# Monomer Purity

## Concerning
## Odour and Taste

Edith Renöckl

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DIPLOMARBEIT

zur Erlangung des akademischen Grades einer

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der Studienrichtung Technische Chemie

erreicht an der

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in Kooperation mit

BOREALIS

Betreuer: Ao.Univ.-Prof. Dipl.Ing. Dr.techn. Erich Leitner

Institut für Analytische Chemie und Lebensmittelchemie
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2009

TU Graz

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Concerning
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Master's Thesis

at

Graz University of Technology

in Cooperation with

submitted by

**Edith Renöckl**

Advisor: Ao.Univ.-Prof. Dipl.Ing. Dr.techn. Erich Leitner

Institute of Analytical Chemistry and Food Chemistry
Graz University of Technology

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# Abstract

The company Borealis and the working group Food Chemistry and Human Sensory Analysis at the Institute of Analytical Chemistry and Food Chemistry (former Institute of Food Chemistry and Technology) of TU Graz are long term partners in investigating odorous behavior of Borealis products. Within this partnership a PhD thesis was started to run a root cause analysis of odour problems in Borealis products. Since this project the idea analyzing the monomer purity of Borealis plants emerged. In this work many samples from plants all over Borealis were analyzed in different approaches. Besides samples from overall Borealis the objectives were the analysis of time dependency or purification samples. Additionally some diluent and comonomer samples were analyzed.
In this thesis the big differences are outlined, beginning from the in-between differences in ethylene and propylene samples, followed by the differences between the different plants, the development within a time range of 5 months and at last the non-existent influence of purification on odour relevant substances in monomers. The measurement of the comonomers and diluents could not show big influences on the whole odour composition.
Additionally to the original outline of the thesis, some quantification experiments were done on 1-hexene-3-one and 2-hexenal in 1-hexene.

In the end it could be shown, that many of the substances which already occurred in the polymer related thesis of Helene Hopfer are also occurring in the monomer.

# Kurzfassung

Die Firma Borealis und der Bereich Lebensmittelchemie und Humansensorik des Institut für Analytische Chemie und Lebensmittelchemie (vormals: Institut für Lebensmittelchemie und -technologie) der TU Graz sind langjährige PartnerInnen bei der Untersuchung des Geruchs von Borealisprodukten. Im Rahmen dieser Partnerschaft hat Helene Hopfer {Hopfer, 2010} eine Dissertation zur Ursachenanalyse dieser Geruchsprobleme begonnen. Nun wurde - in engem Zusammenhang mit dieser Dissertation - eine Diplomarbeit vergeben, die sich mit der Reinheit von Monomeren in geruchsrelevanter Hinsicht beschäftigen soll. In diesem Projekt werden neben Proben aus verschiedenen Standorten auch Proben zur Untersuchung von Zeitabhängigkeiten und Reinigungswirkung untersucht. Zusätzlich werden noch einige Lösungsmittel- und Comonomerproben untersucht.
In dieser Diplomarbeit werden Unterschiede aufgezeigt, beginnend bei den Unterschieden von Ethylen- und Propylenproben untereinander, gefolgt vom Vergleich der verschiedenen Anlagen und einer Untersuchung der qualitativen Veränderungen über einen Zeitraum von 5 Monaten. Es wird erkannt, daß die momentane Reinigung keinen Einfluß auf geruchsaktive Substanzen hat, so wie auch die Messung der Comonomere und Lösungsmittel keinen wesentlichen Einfluß ergeben hat.
Zusätzlich werden noch einige Quantifizierungsexperimente anhand von 1-Hexen-3-on und 2-Hexenal in 1-Hexen durchgeführt.

Am Ende kann gezeigt werden, daß viele Substanzen, die in Helene Hopfers Dissertation auftauchen auch in den Monomeren gefunden werden können.

## Statutory Declaration

*I declare that I have authored this thesis independently, that I have not used other than the declared sources / resources, and that I have explicitly marked all material which has been quoted either literally or by content from the used sources.*

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Ort
Datum
Unterschrift

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# List Of Used Abbreviations

| | |
|---|---|
| CAR | Carboxene™ |
| DVB | Divinyl benzene |
| FID | Flame Ionisation Detector |
| FPD | Flame Photometric Detector |
| GC | Gas Chromatography |
| GC-O | Gas Chromatography Olfactometry |
| HPPO | High Purity Polyolefins |
| MS | Mass Spectrometry |
| NPD | Nitrogen Phosphorus Detector |
| OAV | Odour Activity Value |
| PA | Polyacrylate |
| PAH | Polycyclic Aromatic Hydrocarbons |
| PDMS | Poly(dimethyl)siloxane |
| PEG | Polyethylene glycol |
| PUA | Polyurethane acrylate |
| RI | Retention Index |
| SPME | Solid Phase Microextraction |

# Acknowledgments

I especially wish to thank my advisor, Erich Leitner, for his immediate attention to my questions, sharing the potency of his nose and participation of his endless knowledge.

Special mention goes to Helene Hopfer for her patience and her always available, friendly help; Nina Haar and Eva Schrampf for their helpfulness in sniffing and Wolfgang Stockreiter for his encouragement and assistance.

Without the support and understanding of my parents - Dr. Edeltraud Renöckl and Dr. Helmut Renöckl - the caring support and sometimes very needed helpfulness of Christian and the fortitude of my friends, this thesis would not have been possible.

Edith Renöckl
Graz, Austria, May 2009

# Credits

*“ Let me tell you the secret that has led me to my goal.*
*My strength lies solely in my tenacity. ”*

[ Louis Pasteur, French biologist & bacteriologist, (1822 - 1895) ]

I would like to thank all the colleagues from “my” institute - I loved to come to work every day which is completely to be contributed to the nice working atmosphere.

I would also like to thank all the people from Borealis who gave me the feeling of doing something useful and necessary.

This thesis was written using Keith Andrews’ skeleton thesis {Andrews, 2006}.

Special thanks goes to the person who invented the automatic espresso machine - without you there would not be that much of a thesis.

# Chapter 1

# Introduction

> *“Begin at the beginning and go on till you come to the end; then stop.”*
>
> [Lewis Carroll, Alice in Wonderland]

The main idea of this project was outlined in the so called *HPPO meeting* of Borealis within the 13th and 14th of march 2008 in Mechelen, Belgium. The *HPPO meeting* designated this project to get a deeper look into monomer purity concerning odour and taste. This work is strongly embedded into the PhD thesis of Helene Hopfer {Hopfer, 2010}. The thesis started prior to this project at Graz University of Technology and is intended to end in march 2010.
Borealis took and takes many efforts in the development of high purity polyolefins purposed to develop new highly valuable materials for food packaging, water pipes and many other applications.

In estimation of the possible results of Helene Hopfers work, the influence of monomer purity on the resulting odour of polyolefins attracted attention. This master thesis should now give a starting point of investigating the wide field of monomer purity in a qualitative way. To attain this goal several tasks were established.

- **Monomers**: *This task should give a first impression on monomers used all over the company. The postulation of having the ‘same’ monomer anywhere in the company is subjected to a reality check here.*
  The following samples were used for the investigation:
  - ***Ethylene (PE monomers) from Borouge, Stenungsund and Schwechat***
  - ***Propylene (PP monomers) from Burghausen, Porvoo and Kallo***
- **Time Dependency**: *Monomer supply is a process which undergoes several changes over the time. This task was outlined to find out if the monomers in the plants stay constant in odour relevant aspects.*
  The following samples were used for the investigation:
  - ***Ethylene from Schwechat***
  - ***Propylene from Porvoo***

- **Purification**: *Purification is a process which is intended to clean monomers from catalyst poisons and other substances which may have a bad influence on purification. This task should check up the influence of purification on monomers in an odour relevant way.*
  The following samples were used for the investigation:
  - ***Ethylene from Schwechat***
  - ***Propylene from Porvoo***
  - ***Propylene from Kallo***
- **Comonomers And Diluents**: *Since polyolefins are not exclusively made of ethylene and propylene some very relevant comonomers and diluents were also evaluated in this project.*
  The following samples were used for the investigation:
  - ***1-Butene from Stenungsund***
  - ***1-Hexene from Stenungsund***
  - ***Propane from Stenungsund***

Additionally a set of process chemicals supplied by Borealis should be inspected for obvious sources of malodour.

# Chapter 2

# Embedding

> *“I don’t understand anything about the ballet; all I know is that during the intervals the ballerinas stink like horses.”*
>
> [Anton Chekhov, Russian dramatist & short story author, (1860 - 1904)]

Odour influences our whole life, including our decisions and our well-being. Investigation of odour, its perception and analytics were longterm neglected by academic research. Especially the influence of odour on our purchase decisions is an object of steadily increasing interest. Nowadays we are under the well-directed influence of selected fragrances, if we like it or not, the fresh food counter at the supermarket is - for example - surrounded by a cloud of artificial bread smell. Also - if people would believe the widespread “information” coming from TV commercials - “air deodorants” were absolutely indispensable.

But not only this more or less obvious smelly influences in our life are of interest for manufacturers of consumable goods, also packaging materials of food, pharmaceuticals or medicinal goods are a rewarding research goal. An optimal behaving packaging material is of low odour or better odour-less.

## 2.1. Food Packaging

Food Packaging and its influence on food quality is a topic of imminent importance. Chemical stability, the duration of shelf-life and ‘quality’ are some of the various packaging-correlated aspects of food as well as pharmaceuticals or medical products.lated aspects of food as well as pharmaceuticals or medical products.

## 2.2. Plastics

Plastics are - commonly speaking - highmolecular synthetically manufactured materials. For manufacturing plastics various precursors and many additives are needed. All these substances can and do have an influence on the odour of the product and therefor an influence on the foods quality. This influences can be subsumed under the concept of migration[1] and permeation[2]. Prevention of permeation is the main function of food packaging and what it is developed for. The packaging material itself should not influence the food quality by migrating substances.

Following {Piringer, 1993} addition polymerization is the main manufacturing process for polyolefins. Besides ethylene for food contact material and consumer products some higher $\alpha$ -olefins like propylene, butylene or propene, 1-butene or 1-hexene could be used. Polyethylene (PE) is mainly used for film applications like shrink film, disposable bags or wrapping foil. Because of its low cold resistance standard polypropylene (PP) films have only few applications. To improve this and some other characteristics mainly copolymers are used.

## 2.3. Establishment Of Analytical Methods

Since the analysis of odour relevant substances is a field on which Borealis did not work so far, the current analytic competency is not sufficient for the analysis of odour relevant substances (shown in figure 2.1).

The establishment of analytical methods to deal with gaseous monomer samples was the projects goal at the very beginning. Solid phase microextraction (SPME) as a tool of analyte enrichment should be tested for its appropriateness for analyzing gaseous samples in routine analysis.

With regards to the work of {Hopfer, 2010} should be checked if the substances found in polymers are already present in the monomers. However this project did not deal with the question if those substances survive the polymerization process or not.

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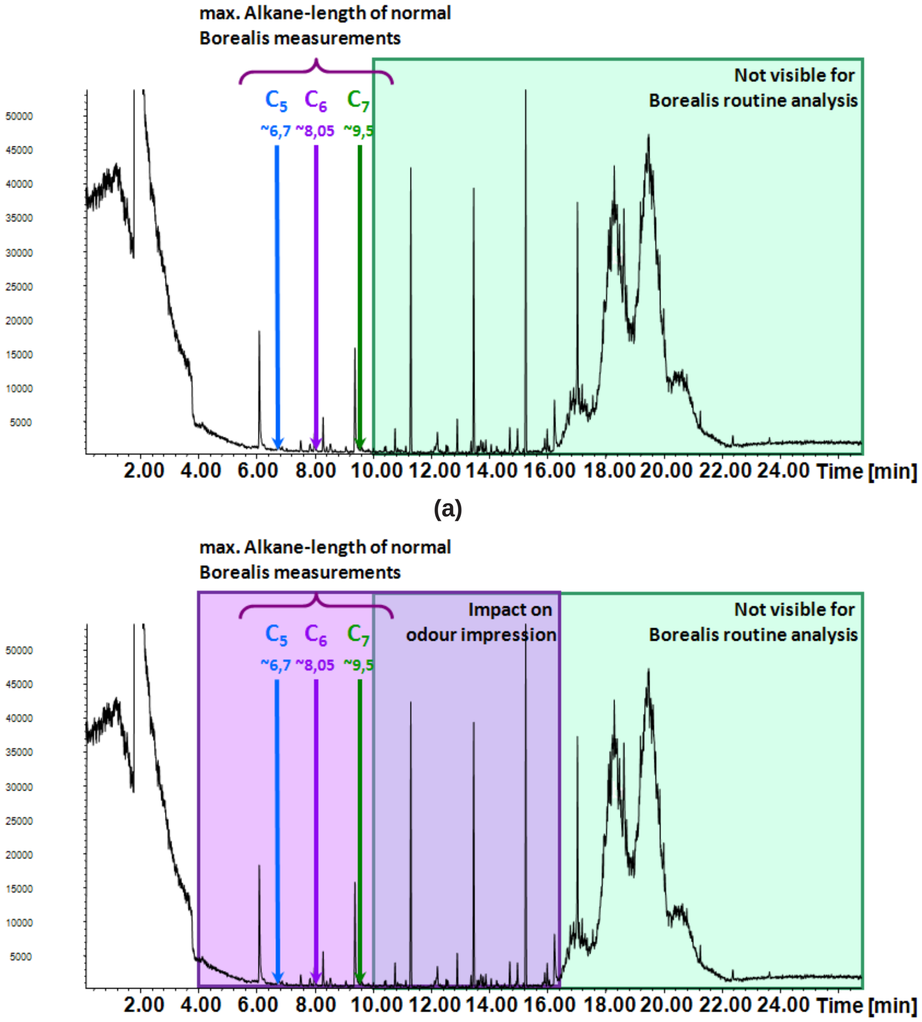
[1] from latin ‘migrare’= marching, hiking

[2] from latin ‘permeare’= to go through, to pass through



(a)

(b)

Figure 2.1.: Illustration of Borealis routine analysis of monomers describing the parts of the chromatograms which are invisible to Borealis in (a) and the parts which have a impact on odour impression in (b)

# Chapter 3

# Theoretical Approach

> “ *The most exciting phrase to hear in science, the one that heralds new discoveries, is not ’Eureka!’ (I found it!) but ’That’s funny ...”’*
>
> [Isaac Asimov, US science fiction novelist & scholar (1920 - 1992)]

## 3.1. Solid Phase Microextraction (SPME)

In this section the basic principles of SPME should be outlined and explained. The inputs and equations of this section were taken from {Pawliszyn, 1997}.

### 3.1.1. Basics On Principles And Construction

Since the transport of the analyte into the coating of the fiber begins immediately after exposure, the extraction is considered to be complete when the concentration of the analyte has reached equilibrium.

$$n = \frac{K_{fs} V_f V_s C_0}{K_{fs} V_f + V_s} \tag{3.1}$$

$n$ = *amount extracted by the coating*
$K_{fs}$ = *fiber coating/sample matrix distribution constant*
$V_f$ = *fiber coating volume*
$V_s$ = *sample volume*
$C_0$ = *initial concentration of a given analyte in the sample*

Equation 3.1 shows that the matrix can be represented as a single homogeneous phase (no headspace). Of course extraction can be interrupted and the sample can be analyzed prior to equilibrium.

In addition, when the sample volume is very large ($K_{fs}V_f << V_s$), equation 3.1 can be simplified to:

$$n = K_{fs} V_f C_0 \tag{3.2}$$

Equation 3.2 points out the usefulness of the technique in field applications, the amount of extracted analyte is independent of the volume of the sample. In practice, the collection of defined samples is no longer needed as the fiber can be exposed directly to ambient air, water, production streams, etc.

### Basic Configuration

Figure 3.1 shows the layout of a common, commercialized SPME liner. In this case, the SPME liner is placed on a liquid filled vial to be exposed to the emerging headspace.

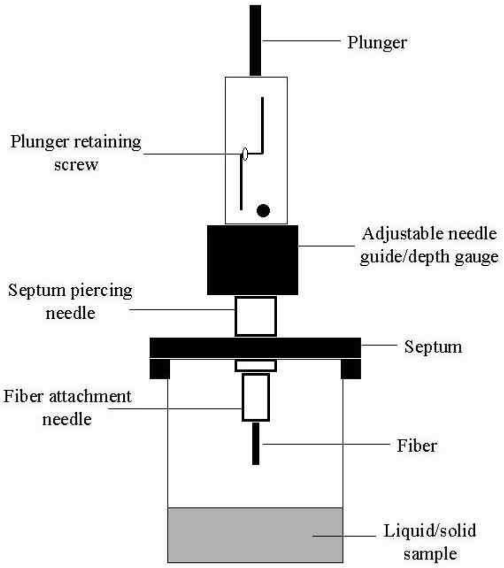


Figure 3.1.: Configuration of a common SPME liner shown from {Randolph C. Galipo et al.}

### Extraction Modes

SPME can be used in different extraction modes. In the direct extraction mode (Figure 3.2a) the coated fiber is directly inserted to the sample, which means direct transport of the analyte to the extracting fiber but also (quoting Erich Leitner) '*...reduction life-time rapidly...*'. To improve extraction time, some level of agitation is needed to force transportation time of the analyte to the extraction phase. *For gaseous samples, natural convection of air is sufficient to facilitate rapid equilibration*. Agitation, rapid vial or fiber movement, stirring or sonication are needed to reduce an effect called 'depletion zone', which produces a fluid shielding and slow diffusion coefficients of analytes in liquid matrices.

In headspace mode the analytes need to be transported through the barrier of air before they can reach the coating. This protects the fiber from damage by high-molecular-weight and other nonvolatile interferences present in the sample matrix, such as humic materials or proteins. Headspace extraction also allows matrix modifications without fiber damaging. At equilibrium the amount of extracted analyte, compared between direct and headspace extraction, is identical as long as the headspace volume and the sample volume are the same. The choice of sampling mode has a very significant impact on extraction kinetics however. When the fiber coating is in the headspace, the analytes are removed from the headspace first, then followed by the analytes from the matrix (shown in Figure 3.2b). Therefore more volatile

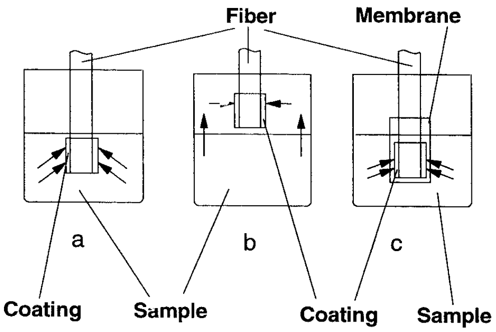


Figure 3.2.: Modes of SPME operation: (a) direct extraction, (b) headspace SPME, (c) membrane-protected SPME as shown in {Pawliszyn, 1997} on p.17

components are extracted much faster than than semivolatiles since they are on higher concentration on the headspace. Temperature has an significant impact on the vapor pressure of the analytes.

Figure 3.3 shows the influence of agitation on the extraction time profile obtained for polynuclear aromatic hydrocarbons (PAHs). Comparing figure 3.3a and 3.3b the equilibration time decreases from 8 to 3 minutes and from 25 to 10 minutes (For phenanthrene and chrysene the equilibrium in this experimental layout is not reached).

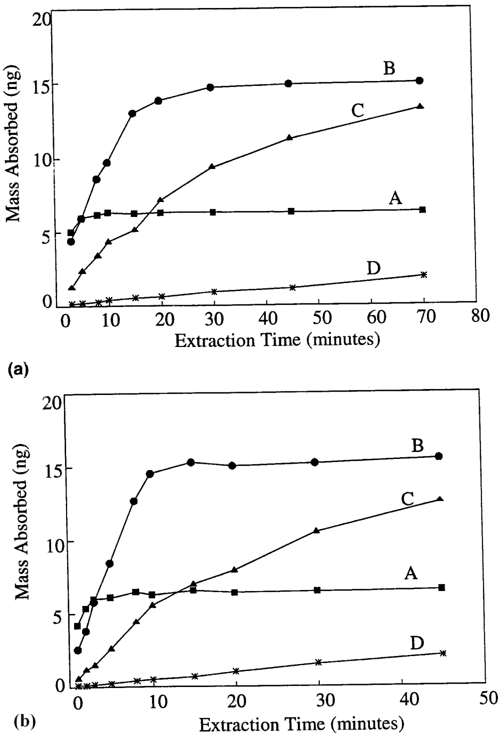


Figure 3.3.: Time extraction profile obtained for headspace solid phase microextraction of several PAHs from aqueous samples at (a) 75% and (b) 100% stirring rates: A naphthalene; B acenaphthalene; C phenanthrene; D chrysene as shown in {Pawliszyn, 1997} on p.18

### Coatings

Equation 3.1 and 3.2 show that the efficiency of the extraction is dependent on the distribution constant $K_{fs}$. This parameter describes the properties of the coating and its selectivity towards the analyte. Additionally the coating volume leads to higher sensitivity but also longer extraction times. This makes the proper selection of the right fiber coating essential to the successful implementation of SPME into a valuable experimental layout.

Figure 3.4 shows the evident influence on two different coatings on a mixture of polar and nonpolar compounds in an aqueous matrix.

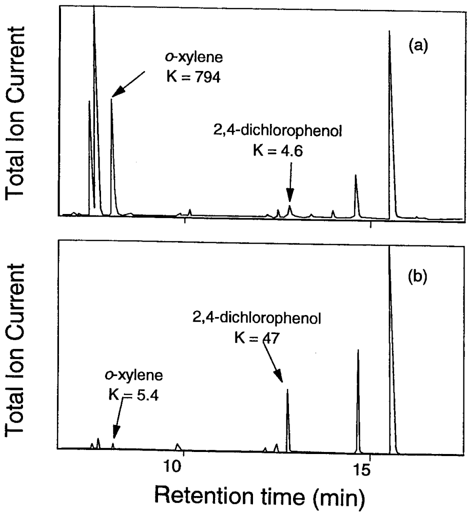


Figure 3.4.: Comparison of total ion current GC/MS chromatograms (TIC) of benzene, toluene, ethyl benzene, o,m,p-xylenes and phenol in water extracted with (a) a poly(dimethylsiloxane) coating and (b) a poly(acrylate) coating shown in {Pawliszyn, 1997} on p.23

### Interfaces To Analytical Instrumentation

For the reason of its solvent-free nature, SPME fibers can be interfaced to analytic instruments of various types, there is no need of injectors capable of large solvent amounts. The mainly used analytical instrument is the GC, in this context it is proposed to work in splitless mode. The desorption time from the analytes from the fiber is very rapid, not only because of the thickness of the coating but also because of the decrease in the coating/gas distribution constant and an increase in the diffusion coefficients. The speed is mainly limited by the introduction time of the fiber into the heated zone.

One of the two possibilities of dealing with this problem is the usage of automatic injection systems with very rapid injection times. The alternative way of using a dedicated injector with a very high heating rate is shown in Figure 3.5.

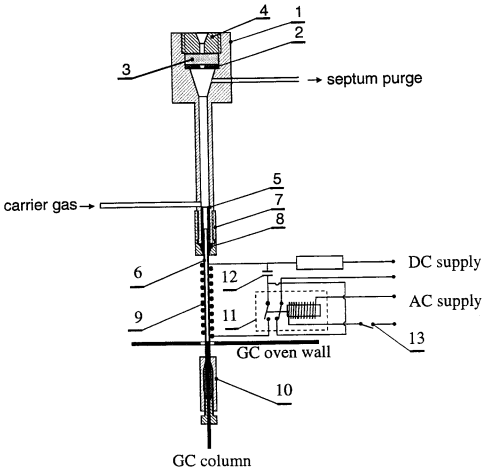


Figure 3.5.: Schematic diagram of the flash SPME injector: 1: injector body; 2: washer; 3: septum; 4: nut; 5: needle guide; 6: fused silica capillary; 7: nut; 8: ferrule; 9: heater; 10: butt connector; 11: relay; 12: capacitor; 13: switch as shown in {Pawliszyn, 1997} on p.32

### 3.1.2. Theory Of Solid Phase Microextraction

To make basic principles of SPME easier to understand and to simplify mathematical relations in the following idealized conditions are assumed. Theoretic approaches are based on fundamentals of thermodynamics and mass transfer.

#### Equilibria in SPME

SPME is a multiphase equilibration process, to simplify the system three idealized phases are considered: the fiber coating, the gas phase or headspace and a homogeneous matrix such as pure water.

The mass of the extracted analyte is directly related to the overall equilibrium in the three phase system of matrix (sample), headspace and coating (fiber). Since the total amount of the analyte should remain the same during extraction, we have:

$$C_0 V_s = C_f^{\infty} V_f + C_h^{\infty} V_h + C_s^{\infty} V_s \tag{3.3}$$

$$\begin{aligned} C_0 &= \textit{initial analyte concentration in the matrix} \\ C_f^{\infty}, C_h^{\infty}, C_s^{\infty} &= \textit{equilibrium coating, headspace \& matrix analyte concentrations} \\ V_f, V_h, V_s &= \textit{coating, headspace \& matrix volumes} \end{aligned}$$

if we define

$$K_{fh} = \frac{C_f^{\infty}}{C_h^{\infty}} \quad \text{as coating/gas distribution constant} \quad \text{and}$$

$$K_{hs} = \frac{C_h^\infty}{C_s^\infty} \quad \text{as gas/sample matrix distribution constant}$$

the mass of the analyte absorbed by the coating

$$n = C_0 V_s \quad \text{can be expressed as}$$

$$n = \frac{K_{fh} K_{hs} V_f C_0 V_s}{K_{fh} K_{hs} V_f + K_{hs} V_h + V_s} \tag{3.4}$$

In the following text an analyte in a multiphase system including a liquid polymer, headspace and an aqueous matrix is used for the discussion of the basic principles of equilibration theory.
The chemical potential of an analyte in the headspace can be expressed as:

$$\mu_h = \mu^0(T) + RT \ln \frac{p_h}{p^0} \tag{3.5}$$

$\mu_h$ = *analyte chemical potential in the headspace*

$p_h$ = *analyte vapour pressure in the headspace*

$\mu^0(T)$ = *analyte chemical potential at standard pressure*

$p^0$ = *standard pressure, usually* $p^0 = 1$ *and temperature T*

The analyte chemical potentials in the coating and the aqueous matrix can be expressed as:

$$\mu_f = \mu^0(T) + RT \ln \frac{p_f}{p^0} \tag{3.6}$$

$$\mu_s = \mu^0(T) + RT \ln \frac{p_s}{p^0} \tag{3.7}$$

$\mu_f, \mu_s$ = *analyte chemical potential in the coating & the matrix*

$p_f, p_s$ = *analyte vapour pressure at equilibrium in the coating & the matrix*

When the three-phase system is at equilibrium the chemical potentials of the analyte in all three phases must be equal:

$$\mu_f = \mu_h = \mu_s \tag{3.8}$$

From equation 3.5 to 3.7 we can write:

$$p_f = p_h = p_s \tag{3.9}$$

$$p_f = K_F C_f^{\infty} \tag{3.10}$$

$$p_s = K_H C_s^{\infty} \tag{3.11}$$

where $K_F$ and $K_H$ are Henry's Law constants of the analyte in the coating and the matrix. Assuming the ideal gas law $p_h V_h = n_h RT$ is valid for the analyte vapour in the headspace:

$$p_h = C_h^{\infty} \tag{3.12}$$

If we connect the distribution constants with Henry's constants we get:

$$K_{fh} = \frac{C_f^{infty}}{C_h^{infty}} = \frac{RT}{K_f} \tag{3.13}$$

$$K_{hs} = \frac{C_h^{infty}}{C_s^{infty}} = \frac{K_H}{RT} \tag{3.14}$$

In the case of the direct SPME sampling from an aqueous solution, we have $\mu_f = \mu_s$ or $p_f = p_s$ at equilibrium. The distribution constant of the analyte between the coating and the aqueous solution $K_{fs}$ can be expressed as $K_{fs} = \frac{C_f^{\infty}}{C_s^{\infty}} = \frac{K_H}{K_F}$ since $p_f = K_F C_f^{\infty}$, $p_s = K_H C_s^{\infty}$ and $p_f = p_s$ when equilibrium is reached.

$$K_{fs} = \frac{K_H}{K_F} = K_{fh} K_{hs} = K_{fg} K_{gs} \tag{3.15}$$

Since $K_{fh}$ the fiber/headspace distribution constant can be approximated by $K_{fg}$ the fiber/gas distribution constant and $K_{hs}$ the headspace/sample distribution constant can be approximated by $K_{gs}$ the gas/sample distribution constant. Then 3.1 can be rewritten as:

$$n = \frac{K_{fs} V_f C_0 V_s}{K_{fs} V_f + K_{hs} V_h + V_s} \tag{3.16}$$

*The equation states, as expected from the equilibrium conditions, that the amount of extracted analyte is independent of the location of the fiber in the system as long as the volumes of headspace, fiber coating and sample are kept constant.*

$$n = \frac{K_{fs} V_f C_0 V_s}{K_{fs} V_f + V_s} \tag{3.17}$$

Both Equation 3.16 and 3.17 describe the mass absorbed by the polymeric coating after equilibrium has been reached.

### Effect Of Extraction Parameters

Theory can be used to optimize the extraction conditions with a minimum of experimental expenses. If both sample and fiber change *Temperature* from $T_0$ to T, the distribution constant changes according to:

$$K_{fs} = K_0 \exp \frac{-\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \tag{3.18}$$

where $K_0$ is the distribution constant when both fiber and sample are at temperature $T_0$ (in Kelvin); $\Delta H$ is the change in enthalpy of analyte when it moves from sample to fiber coating, R is the gas constant. Two common techniques to enhance extraction are *Salting* and *pH Adjustment*. Salting effects on SPME are just determined by experiments to date. In general, the salting effect increases with increasing compound polarity. The Presence of an organic solvent in water changes K according to:

$$K_{fs} = 2.303 K_{fw} \exp \left( \frac{P_1 - P2}{2} \right) \tag{3.19}$$

where $K_{fw}$ is the distribution constant for pure water, $P_1 = 10.2$ is the polarity parameter for water, and $P2 = cP_s + (1-c)P_1$ is the water/solvent mixture polarity parameter for a solvent of concentration c and polarity parameter $P_s$. Equation 3.19 allows the prediction of the distribution constants for water with miscible solvents, assuming that the solvent does not cause the coating to swell. The theory developed following the explanations by $\{$Pawliszyn, 1997$\}$ assumes ideal conditions and neglects factors like *Thermal Swelling*. Thermal swelling should cause the fiber coating radius to change according to:

$$r = r_0(1 + \alpha T) \tag{3.20}$$

where $r_0$ is the radius at 0°C and $\alpha$ is the linear thermal expansion coefficient.

### Coating Selection

$\{$Pawliszyn, 1997$\}$ gives some rules for the coating selection during the establishment of the analysis method.

- **Chemical Nature of Analyte Determines Coating Type (‘*similar attracts similar*’)**
- **PDMS is the Most Useful Coating:** *The advantages of a poly(dimethyl)siloxane are similar to their advantages if they are used as GC stationary phase. They are able to withstand high injector temperatures*
- **The Thinnest Coating which Achieves Required Detection Limits Should Be Used**
- **PA Phase is Suitable for Polar Analytes**
- **Mixed Phase Coatings are more Suitable for Volatile Compounds**
- **DVB Template Resin is Designed to Reduce Molecular Weight Distribution**
- **Method Development for Groups of Analytes Requires the Primary Consideration Be Given to the Most Difficult Analyte**
- **Sometimes Coatings Must Be Custom-Made**

## 3.2. Gas Chromatography

Following {Schomburg, 1990} and {Schwedt, 1994} the basis principle of chromatography is the separation of compounds between a mobile and a stationary phase. Various combinations between mobile and stationary phase are possible, also the physical and chemical principles which are used to do the separation of interest. In the case of this thesis gas chromatography - where gas is the eponymous mobile phase - on a solid stationary phase is used.

After the chromatographic separation process many different detectors can be used. These detectors are dedicated to transform physical properties of the sample-gas mixture (***concentration dependent detectors***, output is given for example in $\frac{g}{mL}$) or of the sample alone (***mass selective detectors***, signal output is given for example in $\frac{g}{s}$) into a electric signal. Another differentiation possibility of detectors is the diversion via usage as ***universal*** or ***selective detector***. A selective detector is sensitive to specific elements (normally one or two “per detector”) and are only responding to the specified element. This means in case of a sulfur selective detector, that non sulfuric size and/or mass of the sulfur containing component is irrelevant to the detector - a big molecule with one sulfur atom is giving the same signal as a small molecule with one sulfur atom. An universal detector is responding to “mass” independently to what element the mass comes from.

In this thesis an universal detector (Flame Ionisation Detector (FID) described in chapter 3.2.1) and two selective detectors (Flame Photometric Detector (FPD) described in chapter 3.2.2 for sulfur or phosphor containing substances and Nitrogen Phosphorous Detector (NPD) described in chapter 3.2.3 for nitrogen or phosphor containing components) are used. For identification of the unknown samples a combination of gas chromatography and mass spectrometry as described in chapter 3.2.4 is used.

For characterization these parameters are used in the several following sections:

- **Linearity -** the signal should be proportional to the measured mass or concentration flow.
- **Detection Limit -** is defined as the ratio of the noise signal and the sensitivity, which is expressed by the smallest concentration or mass flow of an eluted solute which detectable above the noise.
- **Specifity -** Specific detectors are giving a comparatively high signal to the according element. The signal to other elements is cero or nearly cero.

