DEVELOPMENT AND APPLICATION OF A PORTABLE VOLATILE ORGANIC COMPOUND ANALYSER

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Abstract

The subject of this PhD is the development and testing of a portable membrane inlet mass spectrometer (MIMS), for the in-situ measurement of volatile organic compounds (VOCs) in air.

There are several types of VOC monitor available, but few are able to monitor in-situ with near real-time measurements at concentrations around or lower than ppm levels. This PhD focuses on the development of the MS-200 and demonstrates its performance in laboratory and field conditions to analysis a range of VOCs.

The first chapters of this thesis describe the design considerations that led to the development of the MS-200. It also discusses the working principles of the instrument and the laboratory based performance tests that compare the performance of the MS-200 with the industry standard VOC monitor.

As the MS-200 has sensitivity and detection limits down to ppb levels, it overcame the limitations of many other instruments, and enabled its use for many new applications. For example, aromatic and chlorinated hydrocarbons report detection limits of between 600ppt to 20ppb, other VOCs investigated, reported detection limits between 20 to 300ppb, low molecular weight alcohols report detection limits of 0.4 to 6ppm. However, some applications require even lower detection limits, so an alternative inlet system was developed to increase the sensitivity but at the expense of the near real-time measurement capability. Typically the alternative inlet system reduces detection limits by two orders of magnitudes compared with the standard MS-200.

Subsequent sections of this thesis describe and discuss a range of real world applications for the MS-200. Most of these investigations were successful, although a number would need some further work before the MS-200 would be capable to perform such applications routinely in a commercial environment.

The applications discussed include: Investigations into arson where the instrument can be used to detect remnants of accelerants used without needing to return samples to the lab, giving the potential to save both time and money; Monitoring personal exposure to benzene when refuelling a petrol car, where the MS-200 demonstrated the advantage of portable real-time monitoring. It was found that during refuelling the operator could be exposed to benzene concentrations of a few hundred ppb to 4ppm for a duration of about 3 minutes; Measuring VOC markers in human breath as a diagnostic tool for cancer and other illnesses; The use of the MS-200 as an "artificial nose" in the food quality and flavour analysis.

The thesis discusses the advantages and limitations of this technology as well as providing a series of recommendations for its future development.

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1. Introduction

This chapter provides an overview of the nature of Volatile Organic Compounds (VOCs) and their importance in the atmosphere, the environment and health of humans. As a result of environmental and health implications, VOCs are routinely measured at the work space and sources of emission. Additionally concentrations of selected atmospheric VOCs are routinely measured through local and large-scale national networks of VOC monitors. VOCs are a complex group of chemicals and hence require sophisticated measuring methods to quantify their concentrations in the atmosphere. This PhD investigates a novel instrument that measures VOCs, together with its working principles and its uses.

This chapter will discuss the nature and source of VOCs, their effects on nature and humans. In addition it will introduce some current technologies commonly used for measuring VOCs.

1.1. Nature and Sources of VOCs

VOCs are defined by the Department of the Environment as "a wide range of carbon-containing gaseous pollutants, including hydrocarbons and their oxygenated and chlorinated derivatives" (DEFRA 2003).

VOCs have natural, as well as man made sources. The most abundant VOC emitted into the atmosphere is methane, produced by various bacteria, when breaking down and digesting organic matter (DEFRA 2003). Other natural VOCs include chemical emissions from plants, for example isoprene and mono-terpenes (Owen et al. 2003, Komenda et al. 2001), emissions from volcanic sources and fires (Schauer et al. 2001, Austin et al. 2001, Ciccioli et al. 2001). Man made (anthropogenic) sources of VOCs include the use of solvents (for example methanol, propanol), road traffic (1,3-butadiene, benzene, toluene, xylene) (Sadler et al. 2002, Pfeffer et al. 1995, AEAT 2003, Batterman et al. 2002, Mohamed et al. 2002), the production, distribution and use of fossil fuels (benzene, toluene, xylene) (CONCAWE 1999, Jones 2000, DEFRA 2001, DEFRA 2002) as well as other many industrial processes (phosgene, trichloroethane, alkanes) (Sadler et al. 2002, Katzenstein et al. 2003, AEAT 2003).

The estimated annual emission of VOCs (excluding methane) in the UK in 1997 was 2,130kilotonnes. The amounts for different VOC sources in the UK are shown in Figure 1 and are taken from the national emission inventory (AEAT 2003). The national emission inventory estimates the quantity and location of emissions of all quantifiable sources of most of the pollutants of concern for the UK government, such as VOCs, benzene, 1,3-butadiene, methane, as well as inorganic pollutants such as nitrogen oxides and carbon dioxide.

