Determination of volatile organic compounds (VOC) in work-room air using direct-reading PTR-MS and traditional air sampling methodologies

Bestemmelse av flyktige organiske stoffer i luft ved bruk av direktevisende PTR-MS og tradisjonelle luftprøvetakingsmetodologier.

Anette Sauve

Norwegian University of Life Sciences
Department of Chemistry, Biotechnology and Food Sciences
Master Thesis 30 credits 2010

Preface

The thesis was performed as a master thesis at Department for the Chemical and Biological Work Environment at the National Institute for Occupational Health in collaboration with department for Chemistry, Biotechnology and Food Sciences at the Norwegian University for life Sciences (UMB) during the period January 2010 – April 2010.

I would like to thank my advisor at UMB, Dag Ekeberg, for helpful advice, motivation and guidance towards finishing writing this thesis.

To Raymond Olsen, my advisor at NIOH, and Mikolaj Jankowski: I want to thank you for all your input and help with the experiments and especially the interpretation of the results. You have been incredibly generous with both your time and your knowledge. I could not have finished this thesis without your support.

Thank you Merete Hersson for sharing some of your knowledge on gas chromatography and preparation of samples with me.

I want to thank my family for all your support and motivation. Last but certainly not least I want to thank Jørn Inge for all your patience, generosity and support these months but most of all I want to thank you for giving me the much needed incentive to start writing.

Ås, May 12th 2010

Table of Contents

Abstract

PTR-MS was evaluated up against traditional air sampling methodologies by choosing compounds that were tested by injecting a known amount of reference compounds into the test chamber to create artificial atmospheres. Measurements were taken by means of traditional air sampling methodologies and by sampling straight from the chamber using PTR-MS. The traditional methods consisted of active sampling with sorbent tubes, overnight desorption using carbon disulphide/carbon disulphide with 2% Dimethylformamide followed by analysis using gas chromatography. The results were calculated as recovery using the total theoretic concentrations and compared.

The purpose of the experiments was to explore the possibility in using PTR-MS as a direct-reading alternative to the traditional more time consuming methods in use at The National Institute of Occupational Health (NIOH). An additional purpose was to evaluate the test chamber for volatile organic compounds at a concentration area of 1-2 ppm. The advantage of using PTR-MS is avoiding sample preparation and monitoring compounds in seconds compared to the traditional methodologies that use gas chromatography and require sample preparation.

Based on the experiments it may seem that the set-up for the test chamber will be best suited for compounds with a boiling point less than 120 °C. PTR-MS seems to work well with a great amount of the compounds tested but it may seem as if the instrument overestimates the concentrations in some cases and knowledge regarding the fragmentation patterns is important to achieve an accurate quantification. The ability to detect peak exposures as a result of the short response time (seconds) is a great advantage of using PTR-MS and may aid in the elucidating the sources of exposure in production processes. These peaks will be invisible when using traditional averaged air sampling methods; consequently PTR-MS can identify and help remove the peak exposures and thus the total exposure.

Sammendrag

PTR-MS ble testet opp mot tradisjonelle luftprøvetakningsmetoder ved å velge ut forbindelser som ble testet ved å injisere kjente mengder av referansestoffer i et prøvekammer for å lage kunstige atmosfærer. Det ble tatt prøver fra med tradisjonelle metoder og ved å ta målinger direkte fra kammeret med PTR-MS. De tradisjonelle metodene består av prøvetaking med kullrør, desorbering av kullet over natten i karbondisulfid/karbondisulfid med 2% dimetylformamid før analyse ved gasskromatografi. Resultatene ble beregnet opp mot teoretisk konsentrasjon og sammenlignet ved hjelp av ”recovery”verdiene.

Målsetningen var å utforske muligheten for å anvende PTR-MS som et direktevisende alternativ til de mer tidkrevende tradisjonelle luftprøvetakingsmetodene i bruk ved Statens Arbeidsmiljøinstitutt (STAMI). I tillegg var det ønskelig å evaluere prøvekammeret for flyktige organiske forbindelser i konsentrasjonsområdet 1-2 ppm. Fordelen med å bruke PTR-MS er at man unngår prøveopparbeiding og at man kan identifisere og kvantifisere forbindelser i løpet av sekunder sammenlignet med de tradisjonelle metodene som benytter gasskromatografi og krever prøveopparbeidelse.

Basert på eksperimentene utført kan det virke som oppsettet for prøvekammeret fungerer best for forbindelser med kokepunkt under 120 °C. PTR-MS ser ut til å fungere godt for en god del av forbindelsene testet, men det kan virke som den overestimerer konsentrasjonene i en del tilfeller og det er viktig å ha kunnskap om fragmentasjonsmønstre. Evnen til å detektere topper i eksponering på grunn av den korte responstiden er en stor fordel ved bruk av PTR-MS og kan hjelpe til med å identifisere kilder til eksponering i produksjonsprosesser. Disse toppene vil være usynlige i de tradisjonelle prøvetakingsmetodene da de benytter seg av gjennomsnittsverdier over større tidsrom. PTR-MS kan derfor identifisere og hjelpe til med å fjerne topper i eksponering og dermed senke totaleksponeringen.

1 Introduction

The Act relating to working environment, working hours and employment protection (Working Environment Act) of June 17th, 2005, section 4-5 Chemical and biological health hazards, § 1 states: " *When handling chemicals or biological substances, the working environment shall be so arranged that employees are protected against accidents, injuries to health and excessive discomfort....*". The occupational exposure limits (OELs) for exposure to chemical hazards are governed by the Norwegian Labour Inspection Authority. To ensure that no workers are exposed to concentrations exceeding the norms analysis of the workplace air may be required to undergo a chemical analysis. There are a growing amount of substances that are listed in the administrative norms with various effects on the human body (The Norwegian Labour Inspection Authority 2009). Some compounds as for example benzene has been shown to be carcinogenic (Maltoni et al. 1983). The OEL for benzene is currently set to 1 ppm averaged over an 8 hour period(The Norwegian Labour Inspection Authority 2009).

Table 1-1: Areas of use and OELs for the compounds analysed

Name	Common uses	OEL (ppm)*
Benzene	Production of plastics, rubbers, resin. Solvent for paints and printing(1	1
Toluene	Production of benzene and xylene. Solvent and octane booster(2	25
m-Xylene	Solvent in wood stains and varnishes(3	25
Ethyl Benzene	Production of styrene. Solvent for coatings, rubber and plastic wrap production(1	5
Styrene	Production of polymers used in paints, coatings, plastics and resin(1	25
1,2,4-Trimethylbenzene/1,3,5-Trimethylbenzene	Paint thinners(3	20
1,4-Dioxane	Solvent in varnishes and polystyrene production(3	5
n-Butyl-acetate	Solvent in paints(3	75
Acetone	Solvent in production of pharmaceuticals, paints,	125

	polystyrene production and printing[3	
Butan-2-one	Solvent in adhesives, paints and printing[3	75
4-Methylpentan-2-one	Solvent in paints, pharmaceutical industry, rubber manufacture [3	25

* (The Norwegian Labour Inspection Authority 2009) [1 (U.S. Environmental Protection Agency 2010), [2)] (ICIS.com 2008), [3(Scorecard.org 2005)

There is a great need for accurate and precise methods for monitoring workplace air. The methods used at The National Institute of Occupational Health (NIOH) for monitoring volatile organic compounds(VOC) currently involves GC-MS, GC-FID and LC-MS/MS where samples are collected in various methods such as for example diffusive or active samplers. These methods involve use of chromatography which requires time in order to separate the analytes. This makes monitoring of VOCs over short time intervals difficult. Monitoring air over short time intervals requires the use of mass-spectrometric methods (Lindinger, W. et al. 1998a). Using a PTR-MS will also enable identification of exposure sources in production processes and to screen workplace air facilitating the choice of the proper traditional air sampling methodologies. The response time for the PTR-MS instrument used is 100 ms (Ionicon Analytik GmbH 2010).

The PTR-MS is used in several contexts within monitoring of VOC is environmental applications due to its low detection limits but there are currently no published articles regarding the use of PTR-MS in the occupational health area.

The compounds selected for analysis in the experiments are selected based on some limitations. The compounds had to be within the mass area for the PTR-MS used and show baseline separation in the chromatographic method.

1.1 Aim

The aim was through these experiments to explore the possibility of using Proton Transfer Reaction Mass Spectrometry (PTR-MS) as a direct-reading alternative to the more time consuming traditional air sampling methodologies used within the occupational health area at The National Institute of Occupational Health (NIOH). A Proton Transfer Mass Spectrometer is due to its short response time able to monitor peak exposures over short time intervals which will be invisible in a time-averaged analysis method. An additional aim was to evaluate the test chamber for volatile organic compounds in a concentration area of 1-2 ppm.

The purpose of using PTR-MS is to avoid sample preparation and to provide monitoring of compounds in minutes compared to the traditional methods which require a given time for sampling, overnight desorption of samples and analysis via gas chromatography. The work presented in this thesis is performed at The National Institute of Occupational Health (NIOH) in collaboration with The Norwegian University of Life Sciences (UMB).

1.2 Analytical methods

1.2.1 Air samples and sampling

Sampling of volatile organic compounds in workplace air may be performed in several ways. There are instrumental methods that may involve a fixed, portable or semi-portable instrument, there are gas detector tubes and there are canisters or gas bag or impingers that is analysed by gas chromatographic methods(Brown 2002). According to Brown (2002) are the most versatile methods the ones where the VOCs are collected on a solid sorbent and analysed by gas chromatography. The sampling on solid sorbents may be active or passive where the active denotation involves pumps and the passive involves diffusion(Brown 2002).

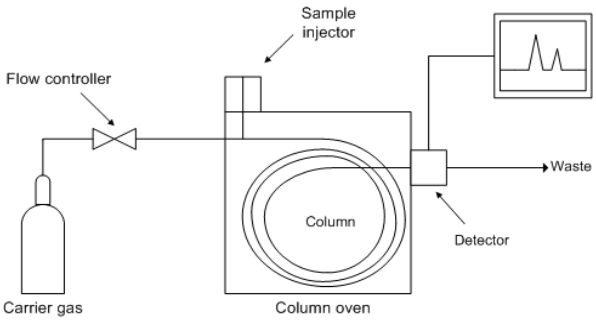
The methods used for air sampling in this thesis are built on the methods developed or adapted by NIOSH and published in the NIOSH Manual of analytical methods(NIOSH 2003) and is also described by ISO (International Organization for Standardization 2001). NIOSH have developed several methods for analysing volatile organic compounds in workplace air, the method used in this thesis are built on the following NIOSH methods: 1501, 1450 1602 and 2555. The sampling is active and performed with solid sorbents. Desorption of analytes from the solid is done with solvent desorption. In general: a known amount of air is pumped through a glass tube containing a solid sorbent over a given period of time. The sorbent is removed from the glass tube and desorbed overnight in carbon disulfide (CS_2 or CS_2 containing 2% dimethylformamide (DMF)) before analysis on a gas chromatograph. The choice of sorbent is dependent on the compounds to be analysed which is also the case for the desorption agent but in the case of the compounds analysed in this thesis CS_2. Pure dimethylformamide is a solvent more suitable for polar compounds than carbon disulphide which is more suited for non polar compounds (Johansen & Wendelboe 1981)

The sorbent tubes are flame sealed glass tubes of 70 mm length, 6 mm outer diameter (o.d.) and inner diameter (i.d.) 4 mm where the sorbent is divided into two sections of 100 and 50 mg by a 2 mm urethane foam plug(NIOSH 2003). The front section with 100 mg sorbent is protected by silylated glass wool plug and is the part generally used for analysis of the samples and is always placed towards the sampling mechanism. The back section containing 50 mg sorbent is placed between the 2 mm urethane foam plug and another 3 mm urethane foam plug and is generally used for control of breakthrough and sample loss (NIOSH 2003).

1.2.2 GC-FID

Following Ahuja (2003) the definition of chromatography is as following: "*Chromatography is essentially a physical method of separation in which components to be separated are distributed between two phases, one of which does not move (appropriately called the stationary phase) and the other that moves through it in a definite direction (commonly called the mobile phase)*." In gas chromatography is not surprisingly a gas whereas the stationary phase may be solid or liquid. The requirements in order to run gas chromatography are that the analyte has to be volatile at the operational temperature or derivatised in order to be volatile or thermally stabile(Ahuja 2003).

A gas chromatographic system consists of a carrier gas tank, an injection chamber, the column, a detector and a data system. The carrier gas can vary, but the most common is helium(Skoog et al. 2007). The requirements for a carrier gas is that it is inert and does not interfere with detection of the analyte (Ahuja 2003).



1.2-1: Diagram of a gas chromatograph(Wikimedia Commons 2009)

Injection of a sample in GC is nowadays usually done by an autosampler with an automated injector to limit the possibilities for errors due to injection technique and provide as similar as possible conditions for all samples. There is possible to perform both a split and a split-less injection depending on the samples in most GC-systems. A split injection is perhaps the most common where only a given part of the injected volume is allowed to enter the column; this can be regarded as a dilution. Split injections are necessary as capillary columns often require very small sample loads and to inject sample loads of a microgram or less would lead to highly increased inaccuracies in the analyses. Split-less injection however allows the entire volume injected in to the system to be separated on the column. A split-less injection requires samples that are free of impurities that may cause problems with the column and low levels of analytes and are most used for trace analysis.

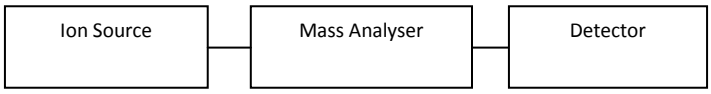
GC-columns may be packed or open-tubular (often called capillary) columns. The column is one of the most important parts in a GC as it is the only part directly responsible for separation of

compounds. The choice of column is based on what kind of compounds that are to be separated and whether the separation is for analytical reasons or if it is part of a preparative system. How the analytes interact with the stationary phase in the column determines their retention time, they may be retained by f. ex polarity or size. The stationary phase in a GC-system may be solid or liquid.

There are several detectors that may be used with a gas chromatograph such as thermal conductivity, flame ionisation, mass spectrometer et cetera. Most detectors used in conjunction with gas chromatography do only provide quantitative information and no qualitative info. The exception is MS which provide both. The detector used in the experiments in this thesis is a flame ionisation detector (FID). The FID burns the column effluent to produce ions which are collected by an electrode which produces a signal correlated to the concentration of ions(Ahuja 2003). The effluent from the column is mixed with hydrogen and burned at the tip of a nozzle surrounded by a surplus of air to aid the combustion(Ahuja 2003). The collecting electrode is kept at a electric potential difference of + 300 V to the flame to attract the ions(Ahuja 2003). The burning of the effluent implies that FID is a destructive detector. FID works with organic compounds, i.e. most carbon-containing compounds with a few exceptions.

1.2.3 General mass spectrometry

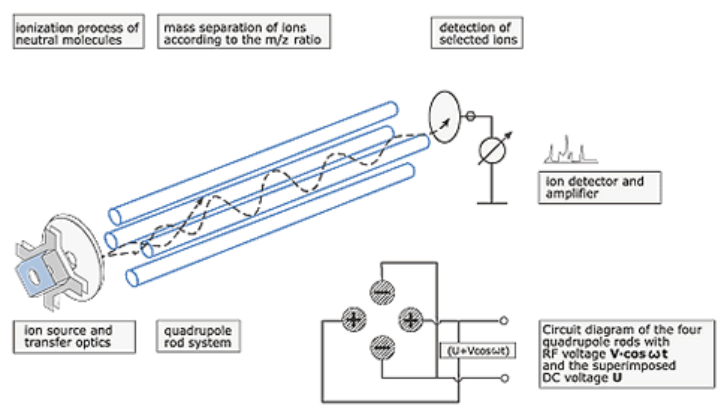
Mass spectrometry is an analytical technique that can give both quantitative and qualitative information. An analytes mass-to-charge-ratio and in some applications its fragmentation or isotope pattern will identify the analyte at the same time as the detector quantifies the analyte. In general mass spectrometry can be described as a technique operating in high vacuum that ionises the analytes and separates them according to their mass-to-charge-ratio by means of electrical or magnetic fields or a combination of both. The sample may be in gaseous or solid form depending on the ion source and sample introduction system. Liquid or aqueous samples must be vaporised as the ions need to be in gas phase in order to be separated in the mass analyzer. There are a number of different mass spectrometers in use today but they are all built after the following principle:



1.2-1: Simple schematic of a mass spectrometer

The ion source is where the ions are formed, they can be formed using various methods such as for example electron ionization (EI) where the analytes are ionised by direct impact with electrons or chemical ionization (CI) where the analytes are ionised by a pre-ionised reactant (Downard 2004). A mass spectrometer is as previously mentioned operated under low pressure, this is to prevent any collisions between ions or ions and contaminants which will lead to a loss of analyte as neutral species will not pass through the mass analyzer and hit the detector. This is not the case when one uses a CI-source. In this source, collisions between the analyte and the reactant gas are wanted so the pressure in a CI-source will be somewhat higher than in an EI-source.

The mass analyzer does always operate in high vacuum. This part of the instrument separates the ions based on their mass-to-charge ratio (*m/z*) using electrical fields, magnet fields or a combination of the two. One of the most common mass analyzers and coincidently the one used in these experiments is the quadrupole. The quadrupole mass filter consists of 4 parallel rods where the oppositely facing pairs are connected electrically, one pair is connected to the positive output of the variable DC source and the other to the negative (Skoog et al. 2007)



1.2-2: Diagram of a quadrupole(InProcess Instruments 2010)

An oscillating radio-frequent field is applied to the rods as well. Increasing these field voltages whilst keeping the ratio between the fields constant leads to an alteration of the trajectory of the ions that are accelerated through the mass filter(Skoog et al. 2007). As ions are electrically charged they will be deflected or attracted by an electrical field, an ion that does not have the *m/z*-ratio required to pass through the ion source at that time will hit one of the rods that has the opposite charge and be neutralised. Altering the voltages will allow the mass filter to scan through a mass range up to 5000(Downard 2004).

The detector used in the experiments is an electron multiplier. An electron multiplier may consist of several discrete plates that are connected by means of a chain of resistors(Downard 2004). A high voltage is applied so that an equal voltage difference is created between each

plate, causing increasingly higher voltages (Downard 2004). When an ion strikes the first plate of the detector an electron is emitted, this electron will hit the next plate where the impact will release more electrons. This process continues throughout the detector and achieves gain of about 10^5 in signal(Downard 2004). The mass spectrometer is usually coupled to a computer that provides the mass spectrum.

1.2.4 Proton Transfer Reaction Mass Spectrometry

Proton Transfer Reaction Mass Spectrometry (PTR-MS) was developed by Professor Werner Lindinger and his colleagues at the University of Innsbruck in Austria in the middle of the 1990s and is an instrument designed for monitoring volatile organic compounds (VOC) in air(Blake et al. 2009).