All the values for linearity, detection limits and specifity in the following sections concerning FID, FPD and NPD are taken from {Schomburg, 1990}

### 3.2.1. Gas Chromatography-FID

The flame ionization detector (see figure 3.6) is a mass flow-dependent detector which responds to substances which are ion-producing when they are burnt in a flame consisting of $H_2$ and synthetic air. The FID is the most prominently and widely used universal detector in gas chromatography.

| | |
|---|---|
| *detection limit* | $2 * 10^{-12} \frac{g}{mL}$ |
| *linearity of the detector* | $> 10^7$ |

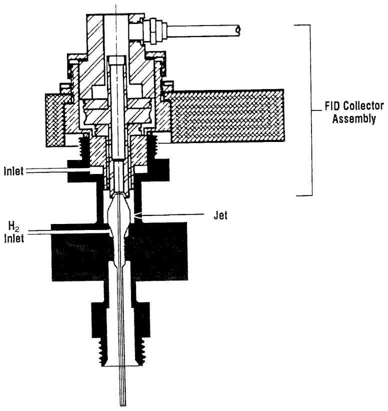


Figure 3.6.: Configuration of a Flame Ionization Detector (FID) liner shown from {Hewlett-Packard, 1993} p.7-3

### 3.2.2. Gas Chromatography-FPD

The flame photometric detector is a highly specific detector for sulfur or phosphorus containing molecules. Figure 3.7 shows a schematic setup of a FPD detector. In this thesis the FPD was used as sulfur selective detector. Sulfur selective measurement is very tricky because substances containing a SH-end are tending to dimerize very fast to a -S-S- containing molecule if they are heated up.

| | |
|---|---|
| *detection limit for S & P* | $2 * 10^{-11} \frac{g}{s}$ & $3 * 10^{-13} \frac{g}{s}$ |
| *specifity* $\frac{P}{C}$ & $\frac{S}{C}$ | $> 10^5$ & $10^3$ to $10^6$ |
| *linearity* | 105 for phosphorus-compounds |

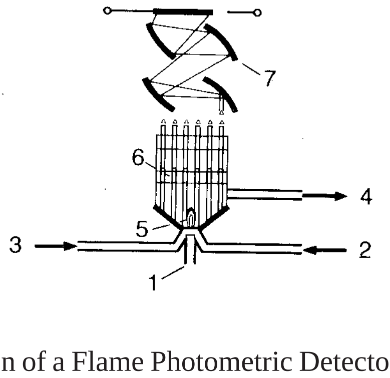


Figure 3.7.: Schematic configuration of a Flame Photometric Detector (FPD) liner; 1: column outlet; 2 & 3: synthetic air/$H_2$-inlet; 4: exhaust; 5: flame; 6: bandpass filter; 7: photomultiplier shown from {Schomburg, 1990} p.68

### 3.2.3. Gas Chromatography-NPD

The nitrogen-phosphorus detector has a similar setup to a flame ionization detector (see section 3.2.1). In the case of our laboratory, the NPD is attached to the same gas chromatograph as the FID. The electrically heated *active element*, which is pointed out in figure 3.8, is a aluminia cylinder coated with a rubidium salt. Nitrogen- and phosphorus-containing molecules are selectively ionized and detected.

| | |
|---|---|
| *detection limit* | $2 * 10^{-14} \frac{N}{s}$ |
| *specifity*$\frac{N}{C}$ & $\frac{N}{P}$ | $> 10^6$ & $> 10^2$ |

The linearity of the detector is similar to a FID-detector.

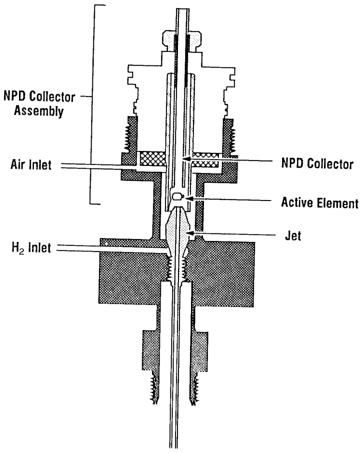


Figure 3.8.: Configuration of a Nitrogen-Phosphorus Detector (NPD) liner shown from {Hewlett-Packard, 1993} p.7-6

### 3.2.4. Gas Chromatography-MS

Mass Spectrometry is used in this project to identify the odour active substances in the samples. In figure 3.9 the principle configuration of a gas chromatograph/ mass spectrometer combination is shown. The sample is separated via gas chromatography; these fractions are transferred to the mass spectrometer. The mass spectrometer is a vacuum system.

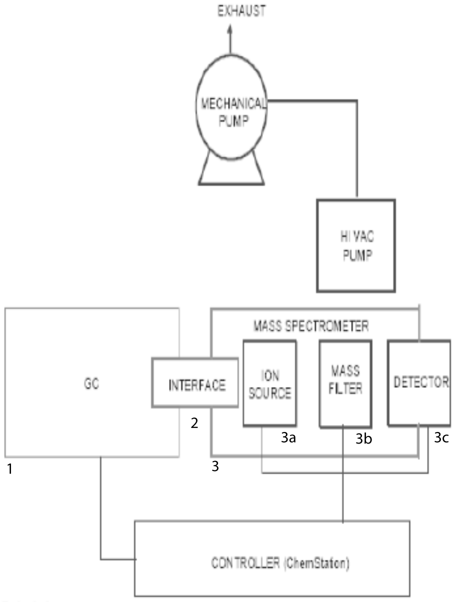


Figure 3.9.: Overview on a GC-MS: 1:gas chromatograph (GC); 2: interface to mass spectrometer (MS); 3:gas chromatograph consisting of 3a:ion source; 3b:mass filter and 3c:detector, taken from {Leitner, 2007}

In the ion source an electron beam of 70 eV collides with the molecules and generates about 0.01% ionized radicals. The generated radicals decompose to defined fragments as shown in figure 3.10.

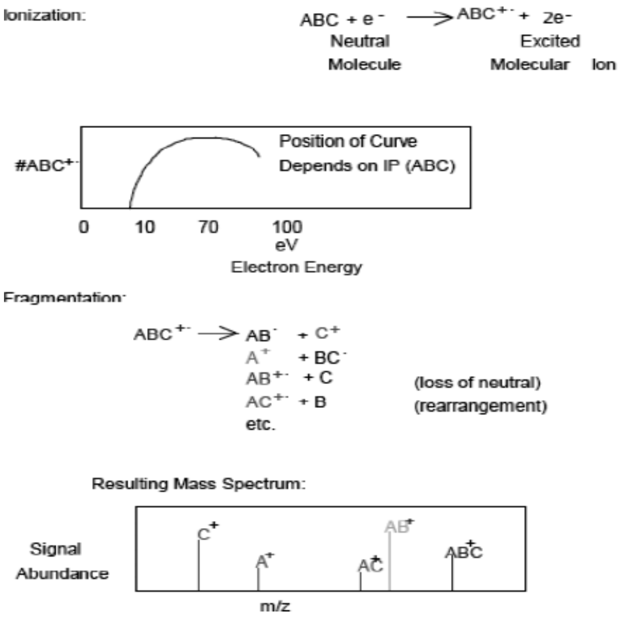


Figure 3.10.: Process of Ionisation taken from {Leitner, 2007}

These fragments are deflected through the mass filter (3.9 in 3b) and 3.11 which consists of quadrupol rods in our laboratory.

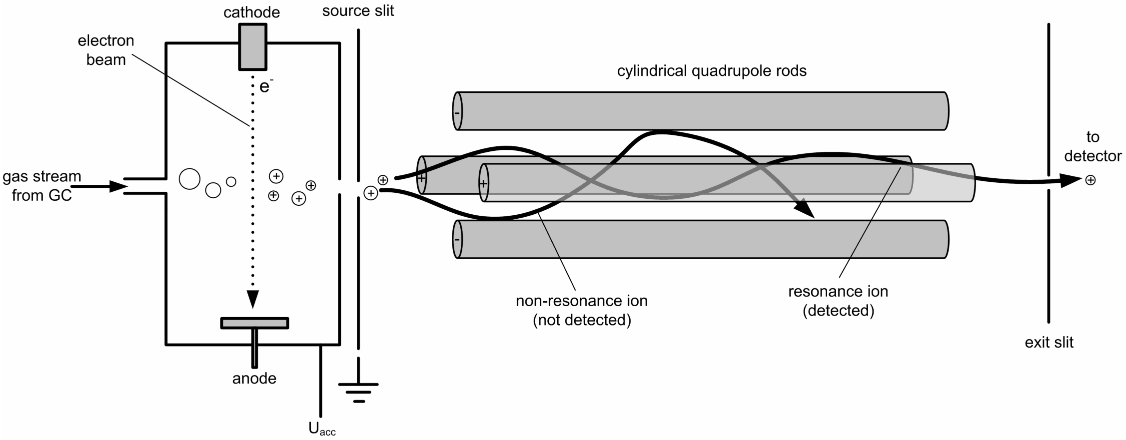


Figure 3.11.: Configuration of a quadrupol-MS with electron impact ionization (EI) as shown in {Wittmann, 2007}

The “impact pattern” - which is the so called “spectrum” - in the detector is characteristic for the substance and compared to data bases[1]. This comparison gives the result of the mass spectrometry analysis which is in fact a probability of correlation between the measurement of the reference substance in the database and the measured component of the sample.

---

[1] Wiley138, Wiley7Nist05

### 3.2.5. Comparison Of The Different Detectors

People who are not kept busy with trace analysis often consider mass spectrometry as an universal remedy for all identification problems. A significant odour impression is induced by a dramatically low amount of substances which is potentially leading to spectral interferences which may cause ambiguous or non significant results.

Finally a sample should be given to see the the different measurement types compared in figure 3.12. Obviously the sulfur and nitrogen levels in the ethylene sample from Borouge are not very high.

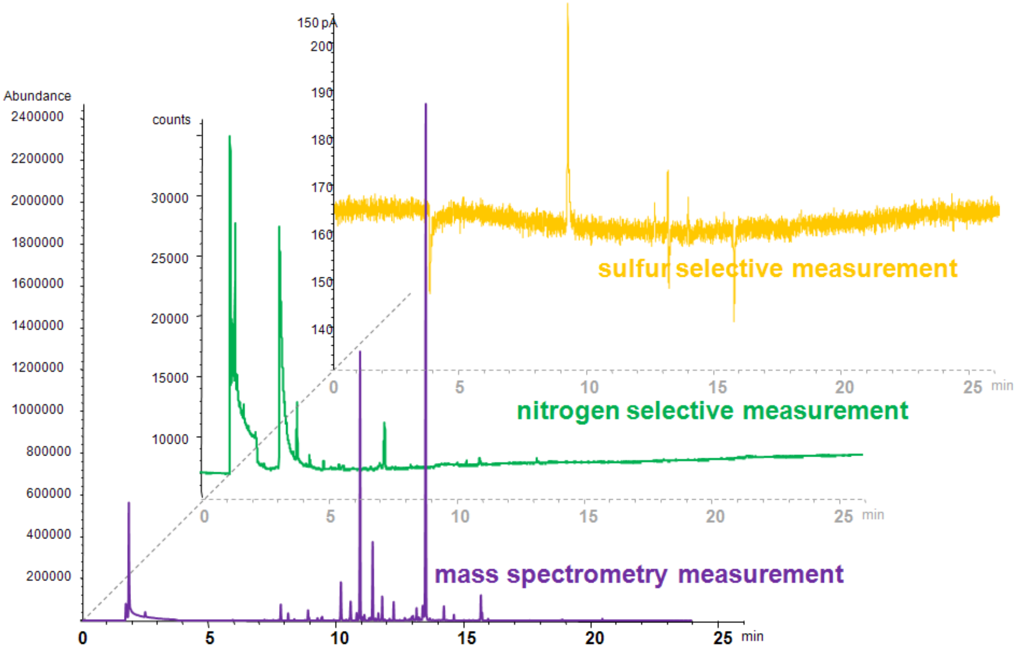


Figure 3.12.: Chromatograms of ethylene from Borouge obtained with a sulfur selective and a nitrogen selective detector and a mass spectrometer

The analysis of the given samples with the “mechanical” detectors does not give a satisfying impression of the odour causing substances. This shows the necessity to use a much more sensitive detector - *the HUMAN NOSE*

## 3.3. Gas Chromatography-Olfactometry

### 3.3.1. Odour Perception

In figure 3.13 the principle of human odour perception is shown. This very complex process is not just influencing our subjective well-being or our purchase decisions; it is also our most efficient warning system concerning the possible intake of toxic substances.

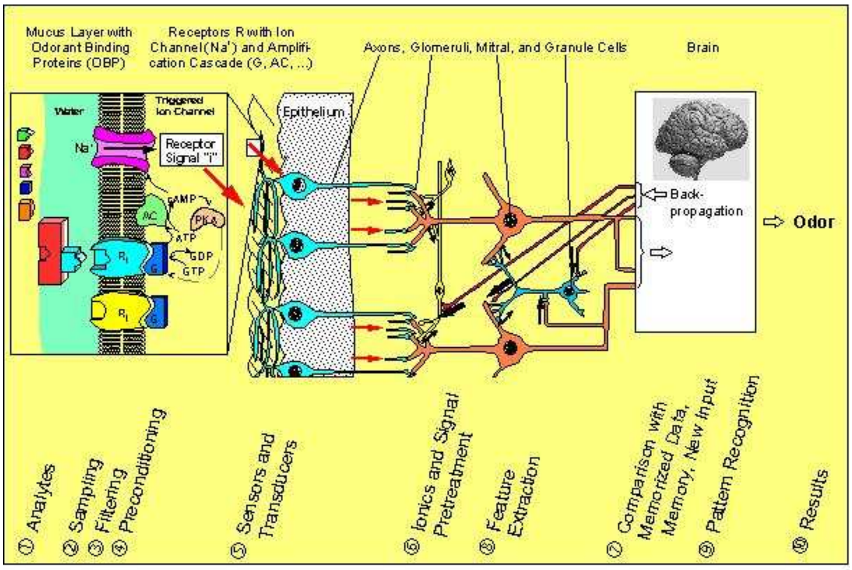


Figure 3.13.: Schematic of the human smelling process taken from {Tübingen, 2003}

Besides several “classic” GC detectors the gas chromatography olfactometry (GCO, GC-’sniffing’) was used. This method uses the human nose as a highly specific detector. The gas flow coming from the GC column is splitted into two parts. One stream leads to a common detector (in our laboratory a FID detector shown in 3.6 or a NPD detector shown in 3.8) and the other stream leads to the sniffing port shown in 3.15 which effectively means to a human nose. The concept of gas chromatography olfactometry makes the correlation between odour active substance and “chromatography peak” possible. The configuration used in our laboratory is shown in the figures 3.14 and 3.15.

### 3.3.2. Detection Frequency

Since odour and malodour are very subjective phenomenons a concept of objectification the odour measurement is necessary. In this concept different operators are sniffing the same sample. Simultaneously the signal of “smelling something” by pressing a button and the verbal odour description are collected by a microphone. The concept of detection frequency has many advantages.

- “Average” odour impression
- Not very time consuming
- Not very exhausting
- Reduction of anosmia[2] problems

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[2] partial or total loss of olfaction

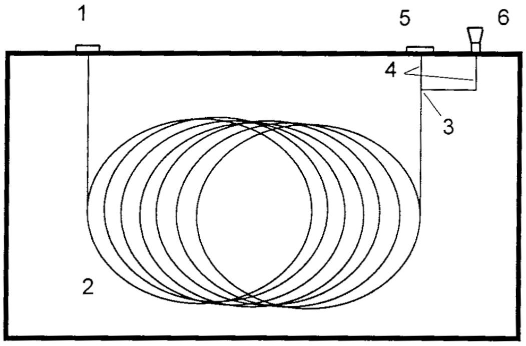
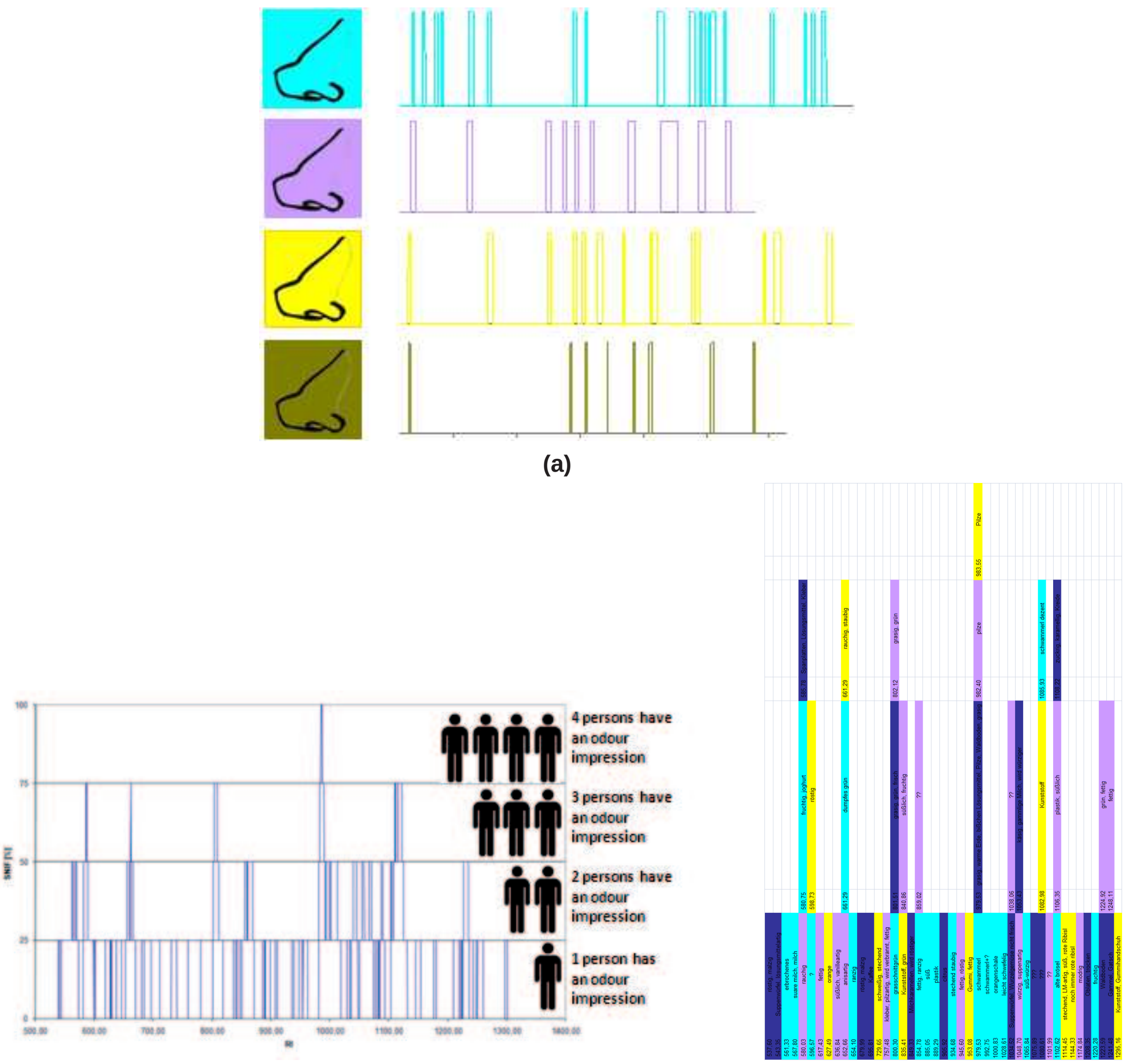


Figure 3.14.: Schematic of a gas chromatograph with FID or NPD and sniffing port with: 1: injector; 2: capillary column; 3: variable splitter; 4: interface line; 5: FID or NPD detector; 6: sniffing port adapted from {Siegmund, 1997} p.20

Figure 3.15.: Schematic of a sniffing port with: 1:sniffing cone (“nose”); 2:column leading to GC adapted from {GERSTEL, 2009}

Figure 3.16a shows the single signals which are collected while the different operators (in this case 4 persons) are sniffing each sample and pressing a button when they have an odour impression. In figure 3.16b the overlay of this signals shows, how this concept gives a very important information. In the lowest quarter of the diagrams are all the signals located which are sniffed by one person, the second quarter contains the signals which are sniffed by two persons, the third quarter shows the signals which lead to impression with three people, the fourth and last quarter shows the signals which impressed all the sniffers. This kind of a ranking displays very clearly the signals with the highest impact (signal in quarter three and four) on the overall odour impression. In this project all the substances with so called “high impact” (quarter three and four) are worked on.

Figure 3.16 (b) and (c) also shows the correlation between “the signal” and the verbal description of the odour impression. This separation of the information “there is something”(“signal”) and “it smells like...”(“verbal description”) prevents the loss of data which may be caused difficulty to describe the odour impression within some seconds.



(a)

(b)

(c)

Figure 3.16.: Illustration of detection frequency: (a) is showing the single signals given by the different operators, (b) is showing the resulting detection frequency diagram, (c) is showing the diagram generated by the verbal descriptions of the different operators represented by different colors

### 3.3.3. Retention Indices (RI)

Mass spectra of aroma active substances are often not specific enough because the concentration of the needed substance is too low. This certainty leads to problems with identification via databases (very low probabilities, equivalent propositions) or an apparently non-existence of the substance of interest. This problem gave rise to the development of the so called *Retention Indices* following {H. Van den Dool, 1963} and {P. Farkas and Kovac, 1994}. This system of *linear retention indices* describes the retentional behavior of substances in correlation to n-alkanes ({see Leitner, 2003} p.42). The number of C atoms in each alkane is multiplied with 100 which leads to a retention index for ethane of 200 (2 C atoms x 100) or 700 for heptane. The retentional behavior of the substances of interest is now set into correlation to the alkanes and a retention index is allocated to the substance.

$$RI = 100 \times \frac{T_x - T_z}{T_{z+1} - T_z} + 100z \tag{3.21}$$

$$\begin{aligned}
RI &= \textit{retention index of component x} \\
T_x &= \textit{retention time of component x} \\
T_z &= \textit{retention time of the n-alkane eluting BEFORE component x} \\
T_{z+1} &= \textit{retention time of the n-alkane eluting AFTER component x} \\
z &= \textit{number of C atoms of the n-alkane eluting BEFORE component x}
\end{aligned}$$

The initially used isothermal retention indices are nowadays substituted by temperature programmed retention indices. Temperature programming allows optimization of analysis time which is necessary while analyzing samples consisting of complex substances mixtures. Retention indices are evidently dependent on the column polarity. Keeping that in mind is important while using databases and comparing results.

To make sure, that the results of the RI calculation done with the equation 3.21 are correctly comparable to the used databases, the systems were constantly checked following {P. Farkas and Kovac, 1994}. The calculation results were compared to several databases.[3]

---

[3] www.flavornet.org, www.kovats.org, SKAF Flavour Database

# Chapter 4

# Instrumental & Evaluation Setup

> *"There are no such things as applied sciences, only applications of science."*
>
> [Louis Pasteur, French biologist & bacteriologist, (1822 - 1895)]

## 4.1. Solid Phase Microextraction - SPME

To find the optimal setup for solid phase microextraction, there was several testing to be done at the very beginning of the work. Since the fiber thermostatting and exposuring is a very time consuming process, the best compromise between optimal enrichment of analytes on the fiber coating and acceptable expenditure of time was to be found.

The thermostatting and exposuring of the fiber was performed by *CTC Analysis PAL systems* which is the standard autosampling system in our laboratory.

### 4.1.1. Coating Test

Table 4.1 shows several SPME fiber coatings which were tested. The polyethylene and the carboxene™/ divinyl benzene coatings showed good results while the testing. Due to the importance of endurance and availability (and also with respect to the knowledge provided by {Pawliszyn, 1997} and outlined in 3.1.2) the divinyl benzene/ carboxene™/ poly(dimethyl)siloxane (DVB/CAR/PDMS) fiber coating was chosen to carry out some testings on temperature and time ratios to find the optimal setup.

All the fibers were supplied by *SUPELCO*.

Table 4.1.: Overview on tested SPME coatings

| **colour** | **material** |
|---|---|
| orange | carboxene™/ divinyl benzene |
| gray/plain | divinyl benzene / carboxene™/ poly(dimethyl)siloxane |
| purple | polyethylene glycol |
| light blue | carboxene™/ poly(dimethyl)siloxane |
| dark red | polyurethane acrylate |
| white | polyacrylate |

The finally chosen fiber was

*SUPELCO*
*SPME Fiber Assembly*
*2cm - 50/30um DVB/Carboxen™/PDMS StableFlex™*
*For Manual or Auto Holder Notched Gray*

### 4.1.2. Time & Temperature Test

Additionally to the testing of the coating some time and temperature testing of the fiber thermostatting and its exposure was carried out.

Table 4.2.: Tested times & temperatures

| **time [min]** | **temperature [$^\circ C$]** |
|---|---|
| 5 | 10 |
| 10 | 20 |
| 15 | 30 |
| 20 | 40 |

Keeping the thermostatting time constant at 5 minutes at 20°C, the fiber exposure time was variated from 5 to 20 minutes at 20°C. The resulting chromatograms are shown in figure 4.1. Since there did not occur any surprising changes onto the different exposure times the 10 minute alternative was chosen to stay on an time and result efficient track. In a second step the thermostatting and exposure temperature was variated from 10°C to 40°C. The resulting chromatograms are shown in figure 4.2. Considering the huge influence of the time spent on fiber preparation on time consumption of the whole analysis the chosen SPME thermostatting and exposuring setup was:

*thermostatting for 5 minutes at 40°C*
*and*
*exposuring for 10 minutes at 40°C.*

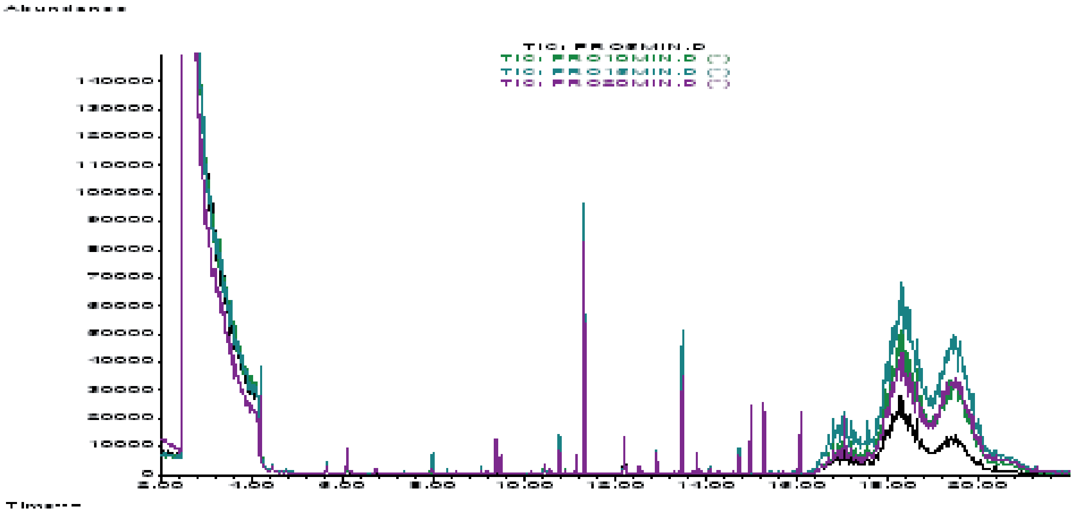


Figure 4.1.: Overlay of chromatograms, showing the results with steady temperature (20°C) and variable time: black:5 minutes, green:10 minutes, blue:15 minutes, violet:20 minutes

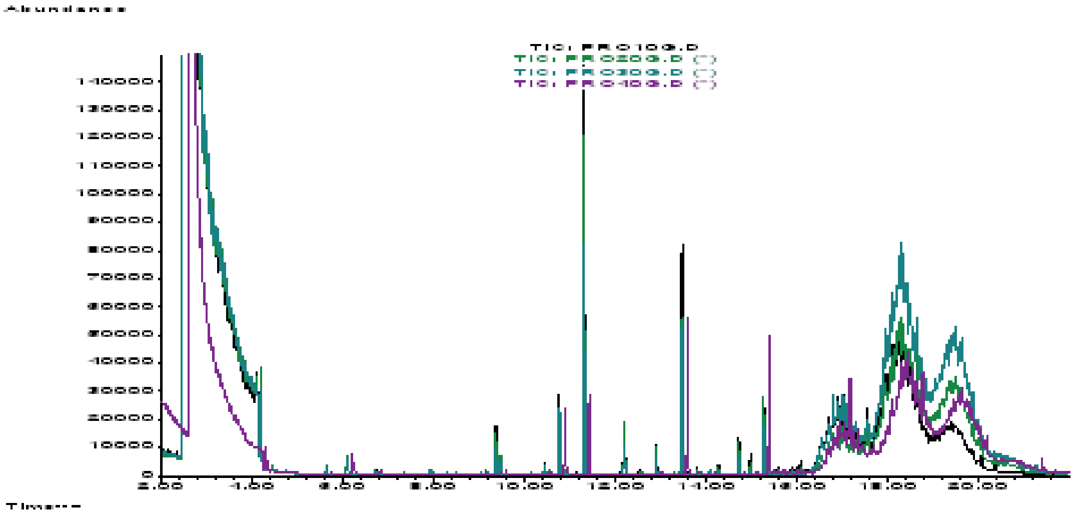


Figure 4.2.: Overlay of chromatograms, showing the results with steady time (10 minutes) and variable temperature: black:10°C, green:20°C, blue:30°C, violet:40°C

## 4.2. Gas Chromatography - GC

### 4.2.1. Equipment

For gas chromatographic analysis the machines shown in table 4.3 were used. With exception of the *HewlettPackard 5890 Series II*, which was run with manual injection, all the gas chromatographs were run with the autosampling system *CTC Analysis PAL systems*.

Table 4.3.: Overview on used Gas Chromatographs

| **Apparatus** | | **Column** | | | | |
|---|---|---|---|---|---|---|
| Gas chromatograph | Detectors | Type | Dimensions | | | Supplier |
| | | | Length [m] | I.D. [mm] | Film [$\mu$m] | |
| HewlettPackard 5890 Series II | FID, NPD, ODP | HP 5 | 30 | 0.32 | 0.25 | J&W Scientific |
| HewlettPackard 5890 Series II Plus | HP 5972 Series Mass Selective Detector | ZB-5MS | 30 | 0.25 | 0.25 | Zebron/Phenomenex |
| GCD Series Gas Chromatograph | Electron Ionization Detector (Mass Selective Detector) | HP 5 | 30 | 0.25 | 1.00 | J&W Scientific |
| Agilent 6890A (G1530A) | FPD, FID | VF-5MS | 30 | 0.25 | 1.00 | VarianFactorFour |

*FID: Flame Ionisation Detector; NPD: Nitrogen-Phosphorus-Detector; ODP: Olfaction-Detection Port; FPD: Flame Photometric Detector*

### 4.2.2. Methods

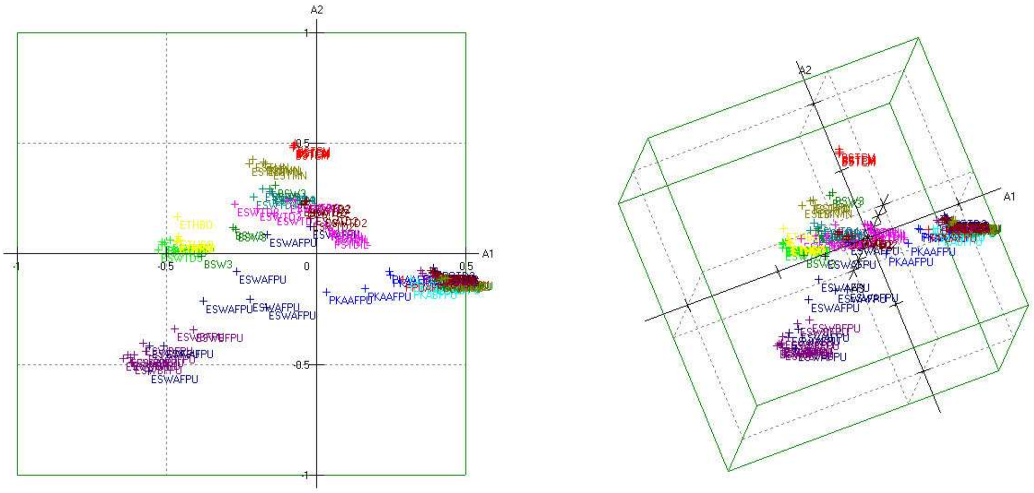
In table 4.4 the used methods of analysis are shown. Both tables 4.3 and 4.4 are pointing out the idea of using the same apparative and methodic setup for the different analyses. Just the olfactometric analysis steps out the line - sniffing analysis makes this necessary. All the measurements were done by SPME injection (desorption temperature of the injector 270 °C for 10 minutes) except the quantification experiments outlined in $MS_{liquid}$ and chapter 7 which were done by liquid injection.

Table 4.4.: GC analysis methods with MS, FPD, FID and ODP detectors

| | **initial temperature** [°C] | **hold time** [min] | **heating rate** $\frac{[^\circ C]}{[min]}$ | **final temperature** [°C] | **hold time** [min] | |
|---|---|---|---|---|---|---|
| MS<sub></sub>$_{\text{SPME}}$ | -30 | 1 | | | | *Pressure=48 kPa* |
| FPD | | | 15 | | | *Total Flow= 34,2* $\frac{[mL]}{[min]}$ |
| FID | | | | 280 | 5 | *Gas Type= Helium* |
| ODP | 35 | 1 | | | | *Pressure*$_{primary}$*=95kPa* |
| | | | 10 | | | *Temperature*$_{detector}$*=280 °C* |
| | | | | 280 | 1 | *Gas Type = Helium* |
| MS$_{\text{liquid}}$ | 20 | 1 | | | | |
| | | | 5 | | | *Pressure*$_{primary}$*=81 kPa* |
| | | | | 40 | 0 | *Pressure*$_{constant}$*=26 kPa* |
| | | | 25 | | | *Gas Type = Helium* |
| | | | | 270 | 0 | |

*FID: Flame Ionisation Detector; NPD: Nitrogen-Phosphorus-Detector; ODP: Olfaction-Detection Port; FPD: Flame Photometric Detector; MS: Mass Selective Detector*

## 4.3. Multivariate Data Analysis



**(a)** **(b)**

Figure 4.3.: Illustration of cluster analysis: (a) 2D cluster and (b) 3D cluster of all measured samples in this project. Cluster analysis is used here as a ‘easy to understand’-picture making tool to make similarities and differences within the samples more obvious.

