shortly described and compared.

4.6.2 Absorption

Absorption is a process of material exchange, where one or more components are separated from a gas mixture by solving in a liquid, called absorbent. Remaining components in the gas mixture behave as inerts towards the solvent. The process of solvent regeneration by separating the dissolved components from the solvent is done by stripping or rectification. Physical absorption is based on the solubility of gas components, here the odorants, in a washing liquid. If the washing liquid reacts with the gas components and forms a stable compound the process is called chemisorption. Basics of absorption, types of absorbents and devices for applications are presented in chapter 4.7.

Absorption techniques are widely spread in the field of odour control. Since most odorants are organic, they are normally very well biologically degradable. Consequently, bioscrubbers are often used for this purpose. This technique combines an effective way of regenerating the washing liquid and a cost-saving disposal of the separated odorants. On the other hand, the effectiveness of bioscrubbers using water as absorbent is limited by low solubility of most odour substances in water. Therefore a combination of a bioscrubber with a downstream biofilter is often used (Heining, K., 1998). Hardly water soluble substances pass the scrubber and are separated in the biofilter by adsorption to biomass. The major disadvantage of this combination is the huge area consumption of the biofilter. One possibility for improving the solubility of odorants in water is the addition of organic liquids like silicone oil (Hekmat and Vortmeyer, 1999; Schippert, 1994) or high-boiling alcanes (Schraeder, 1993) to the water phase. Beside an improvement in absorption, these processes showed two disadvantages. Firstly, during separation the presence of two immiscible phases lead to an addition mass transfers restriction, which leads to a longer retention time and larger reactor volumes. Secondly, the applied oils attach to the biomass contained in the system; which produces an oil sludge that has to be disposed for high costs. Therefore, this combination was not successfully established on the market.

Another area of waste air treatment is the solvents recovery from waste air. In this area organic high-boiling absorbents, like tetraethylene glycol dimethyl ether (TEGDE),

propylene carbonate (PLC) and bis(2-ethyl hexyl) adipate (BEHA), were successfully tested (Kalina,1997; Weisweiler et al., 1992). An application to odour separation has not been reported jet and will therefore additionally be tested within this work. Newer studies (Grigull et al., 2002) examined the suitability of high-boiling substances from renewable raw materials like rapeseed methyl ester (biodiesel) or methyl oleate (leading component of rapeseed methyl ester) for solvent separation. Aim of the study was to decrease operational costs by using lower-cost absorbents. By determining the activity coefficient it has been proofed that these new absorbents have solving properties comparable to those of established absorbents. Since rapeseed methyl ester is insufficiently stable against oxidation at higher temperatures, which would be necessary for regeneration, a technical implementation was not pursued further.

Table 3: Odorants and applied absorbents (Cheremisinoff, 1993; Lazaridis, 1990)

Target components	washing liquids
organic solvents	alkaline solutions
organic acids	sodium hydroxide (NaOH)
aldehydes	bisulphite solutions
thioles	sodium hydroxide (NaOH)
	hydrochloric acid, hydrogen peroxide
hydrogen sulphide (H_2S)	amine solutions
	oxidizing chemicals: H_2SO_4, H_2PO_5, NaOCl, NaOH, $KMnO_4$
	sodium hydroxide (NaOH), lime water, caustic soda solution
thioles, amines	chlorine (gas)
amines + ammonia-based compounds	diluted acid solution, sulphuric acid
H_2S, thioles	diluted caustic solution

Chemical absorption is mainly used for selective separation and recovery of one or more gas components (Table 3). In this context, odour reduction is not the main focus, although target components may be very odorous like hydrogen sulphide, thioles and

amines. Washing liquids are typically acids or bases. Examples of applications are found in the textile industry or in coal fired power stations.

Cheremisinoff (1993) reports of a multiple-step scrubber installed in a fishmeal plant, which is a good example of purposeful choice of washing liquids related to specific odorants. The application consists of a packed cross-flow scrubber with three different scrubbing liquids. In the condenser, as the first step, the hot gases from driers are cooled down with seawater. Herewith, particulate matter and well water-soluble compounds are separated. Then in the reaction section, raw chlorine gas is dosed to oxidize less soluble substances, like thiols, amines etc., to decrease their odorous character and to improve their solubility. In the second scrubber section a diluted acid is applied to absorb amine and ammonia-based compounds and in the third section a diluted caustic is used to absorb H_2S, thiols and not reacted chlorine.

4.6.3 Adsorption

Gas adsorption is a process where one or more components are removed from a gas stream through adherence to a solid surface. The attractive force holding the gaseous molecule at the surface may be either physical (physical adsorption) or chemical (chemisorption) by nature. Adsorption finds wide application in the field of odour reduction. Physical adsorption is a completely reversible process which occurs as a result of physical attraction between gas molecules and molecules of the solid surface. If the gas-solid intermolecular attraction is greater than the intermolecular attractions in the gas phase, then the gas will condense on the solid surface, even though its pressure is lower than its vapour pressure at the prevailing temperature. Therefore, small concentrations of contaminates can be removed from gas streams by adsorption.

In industrial applications, three types of adsorber are commonly used for obtaining effective gas-solid contact. These are the fluidized bed, the continuous moving bed, and the unsteady-state fixed-bed. The latter is by far the mostly applied type in the field of odour control. In this system, the contaminated gas is passed through a stationary bed

of adsorbent. The bed is operated until the contaminant level in the effluent begins to rise, which is called a break through. Then the adsorber must be exchanged and regenerated. Generally, gas flow is diverted to a second parallel bed to allow a continuous operation during change and regeneration of adsorbent. Adsorbent beds range in size and form from disposal cartridges to dumped beds contained in large vessels. Unsteady-state fixed-bed adsorbers have the advantage of being relatively simple and economical, particularly at low adsorbate rates. Since the bed is stationary, the adsorbent is handled only during replacement. Gas flows rates through fixed beds are limited by pressure drop. High flow rates require uneconomically large beds.

The most commonly used adsorbent in odour control is activated carbon. Due to its relatively uniform distribution of surface electrical charge, it is not selective toward polar molecules, so it can be used to remove organic components from waste gas streams with relative high water steam contents. Activated carbon is most effective for adsorbing organic materials which boil at normal ambient temperatures or higher. In general, separation effectiveness increases with increasing molecular weight of the pollutants (Cheremisinoff, 1993).

Another group of adsorbents are siliceous adsorbers, which are silica gels and synthetic zeolithes. These materials are available over a wide range of adsorbent capacities, which is at maximum in the range of highly activated carbon. On the other hand siliceous adsorbers exhibit a greater selectivity for polar molecules than activated carbon. Since metals are less electrophilic than silicon, metal oxide adsorbents show even stronger selectivity for polar molecules. The most commonly used metal oxide adsorbent is activated alumina, used primarily for gas drying.

4.6.4 Biological Odour Control

Most odorants are organic and very well biologically degradable. That is the case especially in the field of waste treatment, farming or food and beverage industry. Therefore, technologies using biological degradation processes are commonly applied

in the field of odour control. Technical devices are bioscrubbers and biofilters. Bioscrubbers provide an effective and cost-efficient way to regenerate the washing liquid while at the same time the separated odorants can be disposed. Only separation efficiency of scrubbers using water as the absorbent is limited due to the low water solubility of many odorants. Biological methods for cleaning exhaust air use both absorptive and adsorptive separation mechanisms. Bioscrubber have the highest sprinkling rates of biological methods, and therefore the highest percentage of absorptive separation. Trickling filters and biofilters have lower sprinkling loads so here the percentage of adsorption is much higher. The focus of this work is on absorption, so experiments are limited on bioscrubbers.
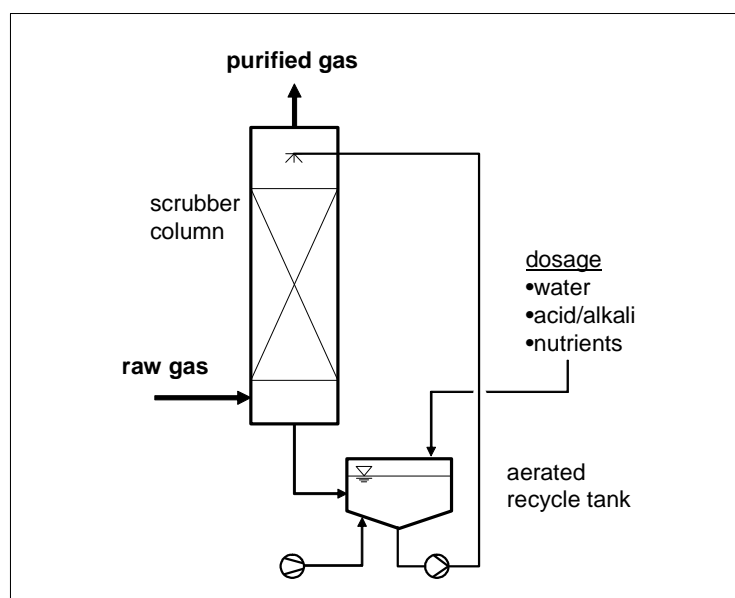
Figure 3: Scheme of a bioscrubber

In bioscrubbers the exhaust air stream to be treated is brought into intensive contact with water. In most cases a scrubber with filling material is used for this purpose in a counter-current operation. Exhaust air passes structured filling material from below, while this material is sprinkled with water from above. The water is diverted at the bottom and fed into a recycle tank, from where it is pumped back again to the head of the scrubber (Figure 3). Due to an intensive contact with water the odorants are solved in the aqueous phase. The filling material offers a high surface (about 200 m²/m³) for mass transfer. Odorants are decomposed by sessile micro-organisms which form a biofilm on the filling material and by suspended micro-organisms in the liquid phase.

Degradation by suspended micro-organisms takes place mainly in the recycle tank, so the recycle tank is aerated in most cases to prevent formation of anaerobic conditions. Detailed descriptions of construction variants like absorptive bioscrubber, trickle-bed reactor or trickling filter reactor are covered in detail by Heining (1998).

Mass transport and biological decomposition in trickle-bed reactors were evaluated by Wagner (1993). He divided the separation process of into the following partial steps:

1. Physical absorption of gaseous contaminants in the liquid
2. Transport of contaminant molecules to the biofilm by convection and diffusion
3. Diffusion and biological decomposition of contaminants inside the biofilm.

Influence of the trickle density on separation behaviour of a biological waste air cleaning process by bioscrubbers, trickling filters and biofilters has been examined by Rutenfranz (1996). He has shown by experiments that hardly water-soluble components of exhaust air, e.g. toluene can be eliminated better with processes with low trickle densities like trickling filters or biofilters. Highly water-soluble substances, e.g. butyl acetate, can be separated better with processes using a high trickle density, like bioscrubbers. It is most likely that separation of oleophile components is better, if a contributing adsorptive effective is higher, which is the case if the trickle density is lower and a direct contact of gaseous components to solid material happens more often.

Conventional bioscrubbers are mostly used for cleaning industrial exhaust air with volume flows of more than 5000 m^3/h and concentrations of pollutants of less 1 to 2 g/m^3 (Schippert, 1993). In case of very high concentrations of pollutants, combustion especially a catalytic combustion may be a more cost-effective alternative. The advantage of bioscrubbers is that they can be easily controlled. Nutrients, which are mainly nitrogenous and phosphoric nutrients, can be added, inhibitants and decomposition products can be discharged with the effluent and fresh water can be added when being needed. The largest bioscrubber in operation cleans 150,000 m^3/h of exhaust air of a printing plant which is loaded with up to 27 kg/h water-soluble solvents (ethyl acetate, ethanol, 2-methoxypropanole). The volume of packing material is 125 m^3.

The aerated recycle tank is designed as a tower-biology (2 x 500 m^3) to save space and to cut down energy expenses for aeration (Schippert, 1993).

4.6.5 Thermal Oxidation

In thermal oxidation techniques, flammable odour components such as hydrocarbons are burned, oxidized, or cracked into water and carbon dioxides. This method is divided into direct incineration and catalyst incineration with and without heat recovery. Heat recovery by an added heat exchanger is mainly used to reduce energy consumption.

Direct incineration is a method where flammable odour components are burned and decomposed by a combustion furnace or by separate afterburners. If the burner characteristics, like mixing behaviour of flame and pollutants, combustion temperature, and retention time are properly designed, this method is very reliable. Although this method requires high energy consumption and emits an odour of combustion exhaust gas, it is a method often applied to odorous waste gases (Yamamoto et al., 2005).

By catalyst incineration, flammable odour components such as hydrocarbons are burned at lower temperatures with an activated catalyst. This method can achieve stable deodorisation effects under relatively lower temperatures of 250-300°C. If cold odorous gas is treated, catalyst temperature needs to be elevated using a furnace or electrical heater. Oxidation catalyst such as Pt, V_2O_5, Co, Mn, Fe, Ni, and others such as CO_3, MnO_2, FeO_3, and NiO are used, held in ceramic pellets or ceramic honeycombs. The main problem of this method is poising and fouling of the catalyst. A system with a three-way catalyst is successfully used for odour control in a painting factory, a sewage disposal plant, and for diesel engine exhaust gas (Yamamoto et al., 2005). Combined systems with catalyst incineration and pre-treatment by adsorption using activated carbon or zeolithe adsorption are applied. The pre-treatment focuses the removal of mist, which is difficult to oxidize and seemed to transport odours components, so that its removal was important to achieve high performance (Yamamoto et al., 2005). At catalytic cracking facilities, combustion is a standard method to remove

sulphides and amines from operations and to convert them into oxides of sulphur and nitrogen. Problems occur when combustion is incomplete and aldehydes are formed which cause a new significant odour. At refineries flare combustion is used to oxidize thioles and hydrogen sulphide to avoid odour generation. In case there are gaseous compounds remaining not oxidized, then nascent oxygen is added to ensure complete combustion and prevent odour emission (Cheremisinoff, 1993).

4.6.6 Radicals Oxidation methods

Several odour control techniques are developed within the last years, which are based on the formation of radicals from air molecules such as active Oxygen (O) or Nitrogen (N), hydroxide ions OH, ozone (O_3) and H_2O_2, which oxidize and decompose organic odour components, when being exposed to contaminated waste gas. Investigations of this method just started, so that reliable data are rare, although some of these methods are several times applied. The non-thermal plasma method, the ozone injection and the photocatalysis belong to this group.

Non-thermal plasma or non-equilibrium plasma describes an electrical neutral and chemical activated ionization state, which is induced by an AC high voltage or a pulsed high voltage at atmospheric pressure and ambient temperature. This technology was commercialized as the pulse corona-induced plasma chemical process (PPCP) for treatment of hazardous air pollutants. Reporting of performance data of this method is limited to laboratory tests so far. Yamamoto (2005) reports of a laboratory-scale application for waste gas treatment of a sewage disposal plant, a refuse disposal plant, and a livestock farm. Okubo (Okubo et al., 2001) found reduction rate > 95%, when being applied to a dry air flow containing 100 ppm acetaldehyde in a test series.

At the method of ozone injection, ozone radicals are produced and supplied into odorous air. Other names of this technology are radical injection or indirect plasma method. This method is commercially applied to indoor air treatment. Proofed application of ozone for oxidation of organic compounds in an aqueous phase can be

found in the field of waste water treatment (Gulyas, 2003; Libra et al., 2000; McKetta, 1999).

An example of photocatalysis for odour control is applied in commercial indoor electric air cleaners using the photo-catalyst (TiO2) (Yamamoto et al., 2005). Here, an inverter lamp emits an ultraviolet ray on the photo-catalyst, which becomes a strong oxidation power. By contact with the catalyst, hydroxide ions (OH-) from air moisture are transferred to OH radicals, which are very unstable and chemically reactive. These radicals are used to oxidize organic odour components. A disadvantage of the radicals oxidation methods in the field of odour control is the risk when being applied to an unknown or a varying gas composition, that oxidations products may be formed, which even have a more intensive odour than the original substances.

4.6.7 Comparison of methods

Table 4: Methods of odour control

Method	Preferred raw gas conditions	Advantages	Disadvantages
physical absorption	T: low H: tolerant	• high-volume flows • low concentrations can be treated • separation of particulate matter possible • combinations of different liquids in a multiple-step system possible	• no complete separation possible (equilibrium) • may need secondary-treatment
chemical absorption	T: low H: tolerant	• low off-gas concentrations are reachable • regaining of gas components possible	• only applicable, if one or few known target compounds have to separated • odour control not main focus
bioscrubber	T: medium H: tolerant	• low operational costs • change of odour by degradation (untypical odour) • no critical waste to be deposited • high acceptance at authorities (operational permit)	• odorants need to be water-soluble and biological degradable • deactivation by poison or inhibition substances possible • risk of odour effect from degradation products

Method	Preferred raw gas conditions	Advantages	Disadvantages
biofilter	T: medium H: tolerant	• long-term operation without shutdown possible (2-8 years) • very low operational costs • changed odour by degradation (untypical odour) • no critical waste to be deposited • high acceptance at authorities (operational permit)	• large areas required • odorants need to be biological degradable • deactivation by poison or inhibition substances possible • risk of odour effect from degradation products • required continuous and equalized water feed
adsorption	T: low H: low	• complete separation possible • regaining of gas components possible • gases with high water steam content can only be treated by non-polar adsorbents	• limited to small flows • critical to particulate matter • regeneration of adsorbents limited (waste disposal)
thermal oxidation	T: high H: low	• high concentrations can be treated • high temperatures can be treated	• limited to substances, which can be oxidized • incomplete combustion may cause new odours • high investment costs • very high energy consumption (lower if concentrations are higher) • explosion risk, if gas has explosive concentration
catalytic oxidation	T: high H: low	• high concentrations can be treated • high temperatures can be treated • higher separation efficiency and lower energy consumption than thermal oxidation	• very high investment costs • risk of deactivation of catalyst by catalyst poisons • catalyst aging • critical to particulate matter • needs pre-heating, if cold gases should be treated • explosion risk, if gas has explosive concentration

Legend: T = temperature, H = humidity

4.7 Absorption – fundamentals and technical applications

4.7.1 Gas solubility

Gas solubility in a liquid phase is described by the Raoult's law and by the Henry's law (Figure 4). Both laws state that the vapour pressure of a component p_i is proportional to its concentration.
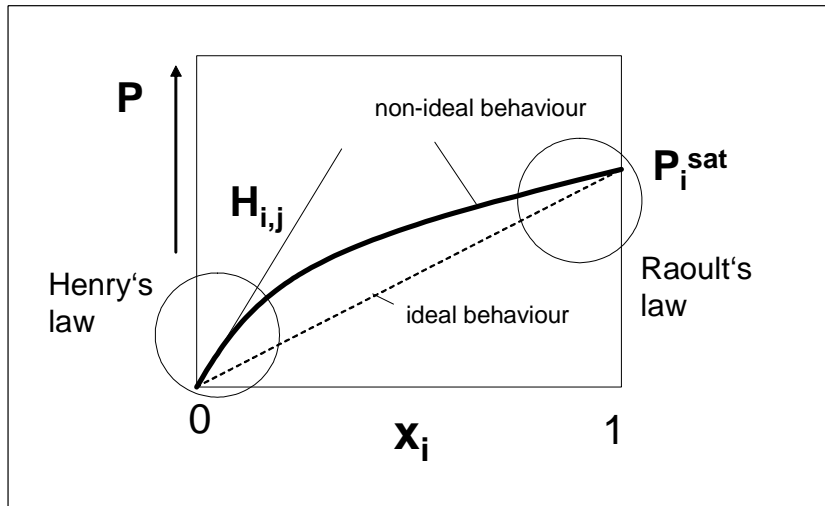
Figure 4: Gas solubility described by Henry's law and Raoult's law

If the solution shows an ideal behaviour, both components follow Raoult's law (eq. 3), which says, that the vapour pressure p_i is dependent on the vapour pressure p_i^{sat} of the pure component and the mole fraction x_i of the component in the solution

$$p_i = p_i^{sat} \cdot x_i \qquad \text{eq. 3}$$

If the solution's behaviour differs from ideal behaviour the Henry's law (eq. 4) is used, which uses an empirically-derived constant $H_{i,j}$ based on an infinitely-dilute solution, that is specific to the components i in the liquid j for a specific temperature.

$$p_i = H_{i,j} \cdot x_i \qquad \text{eq. 4}$$

In most systems, the laws can only be applied over very limited concentrations at the extreme ends of the mole-fraction range. Raoult's law, which uses the vapour pressure of the pure component, is best used for the major component (solvent) and in mixtures of similar components. Henry's law applies to the minor component (solute) in dilute solutions.

Interactions with a third substance or a behaviour deviating explicitly from the ideal gas behaviour cannot be described by the Henry's law. With respect to the very low concentrations of odorous gases in exhaust air the Henry's law can be applied mostly with a sufficient accuracy. For many technically interesting substances Henry coefficients are determined and listed in reviews (Sander, 1999) or data bases. Background information and the derivation of Henry's law can found in numerous studies and monographs (Zarzycki and Chacuk, 1993; Reid et al., 1989; Sattler and Feindt, 1995).

The solubility of an odorant is determined by its polar groups. Their characteristic distribution of electrons attributes an electrical dipole moment to the molecule. This causes the affinity to other polar chemical compounds or to polar interfaces like water (Römpp, 1999). Most organic components are only miscible with water up to a certain degree. Water is a polar solvent and therefore tends to be a good solvent for other polar substances, for example substances containing functional groups like –OH, -CHO, -COOH, $-NO_2$ or $-NH_2$. Molecules containing only carbon and hydrogen are called non-polar. The lipophility of substances is described quantitatively with the octanol/water distribution coefficient. This coefficient specifies the ratio of concentrations of a substance in equilibrium in two adjacent phases, here octanol and water. It is stated in literature mostly in logarithmic notation (log K_{OW}). Substances with a positive logarithmic octanol/water distribution coefficient are therefore lipophiles. This applies to most odorants that have been used in experiments in the course of this work (Table 35 in the annex).

29

4.7.2 Absorbents

4.7.2.1 Requirements on absorbents

In gas absorption the choice of the absorbent is of fundamental importance. Generally a technical applied absorbent has to fulfil the following requirements (Table 5).

Table 5: Requirements on technical absorbents (Sattler and Feindt, 1995)

gas solubility	a high gas solubility (small Henry coefficient) is desired since this increases the absorption rate and minimizes the required absorbent flow
volatility	a low absorbent steam pressure is desired to minimize absorbent losses and contamination of the treated gas
viscosity	low viscosity is preferred for faster material exchanges, lower pressure drops, improved flooding characteristics and good heat transfer characteristic
heat conductivity	should be high for a good distribution of the absorptive heat and for a better heating or cooling, if a thermal regeneration will be used
heat capacity	should be high to reduce temperature heat of absorption
corrosiveness	corrosiveness of the absorbent and the absorbates (solutes) determines the choice of materials, which is a main cost driver
chemical stability	the degree of chemical stability determines the choice of regeneration techniques. Only temperature resistant absorbents can stand a regeneration by steam stripping or rectification. Additionally the absorbent should be non-flammable.
toxicity	the absorbent should be non toxic for safety reasons
odour	the absorbent should not be odorous especially in the field of odour control
foam formation	if an absorbent has a tendency to foam formation it is not applicable for usage in scrubbers
availability	availability must be long-termed ensured
costs	costs for absorbents will always be compared to water as a reference

4.7.2.2 Water

Water is the most important absorbent of physical absorption. It fulfils the requirements on absorbents in an outstanding way. Water molecules are polar and have a distinctly di-polar character. Thus, water molecules attach to all polar substances and reduce the volatility of these substances and separate them from air. For that reason organic acids and ketones can be absorbed by water very well and non-polar gases or steams, like hydrocarbons, cannot. Water steam is the only steam that is allowed to be discharged into atmosphere without limitations.

4.7.2.3 Solubility agents in aqueous solutions

Bioscrubbers are limited in treatment to highly water soluble contaminants as described above. If the distribution equilibrium, expressed by the distribution coefficient K_H in $(g/l_{air})/(g/l_{water})$, is above $5 \cdot 10^{-3}$, the required amount of washing water increases. This leads to higher energy consumption and requires complex applications with higher numbers of mass exchange units. The ability of suspended micro-organisms for absorbing hydrophobic contaminants increases by 2 or 3 magnitudes by addition of a high-boiling solvent in a percentage of 10 – 30% to the washing liquid of a bioscrubber (Schippert, 1993). According to the author, the high-boiling phase dispersed in the bacteria suspension functions as an accumulator. In this phase most of the contaminant to be separated (here toluene) are solved. By addition of about 10% of the solubility agent separation efficiency of toluene could be increased from less that 5% to 85% in a pilot plant designed for a throughput of 1000 m^3/h exhaust air.

4.7.2.4 Washing oils

High-boiling hydrocarbons, also labelled as washing oils, are used as absorbents in the field of solvents recovery. These washing oils are non-polar and so they solute non-polar gases like aliphatic hydrocarbons very well. Disadvantage of the washing oils is that they have a relatively high vapour pressure, which does not lead to bigger absorbents losses, but to a contamination of treated gases above permission limits. So applications using washing oils always need to have low absorption temperatures

Table 6: Applications of washing oils as absorbents

Absorb. type	Absorbent	Absorbat	Reference
PEG-DME	PEG-DME (Genosorb 300)	toluene, dichloroethane	Kalina, 1997
PEG-DME	glycol ether (Kerasorbon 7)	methanol, methyl chloride, n-hexane, xylene, diethyl ether, u.a.	Schmitter, 1993
PEG-DME	TEGDE	hexane, toluene, benzene, xylene, other aromatic compounds	Winterbauer, 1994
PEG-DME	TEGDE	methyl chloride	Schaber et al., 1996
PEG-DME	Genosorb 1753	acetone, toluene, methyl chloride	Schaber et al., 1996
Alcanes	Parex (alcane mixture)	toluene, methyl chloride	Kalina, 1997
Alcanes	HC10 (mineral oil fraction)	toluene, methyl chloride	Kalina, 1997
Silicone oil	Kerasorbon 313 and Kerasorbon 20	methanol, methylene chloride, n-hexane, xylene, diethyl ether, etc	Schmitter, 1993
Propylene carbonate	PLC	hexane, toluene, benzene, xylene, other aromatic compounds	Winterbauer, 1994
Propylene carbonate	PLC	methyl chloride	Schaber et al., 1996
Ester	Kerasorbon 218	methanol, methylene chloride, n-hexane, xylene, diethyl ether, u.a.	Schmitter, 1993
others	BEHA	hexane, toluene, benzene, xylene, other aromatic compounds	Winterbauer, 1994
others	EHS	hexane, toluene, benzene, xylene, other aromatic compounds	Winterbauer, 1994
others	NMP	hexane, toluene, benzene, xylene, other aromatic compounds	Winterbauer, 1994
others	Dialcyl ester, others	hexane, toluene, benzene, xylene, other aromatic compounds	Winterbauer, 1994

Legend: PEG-DME = polyethylene glycol dimethyl ether, PLC= propylene carbonate, NMP = n-methyl pyrrolidon, EHS= 2-ethyl hexane acid, BEHA= Bis(2-ethyl hexyl) adipate. References, which are not listed in the annex, are citied in (Kalina, 1997).

Polyethylene glycol dimethyl ethers (PEG-DME) is a famous group of these washing oils (Table 6). Tetra ethylene glycol dimethyl ether (TEGDE) is one member of this group, which is often investigated and also used for experiments within this work.

Another group of washing oils are silicone oils (Dimethyl siloxanes). They have very low vapour pressures and some of them have an acceptable viscosity. Silicone oils can be used in combination with a steam regeneration under normal pressure, since they are nearly non-water-soluble. Since PEG-DME have higher solubilities of most organic compounds they are preferred and examples of silicone oil applications are limited. Some other organic absorbents, like high-boiling esters of adipin acid or phthal acid are tested with good results. So far no technical applications of these absorbents are known.

4.7.3 Regeneration of absorbents

Absorption is a separation technique, which can be used to transfer pollutants from exhaust air into a liquid medium, where they have to be separated again. So, for application as a technology of environmental protection, absorption has to be combined with a second separation step called regeneration. Therefore absorption is only useful as a method for cleaning waste air if the consecutive problems can be more easily dealt with than the original exhaust air problem. Basically there are three ways of desorption of physically absorbed absorbents:

- expanding (after pressure absorption) or evacuation, respectively
- stripping, meaning desorption with an inert gas, or
- distillation or rectification

Regeneration by expansion is not applied technically, since the degree of cleaning is not sufficient for further usage of the absorbent. Stripping leads to new polluted gas, so this technique can only be used for regeneration if the desorbat can be disposed cost-effectively. Rectification is the process most often used for regenerating absorbents. A simple distillation is often not sufficient, because too much absorbent is discharged from the head of the column. In case of a high-boiling absorbent, rectification can be carried out under vacuum to stay at low temperatures and to avoid thermal damages.

33

Rectification and stripping with water steam can be combined, to achieve good conditions for mass transfer inside a rectification column. Here water steam and absorbent are condensed at the column head. In this case the condensate consists of two liquid phases, the organic phase can disposed e.g. by combustion and the aqueous phase can be decontaminated in a biological waste water treatment plant.

4.7.4 Operational parameters

The stripping factor S (eq. 7) is an operational parameter for comparison of different absorption processes. It is the ratio of the slope of the equilibrium line (m=$H_{i,j}$/p) and the slop of the operating line (L/G). With decreasing stripping factor S the operational costs increase due to higher liquid flows, while the number of required separation steps decreases, which leads to smaller scrubber columns and by that to lower investment costs (Sattler and Feindt, 1995). The economically optimal stripping factor S can only be calculated for a specific system considering the sum of operational costs and investment costs. In this work the stripping factor is used to describe both absorption (S_{abs}) and regeneration (S_{reg}) by stripping.

Table 7: Evaluation parameters of absorption and desorption

separation efficiency	regeneration efficiency	Stripping factor S	concentration factor f
$\eta_{abs} = \dfrac{y_1 - y_2}{y_1}$	$\eta_{reg} = \dfrac{x_1 - x_2}{x_1}$	$S = \dfrac{G}{L} \cdot \dfrac{H_{i,j}}{P}$	$f = \dfrac{y_{stripp}}{y_1}$
eq. 5	**eq. 6**	**eq. 7**	**eq. 8**

with: y_1=raw gas concentration [ppm], y_2=purified gas concentration [ppm], y_{stripp}=stripping gas concentration [ppm], x_1: absorbent effluent concentration [ppm], x_2: absorbent feed concentration [ppm], G=Gas mol flow [kmol/h], L=absorbent mole flow [kmol/h], $H_{i,j}$ = Henry coefficient [bar], P = operating pressure [bar]

Alternatively to the stripping factor, the volumetric solvent ratio ν_v or the molar solvent ratio ν_m can be used as a characteristic parameter for scale up.

$$\nu_v = \frac{Q_L}{Q_G} \qquad \textbf{eq. 9} \qquad\qquad \nu_m = \frac{L}{G} \qquad \textbf{eq. 10}$$

This is the case if multi-components are absorbed and no Henry coefficients are available or the focus is on flow characteristics, e.g. for engineering of bioscrubbers.

4.7.5 Technical applications

Absorptive waste gas treatment is done in various types of wet scrubbers including spray scrubbers and packed towers. Scrubbers are also able to separate particulate matter by suspension in the liquid. In spray scrubbers the washing liquid is spread by one or more banks of high pressure spray nozzles so that it completely covers the gas stream. Typically, this device includes a two stage separation. In the first chamber a diffuser creates a uniform gas flow at the entrance. Then it gets into an intensive contact with the washing liquid. The first chamber is followed by a device which separates the liquid droplets from the air stream and provides further intimate contact between gas and liquid. A second chamber, containing the same equipment, often utilizes a different absorbent. Spray scrubbers are generally viewed as low to medium efficiency devices, with high gas velocities and medium static pressure drops.

The standard absorption device is a packed tower scrubber. It has been extensively applied in odour control applications with a wide variety of absorbents. Two types are utilised, the counter-current packed tower and the cross-flow packed tower. The counter-current packed tower is a device which has a bottom gas entry and a top gas outlet (Figure 5). Scrubbing liquid is introduced on top and flows through the packed bed by gravity counter-current to the gas flow. The packaging provides intimate contact of gas and scrubbing liquid. Selection of packaging material is very critical, since it affects the pressure drop and provides liquid surface regeneration for maximum absorption rates. In cross-flow packed tower the gas streams horizontally through a tower, while the scrubbing liquid enters the top and flows by gravity to the bottom across

the gas stream. Since the pressure drop at packed tower scrubber is relatively low and so is the power demand to transport the scrubbing liquid to the top of the tower, the overall power consumption is minimal.
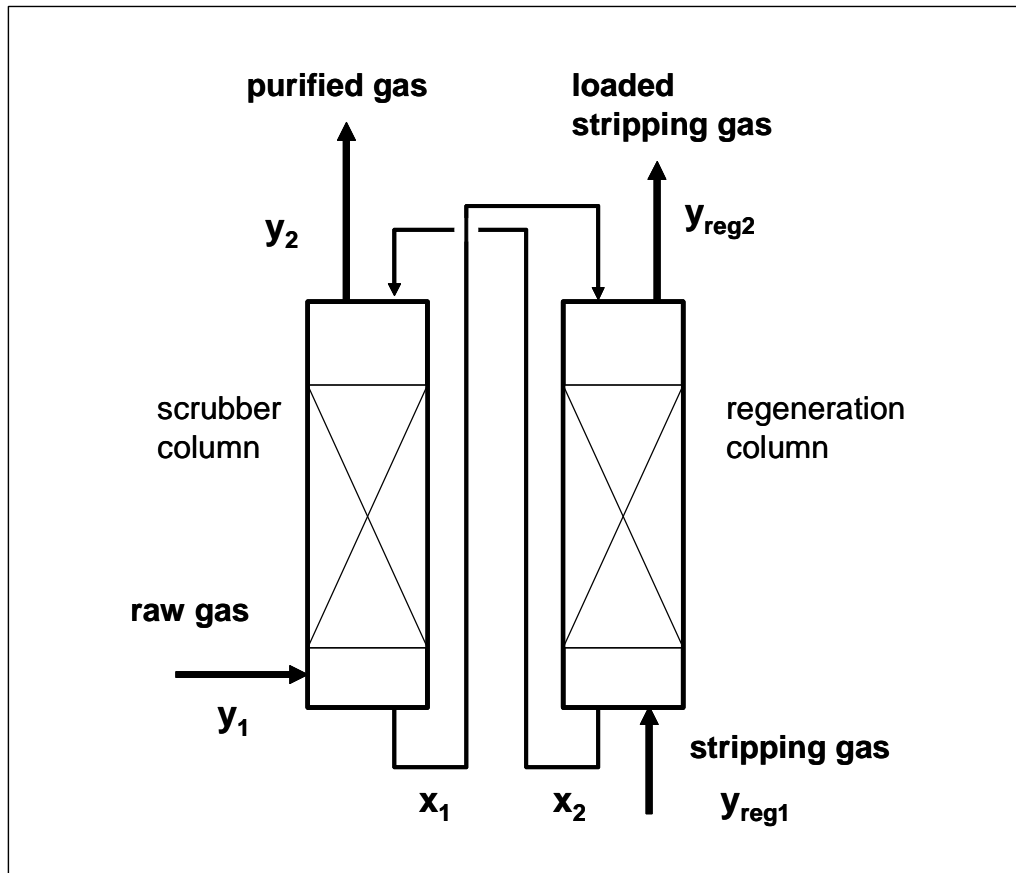
Figure 5: Flow sheet of an absorption and a regeneration column

The venture scrubber is another type of scrubber, which is rarely used for odour reduction, since absorption efficiency is relatively low, but it is reported as one of the best devices for particulate removal. So, its usage in the field of odour reduction is limited to cases, when odours are related primarily to particulate matter (Cheremisinoff, 1993). The venture scrubber employs a constriction in form of a throat where the gas is accelerated to very high velocities. Washing liquid is introduced ahead of or directly into the venture throat. The high velocity of the gas shears the liquid droplets and creates high turbulence in the throat. As a result of turbulence, intimate mixing and effective collisions take place between particulate and scrubbing liquid. The throat is usually

followed by an expanded section where some static pressure is regained and contact between gas and liquid continues. The venture is then followed by an entrainment separator which removes the liquid droplets entrained by the gas stream.

4.8   Design of counter-current absorption columns

There are several methods of calculation of the required height H_C of absorption columns. In this work the theory of theoretical separation stages (chapter 4.8.1), the theory of transfer units (chapter 4.8.2) and a kinetic 1st order method (chapter 4.8.3) are used. A method to determine the second dimension of the column, the diameter D_C or cross sectional area A_C respectively is presented in chapter 4.8.4.

4.8.1   Theory of theoretical separation stages

A theoretical separation unit is defined as that part of a separation apparatus where heat or mass transfer occurs between two phases in contact. Both phases leaving the theoretical separation unit are in phase equilibrium. Normally the required purity of a phase is not achieved by a single separation stage. To increase the separation efficiency, single stages are connected in series to form a cascade. If separation is carried out in a counter-current flow column, the theoretical height for heat and mass transfer depends on the number theoretical separation units connected in series. This design method by multiplying single separation units is a practical, simple and economic method. Historically this method is developed for calculation of a stage wise contact in tray towers, but it is also applicable for continuous contact in columns with packing.

The McCabe-Thiele method is a graphical method to determine the number of theoretical separation units of a counter-current flow column. It is applied for calculation of separation processes of binary mixtures with immiscible liquid and gas phases L and G and if only one component is absorbed from the gas into the liquid phase.