The development of PTR-MS is based on the development of earlier techniques such as flowing afterglow and SIFT (Blake et al. 2009). Flowing afterglow was a technique for studying ion molecule reaction kinetics where ions were injected into an inert buffer gas which contained small amounts of neutral reactants in order to achieve reactions at thermal or near-thermal collision energies (Blake et al. 2009). Ions were produced by an electrical discharge .(Blake et al. 2009) The flowing afterglow technique posed a problem in the ion selection, the technique provided no selection of ions before reaction leading to difficulties in the analysis. This problem was solved by Adams and Smith who introduced selection of ions using a quadrupole filter to allow only ions with a certain mass-to-charge ratio through to the flow tube(Adams & Smith 1976). This technique is called Selected Ion Flow Tube (SIFT). The SIFT-MS was originally used for kinetic studies but is still used today for studies of ion molecule reaction kinetics and for detecting and quantifying trace gases in air (Blake et al. 2009). Using H_3O^+ as a primary ion in SIFT will provide the following equation given that: $[H_3O^+] \gg [RH^+]$

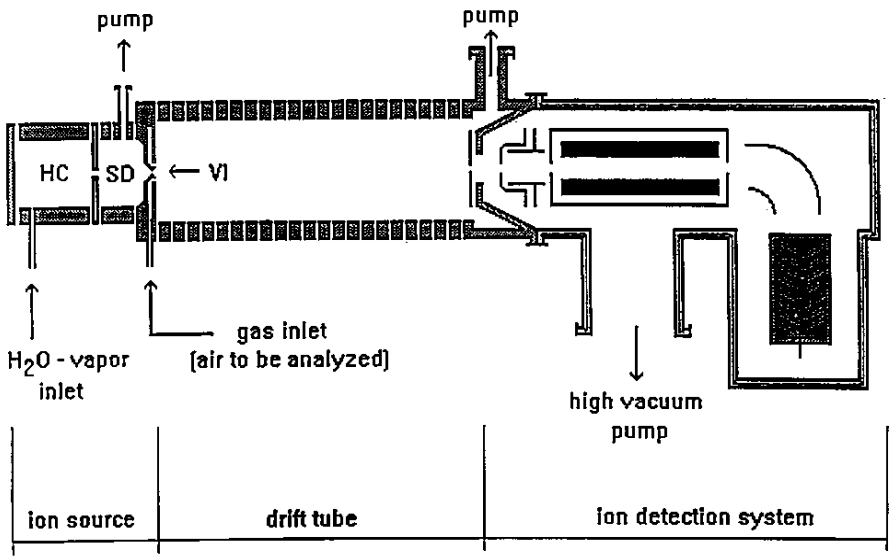
$$\frac{[RH^+]}{[H_3O^+]} = kt[R] \qquad \text{Equation 1.2-1}$$

Where k is the proton transfer reaction rate coefficient and t is the reaction time(Blake et al. 2009). This equation is used for quantification in PTR-MS. This is the inverse of the original use of SIFT as the result in many experiments was to determine the k-coefficient.

The k-values from SIFT can be used in PTR-MS but for most applications theoretical values are utilised(Lindinger, W et al. 1998a).The SIFT consists of an electrical discharge ion source, a

quadrupole mass filter, a flow tube where ions, carrier gas and neutral reagent are mixed and a second mass filter and detector(Blake et al. 2009). Where the SIFT uses a flow tube, PTR-MS uses a drift tube, the main difference between these two are that a flow tube uses carrier gas flows to transport the ions and reactant through the tube whereas the drift tube uses an electrical field to transport ions and analytes(Lagg et al. 1994).

The PTR-MS employs a different ion source than SIFT. In PTR-MS a hollow cathode discharge source generates H_3O^+ions with great efficiency (>99,5 %) so the need for a mass filter to select the ions prior to reaction is eliminated(Lindinger, W. et al. 1998a).



1.2-3: Schematic of a Proton Transfer Reaction Mass Spectrometer (Lindinger, W et al. 1998b)

The schematic above shows the main components of the PTR-MS where HC is the hollow cathode, SD is the source drift region and VI is the Venturi inlet(not used by all research groups working with PTR-MS(Blake et al. 2009). The venture inlet is utilized to minimise diffusion of gases from the drift tube into the source drift region. As the venture inlet is not operating at true venturi conditions there are some diffusion where O_2^+ is the main concern as it does not react with H_2O(Lindinger et al. 1998b). The elimination of the carrier gas from SIFT leads to no dilution of the air to be analysed. In SIFT it was necessary to dilute the gas in order to avoid clusters ions, especially from residual water vapour ($H_3O^+(H_2O)_n$) (Blake et al.2009). A drift tube causes higher ion molecule collision energies thus minimising the cluster ions, but the higher collision energies may lead to some product ion fragmentation(Blake et al. 2009). However the PTR-MS provides better detection limits than the SIFT, as low as a few parts per trillion(Lindinger et al. 1998a).

Using electron impact ionisation in the analysis of air samples poses a couple of difficulties. EI is considered to be a rather hard ionisation technique which leads to a higher degree of fragmentation in the mass spectra. This may be used to identify a compound if the compound is pure, i.e. not in a mixture or in a mixture with very few compounds. In a more complex mixture, a high degree of fragmentation will complicate both identification and quantification. Use of EI in air samples will lead to ionisation of the main constituents of air such as N_2 (roughly 78 % of air) and O_2. These are present in much higher concentrations than the VOCs and may overwhelm the detector at the lower mass end of the spectrum (Blake et al. 2009). These problems with EI have lead to development of several chemical ionisation-techniques. The proton transfer reaction is a form of chemical ionisation that can be described in general by the following reaction where M is any molecule and XH^+ is a donor ion:

$$M_{(g)} + XH^+_{(g)} \rightarrow MH^+_{(g)} + X_{(g)} \qquad \text{Reaction 1.2-1}$$

This process needs to be energetically favoured in order to ionise the analytes. To determine whether or not a reaction is favourable one should always consider the Gibbs energy change for the given temperature, $\Delta G^{\ominus}_T$ (Harris 2007). A negative Gibbs energy change implies a spontaneous reaction. Gibbs energy changes are calculated from the following equation:

$$\Delta G = \Delta H - T\Delta S \text{ (Harris 2007)} \qquad \text{Equation 1.2-2}$$

Where ΔH is the change in enthalpy, T is temperature in Kelvin and ΔS is the change in entropy. In proton transfer reactions the change in entropy is regarded to be small and not vary much from reaction to reaction (Hunter & Lias 1998). This implies that the last part of the formula for Gibbs energy change will not have a great impact on the Gibbs energy change of the reaction. Following this the enthalpy is the most important aspect in proton transfer reactions. The enthalpy can be described by the proton affinity which is defined as the negative of the enthalpy for reaction 1.2-1(Downard 2004) This leads to the use of proton affinities rather than calculations of Gibbs energy change to determine whether or not a reaction will be spontaneous or not in PTR-MS. As a result PTR-MS can only analyse species with a higher proton affinity than water. Table 1.2-1 shows why PTR-MS is transparent to the common constituents of air.

Table 1.2-2: Some selected proton affinities, table adapted from (Hunter &Lias 1998)

Compound	Proton Affinity (kJ/mol)
Helium	178
Oxygen	421
Nitrogen	494
Carbon dioxide	541
Water	691

Benzene	750
Toluene	784
Xylene	795
Acetone	812

The quantification in PTR-MS relies on the assumption that the concentration of H_3O^+ions in the drift tube is so high that the loss of primary ions to proton transfer reaction with the analyte is negligible. The proton transfer coefficient or collision rate coefficient may be determined experimentally or calculated as a theoretical value, following Lindinger et al. (1998) the calculated values are used instead of the reported values. There are several methods for calculating the proton transfer coefficients such as the Langevin theory and the Su and Chesnavich parameterised trajectory studies(Langevin 1905; Su & Chesnavich 1982).

The Langevin theory is applicable for ion molecule reactions of non-polar neutral molecules only and is derived from the Langevin model of the long range interaction between a point charge and a polarisable molecule (Blake et al. 2009; Langevin 1905).

$$k_L = \sqrt{\frac{\pi\alpha e^2}{\mu\varepsilon_0}} \qquad \text{Equation 1.2-3}$$

Where α is the polarizability of the neutral reactant molecule, e is the fundamental unit charge, μ is the reduced mass of the colliding partners and ε_0 is the permittivity of free space (Blake et al. 2009). In the case of a polar molecule, this equation will underestimate the collision rate coefficient as it does not consider the interactions between the positive charge and the permanent dipole moment of the neutral molecule (Blake et al. 2009) An approach that is more in compliance with the experimental values is the Su and Chesnavich parameterised capture rate coefficient(Chesnavich et al. 1980; Su & Chesnavich 1982):

$$k_{SC} = K_{cap} k_L \qquad \text{Equation 1.2-4}$$

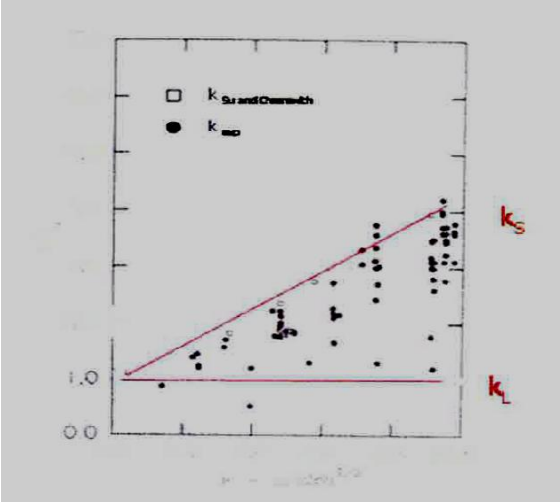
Where:

$$K_{cap} = \begin{cases} \frac{(x+0.5090)^2}{10.526} + 0.9754 & x \leq 2 \\ 0.4767x + 0.6200 & 2 \leq x \leq 3 \\ 0.5781x + 0.3165 & 3 \leq x \leq 35 \\ 0.6201x - 1.153 & 35 \leq x \leq 60 \\ 0.6347x - 2.029 & x \leq 60 \end{cases} \qquad \text{Equation 1.2-5}$$

Where:

$$x = T_r^{-1/2} = \left(\frac{2\alpha k_B T}{\mu_D^2}\right)^{-1/2}$$ Equation 1.2-6

T_r is the reduced temperature, μ_D is the dipole moment of the neutral molecule and k_B is the Boltzmann constant. This value combined with equations above is the basis for quantification for PTR-MS when the condition $[H_3O^+] \gg [RH^+]$ is true. The time in equation 1.2-1 is the time the ions need to travel through the drift tube and can be measured by pulsing the entrance and exit slit of the tube and monitoring the arrival spectrum it can be calculated from mobility values of $[H_3O^+]$ in air (Ellis et al. 1976; Lindinger et al. 1998a).

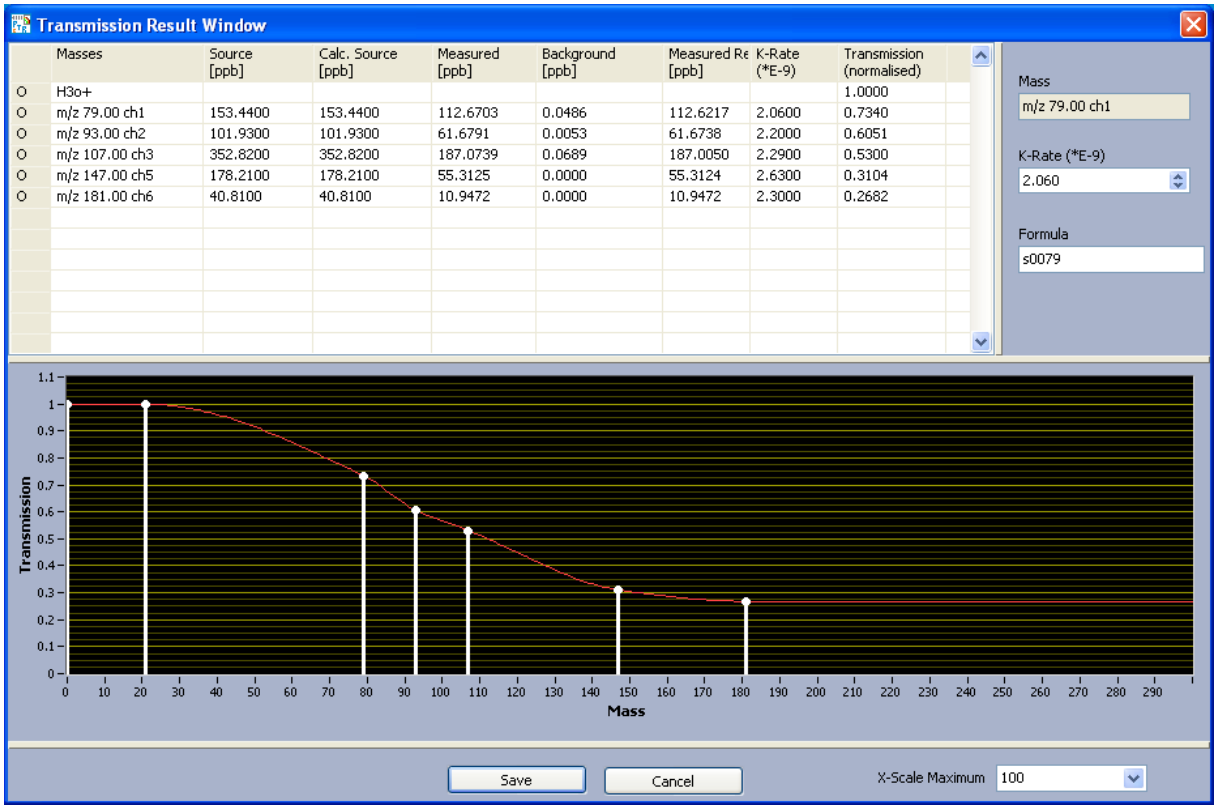


1.2-4: A comparison between the two models for calculating k. Adapted from (Ausloos & Lias 1987)

During the experiments the ratio between the electric field and the density of the buffer gas (i.e. air in PTR-MS), E/N was held between 110 and 140 Townsend (Td) where $1\ Td\ = 10^{-17}\ \frac{cm^2}{Vs}$. This is a compromise between to high cluster formation ($(H_3O^+ \cdot H_2O)_n$, n=1,2,3...) where ligand switching reactions would occur (Praxmarer et al. 1993) and fragmentation due to collisions with neutral species in the drift tube (Lau et al. 1982; Viggiano et al. 1988)

As briefly previously mentioned the density of RH^+ ions compared H_3O^+ ions needs to be so low that the concentration of H_3O^+ can be considered constant as the assumptions for the quantification depends on this (Lindinger et al. 1998a). At higher concentrations of analyte these assumptions are no longer valid as the RH^+ exceeds a negligible concentration compared to the concentration of H_3O^+ ions. For the instrument used in these experiments the linear range is 500 pptv – 10 ppmv (Ionicon Analytik GmbH 2010). Given that the assumptions are valid, i.e. measurements within the linear area of the instrument, the quantifications will be shown directly in the PTR-MS software represented as a graph with concentration on the y-axis.

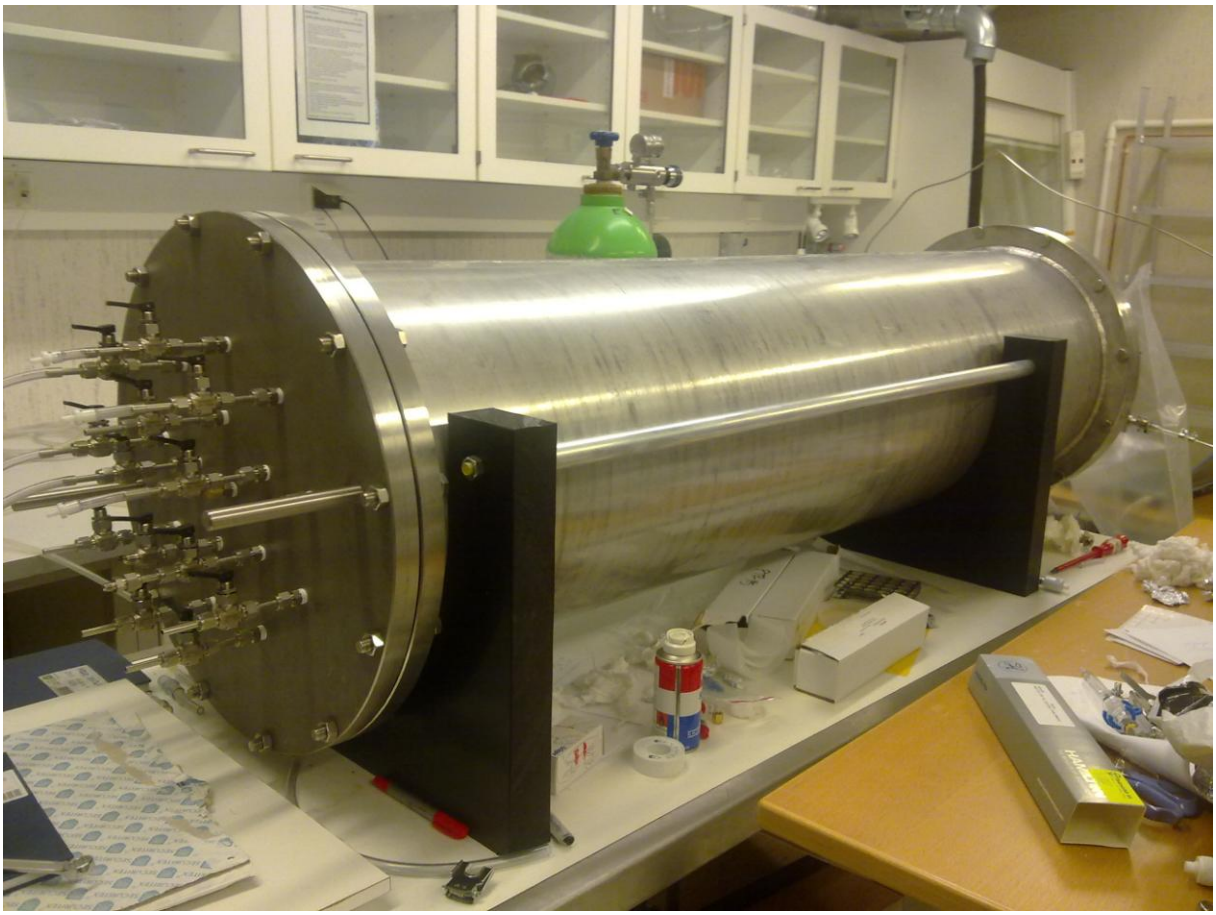
As the collisional energies in the drift tube may cause fragmentations in PTR-MS it is important to be aware of this fact as it will have a great impact on the quantification. Another aspect is isotopes, most elements have several isotopes. In mass spectrometry in general this may be used to define the amount of for example carbon atoms in an unknown compound and is not a problem when using a standard curve for quantification. As PTR-MS is a direct-reading technology where standards are not used when quantifying compounds this aspect needs to be taken in to consideration. The problem is solved by calculating the probabilities for the given *m/z* values and correcting the total concentration according to the probabilities. The probabilities were calculated using Isotope Distribution Calculator and Mass Spec Plotter (Scientific Instrument Services 2010). Another aspect of not using standards is the impact transmission in the quadrupole has on the quantifications; this may be solved by correcting for the transmission. This is illustrated in Figure 1.2-5. The figure does also show the mass area for the quadrupole. It is a narrow mass area due to the size of the quadrupole as the quadrupole installed in the instrument is a smaller one as the instrument is designed for small size and field measurements.