Thinking of analytic chemistry often results in the picture of calculating results via calibration functions. After a calibration and validation of the used analysis system, unknown samples are submitted to this process. The univariate ansatz follows the scheme

*x-data* + *y-data* → *calibration function b*
*x-data* + *calibration function b* → *y-data*

This ansatz does not give any information if the used calibration structure fits to the given questions. Following {Leitner, 2003} p.78-79 and {Conzen, 2001} results calculated with this approach can seem to give a correlation between while disturbing influences or signal noises may stay undetected or are even undetectable. Statistical variations have to be minimized by manifold measurements and building the mean value. Multivariate data analysis[1] is the proper instrument to “use” the manifold quantities of data resulting - in this case - of gas chromatography (examples for those variables are time, mass, intensity). One decisive aspect of this method is the reduction of dimensions. In cluster analysis the objects are aggregated stepwise according to the similarity of their features ({see Otto, 1999}). *A cluster describes a group of objects, that are more similar to each other than to objects outside the group.* For generating clusters like shown in figure 4.3 the software package MASstat™provided by {Analyt-MTC, 2002} was used for analyzing the various datasets with the following statistic choices:

*norm / all peaks* - *geom. display* - *scope: 10*
*Masses selection: automatic selection*
*disabled masses: 28 32 73 77 131 155 207 268 281*
*enabled masses: 29 44 69 83 91 93 106*

---

[1] from *http://www.merriam-webster.com/dictionary/Multivariate* having or involving a number of independent mathematical or statistical variables (last visit: 25/05/2009)

# Chapter 5

# Survey of Samples

> *“Every day you may make progress. Every step may be fruitful. Yet there will stretch out before you an ever-lengthening, ever-ascending, ever-improving path. You know you will never get to the end of the journey. But this, so far from discouraging, only adds to the joy and glory of the climb.”*
>
> [Sir Winston Churchill, British politician, (1874 - 1965)]

To follow the tasks given in chapter 1, with the following samples was dealt within the project. The investigated gases were collected at Borealis in Linz. *Wolfgang Stockreiter* from Borealis filled them into headspace vials and sent them to Graz. In Graz over 400 measurements were done on this project. Figure 5.1 shows the way of the samples through the whole project; the samples are outlined in table 5.1.

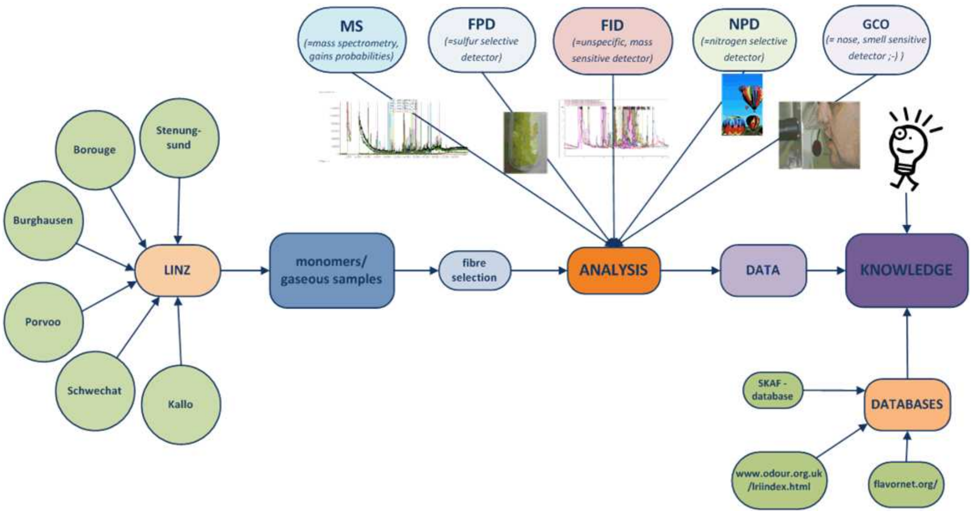


Figure 5.1.: Schematic of the samples way through the whole preparation and examination process

Table 5.1.: Samples used in the master thesis

| **Gas** | **Origin** | *BP* | *AP* | **monomers** | | **time dependency** | | **purification** | | | **comonomers/ diluents** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | PE | PP | SW | PO | SW | PO | KA | |
| Ethylene | Borouge | x | | x | | | | | | | |
| | Stenungsund | x | | x | | | | | | | |
| | Schwechat | x | | x | | April | | x | | | |
| | Schwechat | x | | | | May | | | | | |
| | Schwechat | x | | | | June | | | | | |
| | Schwechat | x | | | | July | | | | | |
| | Schwechat | x | | | | August | | | | | |
| | Schwechat | | x | | | | | x | | | |
| Propylene | Burghausen | x | | | x | | | | | | |
| | Porvoo | x | | | x | | April | | x | | |
| | Porvoo | x | | | | | May | | | | |
| | Porvoo | x | | | | | June | | | | |
| | Porvoo | x | | | | | July | | | | |
| | Porvoo | x | | | | | August | | | | |
| | Porvoo | | x | | | | | | x | | |
| | Kallo | x | | | x | | | | | x | |
| | Kallo | | x | | | | | | | x | |
| 1-Butene | Stenungsund | x | | | | | | | | | x |
| 1-Hexene | Stenungsund | x | | | | | | | | | x |
| Propane | Stenungsund | x | | | | | | | | | x |

*BP= ‘before purification’, AP= ‘after purification’; SW= Schwechat; PO= Porvoo; KA= Kallo*

# Chapter 6

# Monomer Purity Investigation Tasks

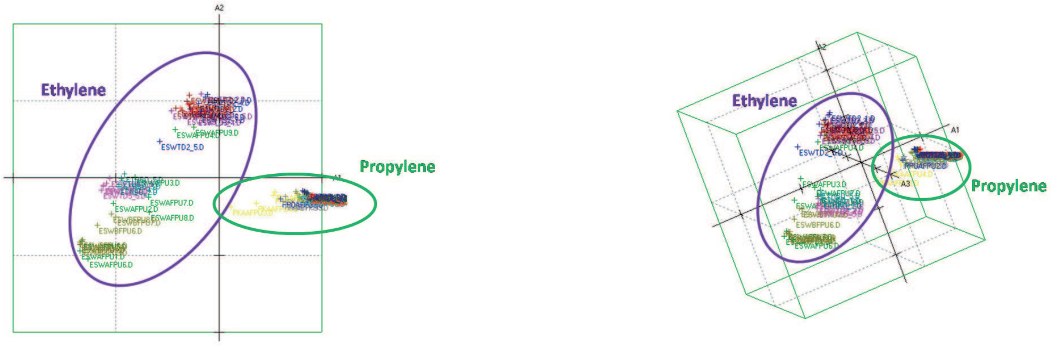
> *"The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them."*
>
> [Sir William Bragg, British physicist, (1862 - 1942)]

To get a deeper look into the problem of odour active monomer impurities, the project was grouped into several tasks. These tasks are intended to overview the problem of (mal-)odorous substances in monomers on the one hand and to give a starting point for deeper investigation on the other hand.

The given (sub-)tasks were:

- **Monomers**
  - PE monomers (Ethylene from Borouge, Stenungsund and Schwechat)
  - PP monomers (Propylene from Burghausen, Porvoo and Kallo)
- **Time Dependency**
  - Ethylene from Schwechat (from April, May, June, July and August)
  - Propylene from Porvoo (from April, May, June, July and August)
- **Purification**
  - Ethylene from Schwechat (Samples before and after purification)
  - Propylene from Porvoo (Samples before and after purification)
  - Propylene from Kallo (Samples before and after purification)
- **Comonomers and Diluents**
  - 1-Butene, 1-Hexene and Propane from Stenungsund

One of the "Borealis-wide" usual assumptions was the idea of having similar monomers all over the company. Figure 6.1 shows that especially the ethylene samples are varying simply through their MS-chromatograms throughout a wide range. Propylene samples give a more homogeneous picture in this context. Deeper investigations on monomer quality were "just" done when the quality began to influence the polymerization process in a bad way. Up to now many different approaches and ideas were invested into the idea of less odorous products. Helene Hopfers thesis is dealing with negative effects on odour and taste from chemicals and polymer processing steps like additives, degradation, compounding and many more. The access to get a deeper understanding of possible sources by investigating the monomer purity in terms of odour and taste is new.



**(a)** **(b)**

Figure 6.1.: Illustration via (a) 2D cluster and (b) 3D cluster of all ethylene and propylene samples. Violet lines are framing ethylene samples, green lines are framing propylene samples.

For the outline of the given tasks different methods of analysis and reporting the results are used. For all the tasks respectively subtasks MS chromatograms, the 2D and 3D clusters and the detection frequency patterns are shown. In the total volatile analysis the overall area of volatiles (the integration parameters are set to exclude the monomer area respectively peak itself) is compared with the number of peaks. The overall area of volatiles[1] is a good indicator for the overall purity of the monomer, while the number of peaks gives information about the number of different substances in the monomer sample. Sometimes occurring not (fully) resolved peak agglomerations are *not* counted as separate peaks. All the chromatograms shown in this chapter are accentuated with two marker lines for n-alkanes with 8 respectively 16 C atoms. Prominent substances which are not considerably contributing to the monomer odour impression are highlighted in the chromatograms. In chapter A.2.1 for every sample the combination of information (chromatograms, detection frequency pattern and found substances) is given.

---

[1] excluding the monomer itself

## 6.1. Total Volatile Impurities

The cluster shown before in figure 6.1 and its immanent picture of very divergent types of monomers gave the impetus to look into the monomers from a more macroscopic point of view. The analysis of volatile impurities in the given monomer samples is outlined to give a first impression on the handled substances and to accentuate the huge varieties of monomers which occurred in this project. As outlined in chapter 1 the several tasks were given to investigate *IF* there are any information patterns or trends in composition on several given contexts.

The term “sum of area” describes the area which is found under the peaks which is the total amount of volatiles (without the monomer itself) in the sample. The term “number of peaks” describes how many peaks are in the chromatogram which is the number of substances in the sample. Table 6.1 shows how to read this information patterns, which are maybe giving a new sight of looking onto the samples.

Table 6.1.: How to read the volatile information patterns

| | **few peaks** | **many peaks** |
|---|---|---|
| **low area** | some substances/ low amount of each | many substances/ low amount of each |
| **high area** | some substances/ high amount of each | many substances/ high amount of each |

However, this should not mislead to a speculation about odour active substances. Volatile substances are *NOT* automatically odour active, in fact that odour active substances in this amount would have a narcotic effect. One of their most characteristic attributes in a technical-analytical way of thinking is their low and mechanical hard to find amount.

Gas chromatography is detecting *ALL* substances which are volatile - so is air - or can become volatile at increasing temperature.

## 6.2. Monomers

This task was intended to give an overview on ethylene and propylene used in different Borealis plants. Samples are taken at a single point of time; due to this fact, that monomer quality can change dramatically during very small time units, the following statements do not lead to a representative picture. Samples not marked as "after purification" were taken before Borealis purification.

### 6.2.1. PE monomers

The samples used in this subtask are:

- Ethylene Borouge
- Ethylene Stenungsund
- Ethylene Schwechat

**Volatile Impurities in PE Monomers**

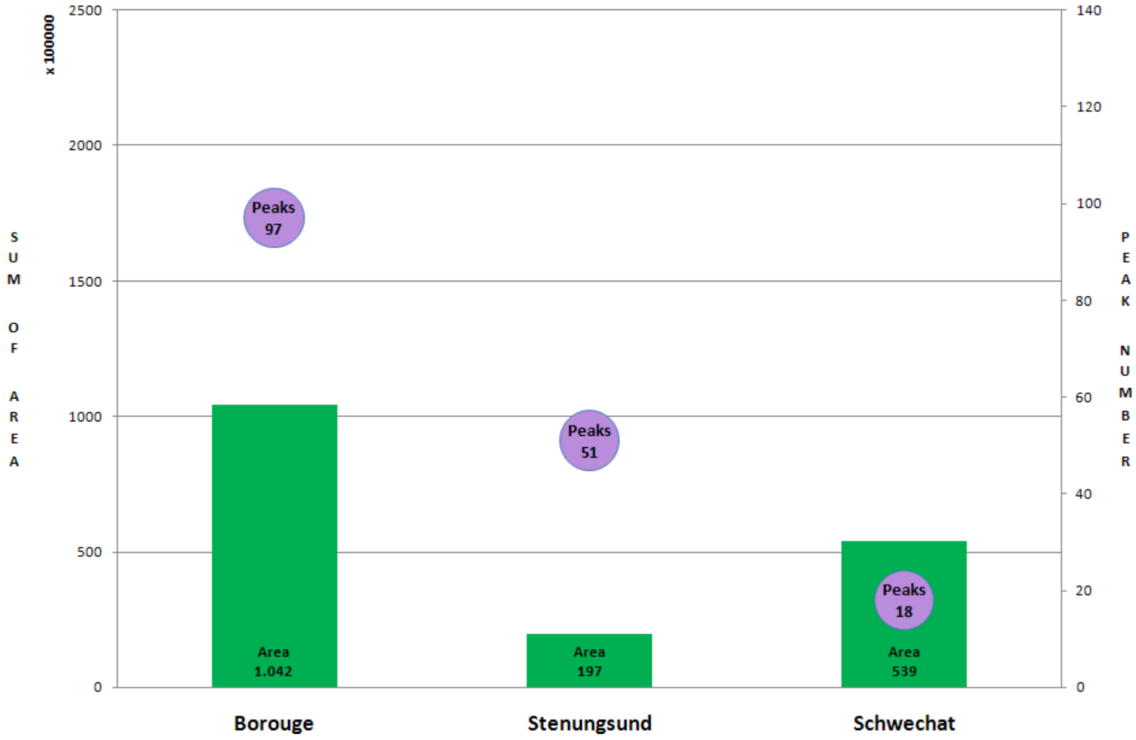


Figure 6.2.: Diagram of total volatiles in a vertical-bar plot for the sum of area and a scatter plot for the sum of peaks of PE monomers

The diagram given in figure 6.2 show, that there is no correlation between the overall sum of area and the number of peaks for the case of ethylene monomers. The Borouge sample is unchallenged the one with the biggest area sum and the most peaks. But the samples from Stenungsund and Schwechat are taking turn within the $2^{nd}$ and $3^{rd}$ place. Schwechat has the 3-fold of sum area, Stenungsund the 3-fold of peaks.

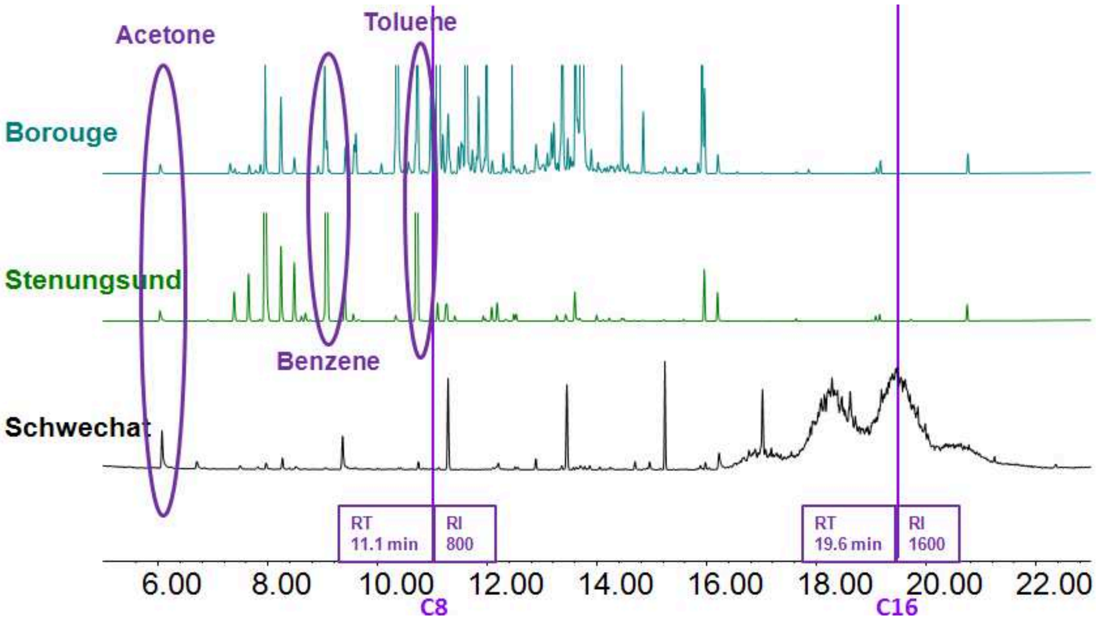
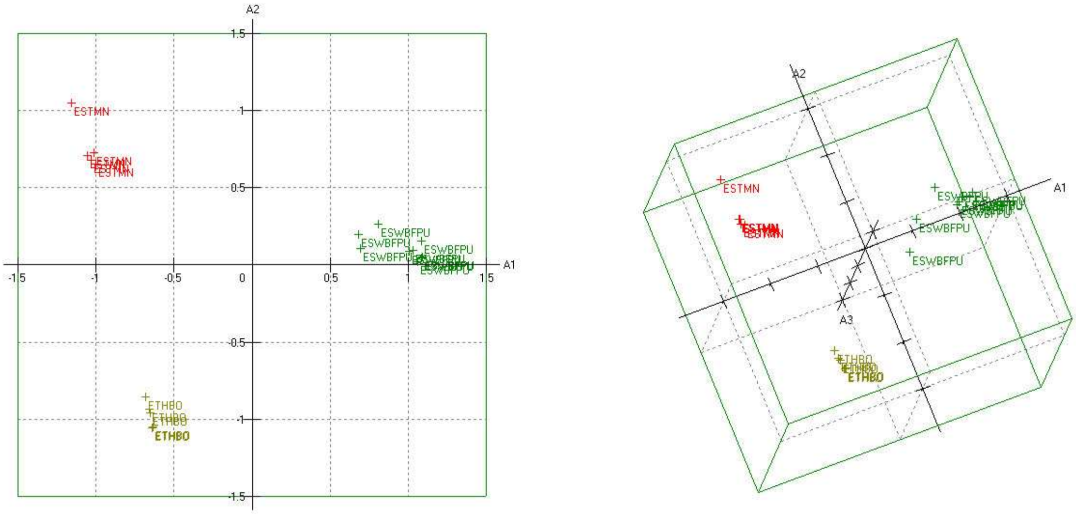


Figure 6.3.: Chromatograms of PE monomers

The chromatograms in figure 6.3 show the big differences between the different plants. In Schwechat occurs a agglomeration of unresolved peaks (so called “Ölberg”[2]) in the long-chain molecules region of the chromatogram. This “Ölberg” also contributes to the volatile results in figure 6.2, the big area ( 75%) value for this samples mainly derives from it. The samples from Stenungsund and Borouge are much cleaner in this areas while the samples from Schwechat have a much lower amount of peaks in the earlier eluting part of the chromatogram.



(a)

(b)

Figure 6.4.: 2D (a) and 3D (b) clusters of PE monomers. red: Stenungsund; yellow: Borouge; green: Schwechat

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[2] This german term comes from the fact, that the hill-like region (“-berg”) of the chromatograms belongs to long-chain molecules (“Öl”)

The clusters shown in figure 6.4 clearly demonstrate the difference between the compared plants but also the good reproducibility of the measurements. Ethylene samples from Schwechat are measured more often because of filling volume problems in the beginning of the project.

### Odour Impression from PE Monomers

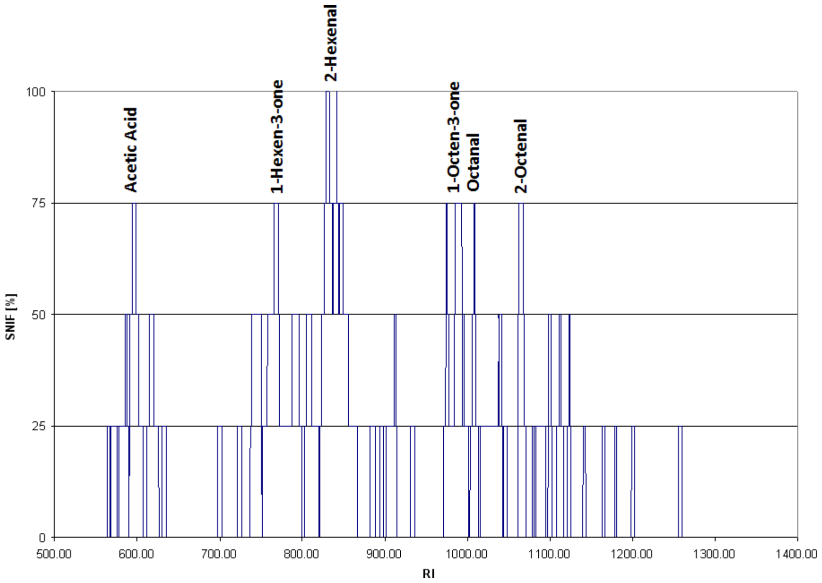


Figure 6.5.: Detection frequency of PE monomers from Borouge

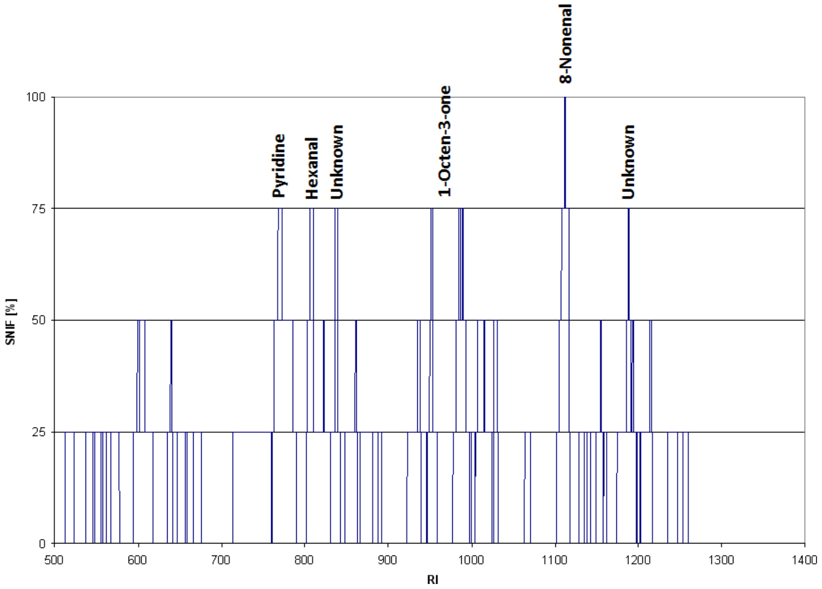


Figure 6.6.: Detection frequency of PE monomers from Stenungsund

Also the odour impressions (shown in figure 6.5, 6.6 and 6.7) from the plants differ within a wide range. The peak number in the chromatograms do not correlate with the overall odour impression. Comparing the detection frequency patterns shows that some of the occurring substances with high impact are the same, but that there are also differences.

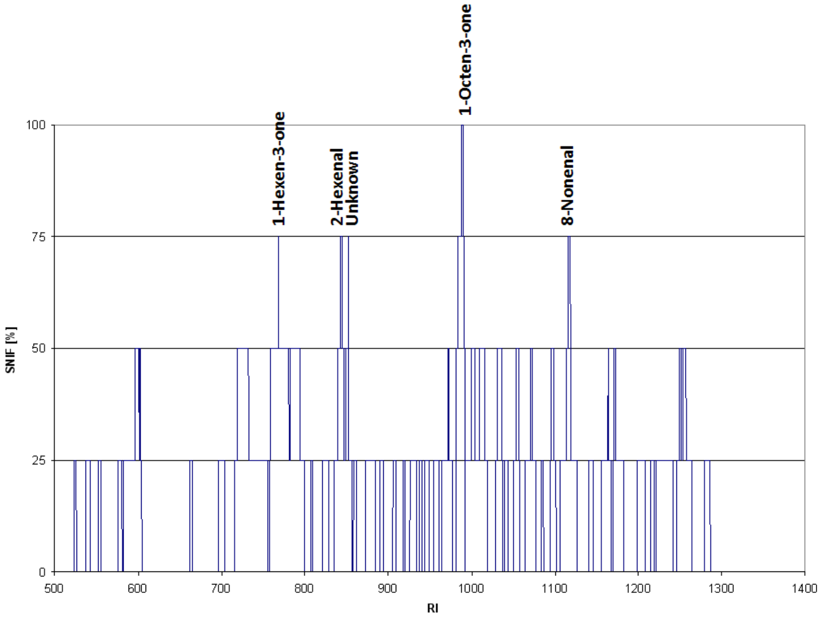


Figure 6.7.: Detection frequency of PE monomers from Schwechat

### 6.2.2. PP monomers

The samples used in this subtask are:

- Propylene Burghausen
- Propylene Porvoo
- Propylene Kallo

#### Volatile Impurities in PP Monomers

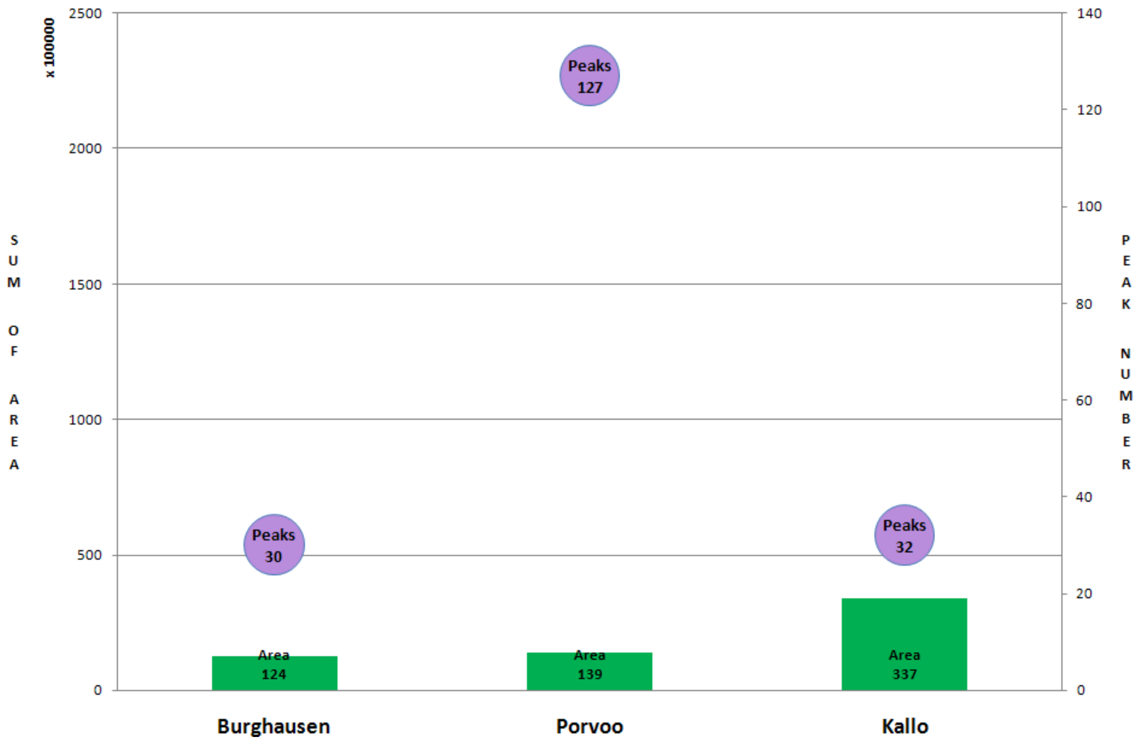


Figure 6.8.: Diagram of total volatiles in a vertical-bar plot for the sum of area and a scatter plot for the sum of peaks of PP monomers

In the diagram shown in figure 6.8 appears an interesting picture concerning the correlation between sum of area and peak number. The given samples are very much the same in the point of sum of area while the number of peaks in the Porvoo sample is up to 4 times higher than the samples from Burghausen and Kallo.

The chromatograms in figure 6.9 point out the reason for this observation, in the Porvoo sample there are many small peaks occurring from methyl- and ethyl branched derivates of the occurring main substances. In the chromatograms shown in figure 6.9 there also occurs a small “Ölberg” in Burghausen and Kallo. Generally speaking, the chromatograms of the propylene samples are more similar to each other than those of the ethylene samples.

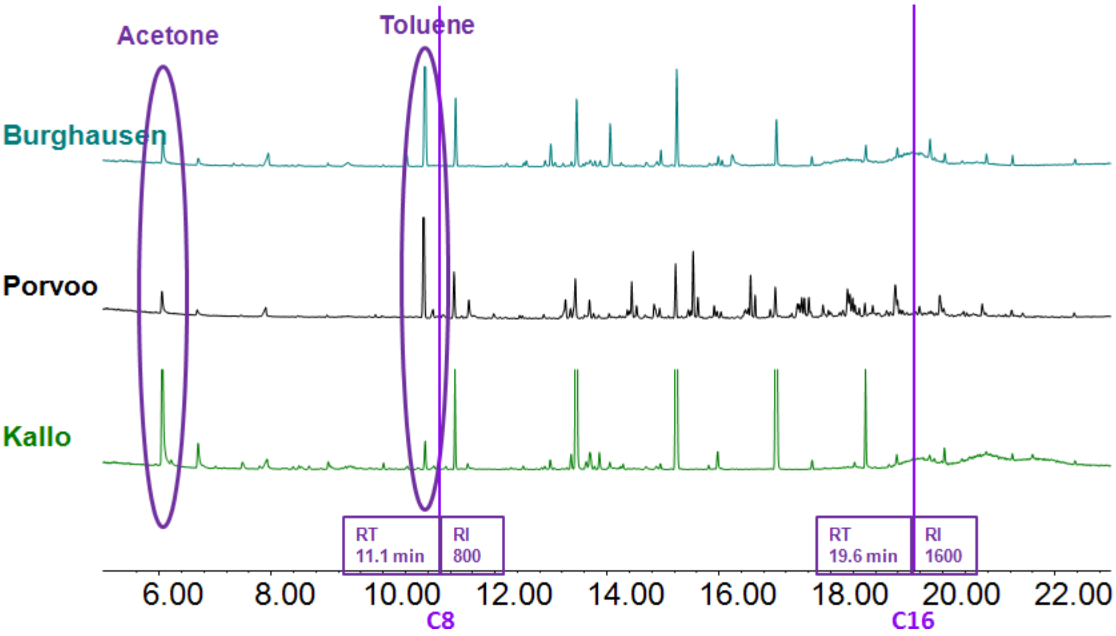
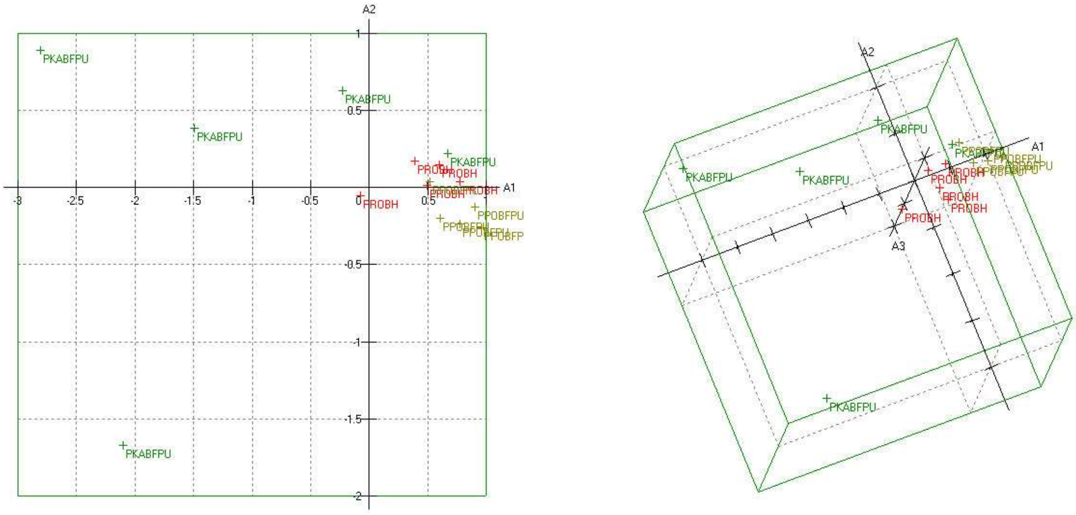


Figure 6.9.: Chromatograms of PP monomers



(a)

(b)

Figure 6.10.: 2D (a) and 3D (b) clusters of PP monomers. green: Kallo; red: Burghausen; yellow: Porvoo

The clusters in figure 6.10 show very clearly that the propylene samples have much more similarities than the ethylene samples. Besides some outliers the single measurements are lying close to each other.

### Odour Impression from PP Monomers

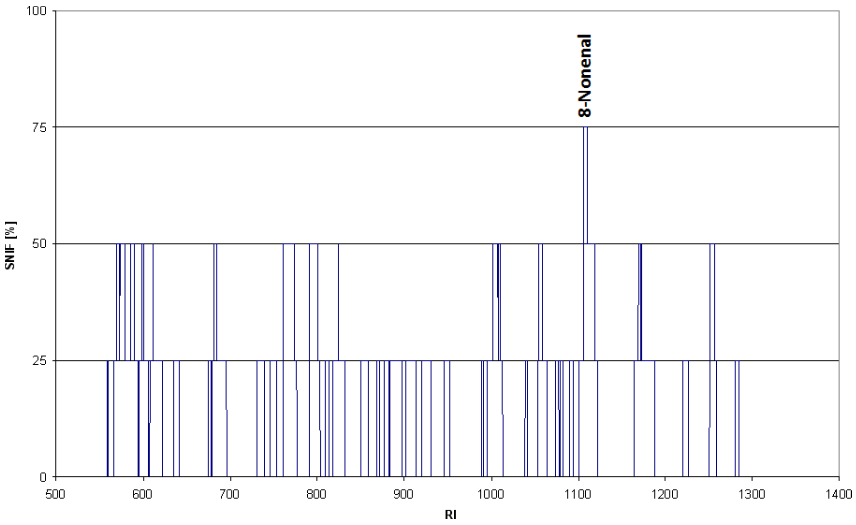


Figure 6.11.: Detection frequency of PP monomers from Burghausen

Figures 6.11, 6.12 and 6.13 give an idea on the odour impressions the samples made. The sample from Burghausen show only one substance with a high impact on the entire odour impression while the samples from Porvoo have eight substances mainly contributing to the overall odour impression. The Kallo sample is giving a rather unimpressive chromatogram (see figure 6.9), but the detection frequency pattern (see figure 6.13) gives a different picture. This points out the fact, that the solely use of MS-chromatograms is does not give a good impression of the odour.