The total mass balance of the transferred component is given for the whole column by the following equation in loading notation:

$$G \cdot (Y_1 - Y_2) = L \cdot (X_1 - Y_2) \qquad\qquad \text{eq. 11}$$

material balance at absorber

$$G \cdot Y_1 + L \cdot X_2 = G \cdot Y_2 + L \cdot X_1$$

equation of operating line

$$Y_1 = \frac{L}{G}(X_1 - X_2) + Y_2$$

Legend
X: molar loading of absorbant
Y: molar loading of waste gas
EL: equilibrium line
OL: operating line
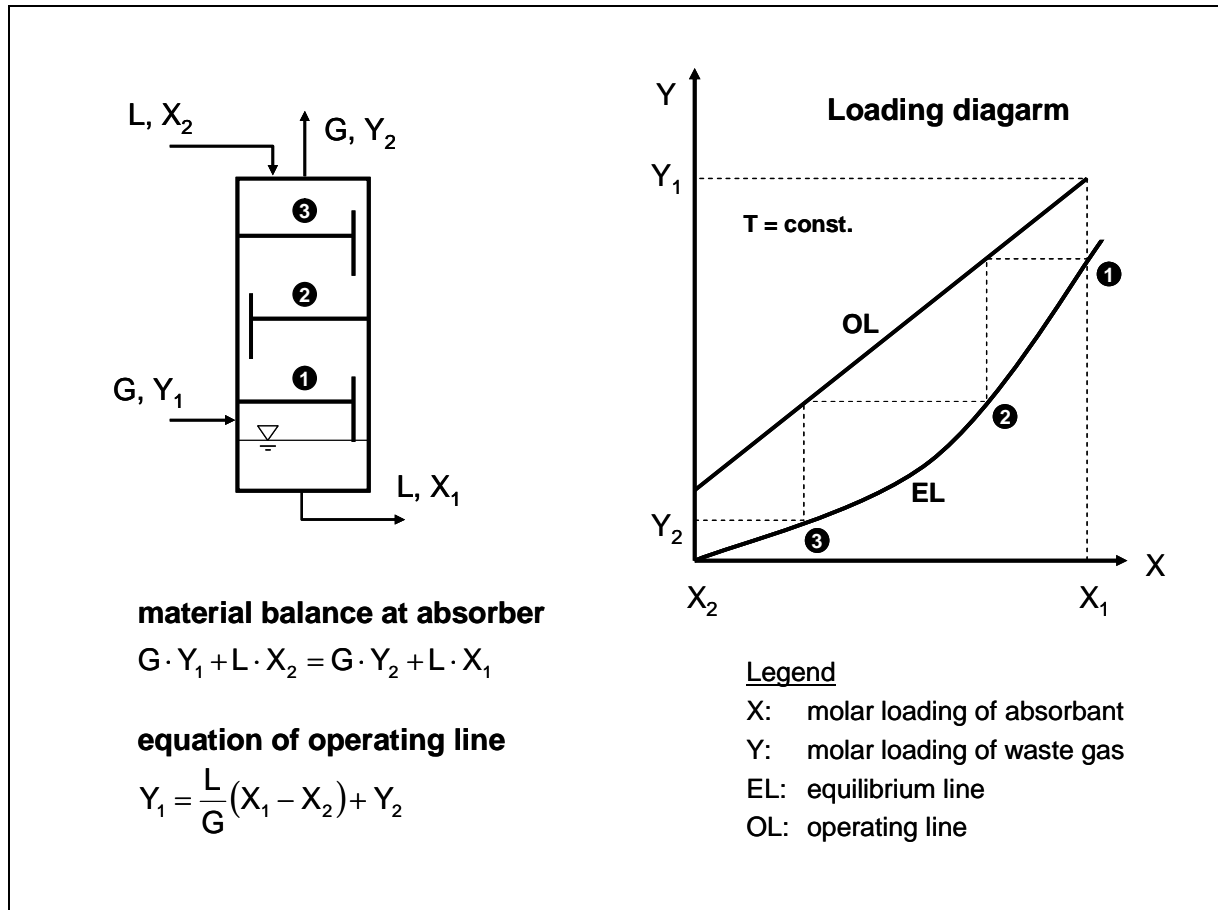
Figure 6: Absorption loading diagram

The absorption loading diagram (Figure 6) demonstrates the separation principle of a counter-current flow process. It shows the graph of eq. 11 in a X, Y coordinate system and a straight line is produced between the points $P_1(X_2, Y_1)$ and $P_2 (X_1, Y_2)$, which is the balance line or operating line with the slope m = L/G, which is the ratio of flow rates of the phases. Points on the operating line link related mole loadings X and Y at any cross section of the column. If the components of the mixture have equal molar vapourisation enthalpies and if they exhibit ideal behaviour and if enthalpy changes of the steam or the liquid phase are negligible, then the operating line is straight (Sattler

and Feindt, 1995). Desorption or stripping can be calculated with the same method in opposite direction. Using the McCabe-Thiele method the number of theoretical separation units N_t can be determined graphically. Alternatively the column height can be calculated based on the number of theoretical separation units N_t with eq. 12, if the molar solvent ratio ν_m and the slope m of the equilibrium curve are constant in the concentration range $Y_2 > Y > Y_1$.

$$N_t = \frac{\ln\left[\frac{Y_1 - m \cdot X_2}{Y_2 - m \cdot X_2}(1-S)+S\right]}{\ln\left(\frac{1}{S}\right)} \qquad \text{eq. 12}$$

If the molar solvent ratio ν_m and the slope m of the equilibrium curve are constant, then the stripping factor S is constant too (eq. 13).

$$S = \frac{m}{\nu_m} = \frac{H_{i,j}/pP}{L/G} \qquad \text{eq. 13}$$

To calculate the height of the absorption column H_C (eq. 14) additionally the height of a theoretical separation stage (HETS) is required, which is found by experiments under conditions as close as possible to further operating conditions.

$$H_C = N_t \cdot HETS \qquad \text{eq. 14}$$

4.8.2 Theory of transfer units (HTU-NTU method)

If column internals, such as filling or packing material, are used to increase the phase boundary area, the liquid phase and the gas phase are in constant contact over the column height. Therefore, a constant contact should be considered in column calculation, using the kinetic theory for a counter-current separation based on mass transfer. In contrast to the theory of theoretical separation stages, this method is continuous and does not take single stages into account. In an absorption process substances are usually only transported from the gas phase to the liquid phase.

Here, for the molar flow rate dn_i of the key component i in the height element the molar balance is

$$dn_i = G \cdot dy \qquad\qquad \textbf{eq. 15}$$

Introducing an overall mass transfer coefficient k_G, related to the overall mass transfer resistance in the gas phase, it becomes

$$dn_i = k_G \cdot \left(y - y^*\right) \cdot dA_C \qquad\qquad \textbf{eq. 16}$$

where y is the gas concentration and y^* is the theoretical gas concentration in equilibrium with the liquid concentration at that point. dA_C is the incremental cross area in height element dh for mass and heat transfer. Using a specific volumetric surface a [m²/m³] of the column packing and a cross sectional area of the column A_C the contact area dA can be calculated with

$$dA = \eta_a \cdot a \cdot A_C \cdot dh \qquad\qquad \textbf{eq. 17}$$

Generally the specific surface a is not completely available for heat and mass transfer it is corrected by Sattler and Feindt (1995) with an area efficiency factor $\eta_a < 1$, which is the ratio of the physical wetted surface and the theoretical wetted surface. The factor η_a depends on the type of packing, the properties of the phases in contact, the distribution of the phases across the sectional area of the column and the loading of the cross section by the phases. Neither the overall mass transfer coefficient k_G nor the physical wetted surface or the efficiency factor η_a could be determined separately by the experiments. So, here all parameters are condensed to the parameter k_Ga, which can be determined by experiments.

$$k_G \cdot \eta_a \cdot a \equiv k_Ga \qquad\qquad \textbf{eq. 18}$$

From equations eq. 15 to eq. 18 it follows

$$G \cdot dy = k_Ga \cdot \left(y - y^*\right) \cdot A_C \cdot dh \qquad\qquad \textbf{eq. 19}$$

Integration with respect to dh gives the height H_C of the column for mass and heat transfer.

$$H_C = \frac{G}{k_G a \cdot A_C} \cdot \int_{y_2}^{y_1} \frac{dy}{y - y^*}$$ eq. 20

According to Chilton and Colburn (citied in Sattler and Feindt, 1995) the integral factor of eq. 20 is the number of transfer units NTU_{OG}, which describes how often the driving force $y-y^*$ is needed in the overall interval from y_1 to y_2 between the entry and the exit ($h = 0$ and $h = H_C$)

$$NTU_{OG} = \int_{y_2}^{y_1} \frac{dy}{y - y^*}$$ eq. 21

Consequently the height of a transfer unit HTU_{OG} is given by

$$HTU_{OG} = \frac{G}{k_G a \cdot A_C}$$ eq. 22

so that the height H_C of the column is

$$H_C = HTU_{OG} \cdot NTU_{OG}$$ eq. 23

With an approximately linear equilibrium curve, which is the case in the range of Henry's law, the driving force can be calculated for the entry of the column with

$$\Delta y_1 = y_1 - y_1^* = y_1 - x_1 \cdot \frac{H_{i,j}}{p}$$ eq. 24

and analogues for the exit. If the balance line is approximately linear too, the driving fore $y-y^*$ in the integral can be replaced sufficiently by the logarithmic mean $(\Delta y)_m$ with

$$(\Delta y)_m = \frac{\Delta y_1 - \Delta y_2}{\ln(\Delta y_1 / \Delta y_2)}$$ eq. 25

and that the number of transfer units becomes

41

$$NTU_{OG} = \int_{y_2}^{y_1} \frac{dy}{y - y^*} \approx \frac{y_1 - y_2}{(\Delta y)_m}$$

<div align="right">eq. 26</div>

So finally the height of the column H_C can be calculated with

$$H_C = \frac{G}{k_G a \cdot A_C} \cdot \frac{y_1 - y_2}{(\Delta y)_m}$$

<div align="right">eq. 27</div>

4.8.3 Kinetic 1st order method

Based on the results of Heining (1998) for the biological degradation of odours substances in a bioscrubber a linear dependency of the degradation rate r [mg/(m³*h)] on the mean gas concentration c_M in [mg/m³] or [OU/m³] respectively can be assumed. So a 1st order method with a kinetic constant k_1 [h^{-1}] is to be tested as a simple and practical method for a scale-up of bioscrubbers (eq. 28).

$$r = k_1 \cdot c_M$$

<div align="right">eq. 28</div>

On the basis of measurements from Heining with waste gas from compost plants this behaviour is proofed for various concentration ranges. The mean gas concentration c_M is calculated as a mean logarithmic concentration with the raw gas concentration c_1 and the purified gas concentration c_2 of the bioscrubber.

$$c_M = \frac{c_1 - c_2}{\ln(c_1 / c_2)}$$

<div align="right">eq. 29</div>

From the mass balance the required reactor volume V_R in [m³] can be calculated by the ratio of mass flow M of degraded substances and the degradation rate r.

$$V_R = \frac{M}{r}$$

<div align="right">eq. 30</div>

4.8.4 Calculation of cross sectional area

The cross sectional area A_C of the column and its diameter D_C result from the equation of gas flow rate

$$A_C = \frac{D_C \cdot \pi}{4} = \frac{Q_{g,max}}{w_{g,max}}$$

eq. 31

where $Q_{g,max}$ is the maximum gas flow rate in the absorber. The maximum feasible gas flow velocity $w_{g,max}$ refers to the superficial cross sectional area of the column. It is given by a loading limit which depends on type and geometry of the packing and on properties of the counter flow phases. The upper load limit, which is called the flooding limit, must not be exceeded or the liquid will be hold back in the packing and effuse with the gas phase at the head of the column. On the other hand packed towers operate the most effective slightly below the flooding limit, so in practice an operational load of 60-85% of the flooding limit is chosen. If typical gas flow velocities are known for similar cases, then they can be taken for calculation of the cross sectional area of the column A_C. As an alternative to this method, if no reference is available, characteristic diagrams or standard values can be used, which are given by manufactures of packings for each packing type. For example, data of the gas load factor F is typically given by the manufacturer of packings referring to the empty column, which can be used as a standard value to calculate the range of operational loading based on gas velocity w_g and density ρ_g with

$$F = w_g \cdot \sqrt{\rho_g} \quad \text{in } [Pa^{0.5}].$$

eq. 32

If a scale-up is done based on experimental properties, e.g. transfer-constants k_Ga, then it must be considered, that these properties depend strictly on the flow velocities of the gas and the liquid phase. So they can only be taken as constants within narrow confines for the specific loads where they are determined.

5 Experiments

5.1 Methods and Materials

At the beginning the applicability of solubility agents and alternative washing liquids is tested in principle. This is done by determination of Henry coefficients in laboratory experiments for single odorants in pure washing liquids (chapter 5.2). Then chosen solubility agents are tested for usage in bioscrubbers (chapter 5.3) with laboratory experiments using single odorants and by on-site experiments using industrial waste gas. Analogues, experiments are done to test washing oils in physical scrubbers (chapter 5.4). For this application regeneration by stripping with water steam and air respectively is evaluated. Kinetic constants are determined for both bioscrubber and physical scrubber for calculation of a scale-up (chapter 6). Subsequently a screening test is presented for evaluation of the applicability of washing liquids to industrial waste gases (chapter 5.5).

5.1.1 Analytics

5.1.1.1 Analysis by GC/FID

Concentrations of single odorous components in a gas mixture are determined with a type 3600 gas chromatograph equipped with a FID (Varian, Darmstadt, Germany). Helium was used as a carrier gas and nitrogen as a make-up gas. Compounds were separated with a SE-54 column (50 m x 0.4 mm I.D., 0.25 µm film thickness, Macherey-Nagel, Düren, Germany). The injector was operated in a split mode 1:40 at 110°C. Oven temperature was held constantly at 120°C. Data were calculated by an internal integrator in the standard modus. For analysis of gaseous samples a GC micro-litres syringe (1ml) was used for manually on-column injection. For the analysis of liquid samples a headspace auto-sampler type DANI HSS 3950 was used. Injection frequency was once every three minutes. To minimize losses of substances by condensation the temperature was adjusted at a minimum of 5 K above the boiling point of the odorant, which is between 40°C (DMS) and 95°C (TEA).

To gain an acceptable accuracy, it was required to manufacture a set of standards each day to determine a calibration line. For calibration of liquid samples analysis, eleven empty vials were closed with teflon septum. A volume of 10 µl of an odorant was injected via a GC micro-litres syringe into three vials (sample S1 to S3) and the content was determined by weighting. All vials were tempered in the headspace for at least 15 minutes. Afterwards the empty vials were charged with samples from the other vials with a GC micro-litres syringe (1000 µl) as follows. A gas sample (1 ml) was transferred from S1 into an empty vial (sample B1). That was repeated twice (sample P1.1 and P1.2). Then a gas sample (1 ml) was transferred from B1 into an empty vial (sample B2). Again this was repeated twice (P2.1 and P2.2). At least a gas sample (1 ml) was transferred from B2 into two empty vials (sample P3.1 and P3.2, respectively). Whenever a sample was drawn out of a vial, pressure equalization was accomplished by penetrating the septum with a syringe needle for a second. This procedure was found to be necessary to ensure a reproducibility of dilution. The analysis of calibration samples followed the procedure of analysis of liquid samples. The calculation of the theoretical amount of odorants was based on the determined weight of the substance while taking a concentration decrease into account caused by sampling multiple times and pressure equalization. For the calibration of gaseous samples all samples were prepared according to the procedure of the calibration of liquid samples with the exception of the analysis, which was done manually according to the analysis of gaseous samples.

5.1.1.2 Analysis by SPME/GC/MS

For identification of a single gas compounds a GC/MS system combined with enrichment by solid-phase micro-extraction (SPME) is used, which is described by Kleeberg et al. (2003). Identification of substances is done by matching mass spectra versus the Wiley mass spectra library.

5.1.1.3 Analysis by Olfactometer

Determination of odour concentration is executed with a computerised olfactometer, type TO6-SIH (Mannebeck, Kiel, Germany) with four test persons, as described in DIN EN 13725 (Anonymous, 2003). Sample bags of polyterephtalic ester (Nalophan®, K. Nalo, Wiesbaden, Germany) were used.

5.1.1.4 Analysis by Electronic Nose

A sensor array or an electronic nose resp., type i-Pen from WMA Airsense equipped with10 sensors of three different sensor types, was used in on-site experiments (see chapter 5.3.4). The electronic nose was equipped with a sampling periphery as shown in Figure 7. Gas samples were taken at three sample points which were raw gas and treated gas behind two bioscrubbers plus calibration gas. Samples were transported through teflon lines by vacuum of a centrifugal gas pump, which was installed down flow of the electronic nose. Changing of sample points was done by magnetic driven sample valves, which are controlled by a PC, which was also used for data storage and data visualization of the electronic nose. To protect the electronic nose from moisture from gas flow, all sample lines were equipped with 500 ml-condensate traps. Calibration gas was gained on site by taking out side air purified by passing an activated carbon filter. Gas flows were measured by flowmeters and manually controlled by needle valves.
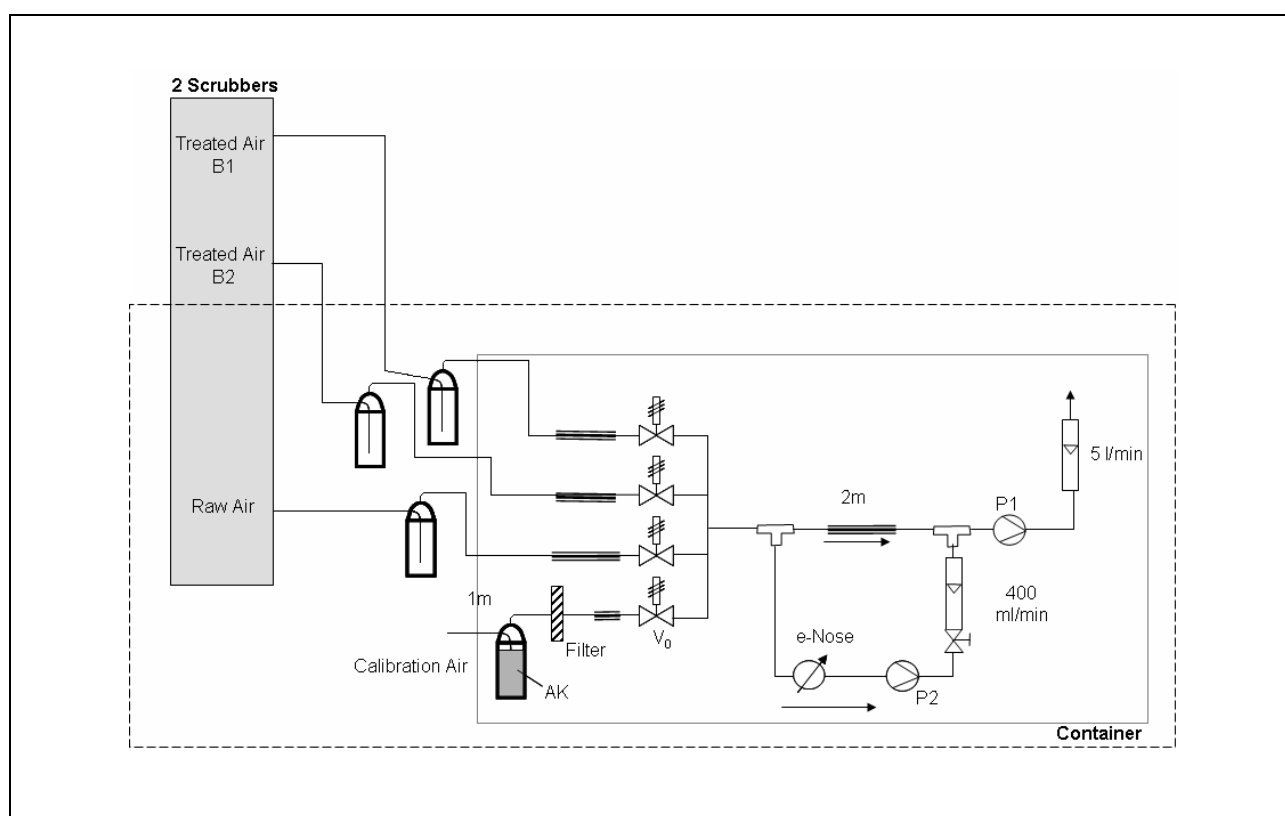
Figure 7: Electronic nose with sampling periphery for continuous monitoring of a bioscrubber

5.1.1.5 Analysis by TOC Analyzer

TOC of gaseous samples were determined by a Hydrocarbon Analyzer, Model 3002, made by Bernath Atomic.

5.1.2 Chemicals

5.1.2.1 Odorants

For laboratory experiments the following chemicals were used: dimethyl sulphide (DMS), CAS 75–18–3, 99%; pentane ethiol (PT), CAS 110–66–7, 98%, triethyl amine (TEA), CAS number 121-44-8, 99.5%, acetic acid (glacial) 100%, CAS number: 64-19-7, furfuryl thiol (FFM), CAS 98-02-2, 95%.

5.1.2.2 Washing liquids

HC10 is a mixture of mineral oil raffinates, Addinol Lube Oil GmbH; tetraethylene glycol dimethyl ether (TEGDE), CAS 143-24-8, 99%, propylene carbonate (PLC), CAS 108-32-7, Biesterfeld GmbH, bis(2-ethyl hexyl) adipate (BEHA), CAS 103-23-1 99%; silicone oil AP 100, CAS 63148-58-3

5.1.2.3 Additives

Humic acids potassium salt (product name POW), CAS 1415-93-6, Humintech GmbH; Humic acids sodium salt (product name Nussbeize), CAS 68131-04-4, Bakelite AG, dimethyl sulfoxide (DMSO), CAS 67-68-5, 99,9%. Physical data of the additives are listed in Table 36 in the appendix.

5.2 Determination of Henry coefficients

As explained in chapter 4 the Henry's law can be used to describe the solubility of a gas in a liquid. Although for many technically interesting substances the Henry coefficients

are determined, normally they are not available for pairs of odorants and washing liquids. Within this work five substances have been selected as typical odorants, with which the suitability of chosen washing liquids is examined. The particular Henry coefficients are determined to compare the suitability of the washing liquids.

5.2.1 Method

Henry coefficients were determined using a headspace GC-FID system. For this method defined amounts of an odorant and of a washing liquid are transferred into a GC vial, closed with a septum and weighed, then tempered in the headspace. Depending on the used substances the odorant dissolves into the liquid. The depletion of odorant concentration in the gas phase is measured after it reaches the equilibrium. Thereby, the distribution of odorous substances within the two phases can be determined. Then the Henry coefficient can be calculated from the ratio of the concentrations in two phases multiplied with the atmospheric pressure.

5.2.2 Preparation of samples

For determination of Henry coefficients, several solutions containing odorants were prepared for analysis. To prepare solution A with the lowest concentration, an amount of 2000 g of pure washing liquid was weighed and transferred into a screw top glass bottle. The two other solutions, B and C, were made up with 300 g of washing liquid. Screw tops of the bottles were equipped with teflon membranes so that an odorant could be added by penetrating the membrane with the needle of a gas-tight micro-litres syringe. Solution A was prepared with an amount of 1 µl of odorant and solution B and C with 5 µl and 50 µl, respectively. To determine the exact amount of odorant the filled syringe was weighed each time. Solutions were stirred with magnetic stirrer, for a period of 20 minutes with a high rotational speed. Subsequently three samples (10 ml) of each solution were drawn with a syringe by penetrating the teflon membrane and transferred into GC vials, which were closed with teflon-septum immediately. The vials were weighed afterwards. The measured peak areas were converted into concentrations based on data of calibrations. Concentrations of the odorant in the washing liquids were calculated as the difference of total amount, being weighted, and the amount in the gas phase. It was assumed that the amount of odorant was completely present either in the gas or in the liquid phase and not clinging to the vial's wall or adsorbed on the septum.

5.2.3 Results

Henry coefficients were calculated for very low liquid concentrations ($x_i \rightarrow 0$) according to the Henry's Law., here transferred for determination of the Henry coefficient.

$$H_{i,j} = \frac{y_i}{x_i} \cdot p, \qquad \forall \; x_i \rightarrow 0$$
$\qquad$ **eq. 33**

To achieve the best accuracy the Henry coefficient are determined at the limit value of $x_i = 0$ according to Gmeling and Kolbe (1992). This limit value can be estimated by a diagram where the ratio y_i/x_i is plotted versus the liquid concentration x_i and a partial regression line is computed for the pairs of variables. The axis intercept $y_{(x=0)}$ multiplied with the total pressure p yields to the Henry coefficient. As an example this kind of diagram is shown for DMS in Water (Figure 8). All Henry coefficients calculated by this procedure are shown in Table 8.
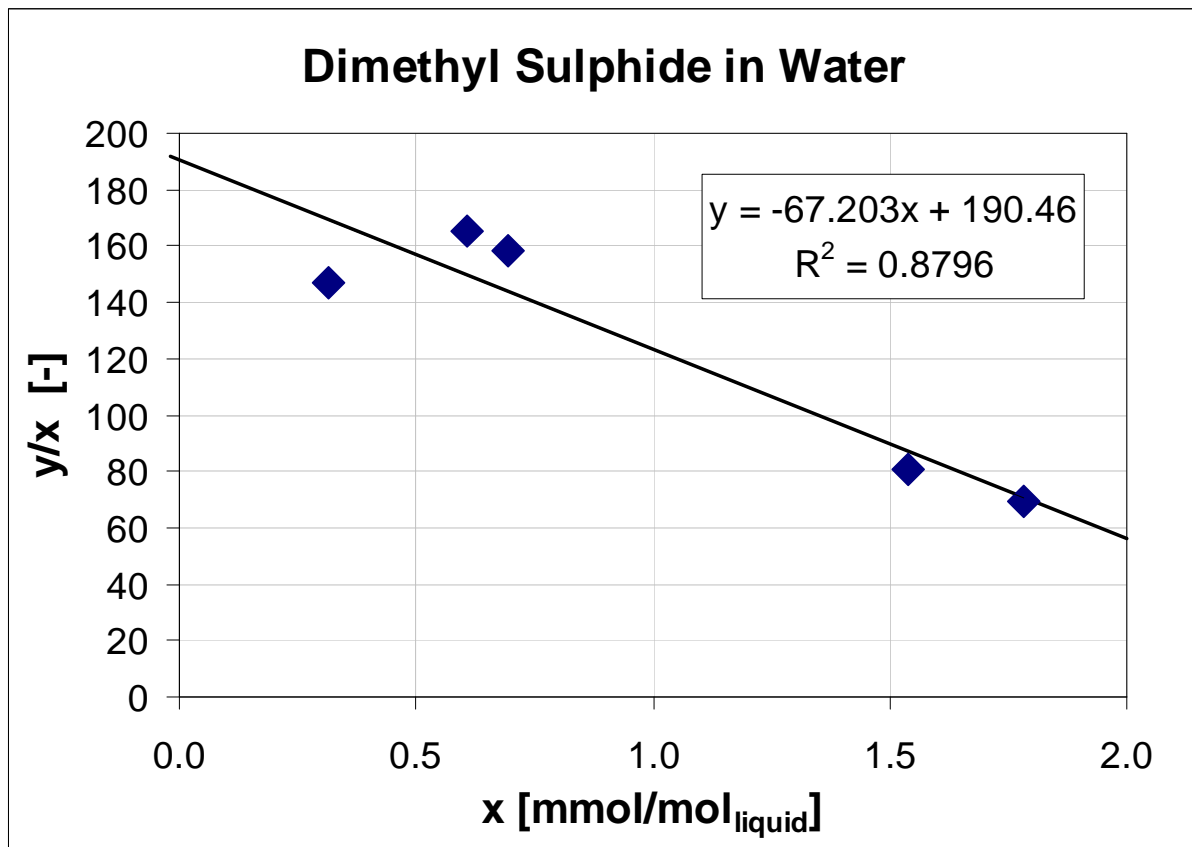
Figure 8: Diagram for determination of the Henry Coefficient of Dimethyl Sulphide (DMS) in water

49

Table 8: Henry coefficients [bar], determined for p= 1,013 bar, T = 30°C (Klingner, 2002)

Absorbents		Odorants				
	weight-conc. [B] :	dimethyl sulphide	triethyl amine	pentane thiol	furfuryl thiol	acetic acid
water	100 %	193	37	> 1000 [C]	318	0.115
Silicone oil [A]	100 %	13.2	5.11	1.62	5.29	8.52
HC10	100 %	1.10	0.270	0.196	0.294	-
DMSO	10 %	158	53	- [D]	- [D]	0.124
POW (A)	5 %	100	8	> 5000 [E]	0.698	0.095
Nussbeize [A]	5 %	107	16	60.8	5.77	0.109
TEGDE	100%	0.950	1.20	n.d.	n.d.	n.d.
PLC	100%	2.91	3.38	n.d.	n.d.	n.d.
BEHA	100%	0.681	0.562	n.d.	n.d.	n.d.

Legend:

	(A):	this Henry coefficient is calculated using the weight concentration [g/g] instead of molar concentration in [mol/mol], because no molar weight was available
	(B):	explanations to concentration mean: 100% = pure liquid, 5 and 10% = aqueous solution
	(C):	the calculated value ($H_{PT,W}$ = 1518 bar) has a higher inaccuracies
	(D):	Henry coefficient could not be calculated, because a chemical reaction happens accompanied with the formation of new substances (no physical absorption)
	(E):	the calculated value ($H_{PT,W}$ = 10173 bar) has a higher inaccuracies
	n.d.	not determined

5.2.4 Discussion

Silicone oil, which is the only investigated liquid which has already been applied in bioscrubbers, shows a good solubility performance, which is between 10 and 60 times higher than that of water, with Pentane thiol even a 600 times higher. The solubility of humic substances solutions is better than that of water but less than that of silicone oil. Compared to water, it has an absorptive capacity about 2 to 15 times higher.

Humic substances solutions show a promising performance, when they are applied to furfuryl thiol, where they have about 55 to 450 times higher solubility than water. These substances will be tested in bioscrubbers in the next chapter.

DMSO showed no improvement at any tested combination, so this substance will not be tested further on. TEGDE, PLC and BEHA have already been used as absorbents in the field of solvent recovery. These substances show very absorptive capacities, which are in the measured combinations about 10 to 280 times higher than that of water. Due to this high performance TEGDE is chosen to be investigated in detail in experiments. Disadvantage of these three substances is that they are water-soluble, so that they cannot be regenerated by steam stripping. HC10 shows the best solubility for the odorants being investigated. This alcane fraction has a solubility, which is between 140 and 1,000 times higher than that of water, with pentane thiol even 5,100 times higher. This absorbent will be investigated in detail in experiments in a physical scrubber and compared with TEGDE (see chapter 5.4).

The only odorant where no better absorbent could be found than water is the hydrophilic substance acetic acid. This substance is a typical compound in waste gases from food industry. If it is identified as a key compound, an aqueous solution is generally a good choice as an absorbent.

5.2.5   Conclusions on Henry coefficients

As expected the absorptive capacities of the washing liquids differ strongly depending on the gaseous substance. Nevertheless, laboratory results indicate that there are applications in the field of odour control, where the performance of gas scrubbers can be improved by usage of one of the investigated washing liquids instead of water. Due to the fact that an all-purpose washing liquid could not be found, a technical implementation in a gas scrubber will always need an adaptation of the absorbent to the waste gas.

5.3   Test of Solubility agents for usage in Bioscrubbers

Humic substances in aqueous solutions fulfil the requirements for usage as solubility agents in bioscrubbers and they showed good results when Henry coefficients were determined in combination with chosen odour substances. So, in the following humic substances are tested as additives in bioscrubbers in four long-term series of measurements.

5.3.1   Bioscrubber – experimental plant

An experimental plant is built up with two identical scrubber columns (W1 and W2) with separate loops of washing liquids (Figure 9). The columns are constructed of PVC-U pipes with inner diameters of 110 mm. The columns consist of three identical segments each of a length of 660 mm. They are filled with a random packing of about 550 mm height filled with Hiflow-Rings (material PP, diameter 15 mm). Air supply is done in laboratory by a pressured air header of the building to produce a synthetic waste air. In on-site experiments the air supply is done by a side stream blower to transport original industrial waste gas from the sampling point to the plant. The production of synthetic waste air is done by a gas generator, which consists of a glass pipette being filled partly by a pure liquid odour substance. This pipette is placed in a closed 1000 ml glass vessel with three flanges for gas inlet and outlet and a thermometer for gas temperature measurement.

A bypass gas stream is transported through the headspace of the generator vessel by pressure drop of a ball valve in the main gas stream. There, it picks up evaporated odour components and get re-mixed with the main gas stream. Subsequent the main gas stream is split into two equal gas streams feeding the two scrubber columns. Gas flows of the main stream and the bypass are measured with flowmeters. Gas feed flows of the columns are measured by thermal velocity sensors. All gas flows are manually controlled by ball valves. Washing liquids are transported by circular pumps from the sumps of the scrubbers to their heads, where they pour down through the fixed beds in counter-current to the waste air. Liquid flows are measured by inductive flowmeter and

controlled by ball valves. Scrubber column W1 was operated as a classic bioscrubber as a reference. In Column W2 humic substances were added to the system. Beside that, both columns were operated under the same operational conditions.

5.3.2 Bioscrubber performance test in laboratory

In these measurement series the effect of solubility agents on the performance of bioscrubbers in odour reduction was evaluated. Additionally optimisation of process conditions and measuring micro-biological degradation rates were done.

5.3.2.1 Method

A synthetic waste air was produced by the described gas generator. In these series dimethyl sulphide (DMS) was added as an odorant to the raw gas stream. Three series were run, which differed by concentration of humic substances and concentration of DMS in the gas feed (Table 9). The bioscrubbers were operated with gas flows of 8.5 m³/h and liquid flows of 0.51 m³/h. Target for pH value control was a range of 6.8 – 7.5. Within series V1 and V2 the pH value was measured daily and corrected by dosing acid or alkaline solution. Within series V3 an automated pH value control was established. Determination of gas concentrations was done by GC/FID. Due to a relative high determination limit (about 3 ppm DMS) of the GC/FID system the bioscrubbers had to be fed with high raw gas concentrations, to enable the quantification of the treated gas concentration too.

Table 9: Process conditions of bioscrubber experiments in laboratory

Series	Duration of measurements	Concentration of humic substances
V1	14 days	5 % w/w
V2	11 days	5 % w/w
V3	11 day	1.5 % w/w

① laboratory bioscrubber   ② DMS dosage

③ liquid flow sensor   ④ pH and O_2 sensor
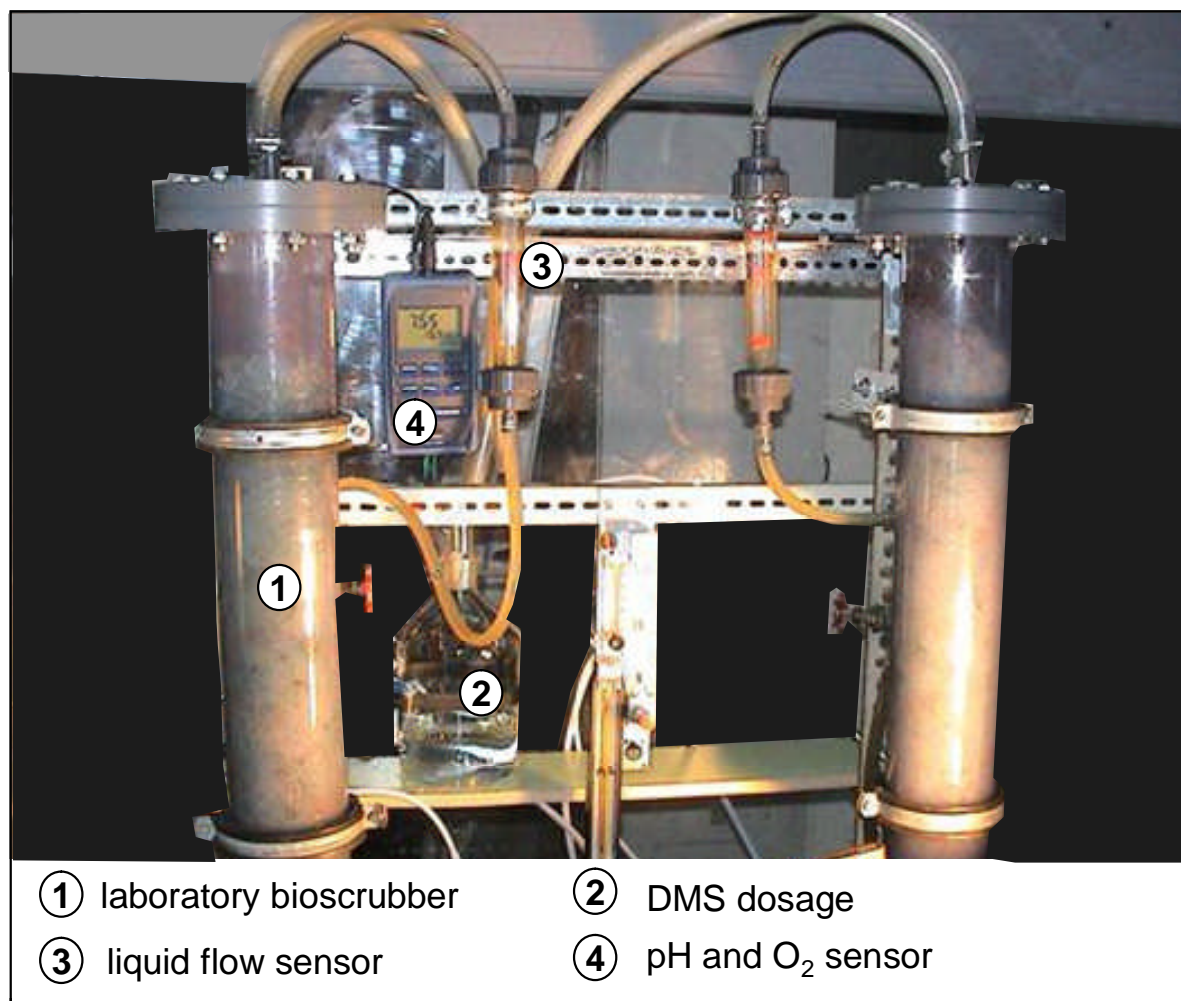
Figure 9: Laboratory Bioscrubber set-up

5.3.2.2 Results

During operation of the bioscrubbers a deviation in produced raw gas concentration could not be prevented. Also pH values varied within 4.5 and 7.5 being measured before the daily manually correction. Nevertheless, the same tendency in correlation was observed within all three series at all raw gas concentrations (Venkov, 2003). Firstly, degradation rates of the bioscrubbers increase with increasing raw gas concentrations. Secondly, degradation rate of scrubber W2 with humic substances was permanently higher than the rate of reference scrubber W1. Thirdly, the effect of the humic substances was higher at higher concentration of humic substances. With a concentration of 1.5% w/w the performance improvement by humic substances was about 34% in average, while a concentration of 5.0% w/w let to an improvement of 47% or 50% respectively (Figure 10, Table 10 and in annex Figure 38 and Figure 39).

5.3.2.3 Discussion

Within these series the raw gas concentration varied strongly. One of the reasons for that was the temperature fluctuation due to a missing temperature regulation in the gas generator. Therefore the odorant evaporated with not constant rates.