1.2-6: Correction of transmission for PTR-MS

1.3 The Test Chamber

In order to control the experiments, a test chamber was needed. A test chamber will allow control of the volume and thus the concentration of analyte(s), pressure, and temperature and may also provide control of humidity if that is an important factor in the experiment. As test chambers are not readily commercially available the chamber utilized in these experiments were built by Sofus E. Kristiansen Eftf. AS (Oslo, Norway). The chamber consists of a steel cylinder rolled from a 6 mm stainless steel sheet. The steel was electro-polished in order to minimise adsorption to the walls of the chamber The cylinder has an inner diameter (i.d.) of 420 mm and a length of 1500 mm. Each end has a flange which has an outer diameter of 520 mm, an inner diameter of 420 mm and a thickness of 25 mm. The cylinder is sealed in both ends with 10 mm expanded Teflon strips provided by A. W. Chesterton Company (Woburn, Massachusetts, USA) serving as gaskets and stainless steel circular plates (d= 520 mm, thickness = 25 mm).

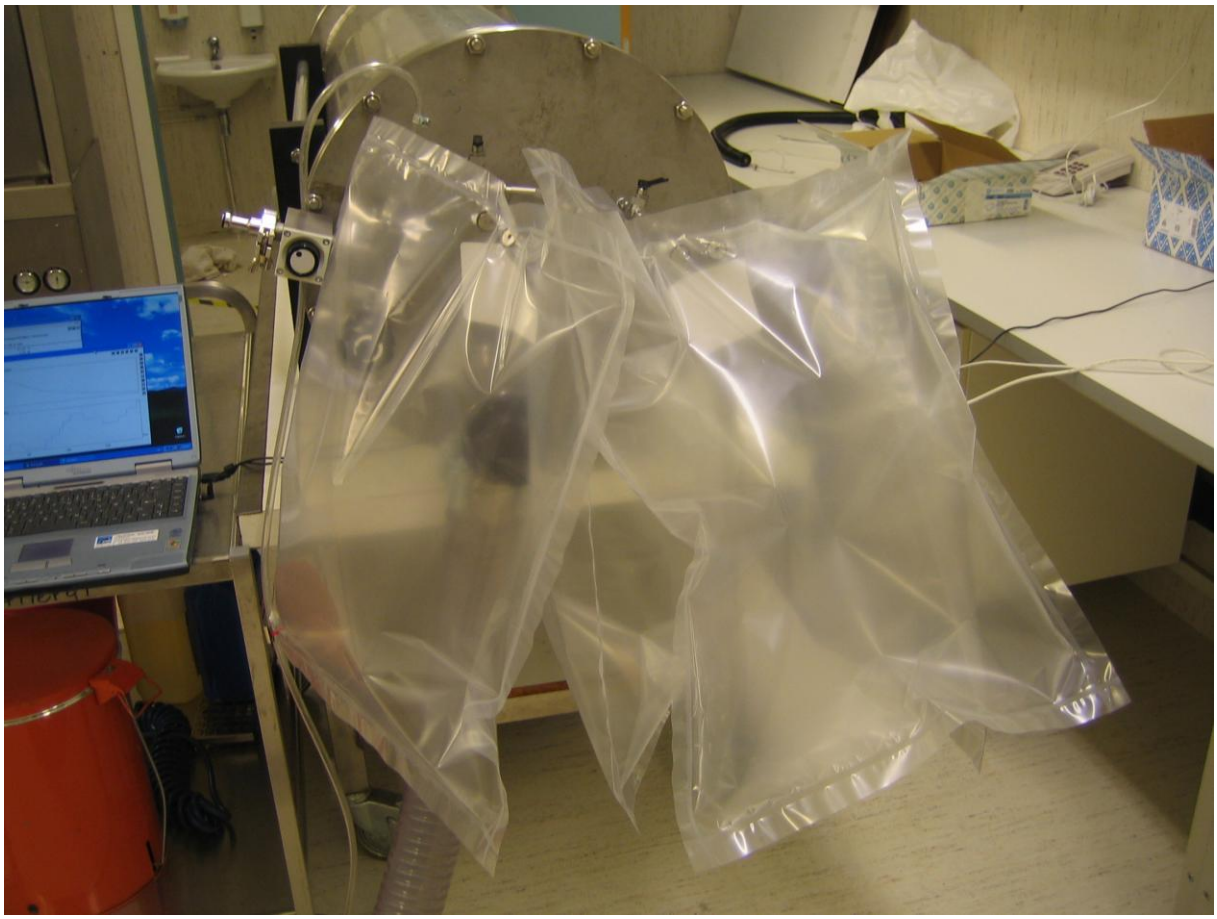


1.3-1: The test chamber

The Test chamber was further modified at NIOH. 2 stainless steel Lesker angle-valves were fitted at the first endplate, where one (DN 63 ISO flange) was further connected to a Sogevac SV65 Vacuum pump (Leybold Vakuum GmbH, Köln, Germany) through a 7m vacuum hose (i.d. 76 mm) and the other (DN 16KF flange) served as inlet for compressed gas. The vacuum parts were supplied by Vacuum-Service AS (Lørenskog, Norway).

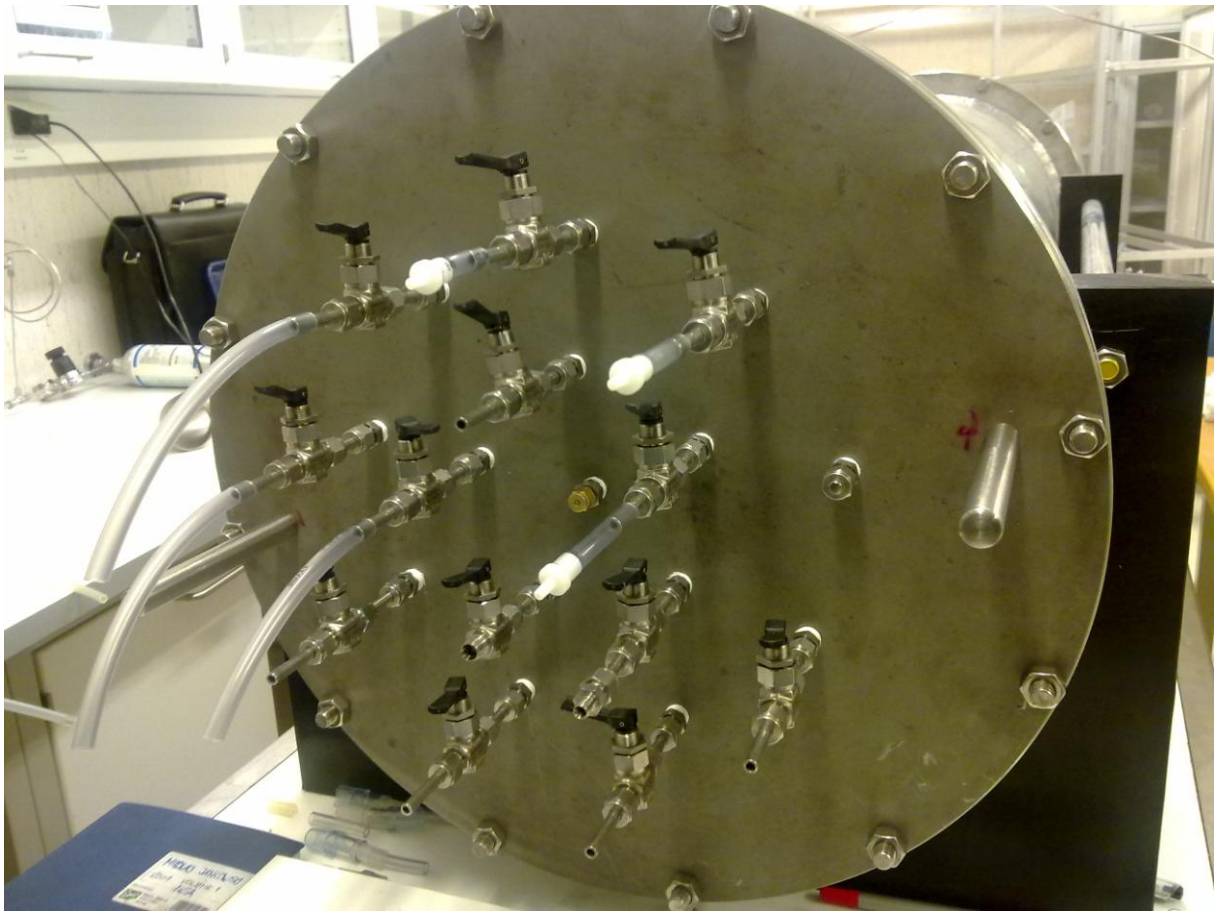
The sensors were fitted at the same endplate. A HumidiProbe (Pico, Cambridgeshire, UK) was suspended 30 cm into the chamber to monitor temperature and humidity. The pressure in the chamber was monitored by two pressure sensors, MPXA4115A (range 66-910 torr.) and MPX4250GP (range 710–1500 torr.). The sensors were connected in parallel to a 2 mm i.d. polypropylene tube. The ambient pressure was monitored using a MPXA4115A pressure sensors, The sensors were acquired from Freescale Semiconductor (Austin, Texas, USA), and the output was recorded using the data program PicoLog (Pico, Cambridgeshire, UK).

Stainless steel ¼” Swagelok toggle valves were fitted to the endplate via two stainless steel ¼” Swagelok to ¼” NPT unions. These two toggle valves were connected to 45 mm x 1/4” o.d. stainless steel tubing providing two and three open end tubes with 1/4” Swagelok as splits.



1.3-2: Endplate with connection to vacuum pump shown with gas bags filled

The other endplate was fitted with 15 stainless steel 1/4” Swagelok to 1/4” NPT unions connected to ¼” Swagelok toggle valves with short pieces of ¼” stainless steel tubing. At the centre of the endplate a stainless steel 1/8” Swagelok to 1/4” NPT union was fitted. All toggle valves, unions and stainless steel tubing were delivered by Teknolab AS (Kolbotn, Norway).



1.3-3: Endplate with toggle valves

2 Experimental

2.1 Equipment and apparatus

A proton transfer reaction mass spectrometer (Compact PTR-MS, Ionicon Analytik G.m.b.H., Innsbruck, Austria) was used for monitoring and quantification, figure 2.1-1. A gas chromatograph Agilent 6890N, Agilent Technologies Inc., Santa Clara, CA, USA) with autosampler and injector (Agilent 7683, Agilent Technologies Inc, Santa Clara, CA, USA) was used for determination of the reference samples, figure 2.1-2

Figure 2.1-1 Compact PTR-MS shown with Supelco gas trap

Figure 2.1-2: Agilent 6890N with Agilent 7683

Table 2.1-1: Equipment used in the experiments

Name	Product	Supplier
Pipettes	Fullpipette 1.5 mL	VWR
Electronic pipette	Biohit eLine 73010X	VWR
Sample vials	Grace 12-14 mL vials with screw caps	Teknolab
Sample vials GC	2 mL with rubber/PTFE-septa	Teknolab
Syringes	Hamilton gastight 1710	Teknolab
Syringes	Hamilton gastight 1705	Teknolab
Syringes	Hamilton gastight 1801	Teknolab
Volumetric flasks	10 mL	VWR
Heating block	Talboys Standard 1 Block Heater	Talboys
Injection unit	ATIS Extraction Glassware with Ground Joint Connector	Sigma-Aldrich
Pumps	SKC Pocket pump 210-1002	Teknolab
Tubes	Polyvinyl chloride tubing for pumps	Teknolab
Pump calibrator	Bios Drycal DC Lite	Teknolab
Sorbent tube	Anasorb CSC 226-01 with caps	Teknolab
Sorbent tube	Anasorb 747 226-81A with caps	Teknolab
Gas bags	SKC Tedlar with dual Stainless steel septum fitting 231-15	Teknolab
Gas trap	Supelco supelpure 22445U	Teknolab

2.2 Reference compounds and chemicals

Table 2.2-1: Reference compounds used in the experiments

Name	Quality	Supplier
Benzene	Analytical grade	Merck(VWR)
Toluene	Analytical grade	Merck(VWR)
m-Xylene	Analytical grade	Fluka
Ethyl benzene	Analytical grade	Fluka
Styrene	Analytical grade	Fluka
1,2,4-Trimethylbenzene	Analytical grade	Fluka
n-butyl acetate	Analytical grade	Merck
1,4-Dioksan	Analytical grade	Fluka
1,3,5-Trimethylbenzene	Analytical grade	Fluka
Acetone	Analytical grade	Merck(VWR)
Butan-2-one (MEK)	Analytical grade	Fluka
4-methylpentan-2-one (MIBK)	Analytical grade	Merck(VWR)

Table 2.2-2: Gases and chemicals used in the experiments

Name	Quality	Supplier
Carbon Disulphide	Glass distilled grad	Rathburn
Dimethylformamide	Analytical grade	Rathburn
Helium	99.9999%	Yara Praxair
Nitrogen	99.999%	Yara Praxair
Synthetic air	99.999%	Yara Praxair
TO-14A Aromatics mixture for PTR-MS calibration	Analytical grade	Scotty Specialty Gases

Table 2.2-3: Some selected physiochemical parameters for the compounds analysed

Chemical	Molecular weight (g/mol)*	Boiling point (°C)*	Density (g/mL)*	Proton Affinity (kJ/mol)**	k_{SC}
Benzene	78.11	80.1	0.8787	750.4	2.06[1)]
Toluene	92.14	110.6	0.866	784.0	2.20[1)]
m-Xylene	106.17	139.3	0.8684	812.1	2.29[1)]
Ethyl benzene	106.17	136.25	0.866	788.0	2.29[1)]
Styrene	104.15	145-146	0.9059	839.5	2.30[1)]
1,2,4-Trimethyl-benzene	120.19	169-171	0.8761		2.35[1)]
n-butyl acetate	116.16	125-126	0.8826		3,16[2)]
1,4-dioxane	88.11	101.1	1.0329	797.4	1.90[3)]
1,3,5-Trimethyl-benzene	120.19	164.7	0.8637	836.2	2.35[1)]
Acetone	58.08	56.5	0.788	812.0	3.82[3)]
Methyl Ethyl Ketone (MEK)	72.11	79.6	0.805	827.3	3.68[3)]
Methyl Isobutyl Ketone (MIBK)	100.16	117-118	0.801		3.69[3)]

*(O'Neil et al. 2006) , ** (*NIST chemistry webbook [electronic resource]*), [1)] k_{SC} rate calculated by Ionicon Analytik, [2)] Calculated using the Su & Chesnavich method (equations 1.2-4 and 1.2-5), dipole moments and polarisability were calculated using Gaussian 03, Revision B.03. (Gaussian Inc. 2004), [3)] (Lindinger et al. 1998)

2.3 Experimental layout

There was performed in total 4 experiments in that formed the basis for this thesis. The experiments were designed to explore how the PTR-MS performed compared to the traditional sampling methods. Several compounds grouped according to their physiochemical parameters were tested.

2.4 Standards and injection solutions

2.4.1 Standards

Standards to the different experiments were made by making a stock solution with 50 µL of each analyte and CS_2 for the given experiment and diluting the stock solution dependent on the theoretical concentrations in the samples given by the injection volume and sample time in 10 mL volumetric flasks. The acetone, butan-2-one and 4-methyl-pentan-2-one standards were diluted in CS_2 containing 2% dimethylformamide. Hamilton syringes were used to transfer the small volumes. The standards were transferred to 2 mL GC-vials containing sorbent from the analysis part of the sorbent tubes. There were made three standards for each experiment where the middle standard had about the same concentration as the samples.

2.4.1.1 Injection solution for experiment 1 – benzene, toluene, m-xylene

The injection solution was made by mixing 1.5 mL Benzene, 1.5 mL Toluene and 2 mL m-xylene (highest molar mass) by adding the compounds to a 12-14 mL sample vial using an electronic pipette.

2.4.1.2 Injection solution for experiment 2 – ethyl benzene, styrene, 1,2,4-Trimethylbenzene

The injection solution for experiment 2 was made by mixing 1.5 mL ethyl benzene, 1.5 mL styrene and 2.0 mL 1,2,4-Trimethylbenzene (highest molar mass) by adding the compounds to a 12-14 mL sample vial using an electronic pipette.

2.4.1.3 Injection solution for experiment 3 – n-butyl acetate, 1,4-dioxane, 1,3,5-Trimethylbenzene

The injection solution was made by mixing 1.5 mL n-butyl acetate, 2.0 mL 1,4-dioxane and 1.5 mL 1,3,5-Trimethylbenzene by adding the compounds to a 12-14 mL sample vial using an electronic pipette. 1,4-dioxane was chosen as the most abundant compound here as it shows poorer response in the GC-analysis.

2.4.1.4 Injection solution for experiment 4 – acetone, butan-2-one, 4-methylpentan-2-one

The injection solution was made by mixing 1.5 mL acetone, 1.5 mL butan-2-one (methyl ethyl ketone (MEK)) and 2.0 mL 4-methylpentan-2-one (methyl isobutyl ketone (MIBK))(highest molar mass) by adding the compounds to a 12-14 mL sample vial using an electronic pipette.

2.5 Calibration of PTR-MS

The PTR-MS instruments was calibrated (mass and transmission) using a high-quality standard gas mixture (Scotty Specialty Gases, Plumsteadville, Pennsylvania, USA)consisting of 14 aromatic components with known concentrations. The components were Benzene, Chlorobenzene, 1,2-dichlorobenzene, 1,3-Dichlorobenzene, 1,4-dichlorobenzene, ethyl benzene, styrene, toluene, 1,2,4-trichlorobenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, *m*-xylene, *o*-xylene and *p*-xylene. All were in the mass area of 100 ppb. For certificate of analysis see Appendix.