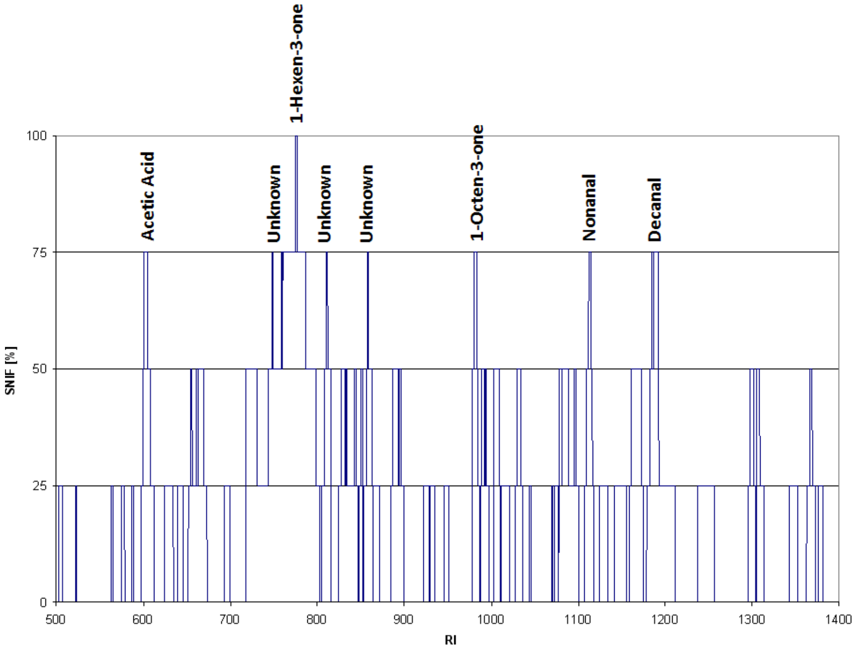


Figure 6.12.: Detection frequency of PP monomers from Porvoo

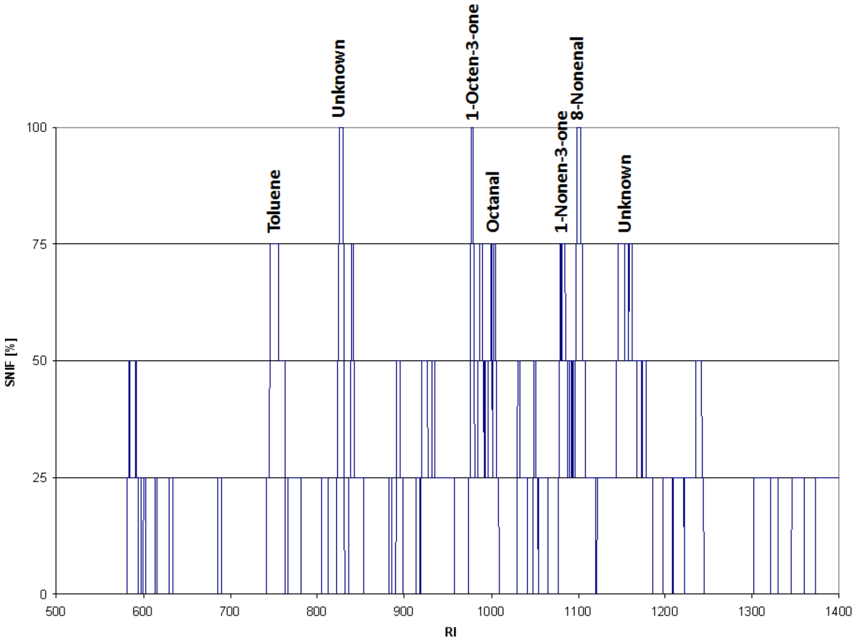


Figure 6.13.: Detection frequency of PP monomers from Kallo

## 6.3. Time Dependency

The Time Dependency samples should deliver insight into the change of monomer composition over the time. Samples were taken before Borealis purification once every month from April 2008 to August 2008.

The samples used in this subtask are:

- Ethylene Schwechat
- Propylene Porvoo

### 6.3.1. Time Dependency - Ethylene Schwechat

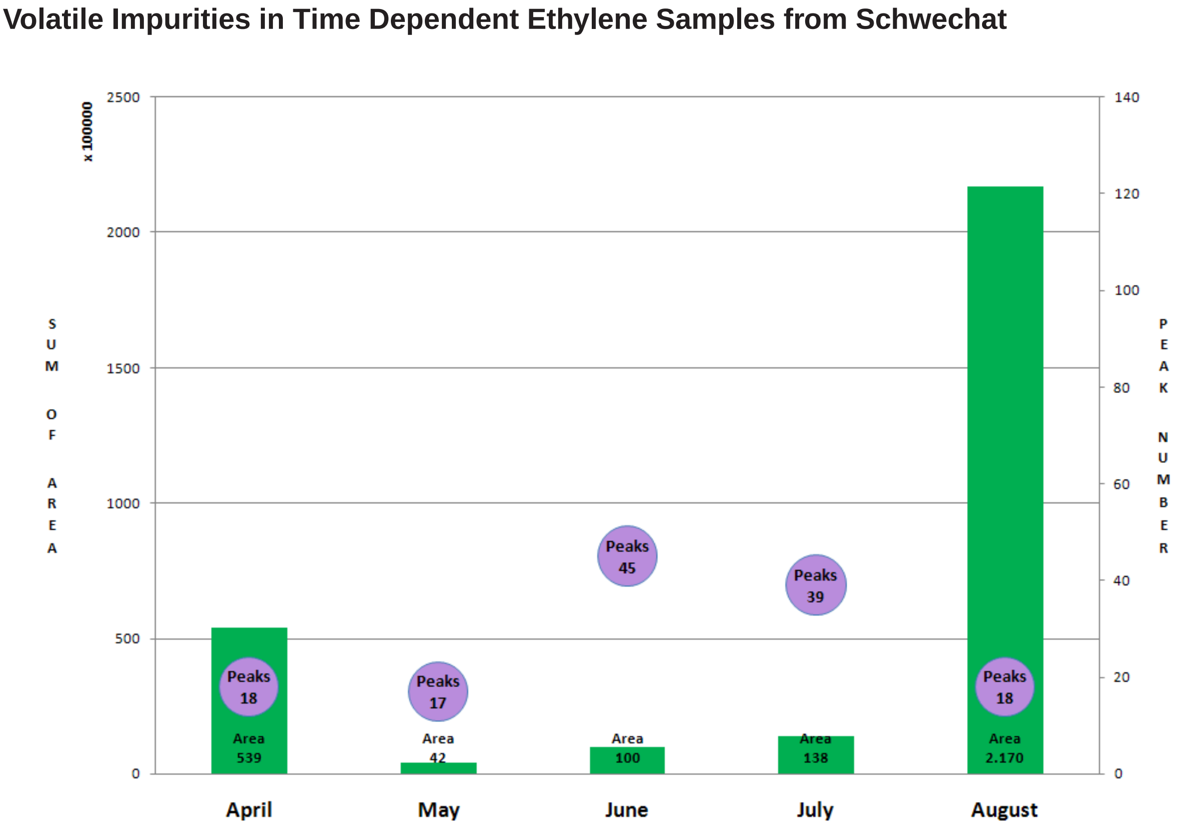


Figure 6.14.: Diagram of total volatiles in a vertical-bar plot for the sum of area and a scatter plot for the sum of peaks of time dependency ethylene samples from Schwechat

Comparing figure 6.14 and 6.15 some things become noticeable; besides total inhomogeneities of the samples the large hills in April and august samples are contributing to the sum of area but not significantly to the number of peaks (this is owed to the fact that these not properly separated peaks are not counted separately though the enclosed area is counted).

As clearly can be seen in figure 6.16 the odour impression changes over the time. Here - due to the fact, that these clusters are made from the MS data - the samples from may, june and july are very much looking the same.

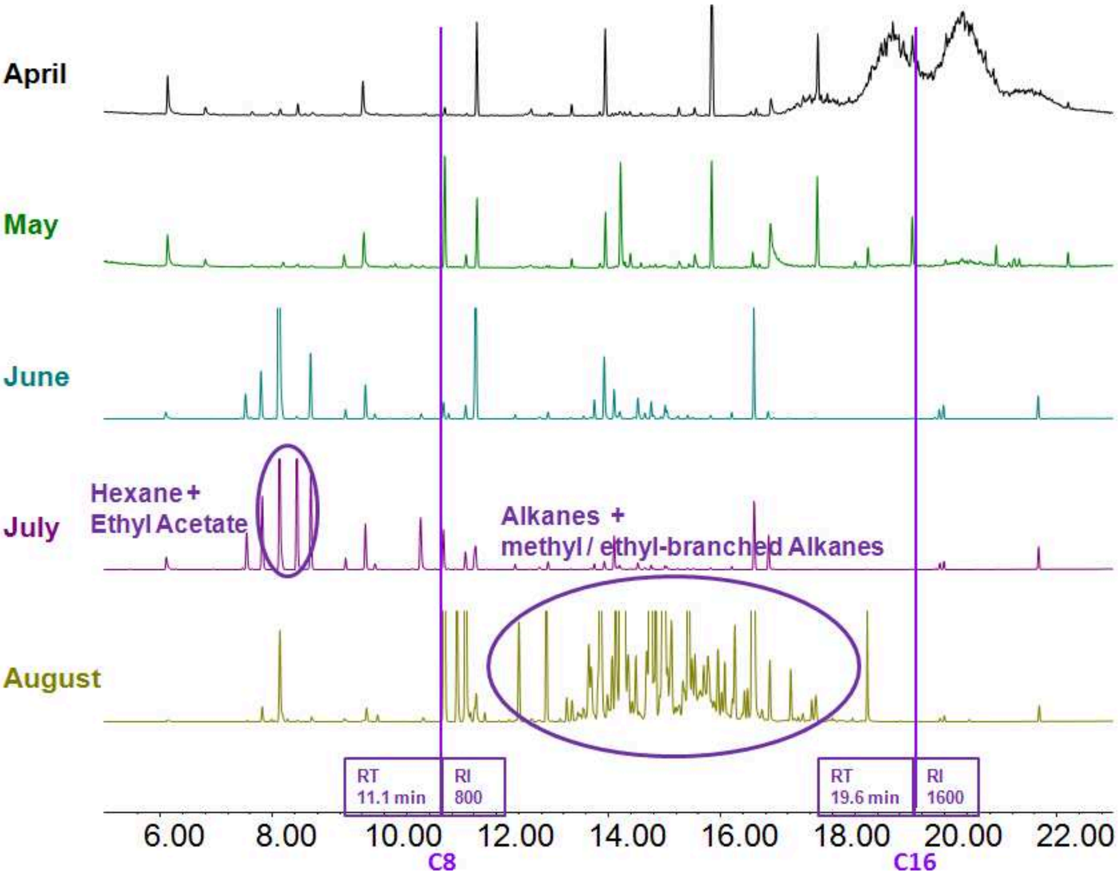
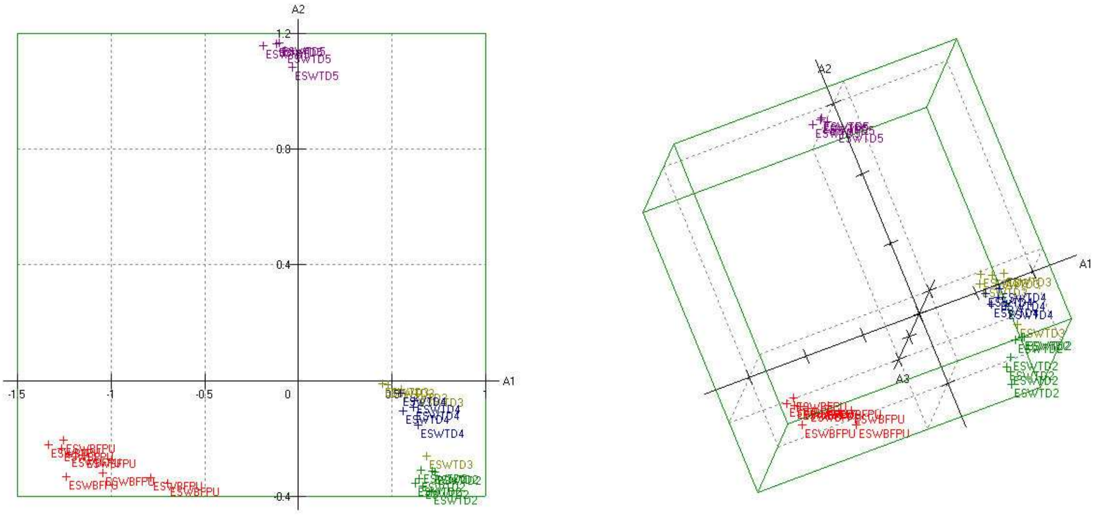


Figure 6.15.: Chromatograms of time dependency samples from Schwechat



**(a)** **(b)**

Figure 6.16.: 2D (a) and 3D (b) clusters of time dependency ethylene samples from Schwechat. red: April; green: May; yellow: June; blue: July; violet: August

### Odour Impression from Time Dependent Ethylene Samples from Schwechat

Although the samples come from the same plant, the composition varies within a wide range (shown in figures 6.17, 6.18, 6.19, 6.20 and 6.21). The ‘Ölberg’ is not always present. The august sample - the highest in sum of area terms- is the one with the fewest high impact odour active substances. The samples from may, june and july which are looking very similar from their chromatograms are really variating in odour relevant terms.

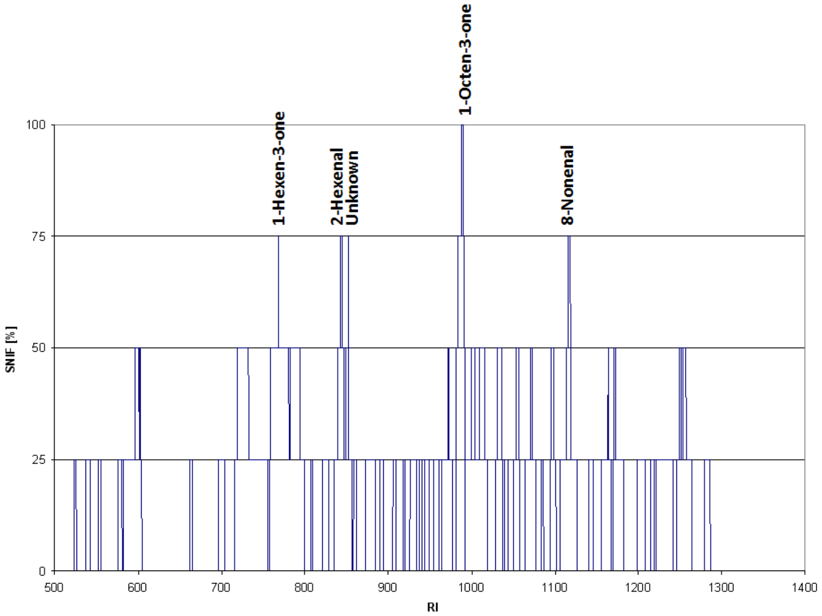


Figure 6.17.: Detection frequency of April ethylene samples from Schwechat

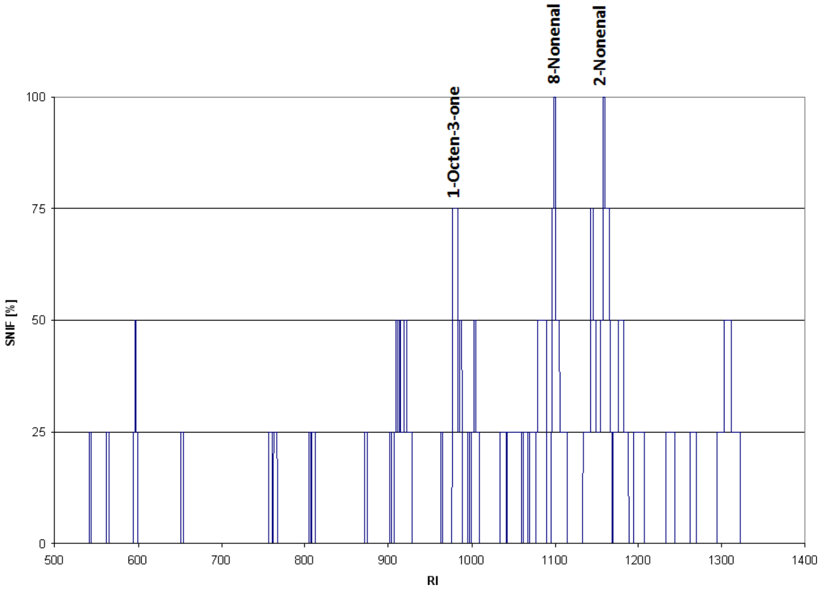


Figure 6.18.: Detection frequency of May ethylene samples from Schwechat

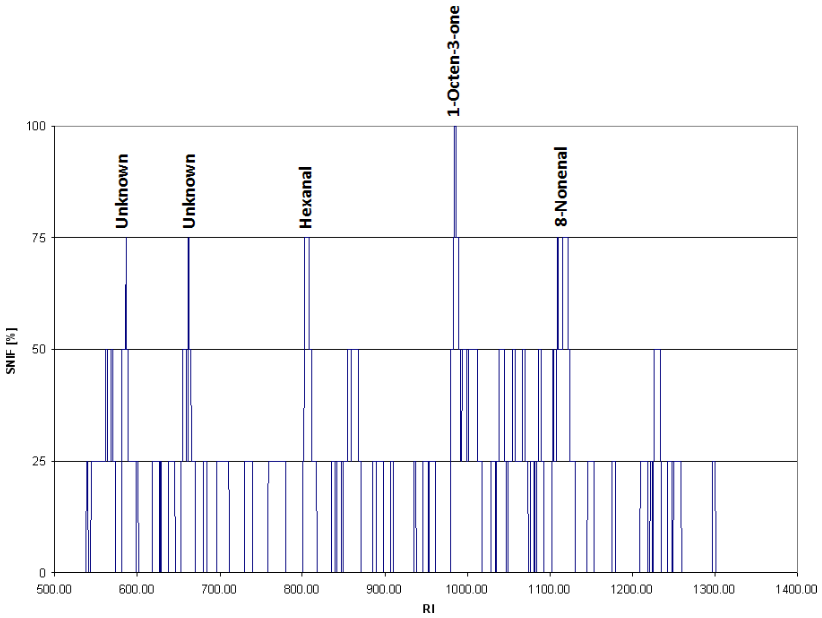


Figure 6.19.: Detection frequency of June ethylene samples from Schwechat

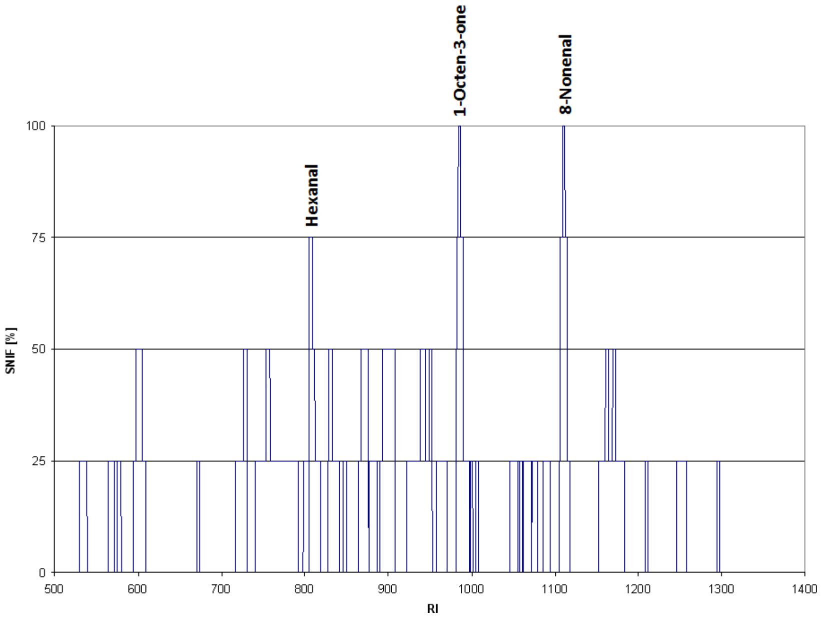


Figure 6.20.: Detection frequency of July ethylene samples from Schwechat

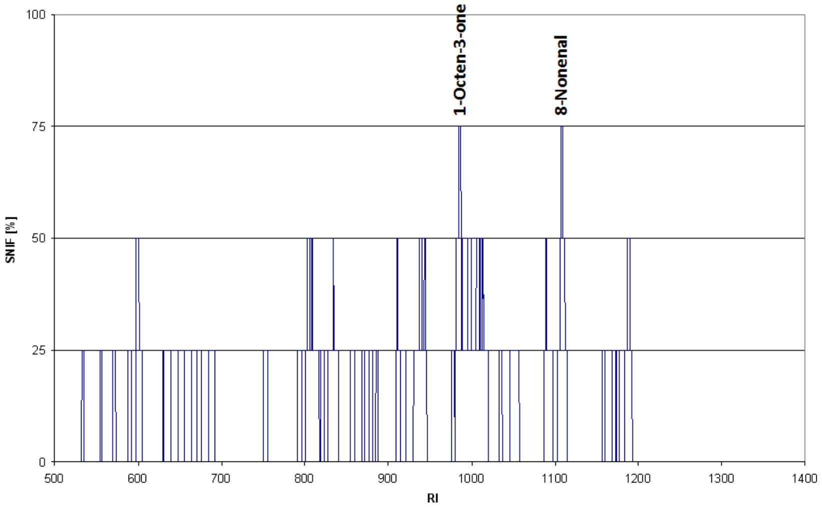


Figure 6.21.: Detection frequency of August ethylene samples from Schwechat

### 6.3.2. Time Dependency - Propylene Porvoo

#### Volatile Impurities in Time Dependent Propylene Samples from Porvoo

In this task the sample from April is the most eye-catching one. Figure 6.22 gives a first idea about the most diverging sample. This is one of the rare samples where the sample with the most peaks is also the sample with most odour impressive substances (figure 6.25). The sum area - which is generally very low - is almost the same throughout all samples.

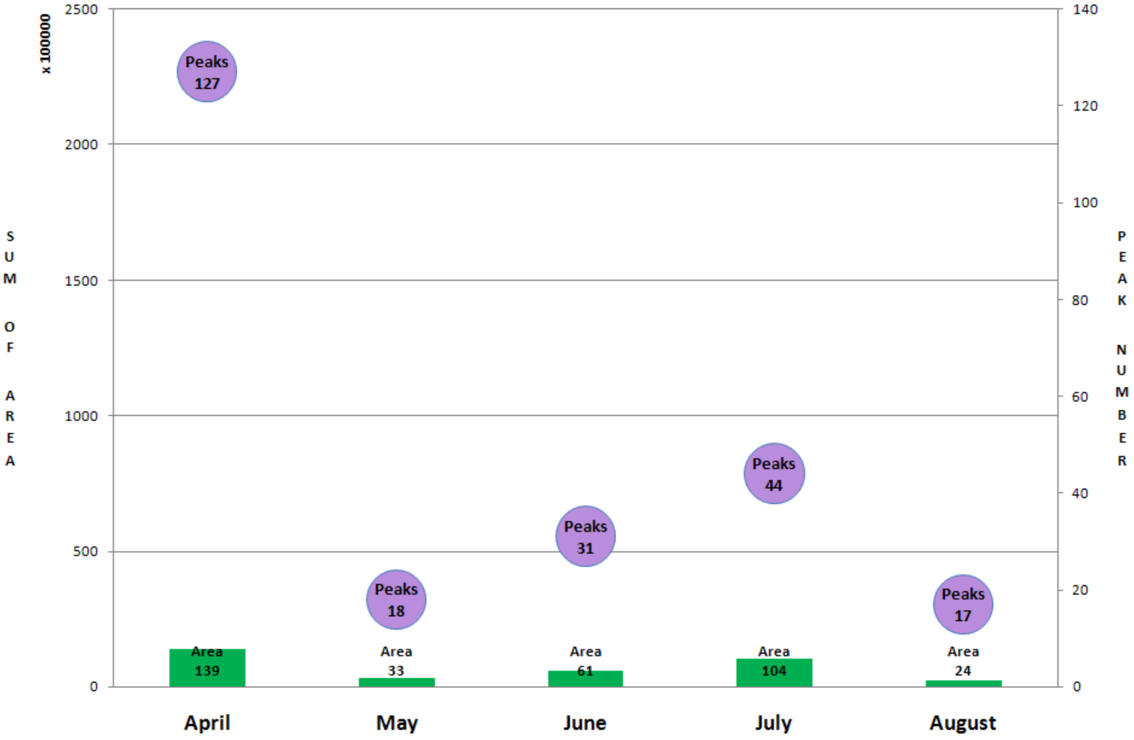


Figure 6.22.: Diagram of total volatiles in a vertical-bar plot for the sum of area and a scatter plot for the sum of peaks of time dependency propylene samples from Porvoo

The clusters in figure 6.16 show a phenomenon which may lead to questions. The samples from April and may seem to build a group compared to the samples from june, july and august although the April sample is the one with the highest number of peaks and the may sample with the lowest number - cero - of substances with high impact on odour all over the project. The reason for this effect could be founded in the fact, that the injection mode had to be changed from automatic to manual because of problems with the septa used in the later delivered sample vials. Nevertheless also in this case the variation of the different samples is very obvious.

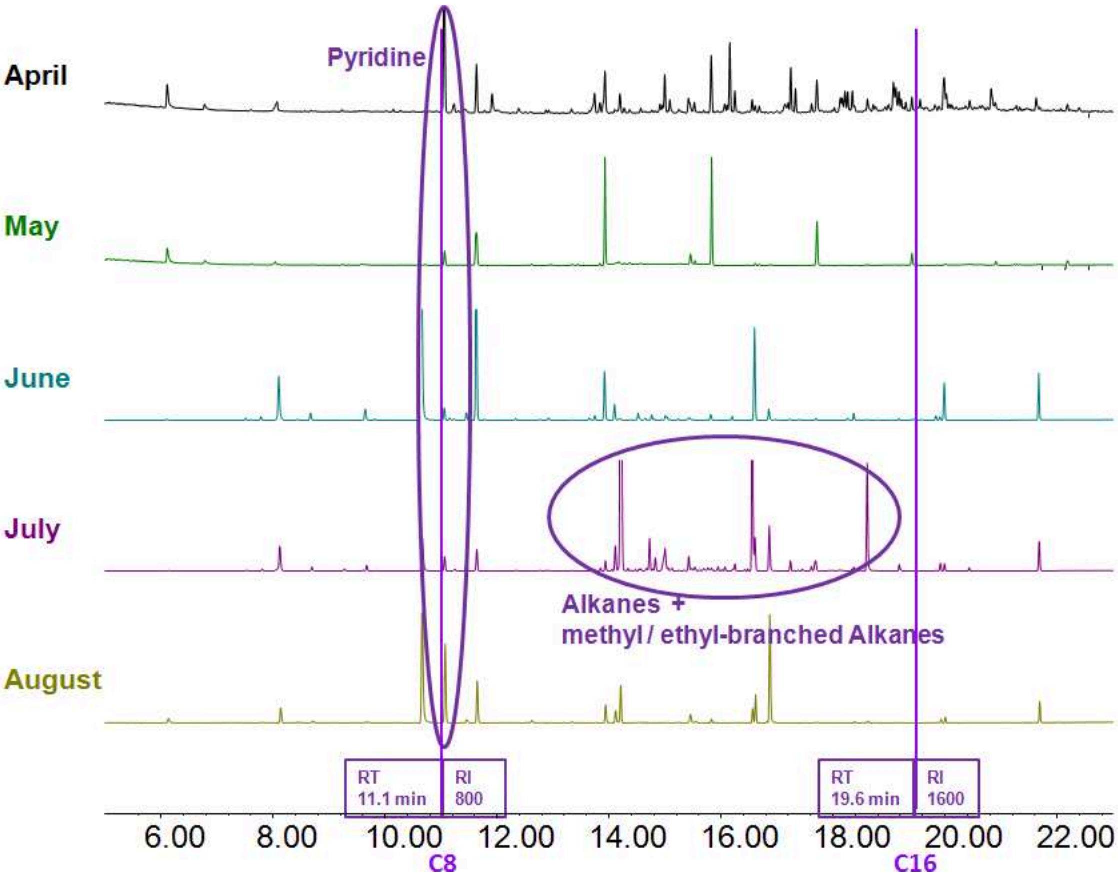
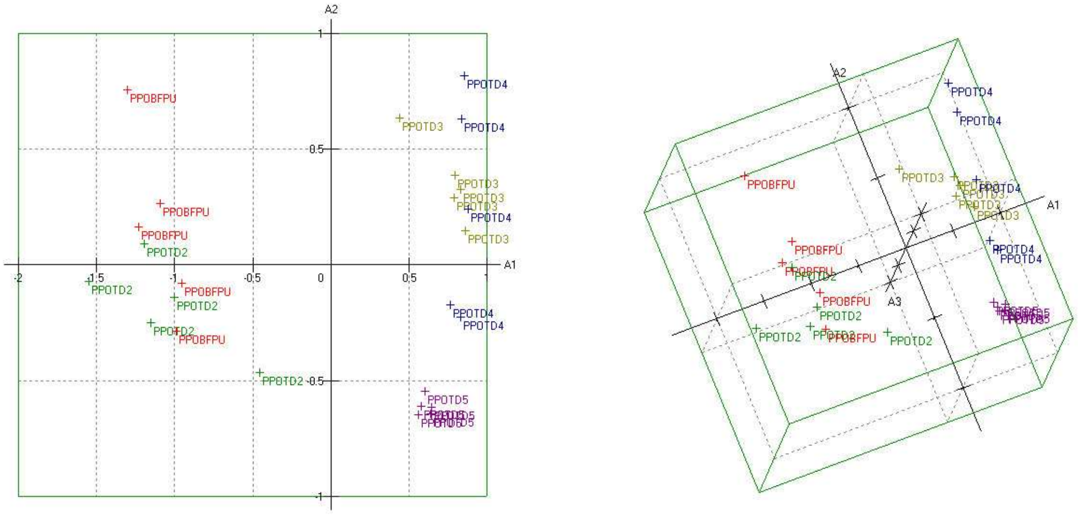


Figure 6.23.: Chromatograms of time dependency samples from Porvoo



**(a)**

**(b)**

Figure 6.24.: 2D (a) and 3D (b) clusters of time dependency propylene samples from Porvoo. red: April; green: May; yellow: June; blue: July; violet: August

### Odour Impression of Time Dependent Propylene Samples from Porvoo

The samples from Porvoo show a much more homogeneous composition than the samples from Schwechat. In the figures 6.25, 6.26, 6.27, 6.28 and 6.29 can also be seen that the may sample is significantly lower in odour than the other samples; there are no substances with high impact on the overall odour impression. On the other hand the sample from April is impressively high with odour active substances with high impact.