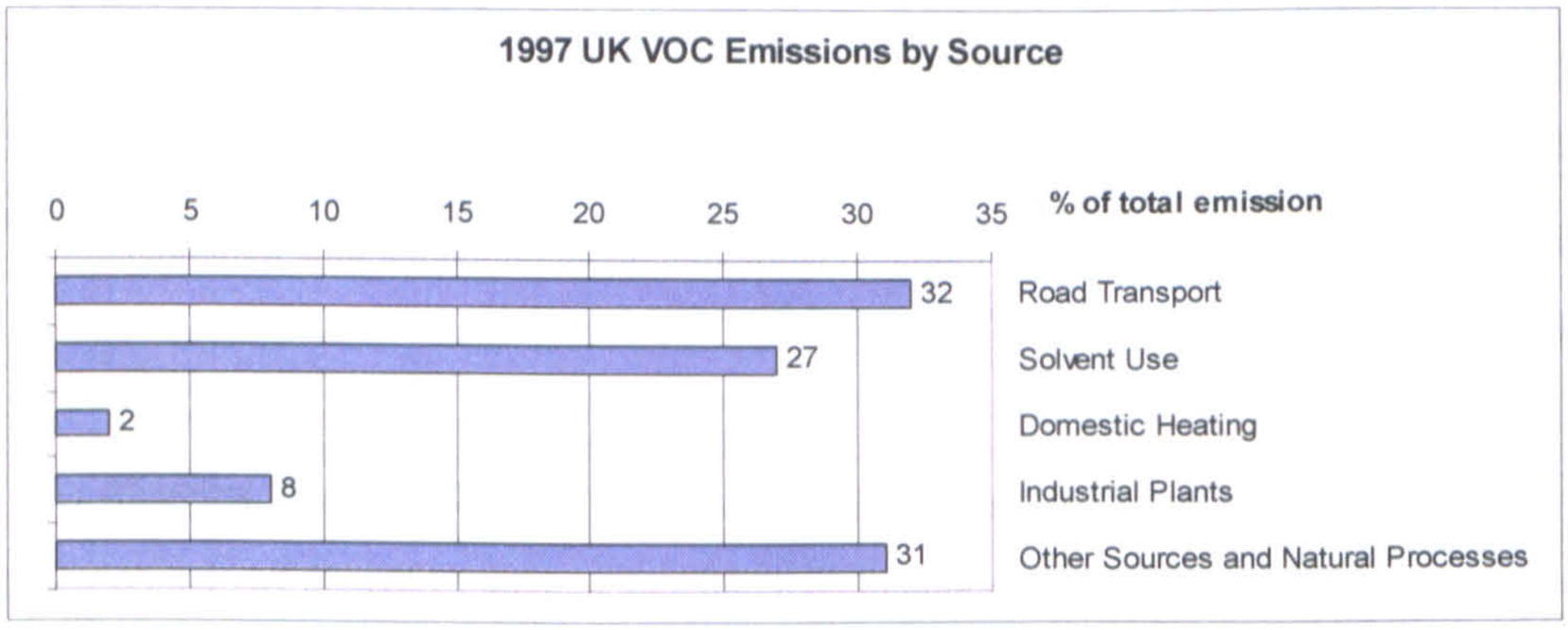

Figure 1: 1997 Emissions of non-Methane VOCs in the UK (data extracted from AEAT 2003)

From this figure it can be seen that the majority of the VOCs are from road transport, although a significant proportion are from natural processes (such as isoprene and mono-terpenes emissions from vegetation, which are not desirable to be reduced, but still play a part in the formation of ozone (Gan, Hopke 2003)). Most of the VOCs will have an effect on the formation of ozone. However, if only the VOCs of direct health impact are considered, then these proportions would be very different, for example 71% of benzene and 85% of 1,3-butadiene emissions are from road transport (AEAT 2001). These numbers are often not so different in urban areas, for example in London where the proportions are 74% and 93% respectively - although it should be noted that the London inventory includes the area up to the M25 (motorway ring around London), a significant proportion of which is fairly rural (Sadler et al. 2002).

The above discussion is about estimated emissions of VOCs. Real concentrations are monitored throughout the UK by the Government and local authorities, as well as universities and airports. The results from the Government networks are provided on the web on the UK Air Quality Archive (DEFRA 2003a)

1.2. Effects of VOCs

VOCs have different effects on nature and humans. These effects include playing a role in the formation of photochemical smog, by assisting in the formation of ground level ozone [Gan, Hopke 2003, DEFRA 2001a], which adversely affects human health and plant growth. VOCs, dissolved in water or soil adversely affect fauna and flora. Methane and a number of other VOCs are greenhouse gases and the Intergovernmental Panel on Climate Change extensively researches their effects [IPPC 2001].