2.6 Set-up and sampling

The injection unit was installed in the heating block which was turned on prior to the experiments to achieve a high temperature and mounted to the test chamber. The pumps were calibrated using the Dry Cal Lite. A gas bag was filled with nitrogen and attached to the injection unit. The pressure sensors in the chamber were tested prior to injection

2.-1: An illustration of the set up for injection showing the injection unit (installed in the heating block) connected to the test chamber and a gas bag with N_2

A known amount of sample was injected through the septum as the toggle valve leading in to the chamber was opened. The amount of sample injected was calculated to correspond to approximately 1 or 2 ppm. Nitrogen flushed through the injection unit and into the chamber as the chamber was held at near vacuum to ensure that all of the analyte was transferred to the chamber. The toggle valve was closed and the test chamber was filled with synthetic air to create an artificial atmosphere. The amount of air was controlled by calculating the relevant pressure needed to achieve an atmosphere with the volume required for sampling (100 L). Gas bags were mounted as shown in figure 1.3-2 and the toggle valves were opened allowing the pressure in the chamber to equalise to the ambient pressure.

The sorbent tubes were cut open by removing the sealed ends and connected to the test chamber and the tubes leading from the pumps. The toggle valves were opened and the pumps started. After a given time the sampling was ended, the pumps were turned off and the toggle valves capped. The sampling time was varied from 60 to 120 minutes

The PTR-MS inlet was detached from its carbon trap and connected to the central outlet of the test chamber where the toggle valve was opened. The PTR-MS instrument was operated in monitored ion detection (MID) mode at the start of sampling and at the end of the sampling. In addition a scan was performed at the end of the sampling.

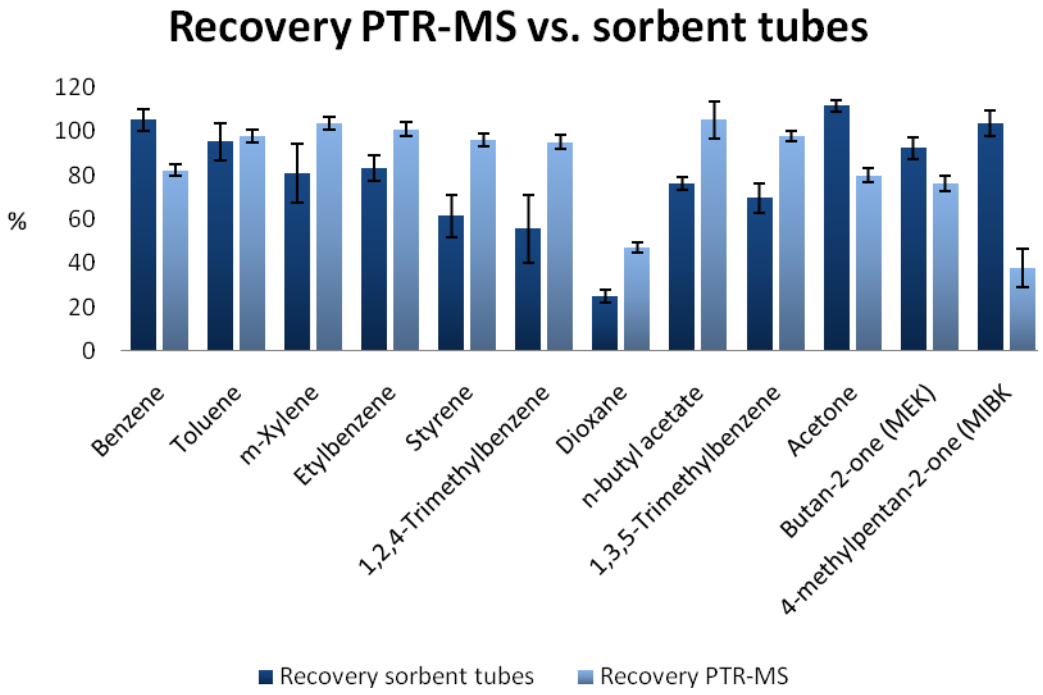
2.7 Preparation of reference samples

The sorbent tubes were capped immediately after sampling using caps supplied in the sorbent tube package. The analysis and the control section of each tube were transferred to 2 mL GC-vials where 1.5 mL CS_2 was added before the vials were capped. The Acetone, MEK, MIBK samples were desorbed using CS_2 with 2 % dimethylformamide for better desorption. A blind sample was made by desorbing the sorbent of an unexposed tube with the same lot number as the exposed tubes. The samples and standards were left to desorb overnight before analysis. The pumps were calibrated after sampling.

2.8 GC-Analysis

A Chromapack 7525 TCEP column (50m x 0.25mm d_f 0.40 µm) was used for the analysis. The injection was splitless due to low concentrations of sample. Helium was used as carrier gas. The temperature program started at 35 °C for 10 minutes, a rate of 4 °C/min until reaching 100 °C where the column was kept for another 10 minutes. 1 µL of desorbed sample and standards were injected. 3 standards were used for quantification except for the last experiment where 4 were chosen. 1 blind sample was analysed as well as controls for each sample.

3 Results and discussion



3-1: Graphical reproduction of recovery data. PTR-MS data are averaged except for n-butyl acetate.

As the graph shows there is a noticeable difference in the results from the sorbent tubes and PTR-MS. They do seem to show similar trends for recovery with benzene and MIBK as the two exceptions. The most apparent difference other than the differences in recovery is the differences in relative standard deviation(RSD) represented by the error bars. The relative standard deviation is higher for the sorbent tubes than the PTR-MS. This is a result of the amount of measurements taken. The results for PTR-MS are calculated from approximately 30 cycles. A high amount of measurements taken will lead to a lower standard deviation and relative standard deviation as the eventual outliers will have less impact on the result. The higher standard deviation for the sorbent tubes will be discussed in the sorbent tube section.

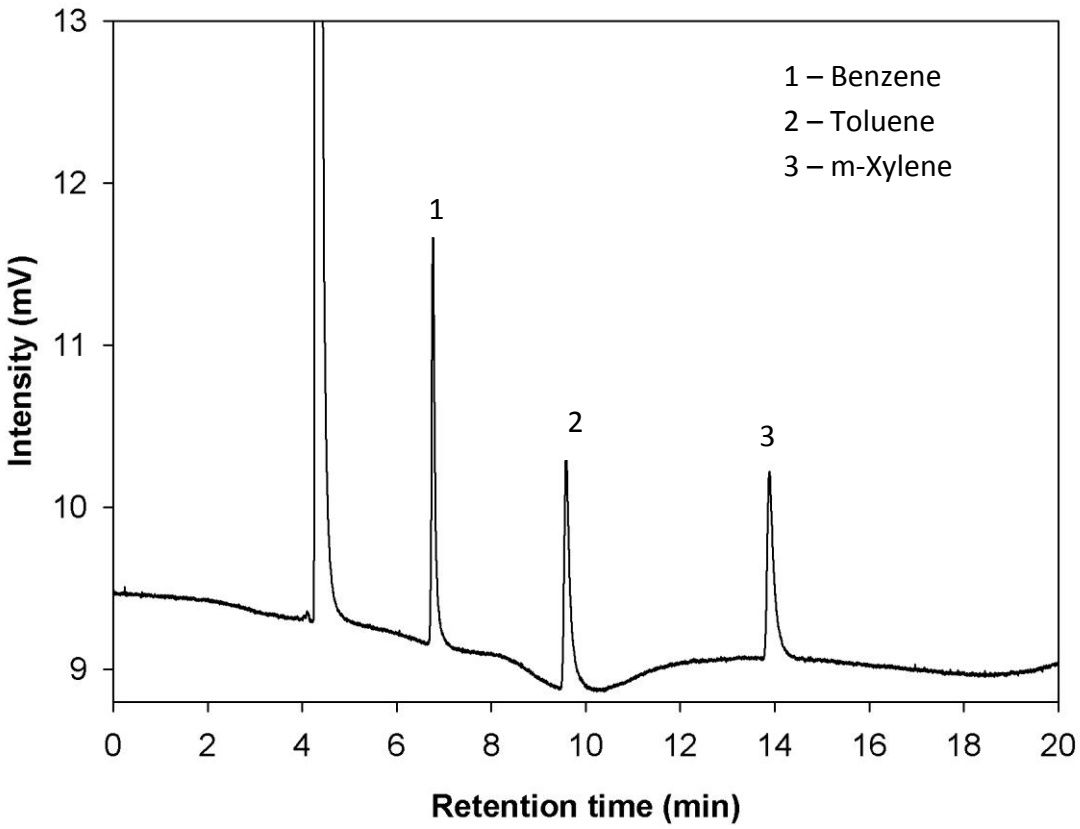
3.1 Sorbent tubes and GC-analysis

Table 3.1-1: Results from analysis of sorbent tubes

Analyte	Average (ppb)	RSD (%)	Recovery (%)
Benzene	2 779	4.9	105
Toluene	2 103	8.4	95.1
m-Xylene	2 051	14	80.8
Ethyl benzene	1 596	5.8	83.2
Styrene	1 256	9.5	61,4
1,2,4-Trimethylbenzene	1 268	15	55.5
1,4-dioxane	923	3.0	25.1
n-butyl acetate	1 358	2.8	76.3
1,3,5-Trimethylbenzene	1 176	6.6	69.6
Acetone	1 189	2.7	112
Butan-2-one(MEK)	806	5.0	92.2
4-methylpentan-2-one (MIBK)	648	5.8	104

The first experiment where benzene, toluene and m-xylene were analysed shows a high recovery percentage for the analytes using sorbent tubes and GC as method. This points to that the injection was successful as a high amount of analyte is transferred to the test chamber and that the gas bags and the chamber do not retain the analytes. The recovery decreases with increasing boiling point of the analyte (ref

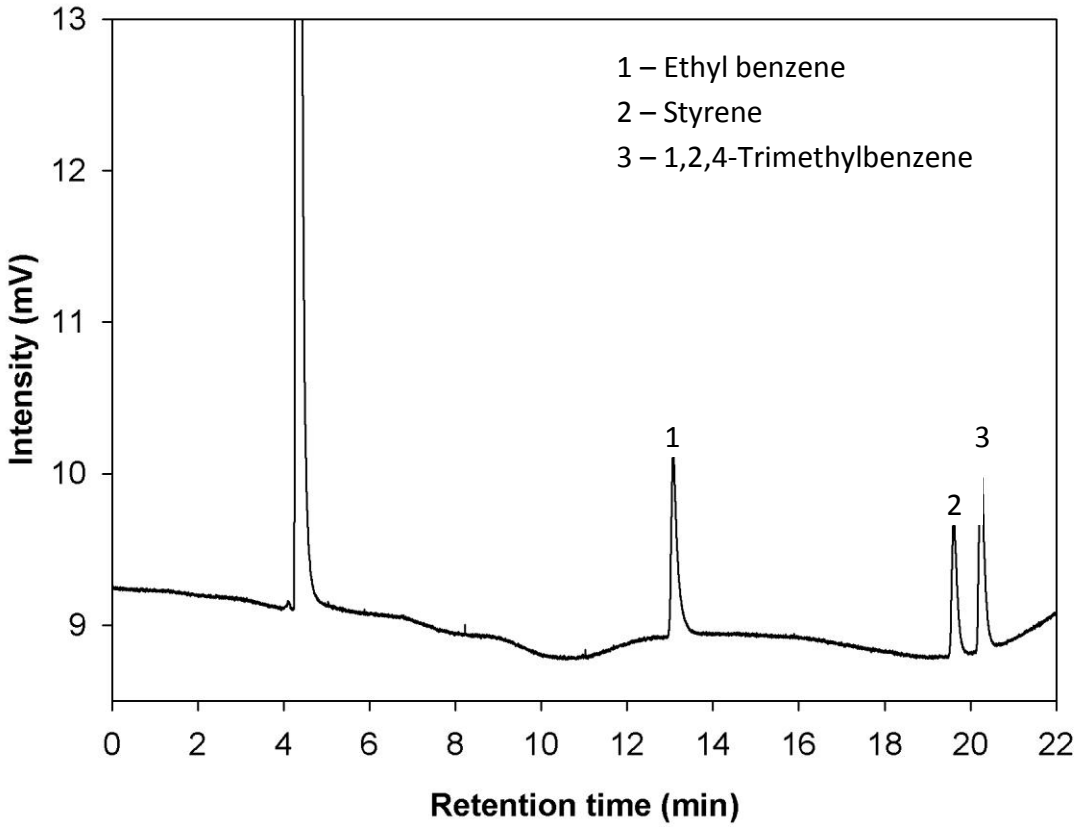
Table 2.2-3), this may be caused by the heating block which has a maximum temperature of 150 °C. It is not unreasonable that the heating block had a temperature somewhere around the boiling point of m-xylene (139.3 °C) as it takes a certain amount of time for a heating block to reach its maximum temperature. The blind sample contained no amount of analyte.



3.1-1: Chromatogram showing the peaks for benzene, toluene and m-xylene.

The chromatogram shows that the resolution was good, all peaks showed baseline separation, there were no overloaded peaks as was expected with the relatively small amounts of sample.

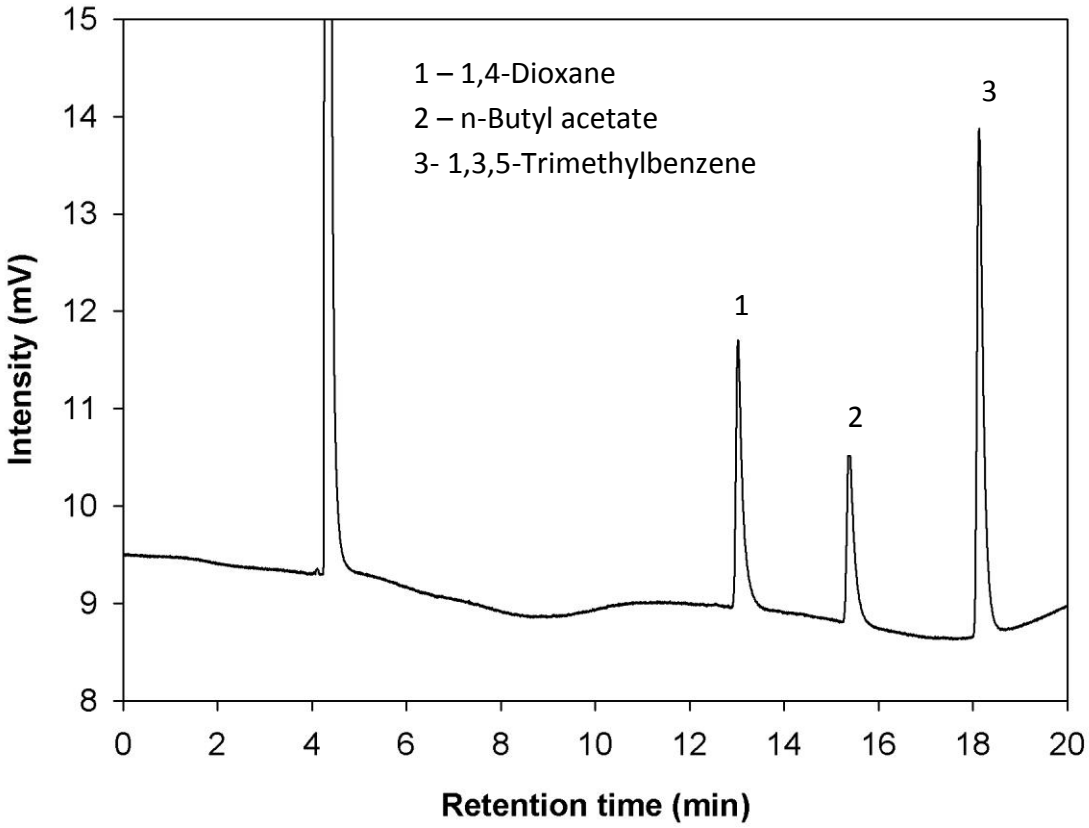
For the second experiment there is also a trend for the sorbent tubes that recovery is related to the boiling points of the compounds as in experiment 1. The lower recovery observed with these compounds further supports the theory of a relation between boiling point and recovery as the compounds have boiling points exceeding the maximum temperature for the heating block. Though there is also a possibility for the compounds to be retained in the test chamber or gas bags or that only parts of the injection solution reached the test chamber.



3.1-2: Chromatogram showing the peaks for ethyl benzene, styrene and 1,2,4-trimethylbenzene

As shown in the chromatogram there were no overlap of peaks and the resolution was good, there is baseline separation between the peaks allowing for an easy integration and good quantitative results.

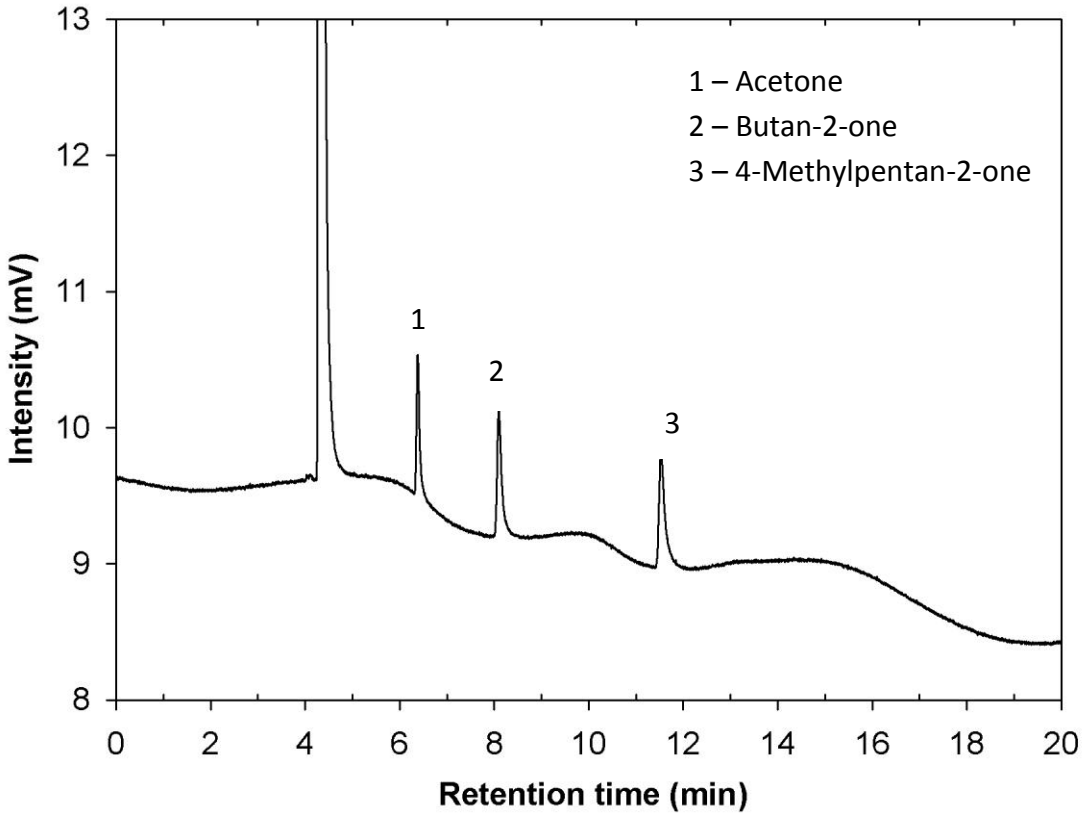
The 1,4-dioxane, n-butyl acetate and 1,3,5-trimethylbenzene samples shows relatively low recovery compared to the other compounds. 1,4-Dioxane generally has a poorer response in the GC method than the other analytes but this should not affect the recovery of 1,4-dioxane to such a great extent. Generally the recoveries are low. 1,3,5-trimethylbenzene has a high boiling point, but n-butyl acetate lies at the same level as the level as the compounds in experiment 1. In other words there may be a loss of sample here. There are two causes that are the most probable here, they are either the injection in to the test chamber or the sample preparation. The sample preparation involves work under a fume hood as the desorption agent CS_2 has toxic effects. If the capping of the vials after addition of desorption agent was not performed immediately some of the compounds may have evaporated. Apart from the 1,4-dioxane this experiment does also seem to support a relation between boiling point and recovery.