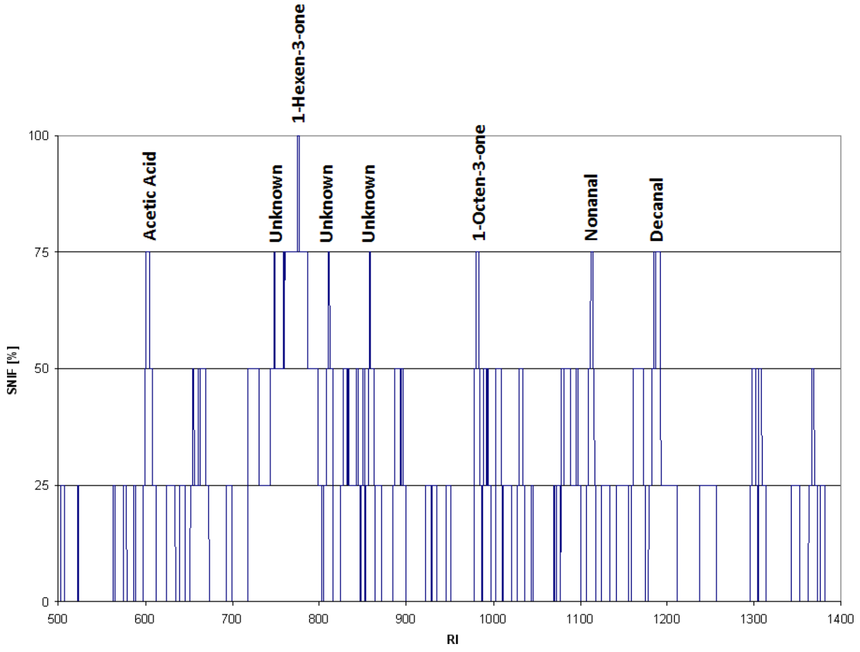


Figure 6.25.: Detection frequency of April propylene samples from Porvoo

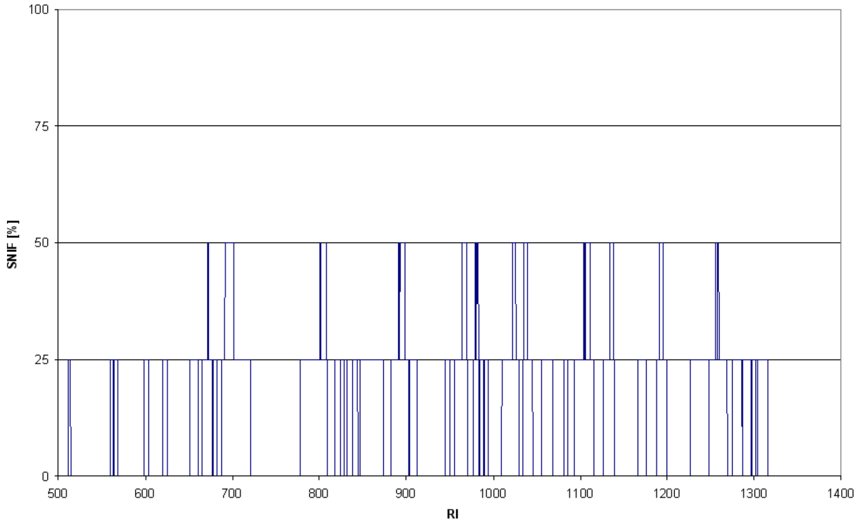


Figure 6.26.: Detection frequency of May propylene samples from Porvoo

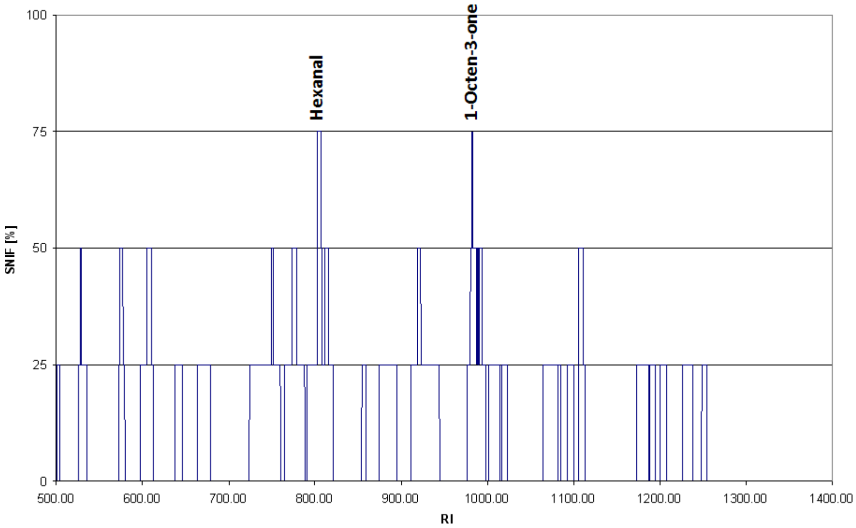


Figure 6.27.: Detection frequency of June propylene samples from Porvoo

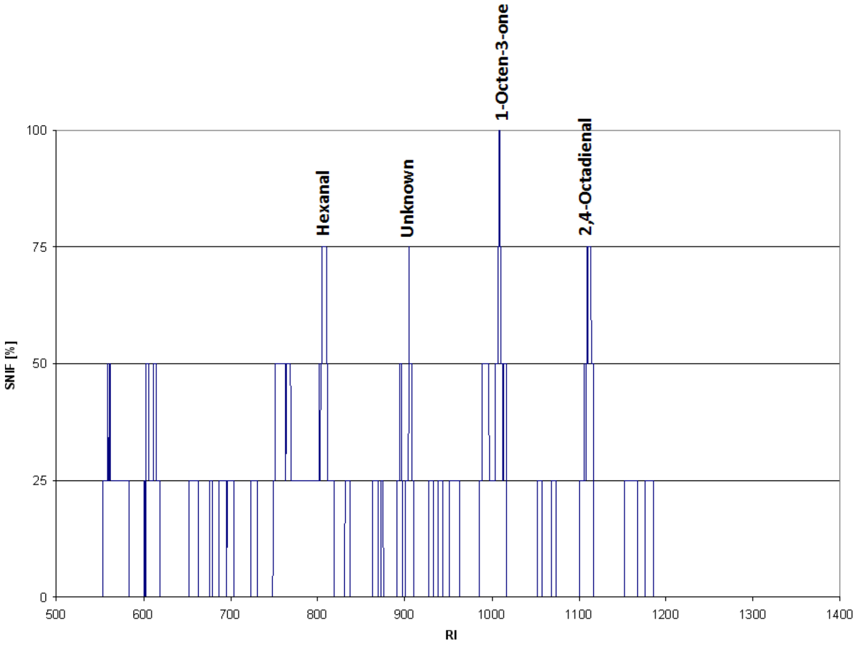


Figure 6.28.: Detection frequency of July propylene samples from Porvoo

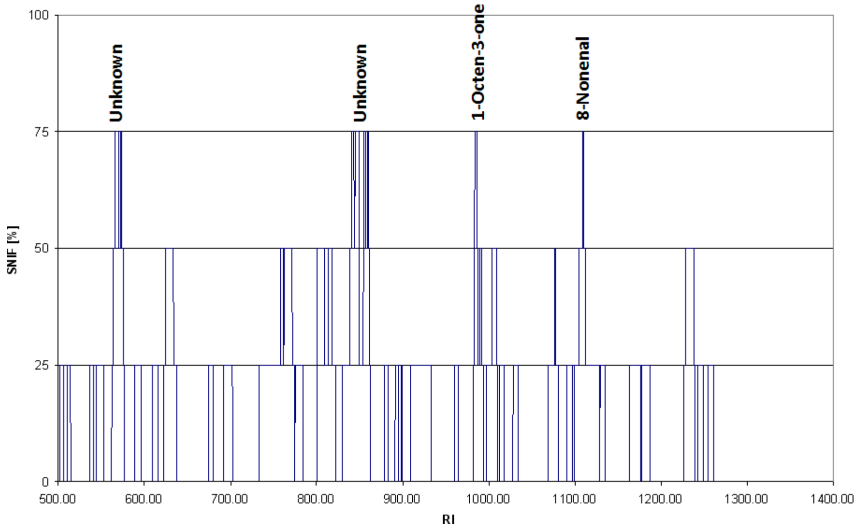


Figure 6.29.: Detection frequency of August propylene samples from Porvoo

## 6.4. Purification

Borealis purification is purposed to clean monomers mainly from polymerization influencing substances such like catalyst poisons. This section should give an impression if there is an effect of Borealis purification on odour relevant substances.

The samples used in this subtask are:

- Ethylene Schwechat
- Propylene Kallo
- Propylene Porvoo

**Volatile Impurities of Purification Samples from Schwechat, Kallo and Porvoo**

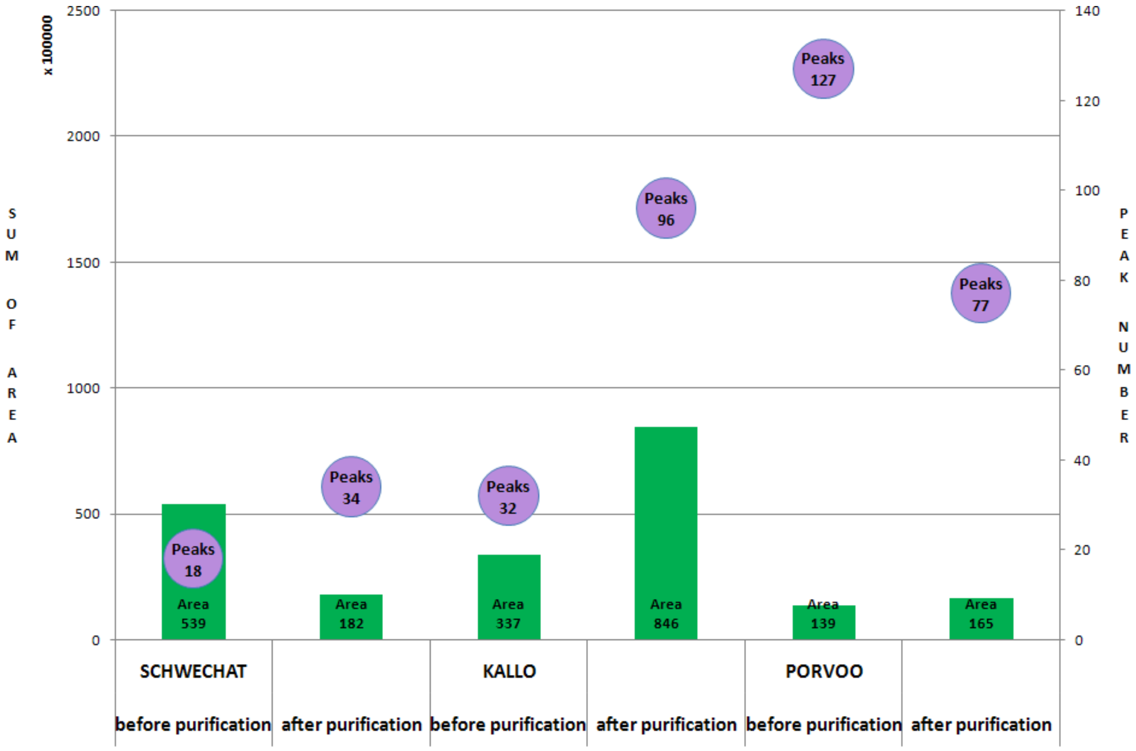
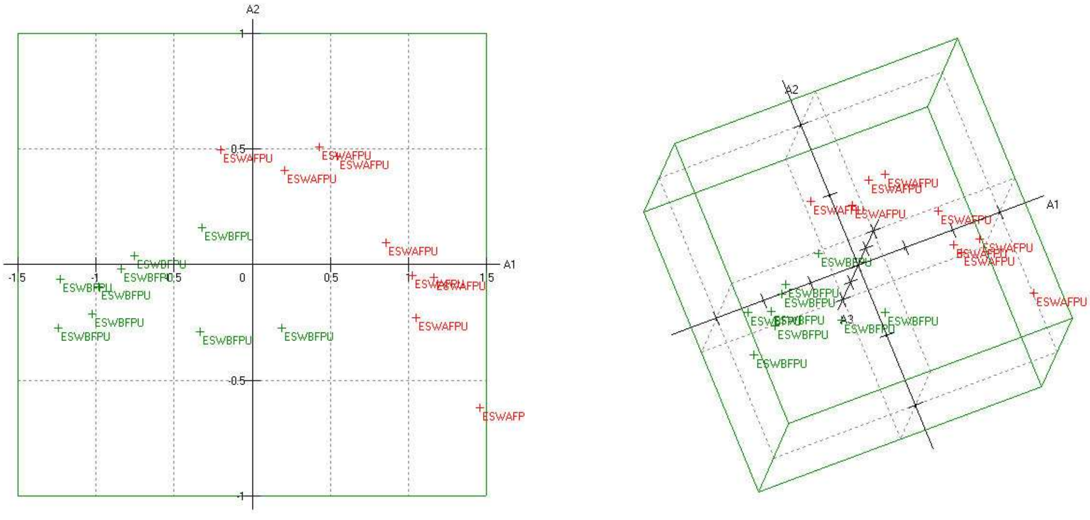


Figure 6.30.: Diagram of total volatiles in a vertical-bar plot for the sum of area and a scatter plot for the sum of peaks of purification samples from Schwechat, Kallo and Porvoo. green/violet: before purification; blue/pink: after purification

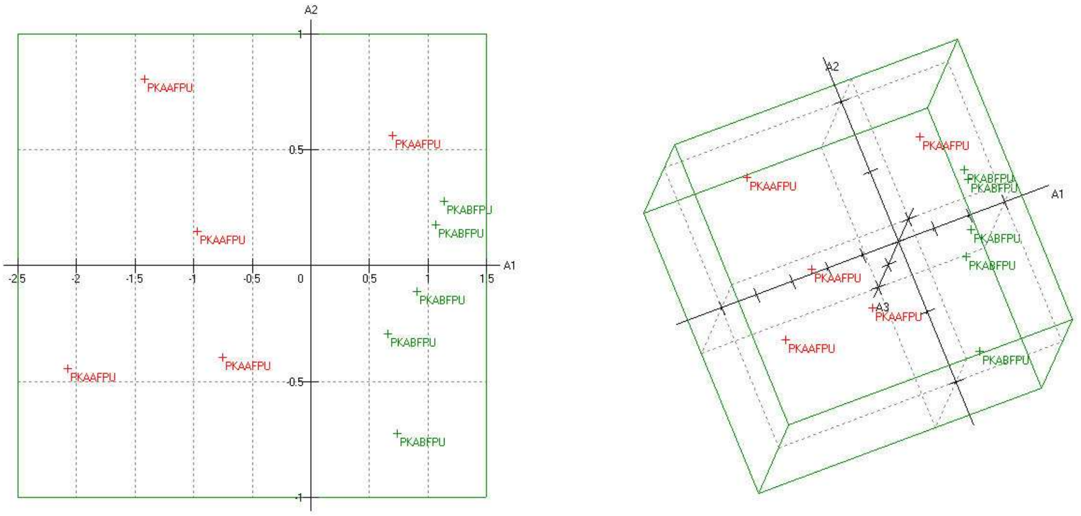
In figure 6.30 the sum of area and peak numbers from the different samples from Schwechat, Kallo and Porvoo before and after purification are shown. Although also the after purification sample from Borouge has a higher number of peaks than the before purification sample, at least the sum of area is lower after the purification; the more significant sample is the one from Kallo, the peak number after the purification is 3-fold higher than before purification.

Figure 6.31 shows that the influence of purification in Schwechat is not of very high impact. The samples do not form real cluster whether before or after purification. This means there is no main influence of purification on the samples because they do not become more homogeneous after purification.



**(a)** **(b)**

Figure 6.31.: 2D (a) and 3D (b) clusters of purification ethylene samples from Schwechat. green: before purification; red: after purification



**(a)** **(b)**

Figure 6.32.: 2D (a) and 3D (b) clusters of purification propylene samples from Kallo. green: before purification; red: after purification

The clustering (shown in figure 6.32) done for the purification samples from Kallo shows a very poor result. Especially the samples after purification, which were intentionally ment to be more similar than before purification are varying very much.

The cluster analysis of the purification for Porvoo in figure 6.33 shows that there are no clusters whether before or after purification. The purification does not have an positive or homogeneity generating effect on the samples.

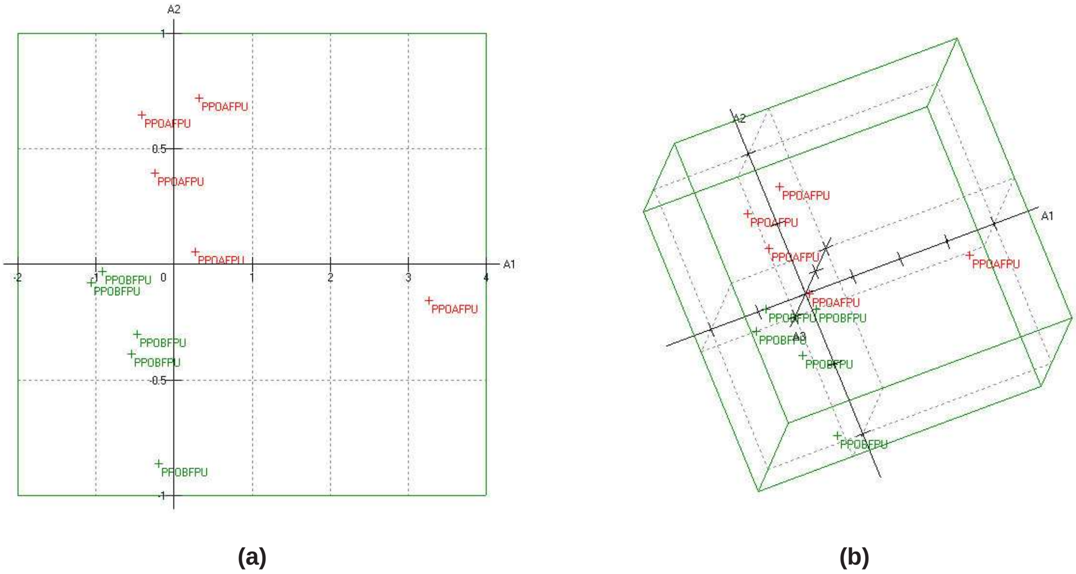


Figure 6.33.: 2D (a) and 3D (b) clusters of purification propylene samples from Porvoo. green: before purification; red: after purification

### 6.4.1. Purification - Ethylene Schwechat

The chromatograms shown in figure 6.34 display vividly the effect of the purification on the long-chain molecules in the later eluting region of the chromatograms. The ‘Ölberg’ is decreasing but all other parts of the chromatogram are not significantly influenced by purification.

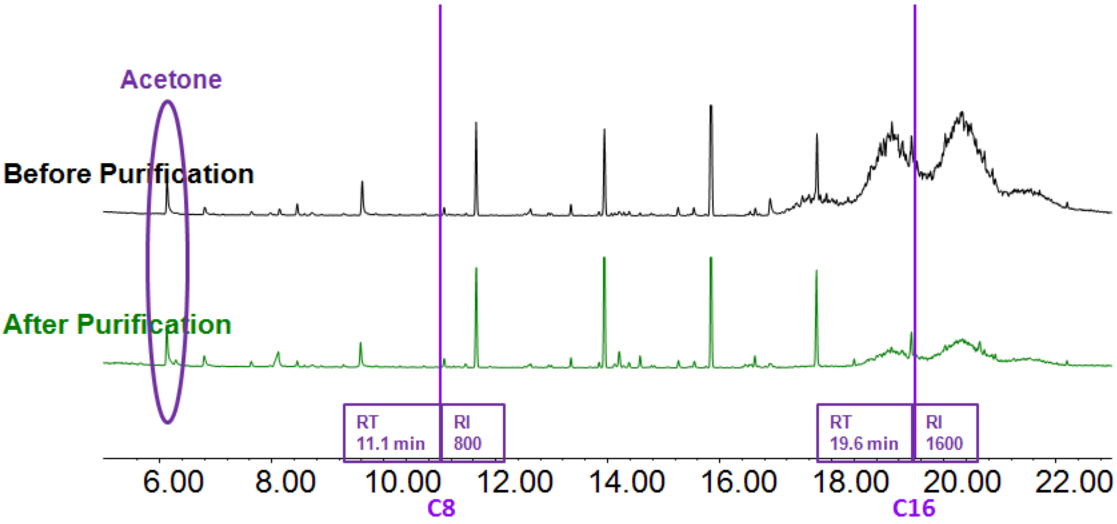


Figure 6.34.: Chromatograms of purification samples from Schwechat

Again can be shown in figure 6.35, that the influence of the purification is not very significant.

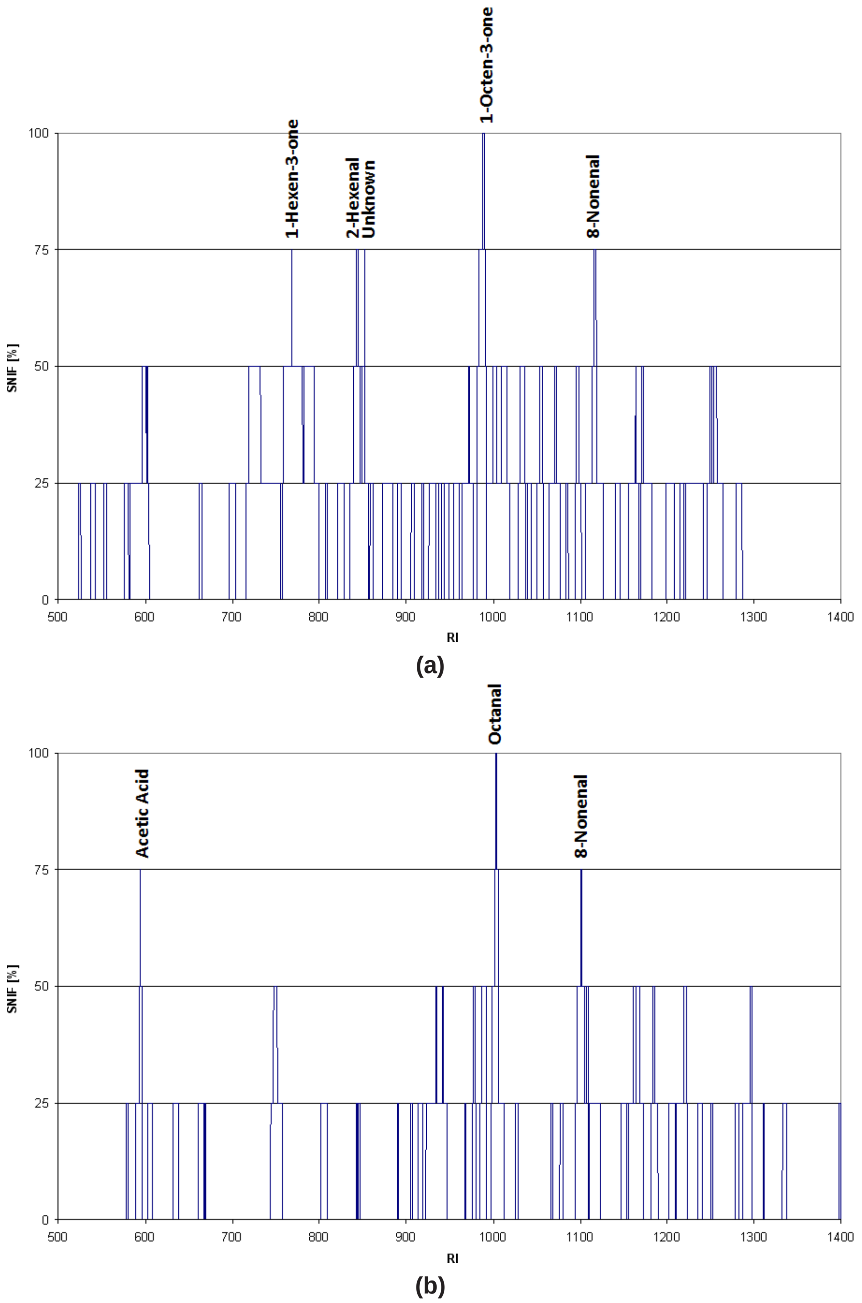


Figure 6.35.: Detection frequency of ethylene Schwechat before (a) and after (b) purification

### 6.4.2. Purification - Propylene Kallo

In the chromatograms of the Kallo samples (figure 6.36) emerges a possible negative effect of purification on odour impression. Since the purification is outlined to clean monomers from catalyst poisons or other substances which are influencing the polymerization negatively, an adverse effect on odour active substances can occur respectively occurs in this case.

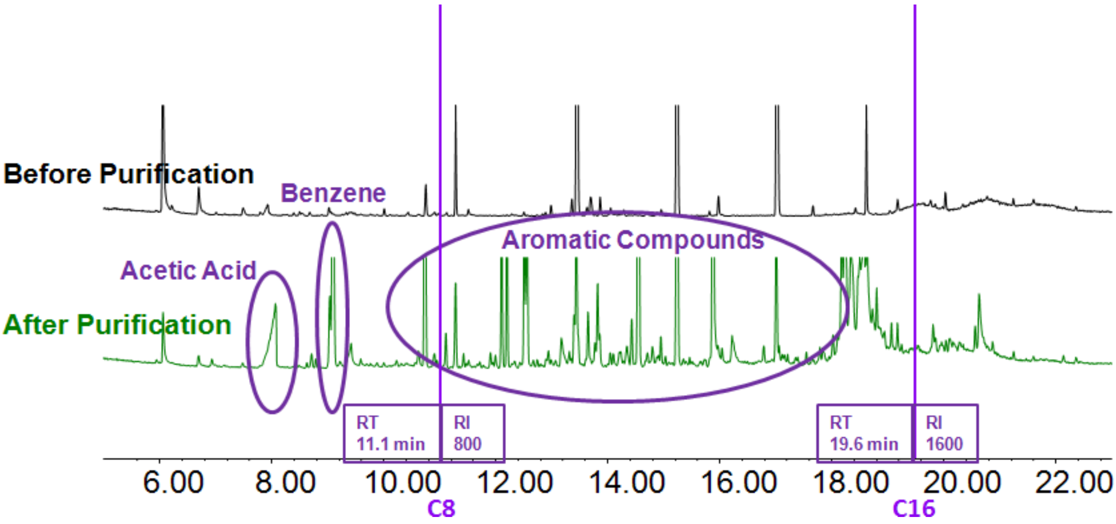
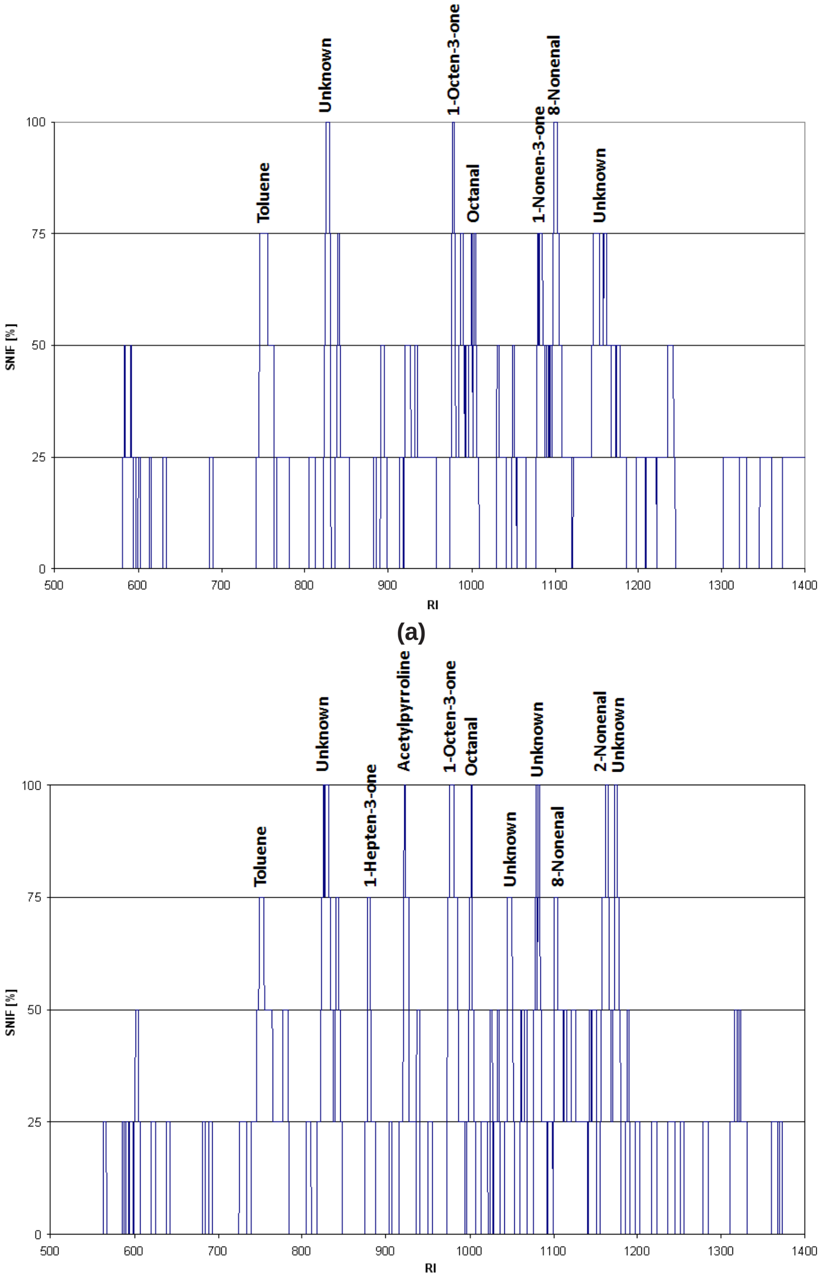


Figure 6.36.: Chromatograms of purification samples from Kallo

Analogue to the chromatograms the detection frequency pattern shown in figure 6.37 shows an increase of high impact substances in the sample taken after purification. One eye-catching fact is the instance of having new substances after purification.



(a)

(b)

Figure 6.37.: Detection frequency of Propylene Kallo before (a) and after (b) purification

### 6.4.3. Purification - Propylene Porvoo

The chromatograms show that the purification (figure 6.38) reduces the amount of methyl-and ethyl-branched molecule derivates which occur as small lines besides the main peaks. But the height and the amount of the main peaks is not influenced by purification.

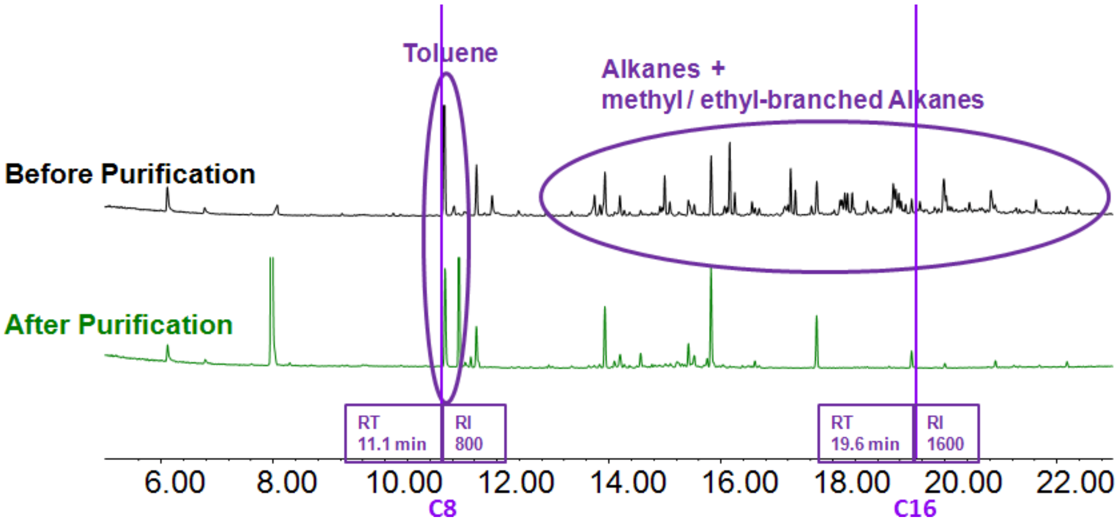
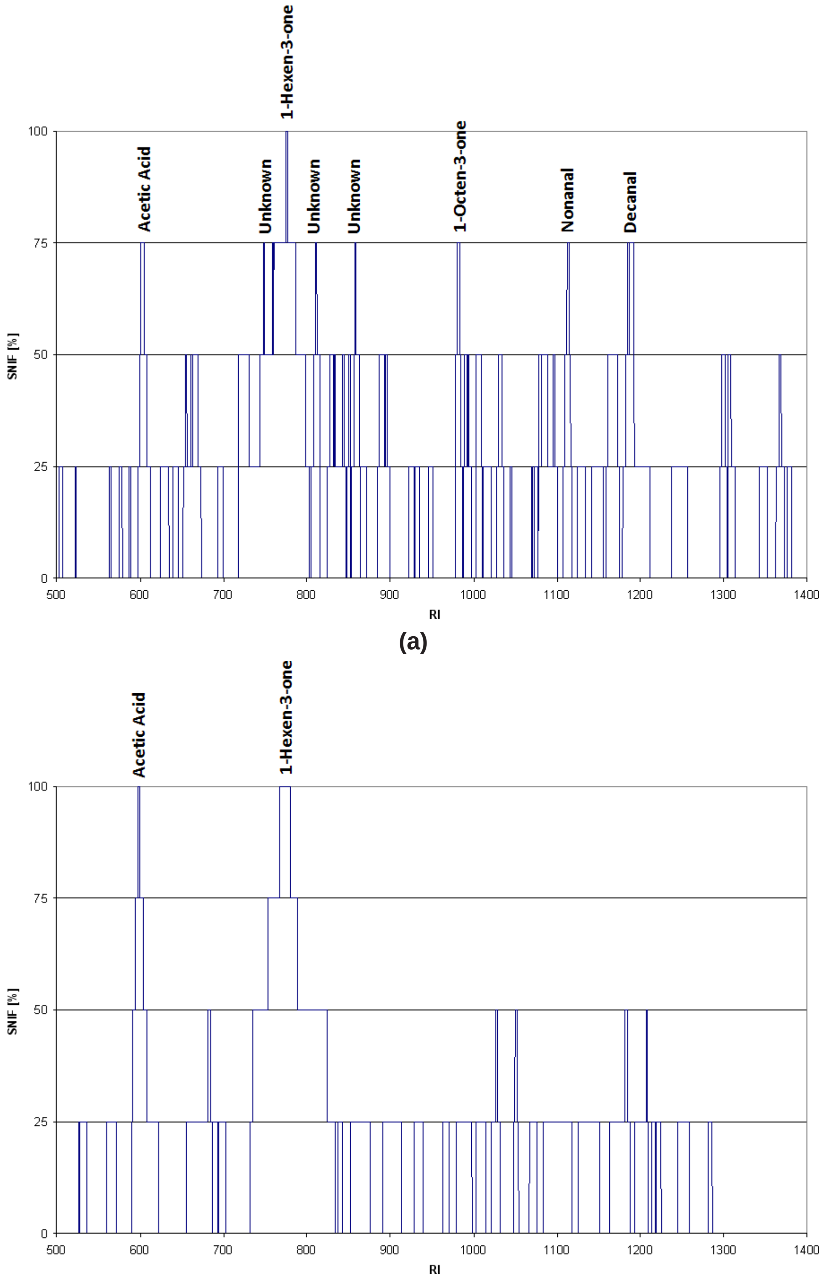


Figure 6.38.: Chromatograms of purification samples from Porvoo

Again can be shown in figure 6.39, that the influence of the purification mainly takes place in the later eluting regions of the chromatogram. Interestingly the purification works on nearly all occurring substances but not on 1-hexene-3-one; the odour impression of this substance seems to be untouched by the purification.



(a)

(b)

Figure 6.39.: Detection frequency of Propylene Porvoo before (a) and after (b) purification

## 6.5. Comonomers And Diluents

Besides the effect of the monomers themselves, comonomers and diluents should be checked on their impact on odour.