Table 10: Odour reduction by bioscrubbers in laboratory tests

	conc. of humic subst. [% w/w]	raw gas conc. min/max [ppm]	raw gas conc. mean value [ppm]	purified air W1- mean value [ppm]	purified air W2- mean value [ppm]	n	separation by W1	separation by W2	improve-ment by humic substances
V1	5 %	20-160	75	62	57	9	17%	26%	50%
V2	5 %	20-370	120	81	59	7	28%	41%	47%
V3	1.5 %	180-530	320	166	107	7	51%	68%	34%

Legend: n: number of days, when 3 gas samples of each sample point were analysed
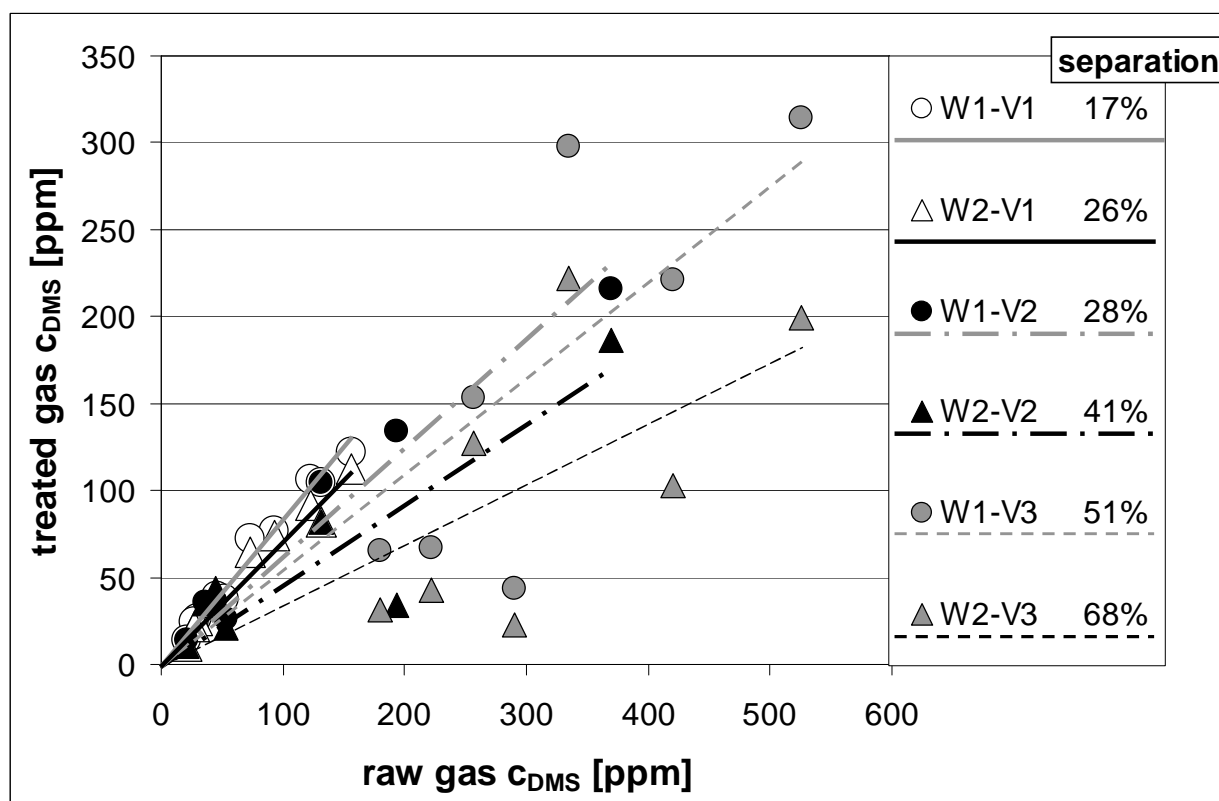
Figure 10: Concentrations in ppm DMS of raw gas and treated gas of the bioscrubbers in laboratory tests

Another reason was a variation in volume flow, which was caused by a simple gas flow control by manually driven ball valves. A few times operation of the plant was also disturbed by fluctuations of the pH value and partial losses of washing liquid. Therefore it has to be assumed that the biocenosis could not develop ideally, thus the scrubbers could not reach their maximum separation performance.

5.3.2.4 Conclusion

Despite the high concentrations of raw gas and the fluctuation in operating conditions good degradation rates could be achieved by the bioscrubbers. This proves that this process is in principle suitable for the decomposition of dimethyl sulphide. While using a solution of humic substances, reduction rate was between 34 and 50% higher than while using water. Therefore it could be shown in principle that separation efficiency of bioscrubbers can be improved by using solutions of humic substances.

5.3.3 Bioscrubber performance test at a fat and oil refinery

In these measurement series the influence of humic substances were tested on separation performance of bioscrubbers treating waste gases from food production facilities. Secondary goal was to optimize process conditions and to determine scale-up parameters.

5.3.3.1 Method

The same bioscrubber experimental set-up which had been used in the laboratory experiments was built up at a fat and oil refinery. There was a highly odorous exhaust air from a caustic potash scrubber, which had been identified as an important local odour emitter by the project partners (Schlegelmilch et al., 2004a). Waste air with the highest odour concentration was determined in the headspace of the scrubber's pumping pit and used as the gas source for the following experiments. To ensure a continuous operation, several design up-grades of the set-up like an automatic liquid level control and an automated fresh water supply were implemented. Again

bioscrubber W1 was operated with water and W2 with aqueous solutions of humic substances. To examine the influence of operating conditions scrubber performance was measured at different air flows (3.5 – 8.0 m³/h) and different flows of washing liquid (0.32 – 0.65 m³/h). Before gas sampling and analysis, operation conditions were kept constant for at least one week. Concentrations of raw gas and pure gas were measured via olfactometry and the separation efficiency was determined on basis of odour reduction.

5.3.3.2 Results

While raw gas concentrations were in the range of 3500 to 32.000 OU/ m³, purified gas concentrations were between 600 and 7,500 OU/m³ (Figure 11). All experiments show that purified gas concentration depended significantly on the raw gas concentration (Figure 12). Reduction rate η_{ou} based on [OU/m³] varied from 70% and 85% with an average of 75% by W1 and 82% by W2. An improvement in reduction efficiency by usage of humic substances is about 10% in average of all seven measurements. The influence of liquid volume flow was low whereas the influence of air volume flow on the reduction rate was found to be significant. The rate dropped continuously from 84% at 4 m³/h to 73% at 8 m³/h with increasing air flow.

There was no negative influence observed of the humic substances on scrubber's operation during experiments. From time to time a foam development was observed inside the columns, but an influence of the humic substances was not seen.

5.3.3.3 Discussion

Again no negative influences of the humic substances on scrubber operation could be detected during operation. The centrifugal pumps were not influenced negatively by the humic substances either. More constant operational conditions like constant pH values of the washing liquids and less varying temperature in the cellar room than in the laboratory supported a good development of the biocenosis. Although few operational draw-backs of on-site experiments occurred, when washing liquid was lost at the

day no.	34	41	49	63	70	77	84
flow air/liquid [m³/h]	5.0 / 0.53	3.5 / 0.42	8.0 / 0.32	5.0 / 0.65	3.5 / 0.63	6.0 / 0.32	4.0 / 0.32
trickling load	0.11	0.12	0.04	0.13	0.18	0.05	0.08
■ raw air [OU/m³]	12,756	24,548	9,742	3,756	31,835	19,484	10,522
□ purified W1 [OU/m³]	5,467	7,512	1,491	683	6,889	4,390	2,814
■ purified W2 [OU/m³]	2,896	3,579	2,170	609	5,014	5,793	1,543
separation W1	57.1%	69.4%	84.7%	81.8%	78.4%	77.5%	73.3%
separation W2	77.3%	85.4%	77.7%	83.8%	84.3%	70.3%	85.3%
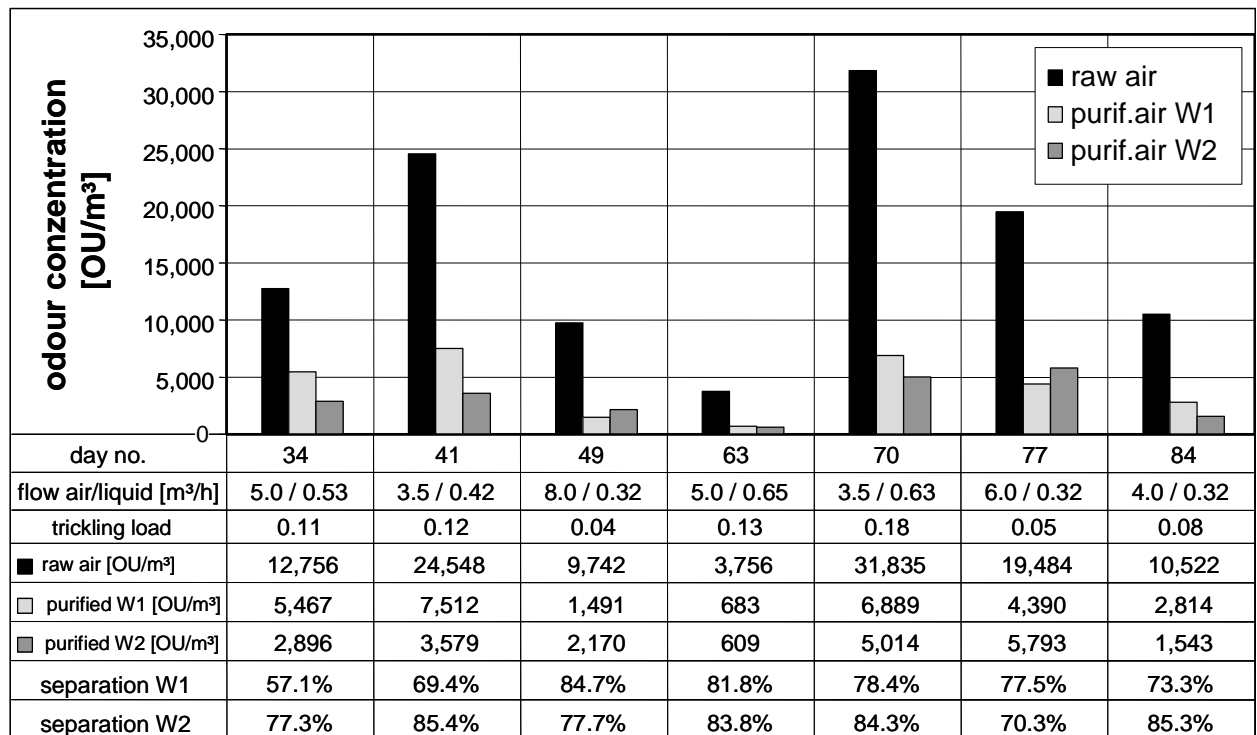
Figure 11: Raw gas and purified gas concentrations of the bioscrubbers W1 (water) and W2 (humic substances) at the fat and oil refinery
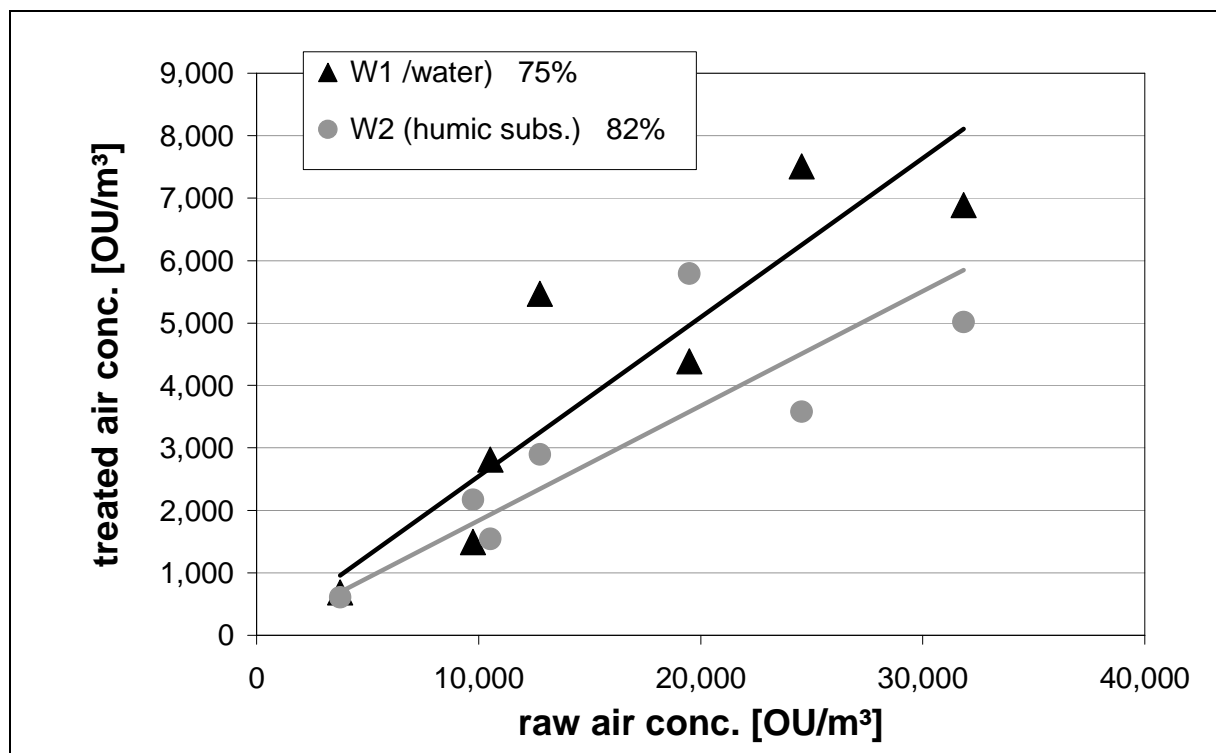
Figure 12: Dependency of purified air concentrations on raw gas concentration based on on-site experiments with bioscrubbers at the fat and oil refinery

58

scrubbers heads during phases of foam formation in both scrubbers. Then fluid level was regulated automatically by addition of water, which lead to losses of biomass and humic substances. Afterwards, concentration of humic substances could be corrected by addition of humic substances and experimental duration between measurement series was increased by at least three days to enable biomass to grow-up again. Nevertheless, odour measurements were carried out only when operational conditions were stable for at least three consecutive days.

Reduction efficiencies by the bioscrubbers were significantly higher within on-site experiments than they were during laboratory experiments. This can be attributed to the lower raw gas concentration at the refinery, which determines directly the degradation rate. Based on the kinetic 1st order method the degradation rate is proportional to the mean logarithmic concentration. The proportional factor is the kinetic constant k_1, which will be determined in chapter 5.3.5 for both measurement series. Although k_1 values are calculated with mass concentration based on laboratory data on and with odour concentration based on on-site data, and although waste gas composition is completely different, it will be shown, that in both cases the k_1 values are nearly the same. In case of the application at the refinery this leads to smaller reduction efficiencies.

Absorption improvement caused by usage of humic substances was less significant at on-site experiments than in laboratory experiments. These findings fit to the results of the screening test (demonstrated in chapter 5.5) where the tested solution of humic substances did not show a significant improved absorptive capacity compared to water for treating the raw gas of the oil and fat refinery. It was impossible to separate most key substances of the raw gas with a satisfying degree by both of the liquids. Before this background the achieved high odour reduction rates are more surprising, indicating that bioscrubbers are also able to separate even less water soluble substance to a certain degree. This can be taken as another indication that separation of gaseous compounds by bioscrubber is not only limited to absorptive process but there are also other contributing effects, like adsorption to biomass or to humic substances and adaptation of biocenosis. This also shows a limitation of the screening test in a situation like this,

which is designed to evaluate differences in absorptive behaviour and underlines the need for on-site test with a pilot plan to gain a reliable data set for planning a full-scale treatment plant.

5.3.3.4 Conclusions

Bioscrubbers are able to work effectively as a first treatment step of odour control at a fat and oil refineries. Reduction rates might not be sufficient to fulfil emission restrictions by a bioscrubber only, due to a high amount of less water soluble odorants. So for this fat and oil refinery a combination of a bioscrubber with a second treatment step, e.g. a biofilter would be an adapted concept of odour control. Separation rate of the bioscrubbers were improved by adding humic substances. This improvement was less significant than it was in laboratory. Optimizing the operation conditions proved to be difficult due to the variation of raw air concentrations. It could be shown, however, that the experimental bioscrubbers were able to treat the exhaust air of the fat and oil refinery with a gas superficial velocity of 0.15 m/s and a trickle density of b = 44 m³/(m²*h), which are in the recommended range (0.5 – 2.5 m/s und 20-60 m³/(m²*h)) for packed bed scrubbers according to VDI 3478 (1996). Based on experiences of these series, higher specific volume flows cannot be recommended because risk of liquid losses at the scrubbers heads increase significantly, especially during phases of foam formation. Operational findings show that dosing of humic substances in a technical application should be done by a dosing station with a manual solid material handling, a material transport by gravity and an automatic dosage to a stirred storage vessel.

5.3.4 Bioscrubber performance test at a starch factory

5.3.4.1 Pilot Plant

Within these test series, the capability and long-term behaviour of humic substances for usage in bioscrubbers were tested. For this purpose a new experimental plant was built in a semi-technical scale by Wessel Umwelttechnik a manufacturer of bioscrubbers (Figure 13). This plant has been operated at a starch factory for one year. Additionally the capability was tested of this process for treating the specific exhaust air of this food

producer and data were collected as a basis for planning a full-scale waste air treatment at this facility. The plant consisted of two identical bioscrubbers of 4,500 mm height and 80 mm in diameter. Lower column parts were located in a 20 ft container together with the aerated recycle tanks and a dosage and measuring technology. An electronic nose, type i-pen, was equipped for a continuous monitoring of the raw air and treated air composition.
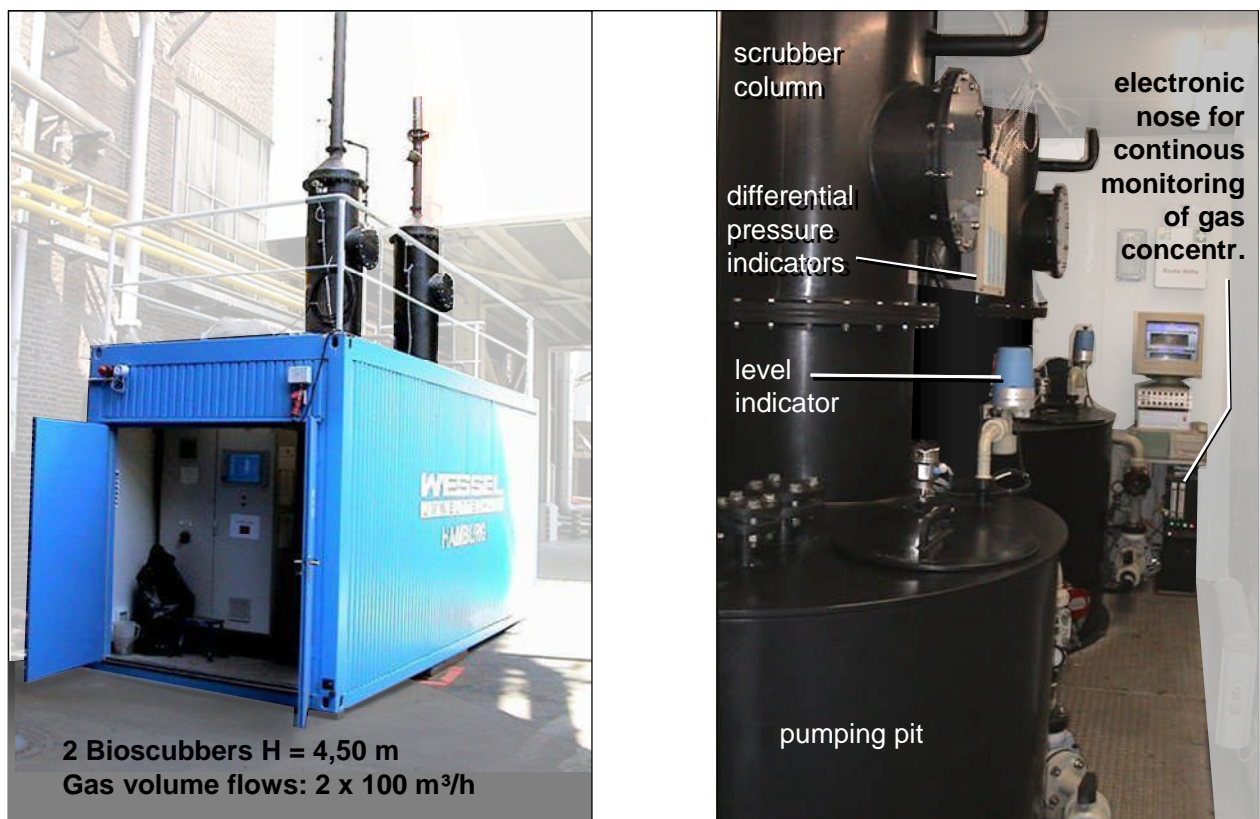
Figure 13: Pilot plant installed at a starch factory (designed by Wessel Umwelttechnik, Hamburg)

5.3.4.2 Process operation

Operation of the bioscrubbers proved to be stable and reliable. Separation performance was permanently high, despite the fluctuating in raw gas concentration. During the on-site experimental series some production downtimes occurred, so the bioscrubbers had to handle with rapidly changing conditions and feed interruptions. But this did not result in a decrease of cleaning capacity or measurable decelerations during starting phases. After the first start-up phase the operational effort to run the experimental plan could be

limited to one inspection per week due to an automated control system of liquid levels and pH values. During measurement phases the effort was higher because inspections were done on a daily basis and more samples were taken and analysed. After a starting phase of several weeks, the pH value remained stable at pH 7.5 – 8.5 without interventions. During the whole period the concentrations of nutrients in the washing liquids were determined regularly. Those were total organic carbon (TOC), total nitrogen (TN) and total phosphorus (TP). To avoid limitations of biological degradation, mineral nutrients were added regularly based on determined nutrients consumption.

The only disturbances during operation occurred by foam formation in the washing liquid, this happened several times after humic substances were added. The first measure to prevent foam formation was the installation of an automated dosing unit of foam inhibitant, but that did not solve the problem reliably. Still a foam formation after dosage of humic substances could be observed. This foam contained a lot of solids and was very stable therefore. It was assumed that these solids were humic substances that were insufficiently mixed. Finally, the problem was solved by an improved manual mixing of the humic substances, by a more smooth dosage and by a reduction of volume flows of washing liquids.

5.3.4.3 Parallel operation of scrubbers

During the first experimental series both scrubbers were operated in parallel. Scrubber W1 was operated as a classic scrubber and scrubber W2 was operated with humic substances. During this series the raw air concentration fluctuated widely (20.000…200.000 OU/m³, typical area: 20.000…40.000 OU/m³). Raw air concentration varied with the daily production process and additionally several downtimes occurred, when less or less concentrated of exhaust air was generated (Figure 14). The measured data show that the cleaning efficiency of both scrubbers increased with increasing raw air concentrations (Figure 15). At relatively low raw air concentrations below 50,000 OU/m³ the cleaning efficiency for was < 60% and it increased to >90% at relatively high raw air concentrations above 250,000 OU/m³.
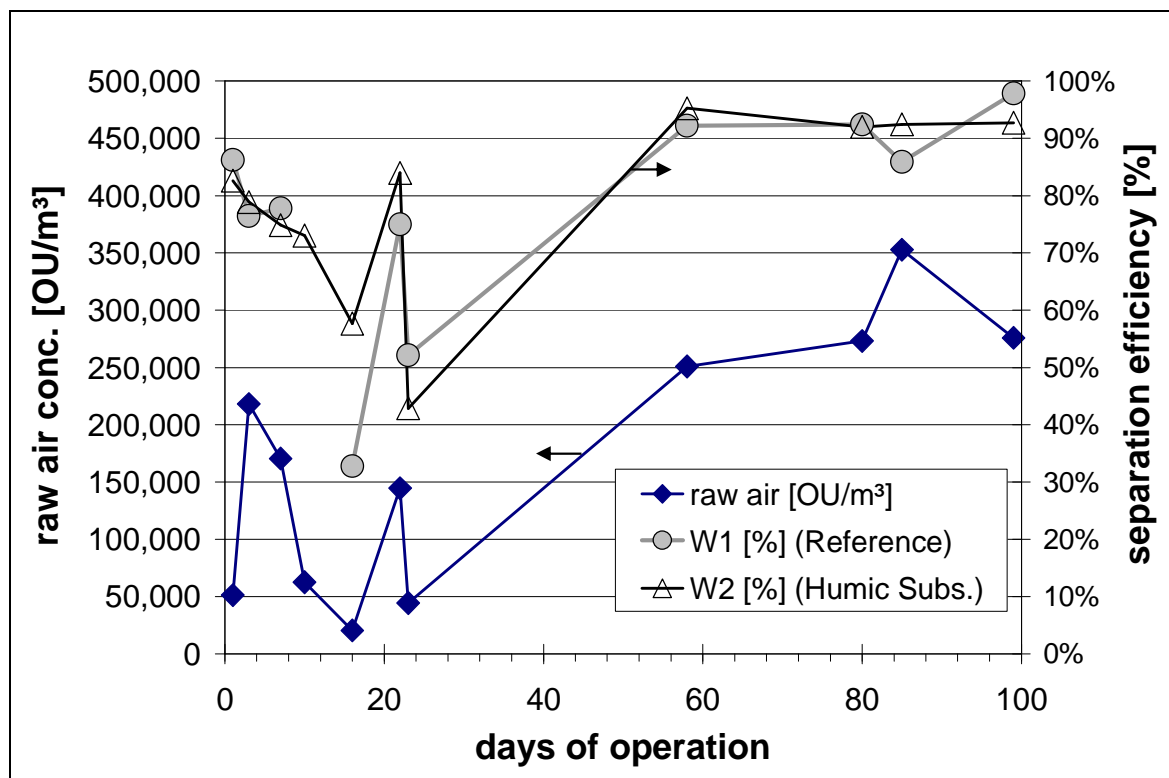
Figure 14: Data of raw gas and purified gas concentrations and separation efficiencies from on-site experiments with bioscrubbers in parallel modus at a starch factory
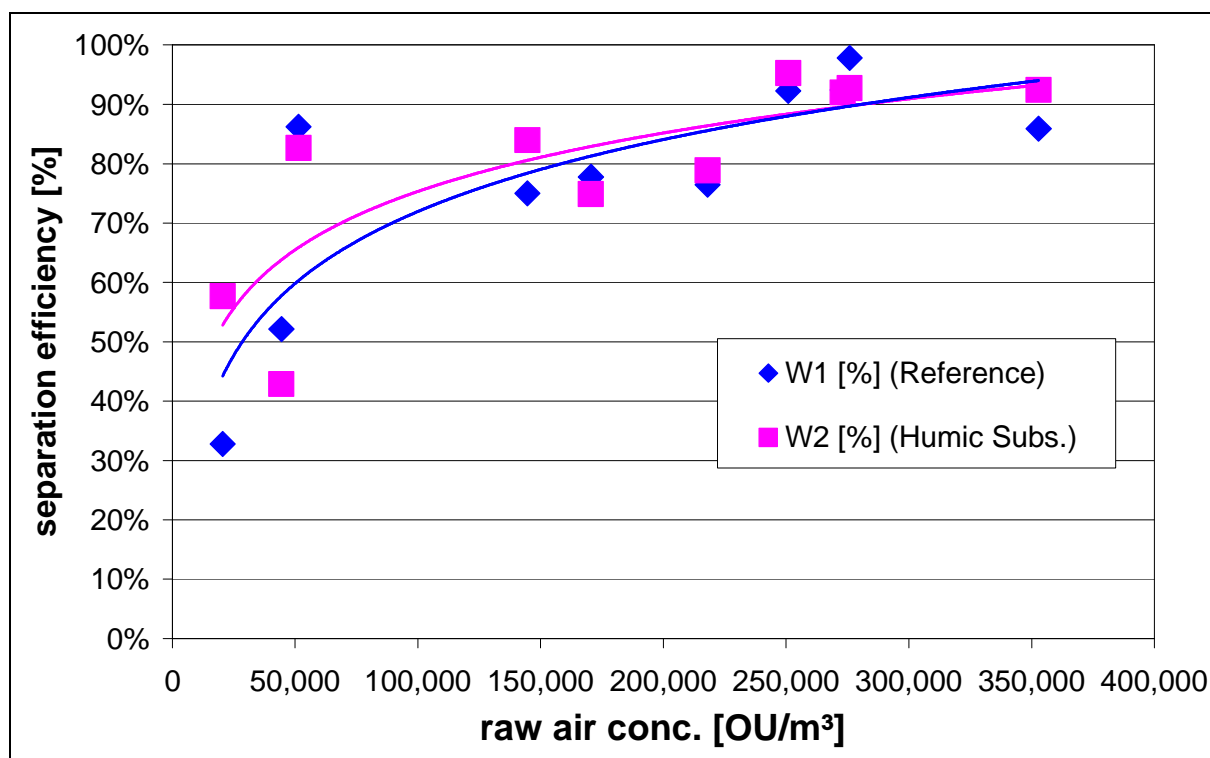
Figure 15: Separation efficiency of bioscrubber in parallel modus at a starch factory

At this series the mean improvement of separation efficiency by humic substances was only 7%. The effect was higher at lower raw air concentrations. At raw air concentrations above 250,000 OU/m³, separation efficiency of both scrubbers was the same. At lower raw air concentrations below 50,000 OU/m³, separation efficiency the scrubber with the added humic substances was about 10% higher compared to those of the conventional scrubber.

5.3.4.4 Serial operation of scrubbers

In this series the two bioscrubbers were run in series. Start-up was done without humic substances (phase 1) as a reference. After one month of operation humic substances were dosed to the second scrubber W2 (phase 2). During both periods no significant disturbances of operation occurred. Nutrients were measured regularly and added if required, also washing liquids were partly exchanged once a week. Additionally the concentrations of total bacteria in the washing liquid were regularly checked.

Measured data show a high variation of raw gas concentration (Figure 16). At 4 of 5 measurements raw gas concentration was below 40,000 OU/m³ which is relatively low compared to concentration of the first series. At one measurement the concentration was above 200,000 OU/m³, which is a more typical concentration at that sampling source. Since no data are available for times in between, it can be assumed, that there were more events with higher concentrations. The scrubbers achieved continuously good separation efficiency with odour reduction >95% in total. The separation efficiency of scrubber W1 was >90%. Although feed concentration was varying, data of phase 1 show that at low raw air concentrations below 50,000 OU/m³ the separation efficiency of a second conventional scrubber W2 is <40% downstream a conventional first scrubber W1. If humic substances were added to the second scrubber W2 (phase 2), then its efficiency increased to >75%. In this case total separation efficiency was raised from 95% to about 98% to 99%.
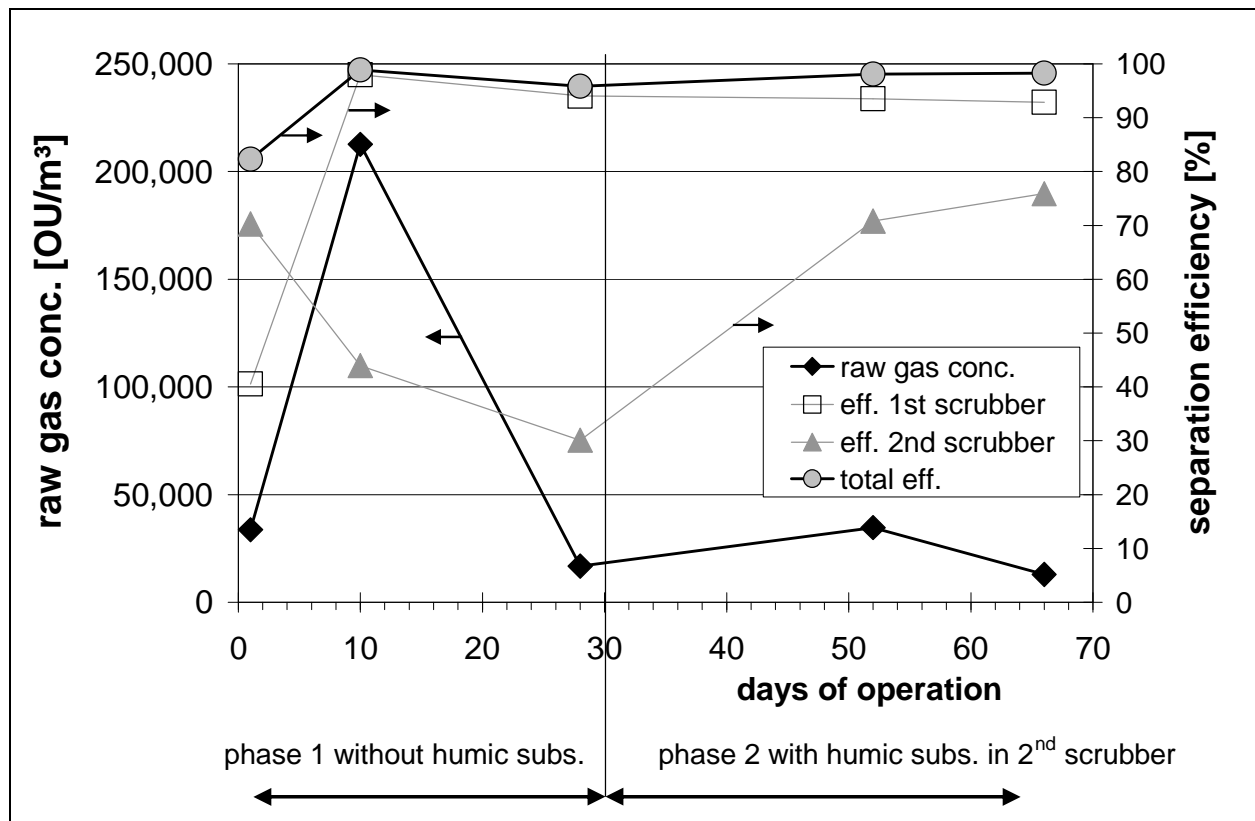
Figure 16: Separation efficiencies from on-site experiments with bioscrubbers in serial modus at a starch factory

5.3.4.5 Electronic Nose

The applicability of a semi-conductor sensor array or an electronic nose respectively, for continuous monitoring of a bioscrubber unit was tested during one month of experiments. An electronic nose, type i-Pen from WMA Airsense, was used with a sampling periphery as described in chapter 5.1.1.4. Experimental set-up was integrated into the container of the bioscrubber and connected to both the raw air stream and the purified air streams. To verify data of the electronic nose, additional odour and TOC measurements from single samples were done. Additionally a protocol of the downtimes was provided by the starch factory, which stated the operating and downtime hours during the entire experimental series. The electronic nose proved to be a continuously working measurement instrument which can be used reliably to monitor operating conditions of a bioscrubber. Phases of production and phases of shut-down could be differentiated easily and changes in gas concentration levels could also be monitored (Figure 17).
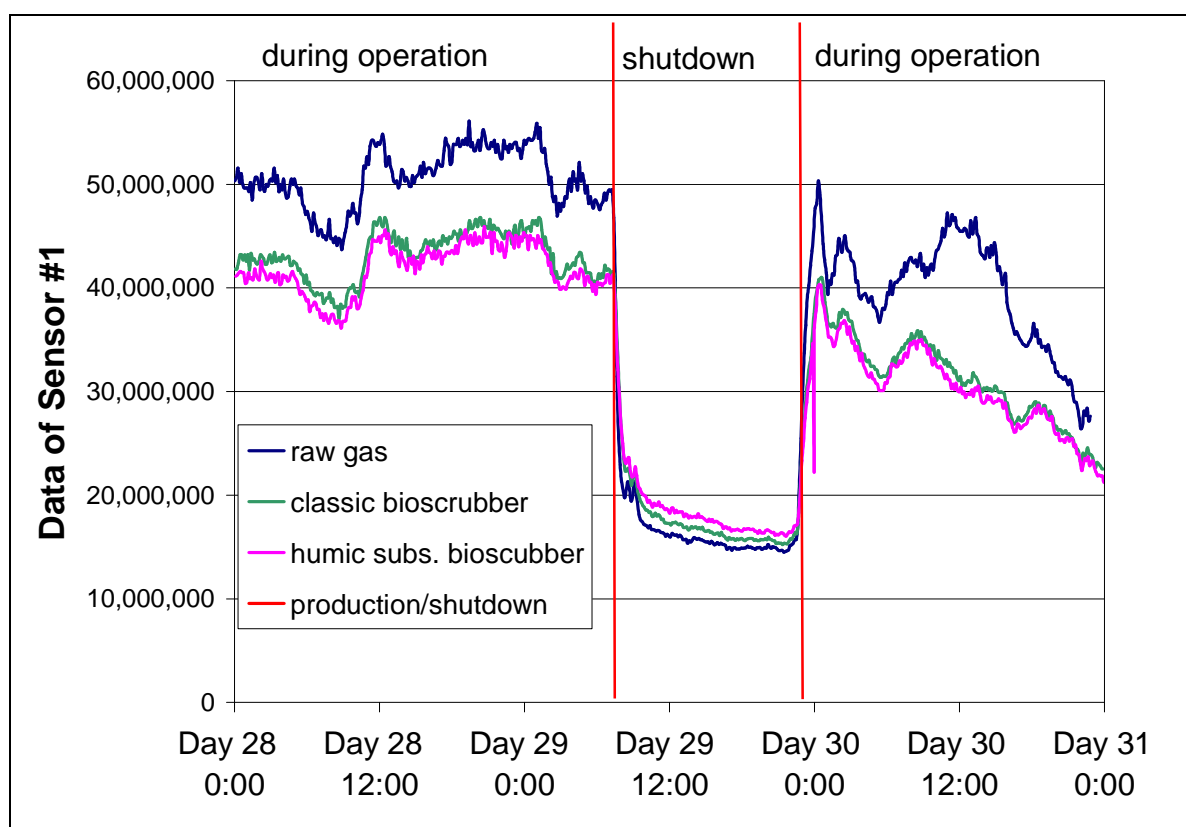
Figure 17: Monitoring of plant operation by usage of an electronic nose

There were several sensors that showed good correlation (R^2 = 0.91) with TOC (Figure 18a, b). On the other hand, correlation with odour concentration was low (R^2 = 0.32) (Figure 18c). One reason for that was the low correlation of odour concentration with TOC (R^2 = 0.40) (Figure 18d) which could have been caused by non odorous or only low odorous components in the exhaust air, which would have been determined by TOC and the electronic nose but not by odour measurement. Since for evaluation only raw sensor data were used and only limited number of laboratory data was available, there is a good chance that with more data and usage of the statistic evaluation software of the electronic nose the correlation of electronic nose data and odour concentration can be improved.
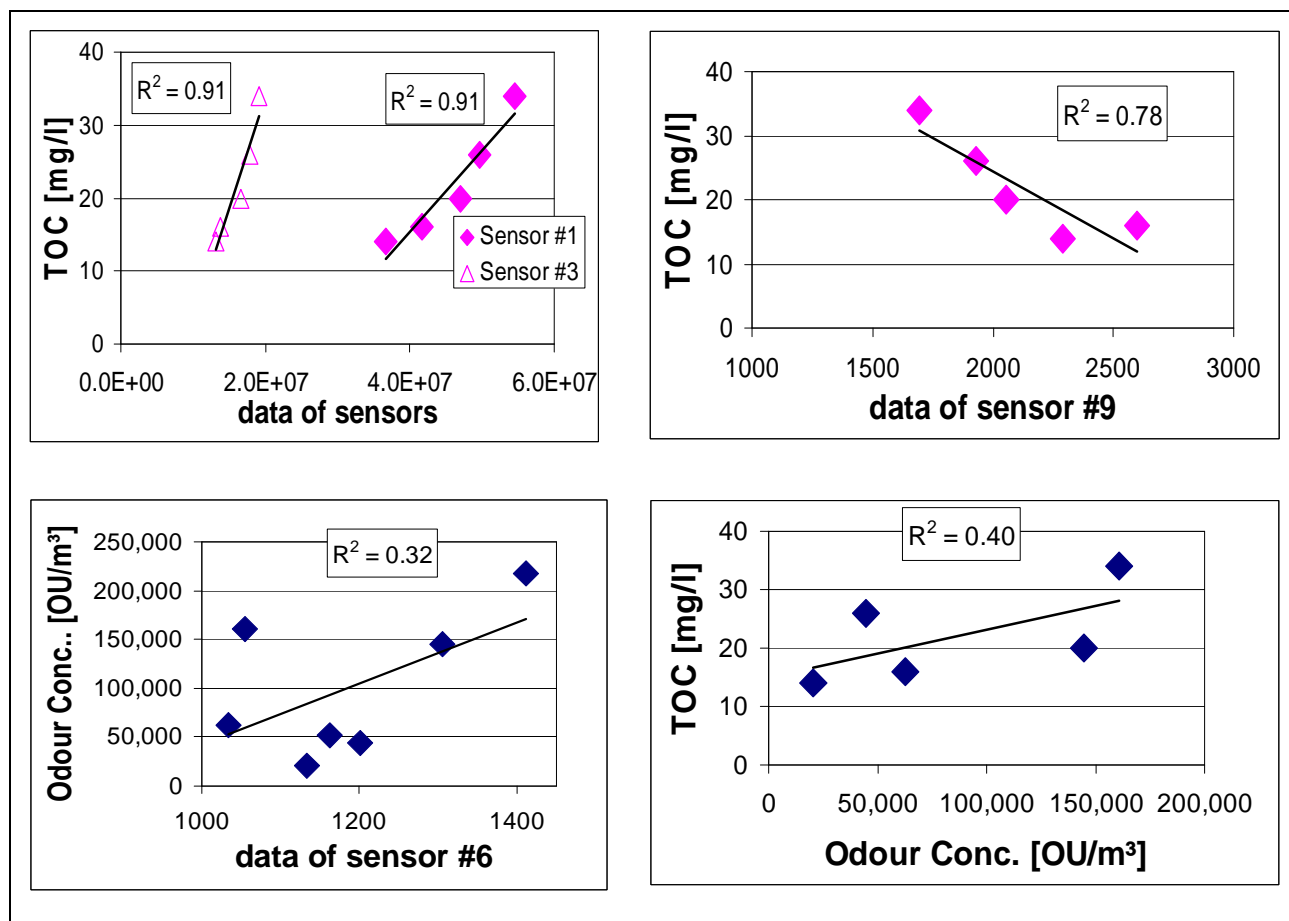
Figure 18a-d: Data of the electronic nose correlated with TOC and odour concentration (Gronek, 2005).