3.1-3: Chromatogram showing the peaks for 1,4-dioxane, n-butyl acetate and 1,3,5-trimethylbenzene

The chromatogram shows well resolved peaks with baseline separation and narrow peaks.

The ketones acetone, butan-2-one and 4-methylpentan-2-one shows a recovery reasonably close to 100 %. The retention of analytes in the chamber or the gas bags is not very likely for these compounds as it would imply that there was injected more of the compounds than the original purpose. Interestingly is this the only experiment not showing a relation between boiling point and recovery as the lowest recovery is observed with butan-2-one and not 4-methylpentan-2-one which has the highest boiling point though, the ketones does have the lowest boiling points of the compounds analyzed and should all be transferred readily into the test chamber.

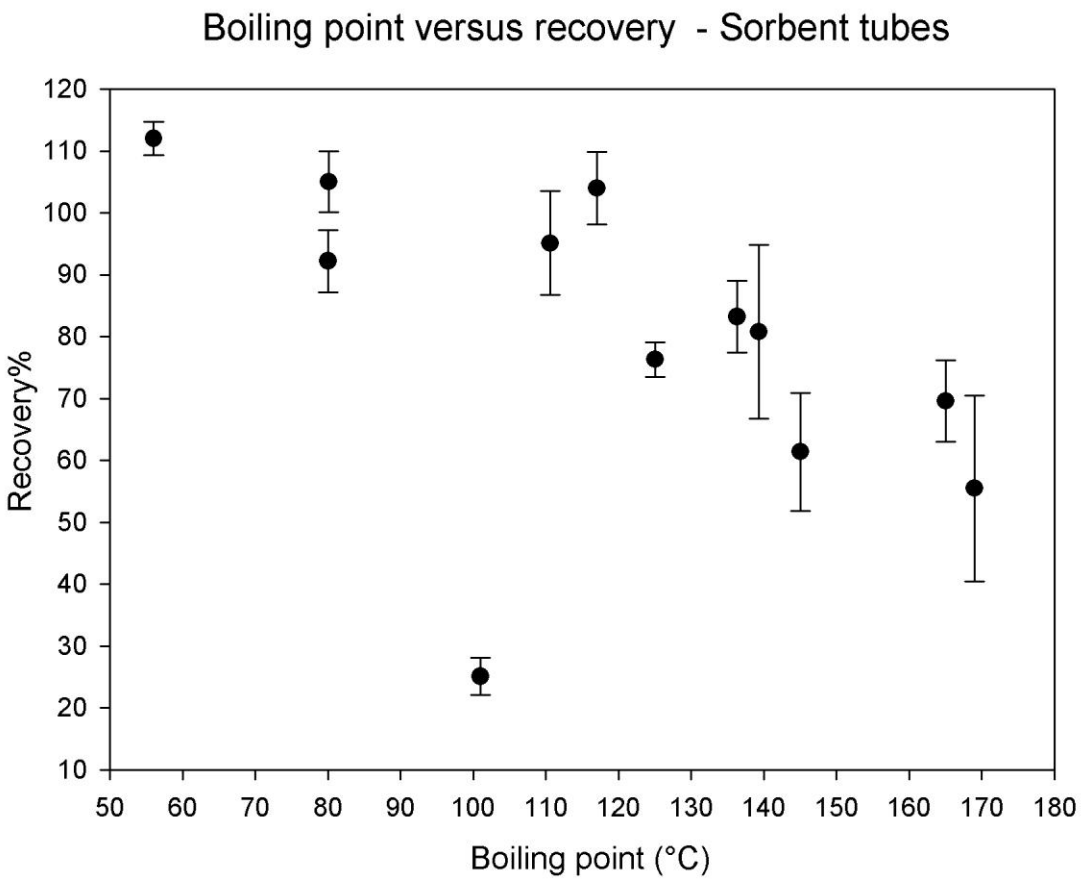


3-1-4: Chromatogram showing the peaks for acetone, butan-2-one and 4-methylpentan-2-one

The peaks in this chromatogram are a bit lower than the others, this is caused by a lower amount of sample as less amount of compounds were injected into the test chamber in the last experiment. The peaks are well separated in this chromatogram to and band broadening does not seem to be an issue at all in these experiments.

The chromatographic method used is the same method used by NIOH for analysis of samples except for the injection which is splitless as the amounts of sample is less than in the real samples.

The chromatograms of the control samples did not contain any analyte, there is in other words no breakthrough which means that the samples can be considered to be valid regarding the quantification.



3.1-5: Recovery plotted against boiling point for the compounds based on sorbent tube analysis

The plot in figure 3.1-5: Recovery plotted against boiling point for the compounds based on sorbent tube analysis shows that there most likely is a relation between the recovery and the boiling point with the current set-up of the test chamber. This is an important observation for further use of the test chamber with the current set-up. In addition to the assumption that the lower recovery observed at compounds with higher boiling points may be caused by the injection there is also a possibility that adsorption may be the cause as loss of compound due to adsorption naturally plays a greater role when sampling at low concentrations. The concentrations sampled in these experiments are in several cases far lower than the OELs for the compounds. The outlier here is 1,4-dioxane whose low recovery is difficult to explain but a possible explanation may be a problem with the reference compound.

A possible cause for the high relative standard deviation for the sorbent tubes in general may be the adsorption to surfaces in the gas bags. The gas bags do have a greater surface than the inside of the test chamber, if they do adsorb some of the compounds that would lead to a concentration gradient in the test chamber as the artificial atmosphere inside the chamber no longer will be homogenous.

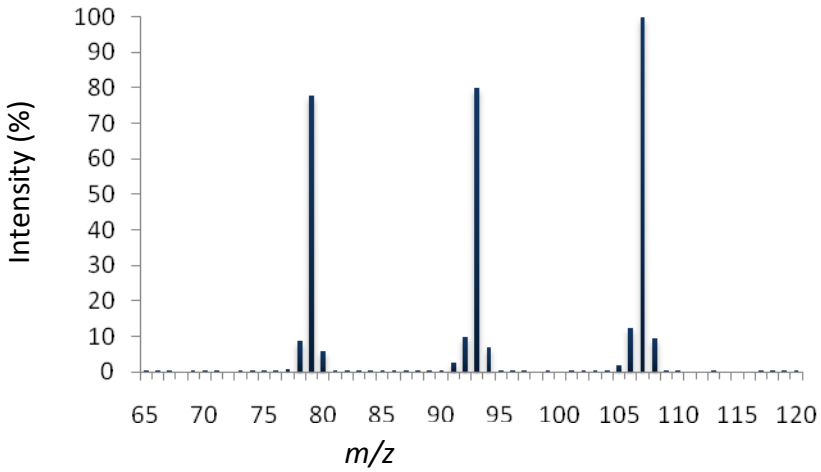
3.2 PTR-MS

Table 3.2-1: Results from PTR-MS

Analyte	PTR-MS start (ppb)	RSD (%)	PTR-MS stop (ppb)	RSD (%)	Recovery (%)
Benzene	2180	2.78	2168	4.2	82.2
Toluene	2168	3.00	2144	4.5	97.5
m-xylene	2678	2.90	2571	4.1	103
Ethyl benzene	1993[1)]	3.36	1875[1)]	3.2	101
Styrene	2222	2.99	1710	4.6	96.1
1,2,4-Trimethylbenzene	2230	3.24	2109	3.8	95.0
1,4-dioxane	1862[(2]	2.35	1610[(2]	2.76	47.2
n-butyl acetate	464[(3]	8.46	1872[(3]	5.90	105*
1,3,5-Trimethylbenzene	1790	2.5	1509	2.90	97.6
Acetone	857	2.46	848	2.09	79.9
Butan-2-one(MEK)	669	3.48	666	2.33	76.3
4-methylpentan-2-one (MIBK)	239[(4]	8.71	235[(4]	2.73	37.8

*Not averaged as fragment at *m/z* 61 was not measured at the start of the experiment. Sum of *m/z*. [1)] Sum of *m/z* 79 and *m/z* 107. [(2] Sum of *m/z* 45 and *m/z* 89. [(3] Sum of *m/z* 41, 43, 61 and 71. [(4] The fragmentation patterns were not established at the time of the analysis so some fragments were not measured.

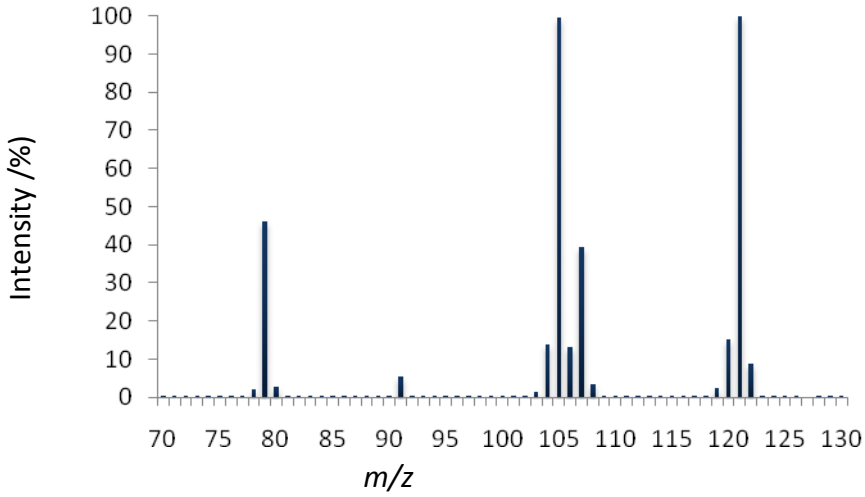
The PTR-MS data shows an opposite trend compared to the sorbent tubes for the first experiment where the compounds benzene, toluene and m-xylene were analysed. The mass spectrum shows that the compounds are not subject to any fragmentation in PTR-MS.



3.2-1: CI-mass spectrum for the compounds benzene (*m/z* 79), toluene (*m/z* 93) and m-xylene (*m/z* 107)

The recovery is much higher than the sorbent tubes recoveries. It seems as though PTR-MS underestimates the concentration of benzene, it is not clear why this is the case. Recovery for toluene is well within the error margin for the sorbent tube recovery. The calibration will have had an impact on the quantification of m-xylene as the gas standard contained all three isomers of xylene, ortho, meta and para. The same k-value was used in this experiment as the k-value during calibration. This implies an overestimation of the m-xylene concentration as the k-value for the three isomers is higher than for m-xylene.

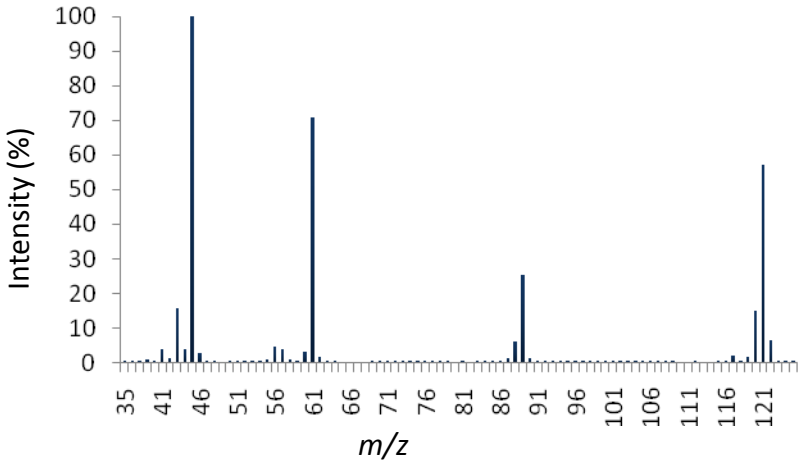
The compounds ethyl benzene, styrene and 1,2,4-trimethylbenzene show the same trend as the sorbent tubes with a recovery related to the boiling point of the compounds, but the recovery is higher than the recovery for the sorbent tubes.



3.2-2: CI mass spectrum for the compounds ethyl benzene (*m/z* 107), styrene (*m/z* 105) and 1,2,4-trimethylbenzene (*m/z* 121)

The mass spectrum for these compounds shows that fragmentation is an issue where analysing ethyl benzene. Ethyl benzene fragments by loss of ethane, leaving a benzene fragment at *m/z* 79. During the experiment, *m/z* 79 was measured and added to the concentration at *m/z* 107. This may pose a problem when quantifying a mixture of ethyl benzene and benzene. It seems as though the PTR-MS overestimates these compounds.

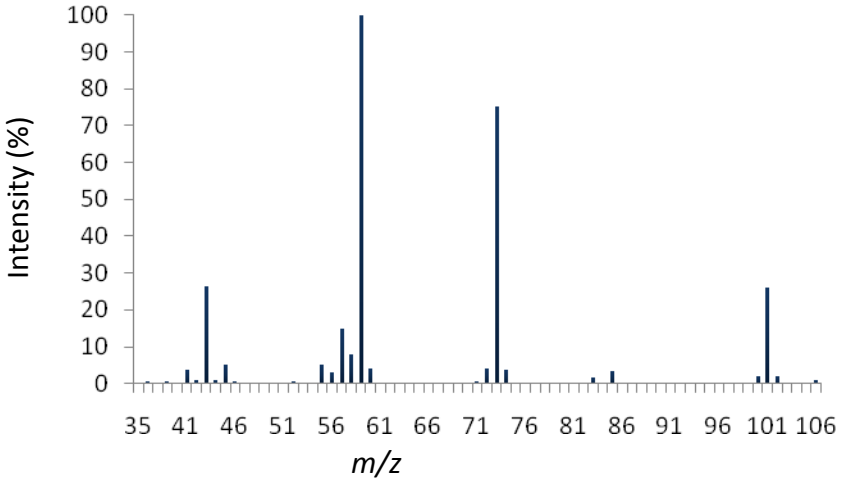
The measurements of 1,4-dioxane, n-butyl acetate and 1,3,5-trimethylbenzene is in compliance with the data from the sorbent tubes but does again show higher recovery. The compounds analysed does show fragmentation as shown in the mass spectrum.



3.2-3: Mass spectrum for the compounds 1,4-dioxane (*m/z* 89), n-butyl acetate (*m/z* 117) and 1,3,5-trimethylbenzene (*m/z* 121)

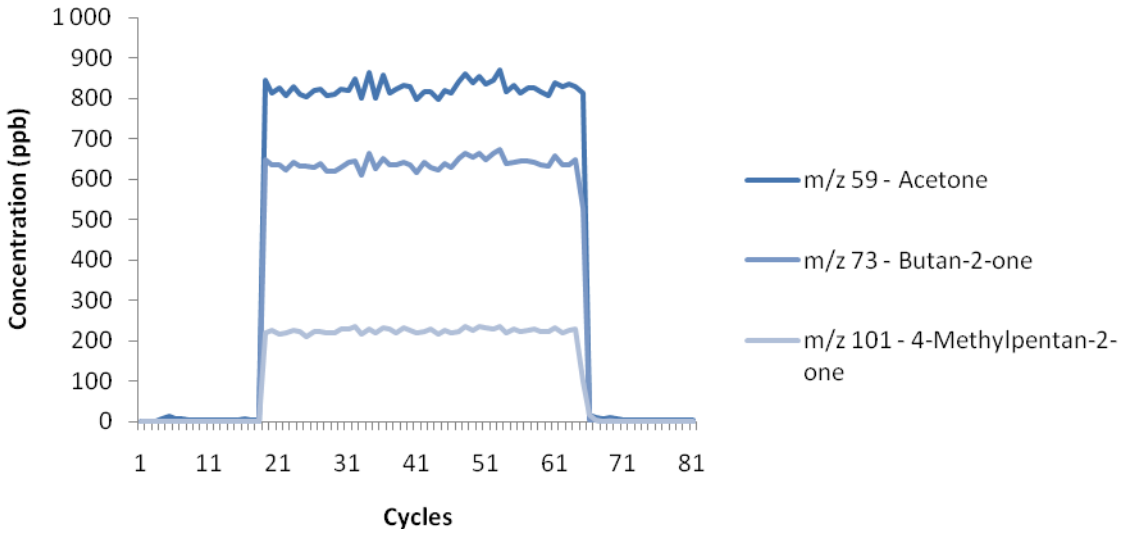
The protonated molecular ion of butyl acetate is barely visible in the mass spectrum. It was discovered that butyl acetate fragments to an acetic acid fragment at *m/z* 61, a fragment at *m/z* 43 which most likely is a ($CH_3CO)^+$ fragment and a fragment at *m/z* 41. At the measurements the fragmentation to acetic acid was not discovered until the end measurement of the experiment, this explains the low recovery at the start measurement. The degree of fragmentation for n-butyl acetate does also explain the elevated RSD for the compound as some of the masses measured had very low concentrations. RSD at low concentrations will often become very large as the average concentration is the denominator when calculating RSD causing the RSD to increase. 1,4-Dioxane fragments to acetaldehyde at *m/z* 45. The recovery for 1,4-dioxane is relatively low measured by PTR-MS as well, this may imply that there is something wrong with the reference compound.