The samples used in this subtask are:

- 1-Butene Stenungsund
- Propane Stenungsund
- 1-Hexene Stenungsund

### Volatile Impurities in Comonomers And Diluents

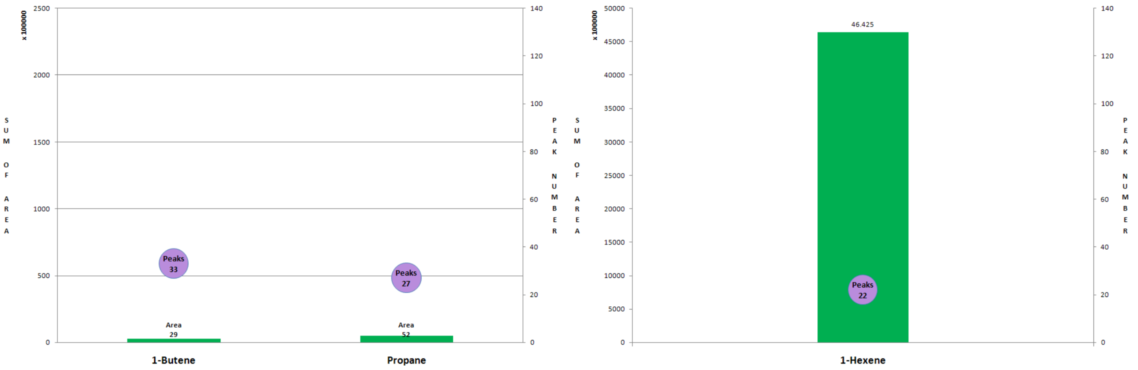


Figure 6.40.: Diagram of total volatiles in a vertical-bar plot for the sum of area and a scatter plot for the sum of peaks of comonomer and diluent samples from Stenungsund; the left plot is showing 1-butene and propane from Stenungsund; the right plot is showing the 1-hexene sample which was liquid (this requires different scaling for the area-axis)

In figure 6.41 the chromatogram of Stenungsund ethylene is also shown to boost significance and comparability of the picture. Since the 1-hexene was the only liquid sample, it was put into a headspace vial as well as the gas samples. Therefore the height and intensity of the peaks (also in the sum of area and number of peaks pattern in figure 6.40) is not directly comparable even though the number of peaks which represents the different occurring impurities gives a good information.

### Odour Impression of Comonomer And Diluent Samples

To bridge to the former tasks which are solely related to monomers, the ethylene chromatogram is added to the picture in figure 6.41. This is also showing, that the contribution of the comonomers are not that high than the ones from the monomer. The detection frequency patterns shown in the figures 6.42, 6.43 and 6.44 point out that 1-butene is compared to propane and 1-hexene very clean in odour relevant terms. The methanethiol was put into the diagram manually because of its definite impact on odour. This substance is eluting together with the solvent in the very beginning of the chromatogram; solvent peaks are generally not sniffed because their tremendously intensive odour impression would block the sniffing persons nose for the whole following substances. The occurring 1-hexene-3-one in figure 6.44 is also object of further investigation in chapter 7.

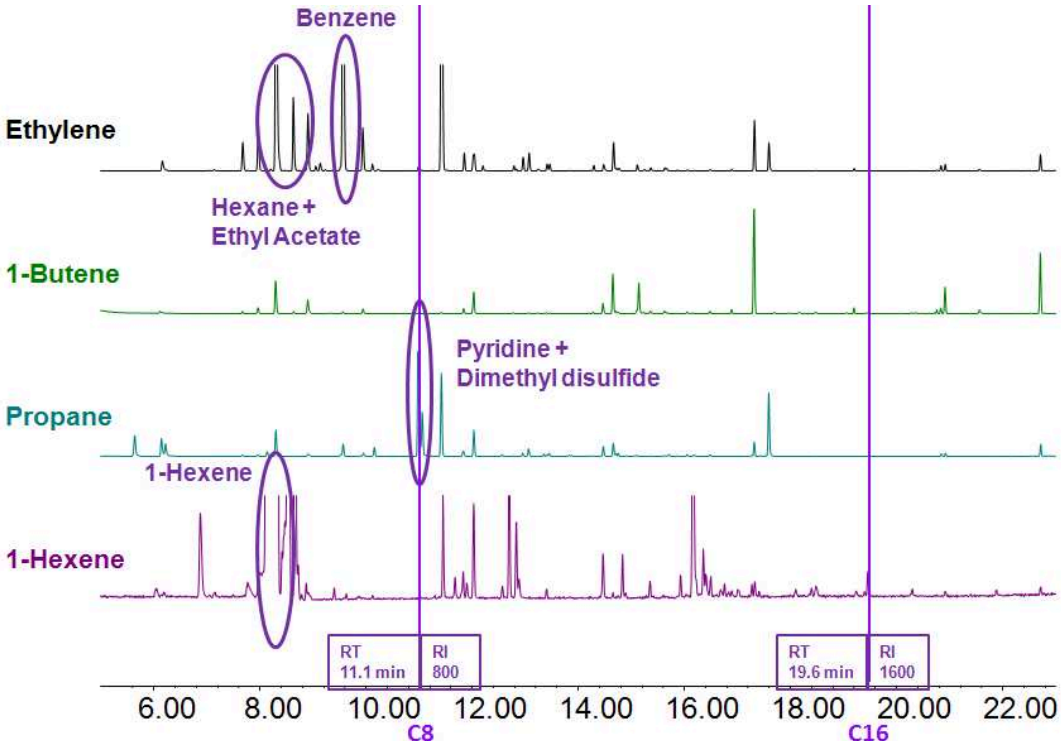


Figure 6.41.: Chromatograms of monomer, comonomers and diluent samples from Stenungsund

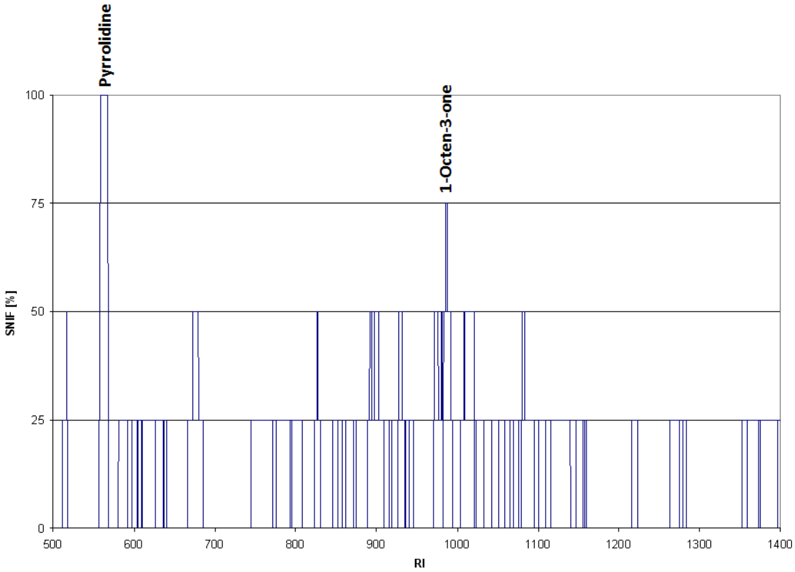


Figure 6.42.: Detection frequency of 1-butene from Stenungsund

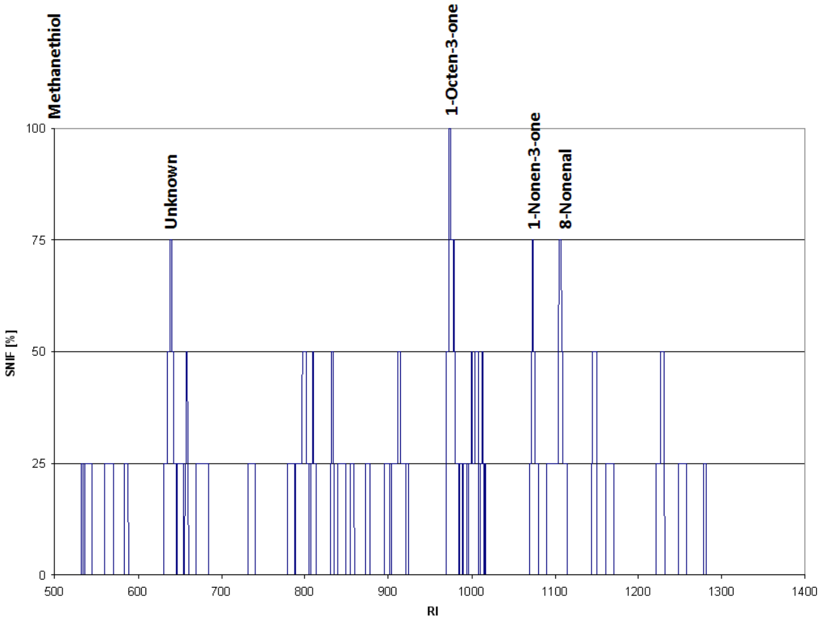


Figure 6.43.: Detection frequency of propane from Stenungsund

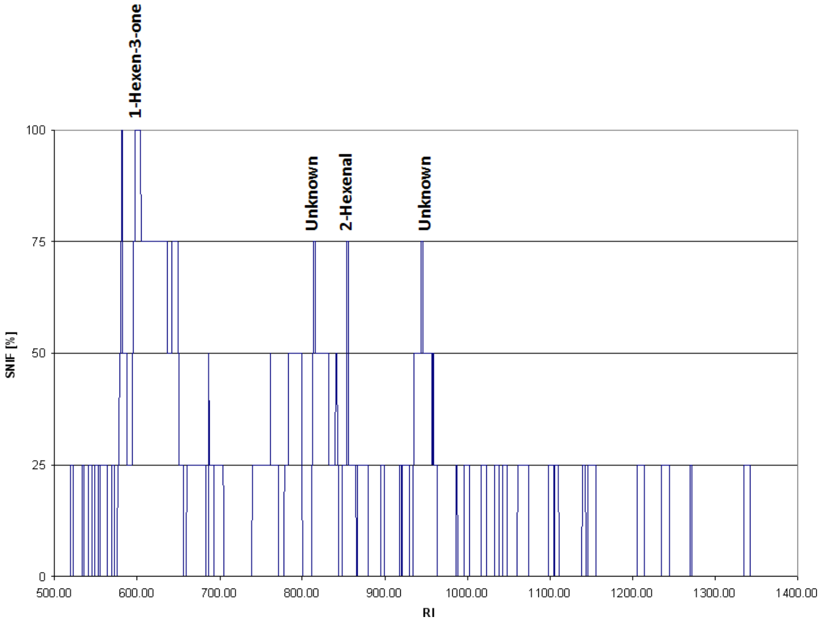


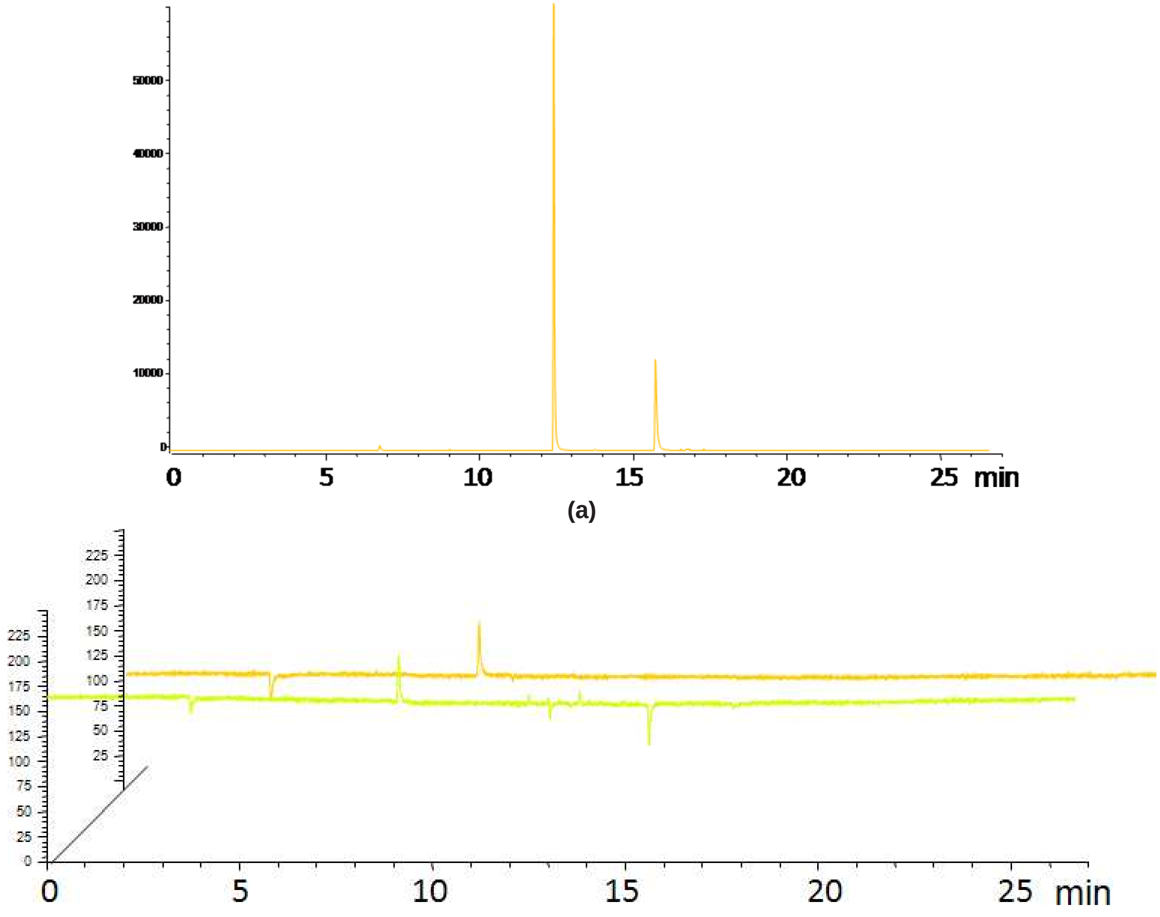
Figure 6.44.: Detection frequency of 1-hexene from Stenungsund

## 6.6. Sulfur and Nitrogen Selective Measurements

Additionally to the previously discussed measurements also measurements on the sulfur selective detector (“FPD”) and on the nitrogen selective detector (“NPD”) were done.

### 6.6.1. Sulfur Selective Measurements

Except for the propane sample from Stenungsund there were no remarkable amounts of sulfur in the samples. Figure 6.45a shows a chromatogram of this sample. The next lower level of barely remarkable sulfur is shown in figure 6.45b which displays a 200-fold lower amount of sulfur than in the propane sample.



(a)

(b)

Figure 6.45.: Sulfur selective measurement of (a) propane from Stenungsund and (b) ethylene from Borouge and Schwechat (July)

### 6.6.2. Nitrogen Selective Measurements

The nitrogen selective measurements were done while the samples were sniffed. The process of sniffing went on for several months, during this time there could not be attained reasonable and reproducible results for the nitrogen selective measurement. By contrast to the other measurements, which were done by one or two runs, the samples do not seem to stay constant over that long time period. Figure 6.46 shows the 3 most significant samples.

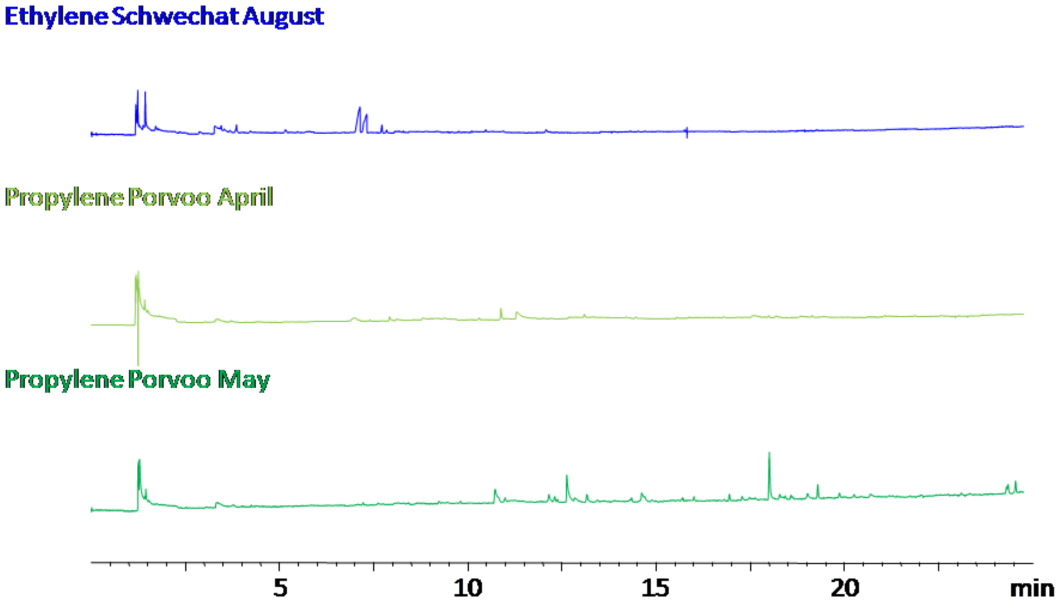


Figure 6.46.: Nitrogen selective measurement of ethylene (August) from Schwechat, propylene from Porvoo (April/before purification and May)

## 6.7. Identified Odour Active Substances

### 6.7.1. List Of Odour Active Substances

A list of identified substances with their odour description, Retention Indices and Odour Threshold is given in table 6.2. In the Appendix section A.2 the origins of the different samples and the occurring substances are outlined in table A.11. The given substances are verified by comparing with the data of Helene Hopfer ({Hopfer, 2010}), comparing it with online data bases[3] and checking the sniffing results by sniffing mixtures of the pure reference substances.

Table 6.2.: List of identified odour active substances in this project sorted by Retention Index; all the used Odour Thresholds in this table are the lowest found values from {van Gemert, 2003}

| **Substance** | **Odour Impression** | **RI** **(HP5)** | **Odour Threshold in Air** $\frac{mg}{m^3}$ |
|---|---|---|---|
| **Pyrrolidine** | *lacquer-like, fuel, heating oil, solvent, leek, intensive, muddy* | **558** | $9x10^{-2}$ |
| **Unknown** | *pungent, glue-like, solvent, burnt, dusty, sweet* | **562** | |
| **Unknown** | *smoky, fruity, yogurt, chipboard, solvent, glue* | **586** | |
| **Acetic acid** | *oil, butter, fatty, pungent, solvent, roasty* | **600** | $3x10^{-2}$ |
| **Unknown** | *glue, milk* | **640** | |
| **Unknown** | *anis-like, dumb green, smoky, dusty* | **662** | |
| **Unknown** | *green , solvent, glue* | **748** | |
| **Pyridine** | *fatty, stinky, dusty, olives, mouldy, solvent, trench coat* | **772** | $2x10^{-1}$ |
| **Toluene** | *solvent, sweet, intensive, dry, glue, pungent, leek, burnt plastic, floating tyre, burnt, sour* | **773** | $4x10^{-1}$ |
| **1-Hexen-3-one** | *mushroom, glue, fruity, wood, burnt, stinky, dust, dry, pungent, sweet, roasty, banner, breadcrumbs, mouldy, plastic, waxy, solvent* | **778** | $2x10^{-5}$ |
| **Hexanal** | *green, grassy, solvent, pungent, fresh, glue, roasty, mouldy, drain, dumb, chip fat, fruity, citrus* | **798** | $2,5x10^{-2}$ |
| **Unknown** | *pungent, sweet, roasty, banner, bread crumbs, mouldy* | **811** | |
| **Unknown** | *solvent, plastic, carpet glue, mouldy, warm solvent, green apple* | **815** | |
| **Unknown** | *stinky, leek, burnt plastic, intensive, roasty, burnt, pungent, plastic, hot wax, dusty, green, glue, wet cloth, mushroom, carpet glue, trench coat* | **826** | |
| **Unknown** | *roasty, mouldy, fatty, dusty* | **839** | |
| **2-Hexenal** | *roasty, burnt, stinky, dusty, mushroom, coffee, malt, green, sweet, fatty, dry cat food, schwimmies, pungent* | **844** | $1,2$ |
| **Unknown** | *sweet, marzipan-like, sticky, alcoholic* | **852** | |
| **Unknown** | *sweet, fruity, sulfuric, fatty, rancid, chip fat, nutty, roasty* | **860** | |
| **1-Hepten-3-one** | *pungent, green, attrited plastic* | **880** | $8x10^{-5}$ |
| **Unknown** | *melted butter, spicy, carrot, soup* | **904** | |
| **Acetyl pyrrolidine** | *soil, mushroom, roasty, intensive, pungent, popcorn, pungent, green, burnt plastic, rubber* | **925** | $2x10^{-5}$ |
| **3-Hepten-2-one** | *fermenting, chemical, dumb, warm plastic, PU-foam, solvent, glue* | **942** | $6^x10-2$ |
| **Unknown** | *stale milk, black currant bonbons, sausage-like* | **952** | |
| **1-Octen-3-one** | *mushroom, soil, mouldy, plaster, roasty, soil, plastic, fatty, dusty* | **984** | $4^x10-4$ |
| **Octanal** | *vinegar, fruity, orange, mandarin-peel, citral, bloomy, woody* | **1007** | $5,8x10^{-3}$ |
| **Unknown** | *warm rubber, plastic, solvent, pungent, lacquer-like* | **1050** | |
| **(E) 2-Octenal** | *fruity, apple, sticky, malt, roasty, fatty, salve-like, rancid* | **1067** | $9x10^{-4}$ |
| **1-Nonen-3-one** | *metallic, lime, mushroom, pungent, burnt plaster, green, fresh, old leather, soily, solvent* | **1077** | $2x10^{-5}$ |
| **Unknown** | *mushroom, organic waste, citral, pungent, dusty, burnt, burnt plastic, urine, dry* | **1083** | |
| **Nonanal**<br>**6-Nonenal**<br>**8-Nonenal** | *green, stink bug, PE fresh, milky, dusty, pulp, mushroom, old breadcrumbs, roasty, pungent, sour, citrus, sweet, burnt plastic, urine, dry, refreshing tissue, plastic, fatty, sweet, caramel, lime, solvent,red currant, not, glue, pastries, burnt, cardboard* | **1104** | $5,2x10^{-3}$ |
| **(E,E) 2,4-Octadienal** | *old breadcrumbs, sugary, caramel, lime, pungent, solvent, sweet, red currant, plastic, warm, PE fresh, barn, sour, smoky, stinky, mouldy milk, rubber, intensive, fatty* | **1113** | $1,2x10^{-2}$ |
| **Unknown** | *dung pile, green, leek, candy floss* | **1150** | |
| **(E)-2-Nonenal** | *PE intensive, fresh, lime, fatty, mouldy, rotten, pungent, dusty, faecale note, burnt, dry, grain, citrus, green, aldehyde, stink bug, mineral oil, fuel* | **1162** | $3,9x10^{-5}$ |
| **Unknown** | *plastic, burnt, dung pile, plaster* | **1175** | |
| **2,4-Nonadienal** | *grassy, warm soil, solvent, mushroom* | **1200** | $2,5x10^{-4}$ |
| **Decanal** | *rotten vegetables, drain, intensive, burnt plastic, gas station, motor oil, fuel, sweet, currant* | **1204** | $6,2x10^{-4}$ |

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[3] www.flavornet.org (last visit: 25/05/2009), SKAF database

### 6.7.2. Comparison of Non Odorous and Odorous Substances

Chapter A.2.1 contains a compendium of information for every single sample. The RI of $C_8$ and $C_{16}$ are indicated in the chromatograms to make the comparison with the detection frequency pattern on the right side easier. Under the chromatogram two tables are given. These tables are listing the volatile impurities on the left side and the odour active substances on the right side.

### 6.7.3. Principal Component Analysis

*The Principal Component Analysis (PCA)* was done by *The Unscrambler* provided by {FaCAMO-Norway}. Following {Otto, 1999} in this method the large number of statistic variables is reduced through approximation with linear combination. These linear combinations are called “principal components”. Differentiation would have been possible if the samples were separated as “clouds”.
All the substances which had an impact of 75 or 100% on the odour impression (the substances which are outlined in the detection frequency patterns) were taken for the analysis. These substances are listed in table 6.2.
Intention of the analysis was to find patterns concerning major odour drivers for a) either ethylene or propylene or b) different plants. Patterns could not be found in the samples, all the samples are sticking together to one cloud. Only the samples from Kallo deviate from the rest by drifting a little bit to the right. PC 1 (“principal component 1”) and PC 2 (“principal component 2”) are not giving a significant evidence for the sample.

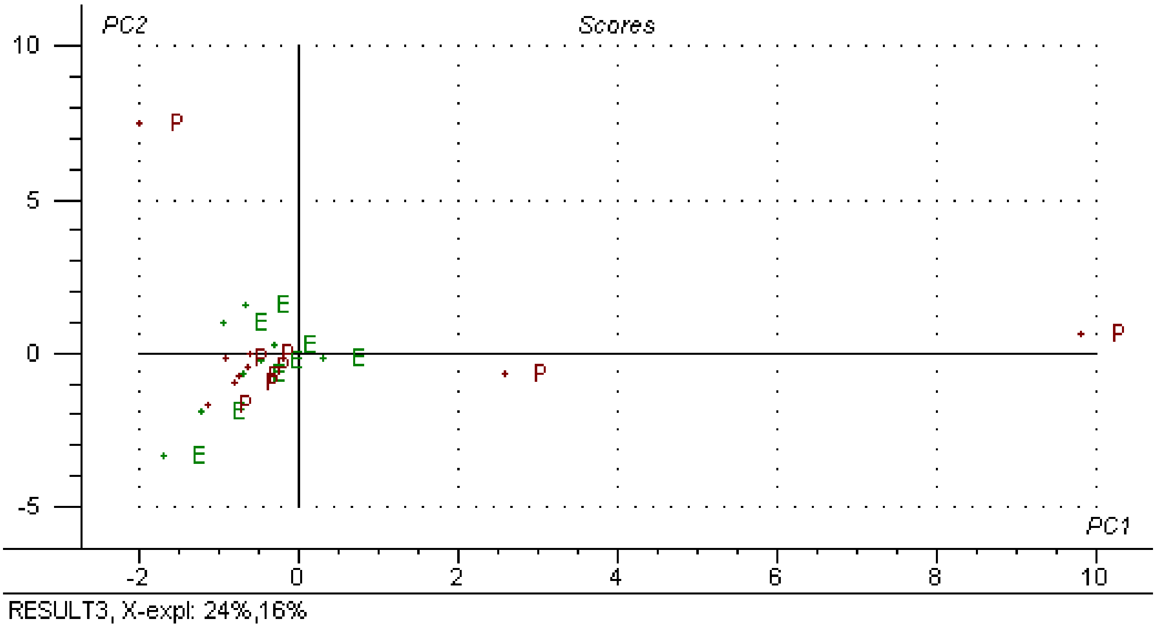


Figure 6.47.: Principal Component Analysis (PCA) obtained from the list of identified odour active substances; PC1: principal component 1 explains 24% of the phenomenons for the sample; PC2: principal component 2 explains 16% of the phenomenons for the sample

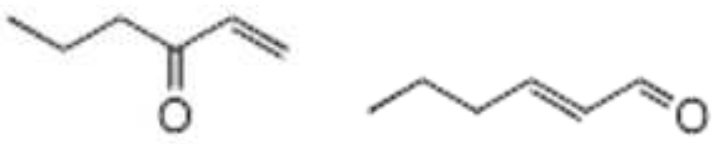
# Chapter 7

# Quantification Experiments

> “*Dosis sola venenum facit.*”
>
> [Philipus Aureolus Paracelsus, German (Swiss-born) alchemist & physician, (1493 - 1541)]

## 7.1. 1-Hexen-3-one and 2-Hexenal in 1-Hexene

Although the project was outlined to be exclusively a qualitative analysis of the samples, in the end the idea showed up to quantify some of the components. To serve this need in the only liquid sample the substances 1-hexene from Stenungsund 1-hexen-3-one and 2-hexenal were picked.



**(a)** **(b)**

Figure 7.1.: 1-Hexen-3-one (a) and 2-Hexenal (b)

The quantification was done by standard addition. The samples were spiked with the questionable substances. With the method *MS*$_{liquid}$ shown in table 4.4 the samples were measured.

$$OdourActivityValue = \frac{Concentration}{OdourThreshold}{}^{1} \tag{7.1}$$

$$OAV_i1 + OAV_i2 + ... + OAV_in \qquad = OAV_m \tag{7.2}$$

*where i1...in: compound 1,....,n in mixture m.*

Equation 7.1 shows the main idea of the *“Odour Activity Value” (OAV)*-concept (see {Grosch, 1993a}, {Grosch, 1993b} and {Rothe, 1963}). The concentration given in $\frac{mg}{kg}$ is divided through the so called

---

[1] all the used Odour Thresholds in this thesis are taken from {van Gemert, 2003}

*"Odour Threshold"* (also given in $\frac{mg}{kg}$). The term "Odour Threshold" describes the concentration of a substance which necessary to have a undifferentiated odour impression ("recognition") or to detect the substance correctly ("detection"). These values are given in literature but they vary from source to source.

Hence, the Odour Activity Value (OAV) describes the impact of a single substance to the overall odour impression. The overall odour impression is the sum of all contributing substance in a sample of interest (see equation 7.2).

Table 7.1.: Quantification of 1-Hexen-3-one and 2-Hexenal in 1-Hexene from Stenungsund; all the used Odour Thresholds in this table are the lowest found values from {van Gemert, 2003}

| | **Concentration** $\frac{mg}{kg}$ | **Odour Threshold** $\frac{mg}{kg}$ | **OAV** |
|---|---|---|---|
| **1-Hexene-3-one** | 1.375 | 0,0000005 | 2749057 |
| **2-Hexenal** | 0.620 | 0,030 | 21 |

Table 7.1 shows demonstratively that the concentration of a substance says nothing about her contribution to the overall odour impression. The concentration of 1-hexen-3-one is "just" 2 times higher than the concentration of 2-hexenal, but its contribution to the total odour impression is about 130000-fold higher. As outlined before in this chapter, the Odour Threshold is the concentration up to this no odour impression occurs. In this sample, the Odour Activity Value also describes the factor of needed reduction of substance amount in the chemical if it should not contribute to the odour impression.

## 7.2. A Thought Experiment

The tables in 7.2 show the theoretically "allowed" amount of the given 1-hexene in the polymer if 1-hexen-3-one and 2-hexenal should not contribute to the odour impression. This is of course a intellectual game, because it is not resolved if the impurities of the comonomer are passing the polymerization process or not.

Table 7.2.: Theoretically allowed amounts of(a) 1-Hexene-3-one and (b) 2-Hexenal if 100% of the substances pass the polymerization

| **1-Hexene** % | **1-Hexene-3-one** $\frac{mg}{kg}$ | **OAV** |
|---|---|---|
| **0,00001** | **0,00000014** | **0** |
| 10 | 0.137 | 274906 |
| 20 | 0.275 | 549811 |
| 30 | 0.412 | 824717 |

(a)

| **1-Hexene** % | **2-Hexenal** $\frac{mg}{kg}$ | **OAV** |
|---|---|---|
| **2** | **0.012** | **0** |
| 10 | 0.062 | 2 |
| 20 | 0.124 | 4 |
| 30 | 0.186 | 6 |

(b)

# Chapter 8

# Potential Odourous Input Through Process Chemicals

> “*The devil is in the detail.*”
>
> [English proverb.]

Borealis provided a list of chemicals which are used as so called ‘process chemicals’ during the polymerization process in Schwechat. This extensive list was separated into subgroups by evaluating the single substances. During this process some information deficiencies emerged. Many of these formulations are kind of blackboxes which were hardly to unseal. The needed information had to be brought from many different sources from all over Borealis company. So this evaluation stucked at a rather theoretic status. The main information of this exercise is the fact that - concerning the monomer impurity results of this whole thesis - the chemicals themselves should not bring a high contribution to the overall odour impression of the products as long as they are *clean*. The generated lists are attached in appendix section A.1.

# Chapter 9

# Outlook

> *"It's very easy to predict the future. People do it all the time. What you can't do, is get it right."*
>
> [Don Norman, The Front Desk, BBC Video, 1995.]

## 9.1. General Trends

The wish of having pure and clean plastic products will surely keep Borealis busy for a long time scale. Costumers and consumers will claim for non odorous products very lasting. So the approach of "we use what we get" won't lead to satisfying results in the attempt of producing non odorous products. Borealis will have to have much more strict claims to suppliers of monomers and will have to think of its own potential of cleaning monomers.

## 9.2. Ideas for Future Work

Although there were no real trends which could be identified, some odour active as well as non odour active substances could be identified as reoccurring throughout the project. If there is an interest in investigating monomer purity more concrete the single tasks should be worked on more detailed for example by shortening the time intervals of time dependency research from once every month to once every day.

Comparing the results of this thesis and the research done at the institute by Helene Hopfer in {Hopfer, 2010} shows that the substances which lead to changes of odour impression during processing and treatment are already present in the monomer. This fact leads to the question if the contribution of the monomer is surviving the polymerization process or not.

Following the monomer molecules through the polymerization process by radioactive isotopes would be a very cost-intensive investigational step with open result. Maybe the result will show that the monomer related impurities are completely destroyed through the polymerization process, maybe it will show that these impurities survive the polymerization. Since the result is not predictable - though the scientific work would not be needed - it is a decision to be made by Borealis scientists and economists.

# Chapter 10

# Concluding Remarks

> *“Everything has an end, only a sausage has two*
> *(Alles hat ein Ende nur die Wurst hat zwei).”*
>
> [German, Danish, and Dutch proverb.]

In the chapters 3, 4 and 5 the theoretical and instrumental setup of the project is outlined and explained. Chapter 6 shows original part of the work done in this project. Simply the look at the differences in between ethylene or propylene samples (see chapter 6.2) gives a good impression. The cluster shown in figure 6.1 indicates from the very beginning of the project that especially the ethylene samples are variating very much just because of their GC-MS data which does not say anything about odour. Various samples were measured and judged here to find that the traditional idea of having consistent monomers over the company or over the time (see chapter 6.3) in the same plant has to be abandoned. In the beginning there was the idea of finding trends in the impurities throughout the time dependency task. In this thesis trends could not be found. It seems to be very evident that the interval of sample taking is much too long. Also the influence of purification (see chapter 6.4) is not - as the term ‘purification’ imparts - always a good one. Since purification is meant to purify monomers mainly from catalyst poisons and other polymerization badly influencing substances this does not mean necessarily to put away odour relevant substances. In chapter 6.5 the possible influences of comonomers and diluents were investigated. The comonomers and diluents do not have an over proportional odour impression compared to the ethylene samples from Stenungsund, which would be necessary to contribute notably to the overall odour impression.

Chapter 7 showed that the simple determination of substance quantities does not give a useful idea of its contribution to the overall odour impression. The concept of Odour Activity Values gives a good idea of a components input on overall odour impression.

Chapter 8 shows the manifold chemicals used in plastics production. Apparently there are not so many substances which are contributing ‘themselves’ to the odour of the products. But - as outlined in the monomer purity investigation - there might be some impurities in the used chemicals which are contributing to odour.