5.3.4.6 Conclusions

For a scale-up of bioscrubbers the results show that a single-stage model of a conventional bioscrubber can purify the specific waste air of the investigated starch factory with a reduction rate of over 90%. Although separation efficiencies over 90% were only reached for high raw air concentrations (above 250.000 OU/ m³) while for low raw air concentrations (from 250.000 OU/ m³) they were in the range of 60%. In case of investigated waste air form the starch factory most components were determined to be relatively good water soluble (see chapter 5.5.4.3). So, here improvement by humic substances was found to be 7% in average, which is smaller than in other examples.

To reach lower treated gas concentrations a secondary treatment step has to be implemented. For this specific application at the starch factory it is proofed that the

combination of a classic bioscrubber as the first step followed by a bioscrubber with humic substances is better than a two classic bioscrubbers in series. Addition of humic substances increased the performance of the second scrubber from about 35% to 80%. Total cleaning performance of a two-step bioscrubber was improved form 94% to about 99% by usage of humic substances at the second scrubber.

5.3.5 Kinetic constants for Scale-up

Scale-up calculations in chapter 6 will be done based on degeneration kinetics determined by the described bioscrubber experiments. Here, the applicability of the 1st order method (chapter 4.8.3) should be tested and if applicable the kinetic constant k_1 should be calculated.

5.3.5.1 Method

Since analysis was limited to the feed and the effluent waste air of the scrubbers it was impossible to determine where exactly the degeneration took place: in the biofilm, the water phase in the bioscrubber (hold-up) or in the water of the recycling vessel. Therefore the evaluation was carried out for the complete system (box model). The 1st order method with a kinetic constant k_1 [h^{-1}] is to be tested as a simple and practical method for a scale-up of bioscrubbers (eq. 28). If the kinetic constant k_1 is to be determined based on experimental data, it is the slope of the partial regression line of the reduction rate over the concentration.

$$k_1 = \frac{\Delta r}{\Delta c_M}$$

eq. 34

The reduction rate r can be calculated from the measured values based on mass concentration of the odorants [mg/m³] with eq. 35 or based on odour concentration [OU/m³] with eq. 36. Mean gas concentrations are calculated with eq. 29.

$$r_m = \frac{c_{M,m} \cdot Q_G}{V_R}$$ 　　　with c_m in [mg/m³] 　　　　**eq. 35**

$$r_{OU} = \frac{c_{M,OU} \cdot Q_G}{V_R}$$ 　　　with c_{OU} in [OU/m³] 　　　　**eq. 36**

5.3.5.2 Laboratory Experiments

Using data of the described laboratory experiments the reduction rate r [mg/(m³*h)] is calculated based on mass concentration of the odorous substance here DMS (Figure 19 and Figure 20). The lab experiments showed relatively good correlation of the measured data with a first order kinetic, so that the kinetic constants k_1 could be determined for each. An exception was experimental series 3, the distribution was too wide (see Figure 39).
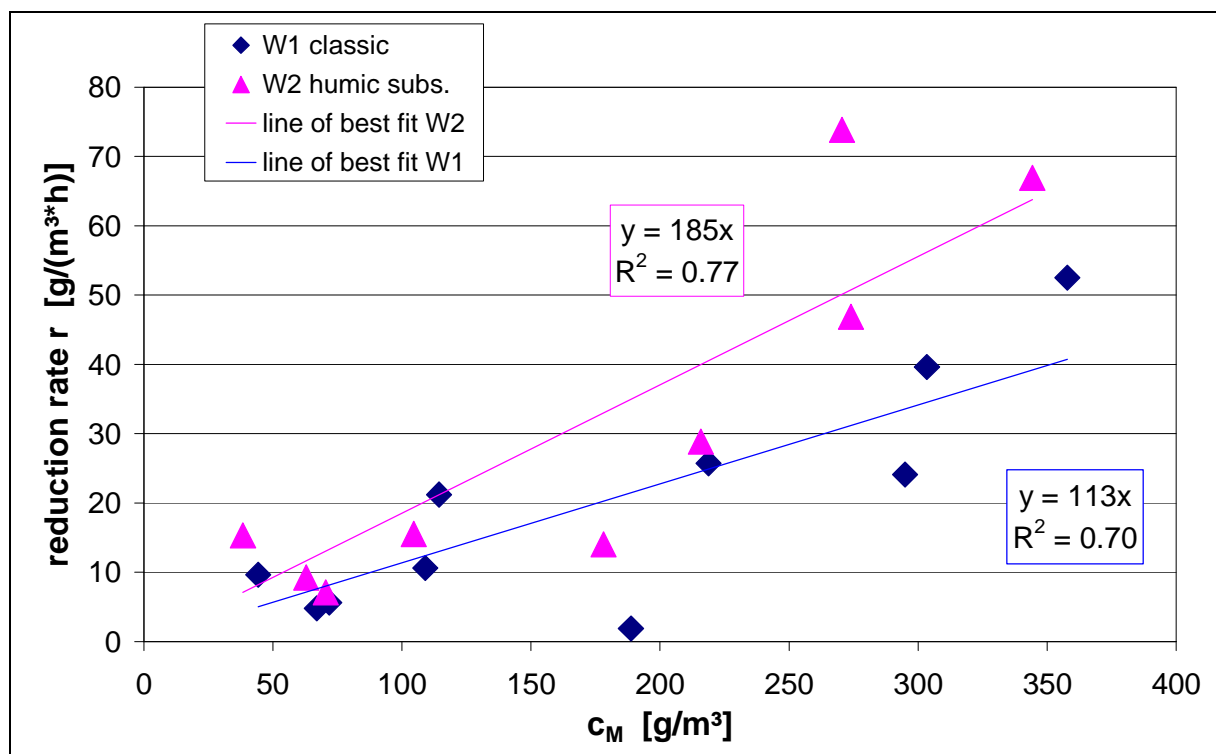
Figure 19: Determination of kinetic constant k1 [1/h] of series V1
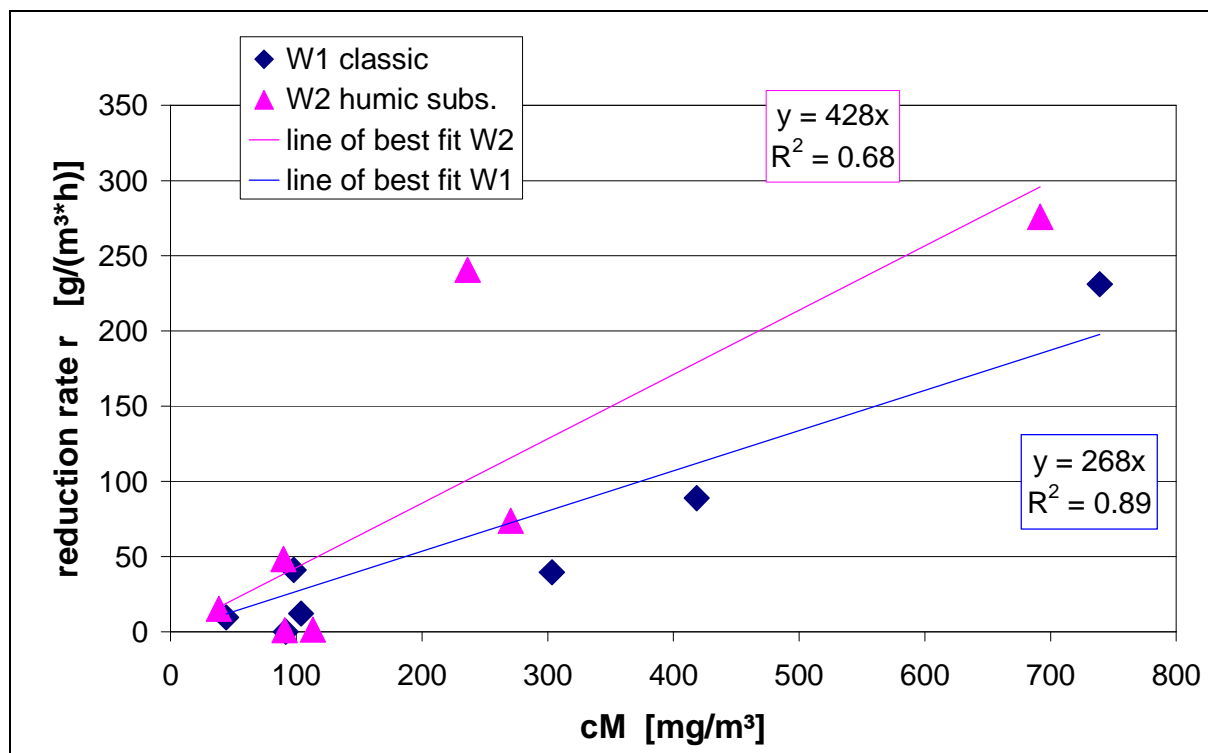
Figure 20: Determination of kinetic constant k1 [1/h] of series V2
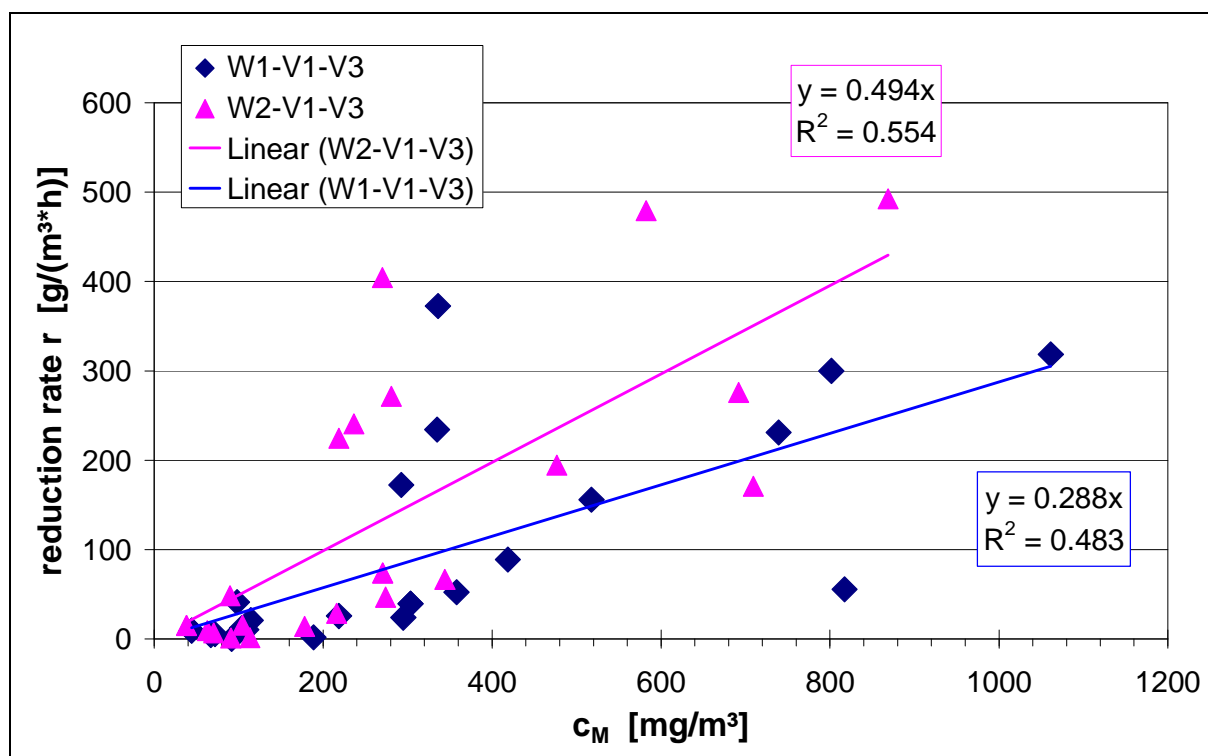
Figure 21: Determination of one kinetic constant k1 [1/h] of all series V1, V2 and V3

Table 11: Kinetic constants k$_{1,mDMS}$ [1/h] based on reduction rates in [g DMS/(m³*h)]

	W1		W2		number of measurements	improvement by humic subs.
	k$_1$ [1/h]	R²	k$_1$ [1/h]	R²	[-]	[%]
V1	113	0.70	185	0.77	9	62%
V2	268	0.89	428	0.68	7	60%
V3	318	-	571	-	7	80%
V1-V3	**288**	**0.483**	**494**	**0.554**	**23**	**72%**

For scale-up calculations in chapter 6 kinetic parameters are chosen which are determined by using data of all three experiments (Figure 21 and Table 11). This is done to increase the number of data points being used and to represent a broader range of operation.

5.3.5.3 On-site experiments

Calculation of the kinetic constant k$_1$ [1/h] from a typical industrial air application is done using data of fat and oil refinery experiments (chapter 5.3.3). Here the reduction rate r in [OU/(m³*h)] is calculated based on odour concentrations and the volumetric solvent ratio ν_v. All process data, e.g. gas concentrations and reduction rates, are listed in Table 41 in the annex. The kinetic constants were determined as shown in Figure 22 as k$_1$(W1) = 330 [h^{-1}] for degradation by the conventional bioscrubber and as k$_1$(W2) = 464 [h^{-1}] for the bioscrubber with humic substances. In this case, the performance improvement by usage of humic substances was about 41%.
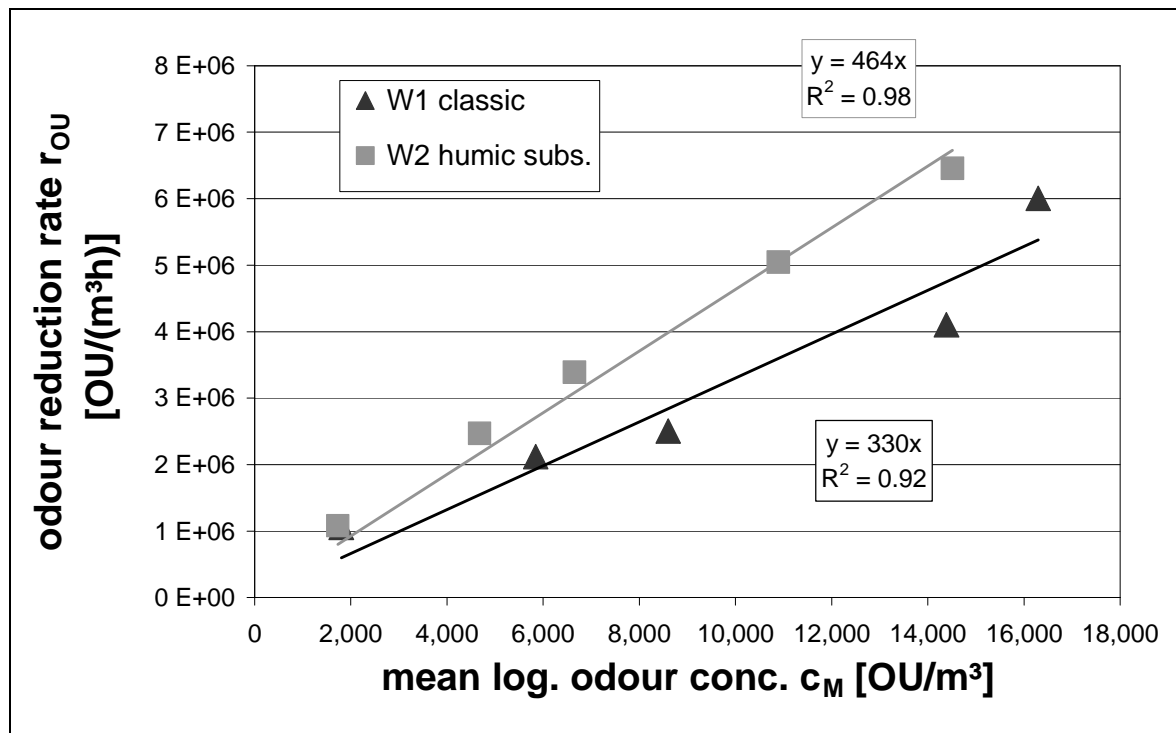
Figure 22: Determination of the kinetic constant k_1 [1/h] based on on-site experiments at a fat and oil refinery

5.3.5.4 Discussion

Comparing the determined k_1 values from laboratory and on-site experiments it becomes obvious how near the values are (Table 12). This surprises because they are determined for completely different waste gas compositions and by different analytical techniques. Data show that degradation behaviours in both cases are very similar and that they are mainly influenced by the biological system, by the growing conditions related to the type of reactor and by the type of absorbent.

Table 12: Comparison of k_1 values

k_1 values	type of concentration for quantification	W1 (classic bioscrubber)	W2 (bioscrubber with humic substances)
laboratory data	mass concentration [mg/m³]	288	494
on-site data	odour concentration [OU/m³]	330	464

5.3.6 Conclusions for Humic substances as solubility agents in bioscrubbers

Comparing the determined Henry coefficients shows that the humic substance, type Nussbeize, is a powerful solubility agent for a broad variety of odorants. This humic substance was chosen for being tested in bioscrubbers in laboratory and on-site experiments. All experimental data show that a biological waste air treatment with bioscrubbers is an effective and reliable process. In all experiments an improvement of the cleaning performance by usage of humic substances was proofed. Degree of improvement varies from small improvements (i.e. 7% improvement at a single step bioscrubber at the starch factory and 10% at the fat and oil refinery), to medium improvements (i.e. between 34 and 50% at a single step bioscrubbers at the laboratory with very high odour concentrations) and to high improvements (>90% improvement at a second bioscrubber step at the starch factory). Since no negative experiences were made with humic substances and material costs are low, a usage can generally be recommended, although the degree of improvement varies with the waste air composition and concentration. It is demonstrated once again that a proper bioscrubbers design can only be done on basis of pre-investigations using on site experiments, no matter if humic substances are used or not. The concentration of the humic substances has a relatively low influence on the effect. There are several results showing that lower concentration might even be more effective. A 1.5% w/w concentration has proofed to be a good starting point, but a subsequent optimization for a specific waste gas should always be done.

5.4 Test of washing oils in waste air scrubbers

5.4.1 Absorbents and treatment concepts

High-boiling absorbents, or washing oils as they are called, have been successfully tested for multiple component absorption in absorption columns. Their principal applicability for absorption of odorants has been proofed by determination of Henry coefficients. In the following chapters HC10 and TEGDE are examined more deeply. HC10 is a high-boiling alcane fraction with a complex composition. Its absorption capacities have been extensively investigated by Kalina (1997) in the field of solvents recovery from waste gas. TEGDE is a widely applied absorbent for separating organic

solvents (Winterbauer, 1994; Weisweiler et al., 1992; Schaber et al., 1996). An important difference between these two absorbents is their regenerability. HC10 can be regenerated by steam stripping due to its hydrophobic character. If TEGDE should be regenerated by stripping, it can only be done with air as strip gas. Water steam cannot be used for regeneration, due to the high water solubility of TEGDE. Within this work, the focus is on testing washing oils combined with regeneration by stripping. Therefore the following 5 concepts (Table 13) are chosen and will be compared.

Table 13: Absorption/Desorption concepts using oils as washing liquids

absorbent	entrainer	regeneration temperature	aim
1.) HC10	steam stripping	100 °C	separation
2.) HC10	air stripping	100°C	concentration
3.) HC10	air stripping	20°C	concentration
4.) TEGDE	air stripping	100°C	concentration
5.) TEGDE	air stripping	20°C	concentration

Only the first process can be used directly for separation of odorants, since they are isolated by condensation together with the steam condensate. At all processes of air stripping for regeneration the odorants are discharged with the stripping air. These processes can only be used for concentration, so a downstream treatment step, e.g. combustion is required.

A laboratory air scrubber using oils as absorbents has been assembled for treatment of synthetic and real waste air streams. Different techniques of online regeneration of the oils like steam stripping and cold or hot air stripping were investigated. Additionally an investigation is presented exemplarily comparing the absorption efficiency of four different absorbents applied to exhaust air of a chocolate factory (chapter 5.5.4.1).

5.4.2 Methods and materials

An experimental set-up is assembled, consisting of a scrubber column in laboratory scale and a heatable stripping column for regeneration of the absorbent. The absorber

is made from a PVC-U-tube, D_i = 27 mm, L = 1500 mm. A geometric packing from Montz, type A3, a = 500 m^2/m^3, is used with a packing height of 1000 mm. The regeneration column was assembled from a Vigreux column made from Duran glass of 600 mm height combined with an intensive cooler of 400 mm height. At the bottom of the regeneration column the supply of stripping gas, water steam and air is provided. The column can be heated from the outside by a trace heating and by water steam which is conducted through the heating coil of the intensive cooler. A steam generator with an electrical power of 1.8 kW and an operating pressure of 1.0 – 1.1 bar is used. Two Dimroth coolers of 400 mm height made from Duran glass were integrated as recuperators. Additionally a water cooler, a condenser and several flowmeters for adjusting the flows are parts of the experimental set-up (Figure 23 and Figure 24). Production of synthetic exhaust air is done by a gas generator, which consists of a 1000 ml glass vessel with an open laboratory flask inside, filled with one pure liquid odorant. A small gas flow is lead through the head space of the glass vessel, where it picks up the evaporating odorant. Then this gas flow is dosed into the raw gas stream. Dosage of odorant can be varied using laboratory flasks with different geometries.

In laboratory 40 series of measurements were carried out with the described set-up (Fenski, 2003). The absorptive and desorptive behaviour were evaluated of the odorants dimethyl sulphide (DMS), triethyl amine (TEA) and pentane ethiol (PT) in the high boiling washing liquids HC10 and TEGDE. Regeneration was done by stripping either with water steam or with air. The influence of operational parameters was examined.

Although the gas superficial velocity w_g should be between 0.2 and 1.0 m/s within operational conditions (Sattler and Feindt, 1995) lower velocities between 0.072 and 0.24 m/s were chosen in the experiments, due to short mean retention times (< 5 s) in the scrubber related to the low height of the packing (1.0 m). A liquid loading was chosen between 13 and 16 $m^3/(m^2 \cdot h)$, which is high above the minimum value of 2 $m^3/(m^2 \cdot h)$ for organic absorbents and 10 $m^3/(m^2 \cdot h)$ for aqueous absorbents. These minima should be exceeded to avoid maldistribution of the liquid (Last, 1999). All ranges of operational parameter are listed in Table 14.
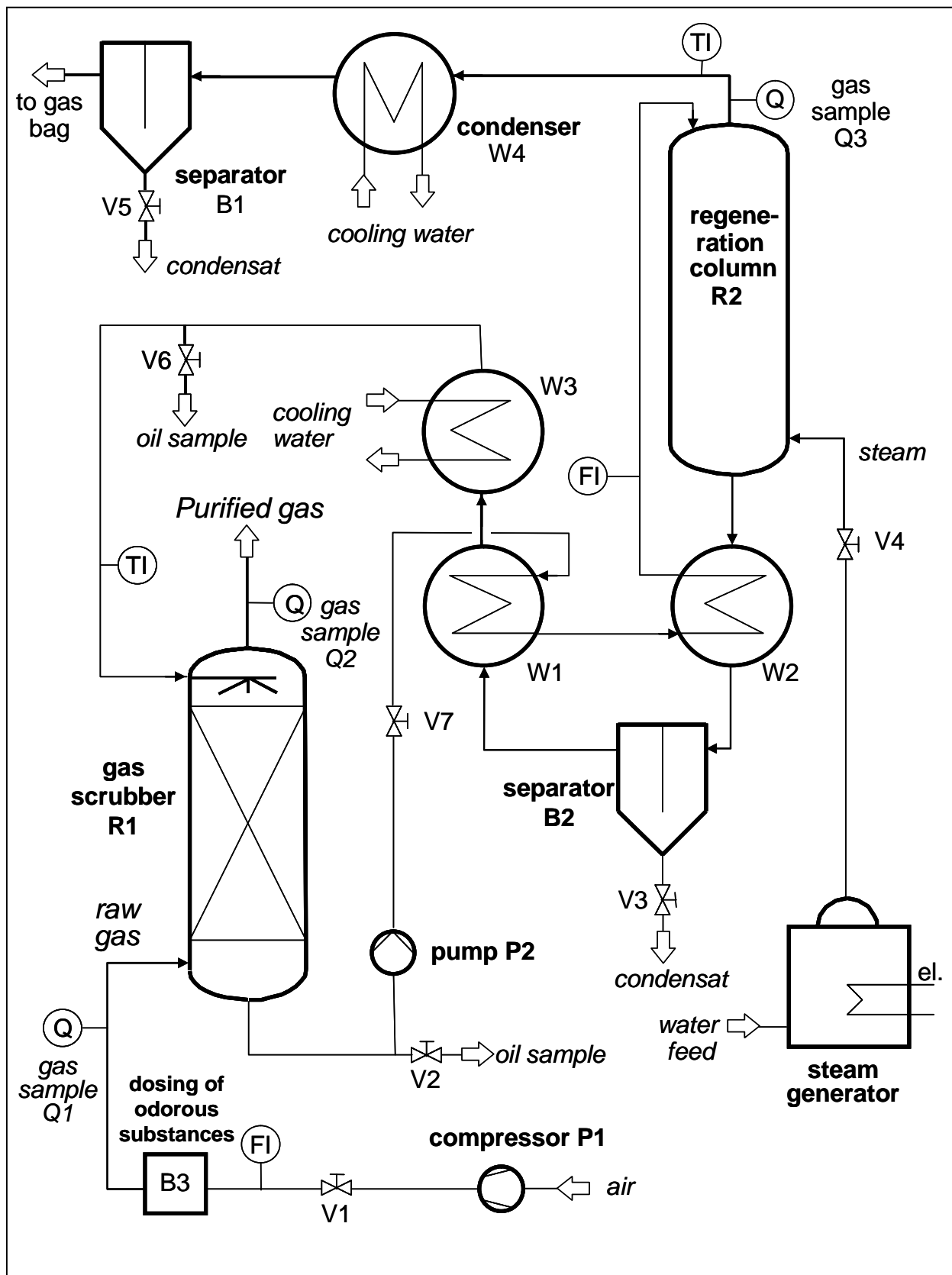
Figure 23: Set-up of oil scrubber with absorption and regeneration columns

①	oil scrubber	②	dosage of odorous subst.
③	regeneration	④	M. Fenski (constructor)
⑤	pump	⑥	steam generator
⑦	condenser	⑧	gas flow sensor
⑨	compressor	⑩	heat exchanger
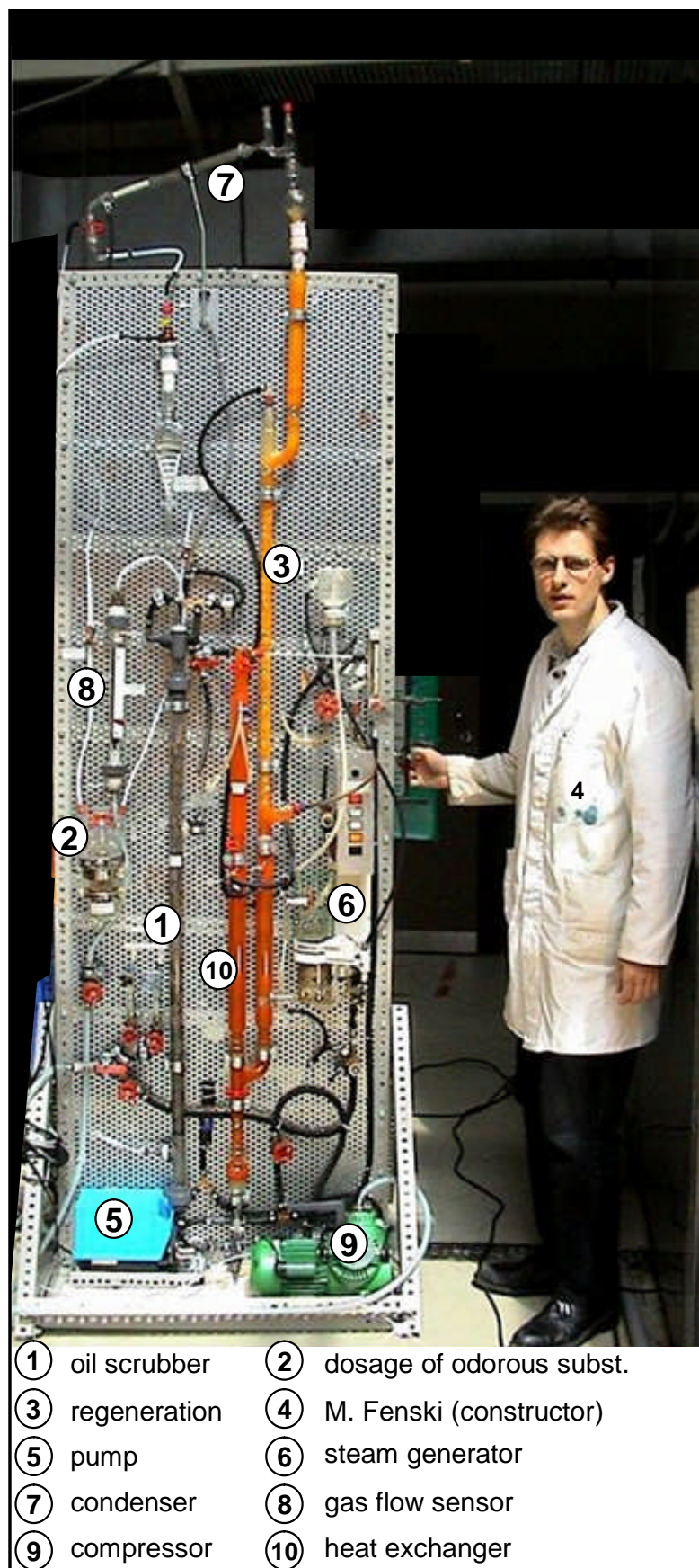
Figure 24: Laboratory oil scrubber

Table 14: Operational settings of laboratory oil absorption experiments

gas volume flow		[l/h]	150, 200, 300, 500
absorbent flow	HC10	[l/h]	6.4, 7.7, 9.3
	TEGDE	[l/h	3.4, 4.5
stripping air flow		[l/h]	0 – 300
odorant	DMS	[g/h]	0.11 – 13.0
	TEA	[g/h]	0.37 – 1.43
	PT	[g/h]	0.11 – 0.12
temperature of regeneration		[°C]	18, 81, 100, 110
steam flow		[g/h]	approx. 500

Gas sampling is carried out with a 1ml gas syringe through the septum of the sampling points Q1 (raw gas) and Q2 (purified gas). After 10, 30, 50, 70, 90, 110 minutes two samples of raw gas and after 20, 40, 60, 80, 100, 120 minutes two samples of purified gas each are taken. Samples are injected into the GC/FID-System immediately after been taken and analysed. After 40, 80, 120 minutes two samples of absorbent before and behind the scrubber, and two aqueous samples from condensates were taken and analysed using the automatic headspace method of the GC/FID system. Dosage of odorant is determined by weighting the flask with the liquid odorant before and after the experiment.

5.4.3 Results and Discussion

All experimental data and an exemplary calculation of the concentration are shown in the annex (Table 37 - Table 40). In Figure 25 the separation efficiencies of DMS by absorption in HC10 and TEGDE are shown depending on the stripping factor S_{abs}. The highest separation efficiency (up to 95%) is achieved using HC10 at low stripping factors (< 0.4) and a regeneration by steam stripping. At higher stripping factors S_{abs} (0.6 – 1.1) the separation efficiency of HC10 is significantly lower η_{abs} (55 – 75%). Similar high efficiencies η_{abs} (70 – 90 %) can be achieved by using TEGDE regenerated by air stripping at 100°C. For this, significantly lower liquid flows are required, which means higher stripping factors S_{abs} (0.9 – 1.3). At lower regeneration temperatures T_{reg} (18°C – 33°C) only minor separation efficiencies η_{reg} (< 50%) were determined in all examined cases.
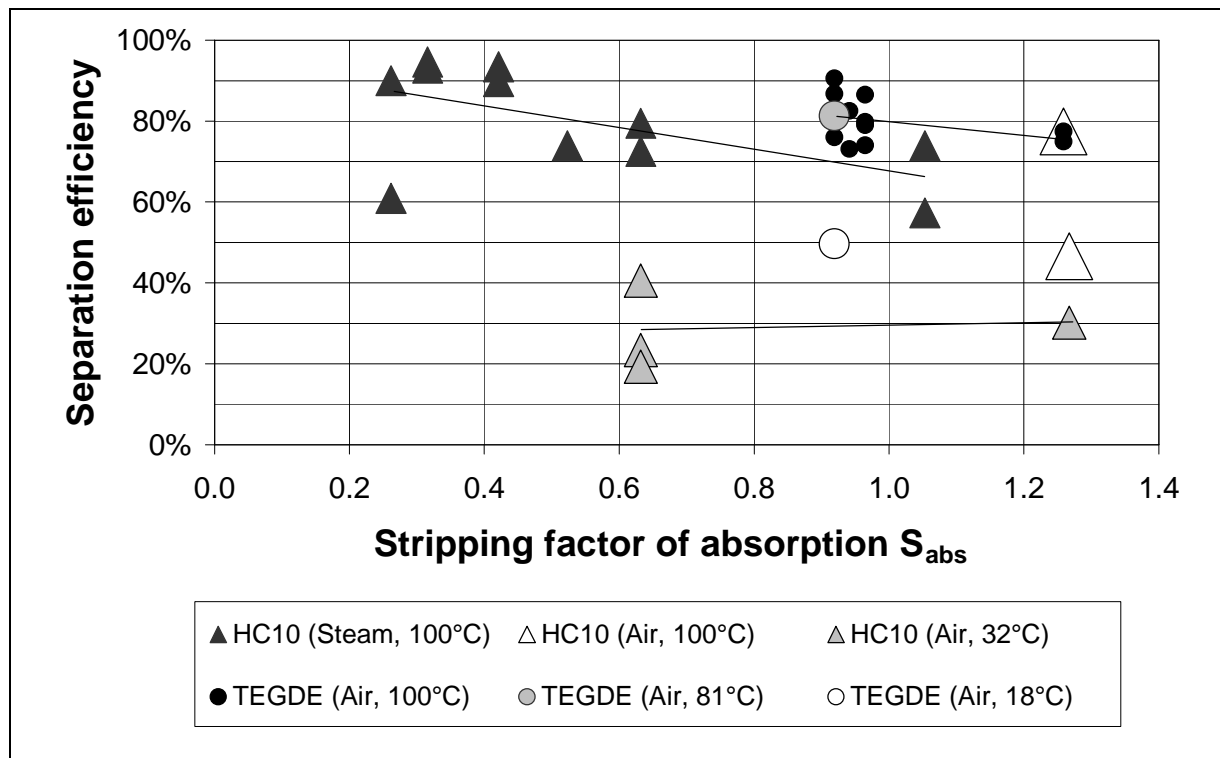
Figure 25: Absorption Efficiency of DMS in HC10 or TEGDE

High separation efficiencies were reached with both absorbents. The positive impact of a high solvent-to-gas-ratio, expressed by low stripping factors S_{abs}, is obvious. In comparison TEGDE with regeneration by air stripping at 100°C shows better results than HC10 with steam regeneration at 100°C. Absorption with TEGDE shows an about 10% higher absorption efficiency η_{abs} than absorption with HC10 with the same stripping factor. From another perspective, absorption with TEGDE needs between 30 and 40% less liquid flow to reach the same separation efficiency than HC10 does.