The last experiment involving the ketones acetone, butan-2-one and 4-methypentan-2-one is the only experiment where the PTR-MS data shows lower recoveries than the sorbent tubes. The 4-methylpentan-2-one shows the lowest recovery. This is due to a fragmentation of the compound shown in the mass spectrum



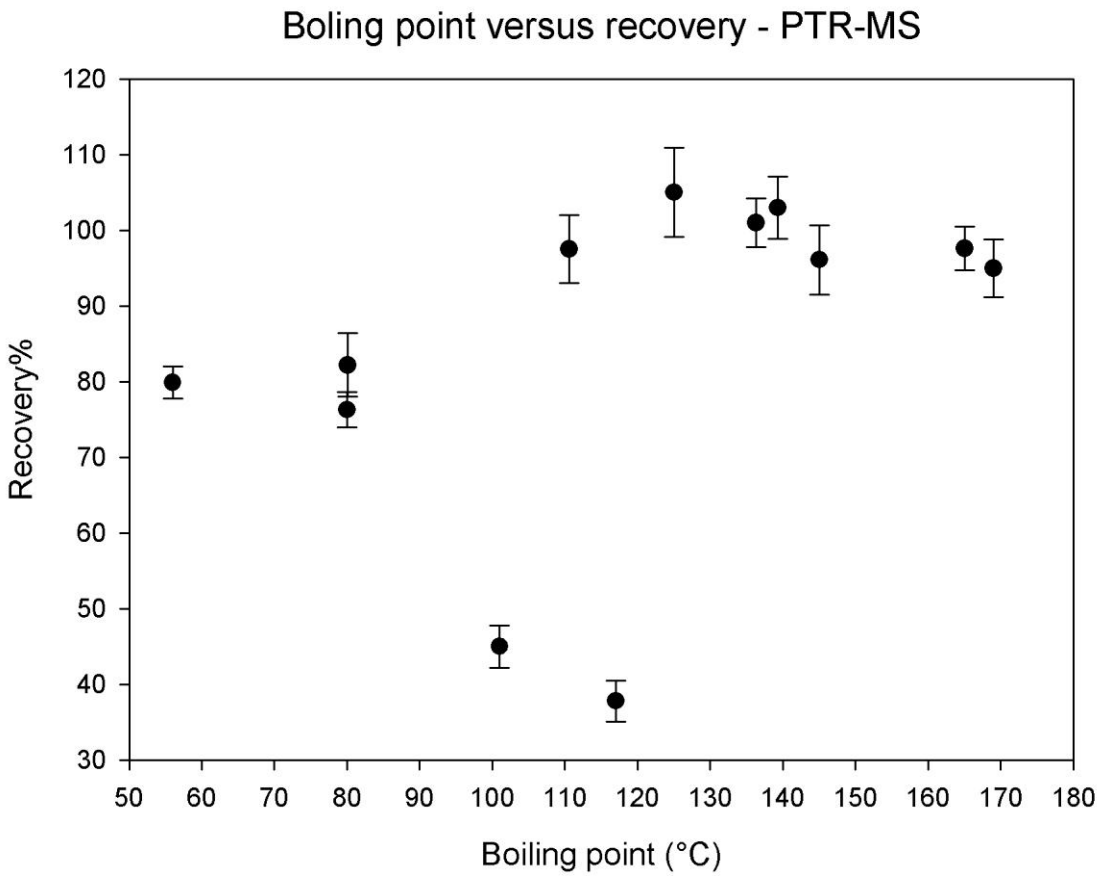
3.2-4: CI mass spectrum for the compounds acetone (*m/z* 59), butan-2-one (*m/z* 73) and 4-methylpentan-2-one (*m/z* 101).

It is obvious from the CI mass spectrum that 4-methylpentan-2-one has fragmented, the most abundant fragment in the mass spectrum is *m/z* 43 which may be a $(CH_3CO)^+$ fragment from 4-methylpentan-2-one. The fragment at *m/z* 57 represents a neutral loss of 43 from protonated 4-methylpentan-2-one or a neutral loss of 15 from protonated butan-2-one where the latter is the more likely as 4-methylpentan-2-one has a methyl group attached to its aliphatic chain making a loss of 43 implausible. *m/z* 43 and 57 were not quantified during the experiment and this is most likely the cause for the low recoveries of butan-2-one and 4-methylpentan-2-one. The quantification cannot be made from scan mode in PTR-MS as the scan mode uses one single proton transfer coefficient throughout the mass area which leads to errors in the quantification. The scan mode is used for detection of compounds only.



3.2-5: The quantification as represented by the PTR-MS. One cycle last 4,2 seconds. The PTR-MS was connected to a hydrocarbon trap prior to and after the measurements of the test chamber

The chart illustrates the monitoring of the concentration of acetone, butan-2-one and 4-methylpentan-2-one. The inlet was connected to the hydrocarbon trap prior to connection to the test chamber. The response is very fast as represented on this graph where the time resolution is 4.2 seconds. The drop in concentration after the inlet was disconnected from the test chamber is observed over 1 cycle. This confirms that the instrument has a short response time. The time taken for the compound to travel the 1.2 m capillary of the inlet is not measured in this experiment but it is not expected to cause a large delay. The net effect is that PTR-MS appears to be a good choice for monitoring peak exposures



3.2-6: Recovery plotted against boiling points for the compounds based on PTR-MS

The trend of lower boiling points giving higher recoveries does not seem to be supported by the PTR-MS data, but as shown earlier on PTR-MS does appear to overestimate recoveries when compared to the sorbent tubes. As sorbent tubes analysed via GC-FID is a confirmed well documented methodology those results are considered to be the more accurate.

4 Conclusion

Based on the results it may seem as the set-up for the test chamber with injector will be best suited for compounds with a boiling point less than 120 °C. PTR-MS appears to work well with a great amount of the compounds tested, but knowledge regarding the fragmentation patterns is required is important to achieve an accurate quantification. It may seem that PTR-MS overestimates the concentrations in some cases, this needs to be explored in each particular instance. Both fragmentation and overestimations of concentrations should be checked prior to the use of PTR-MS. The ability to detect peak exposure as a result of the short response time(seconds) is a great advantage of using PTR-MS and may aid in elucidating the sources of exposure in production processes. These peaks will be invisible when using traditional averaged sampling methods consequently the PTR-MS can identify and help remove the peak exposures and thus the total exposure.

5 References

Adams, N. G. & Smith, D. (1976). The selected ion flow tube (SIFT); A technique for studying ion-neutral reactions. *International Journal of Mass Spectrometry and Ion Physics*, 21 (3-4): 349-359.

Ahuja, S. (2003). *Chromatography and Separation Science*. Separation Science and Technology, vol. 4. San Diego, California, USA: Academic Press. 250 pp.

Ausloos, P. & Lias, S. G. (1987). *Structure/Reactivity and Thermochemistry of Ions* Reidel, Dordrecht, NL: Springer. 508 pp.

Blake, R. S., Monks, P. S. & Ellis, A. M. (2009). Proton-Transfer Reaction Mass Spectrometry. *Chemical Reviews*, 109 (3): 861-896.

Brown, R. H. (2002). Monitoring volatile organic compounds in air - the development of ISO standards and a critical appraisal of the methods. *Journal of Environmental Monitoring* 4: 112-118.

Chesnavich, W. J., Su, T. & Bowers, M. T. (1980). Collisions in a noncentral field: A variational and trajectory investigation of ion--dipole capture. *The Journal of Chemical Physics*, 72 (4): 2641-2655.

Downard, K. M. (2004). *Mass spectrometry a foundation course*. Cambridge, UK: RCS Publishing. 206 pp.

Ellis, H., Pai, R., McDaniel, E., Mason, E. & Viehland, E. H. (1976). At. Data Nuci. *Data Tables*, 17: 77.

Gaussian 03, Revision B.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

Harris, D. C. (2007). *Quantitative Chemical Analysis*. 7 ed. New York, New York, USA: W. H. Freeman and Company. 663 pp.

Hunter, E. P. L. & Lias, S. G. (1998). Evaluated Gas Phase Basicities and Proton Affinities of Molecules: An Update. *Journal of Physical and Chemical Reference Data*, 27 (3): 413-656.

ICIS.com (2008) Toluene Uses and Market Data. Available at http://www.icis.com/v2/chemicals/9076550/toluene/uses.html (accessed 11.05.2010)

InProcess Instruments. (2010). *IPI - InProcess Instruments - Mass Spectrometry/Quadrupole Mass Spectrometry*. Available at: http://www.in-process.com/mass-spectrometry-quadrupole-mass-spectrometry.html (accessed: 12.04.2010).

International Organization for Standardization. (2001). *Workplace air quality -- Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography -- Part 1: Pumped sampling method*, 16200-1: ISO.

Ionicon Analytik GmbH. (2010). *Compact PTR-MS*. Available at: http://www.ptrms.com/products/ptrqms/cptrms.html (accessed: 07/05/2010).

Johansen, I., Wendelboe, J. F. (1981). Dimethylformamide and carbon disulphide desorption efficiencies for organic vapours on gas-sampling charcoal tube analyses with a gas chromatographic backflush technique. *Journal of Chromatography A,* 217: 317-326

Lagg, A., Taucher, J., Hansel, A. & Lindinger, W. (1994). Applications of proton transfer reactions to gas analysis. *International Journal of Mass Spectrometry and Ion Processes*, 134 (1): 55-66.

Langevin, M. (1905). *Ann. Chim. Phys.* , 245: 5.

Lau, Y. K., Ikuta, S. & Kebarle, J. (1982). Thermodynamicsand kinetis of the gas-phase reactions $H_3O^+(H_2O)_{n-1}$ + water = $H_3O^+(H_2O)_n$. *Journal of the American Chemical Society*, 104 (6): 1462-1469.

Lindinger, W., Hansel, A. & Jordan, A. (1998a). On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) Medical applications, food control and environmental research. *International Journal of Mass Spectrometry and Ion Processes* 173: 191-241.

Lindinger, W., Hansel, A. & Jordan, A. (1998b). Proton-transfer-reaction mass spectrometry (PTR-MS): online monitoring of volatile organic compounds at pptv levels. *Chemical Society Reviews*, 27: 347-354.

Maltoni, C., Conti, B. & Cotti, G. (1983). Benzene: A multipotential carcinogen. Results of long-term bioassays performed at th Bologna Institute of Oncology. *American Journal of Industrial Medicine*, 4 (5): 589-630.

NIOSH. (2003). *Manual of Analytical Methods*. Schlecht, P. C., O'Connor, P.F. (ed.), 2003-154 (3rd Supplement): Department of Health and Human Services (National Institute for Occupational Safety and Health).

NIST chemistry webbook [electronic resource]. National Institute of Standards an Technology (eds), Accessed from http://webbook.nist.gov/chemistry/. Washington, D.C. :: National Institute of Standards and Technology.

O'Neil, M. J., Heckelman, P. E., Koch, C. B. & Roman, K. J. (eds). (2006). *The Merck Index: An Encyclopedia of Chemicals, Drugs and Biologicals*. 14th ed. Whitehouse Station, NJ, USA: Merck & Co Inc.

Praxmarer, C., Hansel, A., Jordan, A., Kraus, H. & Lindinger, W. (1993). Reactions of Kr_2^+ with various neutrals. *International Journal of Mass Spectrometry and Ion Processes*, 129: 121-130.

Scientific instruments Services (2010) Isotope Distribution Calculator and Mass Spec Plotter. Available at: http://www.sisweb.com/mstools/isotope.htm (accessed: 11.05.2010)

Scorecard.org (2005). Scorecard Chemical Profile Search. Available at: http://scorecard.org/chemical-profiles/index.tcl (accessed: 11.05.2010)

Skoog, D. A., Holler, F. J. & Crouch, S. R. (2007). *Principles of Instrumental Analysis*. 6 ed.: Thomson Higher Education. 1031 pp.

Su, T. & Chesnavich, W. J. (1982). Parametrization of the ion--polar molecule collision rate constant by trajectory calculations. *The Journal of Chemical Physics*, 76 (10): 5183-5185.

The Norwegian Labour Inspection Authority. (2009). *Veiledning om administrative normer for forurensning i arbeidsatmosfære - fulltekst*. Trondheim, NO.

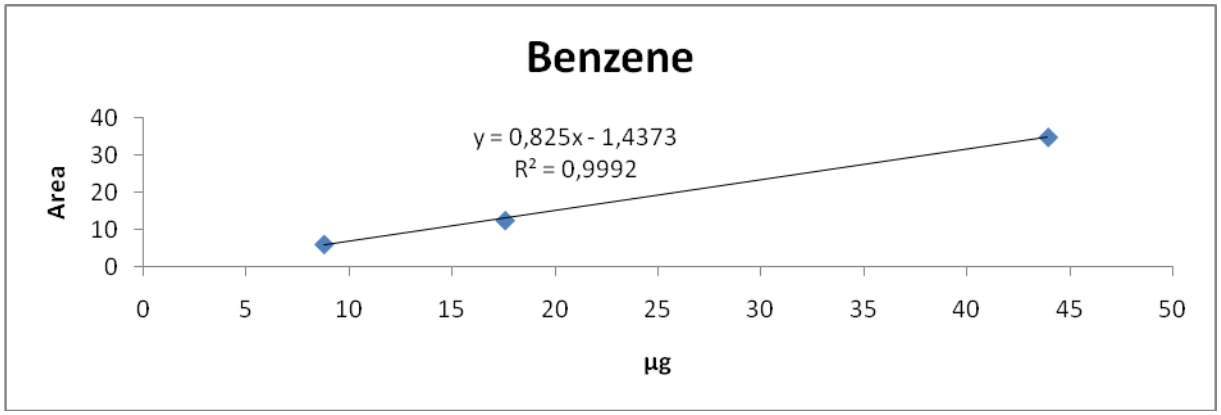
U.S Environmental Protection Agency. (2010). Drinking water contaminants. Available at : http://www.epa.gov/safewater/contaminants/index.html#organic (accessed: 11.05.2010)

Viggiano, A., Dale, F. & Paulson, J. F. (1988). Proton Transfer reactions of $H^+(H_2O)_{n=2-11}$ with methanol, ammonia, pyridine, acetonitrile and acetone. *Journal of Chemical Physics*, 88 (4): 2469-2478.

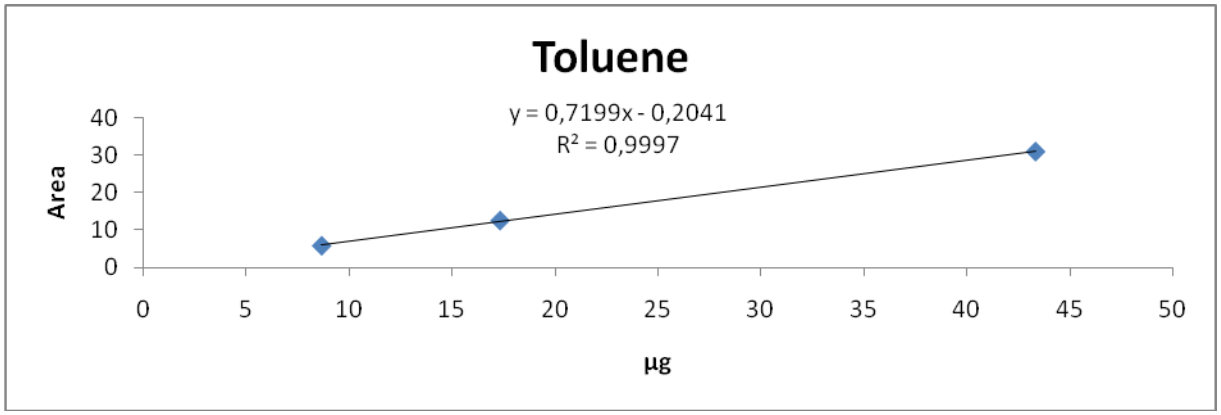
Wikimedia Commons. (2009). *File:Gas Chromatograph.png*. Available at: http://commons.wikimedia.org/wiki/File:Gas_chromatograph.png (accessed: 15.04.2010).