At a glance it can be summed up that monomer purity is not a constant factor which can be counted on in odour relevant terms. Large differences in between plants or over the time have to be expected. Purification is irrelevant for odorous problems.

# Appendix A

# Appendix

*"The point of quotations is that one can use another's words to be insulting."*

[Amanda Cross, US mystery novelist (1926 - )]

## A.1. Lists Of Process Chemicals

Table A.1.: Table of chemicals with characteristic odour but no definite impact on odour in a clean condition, part 1

| line | line no. | substance formulation | synonym | formula | CAS no |
|---|---|---|---|---|---|
| PE4 | B130 | nitrogen | | | |
| var. | | PP polymer granules | | | |
| var. | | PP polymer powder | | | |
| PP3 | 862 | hydrogen | | $H_2$ | 1333-74-0 |
| var. | | carbon monoxide | | CO | 00630-08-0 |
| var. | | carbon dioxide | | $CO_2$ | |
| var. | | hydrogen | | $H_2$ | 1333-74-0 |
| PE4 | B130 | propane liquid | | | |
| PP5 | D 202 | calcium stearate | AS110PWD | | 1592-23-0<br>85251-71-0 |
| PP3 | 863 | calcium stearate / calcium stearate S | | | 1592-23-0<br>85251-71-0 |
| var. | | TEAL (triethyl aluminium 96 %) | triethyl aluminium | | 97-93-8 |

Table A.2.: Table of chemicals with characteristic odour but no definite impact on odour in a clean condition, part 2

| line | line no. | substance formulation | synonym | formula | ingredient 1 | CAS no.1 | ingredient 2 | CAS no.2 | ingredient 3 | CAS no.3 |
|---|---|---|---|---|---|---|---|---|---|---|
| LDPE | | TBPND/ TMBPPI 30m% in iC12 | | | isododecane | 31807-55-3 | tert-butyl peroxy-neodecanoate | 26748-41-4 | 1,1,3,3-tetramethyl-butyl peroxy pivalate | 22288-41-1 |
| LDPE | | TBPEH 30m% in iC12 | | | isododecane | 31807-55-3 | tert-butylperoxy-2-ethyl hexanoate | 3006-82-4 | | |
| LDPE | | TBPIN/BU 30m% in iC12 | | | isododecane | 31807-55-3 | tert-butyl peroxy-3,5,5-trimethyl hexanoate | 13122-18-4 | 2,2 di-(tert-butylperoxy) butane | 2167-23-9 |
| LDPE | | DTBP 30m% in iC12 | | | isododecane | 31807-55-3 | di-tert-butyl peroxide | 110-05-4 | | |
| LDPE | | isododecane | | | hydrocarbons, C4, 1,3-butadiene free, polymerised, triisobutylene part, hydrolysed | 93685-81-5 | 2,2,4,6,6-pentamethyl heptane | 13475-82-6 | | |
| var. | | ethylene | ethylene | $CH_2 = CH_2$ | | 74-85-1 | | | | |
| PE4 | B130 | Isododecane | | | | | | | | |
| var. | | propylene liquid | propylene liquid | $CH_2 = CH - CH_3$ | propylene | 115-07-1 | | | | |
| var. | | propylene gaseous | propylene gaseous | $CH_2 = CH - CH_3$ | propylene | 115-07-1 | | | | |
| PE4 | B130 | steam | | | | | | | | |
| PE4 | B130 | condensate | | | | | | | | |

Table A.3.: Table of chemicals with characteristic odour but no definite impact on odour in a clean condition, part 3

| line | line no. | substance formulation | synonym | formula | ingredient 1 | CAS no.1 | ingredient 2 | CAS no.2 |
|---|---|---|---|---|---|---|---|---|
| PE4 | B135 | TEAL (triethylaluminium 96 %) | | | | | | |
| PE4 | B130 | isopropanol | | | | | | |
| var. | | sodium hypochloride solution | | | | 7681-52-9 | | |
| PE4 | B130 | 1-butene | | | | | | |
| PP5 | D202 | Silica MB | SA452PEL | 40 % SA251 in low molecular weight (wax) carrier | Sodium calcium aluminosilicate, hydrate | 1344-01-0 | ”low molecular weight wax carrier” | |
| PP5 | D202 | SHT | AS400PWD | $Al_2Mg_6(OH)_{16}CO_3 \cdot 4H_2O$ | synthetic hydrotalcite | 11097-49-9 | | |
| var. | | Talkum 97 % (+ Chlorit, Dolomit, Quarz) | | | | 14807-877-9 | | |
| var. | | ethylene glycol 50 % | ethylene glycol | $C_2H_4(OH)_2$ | | 107-21-1 | | |
| PP5 | D 202 | glycerol monostearate | AA120PWD | | | 31566-31-1 | | |
| PP5 | D202 | GMS40 | AA100PWD | | glycerol monostearate | 97593-29-8 (31566-31-1) | | |
| PP5 | D202 | Dimodan HPL 80 | AA191PEL | Composition : AA 120:AA130 = 83,3 : 16,7 | GMS (¿90%) | 31566-31-1(GMS) /97593-29-8 | GML glycerol monolaureate | 142-18-7 (GML), 97593-29-8 |

Table A.4.: Table of chemicals with characteristic odour but no definite impact on odour in a clean condition, part 4

| line | line no. | substance formulation | synonym | formula | ingredient 1 | CAS no.1 | ingredient 2 | CAS no.2 |
|---|---|---|---|---|---|---|---|---|
| PE4 | B130 | AS 100/Ca St | | | calcium stearate (no filtertest requirement) | 1592-23-0 | | |
| PP3 | 862 | paraffin oil | | | | 8042-47-5 | | |
| PP5 | D 201 | vinyl cyclohexane 98 % | ethenyl cyclohexane | $C_8H_{14}$ | | 695-12-5 | | |
| PP5 | D202 | Incroslip C | SA101GRA | $Mg_3[(OH)_2][Si_4O_{10}]$ or $3MgO4SiO_2 \cdot H_2O$ | | 14801-96-6 (98%), 1318-59-8, 83897-85-2, 16389-88-1, 13397-27-7 | | |
| PP5 | D202 | Crodamide SA-150 | SA110GRA | | | 301-02-2 | | |
| PP5 | D 202 | erucic acid amide | SA100GRA | | | 112-84-5 | | |
| PP5 | D202 | silica | | | erucamide (13-docosene amide) | 7631-86-9 / 112-84-5 | silica | |
| PP5 | D202 | erucamide/ silica (pre-blend) | SA304PWD | | erucamide (13-docosene amide) | 112-84-5 | synthetic amorphous silica, chemically prepared | 7631-86-9 |
| | | Incroslip C | SA101GRA | | erucamide (13-docosene amide) | 112-84-5 | | |
| | | 1,3-butadiene | | | | | | |
| var. | | sulfuric acid 96 % | | $H_2SO_4$ | | | | |

Table A.5.: Chemicals listed here might have an input on overall odour impression

| line | line no. | substance formulation | synonym | formula | ingredient 1 | CAS no.1 | ingredient 2 | CAS no.2 | ingredient 3 | CAS no.3 |
|---|---|---|---|---|---|---|---|---|---|---|
| PP5 | D205 | DREWGARD 315 | alk. solution: NaOH, sodium tolyl triazole | | | 7631-95-0<br>64665-57-2<br>1310-73-2 | | | | |
| PP5 | D205 | PERFORMAX 404 E | alk. solution: NaOH, triazole, inhibitors | | | 64665-57-2<br>1310-73-2 | | | | |
| LDPE | | PA | propanal | $CH_3CH_2CHO$ | propanal | 123-38-6 | | | | |
| LDPE | | nBA | acrylic acid butyl ester | $CH_2 = CHCOO(CH_2)_3CH_3$ | acrylic acid butyl ester | 141-32-2 | | | | |
| PP3 | 863 | stabilizer Hostanox SE 10; Alvinox 100; Millad 3988 | AO320, Alvinox, NU230 | | di-octadecyl-disulphide | 2500-88-1 | Alvinox 100 | | 2,4 Bis(3,4-dimethyl benzylidene) sorbitol | 135861-56-2 |
| PP5 | D205 | BIOSPERSE 250 | biocide; isothiazolin mix | | | 55965-84-9 | | | | |

Table A.6.: Chemicals shown in this table are additives used in the process; their odourous effect is unknown, part 1

| line | line no. | substance/ formulation | synonym | formula | ingredient 1 | CAS no.1 | ingredient 2 | CAS no.2 | ingredient 3 | CAS no.3 | ingredient 4 | CAS no.4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PP5 | D202 | Palmarole MBA 115 | OP725PEL2 | AO101 : AO200 : AS110 : AS400 : NU302 : PP pwd = 13,0 : 26,4 : 19,7 : 19,7 : 19,7 : 1,5 | AO101 pentaerythrityl-tetrakis(3-(3’,5’-di-tert. butyl-4-hydroxyphenyl)) propionate | AO101=6683-19-8, AO200=31570-04-4, AS110=1592-23-0, AS400=11097-59-9, NU302=151841-65-5 | AO200 Tris (2,4-di-t-butylphenyl) phosphite | | AS110 calcium stearate thermostable | | AS400 synthetic hydrotalcite | |
| PP5 | D202 | Palmarole MBA 130 | OP729PEL2 | AO101 : AO200 : AS400 : NU302 : co-additive : PP = 14,4 : 14,4 : 8,7 : 48,8 : 12,2 : 1,5 | AO101 | 6683-19-8 | AO200 Tris (2,4-di-t-butylphenyl) phosphite | 31570-04-4 | AS400 synthetic hydrotalcite | 110 97-59-9 | NU302 Hydroxybis (2,4,8,10-tetra-tert. butyl-6-hydroxy-12H-dibenzo(d,g)(1.,3,2) dioxaphosphocin 6-oxidato) aluminium | 151 841-65-5 |
| PE4 | B130 | | OP 163 | AO101 : AO210 : AS100 = 13,3 : 26,7 : 60,0 | AO101 | 6683-19-8 | AO210 | 154 862-43-8 | AS100 | 1592-23-0 | | |
| PP5 | D202 | Irganox CB OP 164 DD | OP164PEL2 | AO103 : AO200 : AS110 = 50,0 : 16,7 : 33,3 | AO103 1,3,5-tri-methyl-2,4,6-tris-(3,5-di-tert. butyl-4-hydroxyphenyl) benzene | 001709-70-2 | Tris (2,4-di-t-butylphenyl) phosphite | 315 70-04-4 | Calcium stearate, thermostable | 1592-23-0 | | |
| PP5 | D202 | Anox NDP OP118 | OP118PEL2 | AO101 : AO200 : AS350 = 29,0 : 58,0 : 13,0 | AO101 pentaerythrityl-tetrakis(3-(3’,5’-di-tert. butyl-4-hydroxyphenyl)) propionate | 6683-19-8 | AO200 Tris (2,4-di-t-butylphenyl) phosphite | 315 70-04-4 | Magnesium oxide | 130 9-48-4 | | |
| PP5 | D202 | Irganox CB3829 FF | OP121GRA | AO200 : AO900 : UV220 = 53,8 : 23,1 : 23,1 | AO200 | 315 70-04-4 | AO900 5,7-di-tert. butyl-3-(3,4-di-methylphenyl)-3H-benzofuran-2-one (90 %) + 5,7-di-tert. butyl-3-(2,3-di-methylphenyl)-3H-benzofuran-2-one (10 %) | 181 314 -48 -7 | UV220=Dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol | 71878-19-8 | | |

Table A.7.: Chemicals shown in this table are additives used in the process; their odourous effect is unknown, part 2

| line | line no. | substance formulation | synonym | formula | ingredient 1 | CAS no.1 | ingredient 2 | CAS no.2 |
|---|---|---|---|---|---|---|---|---|
| PP5 | D202 | Irganox B561 FF | AO500GRA | AO101 : AO200 = 1:4 | AO101 pentaerythrityl-tetrakis(3-(3’,5’-di-tert. butyl-4-hydroxyphenyl)) propionate | 6683-19-8 | AO200 Tris (2,4-di-t-butylphenyl) phosphite | 31570-04-4 |
| PP3 | 863 | Chimasorb 119FL | | UV222 | 1,3,5-triazine-2,4,6-triamine, N,N”’-(1,2-ethane-diylbis(((4,6-bis(butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino)-1,3,5-triazine-2-yl) imino)-3,1-propanediyl))-bis-(N’,N”-dibutyl-N’,N”-bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)) | 90% 106990-43-6 | Dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol | 065447-77-0 |
| PE4 | B130 | Irganox B 215 FF | AO101 : AO200 = 1:2 | | AO101 | 6683-19-8 | Tris (2,4-di-t-butylphenyl) phosphite | 31570-04-4 |
| PE4 | B130 | Irganox B 225 FF | AO101 : AO200 = 1:1 | | AO101 | 6683-19-8 | Tris (2,4-di-t-butylphenyl) phosphite | 31570-04-4 |
| PE4 | B130 | Irganox B 561 FF | AO101 : AO200 = 1:4 | | AO101 | 6683-19-8 | Tris (2,4-di-t-butylphenyl) phosphite | 31570-04-4 |

Table A.8.: Chemicals shown in this table are additives used in the process; their odourous effect is unknown, part 3

| line | line no. | substance formulation | synonym | formula | ingredient 1 | CAS no.1 |
|---|---|---|---|---|---|---|
| PP5 | D 202 | Irganox 3114 | AO106PWD | | 1,3,5-Tris(3',5'-di-tert. butyl-4'-hydroxybenzyl)-isocyanurate | 27676-62-6 |
| LDPE | | 1,7-octadiene | 1,7-octadiene | $CH_2 = CH(CH_2)_4 CH = CH_2$ | 1,7-octadiene | 3710-30-3 |
| PE4 | B130 | Tinuvin 622 FB | | | dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol | 65447-77-0 |
| LDPE | | hexadecyl trimethoxy silan | | $C_{16}H_{33}Si(OCH_3)_3$ | hexadecyl trimethoxy silane | 16415-12-6 |
| PE4 | B130 | Ethanox 330P | | | pentaerythrityl-tetrakis(3-(3',5'-di-tert. butyl-4-hydroxyphenyl)) propionate | 6683-19-8 |
| PP5 | D202 | Irganox 1010 FF | AO101GRA | | pentaerythrityl-tetrakis(3-(3',5'-di-tert. butyl-4-hydroxyphenyl)) propionate | 6683-19-8 |
| PP3 | 863 | NA11 | NU301 | | sodium 2,2'-methylene bis-(4,6-di-tert. butylphenyl) phosphate | 85209-91-2 |
| PP5 | D 202 | Irgafos 168 | AO200 | | tris (2,4-di-t-butylphenyl) phosphite | 31570-04-4 |
| PE4 | B130 | Irgafos 168 | | | tris (2,4-di-t-butylphenyl) phosphite | 31570-04-4 |
| LDPE | | vinyl trimethoxy silane, trimethoxy vinyl silane | | $(CH_3O)_3SiCH = CH_2$ | vinyl trimethoxy silane | 2768-02-7 |
| PP3 | 863 | stabilizer Irganox B 215, 225, B 1411; Irgafos 168; Irganox MD 1024; Alkanox 240 | AO101 : AO200 = 1:2 | | | |

Table A.9.: Chemicals shown in this table are additives used in the process; their odourous effect is unknown, part 4

| line | line no. | substance formulation | synonym | formula | ingredient 1 | CAS no.1 |
|---|---|---|---|---|---|---|
| PP3 | 863 | stabilizer ANOX PP18; Irganox 1010, 1076, 3114; Irgafos P EPQ; BHT | AO101, AO201, AO100 | | | |
| PP5 | D 202 | Irganox PS802FL (TPS) | AO300FLA | | | 693-36-7 |
| PP5 | D 202 | stabilizer Irganox B 215, Anox BB 021, hostanox M102 FF | AO501GRA | AO101 : AO200 = 1:2 | | A: 6683-19-8 B:31570-04-4; Blend A:B=1:1 |
| PP5 | D 202 | Anox BB011, Irganox B-225FF, Hostanox M101 | AO502GRA | AO101 : AO200 = 1:1 | | A: 6683-19-8 B:31570-04-4; Blend A:B=1:1 |
| PP5 | D 202 | Anox NDB BZ4A | OP718PEL2 | AO101 : AO200 : AS400 : NU120 = 9,3 : 37,2 : 14,0 : 39,5 | | |
| PP5 | D 202 | Anox NDP | | | | |
| PP5 | D 202 | Irganox HP 2215 FF | | | | 181314-48-7 |
| PP3 | 862 | cooling agent R 22 | chlordiflour methane | | | 75-45-6 |
| PP5 | D205 | DREWGARD 180 E | Phosphonaten, Polymere, Dispergatoren | | | 37971-36-1 |
| PP5 | D205 | DREWSPERSE 739 | aqueous tenside solution | | | |

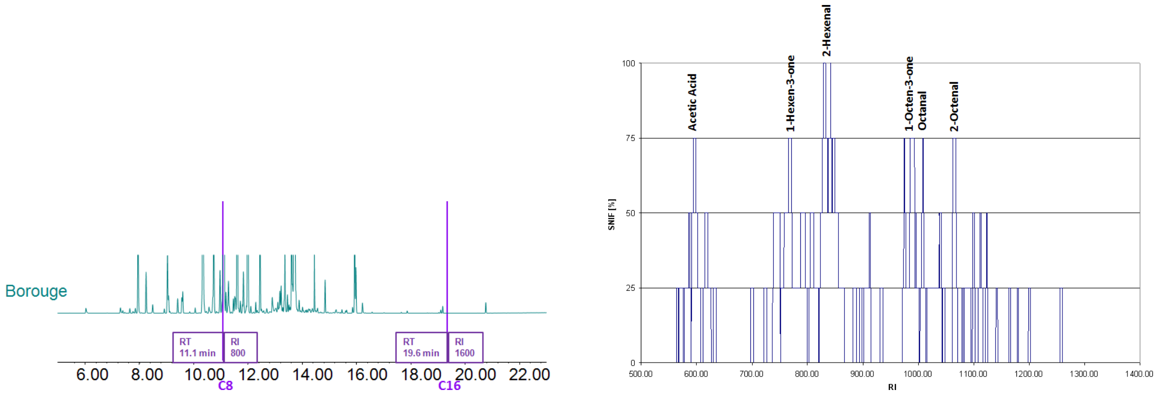
Table A.10.: For the chemicals given in this table not enough information was given by Borealis

| line | line no. | substance formulation | synonym | formula | CAS no.1 |
|---|---|---|---|---|---|
| PE4 | B130 | Octastat | missing | | |
| PE4 | B130 | Primol 352 D | missing | | |
| PE4 | B130 | catalyst BCM 25E | missing | | |
| PE4 | B130 | catalyst BCG 40E | missing | | |
| PE4 | B130 | catalyst BCD 80E | missing | | |
| PP3 | 862 | Donor C | missing | | |
| PP3 | 862 | Donor D | missing | | 126990-35-0 |
| PP3 | 863 | peroxide Trigonox B | missing | DTBP | 110-05-4 |
| PP3 | 862 | catalyst ZN M1 Avant | missing | | |
| PP3 | 862 | catalyst BCF20P | missing | | |
| PP3 | 865 843 | Biosperse 250 | missing | | |
| PP3 | 865 843 | Performax 404 E | missing | | |
| PP3 | 862 | Grinsted PS 432 | missing | | 9007-48-1 330198-91-9 |
| PP5 | D 201 | BCF20P catalyst | missing | | |
| PP5 | D 201 | Grindsted PS 432 | missing | glycerides | 736150-63-3 |
| PP5 | D 201 | mineral oil | missing | | 8042-47-5 |
| LDPE | | cylinder oil KPL 201 | missing | | |
| LDPE | | Primol 352 | missing | | |
| LDPE | | machine oil 220 | missing | | |
| PE4 | B130 | Masterbatch | missing | | |
| | | Shell Cassida HF205 | missing | | |
| | | var. oils | missing | | |

# A.2. Identified Substances

## A.2.1. Correlation between Volatile Impurities & Odour Active Substances

### Ethylene from Borouge



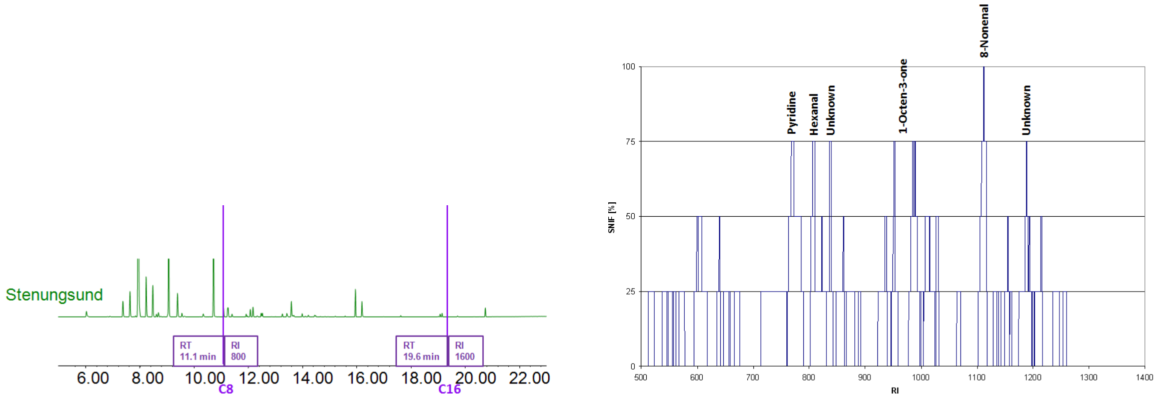
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 2.55 | Cyclopropane | - | | |
| 7.94 | Hexane | 592 | 600 | Acetic Acid |
| 8.23 | Acetic acid ethyl ester | 612 | | |
| 8.48 | Methyl-cyclopentane | 628 | | |
| 9.04 | 1-Butanol | 664 | | |
| 9.41 | 2-Pentanone | 688 | | |
| 9.60 | Heptane | 700 | | |
| 10.35 | Pyridine | 751 | | |
| 10.74 | Toluene | 777 | 778 | 1-Hexen-3-one |
| 10.98 | 1-Butyl-2-methylcyclopropane | 793 | | |
| 11.12 | Octane | 803 | | |
| 11.19 | 2-Octene | 808 | | |
| 11.47 | 5-Methyl-3-hexen-2-one | 829 | | |
| 11.62 | 2-Methyl-2-Pentenal | 840 | 844 | 2-Hexenal |
| 11.73 | 2-Methyl-2-cyclopentenone | 848 | | |
| 11.84 | 2,4-Octadiene | 857 | | |
| 12.29 | 3-Heptanone | 890 | | |
| 12.45 | Nonane | 902 | | |
| 13.22 | 5-Methyl-nonane | 963 | | |
| 13.36 | 3-Methyl-nonane | 975 | 984 | 1-Octen-3-one |
| 13.61 | 1-Decene | 994 | | |
| 13.73 | Decane | 1004 | 1007 | Octanal |
| 14.45 | 2-Methyl-decane | 1067 | 1067 | 2-Octenal |
| 14.85 | Undecane | 1102 | | |
| 15.93 | Dodecane | 1202 | | |

(c)

Figure A.1.: Compilation of volatile and odour active components in Ethylene from Borouge

## Ethylene from Stenungsund



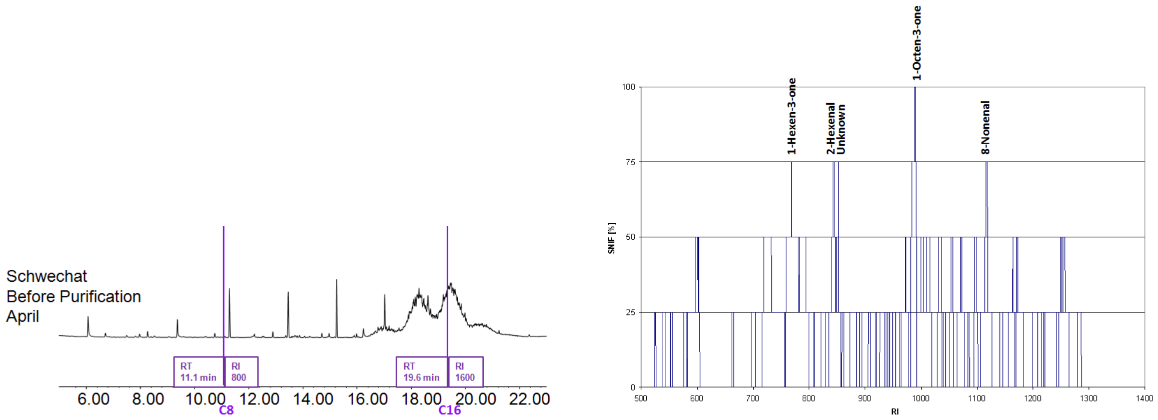
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 2.53 | Propene | - | | |
| 4.04 | 2-Methylpropene | - | | |
| 7.38 | 2-Methylpentane | 549 | | |
| 7.64 | 3-Methylpentane | 568 | | |
| 7.94 | Hexane | 592 | | |
| 8.23 | Acetic acid ethyl ester | 612 | | |
| 8.47 | Methylcyclopentane | 627 | | |
| 9.06 | Benzene | 665 | | |
| 9.40 | 2-Pentanone | 687 | | |
| 10.71 | Toluene | 775 | 772 | Pyridine |
| 11.08 | Hexanal | 800 | 798 | Hexanal |
| 12.17 | Xylene | 881 | 839 | Unknown |
| 13.59 | 2-Octanone | 993 | 984 | 1-Octen-3-one |
| | | | 1104 | 8-Nonenal |
| | | | 1175 | Unknown |

(c)

Figure A.2.: Compilation of volatile and odour active components in Ethylene from Stenungsund

### Ethylene from Schwechat; used in “PE monomers”, “before” Purification & Time Dependency “April”



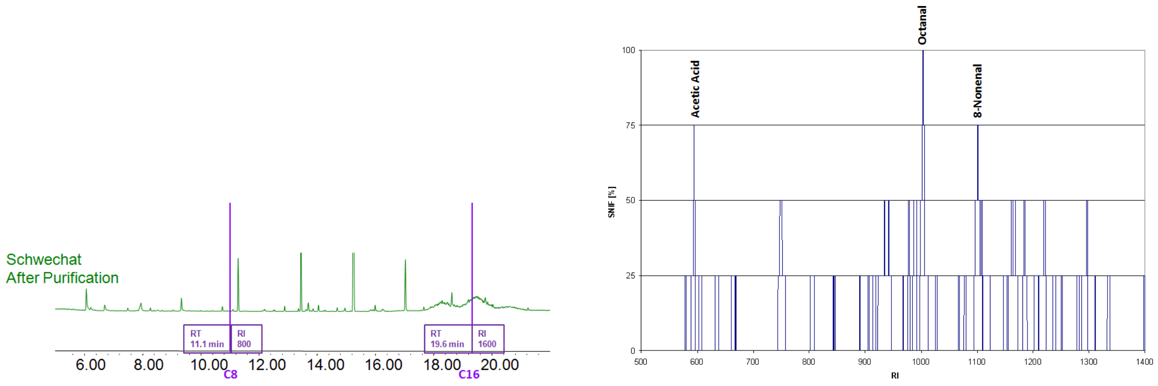
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 6.08 | Acetone | - | 778 | 1-Hexen-3-one |
| | | | 844 | 2-Hexenal |
| | | | 852 | Unknown |
| | | | 984 | 1-Octen-3-one |
| | | | 1104 | 8-Nonenal |
| 17.95 | 7-Hexadecene | 1411 | | |
| 18.39 | 1-Decene | 1461 | | |
| 18.47 | 3-Hexadecene | 1470 | | |
| 19.19 | 3-Heptadecene | 1555 | | |
| 19.54 | 9-Octadecene | 1597 | | |
| 19.62 | 3-Octadecene | 1607 | | |

(c)

Figure A.3.: Compilation of volatile and odour active components in Ethylene from Schwechat; used in the tasks “PE monomers” as sample for Schwechat, “Time Dependency” as April sample for Schwechat and “Purification” as sample “before purification” from Schwechat

## Ethylene from Schwechat; “after” Purification



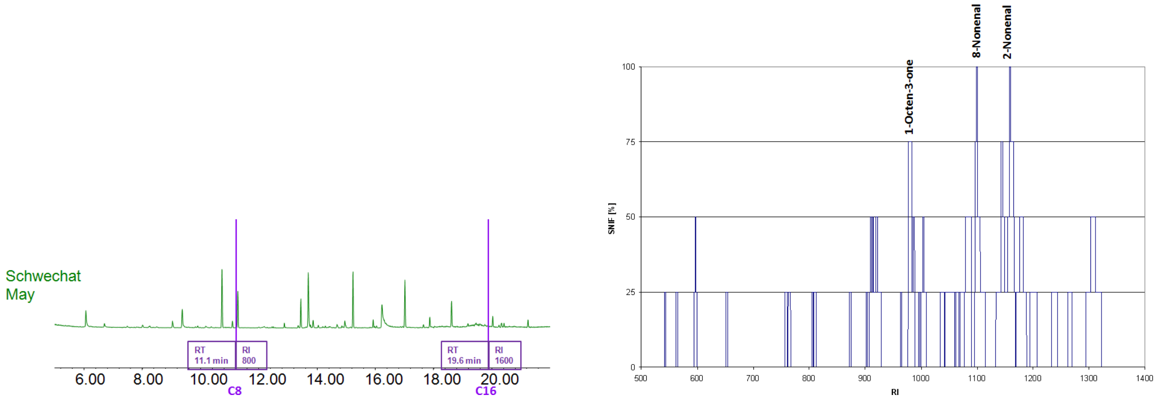
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 6.07 | Acetone | - | 600 | Acetic Acid |
| 13.70 | Decane | 1002 | 1007 | Octanal |
| | | | 1104 | 8-Nonenal |
| 19.45 | 3-Octadecene | 1586 | | |

(c)

Figure A.4.: Compilation of volatile and odour active components in Ethylene from Schwechat “after purification”

## Ethylene from Schwechat; “May”



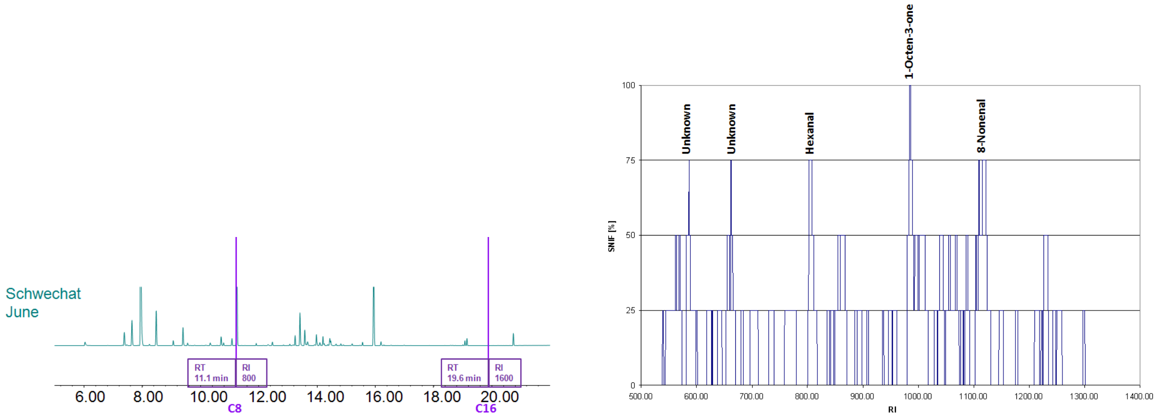
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 10.75 | Toluene | 778 | | |
| 13.71 | Decane | 1003 | 984 | 1-Octen-3-one |
| | | | 1104 | 8-Nonenal |
| | | | 1162 | 2-Nonenal |

(c)

Figure A.5.: Compilation of volatile and odour active components in Ethylene from Schwechat “May”

## Ethylene from Schwechat; “June”



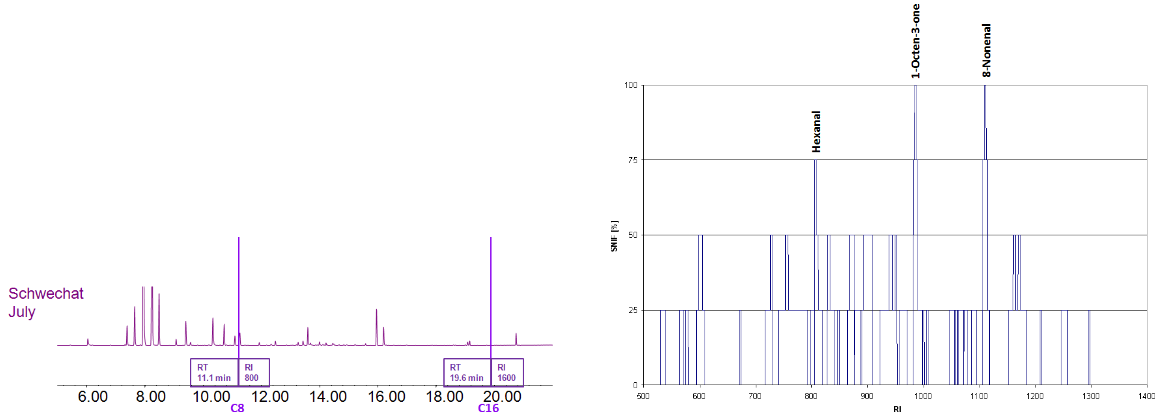
**(a)** **(b)**

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 7.38 | 2-Methyl-pentane | 549 | | |
| 7.64 | 3-Methyl-pentane | 569 | | |
| 7.94 | Hexane | 592 | 586 | Unknown |
| 8.48 | Methyl-cyclopentane | 628 | | |
| 9.40 | 2-Pentanone | 687 | 662 | Unknown |
| 10.72 | Toluene | 776 | 798 | Hexanal |
| 13.59 | 2-Octanone | 993 | 984 | 1-Octen-3-one |
| | | | 1104 | 8-Nonenal |

**(c)**

Figure A.6.: Compilation of volatile and odour active components in Ethylene from Schwechat “June”