In Figure 26 regeneration efficiencies are shown depending on the stripping factor S_{reg} of regeneration. For interpretation it should be considered that higher stripping factors S_{reg} represent higher strip gas flows and by that higher operating costs. High regeneration efficiencies of these absorbents can only be achieved at stripping factors S_{reg} above 1.6 at a temperature of 100°C. For a regeneration efficiency η_{reg} above 95% a stripping factor S_{abs} of 1.8 is required for regeneration of TEGDE by air stripping, whereas regeneration of HC10 by steam stripping needs a stripping factor S_{abs} about 3.0. This means a saving of strip gas of about 40%, when TEGDE is used. Since the

79

slope of the partial regression line of the HC10 regeneration efficiency is low, a stripping factor of S_{abs} 2.0 is supposed to be sufficient to reach a regeneration > 90% and should be used for scale-up.
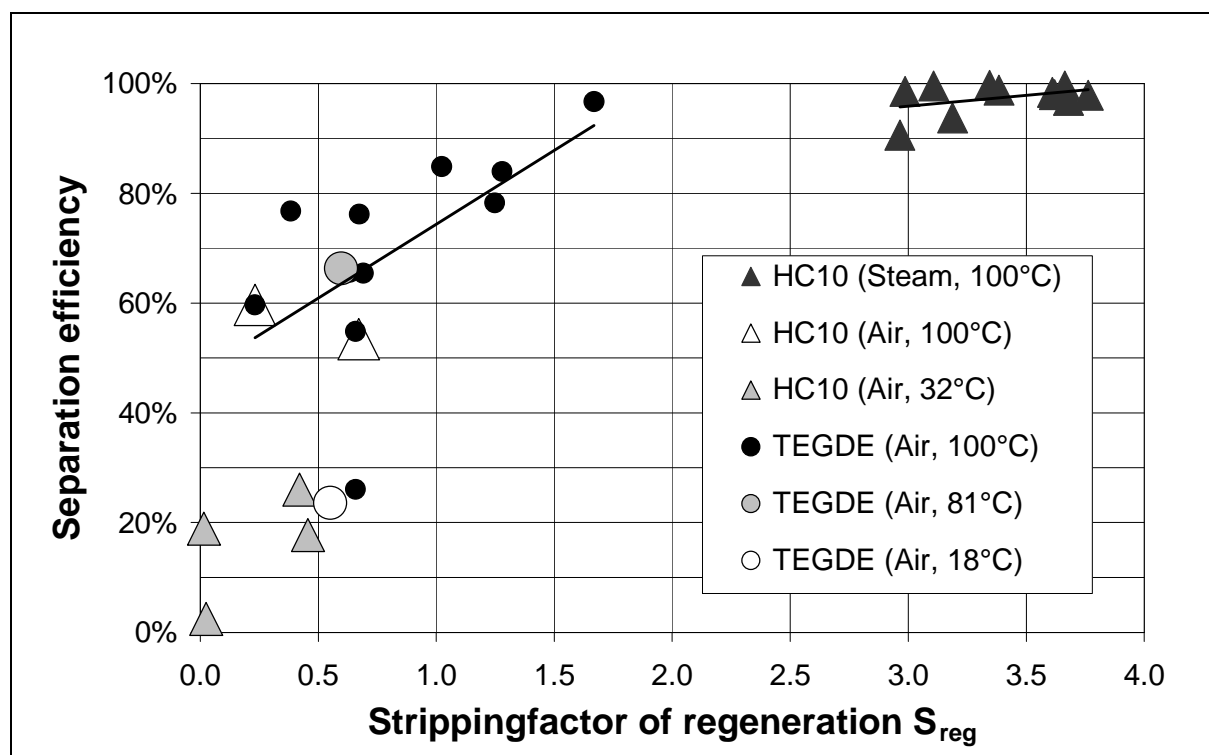
Figure 26: Regeneration Efficiency of DMS with HC10 or TEGDE by steam or air stripping regeneration

Comparison of solubility behaviour of the three odorants DMS, TEA and PT by in HC10 shows at the same range of raw gas concentration that TEA and PT are separated better by trend than DMS. At a stripping factor of S_{abs} = 0.3, DMS is separated by about 90%, while TEA concentration of the treated gas is below detection limit, so TEA is defined as being separated completely (Figure 27). PT is separated by 95 - 98% at a stripping factor of S_{abs} = 0.1. In this case a direct comparison with DMS is not possible, since there are no data of DMS with S_{abs} < 0.25. But it is reasonable to assume by extrapolation of the separation tendency of DMS, that absorption efficiency of DMS would only be in the range of 90 - 95%, just. As a result it can be stated that the absorption efficiency is better for TEA and PT than for DMS when HC10 is used as absorbent. So, DMS is the biggest challenge for absorption with HC10 and should be

used as a reference in further investigations. For scale-up calculations an optimized stripping factor has to be chosen. There are several references in literature defining economical ranges of stripping factors (Table 15). Most authors recommend a minimum stripping factor of $S_{abs} = 0.5$ for absorption. Smaller factors would lead to higher liquid flows and higher operating costs.

Experimental data of show a clear increase of efficiency from about 75% to 90% at absorption with HC10 and smaller stripping factors S_{abs} of 0.4 to 0.6. So a stripping factor of $S_{abs} = 0.5$ for absorption with HC10, which is the minimum recommended value, is a good choice for scale-up calculations. For regeneration a stripping factor of $S_{reg} = 3.0$ is chosen, although it is above most recommended ranges for regeneration, because this is the minimum successfully tested strip gas flow in the described experiments.

Table 15: Economical ranges of stripping factors from other authors

S_{abs} [-]	S_{reg} [-]	reference
0.5….0.9	1.1…2.0	Sattler and Feindt (1995)
0.33…0.67	1.5 …3.0	Fritz and Kern (1990)
0.56…0.77	1.3…1.8	Weisweiler et al. (1992)
0.67…0.83	1.2…1.5	Brauer (1989)
0.5….1.0	1.0…2.0	Bratzler and Doerges (1972)

Since concentration is the intention of the processes using air stripping, the achieved concentration factor f is the most important factor for comparing applications of this process. The highest concentration factor f = 5.35 was achieved using TEGDE at 100 °C with a stripping factor S_{reg} of 0.23. With the same settings an adequate absorption efficiency of 77.5% is reached at a stripping factor of S_{abs}=1.26 (Figure 28).

81
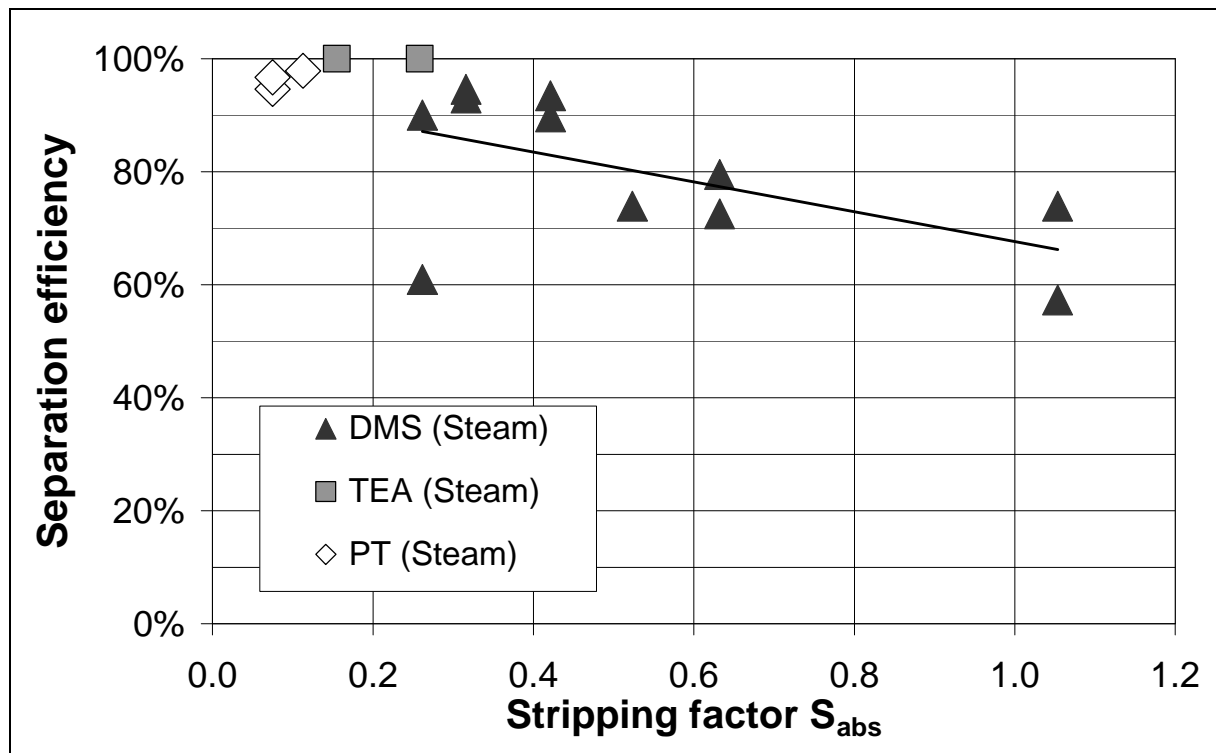
Figure 27: Separation efficiencies of DMS, TEA and PT with HC10 at $T_{reg}=100°C$

5.4.4 Kinetic constants for Scale-up

For scale-up of oil scrubbers and their regeneration two different methods are used within this work. First, the HTU-NTU method is used, which is based on the overall gas-phase mass-transfer coefficient (k_Ga) as the main characteristic parameter and second the theory of theoretical separation stages is used, where the height of a theoretical separation stage (HETS) is to be determined (see chapter 6). The overall gas-phase mass-transfer coefficient of an absorption process (k_Ga_{abs}) and a regeneration process (k_Ga_{reg}) is determined based on laboratory data. All experimental data and all calculation steps of k_Ga_{abs} and k_Ga_{reg} are listed in Table 37 in the annex. In Figure 29 the calculated mass-transfer coefficients are demonstrated for absorption of the odour substance DMS and the absorbent HC10 with steam regeneration. A relatively good correlation with the stripping factor S_{abs} is found. So the mass-transfer coefficient can be calculated within tested range of stripping factors using the calculated partial regression line:

k_Ga (DMS) = 44.93 * S_{abs} + 15.14.
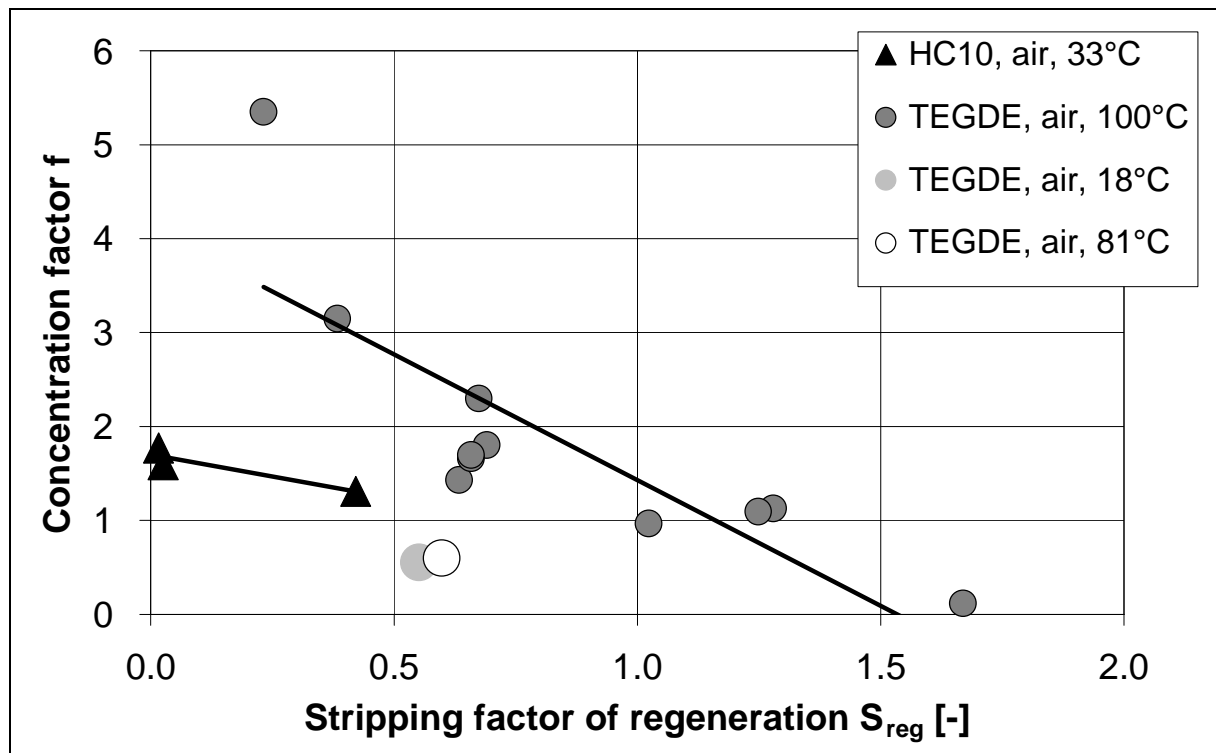
Figure 28: Concentration factor depending on stripping factor of regeneration (DMS in TEGDE)

For economical reasons a stripping factors of S_{abs} of 0.5 is chosen for absorption of DMS by HC10 as described in chapter 5.4.4. For these settings the overall gas-phase mass-transfer coefficient k_Ga is 38 kmol/(h*m³). Compared to values from Bratzler and Doerges (1972) the determined mass-transfer coefficient is in a typical range of chemical absorption with chosen technically applied absorbents (see Table 16). The potential improvement by usage of adapted absorbents instead of water can be seen by assessing values of this table. In this context the determined mass transfer coefficient of HC10 at this application is in a good range, since generally chemical absorption has higher separation efficiencies than physical absorption. Due to the experimental set-up it was impossible to vary the steam flow in a broader range. So all applied steam flows and by that also all stripping factors of the regeneration were in a narrow range of S_{reg} = 3.0…3.8 [-], so the calculated mass-transfer coefficient k_Ga_{reg} of the regeneration does not correlate well with the regeneration stripping factor S_{reg} (Figure 30). For that reason the average value of k_Ga_{reg} (DMS) = 226 (kmol/(h*m³) is used for later scale-up.
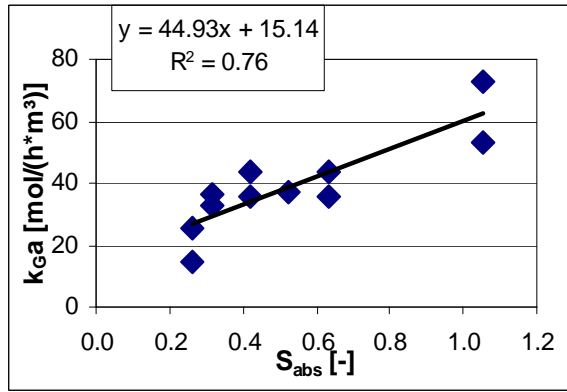
Figure 29: k_Ga_{abs} of absorption process (DMS in HC10)
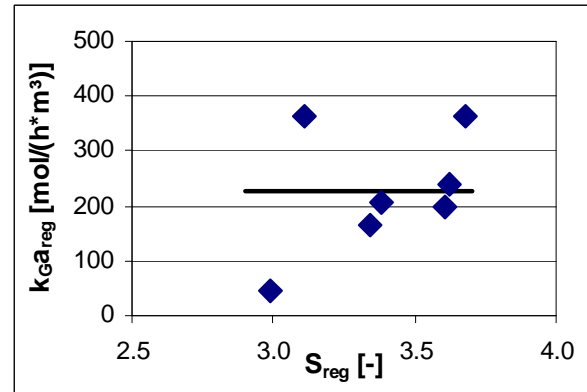
Figure 30: k_Ga_{reg} of regeneration process (DMS in HC10)

Table 16: Overall gas-phase mass-transfer coefficients for chemical absorption (Bratzler, 1972)

Gas	Absorbent	k_Ga [kmol/(h*m³)]
H_2S	$MEA - H_2O$	256
SO_2	$NaOH - H_2O$	240
H_2S	$DEA - H_2O$	160
CO_2	$KOH - H_2O$	95
CO_2	$MEA - H_2O$	63
CO_2	$NaOH - H_2O$	36
H_2S	H_2O	6.4
SO_2	H_2O	5.1
CO_2	$H2O$	1.15

Legend: filling material: 1 ½" Intalox- bridges, 25% conversion, P=1.0197 bar

With the same method the heights of a theoretical separation stages (HETS) are determined. All experimental data and all calculation steps of $HETS_{abs}$ and $HETS_{reg}$ are listed in Table 37. The height of a theoretical separation stage depends on the stripping factor and can be calculated by approximation with HETS= -0.3962*S_{abs} +0.8559 (Figure 31) as the partial regression line.
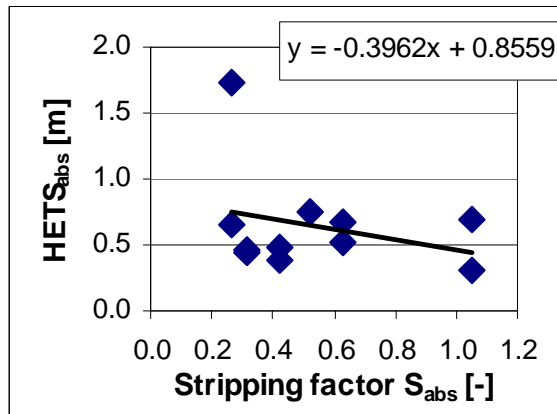
Figure 31: HETS of absorption   Figure 32: HETS of regeneration
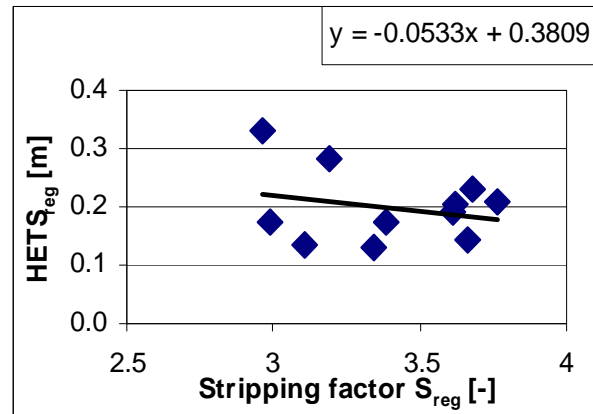
The height becomes $HETS_{abs}$ = 0.66 with a stripping factor Sabs = 0.5. For the same reason as being described for the mass-transfer coefficients, the height $HETS_{reg}$ does not correlate well with the stripping factors S_{reg} and the average value of $HETS_{reg}$ = 0.22 m is used for later scale-up (Figure 32).

5.4.5 Conclusions of washing oil tests

The absorbents HC10 and TEGDE were investigated and compared based on experimental data. Due to their different solubility in water, the absorbents were regenerated by different methods. Results indicate that high absorptive separation efficiencies can be reached with both absorbents and both absorbents can be well regenerated by stripping. In direct comparison, TEGDE showed slightly better absorption efficiency than HC10. The same tendency is identified in effort of regeneration, which means the required strip gas flow. This effort of regeneration is about 40% less for TEGDE than for HC10. On the other side, the relatively poor concentrating factors, which were only between f = 3…5 [-], proofed the process of concentration by air stripping as being not efficient. HC10 has the advantage, that it can be used with a steam regeneration, which is proofed to be an effective method of separating odorants and recovering them in a high concentrated liquid in the condensate phase of the stripper column. Data of HC10 experiments will be used in chapter 6 for scale-up calculations and a comparison with bioscrubbers on basis of two case studies

5.5 Screening test of washing liquids

5.5.1 Introduction

Data of preliminary tests with pilot plants are required for planning a full-scale waste gas scrubber. Since preliminary test are time and costs intensive, the expense must be reduced to an acceptable minimum. For this purpose two types of screening tests are developed within this work for evaluation and comparison of washing liquids, based on absorption rates when being applied to an industrial waste gas. The first one is a static method, where gas samples reach equilibrium with the liquid phase. The second one is a dynamic test method, called scrubber test, where a waste gas gets into a short but intensive contact with the liquid. Here, the mass transfer is also influenced by kinetic parameters. An evaluation of these tests is done with waste gas from a chocolate factory, a fat and oil refinery and a starch factory. Results of the static and the dynamic tests are presented and compared for applicability as a preliminary test to gain design data. Based on these findings, best choices of absorbents for each company are identified.

5.5.2 Key compounds selection procedure

To understand the effectiveness of solubility agents in application to waste air, it is required to identify and quantify single odorants from untreated and treated samples. Since waste air typically consists of a complex composition of substances, key compounds must be identified. With these compounds it is easier to understand and to demonstrate the effects of washing liquids. The selection of key compounds should help to identify main causers of specific smells. From the domain of food and flavour chemistry a technique to identify key compounds is known, which is called depending on the author "odour index" (Goldstein, 2001), "aroma value" (Rothe, 1963), "odor unit" (Guadagni, 1966) or "odour active value" (Acree, 1984). The "odour ratio" (Freudenthal et al., 2004c, 2005a, 2005b) is a further approach developed within our cooperative research project to identify key compounds in a waste gas sample. It is calculated as the ratio of the concentration of a volatile compound to its odour threshold OT_i (eq. 37). Since single substances should not be assessed absolutely but in relation to other substances in the sample, the absolute number of the odour ratio is of no meaning, but

only the participation of the ratio of one component in the sum of all odour ratios of the collective. So the characteristic parameter, which describes the potential contribution of a single component to the cumulative odour impression of a gas sample, is named the "relative odour ratio OR%$_i$", which is calculated by eq. 38 and used in the following discussions.

$$OR_i = \alpha_i \cdot \tau_i$$

eq. 37

$$OR\%_i = \frac{OR_i}{\sum\limits_{j=1}^{n} OR_j}$$

eq. 38

with

$$\alpha_i = \frac{a_i}{\sum\limits_{j=1}^{n} a_j}$$

eq. 39

and

$$\tau_i = \frac{\sum\limits_{j=1}^{n} OT_j}{OT_i}$$

eq. 40

parameters		explanation	units
OR$_i$	:	odour ratio of the compound	[%]
a$_i$	:	peak area of the total ion currency chromatogram of compound i (TIC)	[-]
OT$_i$:	:	olfactory threshold of the compound i	[µg/l]
α_i	:	peak area participation of compound i	[%]
τ_i	:	inverse of the olfactory threshold participation of compound i	[%]

To diminish the analytical effort, the quantification of concentrations is replaced by using the measured peak areas a$_i$ from the total ion currency chromatogram (TIC) of SPME/GC/MS measurements. Data of olfactory thresholds are taken from Devos (1990); Gemert (1977) and Rychlik (1998). To demonstrate the separate influence of the two factors concentration or TIC peak area, respectively and olfactory threshold, the peak area participation α_i (eq. 39) and τ_l as the inverse of the olfactory threshold participation (eq. 40) are calculated in percentage and listed separately for each key

compound. This approach is based on the assumption that first, the TIC peak area of a compound correlates with its concentration and second, that odorants with lower olfactory thresholds have a more intensive odour.

To visualize the composition of a raw gas sample, the key compounds being identified by the odour ratios are included in a radar plot in a star-shaped pattern, which can be termed the finger-print of the gas sample. Each peak represents a key compound of the gas sample. The calculated odour ratios are used to order the substances in the diagram. The lengths of the star's peaks are of no meaning. The number of key compounds can be chosen depending on the gas complexity, but should not exceed 20 compounds.

The effect of washing liquids can be illustrated by changes in the pattern. If the measured TIC peak area of a substance in a treated sample is below a defined selection limit then this substance is defined within this test as being separated. The selection limit must be adapted to the raw gas concentration. A good starting point is a value of 10%. Then the star's peak of this substance is left out the characteristic pattern of the sample. The more peaks are left out the more key compounds are absorbed. Absorption of compounds with higher odour ratios should lead to higher odour reductions then absorption of compounds with smaller odour ratios. So this finger-print diagram represents the key components of a sample and visualizes changes in composition due to application of absorbents.

5.5.3 Method and materials

Within the static screening test, samples of undiluted waste gas are taken at the source. Sampling is done with a sampling device being used for olfactory measurements according to the VDI-guideline 3881-2 (Anonymous, 1995) for static sampling. Before closing a filled sample bag, a washing liquid is added with a dosage of 10 ml per litre air. For equilibration the sample bag is stored for at least 6 hours in laboratory at a

constant room temperature. Subsequently, gas analysis is done by olfactometer, SPME/GC/MS and TOC. One sample of untreated waste gas is analyzed and used as a reference.

Within the dynamic screening test or the scrubber test resp., a transportable experimental set-up with a scrubber column was used for on site investigations. The absorber was made from a PVC-U-tube with an inner diameter of 27 mm and a length of 1500 mm. A geometric packing from Montz was used, type A3 (500 m^2/m^3) with a packing height of 1000 mm. For these experiments only pure or conditioned absorbents were used in a non-recurring cycle, to examine the separation efficiency of the liquids without an influence of regeneration. All scrubber tests were carried out with a gas volume flow of 300 l/h and a liquid flow of 10 l/h at ambient temperature. Gas feed was transported by a gas pump from the source to the experimental set-up by a teflon tube of 20 m length and 5 mm diameter. Samples of treated air from the scrubber outlet were collected in sample bags and analysed as in the static test. As a reference a sample of the raw gas is transported the same way as the treated samples through the pump, the teflon tube and the scrubber before the first liquid has wetted the scrubber packing.

At the chocolate factory, samples were taken from the headspace of a conche which belongs to the raw chocolate production. At the fat and oil refinery a chemical scrubber for odour control is in operation, where a caustic potash is used as a washing liquid. Samples for the screening test were taken from the gas phase above the scrubber recycle tank. At the starch factory samples were taken from two exhaust gas streams from dryers, which are used for conditioning of by-products. All used gas sources of the production facilities were identified before as main odour emission sources by the project partners (Schlegelmilch, 2004a).

5.5.4 Results

5.5.4.1 Results from screening tests at a chocolate factory

Within this measurement series four absorbents were tested. For testing the applicability of bioscrubbers an aqueous solution of humic substances were applied, made from a sodium salt of humic substances (trade name "Nussbeize"). Based on data from determined Henry coefficients and from experiments with the physical scrubber, two promising washing oils, HC10 und tetraethylene glycol dimethyl ether (TEGDE), were chosen to be tested within these series. Water is used as a reference.

Olfactometric data show a raw gas concentration of 10,100 OU/m³ (Table 17), which is in a typical range of an industrial gas, which has to be treated, if it appears in a remarkable gas flow. Application of water showed no reduction. The solution of humic substances reduced the concentration by 70% and HC10 and TEGDE show further slight improvements (76% or 86%, resp). Otherwise absorption was not sufficient, because odour characteristic remained a typical chocolate odour, which indicates that main key compounds were no separated effectively. Identified key substances are listed in Table 18 sorted by relative odour ratios. Separation efficiencies determined by the dynamic screening test show the same tendency as the static test, although all measured odour concentrations in the screening test are higher than in the scrubber test. Since the same gas was probed within both tests the lower concentration of the scrubber tests can only be a consequence of losses by the passage through the telfon tube e.g. by adsorption to the tube wall.

While odour reduction by usage of water is between 0% (screening test) and 50% (scrubber) it can be improved to 60% in the screening test and 78% in the scrubber test by usage of the solution of humic substances. In this experiment HC10 leads to a similar odour reduction of 66% to 76%. Only TEGDE achieves an advanced odour

Table 17: Data on olfactory and TOC measurement of screening test at a chocolate factory

sample	odour impression	Odour conc. [OU/m³]	separation [%]	TOC [mgC/m³]	separation [%]
screenning test					
raw air	chocolate	10100	-	5.6	-
water	chocolate (modified)	10500	-	2.2/2.2	61%
humic subst.	chocolate, spicy	3100	69%	1.1/1.3	79%
HC10	chocolate	2400	76%	3.6/2.8	43%
TEGDE	chocolate, cacao	2000	80%	1.7/1.3	73%
scrubber test					
water	chocolate	5100	50%	1.9/1.8	67%
humic subst.	chocolate	2300	77%	1.7	70%
HC10	sweet	1000	90%	2.3/2.3	59%
TEGDE	sweet, like PVC	270	97%	0.8/0.8	86%
washing liquids with pure air					
water	spicy, mushroom	50	-	0.0/0.0	-
humic subst.	musty, spicy	40	-	0.0	-
HC10	sweet	90	-	0.5/0.1	-
TEGDE	sweet, spicy	210	-	0.1/0.0	-

Table 18: Identified substances in waste air from a chocolate factory with peak areas (α_i), olfactory thresholds (OT_i) and odour ratios (OR_i)

substance	a_i [-]	OT_i [µg/l]	α_i	τ_i	OR_i	$OR\%_i$
3-methyl-butanal	13,329,347	0.005	**15.9%**	8.6%	2,665,869,300	**57.0%**
2-methyl-butanal	14,454,537	0.02	**17.3%**	2.2%	722,726,850	**15.5%**
acetic acid	38,951,887	0.06	**46.5%**	0.7%	649,198,117	**13.9%**
dimethyl trisulfide	168,310	0.0012	0.2%	**35.8%**	140,258,333	3.0%
3-methyl butanoic acid	1,873,421	0.015	2.2%	2.9%	124,894,733	2.7%
2,5-dimethylpyrazine	187,773	0.0017	0.2%	**25.3%**	110,454,706	2.4%
2-methyl propanoic acid	3,454,895	0,037	4.1%	1.2%	93,375,541	2.0%
2,3-diethylpyrazine	303,859	0.0066	0.4%	6.5%	46,039,242	1.0%
hexanal	1,625,121	0.04	1.9%	1.1%	40,628,020	0.9%
dimethyl disulfide	676,139	0.029	0.8%	1.5%	23,315,138	0.5%
2-methyl-propanal	2,853,026	0.14	3.4%	0.3%	20,378,757	0.4%
3-ethyl-2,5-dimethylpyrazine	61,552	0.0036	0.1%	**11.9%**	17,097,778	0.4%
3-methyl-1-butanol	804,154	0.1	1.0%	0.4%	8,041,540	0.2%
benzaldehyde	890,508	0.19	1.1%	0.2%	4,686,884	0.1%
2-methyl-1-butanol	603,529	0.14	0.7%	0.3%	4,310,921	0.1%
2,6-dimethylpyrazine	230,329	0.074	0.3%	0.6%	3,112,554	0.1%
2-heptanone	592,272	0.68	0.7%	0.1%	870,988	0.0%
limonene	104,861	0.2	0.1%	0.2%	524,305	0.0%
2-pentylfuran	53,304	0.27	0.1%	0.2%	197,422	0.0%
methylpyrazine	189,275	2	0.2%	0.0%	94,638	0.0%
2-nonanone	121,193	1.7	0.1%	0.0%	71,290	0.0%
aceton	2,224,231	35	2.7%	0.0%	63,549	0.0%

reduction up to 80% to 89%. In general, data show a narrow correlation of odour concentration and TOC concentration (Table 17), which validates these two measurement techniques. So in a certain range, the odour effect is directly influenced by the concentration of the single compounds neglecting changes in the composition.

Data from the chocolate factory show a high number of single components in the raw air. More than 40 substances showed larger peak areas in the total ion currency chromatogram (TIC), which could be identified with significant plausibility. On the basis of the calculated odour indices, 22 substances were chosen as key compounds. The peak areas (Table 18) show the domineering fraction of acetic acid (α_i=46.5%) and also high fractions of 2-methyl-butanal (α_i=17.3%) and 3-methyl-butanal (α_i=15.9%). In this gas mixture, 3-methyl-butanal has the highest relative odour ratio OR%$_i$ with 57.0% and 2-methyl-butanal has the second highest with OR%$_i$ = 15.5%. Acetic acid has only the third highest relative odour ratio of OR%$_i$ = 13.9% due to its lower olfactory threshold participation of 0.7%. Regarding olfactory thresholds dimethyl trisulphide was identified as the substance with the lowest olfactory threshold (0.0012µg/l$_{air}$) and therefore with the highest olfactory impact (τ_i=35.8%), but the associated peak area is relatively small (α_i=0.2%) and therefore dimethyl trisulphide has only the fourth highest relative odour ratio OR%$_i$ of 3.0%.

Comparing separation efficiencies of the static screening test and the scrubber test, results are quite similar. Data from SPME/GC/MS analysis indicate that there are different reduction rates but the same tendency (Table 19). From 22 key compounds in the waste air from the chocolate factory, 19 substances show the same separation tendency at both tests with water and the solution of humic substances, 21 with the usage of HC10 and 20 with TEGDE. So the average conformance of the results of the both tests was very good with 90%. The fingerprint of the chocolate factory gas sample (Figure 33) shows that water reduces the number of key compounds from 22 down to 9 in the scrubber test which is a reduction of 59%. After treatment with the solution of humic substances the air sample still contains 10 compounds (55% reduction). Better results are gained with HC10, which only remains 4 compounds in the sample (82% reduction) and TEGDE, which reduces down to 1 compound (95% reduction).

Table 19: Separation efficiencies of key compounds of raw air from a chocolate factory with peak areas and percentage of residuals

substance	raw air areas [-]	OR%$_i$	water screentest	water scrubber	humin screentest	humin scrubber	HC10 screentest	HC10 scrubber	TEGDE screentest	TEGDE scrubber
3-methyl-butanal	13,329,347	57.0%	10%	60%	19%	66%	18%	5%	13%	0%
2-methyl-butanal	14,454,537	15.5%	0%	0%	0%	0%	0%	0%	0%	0%
acetic acid	38,951,887	13.9%	0%	0%	0%	0%	63%	7%	0%	0%
dimethyl trisulfide	168,310	3.0%	162%	132%	84%	167%	0%	0%	0%	0%
3-methyl butanoic acid	1,873,421	2.7%	0%	0%	0%	0%	0%	0%	0%	0%
2,5-dimethylpyrazine	187,773	2.4%	0%	0%	0%	0%	0%	0%	0%	0%
2-methyl propanoic acid	3,454,895	2.0%	0%	0%	0%	0%	6%	0%	0%	0%
2,3-diethylpyrazine	303,859	1.0%	0%	0%	0%	0%	0%	0%	0%	0%
hexanal	1,625,121	0.9%	25%	32%	0%	41%	0%	0%	0%	0%
dimethyl disulfide	676,139	0.5%	108%	154%	82%	216%	0%	0%	0%	0%
2-methyl-propanal	2,853,026	0.4%	52%	59%	0%	69%	43%	52%	36%	0%
3-ethyl-2,5-dimethylpyrazine	61,552	0.4%	0%	0%	0%	0%	0%	0%	0%	0%
3-methyl-1-butanol	804,154	0.2%	13%	0%	12%	0%	0%	0%	0%	0%
benzaldehyde	890,508	0.1%	20%	0%	0%	0%	0%	0%	0%	0%
2-methyl-1-butanol	603,529	0.1%	0%	0%	0%	0%	0%	0%	0%	0%
2,6-dimethylpyrazine	230,329	0.1%	0%	0%	0%	0%	0%	0%	0%	0%
2-heptanone	592,272	0.0%	33%	26%	41%	28%	0%	0%	0%	0%
limonene	104,861	0.0%	311%	477%	282%	116%	0%	0%	0%	0%
2-pentylfuran	53,304	0.0%	257%	393%	361%	431%	0%	0%	0%	0%
methylpyrazine	189,275	0.0%	0%	0%	0%	0%	0%	0%	0%	0%
2-nonanone	121,193	0.0%	56%	0%	57%	35%	0%	0%	0%	0%
aceton	2,224,231	0.0%	40%	23%	32%	27%	89%	104%	53%	15%

Legend: grey fields = substances defined as not being separated (conc. >2% at screening test and scrubber test)
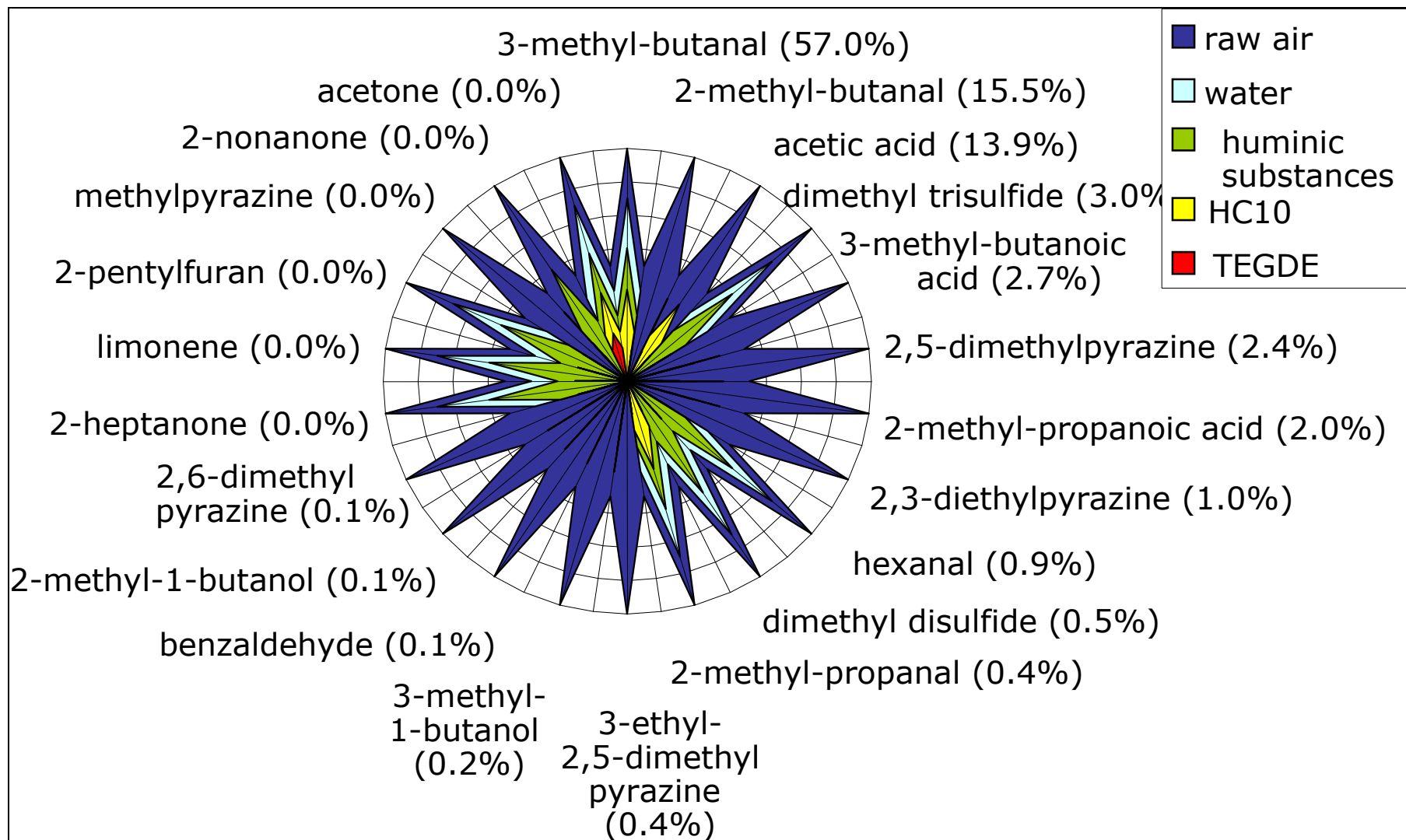
Figure 33: Radar plot of the raw gas of the chocolate factory determined by the scrubber test

Water and the solution of humic substances have only one difference in pattern, which concerns 2-nonanone, the substance with the second smallest odour ratio. That explains why water and the solution of humic substances achieve a similar odour reduction. A predication of the odour reduction by HC10 compared with water cannot be made on the basis of the fingerprint, because the patterns differ strongly from each other. For example, acetic acid, the highly water soluble substance with the largest TIC area and the third largest odour ratio are separated by all liquids except HC10. The substance with the next smaller odour ratio, 3-metyl-butanoic acid, is only separated by the non-aqueous liquids. A very good odour reduction of TEGDE can be seen by the fact that only one substance, acetone the substance with the smallest calculated odour ratio, is not separated.

As a summary of waste gas analysis of the chocolate factory it can be ascertained that TEGDE has the best absorption efficiency of the four washing liquids examined, while water and the solution of humic substances are not adapted very well. On the basis of the olfactory data, the usage of humic substances show a similar absorptive capacity as water has. GC/MS data show the same tendency. Based on the olfactory data, HC10 obtains absorption efficiencies in the same range as water and the solution of humic substances, although the number of key compounds is noticeably reduced.

5.5.4.2 Results from screening tests at a fat and oil refinery

At the fat and oil refinery the same washing liquids were tested as at the chocolate factory. Odour concentration of the raw gas was with 33,400 OU/m³ (Table 20) again in a typical medium range of industrial gases. Odour reduction by water (32%) and the solution of humic substances (42%) was relatively low in both cases. Significant better results were obtained by application of HC10 and TEGDE (both a 97% reduction). Furthermore, the odour impression of treated samples lost the characteristic of the raw gas. While the raw gas was described as "industry" and "soap" like, the characteristic of the sample treated by water changed to "industry, fruity" and "spicy". The sample being treated by the solution of humic substances was characterized as "fruity" and the sample treated by TEGDE smelled like "green apple" and "soap". These descriptions

can be interpreted as losses of odour characteristic step by step from water down to HC10. An odour being described as "soap" is often a combination of a "solvent" and a "fruit" aroma, which is commonly added to household soaps. The "fruity" note at the water sample can be interpreted as a reduction of the "solvent" like smelling components. This effect could also be gained by treatment with TEGDE. The sample treated by solution of humic substances lost its "industry" character.