Appendix

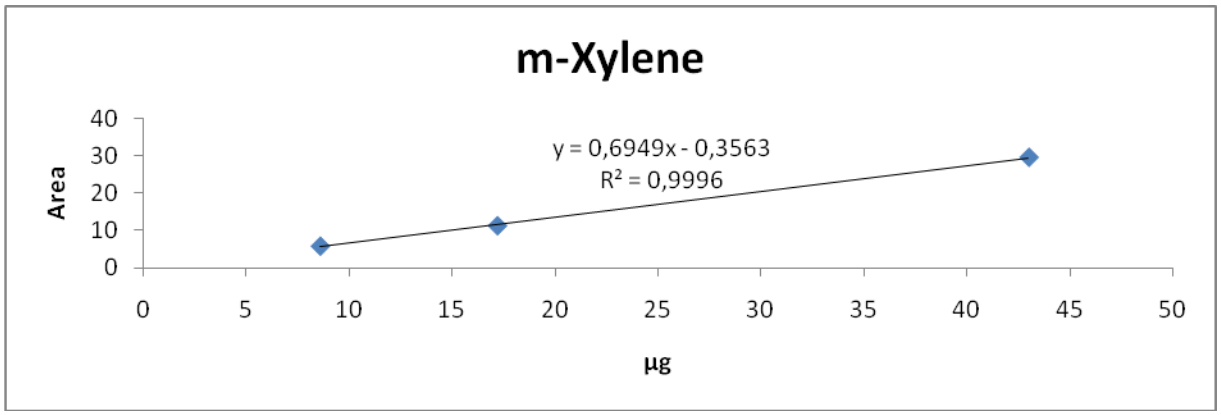
1 Standard curves for GC-FID analysis



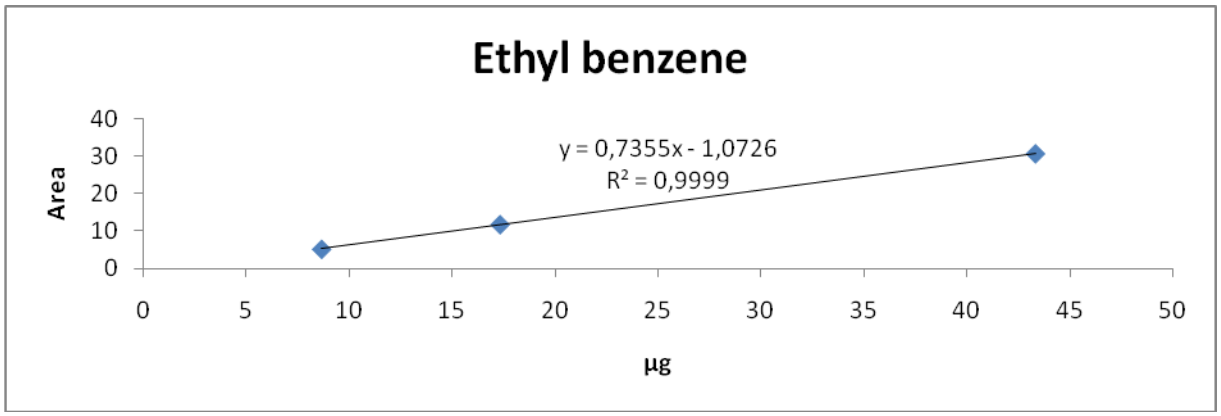
1-1: Standard curve for benzene



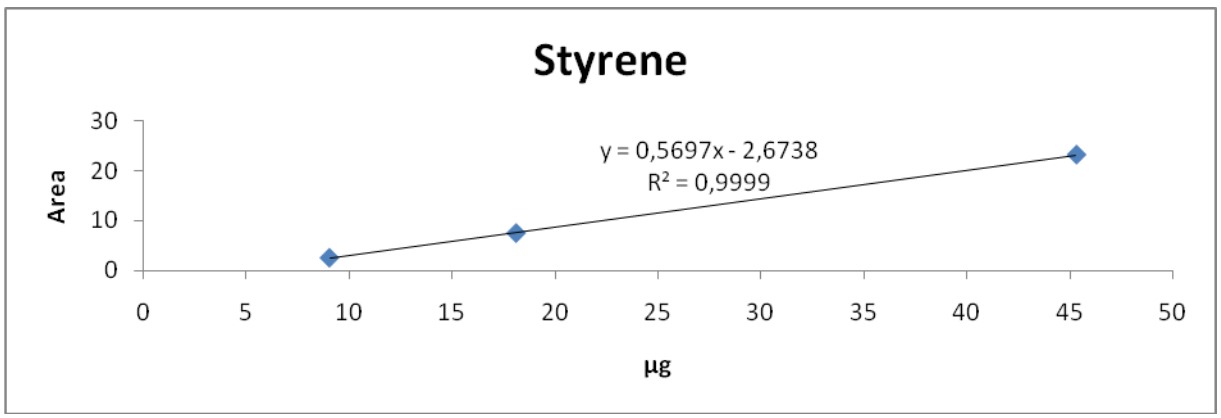
1-2: Standardcurve for Toluene



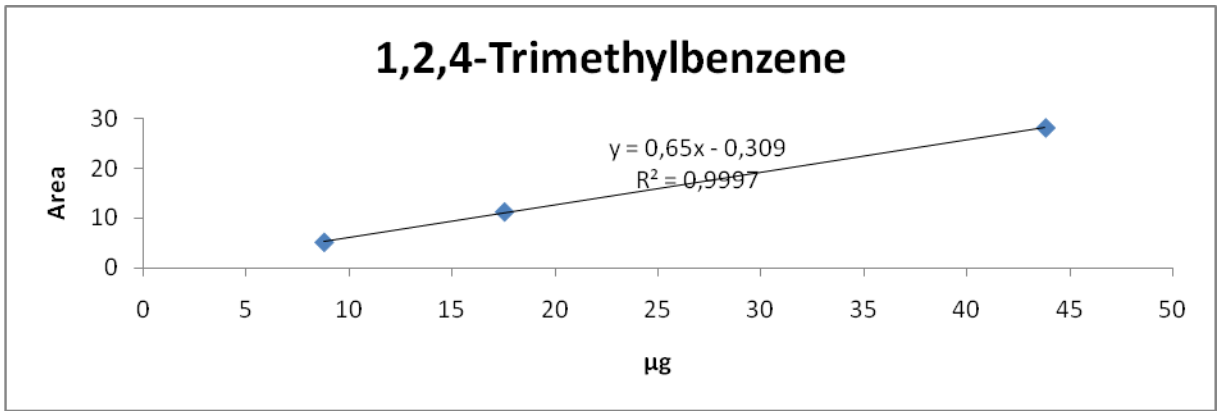
1- 3: Standard curve for m-Xylene



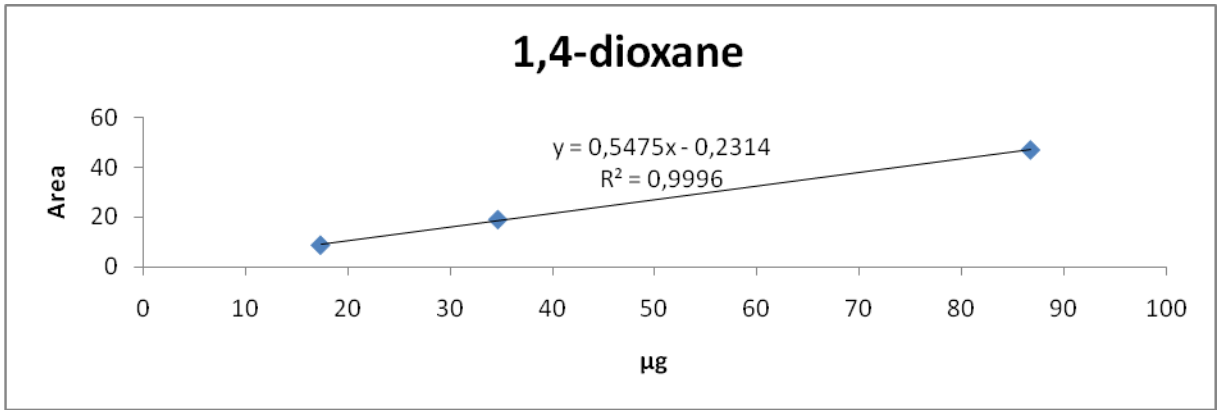
1-4: Standard curve for Ethyl benzene



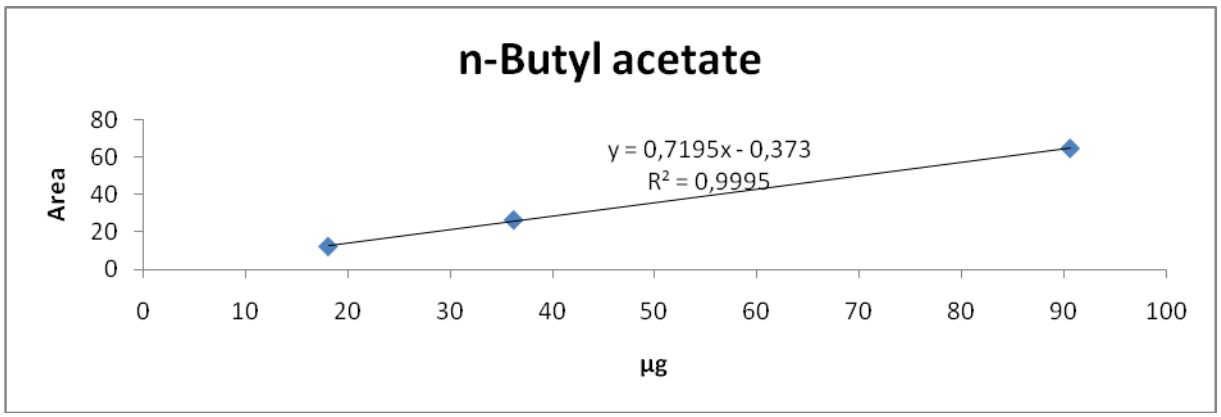
1-5: Standard curve for Styrene



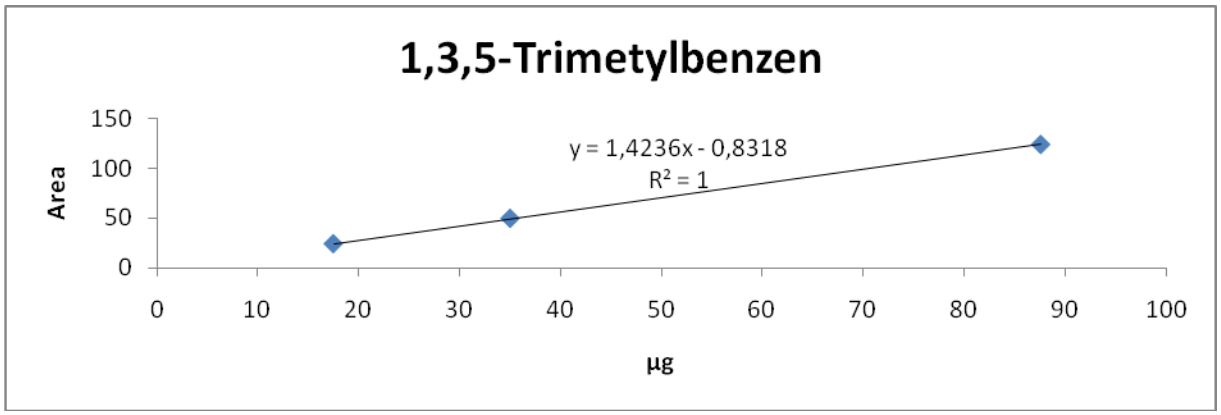
1-6: Standard curve for 1,2,4-Trimethylbenzene



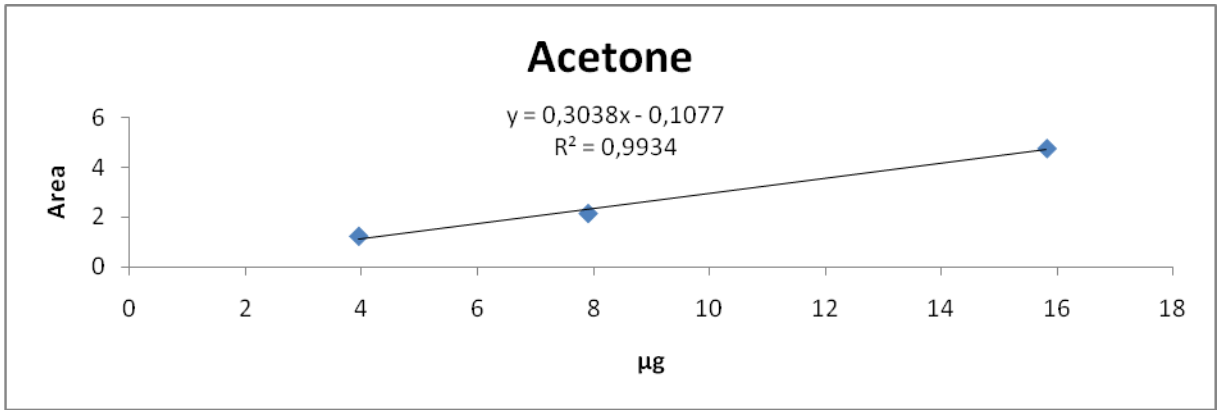
1-7: Standard curve for 1,4-dioxane



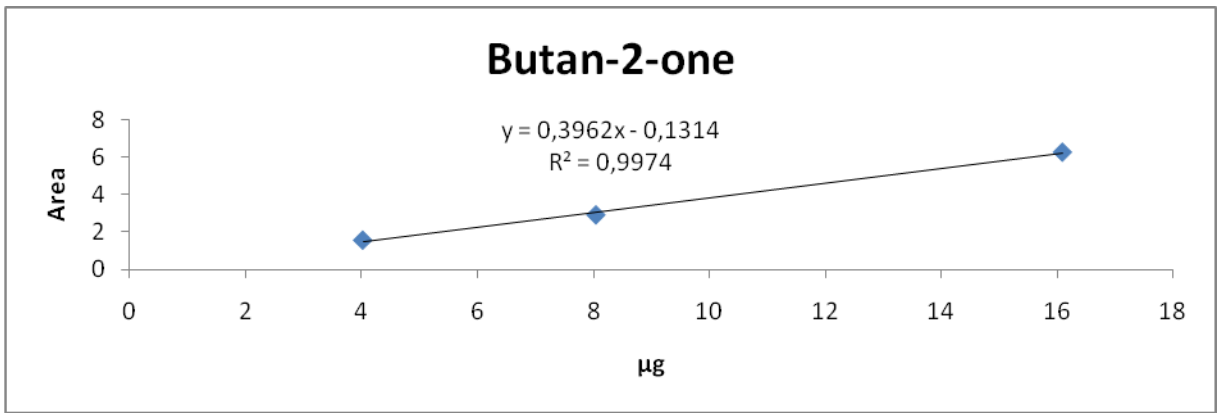
1-8: Standard curve for n-Butyl acetate



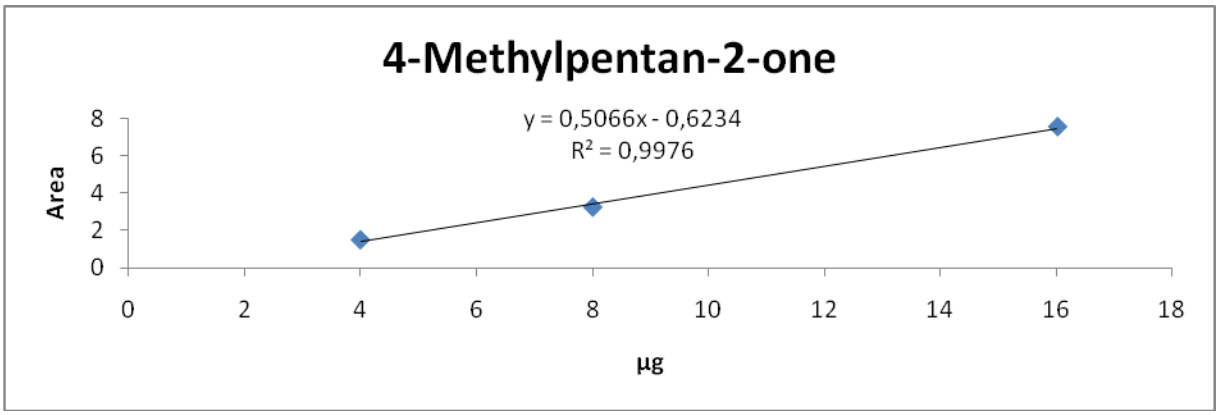
1-9: Standard curve for 1,3,5-Trimethylbenzene



1-10: Standard curve for Acetone



1-11: Standard curve for Butan-2-one



1-12: Standard curve for 4-methylpentan-2-one

2 Calculations of recovery sorbent tubes

2-1: calculations of theoretical concentrations - experiment 1

Analyte	Molecular weight (g/mol)	Density (g/mL)	Boiling point (°C)	Volume injected (µL)
Benzen	78,11	0,8786	80,1	3,0
Toluen	92,14	0,8669	110,6	3,0
m-xylen	106,11	0,8600	139,0	4,0
	208 L chamber + 104 L bags			
	i.e. 0,312 m3			
µg injected	**Air volume (m^3)**	**Molecular weight (g/mol)**	**Concentration (µg/m^3)**	**Concentration (ppb)**
2635,800	0,312	78,11	8448,1	2644,418
2600,700	0,312	92,14	8335,6	2211,904
3440,000	0,312	106,11	11025,6	2540,542

The maximum theoretical concentrations were calculated for each tube using the flow measurements from the DryCal Lite and exact sampling time (62 minutes).

2-2: Calculations of recovery - experiment 1

sample	Area Benzene	Area Toluene	Area m-Xylene	µg Benzene total	µg Toluen total	µg m-Xylen total	
1	14,290	12,595	14,402	28,595	26,667	31,858	
2	14,066	11,616	11,729	28,187	24,629	26,086	
3	11,984	9,973	10,531	24,401	21,205	23,501	
4							
5							
	Volum (m^3)						
sample	Area Benzen	Conc. Benzene (µg/m3)	Conc. Toluene (µg/m3)	Conc. m-Xylene (µg/m3)	Conc. Benzene (ppb)	Conc. Toluene (ppb)	Conc. m-Xylene ppb)
1	0,003	9242,708	8619,644	10297,334	2893	2287	2373
2	0,003	9002,700	7866,125	8331,541	2818	2087	1920
3	0,003	8391,724	7292,285	8082,033	2627	1935	1862
				Average	2779,3	2103,2	2051,6
				Standard deviation	137	177	280
				RSD(%)	4,9	8,4	13,6
				Recovery% of theoretical concentration	105,1	95,1	80,8
				PTR-MS Start	2180	2168	2678
				PTR-MS end	2168	2144	2571
				Recovery% PTR-MS vs sorbent tubes star	78,4	103,1	130,5
				Recovery% PTR-MS vs sorbent tubes enc	78,0	101,9	125,3

2--3: Calculations of theoretical concentrations for experiment 2

Analyte	Molecular weight (g/mol)	Density (g/mL)	Boiling point (°C)	Volume injected (µL)
Ethyl benzene	106,17	0,8670	136,0	3,0
Styrene	104,15	0,9060	145,0	3,0
1,2,4-Trimethylbenzene	120,19	0,8760	168,0	4,0

µg injected	Air volume (m^3)	Molecular weight (g/mol)	Concentration (µg/m^3)	Concentration (ppb)
2601,000	0,312	106,17	8336,5	1,920
2718,000	0,312	104,15	8711,5	2,045
3504,000	0,312	120,19	11230,8	2,285

The maximum theoretical concentrations were calculated for each tube using the flow measurements from the DryCal Lite and exact sampling time (60 minutes)

2 --4: Calculations of recovery – experiment 2

sample	Area Ethyl benzene	Area Styrene	Area 1,2,4-Trimethylbenzene	µg Ethyl benzene totalt	µg Styrene total	µg 1,2,4-Trimethylbenzene total	
1	9,331	3,360	7,706	21,218	15,888	18,497	
2	8,086	3,025	6,684	18,679	15,005	16,137	
3	9,379	3,992	9,468	21,316	17,551	22,562	
4	9,305	3,463	7,259	21,163	16,159	17,465	
5	8,595	2,692	7,055	19,716	14,128	16,993	
	Volume (m3)						
sample	Volume (m3)	Conc. Ethyl benzene (µg/m3	Conc. Styrene (µg/m3)	Conc. 1,2,4-Trimethylbenzene (µg/m3)	Conc. Ethyl benzene (ppb)	Conc. Styrene (ppb)	nc. 1,2,4-TrimEthyl benzene pp
1	0,003	7195,097	5387,551	6272,197	1657	1265	1276
2	0,003	6505,984	5226,421	5620,569	1498	1227	1143
3	0,003	7440,193	6126,004	7875,006	1713	1438	1602
4	0,003	6957,067	5311,924	5741,268	1602	1247	1168
5	0,003	6565,447	4704,625	5658,580	1512	1104	1151
				Average	1596,6	1256,3	1268,1
				Std. Dev.	92	120	194
				RSD (%)	5,8	9,5	15,3
				Recovery% of theoretical concentration	83,2	61,4	55,5

2- 5: Calculation of theoretical concentrations – experiment 3

Analyte	Molecular weight (g/mol)	Density (g/mL)	Boiling point (°C)	Volume injected (µL)
1,4-Dioxane	88,11	1,0340	136,0	4,0
n-Butyl acetate	116,16	0,8800	145,0	3,0
1,3,5-Trimethylbenzen	120,19	0,8640	168,0	3,0

µg injected	Air volume (m^3)	Molecular weight (g/mol)	Concentration (µg/m^3)	Concentration (ppb)
4136,000	0,312	88,11	13256,4	3,679
2640,000	0,312	116,16	8461,5	1,781
2592,000	0,312	120,19	8307,7	1,690