## Ethylene from Schwechat; “July”



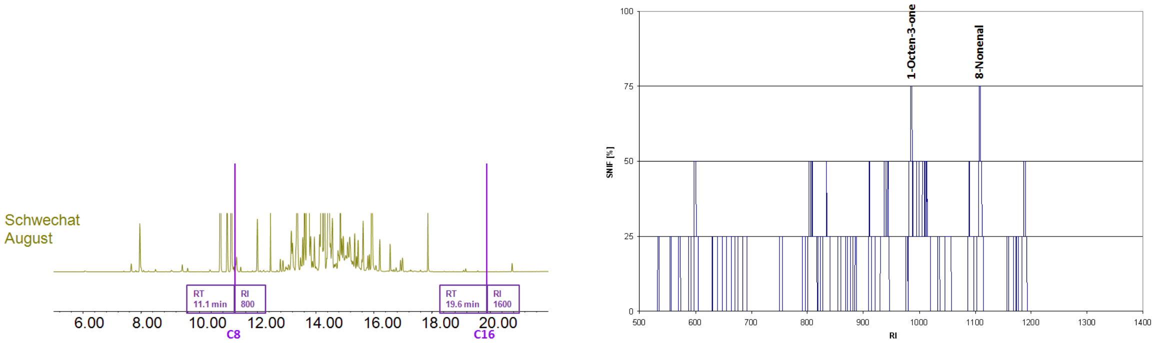
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 4.06 | 2-Methyl-1-propene | - | | |
| 7.65 | 3-Methyl-pentane | 570 | | |
| 7.95 | Hexane | 593 | | |
| 8.25 | Ethyl Acetate | 613 | | |
| 8.49 | Methyl-cyclopentane | 628 | | |
| 9.40 | 2-Pentanone | 688 | | |
| 10.33 | Pyridine | 750 | | |
| 10.72 | Toluene | 776 | | |
| 11.09 | Hexanal | 801 | 798 | Hexanal |
| 13.60 | 2-Octanone | 994 | 984 | 1-Octen-3-one |
| | | | 1104 | 8-Nonenal |

(c)

Figure A.7.: Compilation of volatile and odour active components in Ethylene from Schwechat “July”

### Ethylene from Schwechat; “August”



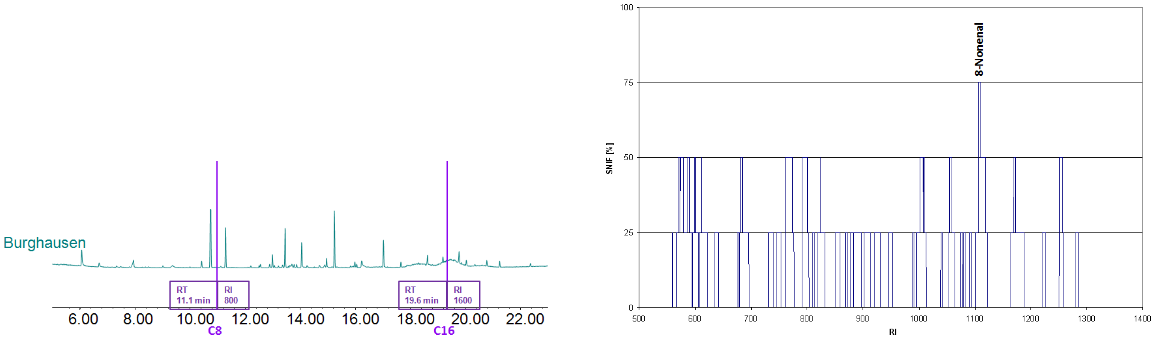
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 4.07 | 2-Methyl-1-propene | - | | |
| 7.96 | Hexane | 593 | | |
| 10.96 | 3-Methylene-heptane | 792 | | |
| 11.10 | Octane | 802 | | |
| 11.99 | 5-Methyl-undecane | 868 | | |
| 12.45 | Nonane | 902 | | |
| 13.22 | 5-Methyl-nonane | 963 | | |
| 13.37 | 3-Methyl-nonane | 975 | | |
| 13.56 | 2,3-Dimethyl-1-hexene | 991 | 984 | 1-Octen-3-one |
| 13.63 | Cyclodecane | 996 | | |
| 13.73 | 3-Ethyl-2-methyl-heptane | 1005 | | |
| 13.84 | 1,2,4-Trimethyl-benzene | 1014 | | |
| 14.45 | 2-Methyl-decane | 1067 | | |
| 14.85 | Undecane | 1102 | 1104 | 8-Nonenal |
| 15.63 | 3-Methyl-undecane | 1174 | | |
| 15.79 | 3-Methylene-undecane | 1189 | | |
| 15.84 | 1-Dodecene | 1194 | | |
| 15.94 | Dodecane | 1204 | | |
| 16.92 | Tridecane | 1302 | | |
| 16.99 | 1,3,5-Trimethyl-2-propyl-benzene | 1309 | | |
| 17.86 | Tetradecane | 1401 | | |

(c)

Figure A.8.: Compilation of volatile and odour active components in Ethylene from Schwechat “August”

## Propylene from Burghausen



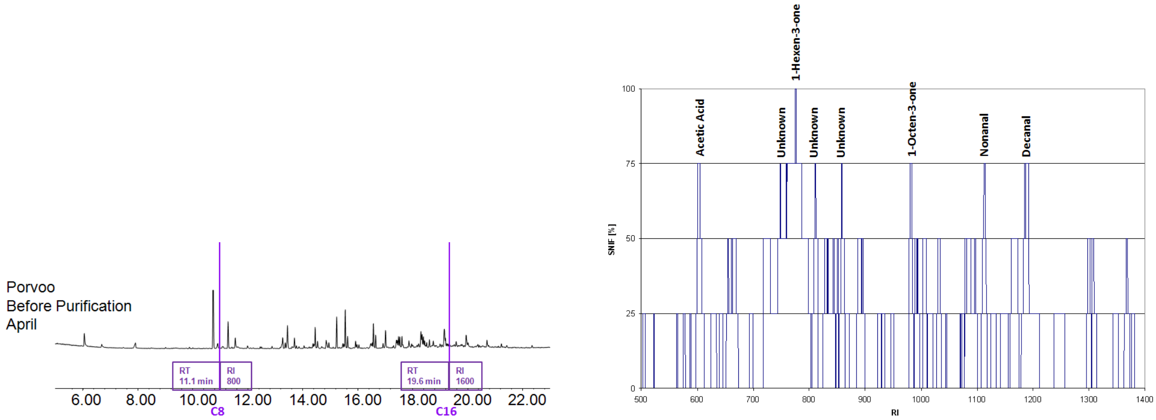
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 6.07 | Acetone | - | | 8-Nonenal |
| 10.74 | Toluene | 777 | | |
| 12.99 | 3-Methyl-3-heptanol | 945 | | |
| 14.05 | 2-Ethyl-hexanol | 1032 | 1104 | |
| 14.96 | Nonanal | 1112 | | |
| 19.77 | Diethyl phthalate | 1626 | | |

(c)

Figure A.9.: Compilation of volatile and odour active components in Propylene from Burghausen

### Propylene from Porvoo; used in “PP monomers”, “before” Purification & Time Dependency “April”



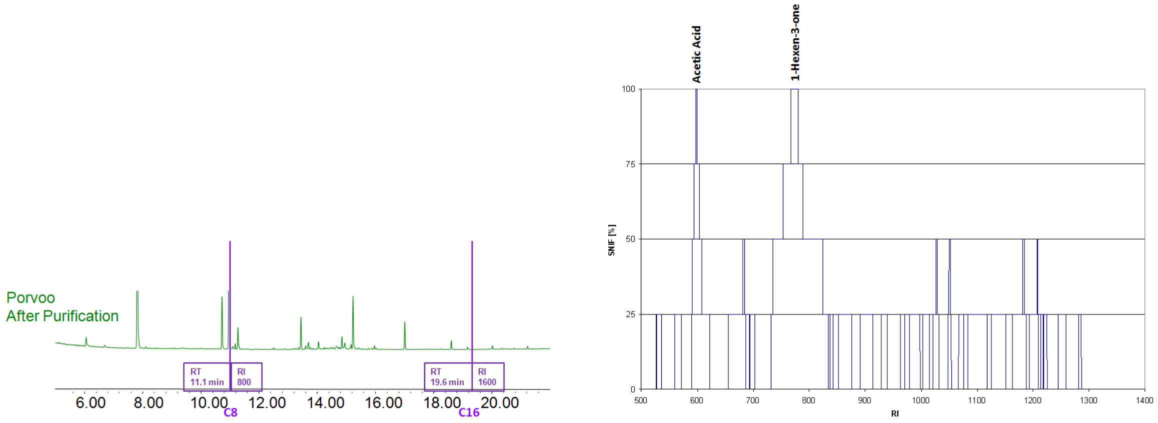
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 6.05 | Acetone | - | 600 | Acetic Acid |
| | | | 748 | Unknown |
| 10.73 | Toluene | 777 | 778 | 1-Hexen-3-one |
| | | | 811 | Unknown |
| | | | 860 | Unknown |
| 13.69 | Decane | 1001 | 984 | 1-Octen-3-one |
| 14.45 | 2-Methyl-decane | 1067 | 1104 | Nonanal |
| 15.54 | 2-Methyl-undecane | 1166 | | |
| 15.63 | 3,8-Dimethyl-decane | 1174 | 1204 | Decanal |
| 16.65 | 2,9-Dimethyl-undecane | 1274 | | |
| 17.61 | 3-Methyl-tridecane | 1374 | | |
| 18.34 | 5-Methyl-tetradecane | 1456 | | |
| 19.15 | Squalane | 1550 | | |
| 19.95 | Hexadecane | 1649 | | |

(c)

Figure A.10.: Compilation of volatile and odour active components in Propylene from Porvoo; used in the tasks “PP monomers” as sample for Porvoo, “Time Dependency” as April sample for Porvoo and “Purification” as sample “before purification” from Porvoo

### Propylene from Porvoo; “after” Purification



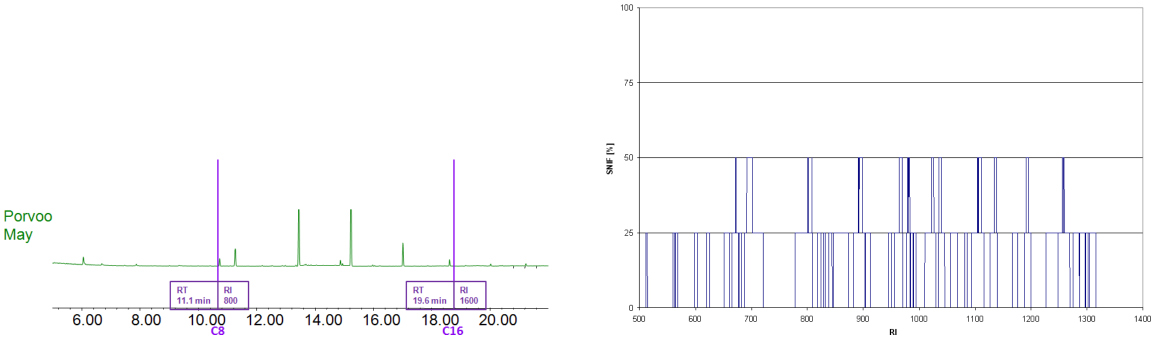
**(a)** **(b)**

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 7.81 | 4-Pentenal | 582 | | |
| | | | 600 | Acetic Acid |
| 10.73 | Toluene | 777 | 778 | 1-Hexen-3-one |
| 10.97 | cis-1-Butyl-2-methylcyclopropane | 793 | | |

**(c)**

Figure A.11.: Compilation of volatile and odour active components in Propylene from Porvoo “after purification”

## Propylene from Porvoo; “May”



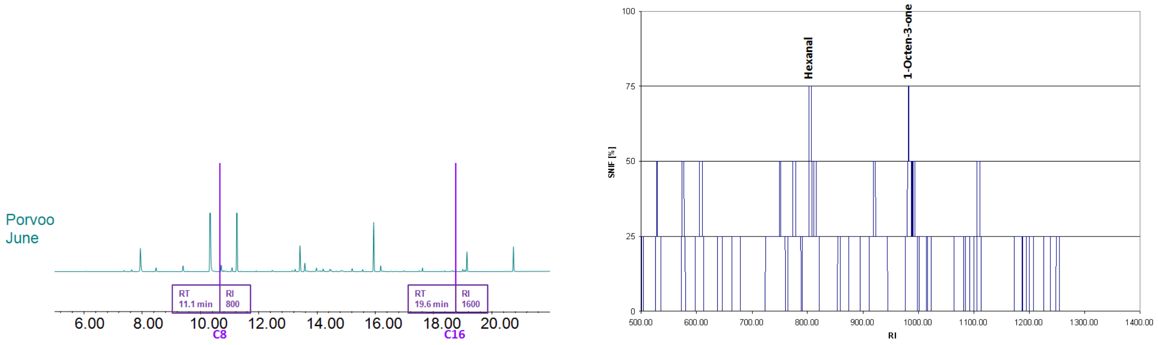
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|

(c)

Figure A.12.: Compilation of volatile and odour active components in Propylene from Porvoo “May”

## Propylene from Porvoo; “June”



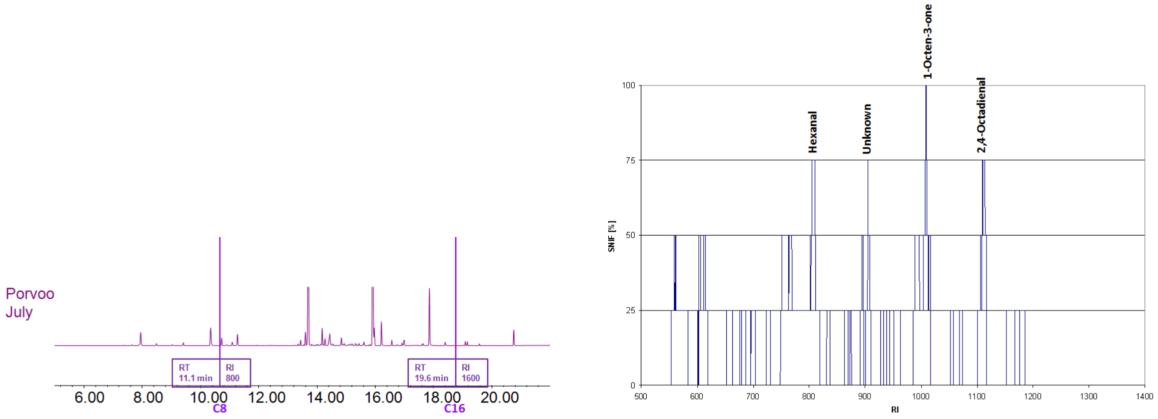
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 7.94 | Hexane | 591 | | |
| 10.33 | Pyridine | 749 | | |
| | | | 798 | Hexanal |
| | | | 984 | 1-Octen-3-one |
| 13.59 | 2-Octanone | 993 | | |

(c)

Figure A.13.: Compilation of volatile and odour active components in Propylene from Porvoo “June”

## Propylene from Porvoo; “July”



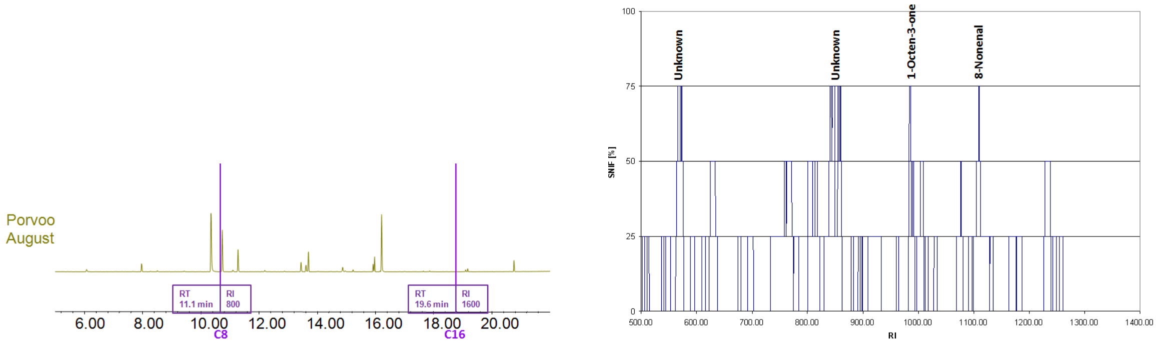
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 7.95 | Hexane | 592 | | |
| 10.35 | Pyridine | 751 | | |
| | | | 798 | Hexanal |
| | | | 904 | Unknown |
| 13.60 | 2-Octanone | 994 | 984 | 1-Octen-3-one |
| | | | 1113 | 2,4-Octadienal |
| 15.92 | Dodecane | 1201 | | |
| 17.85 | Tetradecane | 1400 | | |

(c)

Figure A.14.: Compilation of volatile and odour active components in Propylene from Porvoo “July”

## Propylene from Porvoo; “August”



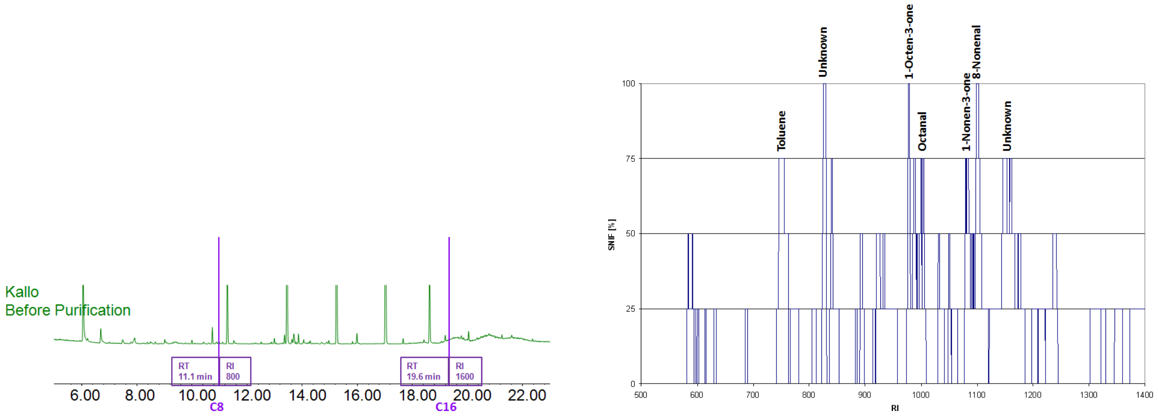
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| | | | 562 | Unknown |
| 10.35 | Pyridine | 751 | | |
| 10.74 | Toluene | 777 | | |
| | | | 844 | 2-Hexenal |
| | | | 984 | 1-Octen-3-one |
| 13.70 | Decane | 1002 | | |
| | | | 1104 | 8-Nonenal |

(c)

Figure A.15.: Compilation of volatile and odour active components in Propylene from Porvoo “August”

## Propylene from Kallo; used in “PP monomers” & “before” Purification



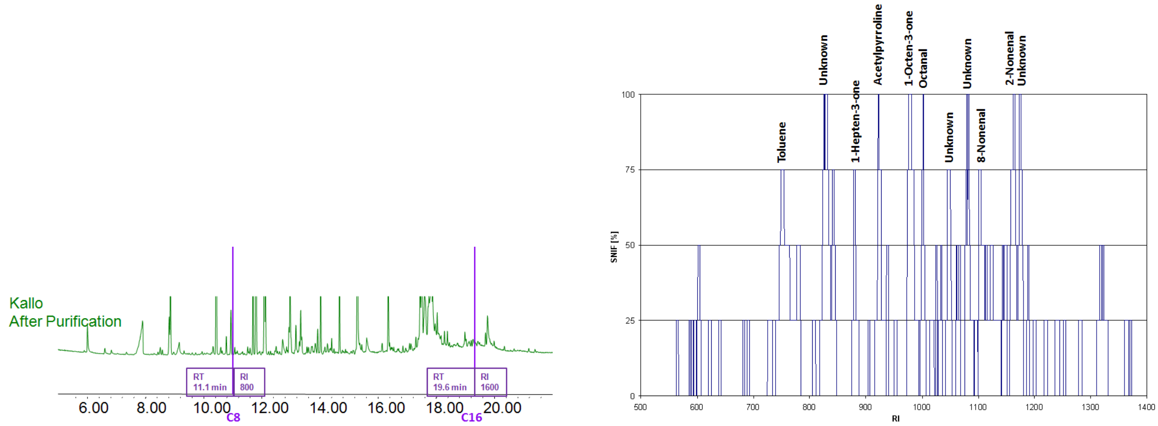
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 6.06 | Acetone | - | | |
| 6.68 | 2-Methyl-2-propanol | - | | |
| 10.74 | Toluene | 773 | 773 | Toluene |
| | | | 826 | Unknown |
| | | | 984 | 1-Octen-3-one |
| | | | 1007 | Octanal |
| | | | 1077 | 1-Nonen-3-one |
| | | | 1104 | 8-Nonenal |
| | | | 1150 | Unknown |

(c)

Figure A.16.: Compilation of volatile and odour active components in Propylene from Kallo; used in the tasks “PP monomers” as sample for Kallo and “Purification” as sample “before purification” from Kallo

## Propylene from Kallo; “after” Purification



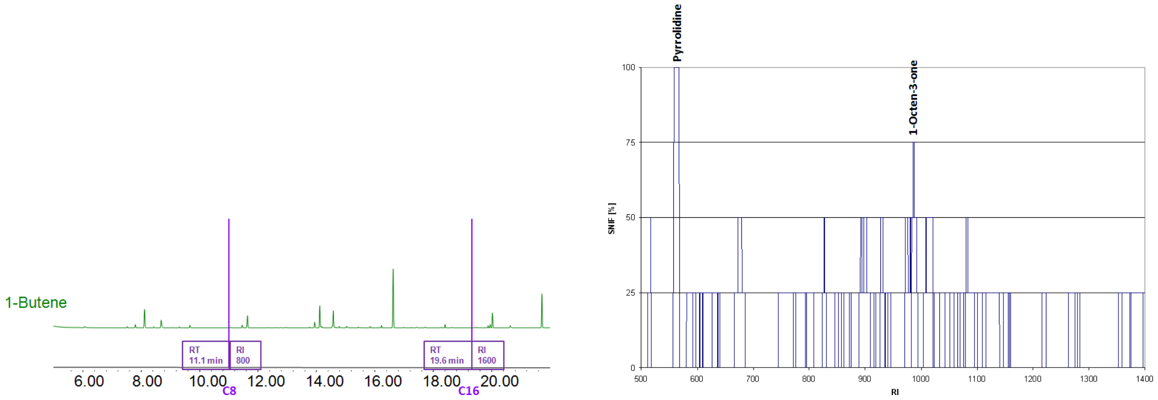
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 6.07 | Acetone | - | | |
| 8.08 | Acetic acid | 602 | | |
| 9.04 | 1-Butanol | 664 | | |
| 9.10 | Benzene | 668 | | |
| 9.41 | Propanoic acid | 688 | | |
| 10.74 | Toluene | 773 | 773 | Toluene |
| | | | 839 | Unknown |
| 12.10 | Ethylbenzene | 876 | 880 | 1-Hepten-3-one |
| 12.20 | Xylene | 884 | | |
| 12.51 | Styrene | 907 | | |
| | | | 925 | Acetylpyrrolidine |
| 13.18 | 5-(1-Methylethylidene)-1,3-cyclopentadiene | 960 | | |
| 13.66 | (1-Methylethenyl)-benzene | 998 | 984 | 1-Octen-3-one |
| 13.83 | 1-Ethyl-2-methyl-benzene | 1013 | 1007 | Octanal |
| 14.36 | 5-exo-Vinyl-5-endo-norbornenol | 1059 | 1050 | Unknown |
| 14.44 | Indane | 1066 | | |
| 14.55 | 1H-Indene | 1076 | 1083 | Unknown |
| 14.81 | 3,4-Divinyl-1-cyclohexene | 1098 | 1104 | 8-Nonenal |
| | | | 1162 | 2-Nonenal |
| | | | 1175 | Unknown |
| 15.89 | 2-(2-Butoxyethoxy)ethanol | 1198 | | |
| 17.79 | 6-Methylquinoline | 1394 | | |
| 17.85 | 1(3H)-Isobenzofuranone | 1400 | | |
| 18.34 | Tridecanol | 1456 | | |
| 18.50 | Pentafluoropropionic acid pentadecyl ester | 1473 | | |
| 18.58 | 1-Dodecanol | 1482 | | |
| 18.79 | Hexatriacontane | 1507 | | |
| 19.06 | Trifluoroacetic acid | 1539 | | |
| 19.17 | Octacosane | 1552 | | |
| 20.63 | 2-(Dodecyloxy)-ethanol | 1736 | | |

(c)

Figure A.17.: Compilation of volatile and odour active components in Propylene from Kallo “after purification”

## 1-Butene from Stenungsund



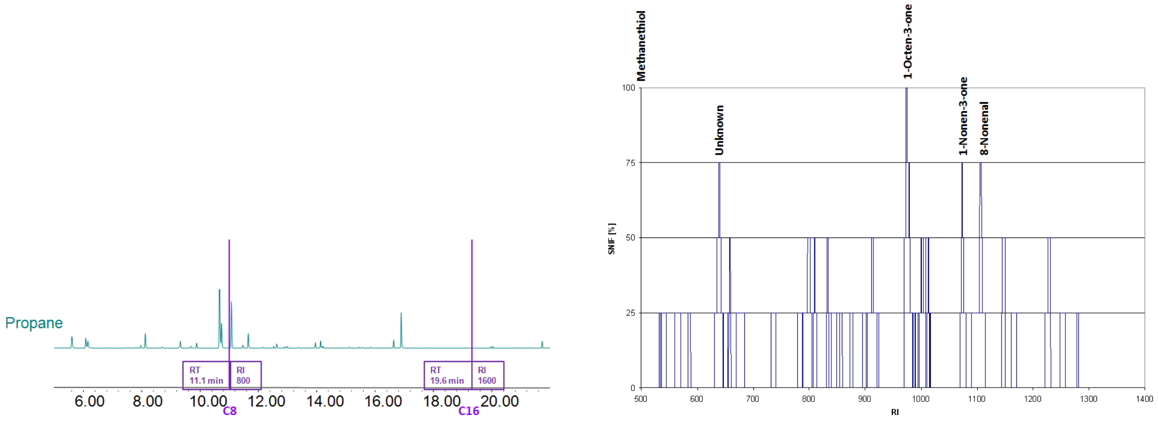
**(a)** **(b)**

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 3.994 | 1-Butene | - | | |
| 4.038 | 2-Methyl-1-propene | - | 558 | Pyrrolidine |
| 7.936 | Hexane | 591 | | |
| 13.582 | 2-Octanone | 992 | 984 | 1-Octen-3-one |
| 14.019 | 2-Ethyl-1-hexanol | 1029 | | |

**(c)**

Figure A.18.: Compilation of volatile and odour active components in 1-Butene from Stenungsund

### Propane from Stenungsund



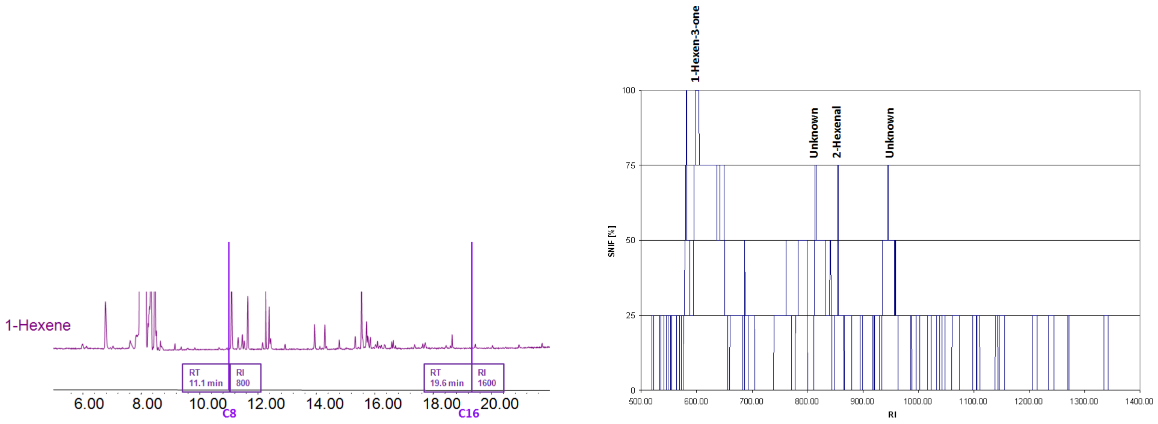
(a) (b)

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 6.02 | Acetone | - | - | Methanethiol |
| 7.94 | Hexane | 591 | | |
| | | | 640 | Unknown |
| 10.33 | Pyridine | 749 | | |
| 10.40 | Dimethyl disulfide | 754 | | |
| 10.72 | Toluene | 776 | | |
| | | | 984 | 1-Octen-3-one |
| | | | 1077 | 1-Nonen-3-one |
| | | | 1104 | 8-Nonenal |

(c)

Figure A.19.: Compilation of volatile and odour active components in Propane from Stenungsund

## 1-Hexene from Stenungsund



**(a)** **(b)**

| RT | Volatile Impurities | RI | RI | Odour Active Substances |
|---|---|---|---|---|
| 6.68 | 1,3-Pentadiene | - | | |
| 10.74 | 1-Hexen-3-one | 778 | 778 | 1-Hexen-3-one |
| | | | 815 | Unknown |
| 11.84 | 2-Hexenal | 844 | 844 | 2-Hexenal |
| | | | 942 | 3-Hepten-2-one |
| 14.22 | 1-Methyl-cyclohexene | 1047 | | |
| 17.84 | Tetradecane | 1399 | | |

**(c)**

Figure A.20.: Compilation of volatile and odour active components in 1-Hexene from Stenungsund

## A.2.2. Identified Odour Active Substances

Table A.11.: List of identified odour active substances and their origins in this project

| | | Monomers | | | | | | Time Dependency | | | | | | | | | | Purification | | | | | | Comonomers | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | PE | | | PP | | | Schwechat | | | | | Porvoo | | | | | Schwechat | | Porvoo | | Kallo | | Stenungsund | | |
| Substance | RI | Stenungsund | Borouge | Schwechat | Burghausen | Porvoo | Kallo | April | May | June | July | August | April | May | June | July | August | Before | After | Before | After | Before | After | 1-Butene | 1-Hexene | Propane |
| **Pyrrolidine** | **558** | | | | | | | | | | | | | | | | | | | | | | | x | | |
| **Unknown** | **562** | | | | | | | | | | | | | | | | x | | | | | | | | | |
| **Unknown** | **586** | | | | | | | | | x | | | | | | | | | | | | | | | | |
| **Unknown** | **600** | | x | | | x | | | | | | | x | | | | | | x | x | x | | | | | |
| **Unknown** | **640** | | | | | | | | | | | | | | | | | | | | | | | | | x |
| **Unknown** | **662** | | | | | | | | | x | | | | | | | | | | | | | | | | |
| **Unknown** | **748** | | | | | x | | | | | | | x | | | | | | | x | | | | | | |
| **Pyridine** | **772** | x | | | | | | | | | | | | | | | | | | | | | | | | |
| **Toluene** | **773** | | | | | | x | | | | | | | | | | | | | | | x | x | | | |
| **1-Hexen-3-one** | **778** | | x | x | | x | | x | | | | | x | | | | | x | | x | x | | | | x | |
| **Hexanal** | **798** | x | | | | | | | | x | x | | | | x | x | | | | | | | | | | |
| **Unknown** | **811** | | | | | x | | | | | | | x | | | | | | | x | | | | | | |
| **Unknown** | **815** | | | | | | | | | | | | | | | | | | | | | | | | x | |
| **Unknown** | **826** | | | | | | x | | | | | | | | | | | | | | | x | x | | | |
| **Unknown** | **839** | x | | | | | | | | | | | | | | | | | | | | | | | | |
| **2-Hexenal** | **844** | | x | x | | | | x | | | | | | | | | x | x | | | | | | | x | |
| **Unknown** | **852** | | | x | | | | x | | | | | | | | | | x | | | | | | | | |
| **Unknown** | **860** | | | | | x | | | | | | | x | | | | | | | x | | | | | | |
| **1-Hepten-3-one** | **880** | | | | | | | | | | | | | | | | | | | | | | x | | | |
| **Unknown** | **904** | | | | | | | | | | | | | | | x | | | | | | | | | | |
| **Acetyl pyrrolidine** | **925** | | | | | | | | | | | | | | | | | | | | | | x | | | |
| **3-Hepten-2-one** | **942** | | | | | | | | | | | | | | | | | | | | | | | | x | |
| **Unknown** | **952** | | | | | | | | | | | | | | | | | | | | | | | | | |
| **1-Octen-3-one** | **984** | x | x | x | | x | x | x | x | x | x | x | x | | x | x | x | x | | x | | x | x | x | | x |
| **Octanal** | **1007** | | x | | | | x | | | | | | | | | | | | x | | | x | x | | | |
| **Unknown** | **1050** | | | | | | | | | | | | | | | | | | | | | | x | | | |
| **(E) 2-Octenal** | **1067** | | x | | | | | | | | | | | | | | | | | | | | | | | |
| **1-Nonen-3-one** | **1077** | | | | | | x | | | | | | | | | | | | | | | x | | | | x |
| **Unknown** | **1083** | | | | | | | | | | | | | | | | | | | | | | x | | | |
| **Nonanal**<br>**6-Nonenal**<br>**8-Nonenal** | **1104** | x | | x | x | x | x | x | x | x | x | x | x | | | | x | x | x | x | | x | x | | | x |
| **(E,E) 2,4-Octadienal** | **1113** | | | | | | | | | | | | | | | x | | | | | | | | | | |
| **Unknown** | **1150** | | | | | | x | | | | | | | | | | | | | | | x | | | | |
| **(E)-2-Nonenal** | **1162** | | | | | | | | x | | | | | | | | | | | | | | x | | | |
| **Unknown** | **1175** | x | | | | | | | | | | | | | | | | | | | | | x | | | |
| **Decanal** | **1204** | | | | | x | | | | | | | x | | | | | | | x | | | | | | |

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