Table 20: Data on olfactory and TOC measurement of fat and oil refinery samples

sample	odour impression	Odour conc. [OU/m³]	separation [%]	TOC [mgC/m³]	separation [%]
screenning test					
raw air	industry, soap	33400	-	112	-
water	industry, fruity	22700	32%	100	11%
humic subst.	spicy, fruity	19500	42%	78	30%
HC10	-	930	97%	12.5	89%
TEGDE	green apple, soap	1100	97%	14	88%
scrubber test					
raw air	industry, soap	8000	-	53	-
water	green apple, tomato	1000	88%	10	81%
humic subst.	green apple, shampoo	2400	70%	11	79%
HC10	Cola, soap	140	98%	0.4	99%
TEGDE	industrial soap	230	97%	31	42%

By this treatment an important aim of odour control is reached, the loss of the characteristic odour, although odour concentration was still at a high level. Treatment by HC10 reduces the odour concentration in the same range as by TEGDE, but in addition HC10 took away the raw gas smell, if the left-out of description can be interpreted in this way. If so, HC10 showed the highest efficiency in this test. The stepwise reduction of the characteristic odour correlates very well with the decrease in odour concentrations. At this point this can be taken as a hint for a stepwise reduction of key compounds.

The measured TIC peak areas of key compounds in the raw gas are listed in Table 21. Again the tendencies in the comparison of the liquids by both tests were similar (Table 22). Differences in concentration ranges of the two test types were also observed within this series as in the measurements of the chocolate factory by olfactometer and

by GC/MS analysis for all compounds. Nevertheless, compositions of the compounds were quite similar in both tests. For calculation of the separation ratio of key compounds, a comparison of data of both tests was done, which showed, that a TIC area reduction of 40% in the screening test corresponded well with a reduction of 98% in the scrubber test. A comparison of both tests shows that 14 from 17 key compounds have the same separation tendency, if water or TEGDE are used. With the solution of humic substances - 13 substances and with HC10 - 15 substances show the same tendency. The average conformance of the results of the two test types was about 82%, which is nearly as good as within the experiments at the chocolate factory.

In this waste gas sample the substances with lowest olfactory thresholds (2-nonenal, 2,4-decadienal and 2,4-nonadienal) are the three most important compounds, because they have the highest relative odour indices $OR\%_i$. The substances with the largest TIC peak areas (p-xylene and limonene) have relatively small relative odour indices $OR\%_i$ due to there high olfactory thresholds. A visualisation of the results of the scrubber test by the fingerprint (Figure 34) shows the reduction effect of the liquids. Water is the only liquid, which was able to separate 2-nonenal, the substance with the highest odour ratio. That gives a hint, why there was an odour reduction by water (80% reduction) although many key compounds remained in the treated sample. The solution of humic substances showed the same pattern as water, except for the first substance. Here odour reduction was worse (70% reduction) what indicates the importance of the key compound 2-nonenal for this specific waste gas. HC10 and TEGDE achieved very good odour reductions, although they did not separate the two substances with the highest odour indices. But they separated all other key compounds except one substance each. By that, the odorous effect of these two substances can be analysed in detail. HC10 which caused the best odour reduction of 98% remained 2-propenal in the gas phase, which has a relative odour ratio $OR\%_i$ of 0.01%. On the other hand, TEGDE which showed nearly the same odour reduction (97%) remained octanal in the gas phase, which had a relative odour ratio $OR\%_i$ of 0.33%. Although accuracy of the analytical techniques is not that high, the two independent results fit very well together and show the applicability of the relative odour ratio in principle.

97

Table 21: Identified substances of waste air from a fat and oil refinery with peak areas (α_i), olfactory thresholds (OT_i) and odour ratios (OR_i)

substance	a_i [-]	OT_i [µg/l]	α_i	τ_i	OR_i	$OR\%_i$
2-nonenal	34,980,253	0.0006	6.18%	**9.73%**	58,300,421,667	69.22%
2,4-decadienal	1,739,194	0.00008	0.31%	**72.95%**	21,739,927,866	25.81%
2,4-nonadienal	476,420	0.0004	0.08%	**14.59%**	1,191,050,744	1.41%
nonanal	4,217,712	0.005	0.75%	1.17%	843,542,329	1.00%
hexanal	23,833,917	0.04	4.21%	0.15%	595,847,919	0.71%
limonene	107,042,886	0.2	**18.91%**	0.03%	535,214,428	0.64%
heptanal	5,981,554	0.02	1.06%	0.29%	299,077,717	0.36%
octanal	1,978,338	0.0072	0.35%	0.81%	274,769,172	0.33%
2-pentylfuran	64,729,075	0.27	**11.43%**	0.02%	239,737,315	0.28%
p-xylene	221,239,766	2.1	**39.08%**	0.00%	105,352,270	0.13%
2-hexenal	1,528,763	0.034	0.27%	0.17%	44,963,623	0.05%
ethylbenzene	5,542,900	0.41	0.98%	0.01%	13,519,268	0.02%
toluene	64,982,554	5.9	**11.48%**	0.00%	11,013,992	0.01%
2-heptanone	13,442,737	1.3	2.37%	0.00%	10,340,567	0.01%
2-propenal	1,825,838	0.2	0.32%	0.03%	9,129,190	0.01%
benzaldehyde	1,395,217	0.19	0.25%	0.03%	7,343,247	0.01%
2-octene	11,134,779	1.6	1.97%	0.00%	6,959,237	0.01%
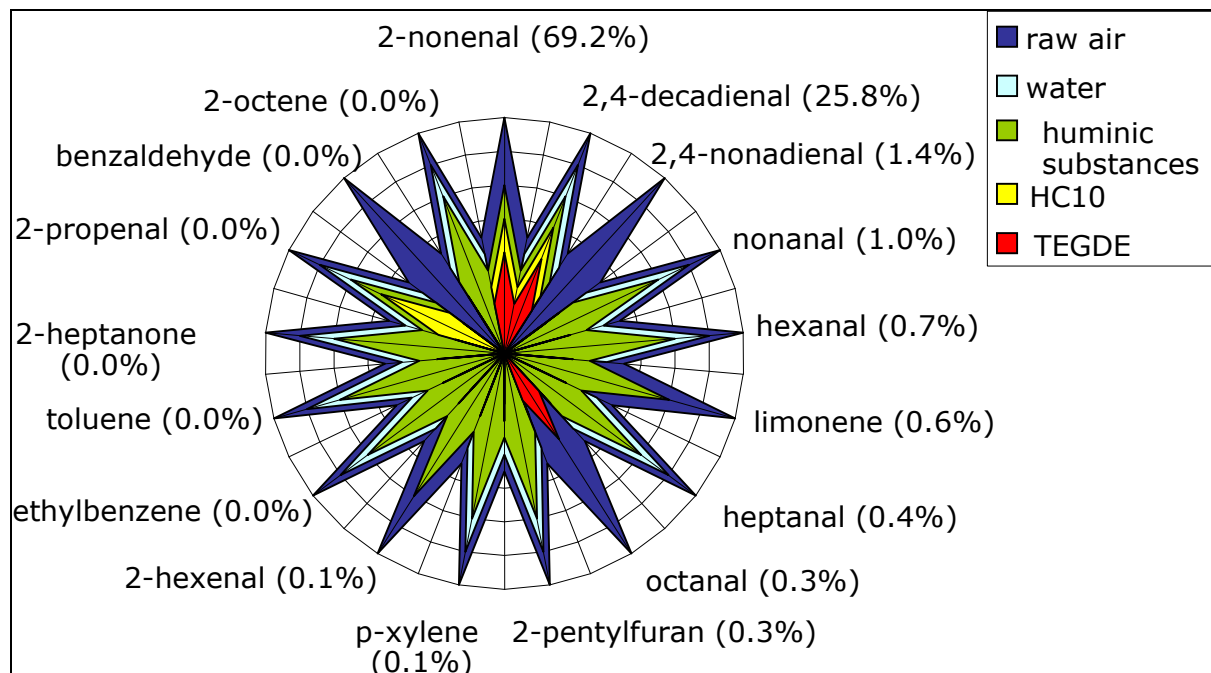
Figure 34: Radar plot of the raw gas a fat and oil refinery and from treated samples (scrubber test)

In summary, for an application of an absorptive waste air treatment at the fat and oil refinery, the best choices of absorbents are HC10 and TEGDE. Both show quite similar performances in treatment of this specific waste air. Water was not good adapted to this treatment scope and the solution of humic substances did not improve the absorption at all.

5.5.4.3 Results from a screening test at a starch factory

This facility was chosen for on-site bioscrubber test. For that perspective the focus was on testing solutions of humic substances within the screening test. Based on the results of the determined Henry Coefficients and bioscrubber tests, both types of humic substances, Nussbeize and POW, were chosen to be tested each in a 1.5% w/w and a 5.0% w/w aqueous solution.

With regard to a later use of the results for implementation of an exhaust air treatment facility, the two most important exhaust air streams were chosen to be examined within this series of experiments. Both exhaust air streams derive from dryers, which are used to treat by-products. The air stream A had high odour concentrations (13,000 - 35,000 OU/m³) at a relatively low volume flow. Its contribution to the total odour emission varied between 50% and 60%. The air stream B had a significantly higher volume flow, so its contribution to the total odour emission was about 5 - 10%, although its odour concentrations (650 - 1,100 OU/m³) were relatively low.

Treatment of sample from air stream A with water lead to an odour reduction of 85% and it was improved to 92 - 95% by usage of humic substances (Table 23). Results of the humic substance type Nussbeize were slightly better. The concentration of humic substances had no significant influence on reduction rate of both products. The gas sample from stream B had a significantly lower odour concentration. In this case, treatment with water only resulted in a moderate odour reduction of 33%. By usage of a 1.5 w/w% solution of humic substances the odour concentration was reduced by 62% and 87% respectively. The separation efficiency of the 5 w/w% solution were

Table 22: Separation efficiencies of key compounds of raw air from oil refinery with peak areas and percentage of residuals

substance	raw air, screen-test areas [-]	raw air, scrubber areas [-]	OR%$_i$ screen test	OR%$_i$ scrubber	water, screentest	water, scrubber	humin, screentest	humin, scrubber	HC10, screentest	HC10, scrubber	TEGDE, screentest	TEGDE, scrubber
2-nonenal	34,980,253	1,015,417	69.21%	46.4%	57%	0%	33%	11%	0%	4%	0%	15%
2,4-decadienal	1,739,194	41,198	25.81%	14.1%	66%	13%	9%	287%	0%	455%	4%	154%
2,4-nonadienal	476,420	19,231	1.41%	1.3%	57%	0%	37%	0%	0%	0%	5%	0%
nonanal	4,217,712	558,108	1.00%	3.1%	88%	16%	63%	7%	0%	0%	3%	0%
hexanal	23,833,917	26,474,342	0.71%	18.1%	89%	27%	102%	53%	26%	0%	15%	0%
limonene	107,042,886	38,988,191	0.64%	5.3%	95%	1%	83%	3%	0%	1%	1%	1%
heptanal	5,981,554	2,295,855	0.36%	3.1%	118%	9%	64%	24%	2%	1%	2%	0%
octanal	1,978,338	271,159	0.33%	1.0%	74%	0%	47%	0%	0%	0%	0%	17%
2-pentylfuran	64,729,075	24,944,106	0.28%	2.5%	101%	2%	83%	14%	0%	1%	1%	0%
p-xylene	221,239,766	165,174,777	0.13%	2.2%	101%	35%	103%	72%	6%	0%	4%	0%
2-hexenal	1,528,763	683,586	0.05%	0.6%	29%	0%	40%	60%	14%	0%	6%	0%
ethylbenzene	5,542,900	6,339,063	0.02%	0.4%	109%	33%	118%	75%	43%	1%	0%	0%
toluene	64,982,554	122,310,865	0.01%	0.6%	116%	54%	142%	93%	55%	0%	27%	1%
2-heptanone	13,442,737	8,023,135	0.01%	0.2%	101%	12%	98%	65%	4%	1%	3%	0%
2-propenal	1,825,838	4,263,077	0.01%	0.6%	46%	10%	11%	27%	169%	9%	22%	0%
benzaldehyde	1,395,217	196,007	0.01%	0.0%	43%	0%	35%	0%	6%	0%	0%	0%
2-octene	11,134,779	26,706,625	0.01%	0.5%	127%	53%	174%	103%	25%	0%	26%	1%

Legend: grey fields = substances defined as not being separated (conc. > 60% at screening test and >2% at scrubber test)

remarkably lower (23% and 47% respectively), which were in the range of the results obtained with water. By a single absorption step, like it is done within the static test, it was not possible to separate the main key compounds of the sample, which can be seen by the unchanged odour description of all samples. Like the raw gas, all treated samples still have the characteristic odour of "grain", "bread" or "chocolate" in slight variations.

The gas sample from stream B had a significantly lower odour concentration. In this case, treatment with water only resulted in a moderate odour reduction of 33%. By usage of a 1.5 w/w% solution of humic substances the odour concentration was reduced by 62% and 87% respectively. The separation efficiency of the 5 w/w% solution were remarkably lower (23% and 47% respectively), which were in the range of the results obtained with water. By a single absorption step, like it is done within the static test, it was not possible to separate the main key compounds of the sample, which can be seen by the unchanged odour description of all samples. Like the raw gas, all treated samples still have the characteristic odour of "grain", "bread" or "chocolate" in slight variations.

Table 23: Olfactory data from static screening test at a starch factory

Gas	Absorbant	Source A [OU/m³]	Odour impression	Source B [OU/m³]	Odour impression	Separation [%] A	B
raw gas	-	231000	grain	790	chocolate, bread	-	-
raw gas	water	34300	bread, chocolate	530	yeast, dough	85%	33%
raw gas	NB-1,5%	13700	chocolate, bread	300	chocolate, earth	94%	62%
raw gas	NB-5%	11900	chocolate, bread	610	chocolate, bread	95%	23%
raw gas	POW-1,5%	16400	chocolate	100	yeast	93%	87%
raw gas	POW-5%	19400	chocolate, bread	420	dough, nuts	92%	47%
pure air	water	10	radiator	10	radiator	-	-
pure air	NB-1,5%	60	n.n.	120	sweet, earth	-	-
pure air	NB-5%	290	acidic	100	earth	-	-
pure air	POW-1,5%	70	sweet	50	dust, wood	-	-
pure air	POW-5%	90	sweet	60	dust, earth	-	-

Legende: NB = "Nussbeize", all concentrations in [%w/w]

About 200 compounds were detected in both raw air samples by GC/MS analysis. In sample A, 52 compounds could be identified with a high accuracy and for 40 substances from this group the odour thresholds could be obtained (Table 24). From sample B, 35 compounds could be identified and for 29 of them the odour thresholds could be obtained (Table 42 and Table 43 in the annex).

Looking at the 10 most important key components of sample A based on the Odour Ratio, it can be seen that exhaust air A was mostly determined by aldehydes, like 3- und 2-methyl butanal and a decadienal, by acetic acid and sulphur organic components, like dimethyl and dimethyl sulphide (DMS). 3-methylbutanal and acetic acid were the two compounds with the largest TIC-peak areas and the highest Odour Ratio participation. Dimethyl trisulphide was the compound with the third highest Odour Ratio participation due to its low odour threshold, although its peak area was only in the mid-range. The odour character of sample A was mainly generated by aldehydes, organic acids and sulphur-organic substances, like dimethyl trisulphide and dimethyl sulphide.

In Table 25 the TIC peak areas are shown of the odour substances in the raw air and their residual concentrations after treatment with the washing liquids. It can be perceived that the residual concentrations of single components turned out to vary widely. For the most important component, 3-methylbutanal, which was reduced by water only by 3%, the application of humic substances resulted only in slight improvements (8% to 14%) (Figure 35). In contrast to that, acidic acid, the substance with the second-highest Odour Ratio, was separated very well with water, and a slight improvement due to humic substances could be observed. The separation of dimethyl trisulphide could be significantly improved by usage of humic substances.

Analysis of odorants of sample B showed a number of odorous components that could also be identified in raw air A. The substances 3-methylbutanal and acidic acid were again two of the five substances with the highest Odour Ratios. The most important substance in this exhaust air was 3-methyl-1-butanol due to its large fraction of the peak area. The only substance that generated a larger peak area was ethanol, which barely

Table 24: Raw air compounds, type A, with TIC areas, odorous thresholds OTi and Odour Ratio OR$_i$

compounds	group of substances	raw air "A" [TIC area]	OT [µg/l]	α_i	τ_i	OR$_i$	OR%$_i$
3-methyl-butanal	aldehyde	29,644,921	0.005	**28.9%**	0.9%	5,928,984,286	**80.1%**
acidic acid	acid	41,842,053	0.06	**40.9%**	0.1%	697,367,550	**9.4%**
dimethyl trisulfide	org. sulphur	343,663	0.0012	0.3%	3.8%	286,385,894	**3.9%**
(E,Z)-2,4-decadienal	aldehyde	50,698	0.00022	0.0%	**20.6%**	230,443,997	**3.1%**
dimethyl sulfide	org. sulphur	802,815	0.0078	0.8%	0.6%	102,925,000	1.4%
2-methyl butanal	aldehyde	7,622,980	0.14	7.4%	0.0%	54,449,856	0.7%
3-ethyl-2,5-dimethylpyrazine	pyrazine	90,248	0.0025	0.1%	1.8%	36,099,200	0.5%
2-methyl-propanal	aldehyde	3,352,113	0.14	3.3%	0.0%	23,943,664	0.3%
hexanal	aldehyde	353,911	0.04	0.3%	0.1%	8,847,765	0.1%
benzaldehyde	aldehyde	1,595,579	0.19	1.6%	0.0%	8,397,782	0.1%
pentanal	aldehyde	212,068	0.036	0.2%	0.1%	5,890,778	0.1%
nonanal	aldehyde	27,655	0.005	0.0%	0.9%	5,531,000	0.1%
decanal	aldehyde	19,867	0.005	0.0%	0.9%	3,973,400	0.1%
dimethyl disulfide	org. sulphur	89,041	0.029	0.1%	0.2%	3,070,379	0.0%
2-pentylfuran	furane	569,863	0.27	0.6%	0.0%	2,110,605	0.0%
3-methyl-1-butanol *	alcohole	46,598	0.1	0.0%	0.0%	465,984	0.0%
2-hexenal	aldehyde	102,420	0.34	0.1%	0.0%	301,235	0.0%
2-methyl propanoic acid	acid	18,784	0.072	0.0%	0.1%	260,889	0.0%
heptanal	aldehyde	37,704	0.26	0.0%	0.0%	145,015	0.0%
tetramethylpyrazine	pyrazine	245,644	2	0.2%	0.0%	122,822	0.0%
2-pentanone	ketone	440,041	5.5	0.4%	0.0%	80,007	0.0%
ethylbenzene	aromate	30,662	0.41	0.0%	0.0%	74,786	0.0%
toluene	aromate	356,341	5.9	0.3%	0.0%	60,397	0.0%
2-hexanone	ketone	27,278	0.71	0.0%	0.0%	38,420	0.0%
p-xylene	aromate	78,423	2.1	0.1%	0.0%	37,344	0.0%
2-heptanone	ketone	25,027	0.68	0.0%	0.0%	36,804	0.0%
aceton	ketone	815,781	35	0.8%	0.0%	23,308	0.0%
ethanol	alcohole	240,588	19	0.2%	0.0%	12,663	0.0%
undecene	alkene	51,765	7.8	0.1%	0.0%	6,637	0.0%
a-pinene	terpene	37,523	18	0.0%	0.0%	2,085	0.0%
3-hydroxy-2-butanone	ketone	57,002	42	0.1%	0.0%	1,357	0.0%
octane	alkane	221,194	224	0.2%	0.0%	987	0.0%
nonane	alkane	21,994	60	0.0%	0.0%	367	0.0%
2-furancarboxaldehyde	aldehyde	7,613,575	n.n.	**7.4%**	0.0%	0	0.0%
phenylacetaldehyde	aldehyde	4,737,822	n.n.	4.6%	0.0%	0	0.0%
2-methyl-furane*	furane	334,509	n.n.	0.3%	0.0%	0	0.0%
2-methyl-3-octanone*	ketone	120,882	n.n.	0.1%	0.0%	0	0.0%
Decanoic acid methyl ester	ester	54,805	n.n.	0.1%	0.0%	0	0.0%
2-Octene (E)	alkene	43,478	n.n.	0.0%	0.0%	0	0.0%
2,6-dimethylpyrazine	pyrazine	37,102	n.n.	0.0%	0.0%	0	0.0%
propylbenzene	aromate	7,269	n.n.	0.0%	0.0%	0	0.0%
(E,E)-2,4-decadienal	aldehyde	0	0.00008	0.0%	**56.5%**	0	0.0%
(E,E)-2,4-nonadienal	aldehyde	0	0.0004	0.0%	11.3%	0	0.0%
(E)-2-nonenal	aldehyde	0	0.0036	0.0%	**1.3%**	0	0.0%
3-methyl butanoic acid	acid	0	0.006	0.0%	0.8%	0	0.0%
m,o-xylene	aromate	0	1.2	0.0%	0.0%	0	0.0%
2-nonanon	ketone	0	1.7	0.0%	0.0%	0	0.0%
2-butanon	ketone	0	5.8	0.0%	0.0%	0	0.0%
2,2,6-trimethylcyclohexanon	ketone	0	n.n.	0.0%	0.0%	0	0.0%
2-ethylfurane	furane	0	n.n.	0.0%	0.0%	0	0.0%
3-methylthiopropanal	aldehyde	0	n.n.	0.0%	0.0%	0	0.0%

Legend: compounds marked with * could only be identified with low certainty

103

Table 25: Separation efficiencies of key compounds of sample A of a starch factory with peak areas and percentage of residuals

compounds	raw air "A" [TIC area]	OR%$_i$	+Water	+NB 1,5%	+NB 5%	+POW 1,5%	+POW 5%
3-methylbutanal	29,644,921	**80.1%**	97%	92%	86%	93%	89%
acidic acid	41,842,053	**9.4%**	6%	1%	2%	1%	2%
dimethyl trisulfide	343,663	**3.9%**	534%	29%	62%	72%	29%
(E,Z)-2,4-decadienal	50,698	**3.1%**	60%	0%	15%	43%	0%
dimethy sulfide	802,815	1.4%	185%	161%	134%	173%	150%
2-methylbutanal	7,622,980	0.7%	105%	99%	90%	94%	94%
3-ethyl-2,5-dimethylpyrazine	90,248	0.5%	0%	0%	0%	0%	0%
2-methylpropanal	3,352,113	0.3%	96%	106%	98%	104%	105%
hexanal	353,911	0.1%	70%	81%	68%	81%	73%
benzaldehyde	1,595,579	0.1%	11%	44%	39%	69%	39%
pentanal	212,068	0.1%	55%	92%	28%	88%	84%
nonanal	27,655	0.1%	864%	279%	90%	0%	68%
decanal	19,867	0.1%	46%	145%	1178%	385%	682%
dimethyl disulfide	89,041	0.0%	3055%	1018%	1084%	874%	783%
2-pentylfurane	569,863	0.0%	113%	83%	66%	94%	96%
3-methyl-1-butanol*	46,598	0.0%	42%	0%	0%	0%	0%
2-hexenal	102,420	0.0%	0%	33%	0%	0%	0%
2-methyl propanoic acid	18,784	0.0%	0%	0%	0%	0%	0%
heptanal	37,704	0.0%	102%	63%	47%	42%	104%
tetramethyl pyrazine	245,644	0.0%	0%	0%	0%	0%	0%
2-pentanone	440,041	0.0%	27%	0%	0%	0%	0%
ethylbenzene	30,662	0.0%	42%	212%	88%	73%	372%
toluene	356,341	0.0%	36%	48%	41%	46%	57%
2-hexanone	27,278	0.0%	0%	0%	0%	0%	191%
p-xylene	78,423	0.0%	53%	121%	130%	79%	135%
2-heptanone	25,027	0.0%	139%	111%	141%	0%	392%
acetone	815,781	0.0%	54%	54%	86%	70%	85%
ethanol	240,588	0.0%	19%	4%	9%	4%	3%
undecen	51,765	0.0%	69%	69%	61%	61%	49%
a-pinene	37,523	0.0%	80%	90%	79%	75%	154%
3-hydroxy-2-butanone	57,002	0.0%	0%	0%	0%	0%	0%
octane	221,194	0.0%	73%	81%	71%	78%	67%
nonane	21,994	0.0%	111%	131%	52%	56%	124%
2-furancarboxaldehyde	7,613,575	0.0%	8%	6%	5%	7%	6%
phenylacetaldehyde	4,737,822	0.0%	4%	0%	0%	0%	0%
2-methylfurane*	334,509	0.0%	22%	26%	42%	21%	14%
2-methyl-3-Octanone*	120,882	0.0%	0%	0%	0%	0%	0%
Decanoic acid methyl ester	54,805	0.0%	42%	32%	37%	23%	48%
2-octene (E)	43,478	0.0%	0%	0%	0%	0%	0%
2,6-dimethylpyrazine	37,102	0.0%	0%	0%	0%	0%	0%
propylbenzene	7,269	0.0%	0%	111%	132%	0%	0%
(E)-2-nonenal	0	0.0%	0	1,104,446	0	0	0
(E,E)-2,4-decadienal	0	0.0%	0	0	22,053	0	0
(E,E)-2,4-nonadienal	0	0.0%	0	0	86,699	0	0
2,2,6-trimethyl cyclohexanon	0	0.0%	0	112,623	260,962	286,809	715,821
2-butanone	0	0.0%	93,574	170,053	357,809	123,417	264,281
2-ethylfurane	0	0.0%	0	0	54,275	0	0
2-nonanone	0	0.0%	0	0	0	12,561	12,012
3-methyl butanoic acid	0	0.0%	33,400	43,559	0	0	0
3-methyl thiopropanal	0	0.0%	0	5,750	4,649	13,290	0
m,o-xylene	0	0.0%	16,144	53,934	19,131	0	0

Legend: areas highlighted grey = compounds with a residual concentration >10% (separation insufficient)
compounds marked with * could only be identified with low certainty
NB: humic substances type "Nussbeize", POW = humic substances type "POW"

Sample A

3-methyl butanal [80.1%] (malty)

benzaldehyde [0.1%] (bitter almond)

acidic acid [9.4%] (vinegar, pungent)

hexanal [0.1%] (grass, apple, rancid)

dimethyl trisulfide [3.9%] (sulfury)

2-methyl propanal [0.3%] (green, pungent, malty)

(E,Z)-2,4-decadienal [3.1%] (deep-fried)

3-ethyl-2,5-dimethyl pyrazine [0.5%] (roasty, earthy)

dimethy sulfide [1.4%] (cabbage, onion, rotten)

2-methyl butanal [0.7%] (chocolate, almond)

sample	OU/m³	n	description
raw air	231.000	10	cereal
water	34.000	5	bread, chocolate
NB 1.5%	14.000	3	chocolate, bread
NB 5.0%	12.000	2	chocolate, bread
POW 1.5%	16.000	2	chocolate
POW 5.0%	19.000	2	chocolate, bread

Legend

in [ ]: Odour Ratio

in ( ): Odour description

n: number of key compounds after absorptive treatment

Figure 35: Fingerprint of sample A of a starch factory

contributed to the Odour Ratio due to its relatively high olfactory threshold. Further of importance were the aldehydes hexanal and nonanal and the alcohols 1-hexanol and 3-methyl-1-butanol. Dimethyl disulphide was the only sulphur-organic key compound. It can be seen that the best separation efficiency were achieved using a solution of 1.5 w/w% Nussbeize, which was more efficient than water for the first 12 key components and also more efficient for most other components as well. The separation of the most important component, 3-methyl-1-butanol, was already very effective with water and could only be slightly improved with the solutions of humic substances (Figure 36).

The highest reduction rate by far was gained with a solution of POW at a concentration of 1.5% w/w. Reduction of the first 12 most important key compounds was higher or even notedly higher than those gained with water. At 9 of the 12 most important compounds the reduction rate was better than those of the other solutions of humic

substances. Only separation of the most important substance, 3-methyl 1-butanol, could not be improved significantly, because it was already separated very well by water.

Based on these series the following substance group specific statements can be made for treatment of the exhaust air of these starch factory emission sources, if a remaining uncertainty by surplus amounts or deviations in determined concentrations is considered. Separation of aldehydes and sulphuric organic substances by water was poor and could be improved by usage of solutions of humic substances (Table 26). Separation of alcohols and organic acids by water was from moderate to good and could even be improved by usage of solutions of humic substances. Ketones were separated moderately by water, too, but here no significant improvement could be observed by usage of solutions of humic substances. Separation of aromatics by water was from poor to moderate without any improvement by solutions of humic substances.

sample	OU/m³	n	description
raw air	790	10	chocolate, bread
water	527	8	yeast, dough
NB 1.5%	304	3	chocolate, earth
NB 5.0%	609	7	chocolate, bread
POW 1.5%	96	7	yeast
POW 5.0%	418	5	dough, nuts

Legend

in [ ]: Odour Ratio

in ( ): Odour description
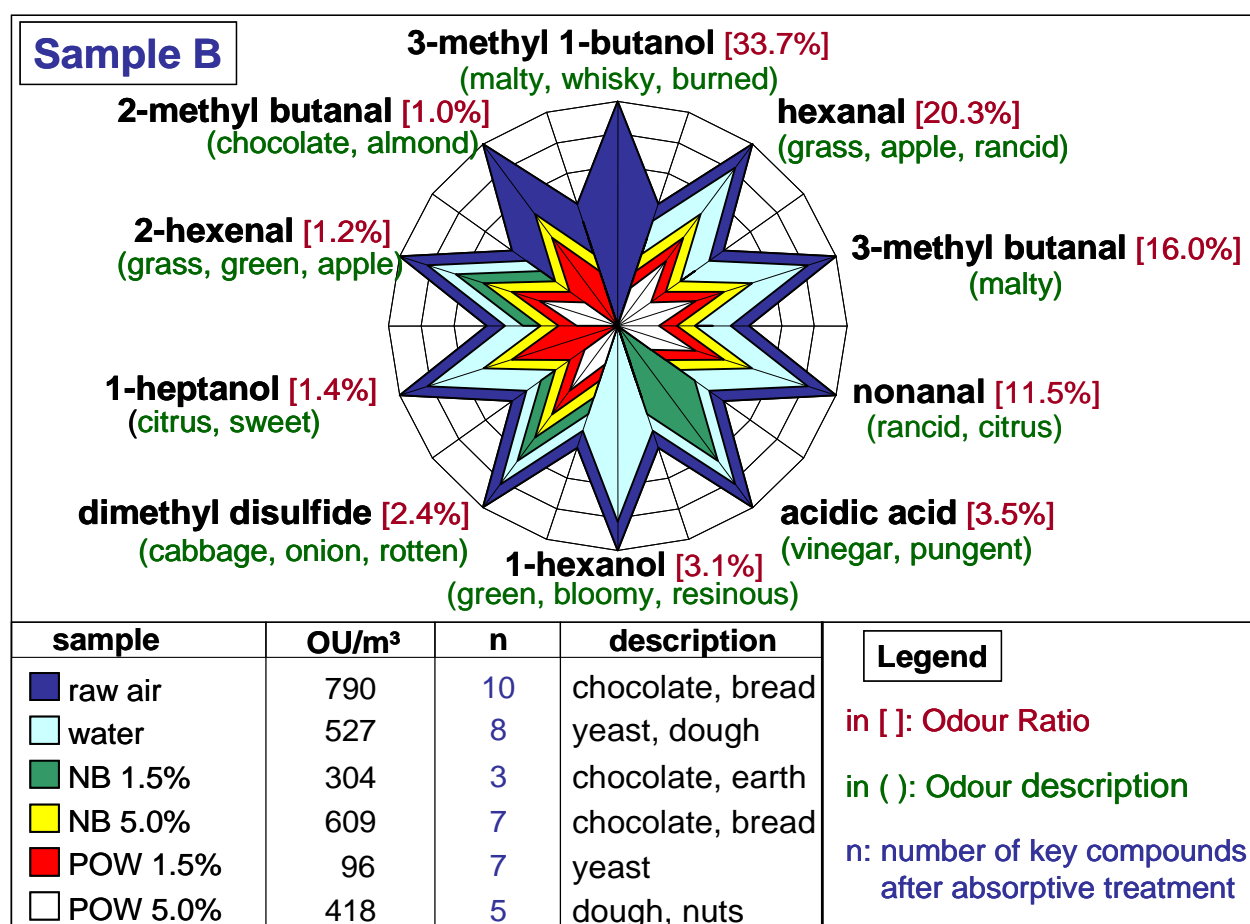
n: number of key compounds after absorptive treatment

Figure 36: Fingerprint of sample B of a starch factory

Table 26: Absorption efficiencies by substance groups based on data from starch factory

compound groups		water	humic subst.
aldehydes	3-methylbutanal (E,Z)-2,4-decadienal	moderate	improved
sulfur-organic compounds	dimethyl trisulfide dimethyl sulfide		
alcohols	3-methyl-1-butanol ethanol	moderate - good	improved
organic acids	acetic acid 2-methyl propanoic acid		
ketones	2-Pentanon 2-Hexanon	moderate - good	not improved
aromatics	Ethylbenzol Toluol	poor - moderate	not improved

5.5.5 Discussion of results

A comparison of identified odour components of the samples from the starch factory, the fat and oil refinery and the chocolate factory show an astonishing similarity. Appropriately, the odour impression of most samples is described with a chocolate note. This surprises at first glance, because at the starch factory and the fat and oil refinery no chocolate or cacao containing raw materials are processed. Based on this observation, it can be assumed that the formation of odorants by processes of material treatment, e.g. by temperature treatment in dryers, has a similar contributive effect to the total odour impression of a waste air stream from a food producing company than the raw materials and products have themselves.

The most important conclusion of these series of experiments was that the examined exhaust air of food producers contained a high percentage of water soluble odorants which can be separated in a bioscrubber. Additionally several times a higher solubility of those substances in the humic substance solutions could be noted, so it can be expected that adding humic substances to the washing liquid will result in improved separation ratios of bioscrubbers. For optimising the concentration of humic substances it can be noted that the "more is better" method is useless for most odorants. No type

and no concentration of humic substances could be identified to be a preferred solution for all applications. So a later optimisation will always be required.

5.5.6 Discussion of the odour ratio approach

Despite the demonstrated benefits and increase of know how by the new method of the relative Odour Ratio, some weak point have to be discussed. Firstly, there is the danger of a misinterpretation by a non-detection of too low concentrated odorants. These substances might have an important impact on the odour, if their odour threshold is very low. Secondly, there is a straight dependency on a broad database, which can never be complete, due to the endless number of organic odorants. Thereby, there will always be odorants, of which the odour threshold is not available, so that in consequence these substances cannot be considered for calculation of the Odour Ratio. Thirdly, there is always the chance of an incorrect identification of a substance by SPME/GC/MS, which would also lead to a misinterpretation. Fourthly, the selection limit to distinguish between separated and not separated substances has always to be adapted to the gas concentration and its choice influences directly the results.

So as the next step, the applicability of the odour ratio for the identification of key compounds will be verified. Therefore, the dependency of the odour concentration on the number of detectable key compounds is calculated and shown for the waste air from the chocolate factory (Figure 37, A) and from the fat refinery (Figure 37, C). Both diagrams show a linear correlation of the odour concentration and the number of key compounds in a good approximation. In experiment with the waste air of the fat and oil refinery, two separate linear regression lines have to be calculated for the screening test and the scrubber test due to different concentration ranges of the odour concentrations in both tests as described before. For data from the chocolate factory one single linear regression line could be determined for both tests.

As a result of all calculated regression lines, which all have accuracy above 70% and which go approximately through the zero points of the diagrams, it can be reasoned,

that the main odorous effect is caused by the chosen key compounds and that contribution of other substances can be neglected. By that it can be adduced evidence that the approach of the odour ratio can generally be used for identification of key compounds in industrial waste gases.
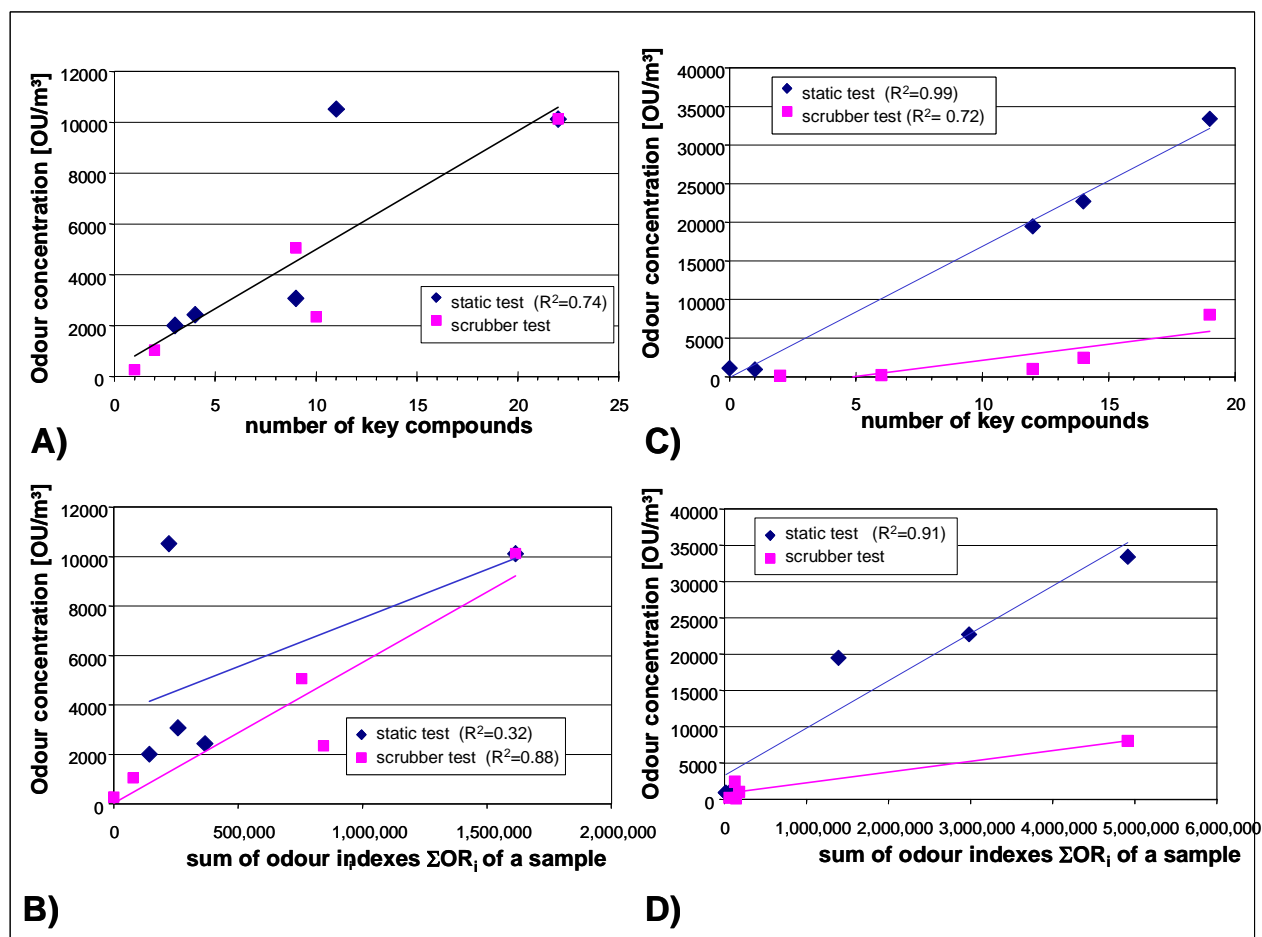
Figure 37: Correlation of odour concentration with the number of key compounds and sum of absolute odour ratios, samples of a chocolate factory (figure A and B) and a fat and oil refinery (figure C and D)

In the following the absolute values of the odour ratios are tested for correlation with odour concentration. Therefore, the absolute odour ratio OR_i (not the relative odour ratio $OR\%_i$) is calculated for each key compound, by dividing the measured TIC area by the odour threshold of the compound. The sum of absolute odour ratio OR_i of all key compounds of a sample represents the odour ratio of the total gas sample. This calculation is done for the raw air sample and all treated samples of one gas source.