The maximum theoretical concentrations were calculated for each tube using the flow measurements from the DryCal Lite and exact sampling time (120 minutes)

2 -6: Calculations of recovery - experiment 3

Sample	1,4-Dioxane	n-Butyl acetate	1,3,5-Trimethylbenzen	µg 1,4-Dioxane total	µg n-Butyl acetate totalt	µg 1,3,5-Trimethylbenzene total	
1	10,126	9,477	14,105	21,940	31,914	33,008	
2	10,552	9,562	12,896	22,805	32,140	30,292	
3	11,606	10,958	16,146	24,946	35,840	37,595	
4	10,650	9,611	13,920	23,005	32,271	32,592	
5	10,915	10,864	14,598	23,542	35,589	34,116	
	Volume (m3)						
Sample	Volume (m3)	Conc. 1,4-dioxane (µg/m3)	Conc. n-Butyl acetate (µg/m3)	Conc. 1,3,5-Trimethylbenzene (µg/m3)	Conc. 1,4-dioxane (ppb)	Conc. n-Butyl acetate (ppb)	Conc. 1,3,5-Trimethylbenzene (ppb)
1	0,005	3994,519	5810,313	6009,598	920	1364	1223
2	0,006	4028,625	5677,663	5351,100	928	1333	1089
3	0,006	4191,159	6021,543	6316,338	965	1414	1285
4	0,006	3989,711	5596,689	5652,380	919	1314	1150
5	0,006	3854,296	5826,626	5585,408	888	1368	1136
				Average	923,85	1358,4	1176,4
				Std.dev	28	38	77
				RSD (%)	3,0	2,8	6,6
				Recovery% of theoretical concentration	25,1	76,3	69,6

2-7: calculation of theoretical concentrations - experiment 4

Analyte	Molecular weight (g/mol)	Density (g/mL)	Boiling point (°C)	Volume injected (µL)
Acetone	58,08	0,7910	56,0	1,0
Mek	72,11	0,8050	80,0	1,0
Mibk	100,16	0,8010	117,5	1,0

µg injected	Air volume (m^3)	Molecular weight (g/mol)	Concentration (µg/m^3)	Concentration (ppb)
791,000	0,312	58,08	2535,3	1,067
805,000	0,312	72,11	2580,1	0,875
801,000	0,312	100,16	2567,3	0,627

The maximum theoretical concentrations were calculated for each tube using the flow measurements from the DryCal Lite and exact sampling time (60 minutes)

2-8: Calculations of recovery - experiment 4

3 Mass probabilities and recoveries for PTR-MS

	START			
Component	mass concentration (ppb)	mass	probability	full concentration (ppb)
Benzene	2042,00	79	100	2180
		80	6,58	
		81	0,18	
Toluene	2009,00	93	100	2168
		94	7,67	
		95	0,25	
m-Xylene	2454,00	107	100	2678
		108	8,78	
		109	0,34	
	END			
Component	mass concentration (ppb)	mass	probability	full concentration (ppb)
Benzene	2031,00	79	100	2168
		80	6,58	
		81	0,18	
Toluene	1987,00	93	100	2144
		94	7,67	
		95	0,25	
m-Xylene	2356,00	107	100	2571
		108	8,78	
		109	0,34	

Calculation of theoretical concentration (3 µL injected)

Analyte	Molecular weight (g/mol)	Density (g/mL)	Boiling point (°C)	Volum injected (µL)	
Benzene	78,11	0,8786	80,1	3,0	
Toluene	92,14	0,8669	110,6	3,0	
m-Xylene	106,11	0,8600	139,0	4,0	
Analyte	**µg injected**	**Air volume (m^3)**	**Molecular weight (g/mol)**	**Concentration (µg/m^3)**	**Concentration (ppb)**
Benzene	2635,800	0,312	78,11	8448,1	2644
Toluene	2600,700	0,312	92,14	8335,6	2212
m-Xylene	3440,000	0,312	106,11	11025,6	2541

Analytt	Theoretically calculated (ppb)	Measured start PTR-M	Recovery start %	Measured end PTR-MS	Recovery end %
Aceton	2644	2180	82,4	2168	82,0
Mek	2212	2168	98,0	2144	96,9
Mibk	2541	2678	105,4	2571	101,2

3-1: Mass probabilities and calculation of recovery for experiment 1

	START		ca. 40 min after start	
Component	**mass concentration (ppb)**	**mass**	**probability**	**full concentration (ppb)**
Benzene	1041,00	79	100	1111
		80	6,58	
		81	0,18	
Etylbenzene	808,00	107	100	882
		108	8,78	
		109	0,34	
Styrene	2037,00	105	100	2222
		106	8,76	
		107	0,34	
1,2,4-Trimetylbenzene	2021,00	121	100	2230
		122	9,88	
		123	0,44	
	END		ca. 2.5 timer after start	
Component	**mass concentration (ppb)**	**mass**	**probability**	**full concentration (ppb)**
Benzene	937,00	79	100	1000
		80	6,58	
		81	0,18	
Etylbenzene	802,00	107	100	875
		108	8,78	
		109	0,34	
Styrene	1567,00	105	100	1710
		106	8,76	
		107	0,34	
1,2,4-Trimetylbenzene	1912,00	121	100	2109
		122	9,88	
		123	0,44	

Calculation of theoretical concentration (10 µL injected)

Analyte	**Molecular weight (g/mol)**	**Density (g/mL)**	**Boiling point (°C)**	**Volum injected (µL)**
Etylbenzen	106,17	0,8670	136,0	3,0
Styren	104,15	0,9060	145,0	3,0
1,2,4-Trimetylbenzen	120,19	0,8760	168,0	4,0

Analyte	**µg injected**	**Air volume (m^3)**	**Molecular weight (g/mol)**	**Concentration (µg/m^3)**	**Concentration (ppb)**
Etylbenzen	2601,000	0,312	106,17	8336,5	1920
Styren	2718,000	0,312	104,15	8711,5	2045
1,2,4-Trimetylbenzen	3504,000	0,312	120,19	11230,8	2285

Korrigert målt verdi PTR-MS mot teoretisk beregnet verdi kammer

Analytt	Theoretically calculated (ppb)	leasured start PTR-M	Recovery start %	Measured end PTR-MS	Recovery end %
Etylbenzen *	1920	1993	103,8	1875	97,7
Styren	2045	2222	108,7	1710	83,6
1,2,4-Trimetylbenzen	2285	2230	97,6	2109	92,3

* Measured value for benzene is added to the ethyl benzene concentration as ethyl benzene fragments to benzene.

3-2: Mass probabilities and calculation of recovery for experiment 2

	START		ca. 5 min after start	
Component	**mass concentration (ppb)**	**mass**	**probability**	**full concentration (ppb)**
1,4-dioxane	792,00	89	100	832
		90	4,6	
		91	0,5	
Acetaldehyd	2010,00	45	100	2058
(fragment av 1,4-dioxane)		46	2,2	
		47	0,2	
n-butyl acetate	33,00	117	100	35
		118	6,8	
		119	0,6	
n-butyl acetate	3,00	71	100	3
fragment 71 m/z		72	4,4	
		73	0,3	
Acetic acid	0,00	61	100	0
(fragment of n-butyl acetate)		62	2,3	
		63	0,4	
n-butyl acetate	415,00	43	100	425
fragment 43 m/z		44	2,2	
		45	0,2	
1,2,4-trimethylbenzenee	1623,00	121	100	1790
		122	9,88	
		123	0,44	
	END	ca. 1 time og 45 min after start		
Component	**mass concentration (ppb)**	**mass**	**probability**	**full concentration (ppb)**
1,4-dioxane	777,00	89	100	817
		90	4,6	
		91	0,5	
Acetaldehyd	1664,00	45	100	1704
(fragment av 1,4-dioxane)		46	2,2	
		47	0,2	
n-butyl acetate	33,00	117	100	35
		118	6,8	0
		119	0,6	
n-butyl acetate	3,00	71	100	3
fragment 71 m/z		72	4,4	
		73	0,3	
Acetic acid		61	100	0
(fragment of n-butyl acetate)		62	2,3	
		63	0,4	
n-butyl acetate	443,00	43	100	454
fragment 43 m/z		44	2,2	
		45	0,2	
1,2,4-trimethylbenzenee	1416,00	121	100	1562
		122	9,88	
		123	0,44	
	END		ca. 2 timer after start	
Component	**mass concentration (ppb)**	**mass**	**probability**	**full concentration (ppb)**
1,4-dioxane	759,00	89	100	798
		90	4,6	
		91	0,5	
Acetaldehyd	1586,00	45	100	1624
(fragment av 1,4-dioxane)		46	2,2	
		47	0,2	
n-butyl acetate	31,00	117	100	33
		118	6,8	
		119	0,6	
n-butyl acetate	6,00	71	100	6
fragment 71 m/z		72	4,4	
		73	0,3	
Acetic acid	1340,00	61	100	1376
(fragment of n-butyl acetate)		62	2,3	
		63	0,4	
n-butyl acetate	446,00	43	100	457
fragment 43 m/z		44	2,2	
		45	0,2	
1,2,4-trimethylbenzenee	1368,00	121	100	1509
		122	9,88	
		123	0,44	

Calculation of theoretical concentration (10 µL injected)

Analyte	**Molecular weight (g/mol)**	**Density (g/mL)**	**Boiling point (°C)**	**Volum injected (µL)**	
1,4-dioxane	88,11	1,0340	136,0	4,0	
n-butyl acetate	116,16	0,8800	145,0	3,0	
1,3,5-trimethylbenzene	120,19	0,8640	168,0	3,0	
Analyte	**µg injected**	**Air volume (m^3)**	**Molecular weight (g/mol)**	**Concentration (µg/m^3)**	**Concentration (ppb)**
1,4-dioxane	4136,000	0,312	88,11	13256,4	3679
n-butyl acetate	2640,000	0,312	116,16	8461,5	1781
1,3,5-trimethylbenzene	2592,000	0,312	120,19	8307,7	1690

Analytt	Theoretically calculated (ppb)	Measured start PTR-M	Recovery start %	Measured end PTR-MS	Recovery end %
1,4-dioxane*	3679	1862	50,6	1610	43,8
n-butyl acetate**1)	1781	464	26,0	1872	105,1
1,3,5-trimethylbenzene	1690	1790	105,9	1509	89,3

* Measured value for acetaldehyd is added to hte 1,4-dioxane concentration as 1,4-dioxane fragments to acetaldehyd.

** Measured values for 41, 43, 61 og 71 m/z are added to n-butyl acetate concentration as n-butyl acetate fragments.

1) Acetic acid not measured at start

3-3: Mass probabilities and calculation of recovery for experiment 3

	START			
Component	**mass concentration (ppb)**	**mass**	**probability**	**full concentration (ppb)**
Aceton	826,85	59	100	857
		60	3,4	
		61	0,2	
MEK	638,41	73	100	669
		74	4,5	
		75	0,3	
MIBK	222,72	101	100	239
		102	6,7	
		103	0,4	
	END			
Component	**mass concentration (ppb)**	**mass**	**probability**	**full concentration (ppb)**
Aceton	818,74	59	100	848
		60	3,4	
		61	0,2	
MEK	635,44	73	100	666
		74	4,5	
		75	0,3	
MIBK	219,10	101	100	235
		102	6,7	
		103	0,4	

Calculation of theoretical concentration (3 µL injected)

Analyte	**Molecular weight (g/mol)**	**Density (g/mL)**	**Boiling point (°C)**	**Volum injected (µL)**	
Aceton	58,08	0,7910	136,0	1,0	
Mek	72,11	0,8050	145,0	1,0	
Mibk	100,16	0,8010	168,0	1,0	
Analyte	**µg injected**	**Air volume (m^3)**	**Molecular weight (g/mol)**	**Concentration (µg/m^3)**	**Concentration (ppb)**
Aceton	791,000	0,312	58,08	2535,3	1067
Mek	805,000	0,312	72,11	2580,1	875
Mibk	801,000	0,312	100,16	2567,3	627

Analytt	Theoretically calculated (ppb)	leasured start PTR-M	Recovery start %	Measured end PTR-MS	Recovery end %
Aceton	1067	857	80,3	848	79,5
Mek	875	669	76,5	666	76,1
Mibk	627	239	38,1	235	37,4

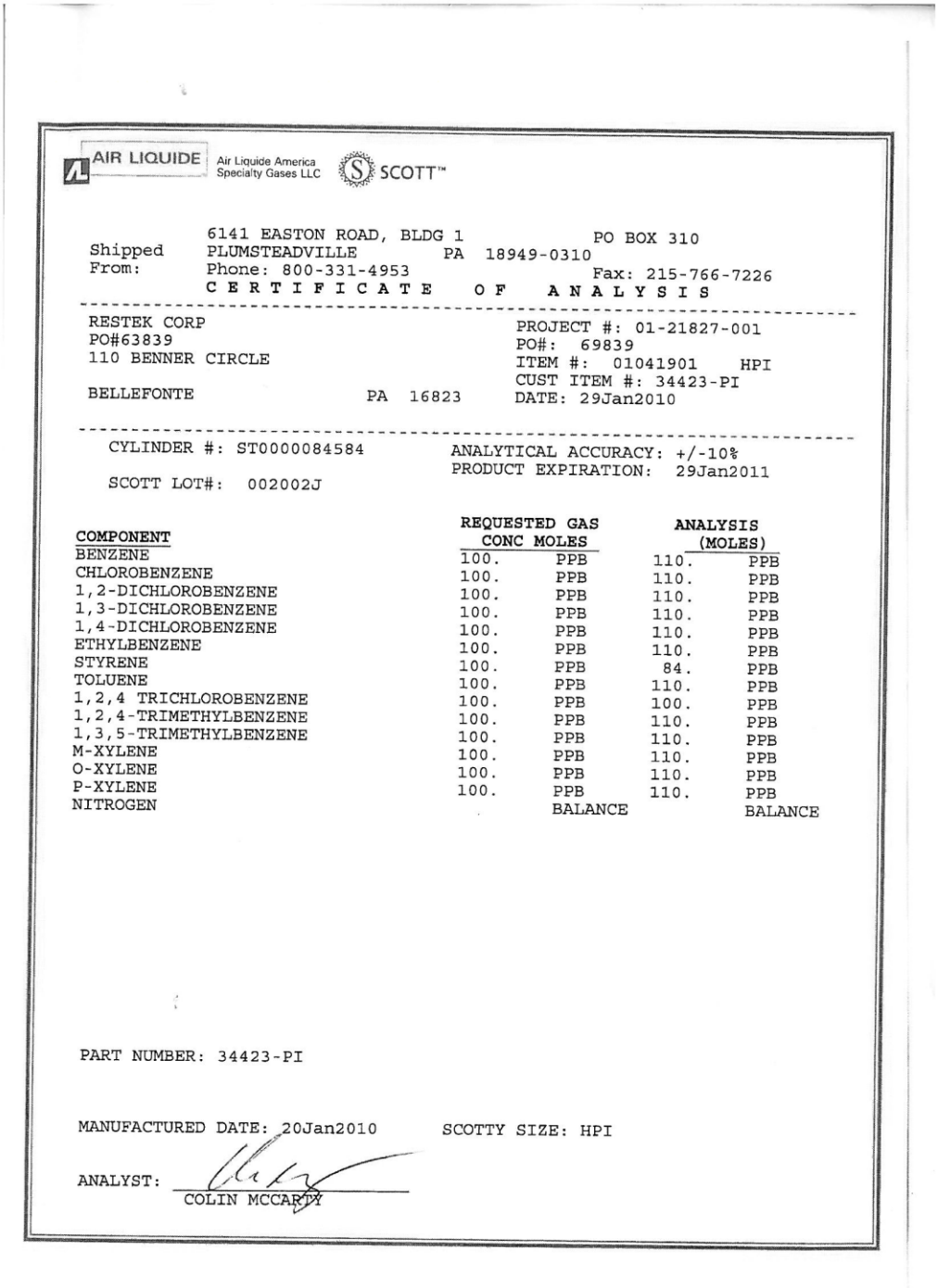
3-4: Mass probabilities and calculations of recovery for experiment 4

4 Calibration of SKC Pocket Pumps

4-1: Results from calibration of pumps used to calculate maximum theoretical values

Experiment	Tube	Before (mL/min)	After (mL/min)
1	1	49.7	50.1
	2	50.4	50.6
	3	46.7	47.1
2	1	48.5	49.8
	2	47.7	48.0
	3	47.5	48.0
	4	50.6	50.8
	5	50.0	50.1
3	1	47.5	47.2
	2	47.9	47.7
	3	50.1	49.1
	4	47.8	48.3
	5	50.9	50.9
4	1	48.4	48.5
	2	52.3	53.4
	3	49.7	54.0

5 Certificate of Analysis for gas mixture used for calibration



AIR LIQUIDE Air Liquide America Specialty Gases LLC SCOTT™

Shipped From: 6141 EASTON ROAD, BLDG 1 PO BOX 310
PLUMSTEADVILLE PA 18949-0310
Phone: 800-331-4953 Fax: 215-766-7226

CERTIFICATE OF ANALYSIS

RESTEK CORP
PO#63839
110 BENNER CIRCLE
BELLEFONTE PA 16823

PROJECT #: 01-21827-001
PO#: 69839
ITEM #: 01041901 HPI
CUST ITEM #: 34423-PI
DATE: 29Jan2010

CYLINDER #: ST0000084584
SCOTT LOT#: 002002J

ANALYTICAL ACCURACY: +/-10%
PRODUCT EXPIRATION: 29Jan2011

COMPONENT	REQUESTED GAS CONC MOLES		ANALYSIS (MOLES)	
BENZENE	100.	PPB	110.	PPB
CHLOROBENZENE	100.	PPB	110.	PPB
1,2-DICHLOROBENZENE	100.	PPB	110.	PPB
1,3-DICHLOROBENZENE	100.	PPB	110.	PPB
1,4-DICHLOROBENZENE	100.	PPB	110.	PPB
ETHYLBENZENE	100.	PPB	110.	PPB
STYRENE	100.	PPB	84.	PPB
TOLUENE	100.	PPB	110.	PPB
1,2,4 TRICHLOROBENZENE	100.	PPB	100.	PPB
1,2,4-TRIMETHYLBENZENE	100.	PPB	110.	PPB
1,3,5-TRIMETHYLBENZENE	100.	PPB	110.	PPB
M-XYLENE	100.	PPB	110.	PPB
O-XYLENE	100.	PPB	110.	PPB
P-XYLENE	100.	PPB	110.	PPB
NITROGEN		BALANCE		BALANCE

PART NUMBER: 34423-PI

MANUFACTURED DATE: 20Jan2010 SCOTTY SIZE: HPI

ANALYST: COLIN MCCARTY

5-1: Certificate of analysis for gas mixture used in PTR-MS calibration