This approach is verified by plotting the odour concentration versus the described odour ratio of the sample (Figure 37, B, D). These two parameters show a linear dependency although the correlation of the odour concentration with the odour ratio of the sample is not as good as with the number of key compounds.

Limits of the applicability of the odour ratio become obvious, if the apparent importance a compound within the gas mixture should be calculated on basis of relative odour ratios. Comparing the odour ratios of all compounds seems to indicate a dominance of the first few compounds due to the big differences in values. This is contrary to the approximate linear correlation of odour concentration and the number of key compounds as described above. So it can be summarised that the odour ratio is appropriate to identify key compounds and differentiate if they are more or less important for the total odour impression of a sample. The odour ratio cannot be used to determine a strict ranking of importance of the odorants based on the values of the odour ratios. At least it cannot be used to forecast odour concentration of a sample based on the concentration of the single compounds. A reason for this is limitation can be assumed to base on the analytical procedure. Firstly, the enrichment by solid phase extraction is not an absolute technique. Here gas compounds have different enrichment factors mainly influenced by their polarity. So, the gas phase, which is sampled and desorbed into the SPME/GC/MS system, has a composition different to the original gas sample. Secondly, the TIC areas are used for calculation instead of concentrations, what might lead to a weighting of compounds.

5.5.7 Conclusions

By the developed static screening test, washing liquids can be directly compared using the specific waste gas. Differences in results of the static screening and the dynamic screening test are found to be small against the effect of the liquids. Results of the dynamic test do not give a hint that kinetic parameters have a major influence on the separation process. So for this purpose, there is no need to run a dynamic test with extensive scrubber experiments. In future a fast selection of washing liquids can be done by the static screening test only. But it should be stressed that the screening is

appropriate to test washing liquids, but cannot be used for a scale up of a technical plant. Determination of single substances by SPME/GC/MS and calculation and comparison of Odour Indices is time consuming and will only be of scientific interest. The screening test can be carried out alternatively with an olfactometric analysis as the only measurement to identify the best adapted absorbent for a specific waste air. Additional analysis with TOC or FID senor or identification of single gas compounds and determination of their concentrations is not required for an engineering purpose, but it is helpful to understand the influence of single compounds to the odorous impression of the sample and it is helpful to understand the differences in effectivity and selectivity of the absorbents.

6 Scale-up

In this chapter the treatment methods of a conventional bioscrubber, of a bioscrubber with humic substances as solubility agent and of a physical scrubber using HC10 with a steam regeneration should be compared. On basis of kinetic and operating parameters determined by experiments, scale-up calculations are carried out for two typical tasks of waste gas treatment. By this approach the advantages and disadvantages of the techniques should be compared and discussed. Finally the best solution for each task should be worked out. For a direct comparison of the calculated scrubber columns the same gas velocity and the same column diameter are chosen. By that approach a comparison of the odour control performance of the techniques can be done by a simple comparison of the calculated column heights. Scale-up of the bioscrubbers is done with the kinetic 1st order method using data from laboratory and on-site experiments. Scale-up of the oil scrubber and its regeneration is done in two ways, with the HTU-NTU method and with method of theoretical separation stages, both based on laboratory experiments only.

6.1 Case 1: Waste air from a Dryer unit

In case 1 a treatment unit for an industrial application with a relatively small gas volume flow and a high raw gas concentration should be designed. A typical example of this

case would be the waste air stream of a product dryer which should be treated after being cooled down to 20°C. In this example the defined gas stream is the only source of the industrial location. As a simplification dimethyl sulphide (DMS) is defined as the only odorants in the exhaust air, so that data of the laboratory experiments of the bioscrubbers and the oil-scrubber can be used directly. For simplification water content is taken as being inert towards the absorption of DMS and is not considered. Conditions of the waste air stream are listed in Table 27. Detailed calculations are in the annex chapter 9.2 and results are shown in Table 28. Chosen operational parameters and concentrations are near to experimental conditions, which are investigated within this work, to minimize failure by extrapolation. For example, the operational pressure would be slightly higher in a technical application due to pressure losses over the packing.

Table 27: Operational parameters of case 1

raw gas concentration	500 ppm, DMS in air, (=1292 mg/m³, about 130,000 OU/m³)
gas volume flow	1000 m³/h
required: treated air concentration	1.93 ppm (= 5 mg/m³, about 500 OU/m³)
T, P	20°C, 1.15 bar

6.1.1 Results and discussion

Comparing results of the bioscrubbers calculated with the kinetic 1st order method shows that the largest reactor height is required for the conventional bioscrubber analogues to the properties of the kinetic constants. The humic bioscrubber needs only 58% of this height. Scale-up of the oil scrubber is calculated in two different ways. The calculated heights are nearly the same. Taking the large scale-up factor from a laboratory plant to a technical plant into account a deviation of less then 30% is acceptable.

For treatment of a small waste gas flow with a high DMS concentration, both the humic bioscrubber and the oil scrubber need column heights which are in the same range and

which are smaller than the conventional bioscrubber. Reduction by usage of humic substances is about 42% and by usage of an oil scrubber it is between 29% and 49%. Compared to the scrubber column the calculated height of the regeneration column is relatively small with between 10% and 20% of the scrubber height. Compared to the bioscrubber concept, where no additional regeneration column is needed, the height is relatively large because a second column has to be installed and operated. The sum of oil scrubber and regeneration volumes is between 21% and 39% less than the volume of the conventional bioscrubber but it is between 4% and 36% more than the volume of the bioscrubber with humic substances. So a simple comparison of volumes shows that costs for a bioscrubber with humic substances would be less than those of the oil scrubber system. So for this case, the concept of the bioscrubber with humic substances is obviously the best choice.

Table 28 Results of Scale-up for Case 1

scrubber type	bioscrubber (reference)	bioscrubber humic subst.	oil scrubber (HC10)		Regeneration (HC10) Steam stripping	
method	**kinetic 1st order**	**kinetic 1st order**	**HTU / NTU**	**HETS / Nt**	**HTU / NTU**	**HETS / Nt**
operataional parameters chosen by experiments	w_g=0.15 [m/s] b=44m³/(m²*h)	w_g=0.15 [m/s] b=44m³/(m²*h)	w_g=0.15 [m/s] S_{abs}=0.5 [-]	w_g=0.15 [m/s] S_{abs}=0.5 [-]	w_g=0.7 [m/s] S_{reg}=3.0 [-]	w_g=0.7 [m/s] S_{reg}=3.0 [-]
design parameters determined by experiments	$k_{1,DMS}$=288 [1/h]	$k_{1,DMS}$=494 [1/h]	k_Ga (DMS) = 44.9*S_{abs} + 15.1 = 38 (kmol/(h*m³))	HETS (DMS)= 0.3962*S_abs +0.8559 =0.66m	k_Ga_{reg} (DMS) =226 (kmol/(h*m³))	$HETS_{reg}$ (DMS) = 0.22 m
experiments for data basis	bioscrubber laboratory	bioscrubber laboratory	oil scrubber laboratory	oil scrubber laboratory	oil scrubber laboratory	oil scrubber laboratory
Ac [m²]	1.85	1.85	1.85	1.85	1.37	1.37
Dc [m]	1.5	1.5	1.5	1.5	1.3	1.3
Hc [m]	10.4	6.1	7.4	5.3	1.1	1.1
V_R [m³]	19.3	11.2	13.8	9.8	1.5	1.5
$V_C/V_{Bioscrub}$.	100%	58%	Scrubber:71%	Scrubber:51%	Reg: 8% total: 79%	Reg: 10% total: 61%

In case 1 a classic bioscrubber would be needed with a diameter of 1.5 m and a height of 10.4 m for treatment of a single gas stream. In this case, usage of humic substances reduces the required height of the bioscrubber to 6.1 m, which is a reduction of 42%. Here the main benefit would be a reduction of operational costs in the same range,

since operational costs are determined by pressure losses at the gas side and pump energy, which are proportional to the pressure height. Installation costs for the smaller scrubber column would be reduced too, but this effect would be smaller.

6.2 Case 2: Waste air from a Facility

In case 2, a relative high gas flow with a moderate odour concentration has to be treated (Table 29). In this case the design parameters from the on-site experiments at the fat and oil refinery should be used. So a typical example of this waste gas would be the collective exhaust gas stream of a fat and oil refinery. Due to the fact, that the design parameters are specific for this company, results cannot be directly transferred to other applications.

Table 29: Operational parameters of case 2

raw gas concentration	10,000 OU/m³
gas volume flow	50,000 m³/h
required: treated air concentration	500 OU/m³
T, P	20°C, 1.013 bar

For this calculation, there are kinetic data only for the bioscrubber scale-up. Facility specific parameters for the oil scrubber and regeneration are not available. Therefore an approach in three steps is chosen. First, the bioscrubbers are calculated based on the specific parameters from on-site experiments. Second, a theoretic gas mass concentration is to be determined for a waste gas with DMS as the only pollutant, which causes the odour concentration, which is given by the task of case 2. Here data from the odour threshold and laboratory experiments with DMS are used for choosing an adapted starting point. A control of the theoretic concentration will be done by comparison of the scale-up results of the bioscrubbers with the same method and kinetic parameters both from the fat and oil refinery and from laboratory. If there are differences in results, then the correlation of odour concentration and mass concentration has to be adapted iteratively. Then, as the third step, the oil scrubber and

the regeneration are calculated with the HTU-NTU method and with the method of theoretical separation stages based on the theoretical DMS mass concentrations. At the end all results are compared. Calculations are shown in the annex chapter 9.2 and results are shown in Table 30.

6.2.1 Results and discussion

First, the conventional bioscrubber is dimensioned based on on-site experimental data. The calculated height is $H_C = 4.90$ m which is taken as a reference. Second, a starting point of the estimated DMS gas mass concentration of 88 mg/m³ is chosen as a corresponding value to the odour concentration of 10,000 OU/m³. Based on this value the height of the scrubber column becomes 5.38 m, so the mass concentration has to be reduced for the next iterative calculation step. At a concentration of 68 mg/m³ the height becomes the same as the conventional bioscrubber.

Comparison of the heights of the bioscrubbers shows in both versions a good improvement by usage of humic substances. The height reduction is about 29% based on the on-site data and 42% based on laboratory data. This fits to the observation that improvements in separation efficiency by usage of humin substances were higher within laboratory experiments. Taking the conventional bioscrubber as a reference, which is dimensioned based on on-site experiments, the height of the oil scrubber would be between 40% and 45% smaller. In this case deviations in calculated heights by the two methods are very small with 7% for the absorption column and 3% for the regeneration column. The regeneration column is chosen thinner than the scrubber column, because strip gas flow is smaller than the waste gas flow. So, comparisons including the regeneration are done based on the column volume not on its height.

Results of case 2 show that the sum of column volumes of the oil scrubber and regeneration is between 42% and 47% smaller than the classic bioscrubber and between 5% and 12% smaller than the volume of the bioscrubber with humic substances. In the second case again, savings in column volume by application of an oil

115

scrubber with a steam regeneration using HC10 are small compared to the absolute volume of the classic bioscrubber. So, the most effective method of odour control is again a bioscrubber with humic substances. Calculated improvement by usage of humic substances is a volume reduction of 29% compared to the classic bioscrubber.

6.3 Conclusions of Scale-up

As a first finding of scale-up calculation, there is a direct dependency of reactor volume on waste gas volume flow. Which is obvious since the flow directly determines the load, which has to be reduced, but it underlines the need for a minimization of waste air volume flow, e.g. by a selective waste gas collection. Each reduction of false air input reduces the volume flow of waste gas, which has to be treated and by that it reduces the required scrubber volume and in the same degree the operational costs.

Comparison of scale-up results of case 1 and 2 shows that the reactor volume of a bioscrubber can be reduced by 30% to 42% respectively by usage of humic substances (Table 31). This reduction would lead to an installation cost reduction (approx. -10%) and ongoing savings in operational costs of (-30% to -40%). This is a high improvement, especially if the effort is considered, which is limited to dosage of solid material.

Oil-scrubbers would need smaller reactor volumes than a classic bioscrubber, but if an additional regeneration column is considered, total volume would be in the same range of the bioscrubber with humic substances. Additional costs for required assemblies like heat exchangers, steam generator, pumps and compressors must be considered. The same is with operating costs, which would be much higher for the oil scrubber, due to heating, cooling and additional pumping energy. So improvement by volume reduction is revoked by installation and operational costs.

Table 30: Results of Scale-up Case 2

scrubber type	conventional bioscrubber (reference)	bioscrubber humic subst.	conventional bioscrubber	bioscrubber humic subst	oil scrubber (HC10)		Regeneration (HC10) Steam stripping	
method	**kinetic 1st order**	**kinetic 1st order**	**kinetic 1st order**	**kinetic 1st order**	**HTU / NTU**	**HETS / Nt**	**HTU / NTU**	**HETS / Nt**
operational parameters chosen by experiments	w_G=0.15 [m/s] b=44m³/(m²*h)	w_G=0.15 [m/s] b=44m³/(m²*h)	w_G=0.15 [m/s] b=44m³/(m²*h)	w_G=0.15 [m/s] b=44m³/(m²*h)	w_G=0.7 [m/s] S_{abs}=0.5 [-]	w_G=0.7 [m/s] S_{abs}=0.5 [-]	w_G=0.7 [m/s] S_{reg}=3.0 [-]	w_G=0.7 [m/s] S_{reg}=3.0 [-]
experiments for data basis	**bioscrubber Fat refinery**	**bioscrubber Fat refinery**	**bioscrubber laboratory**	**bioscrubber laboratory**	**oil scrubber laboratory**	**oil scrubber laboratory**	**oil scrubber laboratory**	**oil scrubber laboratory**
design parameters determined by experiments	$k_{1,OU}$=330 [1/h]	$k_{1,OU}$=464 [1/h]	$k_{1,mDMS}$ = 288 [1/h]	$k_{1,mDMS}$ = 494 [1/h]	kGa (DMS)= 38 (kmol/(h*m³)	HETS (DMS)= 0.3962*S_abs +0.8559 =0.66m	kGa$_{reg}$ (DMS) =226 (kmol/(h*m³)	HETS$_{reg}$ (DMS) = 0.22 m
Dc [m]	10.9	10.9	10.9	10.9	10.9	10.9	9.3	9.3
Hc [m]	4.9	3.5	4.9	2.9	2.9	2.7	0.5	0.5
V_R [m³]	456	324	456	266	273	252	35	34
$V_C/V_{Bioscrub}$.	100%	71%	100%	58%	Scrubber: 60%	Scrubber: 55%	Reg: 8% total: 68%	Reg: 8% total: 63%

Table 31: Comparison of calculated reactor volumes of scale-up case 1 and 2

Parameter	case 1	case 2
gas volume flow	small (1.000 m³/h)	high (50.000 m³/h)
raw gas concentration	high (500 ppm, ca. 130.000 OU/m³)	moderate (10.000 OU/m³)
required discharge gas concentration	1,93 ppm, about 500 OU/m³	500 OU/m³
odour substance	DMS	odorants from a fat and oil refinery
volumes of bioscrubbers classic / humic subst.	19.3 m³ / 11.2 m³	456 m³ / 324 m³
volume reduction by humic substances-bioscrubber	-42%	-29%
volume reduction by oil-scrubber (regeneration included)	-21%	-42%

Comparison of scale-up results of all investigated absorptive odour control techniques proofs that the bioscrubber with humic substances is the most efficient choice, due to smallest column volume and lowest operational costs. On contrast the oil-scrubber is the most expensive concept. Last but not least the concept of using an oil scrubber for odour control requires an additional disposal of the separated odorants, e.g. by combustion of the condensate. This step is already included in the bioscrubber by a biological degradation of odorants by micro-organisms.

7 Summary

Comparing the solubility of the investigated absorbents based on determined Henry coefficients, three substances are identified with high absorptive capacities. First, the alcane fraction HC10 shows the best solubility, which is between 140 and 1000 times higher than that of water. Second, very good solubility for odorants could be confirmed of the following group of absorbents, TEGDE, PLC and BEHA which have already been used in the field of solvent recovery. Third, humic substances in aqueous solutions fulfil the requirements of usage as solubility agents in bioscrubbers and they showed solubilities of odorants about 2 to 15 times higher than water. So, humic substances were tested as additives in bioscrubbers.

Performance improvements by usage of humic substances as solubility agents in bioscrubbers were proofed and verified in several long-term series of measurements. By laboratory tests good reduction rates of dimethyl sulphide (DMS) were measured. In average the reduction rate of a bioscrubber with humic substances was between 34 and 50% higher than the conventional bioscrubber. Variation of the humic substances concentration did not show significant influence on degradation rates.

At second step, bioscrubber experiments were carried out at a fat and oil refinery. As a waste gas source the gas phase above a pumping pit of a caustic scrubber was chosen, which was determined as a main emission source of the facility. During experiments raw gas concentration was between 3,500 und 32,000 OU/m³. Reduction rate η_{ou} based on [OU/m³] was about 75% by a conventional bioscrubber and 82% by a bioscrubber with humic substances. That is an improvement by 10% in average. Experiences in operation did not show any negative aspects of using humic substances. The only operational problem was caused by foam formation happened a few times, but this problem also occurred in the conventional bioscrubber, so it could not be related to humic substances.

As a third step, a bioscrubber pilot plant in half-technical scale was built-up for testing humic substance on site a starch factory treating high concentrated waste air from dryers. The conventional bioscrubber achieved in a single step modus reduction rates above 90% during times with high raw gas concentrations (>250,000 OU/m³). Here the improvement by humic substance was only between 7% and 10%. A reason for that was that in case of investigated waste air from the starch factory most components were determined to be relatively good water soluble. Then, humic substances were tested in a series modus of two bioscrubber. While reduction of the second step was about 35% by a conventional bioscrubber it could be increased up to 80% by usage of humic substances. So, here humic substances doubled the separation efficiency of the second step, which can be explained by the increased relative content of less water-soluble compounds after a first treatment step with water as absorbent. With this combination a permanent cleaning performance between 94 and 99% were achieved. Within the on-site experiments the applicability of an electronic nose for online scrubber performance monitoring was demonstrated.

Reviewing all bioscrubber experiments described, the type and the concentration of the humic substances seems to have a relatively low influence on the treatment effect. There are results showing that lower concentration might even be more effective depending on the type of waste air. A 1.5 weight-% concentration was proofed to be a good starting point, but a subsequent optimization for a specific waste gas should always be done.

A laboratory air scrubber using oils as absorbents has been assembled to examine cleaning performance on synthetic and real exhaust air streams. Results with the absorbents HC10, an alcane fraction, and tetraethylene glycol dimethyl ether (TEGDE) are presented. It is proofed, that high absorptive separation can be reached with both absorbents and both absorbents can be well regenerated by stripping. TEGDE showed slightly better absorption efficiency and the effort of regeneration is about 40% less for TEGDE than for HC10. Due to high water solubility of TEGDE, it was only tested in combination with regeneration by air stripping, whereas HC10 could be tested with regeneration by steam stripping and by air stripping. The

treatment concept with TEGDE and a regeneration by air stripping is determined to be inefficient due to poor concentration factors. HC10 has the advantage, that it can be regenerated by steam stripping, which is proofed to be an effective method of separating odorants. Then theses substances can be recovered in a high concentration as a condensate of the stripper column.

Data of HC10 experiments are used for scale-up calculations and comparison with bioscrubbers on basis of two case studies. Improvements by usage of washing oils, quantified by smaller scrubber columns, are found to be too small to be an efficient alternative to a bioscrubber. The additional effort for regeneration and heating is considerably higher than the savings. Improvements by usage of humic substances in bioscrubber are nearly as high as by usage of washing oils and the additional efforts are much less. They are limited to material costs of humic substances and efforts of material handling and dosage which are all relatively low.

A screening test is developed as a tool of low expense for testing washing liquids on industrial waste gases. A new parameter named the "relative odour ratio $OR\%_i$", is introduced, which describes the potential contribution of single odorants to the cumulative odour impression of a gas sample. This parameter is used to identify key compounds of the specific smells and it can be used to explain the separating effect and selectivity of absorbents. The screening test is verified by experiments at a chocolate factory, a fat and oil refinery and a starch factory.

8 Outlook

Although washing oils show high solubility of odours substances, scale-up results show that oil-scrubbers in a technical application need reactor volumes in the same range like bioscrubbers. Total cost would even be higher than for a conventional bioscrubber due to investment and operating costs as described above. Based on these findings further investigations in alternatively washing oils cannot be recommended for the purpose of odour control.

Bioscrubbers were determined again to be a highly efficient technique of odour control as described by several authors before. By this work, usage of humic substances as solubility agents is proofed to improve the efficiency of bioscrubbers with a small additional effort of material dosage. Applications of humic substances-bioscrubbers should be tested on other waste gas sources with more lipophilic odorants, since there the potential for efficiency improvements is much higher. With a high probability a direct treatment of the waste gas of an oil refinery by a humic substances-bioscrubber would be an interesting test. In the investigated case it was only possible to apply this technique to a secondary emission stream. An application to the primary gas stream, which is now treated by the caustic air scrubber, would probably lead to very good separation efficiency.

Further investigations should be done on testing other humic substances products which might lead to further efficiency improvements. Investigations of secondary separating effects of humic substances on bioscrubbers like surface tension reduction, influence on pH-value buffer capacity, adsorptive effects and others would lead to a deeper understanding the way this additive interacts, which might open the door for new kinds of reactors or new techniques.

9 Annex

9.1 Figures
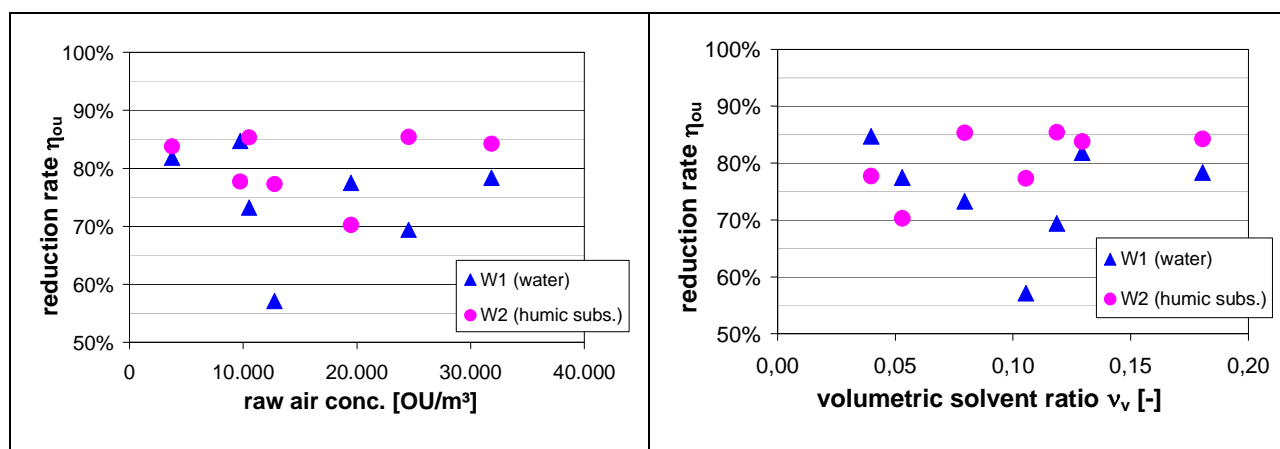
Figure 38: Dependency of odour reduction rate on raw air concentration and volumetric solvent ration based on on-site experiments with bioscrubbers at the fat and oil refinery
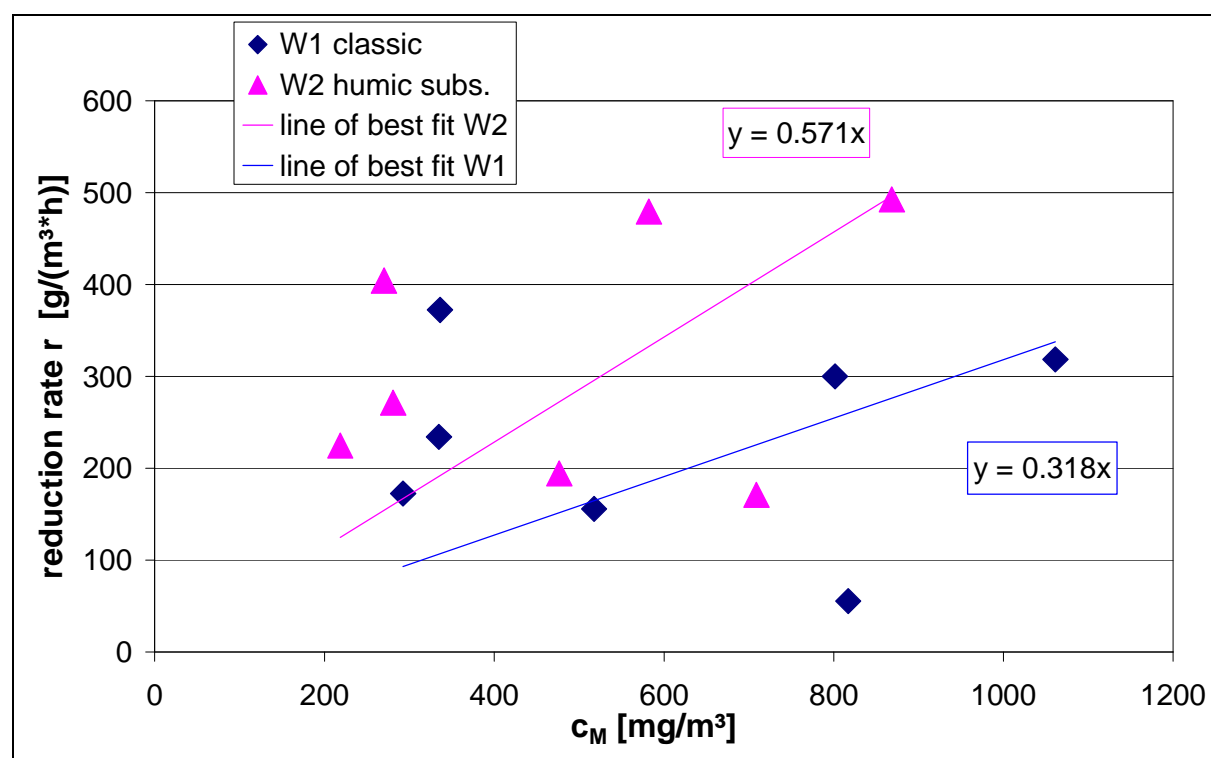
Figure 39: Determination of kinetic constant k1 [1/h] of series V3

9.2 Calculations for scale-up of case 1 (case 2 analogues)

For scale-up the following parameters are chosen from experiments as shown in chapter 4.7.2:

- superficial gas velocity of absorption w_g and regeneration $w_{g,reg}$

- stripping factor of absorption S_{abs} and regeneration S_{reg}

- irrigation load b and

- kinetic constants k_1 and k_Ga

For the bioscrubber a gas flow velocity of = 0.15 m/s is recommended (Heining, 1998) so that the cross sectional area of the column A_C and the column diameter D_C can be calculated as following

$$A_C = \frac{Q_G}{w_G} = 1000 \text{ (m³/h)} / 0.15 \text{ (m/s)} = 0.28 \text{ (m³/s)} / 0.15 \text{ (m/s)} = 1.85 \text{ m²}$$

and column diameter of D_C = 1.54 m.

For a scale-up the oil scrubber, data were used from experiments with a Montz geometric packing, type A3, analogical to the laboratory plant. With a gas load factor F between 0.6 and 2.5 $\left[\sqrt{Pa}\right]$ for operation given by the manufacturer and an air density of ρ_g = 1.293 [g/l at operational pressure and temperature, the range of gas flow velocity can be calculated with eq. 32. A, as following

F	$\left[\sqrt{Pa}\right]$	0.6 (min)	2.5 (max)
$w_g = F / \sqrt{\rho_g}$	[m/s]	0.53 (min)	2.20 (max)

In laboratory tests, gas velocities between 0.07 and 0.24 [m/s] were applied, since higher gas velocities let to problems in gas/liquid separation at the head of the scrubber column and could no tested for that reason. Best results were gained with a stripping factor S_{abs} = 0.4 [-] which was related to a gas velocity of w_g = 0.1 m/s. For a direct comparison with the results of the bioscrubber experiments the same gas velocity of w_g = 0.15 [m/s] and the same column diameter of D_C = 1.54 m are chosen. By this approach, a comparison of the odour control performance of the techniques can be done by a simple comparison of the calculated highs or volumes, respectively.

9.2.1.1 Scale-up of bioscrubbers (case1)

Based on chosen irrigation load b the liquid flow is calculated

Q_L = b * A_C = 44 m³/(m²*h) * 1.85 m² = 81 m³/h.

The mass flow of the odorants being separated can be calculated by a mass balance. Absorbed mass flow of DMS is

M_{DMS} = Q_G * (c_1-c_2) = 1,000 m³/h * (1.292 - 5) mg DMS / m³ = 1.29 mg DMS / h.

Mean gas concentration c_M is calculated with eq. 29

$$c_M = \frac{c_1 - c_2}{\ln(c_1 / c_2)} = (1{,}292\text{-}5)/\ln(1{,}292/5) \text{ (mg DMS / m³)} = 232 \text{ mg DMS / m³}.$$

Degradation rate is calculated with eq. 28 based on kinetic constant k_1 [h^{-1}] from experiments (here for conventional bioscrubbers)

$r = k_1 \cdot c_M$ = 288 (1/h) * 232 mg DMS / m³ = 66.7 mg DMS / (m³*h).

The required column volume V_C is the ratio of absorbed odour emission and degradation rate according to eq. 30

$$V_R = \frac{M_{DMS}}{r} = (1{,}29 \text{ mg DMS / h}) / (66.7 \text{ mg DMS} / (m^3 {*} h)] = 19.3 \text{ m}^3.$$

Column height is the ratio of volume by square area

$$H_C = V_R / A_C = 19.3 \text{ m}^3 / 1.85 \text{ m}^2 = 10.4 \text{ m}.$$

9.2.2 Scale-up of oil scrubber and regeneration (case1)

For a design of the oil scrubber based on the HTU/NTU-concept one more parameter has to be chosen to define the mass balance. So the concentration of the odorant in the oil after the regeneration is chosen to be slightly below the detection limit by $x_2 = 1$ ppm. Calculations are shown in Table 32 to Table 34

Table 32: Calculation of fluid flows and concentrations (case1)

molar gas flow G (ideal gas)	$G = p \cdot Q_G / RT = 1.15 * 10^5$ N/m² *1000 m³/h / (8.314 kJ / (kmol*K) *293 K) = 47.2 kmol/h
molar liquid flow L (eq. 13)	$L = G * H_{i,j} / (S_{abs} * p) = 47.2$ kmol/h * 1.10 bar / (0.5 * 1.15 bar) = 90.3 kmol/h
adsorbed molar flow n_{abs}	$n_{abs} = (y_1 - y_2) * G$ $= (500 - 1.93) * 10^{-6}$ (mol/mol)* 47.2 kmol/h = 23.5 mol/h
molar flow of odorants in absorbent after regeneration	$n_{x2} = x_2 * L = 1 * 10^{-6}$ (mol/mol) * 90.3 kmol/h $= 9 * 10^{-2}$ mol/h
molar flow of odorants in absorbent before regeneration	$n_{x1} = n_{abs} + n_{x2} = n_{abs} = 23.6$ mol/h
concentration in absorbent before Regeneration	$x_1 = n_{x1} / L = 23.6$ [mol/h] / 90.3 [kmol/h] = 261 [ppm]
stripping gas mol flow G_{reg}	$G_{reg} = S_{reg} \cdot L \cdot \dfrac{p}{H_{i,j}}$ $G_{reg} = 3 * 90.3$ kmol/h*1.15 bar / 2.43 bar = 128 kmol/h
stripping gas volume flow Q_{reg} at T=373K (ideal gas)	$Q_{reg} = G_{reg} \cdot R \cdot T / p = 128$ kmol/h * 8.314 (kJ/kmol*K) * 373 K / 1.15 *10^5 N/m² = 3458 m³/h = 0.96 m³/s
y_{reg2}	$y_{reg2} = n_{abs} / G_{reg} = (23.5$ mol/h)/ (128 kmol/h) = 183 ppm

Table 33: Scale-up with theory of transfer units (HTU-NTU method, case1)

Parameters	Absorption column	Regeneration column
characteristics	• $H_{i,j\ (DMS,HC10,20°C)}$ = 1.1 bar • S_{abs} = 0.5 • w_g = 0.15 [m/s]	• $H_{i,j\ (DMS,HC10,100°C)}$ = 2.43 bar • S_{reg} = 3.0 • $w_{g,reg}$ = 0.7 m/s *(based on exp. data with good bubbles distribution)*
	• k_Ga (DMS)= 44.9*Sabs + 15.1 = <u>38 (kmol/(h*m³)</u> *(see chapter 5.4.4 "Kinetic constants for Scale-up")*	• kGa$_{reg}$ (DMS) = <u>226 (kmol/(h*m³)</u>
A_C [m²]	A_C = 1.85 m² (chosen)	$A_{C,reg} = Q_{reg} / w_{reg}$ =(0.96 m³/s) / (0.7 m/s) = 1.37 m²
driving force at point of gas inlet	$\Delta y_1 = y_1 - x_1 \cdot \dfrac{H_{i,j}}{p}$ = 500 ppm - 261 ppm* (1.1/1.15) = 250 ppm	$\Delta y_{reg1} = x_2 \cdot \dfrac{H_{i,j}}{p} - y_{reg1} = x_2 \cdot \dfrac{H_{i,j}}{p}$ *(since y_{reg1} = 0)* = 1 ppm * (2.43 bar/1.15 bar) = 2.1 ppm
driving force at point of gas outlet	$\Delta y_2 = y_2 - x_2 \cdot \dfrac{H_{i,j}}{p}$ = 1.93 ppm- 1 ppm * (1.1/1.15) = 1.0 ppm	$\Delta y_{reg2} = x_1 \cdot \dfrac{H_{i,j}}{p} - y_{reg2}$ = 261 ppm * (2.43 bar/1.15 bar) − 183 ppm= 369 ppm
mean logarithmic concentration	$(\Delta y)_m = \dfrac{\Delta y_2 - \Delta y_1}{\ln(\Delta y_2 / \Delta y_1)}$ = (250-1) ppm / ln(250/1) = 44.9 ppm	$(\Delta y)_m = \dfrac{\Delta y_2 - \Delta y_1}{\ln(\Delta y_2 / \Delta y_1)}$ = (369-2.1) ppm / ln(369/2.1) = 71.0 ppm
required reactor height	$H_C = \dfrac{G}{k_Ga \cdot A_C} \cdot \dfrac{y_2 - y_1}{(\Delta y)_m}$ = 47.2 (kmol/h) * (500-1.93) (ppm) / (38 kmol/h*m³ * 1.85 m²* 44.9 ppm) = **7.4 m**	$H_{C,reg} = \dfrac{G_{reg}}{k_Ga \cdot A_{C,reg}} \cdot \dfrac{y_{reg2} - y_{reg1}}{(\Delta y)_m}$ = 128 (kmol/h)*(183-0) ppm/ (226 (kmol/h*m³)*1.37 m² * 71.0 (ppm)) = **1.1 m**
reactor volume	$V_R = H_C * A_C$ = 7.4 m * 1.85 m² = **13.8 m³**	$V_R = H_{C,reg} * A_{C,reg}$ = 1.1 m * 1.85 m² **= 1.5 m³**

Table 34: Scale-up with theory of theoretical separation stages (HETS, case1)

Parameters	Absorption column	Regeneration column
characteristics	• $H_{i,j \text{ (DMS,HC10,20°C)}} = 1.1$ bar • $S_{abs} = 0.5$	• $H_{i,j \text{ (DMS,HC10,100°C)}} = 2.43$ bar • $S_{reg} = 3$
	• HETS = -0.3962*S_{abs} + 0.8559 = 0.66 m	• HETS = 0.22 m
	(see chapter 5.4.4 "Kinetic constants for Scale-up")	
	• $A_C = 1.85$ m²	• $A_{C,reg} = 1.37$ m²
	(same sizes like with HTU/NTU)	
number of theoretical separation units N_t McCabe-Thiele method	$N_t = \dfrac{\ln\left[\dfrac{Y_1 - m \cdot X_2}{Y_2 - m \cdot X_2}(1-S) + S\right]}{\ln\left(\dfrac{1}{S}\right)}$ **$N_{th} = 8.0$**	$\dfrac{X_1 - X_2}{\dfrac{Y_{reg1}}{m} - X_2} = \dfrac{S^{N_t+1} - S}{S^{N_t+1} - 1}$ (iterative) **$N_{th} = 4.9$**
Column height	$H_C = N_t \cdot HETS = 8.0 * 0.66$ m = **5.3 m**	$H_C = N_t \cdot HETS = 4.9 * 0.22$ m = **1.1 m**
Reactor volume	$V_R = H_C * A_C = 5.3$ m * 1,85 m² = **9.8 m³**	$V_R = H_C * A_{C,reg}$ = 1.1 m * 1.37 m² = **1.5 m³**

9.3 Annex - Tables

Table 35: Substance data of chosen odorants (source safety datasheets of manufacturers)

Substance	CAS	empirical formula	boiling temperature (1,013 bar) [°C]	vapour pressure with temperature information [mbar]	log K_{OW}	molar weight [g/mol]	density [kg/l]
decadienal (trans,trans-2,4-)	25152-84-5	$C_{10}H_{16}O$	115	k.A.	k.A.	152.24	0.868
dimethyl disulfide	624-92-0	$(CH_3)_2S_2$	109	37.0 (25°C)	1.77	94.20	1.046
dimethyl sulfide	75-18-3	C_2H_6S	37	690 (20°C)	0.87	62.13	0.847
furfuryl thiol	98-02-2	C_5H_6OS	155	4.00 (20°C)	k.A.	114.17	1.132
pentan thiol	110-66-7	$CH_3(CH_2)_4SH$	126.8	18.7 (25°C)	k.A.	104.22	0.840
trimethyl amine	75-50-3	$(CH_3)_3N$	2.87	2200 (20°C)	0.16	59.11	0.636
triethyl amine	121-44-8	$C_6H_{15}N$	89.0	70.0 (20°C)	1.45	101.19	0.728
butyric acid	107-92-6	$CH_3(CH_2)_2COOH$	126	36.5 (37.7 °C)	0.79	88.11	0.868
1-butanol	71-36-3	$CH_3(CH_2)_3OH$	117.7	6.7 (20°C)	0.9	74.12	0.810
formic acid	64-18-6	CH_2O_2	100.2	42 (20°C)	-0.54	46.03	1.220
acetic acid	64-19-7	$C_2H_4O_2$	118.1	16 (20°C)	-0.17	60.05	1.050

Table 36: Substance data of applied absorbants (source safety datasheets of manufacturers)

Substance	HC–10	TEGDE	BEHA	PLC	Nussbeize	POW	Silicone oil	Dodecane
name	Alcane fraction	Tetraethylengly-coldimethylether	Bis(2-ethyl hexyl) adipate	Propylencarbonat	sodium salt of humic substances	POW-Humus 85 WSP	Silicone oil AP 100	dodecane
CAS number	64742-14-9	143-24-8	103-23-1	108-32-7	68131-04-4	1415-93-6	63148-58-3	112–40–3
molar weight [g/mol]	ca. 315	222.3	307.6	102.1	n.a.	n.a.	n.a.	170.3
empirical formula	(#)	$C_{10}H_{22}O_5$	$C_{22}H_{42}O_4$	$C_4H_6O_3$	n.a.	$C_{70}H_{46}N_2O_{27}K_7$	n.a.	n.a.
density at 15°C [g/cm³]	0.877	1.01	0.927	1.20	1.3 – 1.4	1000 – 50,000 Da	1.05	0.749–0.753
solubility in water	10 g/l	well soluble	soluble	180 g/l	100 g/l	180 g/l	insoluble	insoluble

(#):mass distribution: aromatic (13.5%), naphthenic (29.0%), parrafinic (57.5%)

Table 37: Data from Laboratory Oil scrubber experiments and calculated values (part1)

Experiment No.		E1	E2	E3	E4	E5	E6	E7	E8	E10	E11	E12
washing liquid		HC10	HC10	HC10	HC10	HC10	HC10	HC10	HC10	HC10	HC10	HC10
odorous substance		DMS	DMS	DMS	DMS	DMS	DMS	DMS	DMS	DMS	DMS	DMS
strip gas in regeneration		steam	steam	steam	steam	steam	steam	steam	steam	steam	steam	steam
temperature regeneration [°C]	T_reg	100	100	100	100	100	100	100	100	100	100	100
raw gas volume flow [l/h]	v_G	300	500	500	300	200	200	150	150	300	150	150
liquid volume flow [l/h]	v_L	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	9.3	9.3	9.3
strip gas volume flow [l/h]		w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o
mass flow of odorous substance [g/h]		0.52	0.77	0.14	0.13	?	0.84	1.08	0.25	0.84	0.84	0.18
raw gas concentration [ppm]	y1	775	485	111	204	473	2260	3129	896	1069	647	2350
treated gas concentration [ppm]	y2	159	207	29	56	31	232	169	62	279	253	235
strip gas concentration [ppm]		-	-	-	-	-	-	-	-	-	-	-
concentration in liquid before scrubber [ppm]	x2	1	1	1	1	1	1	12	8	4	4	4
concentration in liquid after scrubber [ppm]	x1	227	287	49	62	47	213	390	85	324	279	64
concentration in condensate [ppm]		126	154	27	37	60	211	329	100	188	259	61
steam dosing in regeneration [gH2O/kgLiquidl]		74.04	79.66	86.24	86.01	89.64	87.26	87.65	70.62	80.63	71.15	75.94
absorption efficiency [%] (=(y1-y2)/y1	eta_abs	79%	57%	74%	73%	93%	90%	95%	93%	74%	61%	90%
regeneration efficiency [%] (=(x2-x1)/x2)	eta_reg	100%	100%	98%	98%	98%	100%	97%	91%	99%	99%	94%
concentration factor [%] (=y3/y1)	f	-	-	-	-	-	-	-	-	-	-	-
raw gas mol flow [mol/h]	G	12.48	20.79	20.79	12.48	8.32	8.32	6.24	6.24	12.48	6.24	6.24
density liquid [kg/l]	ro_L	0.877	0.877	0.877	0.877	0.877	0.877	0.877	0.877	0.877	0.877	0.877
mass flow liquid [kg/h]	m_L	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	8.2	8.2	8.2
mole weight of absorbant [kg/kmol]	Mi	315	315	315	315	315	315	315	315	315	315	315
mole flow liquid [mol/h]	L	21.4	21.4	21.4	21.4	21.4	21.4	21.4	21.4	25.9	25.9	25.9
mass flow steam [g/h]	m_D	500.0	537.9	582.4	580.8	605.3	589.3	591.9	476.9	657.6	580.3	619.4

Table 38: Data from Laboratory Oil scrubber experiments and calculated values (part2)

Experiment No.		E1	E2	E3	E4	E5	E6	E7	E8	E10	E11	E12
steam superficial velocity [m/s]	w_D	0.59	0.64	0.69	0.69	0.72	0.70	0.70	0.56	0.78	0.69	0.73
mole flow strip gas [mol/h]		-	-	-	-	-	-	-	-	-	-	-
Henry coefficient, absorption at 25°C [bar]	Hi,j (T)	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
Henry coefficient, regeneration, 100°C (steam), 25°C (air) [bar]	Hi,j (T_reg)	2.43	2.43	2.43	2.43	2.43	2.43	2.43	2.43	2.43	2.43	2.43
stripping factor, absorption [-]	S_abs	0.63	1.05	1.05	0.63	0.42	0.42	0.32	0.32	0.52	0.26	0.26
stripping factor, regeneration [-]	S_reg	3.11	3.34	3.62	3.61	3.76	3.66	3.68	2.96	3.38	2.99	3.19
equilibrium gas conc. of x1 (=x1*(H/P)) [ppm]	y1*	246.5	311.6	53.2	67.3	51.0	231.3	423.5	92.3	351.8	303.0	69.5
equilibrium gas conc. of x2 (=x2*(H/P)) [ppm]	y2*	1.1	1.1	1.1	1.1	1.1	1.1	13.0	8.7	4.3	4.3	4.3
d_y1 (=y1-y1*) [ppm]		528.5	173.4	57.8	136.7	422.0	2028.7	2705.5	803.7	717.2	344.0	2280.5
d_y2 (=y2-y2*) [ppm]		157.9	205.9	27.9	54.9	29.9	230.9	156.0	53.3	274.7	248.7	230.7
(d_y)_m [ppm]		306.8	189.2	41.1	89.7	148.1	827.3	893.5	276.6	461.1	293.8	894.7
(y2-y1)/(d_y)_m [-]		2.0	1.5	2.0	1.7	3.0	2.5	3.3	3.0	1.7	1.3	2.4
overall gas-phase mass-transfer coefficient, absorption [kmol/(h*m³)]	kGa	43.8	53.4	72.5	36.0	43.3	35.6	36.1	32.9	37.3	14.6	25.8
absorbed mol flow [mol/h] (=(y2-y1)*V_G)	n_abs	7.7E-03	5.8E-03	1.7E-03	1.8E-03	3.7E-03	1.7E-02	1.8E-02	5.2E-03	9.9E-03	2.5E-03	1.3E-02
y_reg2 (ppm) (=n_abs/D)		277	193	53	57	109	515	561	196	270	76	383
y_reg1* (=x2*(H/P))		2.4	2.4	2.4	2.4	2.4	2.4	28.8	19.2	9.6	9.6	9.6
y-reg2* (=x1*(H/P))		544.5	688.5	117.5	148.7	112.7	510.9	935.5	203.9	777.2	669.3	153.5
d_y_reg1 (=y_reg1*, da y_reg=0,def.)		2.4	2.4	2.4	2.4	2.4	2.4	28.8	19.2	9.6	9.6	9.6
d_y_reg2 (=y_reg2*-y_reg2)		267.9	495.0	64.8	91.5	3.4	-4.3	374.0	7.5	507.5	593.0	-229.9
(d_y)_m		56.3	92.4	18.9	24.5	2.9	n.n.	134.6	12.5	125.5	141.5	n.n.
(y_reg2)/(d_y)_m		4.9	2.1	2.8	2.3	37.9	n.n.	4.2	15.7	2.2	0.5	n.n.
overall gas-phase mass-transfer coefficient, regeneration [kmol/(h*m³)]	kGa_reg	362	166	239	200	3380	n.n.	364	1106	208	46	n.n.
m (=Hij/P)		1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
number of theoretical separation steps, abs [-]	Nt_abs	1.94	1.44	3.28	1.50	2.61	2.09	2.29	2.14	1.33	0.58	1.53
height of a theoretical separation step, absorption [m]	HETS_abs	0.52	0.70	0.30	0.67	0.38	0.48	0.44	0.47	0.75	1.73	0.65
m_reg (=Hij/P)		2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
number of theoretical separation steps, reg [-]	Nt_reg	7.4	7.6	4.9	5.3	4.8	6.9	4.4	3.0	5.7	5.8	3.5
height of a theoretical separation step, regeneration [m]	HETS_reg	0.13	0.13	0.20	0.19	0.21	0.14	0.23	0.33	0.17	0.17	0.28

Table 39: Data from Laboratory Oil scrubber experiments (part3)

Experiment No.		E19	E20	E21	E23	E26	E28	E29	E30	E31	E32	E33	E34
washing liquid		HC 10	HC 10	HC 10	HC10	HC10	Tegde	Tegde	Tegde	Tegde	Tegde	Tegde	Tegde
odorous substance		DMS	DMS	DMS	DMS	DMS	DMS	DMS	DMS	DMS	DMS	DMS	DMS
strip gas in regeneration		Luft	Luft	Luft	Luft	Luft	Luft	Luft	Luft	Luft	Luft	Luft	Luft
temperature regeneration [°C]	T_reg	32	33	33	18	100	100	100	100	100	100	100	100
raw gas volume flow [l/h]	v_G	300	300	300	500	500	500	500	500	500	500	500	500
liquid volume flow [l/h]	v_L	7.7	7.7	7.7	6.4	6.4	3.41	3.41	4.45	4.45	4.45	4.45	4.56
strip gas volume flow [l/h]		12	7.5	200	180	120	36	300	300	90	240	162	162
mass flow of odorous substance [g/h]		0.77	2.30	0.75	4.80	3.47	6.00	5.87	12.94	12.94	3.73	3.73	4.85
raw gas concentration [ppm]	y1	1142	3560	1067	4883	4103	7092	30273	4655	4918	4101	5134	4799
treated gas concentration [ppm]	y2	875	2873	634	3409	2192	1598	7597	976	993	1064	691	1291
strip gas concentration [ppm]		1820	6301	1396			37953	3512	5246	15484	3966	9249	11028
concentration in liquid before scrubber [ppm]	x2	961	2727	569	3427	1060	1054	1072	1390	1612	1592	1905	2029
concentration in liquid after scrubber [ppm]	x1	985	3362	769	4165	2275	2614	32520	8674	6937	10513	5510	8526
concentration in condensate [ppm]		-	-	-	-	-	-	-	7000	13700	-	-	-

Table 40: Data from Laboratory Oil scrubber experiments (part4)

Experiment No.		E35	E38	E39	E40	E36	E37	E14	E13	E17	E15	E16	E18
washing liquid		Tegde	Tegde	Tegde	Tegde	Tegde	Tegde	HC10	HC10	HC 10	HC 10	HC 10	Dodecan
odorous substance		DMS	DMS	DMS	DMS	DMS	DMS	TEA	TEA	PT	PT	PT	DMS
strip gas in regeneration		Luft	Luft	Luft	Luft	Luft	Luft	steam	steam	steam	steam	steam	steam
temperature regeneration [°C]	T_reg	100	100	100	110	18	81	100	100	100	100	100	100
raw gas volume flow [l/h]	v_G	500	500	500	500	500	500	300	500	200	200	300	300
liquid volume flow [l/h]	v_L	4.67	4.67	4.67	4.56	4.67	4.67	7.7	7.7	7.7	7.7	7.7	7.7
strip gas volume flow [l/h]		156	162	162	300	300	300	w/o	w/o	w/o	w/o	w/o	w/o
mass flow of odorous substance [g/h]		4.08	0.63	1.82	5.48	5.26	5.26	0.82	0.37	0.11	0.12	?	0.87
raw gas concentration [ppm]	y1	3553	782	1926	4541	4864	4336	288	180	241	393	232	1552
treated gas concentration [ppm]	y2	853	104	182	793	2449	812	n.n.	n.n.	13	13	<5	188
strip gas concentration [ppm]		5078	1298	3266	4970	2829	5937	-	-	-	-	-	-
concentration in liquid before scrubber [ppm]	x2	949	604	660	640	4957	1296	n.n.	n.n.	n.n.	n.n.	n.n.	**4.000**
concentration in liquid after scrubber [ppm]	x1	2758	817	1461	2942	6489	3845	72	n.n.	n.n.	n.n.	n.n.	311
concentration in condensate [ppm]		17133	2636	3793	7058		10546	36	44	53	53	33	96

Table 41: Data of on-site bioscrubber experiments at a fat and oil refinery

Day#	26	33	41	56	63	70	77
QG [m³/h]	5.0	3.5	8.0	5.0	3.5	6.0	4.0
QL [m³/h]	0.53	0.42	0.32	0.65	0.63	0.32	0.32
v (QL/QG)	0.11	0.12	0.04	0.13	0.18	0.05	0.08
raw gas conc. [OU/m³]	12,756	24,548	9,742	3,756	31,835	19,484	10,522
gas conc. W1 [OU/m³]	5,467	7,512	1,491	683	6,889	4,390	2,814
gas conc. W1 [OU/m³]	2,896	3,579	2,170	609	5,014	5,793	1,543
W1-c_M [OU/m³]	8,603	14,387	4,396	1,803	16,298	10,128	5,844
W2-c_M [OU/m³]	6,650	10,890	5,042	1,730	14,511	11,287	4,677
separation efficiency W1 [OU/(m³*h)]	2.51E+06	4.10E+06	4.54E+06	1.06E+06	6.00E+06	6.23E+06	2.12E+06
separation efficiency W2 [OU/(m³*h)]	3.39E+06	5.05E+06	4.17E+06	1.08E+06	6.46E+06	5.65E+06	2.47E+06
separation efficiency W1 [%]	57%	69%	85%	82%	78%	77%	73%
separation efficiency W2 [%]	77%	85%	78%	84%	84%	70%	85%

Table 42: Identified substances of raw air of starch factory, type B, with TIC areas, odorous thresholds OT_i and Odour Ratio OI_i

compounds	group of substances	raw air "B" [TIC area]	OT [µg/l]	α_i	τ_i	OR_i	$OR\%_i$
3-methyl-1-butanol	alcoholes	1,676,676	0.1	**19.52%**	1.70%	16,766,763	**33.7%**
hexanal	aldehyde	404,189	0.04	4.71%	4.25%	10,104,729	**20.3%**
3-methylbutanal	aldehyde	39,716	0.005	0.46%	**34.00%**	7,943,146	**16.0%**
nonanal	aldehyde	28,713	0.005	0.33%	**34.00%**	5,742,600	**11.5%**
acidic acid	acid	105,939	0.06	1.23%	2.83%	1,765,650	3.5%
1-hexanol	alcoholes	455,832	0.3	5.31%	0.57%	1,519,440	3.1%
dimethyl disulfide	org. sulphur	35,058	0.029	0.41%	5.86%	1,208,889	2.4%
1-heptanol*	alcoholes	33,717	0.05	0.39%	3.40%	674,340	1.4%
2-hexenal	aldehyde	20,039	0.034	0.23%	5.00%	589,387	1.2%
2-methylbutanal	aldehyde	70,462	0.14	0.82%	1.21%	503,300	1.0%
2-methylpropanal	aldehyde	68,378	0.14	0.80%	1.21%	488,414	1.0%
2-pentylfurane	furane	101,467	0.27	1.18%	0.63%	375,804	0.8%
ethanol	alcoholes	4,909,250	19	**57.15%**	0.01%	258,382	0.5%
1-decanol*	alcoholes	21,166	0.1	0.25%	1.70%	211,659	0.4%
benzaldehyde	aldehyde	39,131	0.19	0.46%	0.89%	205,950	0.4%
2-heptanon	ketone	28,493	0.68	0.33%	0.25%	41,901	0.1%
ethylbenzene	aromate	9,564	0.41	0.11%	0.41%	23,327	0.0%
m,o-xylene	aromate	16,281	1.2	0.19%	0.14%	13,568	0.0%
p-xylene	aromate	22,327	2.1	0.26%	0.08%	10,632	0.0%
toluene	aromate	60,617	5.9	0.71%	0.03%	10,274	0.0%
2-butanone	ketone	54,054	5.8	0.63%	0.03%	9,320	0.0%
2-pentanone	ketone	46,850	5.5	0.55%	0.03%	8,518	0.0%
acetone	ketone	80,584	35	0.94%	0.00%	2,302	0.0%
a-pinene	terpene	24,163	18	0.28%	0.01%	1,342	0.0%
undecene	alkene	7,659	7.8	0.09%	0.02%	982	0.0%
3-hydroxy-2-butanon	ketone	13,175	42	0.15%	0.00%	314	0.0%
2-methylfurane	furane	0	n.n.	0.00%	0.00%	0	0.0%
benzene	aromate	0	37	0.00%	0.00%	0	0.0%
1-heptene	alkene	64,870	n.n.	0.76%	0.00%	0	0.0%
nonanol*	alcoholes	12,148	n.n.	0.14%	0.00%	0	0.0%
2-methyl-3-octanone*	ketone	11,901	n.n.	0.14%	0.00%	0	0.0%
2,2,6-trimethyl-cyclohexanone	ketone	0	n.n.	0.00%	0.00%	0	0.0%
1,2,4,5-tetraethyl-cyclohexan *	alkane	0	n.n.	0.00%	0.00%	0	0.0%

Legend: compounds marked with * could only be identified with low certainty

Table 43: Waste air components of raw air, type B, with percental residual concentration [%] of the raw air peak areas

compounds	Raw air "B" [TIC area]	OR%$_i$	+Water	+NB 1,5%	+NB 5%	+POW 1,5%	+POW 5%
3-methyl-1-butanol	1,676,676	**33.70%**	8%	5%	6%	8%	7%
hexanal	404,189	**20.31%**	310%	0%	80%	18%	11%
3-methylbutanal	39,716	**15.96%**	73%	0%	413%	204%	271%
nonanal	28,713	**11.54%**	177%	0%	100%	69%	51%
acidic acid	105,939	3.55%	32%	12%	0%	0%	0%
1-hexanol	455,832	3.05%	13%	3%	4%	8%	4%
dimethyl disulfide	35,058	2.43%	83%	61%	72%	49%	141%
1-heptanol*	33,717	1.36%	76%	0%	61%	49%	0%
2-hexenal	20,039	1.18%	76%	63%	128%	165%	92%
2-methylbutanal	70,462	1.01%	10%	0%	180%	81%	0%
2-methylpropanal	68,378	0.98%	49%	0%	44%	0%	0%
2-pentylfurane	101,467	0.76%	96%	116%	115%	123%	151%
ethanol	4,909,250	0.52%	6%	1%	4%	4%	1%
1-decanol*	21,166	0.43%	0%	0%	0%	0%	0%
benzaldehyde	39,131	0.41%	115%	38%	225%	92%	65%
2-heptanone	28,493	0.08%	43%	52%	57%	47%	153%
ehylbenzene	9,564	0.05%	161%	151%	257%	464%	261%
m,o-xylene	16,281	0.03%	56%	78%	77%	46%	218%
p-xylene	22,327	0.02%	206%	159%	193%	139%	236%
toluene	60,617	0.02%	100%	160%	187%	137%	189%
2-butanone	54,054	0.02%	0%	70%	96%	72%	222%
2-pentanone	46,850	0.02%	0%	0%	41%	34%	33%
acetone	80,584	0.00%	119%	299%	407%	187%	525%
a-pinene	24,163	0.00%	98%	93%	130%	126%	115%
undecene	7,659	0.00%	0%	0%	0%	0%	0%
3-hydroxy-2-butanon	13,175	0.00%	0%	0%	43%	0%	0%
1-heptene	64,870	0.00%	129%	41%	38%	29%	50%
nonanol*	12,148	0.00%	0%	0%	0%	0%	0%
2-methyl-3-octanone	11,901	0.00%	117%	81%	135%	118%	231%
benzene	0	0.00%	0	45,213	0	0	91,922
2,2,6-trimethyl-cyclohexanone	0	0.00%	0	114,639	266,306	257,213	689,983
1,2,4,5-tetraethyl-cyclohexane*	0	0.00%	0	0	0	0	26,490

Legend: areas highlighted grey = compounds with a redidual concentration >10% (separation insufficient)
compounds marked with * could only be identified with low certainty
NB: humic substances type "Nussbeize", POW = humic substances type "POW"

10 References

Acree, T.E.; Barnhard, J.; Cunningham, D.G. (1984): A procedure for the sensory analysis of gas chromatographic effluents. Food Chem. 14, pp. 273-286

Amoore, J.E. (1970): Molecular Basis of Odor. Ed. C.C. Thomas Publisher, Springfield, USA

Anonymous (1995): VDI-Guidelines, Olfaktometrie. Bd. 1-4, Geruchsschwellen-bestimmung, Anwendungsvorschrifften und Verfahrenskenngrössen, Kommission Reinhaltung der Luft im VDI und DIN, VDI-Verlag, Düsseldorf, Germany

Anonymous (1998): VDI-Guidelines, Abgasreinigung durch Adsorption - Prozeßgas- und Abgasreinigung. No. 3674, vol.5, VDI-Verlag, Düsseldorf, Germany

Anonymous (1999): VDI-Guidelines, Naßabscheider - Abgasreinigung durch Absorption. No. 3679, vol.2, VDI-Verlag, Düsseldorf, Germany

Anonymous (2002): Wärmeatlas. 9. Auflage. Berlin, Springer, ISBN: 3-540-41200-X

Anonymous (2003): DIN EN 13725: Air quality - Determination of odour concentration by dynamic olfactometry. German version EN 13725:2003, VDI/DIN-Handbuch Reinhaltung der Luft - Band 1A, Kommission Reinhaltung der Luft (KRdL), VDI-Verlag, Düsseldorf

Behrendt, J. (1994): Biologisch-chemische Behandlung von Prozesswässern der Altlastensanierung sowie von kontaminierten Grundwässern. Diss., VDI-Verl., Fortschritt-Berichte / VDI: Reihe 15, Umwelttechnik ; Nr. 119 Düsseldorf, Germany, ISBN: 3-18-141915-X

Billet, R. (1995): Packed towers in processing and environmental technology. VCH, Weinheim, ISBN 3-527-28616-0

Bockreis, A. und Steinberg, I. (2004): Vom Geruch zum Gestank. Geruch: Messung-Wirkung-Minimierung. 71. Darmstädter Seminar Abfalltechnik, Verein zur Förderung des Institutes WAR (Hrsg.), TU Darmstadt e.V., Schriftenreihe WAR 157, ISBN: 3-932518-53-5, pp. 1-8

Bollag, J.-M. und Myers, C. (1992): Detoxification of aquatic and terrestrial sites through binding of pollutants to humic substances. The Science of the Total Environment 117/118 357-366.

Bratzler, K.; Doergers, A. (1972): Gas purification and Gas separation by absortion (text in German languages). in Ullmanns Encyclopädie der technischen Chemie, Vol.2, Verfahrenstechnik 1 (Grundoperationen), VCH, Weinheim, ISBN 3-527-28616-0

Brauer, H. (1989): Absorptive Abgasreinigung. VDI Berichte, Bd. 730, pp. 275-329, VDI Verlag, Düsseldorf

Brecht, B. (1928): "Ballade von der Unzulänglichkeit des menschlichen Planens"/ "Song of the Insufficiency of Human Struggling" in "Die Dreigroschenoper" / "The Threepenny Opera", Berlin

Cheremisinoff, P.N. (ed.) (1993): Air pollution control and design for industry. Marcel Dekker Inc., New York

Cuno, M., Weigert, B., Behrendt, J., Wiesmann, U. (1995): Biologischer Abbau von Öl/Wasser-Emulsionen und polycyclischen aromatischen Kohlenwasser-stoffen. Vom Wasser, Bd. 84, pp. 105-116

Cuno, M. (1996): Kinetische Untersuchungen zum biologischen Abbau von Mineralölen und polycyclischen aromatischen Kohlenwasserstoffen. VDI-Verlag, Düsseldorf

Daniels, R. (2002): Electronic Noses. Eurocosmetics 10[1], pp. 20-29.

Devos, M.; Gemert, L.J.van.; Patte, F.; Rouault, J. (1990): Standardized Human Olfactory Thresholds. Oxford University Press

Fenski, M. (2003): Einsatz des Dampfstripp–Verfahrens zur Regeneration hochsiedender Waschflüssigkeiten aus der absorptiven Reinigung geruchsbeladener Abluft. DA, AB Abwasserwirtschaft, TU Hamburg-Harburg

Frechen, F.B. (1984): Stellung des Kompostfilterverfahrens zur Abluftdesodorierung im Bereich von Kläranlagen im Vergleich zu anderen Verfahren. Wissenschaft und Umwelt. 7 (1), 17-24

Freudenthal, K., Otterpohl, R., Behrendt, J. (2004a): Improvement in Odour Reduction by Air Scrubbers Using Adapted Washing Liquids. Enviro 04 Convention & Exhibition, proceedings, no. E4187, Sydney

Freudenthal, K., Otterpohl, R., Behrendt, J. (2004b): Entwicklung eines selektiven Absorptionsverfahrens zur Reinigung geruchsbeladener Abluft aus Lebensmittelbetrieben. Hamburger Berichte, Bd.23, Verl. Abfall aktuell, 221-238

Freudenthal, K., Fenski, M., Otterpohl, R., Behrendt, J. (2004c): Investigation of Odour Abatement by Absorption with adapted Oils as Washing Liquids. International Conference „Environmental Odour Management", VDI-Berichte, 1850, VDI-Verlag, Düsseldorf, pp. 503-514

Freudenthal, K., Otterpohl, R., Behrendt, J. (2005a): Absorption of odorants using selective gas-liquid separation processes. Waste Management J., vol. 25, Elsevier, pp.975-984

Freudenthal, K., Otterpohl, R., Behrendt, J. (2005b): Selektive Absorption zur Geruchsminderung bei Produktionsprozessen durch den Einsatz von Löslichkeitsvermittlern in Biowäschern. VDI-Berichte, 1893, VDI-Verlag, pp. 71-184, Düsseldorf

Freudenthal, K., Otterpohl, R., Behrendt, J. (2005c): Selective Absorption for Odour Control of Production Processes by application of Solubility Agents in Bioscrubbers. 10th International Waste Management and Landfill Symposium, proceedings, pp. 527-528, Cagliari, Italy

Fritz, W.; Kern, H. (1990): Reinigung von Abgasen: Gesetzgebung zum Emissionsschutz, Maßnahmen zur Verhütung von Emissionen; mechanische, thermische, chemische und biologische Verfahren der Abgasreinigung, Entschwefelung und Entstickung von Feuerabgasen; physikalische Grundlagen, technische Realisierung, Umwelt-Magazin, Bd. 2, pp. 133-137, Vogel, Würzburg

Gemert, L.J.v.; Nettenbreijer; A.H. (eds.) (1977): Compilation of odour thresholds values in air and water. Nat. Inst. Water Supply, Voorburg, Netherlands

Gmehling, J.; Kolbe, B. (1992). Thermodynamik. 2. Aufl., Weinheim, VCH, ISBN 3-527-28547-4

Goldstein, N. (2001): New frontiers for odor research. Biocycle, September 2001, pp. 46-51, online-version: http://www.jgpress.com/BCArticles/2001/090146.html

Grigull, K.; Weilberg, Chr.; Elsholz, K.; Bryniok, D. (2002): Absorption von Schadstoffen mit regenerativen Waschmedien und anschließeneder Verwertung. VDI-Berichte Nr. 1722, pp. 93-100, VDI Verlag, Düsseldorf

Guadagni, D.G.; Buttery, R.G.; Harris, J. (1966): Odour intensities of hop oil components. J. Sci. Food Agric. 17, pp. 142-144

Gulyas, H. (2003): Organische Problemstoffe in Abwässern: Wirkungen und Behandlungsverfahren. Hamburger Berichte zur Siedlungswasserwirtschaft 42, Gesellschaft zur Förderung der Forschung und Entwicklung der Umwelttechnologien an der Technischen Universität Hamburg-Harburg e.V., Hamburg, ISBN 3-930400-58-8

Hangartner, M (1987): Sensorische Geruchsmessung. Umweltschutz/ Gesundheitstechnik, Bd. 1, pp.20-23, Cicero-Verl., Zürich

Heining, K. (1998): Biofilters and Bioscrubbers – Odour elimination in composting plants. dissertation, Economica Verlag, Bonn, ISBN 3-87081-158-7

Hekmat, D. und Vortmeyer, D. (1999): Biologischer Abbau von schwer wasserlöslichen, flüchtigen aromatischen Verbindungen aus Abluft. Chemie Ingenieur Technik 71 (11), 1290-1294.

Kalina, A. (1997): Verfahrenstechnische Grundlagen der Mehrkomponenten-absorption mit hoch-siedenen Waschflüssigkeiten, dissertation, Merseburg

Kleeberg, K. K., Liu, Y., Schlegelmilch, M., Streese, J., Stegmann, R. (2003): Potential of Solid-Phase Microextraction (SPME) for the Charaterisation of Odourous Waste Gas Emissions. proceedings of Sardinia 2003 -Ninth International Waste Management and Landfill Symposium, Cagliari

Klingner, B. (2002): Untersuchungen zur Verbesserung der Absorptionsleistung für die Behandlung geruchsbeladener Abluft durch Einsatz von Waschadditiven. Diplomarbeit, AB Abwasserwirtschft, TU Hamburg-Harburg

Koglatis, J. (2002): Untersuchungen zum Einfluss von Löslichkeitsvermittlern auf die

Absorptionsleistung von Waschflüssigkeiten anhand von Messungen mit dem GC/FID und der Elektronischen Nase. Studienarbeit, AB Abwasserwirtschaft, TU Hamburg-Harburg

Kruszona, H.-C. (2002): Entwicklung eines Messverfahrens zur indirekten Bestimmung der Lipophilizität von Geruchsstoffen. Vertieferarbeit, AB Abwasserwirtschaft, TU Hamburg-Harburg

Kruszona, H.-C. (2003): Abtrennung von Geruchsstoffen der Lebensmittelindustrie aus dem Absorbens eines Abluftwäschers mittels Flüssig-flüssig-Extraktion. Diplomarbeit, AB Abwasserwirtschaft, TU Hamburg-Harburg

Last, W. (1999): Absorption mit überlagerter chemischer Reaktion in Packungs-kolonnen. Fortschrittsberichte VDI, Reihe 3, Nr. 618. Düsseldorf : VDI Verlag

Lazaridis, A. (1990): Reaktionskinetische Untersuchungen zur simultanen Absorption von NOx und SO2 in Wasser und in wässrigen Eisen-EDTA-Lösungen. Dissertation, Techn. Hochsch., Aachen

Libra, J.A.; Saupe, A. (2000): Ozonation of water and wastewater: A practical guide to understanding ozon and its applications. Wiley, New York

McKetta, J.J. (ed.) (1999): Encyclopedia of chemical processing and design: Wastewater treatment with ozone to water and wastewater treatment. Marcel Dekker, New York, Vol. 66

Neustadt, B., Marr, I. L., Zwanziger, H.W. (1995): Toxicity Testing of Oil-Contamina-ted Drilling Cuttings. Fresenius Journal of Analytical Chemistry 351 (7), 625-628

Ohloff, G. (1990): Riechstoffe und Geruchssinn. Springer Verlag, Berlin, Heidelberg

Okubo, M.; Yamamoto, T.; Kuroki, T. (2001): IEEE Trans. Ind. Applic. 37, 5, pp. 1505-1511, New York

Reid, R.C.; Prausnitz, J.M.; Poling, B.E. (1989): Properties of Gases and Liquids. McGraw-Hill, NewYork

Römpp, H., Falbe, J. (ed.) et al. (1999): Römpp-Chemie-Lexikon. Georg Thieme Verlag, Stuttgart/New York, ISBN: 3-13-734609-6

Rothe, M.; Thomas, B. (1963): Aroma of bread. Evaluation of chemical taste analyses with the aid of threshold value. Z. Lebensm. Unters. Forsch. 202, pp.30-34

Ruentfranz, C. (1996): Einfluss des Luft-Wasser-Verteilungsgleichgewichts von Schadstoffen und weiterer Parameter auf die Kinetik biologischer Abluftreinigungsverfahren. Fortschr.-Ber. VDI Reihe 15 Nr. 160, VDI Verlag, Düsseldorf, Germany (TUB: 2214-9826)

Rychlik, M.; Schieberle, P.; Grosch. W. (1998): Compliation of odor thresholds, odor qualities and retention indices of key food odorants. Inst. of food chemistry, Techn. Univ. Munich, Germany

Sattler, K.; Feindt, H.J. (1995): Thermal separation processes. 1. ed., . VCH Publishers, New York, ISBN 3-527-28622-5

Schaber, K.; Philippe, J.-L.; Weisweiler, W.; Pinter, A. (1996): Verfahrenstechnische Bewertung neuartiger Waschflüssigkeiten zur Absorption von Lösungsmitteln. research report PEF_Projekt, Europ. Forschungszentrum für Maßnahmen zur Luftreinhaltung, Berichte Umweltforschung Baden-Württemberg, Germany

Schippert, E. (1993): Abscheidung von Lösemitteln im Biowäscher. VDI Berichte 1034, Fortschritte bei der thermischen, katalytischen, sorptiven und biologischen Abgasreinigung, pp. 577 - 609, VDI Verlag, Düsseldorf

Schlauer, J.; Kriebel, M. (2003): Absorption. in: Ullmann´s encyclopedia of industrial chemistry, 6. ed., Weinheim, Wiley, ISBN 3-527-30385-5

Schlegel, H. G. (1992): Allgemeine Mikorbiologie. 7. Auflage, Thieme Verlag, Stuttgart, ISBN 3-13-444607-3

Schlegelmilch, M., Kleeberg, K., Streese, J., Stegman, R. (2004a): Odour management at fat and oil processing industries. Waste Management J., Odour Special, Elsevier

Schlegelmilch, M., Kleeberg, K., Streese, J., Stegman, R. (2004b): Geruchsmanagment, Ein Anwenderhandbuch mit Beispielen aus der Lebensmittel-industrie. Hamb. Berichte, Bd.24, Verla Abfall aktuell, Stuttgart, ISBN 3-9808180-7-1

Niemeyer, B.; Matz, G.; Otterpohl, R.; Stegmann, R.; Steinhart, H. (ed.) (2006): Minimierung von Gerüchen, Abschlussbericht des Verbundprojekts "Integrierter Umweltschutz in der Lebensmittelindustrie durch selective Minimierung von Gerüchen". Hamburger Berichte, Band 3, Hamburg, ISBN 3-9810064-5-3

Schraeder, R. (1993): Emissionsminderung mit Biowäscher und Lösevermittlern hinter Imprägnier- und Siebdruckanlagen der Dichtungsfertigung. In: VDI (ed.), pp. 617-662 Düsseldorf

Theodore, L.; Buonicore, A. (1988): Air pollution control equipment, part 2, gases. CRC Press, ISBN: 0-8493-5819-1

Venkov, B. (2003): Verbesserung der Reinigungsleistung von Biowäschern bei der Behandlung geruchsbeladener Abluft durch den Einsatz von Huminstoffen. Diplomarbeit, AB Abwasserwirtschaft, TU Hamburg-Harburg

Wagner, S. (1993): Abluftreinigung im Biorieselbettreaktor. Dissertation, Technische Universität München, München

Weisweiler, W., Pinter, A., Winterweiler, W. (1992): Neuartige Waschflüssigkeitssysteme zur Absorption flüchtiger organischer Kohlenwasserstoffe (VOC). research report, Project No. FZKA-PEF 137 Europäisches Forschungszentrum für Maßnahmen zur Luftreinhaltung, Karlsruhe, Germany

Winterbauer, H (1994): Grundlagen einer Heuristik zur Auswahl von Waschflüssigkeiten für die Absorption flüchtiger organischer Verbindungen (VOC) aus Abluftströmen. dissertation, Univ. Karlsruhe (TH), Germany

Yamamoto, T.; Okubo, M.; Hung, Y.-T.; Zhang, R. (2005): Odour pollution control, form Handbook of Environmental Engineering. Vol. 2: Advanced Air and Noise Pollution Control. edited by: Wang, L.K.; Pereira, N.C.; Hung, Y.-T., The Human Press, Inc, Totowa, NJ, ISBN 1588-2935-99

Zarzycki, R.; Chacuk, A. (1993): Absorption – Fundamentals & Applications. Pergamon Press, Oxford, England, ISBN 0 08 040263 1

CURRICULUM VITAE

Personal Data

Name:	Kai Freudenthal
Address:	Güldensternweg 5
	21682 Stade
Date / Place of birth:	22.01.1970, Hamburg
Marital status:	married, 2 children
	(11 und 8 years old)
Nationality:	german

Professional experiences

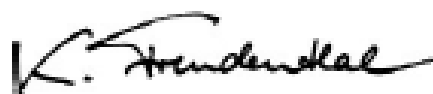|	
11/2008 – present	Run Plant Engineer, DOW Chemical Deutschland, Stade, MDI plant
03/2006 – 10/2008	Reliability Engineer, DOW Chemical Deutschland, Stade, Polycarbonat-, Dowex- and Dowanol plants
09/2001 – 02/2006	Scientific Assistant at Hamburg University of Technology, Institute of Wastewater Management and Water Protection
05/1999 – 09/2001	Project Engineer at Sekoulov, Rohbrecht + Partner (GbR), Consulting Engineers for municipal and industrial Wastewater Management

Education

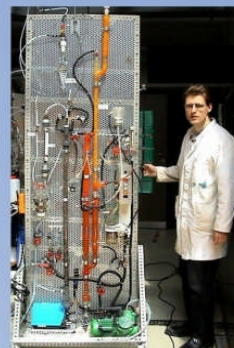|	
1992 - 1999	Study at Hamburg University of Technology, Degree obtained: Diplom Engineer of Process Technology
1989 – 1992	Apprenticeship at Hamburger Electricitäts-Werke AG (HEW) Degree obtained: Process Controlling Engineer
1980 - 1989	Secondary School Uhlenhorst-Barmbek, Hamburg Degree obtained: General Qualification for University entrance
1976 - 1980	Primary School Adolph-Schönfelder, Hamburg

Stade, 12.11.2009

Institute of Wastewater Management and Water Protection

Hamburg University of Technology

Odour control by waste air scrubbers can be improved by optimized choice of absorbents. Applicability of humic substances as solubility agents in bioscrubbers was proofed and verified in several on-site series of measurements at food production companies. Alternatively washing oils were testes in physical scrubbers with regeneration by steam stripping. Both concepts of odour control are compared.