At high concentrations, most VOCs will have a poisonous effect on humans. Prolonged exposure to the many VOCs at low levels can also be hazardous to health as many are suspected of being carcinogens [WHO 1997]. The United Kingdom Expert Panel on Air Quality Standards (EPAQS) recommended that in ambient air, the concentration of benzene should not exceed a 5ppb annual average, and 1,3-butadiene should not exceed a 1ppb annual average [EPAQS 1994]. In the UK the national government has published strict air quality standards for benzene and 1,3-butadiene [DEFRA 2000]. These concentrations, as well as a further target set by the European Union of 1.54ppb annual average of benzene, will have to be met by 2010 [EC 2000]. The US EPA is also concerned about health effects of benzene and other VOCs [EPA 2000]. As a result of the adverse environmental impact of elevated VOC concentrations in the atmosphere many international treaties discuss the reduction in manmade VOC emissions [EC 2001].

Most countries have legislation that controls emission of VOCs into the atmosphere and the exposure to VOCs at the workspace. The UK Health and Safety Executive (HSE) published a list of "Control of Substances Hazardous to Health" (COSHH), including many VOCs [HSE 1997]. For example the 8 hourly time weighted average exposure for benzene should not exceed 5ppm, the one for carbon disulphide is 10ppm and toluene is 50ppm.

1.3. Monitoring VOCs

Wherever VOCs are of interest, there is a need for their concentrations to be monitored. Where there are legislative targets, Governments need to know whether or not VOC concentration targets are met and therefore have monitors placed in representative locations around the country (AEAT 2003). In order to reduce the VOC levels where they are above the relevant targets it is important to monitor their sources. The HSE and employers need to know if the workplace air is within the workplace exposure limits (HSE 1997). It is also important to monitor VOCs at various levels and locations in order to enhance the understanding of their occurrence and concentrations in the environment, and our exposure to them as highlighted by Saarinen et al. (2000) and CONCAWE (1999). People spend considerable time indoors and therefore it is important to monitor and understand the differences between indoor and ambient VOC concentrations (Harrison 1998). As people move around, and hence can be exposed to different sources and/or emission rates, it is also important to monitor and understand the actual personal exposure to VOCs (Na, Kim. 2001).

There are numerous other reasons for monitoring VOCs. These include

- Industry needs to know how their processes are functioning, and so monitoring is part of many production processes (Phan, Auth 1993).
- Food research monitors VOC emissions from foods to identify food quality (Zubritski 2000).
- Law enforcement agencies - such as the police together with the fire brigade use the monitoring of VOCs to identify potential cases of arson or other criminal activities (Bertsch 1996).
- Recently there has been a lot of interest in monitoring VOCs in human breath to be used as a non-invasive diagnosis tool for various diseases (Gordon et al. 2002, Phillips 1992A).

There are several ways of monitoring, either in-situ by analysing a sample directly, or by taking a sample to the analyser. Many current technologies for air pollution or VOC analysis still follow the principle of collecting a sample of the air by collecting and storing it in a canister (EPA TO-14) or adsorbing the

chemical of interest onto a solid adsorbent (EPA TO-1). The samples are stored and transported to the laboratory, where the analysis is performed. One common example of this is employing a passive diffusion tube on a site of interest, which is generally left there for 2 to 4 weeks collecting a sample that is averaged over that time, and which is then sent to the laboratory for analysis (Kesselmeier et al. 2002). For ambient VOC monitoring the need for semi-continuous in-situ monitoring is accepted, and therefore DEFRA operates VOC monitoring stations at selected sites throughout the UK, avoiding sample collection and transport to a central laboratory (DEFRA 2003a).

The Government use, and recommend local authorities to use in-situ sampling monitors, where a sample is taken, but analysed more or less immediately. Monitors for benzene and 1,3-butadiene use a pumped sampling device on to adsorbent cartridge, where analysis is carried out by gas chromatographic determination (DEFRA 2003b).

Concentrations of various VOCs in the above mentioned applications can be within the following ranges:

- ppt (10^{-12}) for environmental applications and VOC measurement in human breath testing (Phillips et al. 1994a).
- ppb (10^{-9}) for ambient and indoor air quality (Lee et al. 2002, Na, Kim 2001, Wiedinmyer et al. 2001).
- ppm (10^{-6}) for personal peak exposures when handling VOCs and industrial emission (Bono et al. 2003, HSE 1997)
- percentage levels in process monitoring.

As seen from this, concentrations of VOCs that are of interest span 10 orders of magnitude and include a huge range of chemicals. This results in a broad requirement onto potential monitoring techniques. The background matrix (i.e. the chemicals or matter around the VOC of interest) can be simply one inorganic gas, like nitrogen, or can be very complex matrixes of inorganic gases, different VOCs, and water or soil. This adds further requirements onto VOC monitors.

Using the common technique of initial sampling of the VOCs followed by analysis off-site can have disadvantages. Samples might change due to adsorption or interactions with other constituents of the sampling matrix during storage. In studies, Taylor (1987) found the collection of air samples and their transport to be the biggest source of errors when analysing air using these methods. The analysis of air in-situ improves the accuracy and simplifies the sampling and analysis process and therefore is able to significantly reduce the possible errors and the cost of analysis (Taylor 1987) (Berkley et al. 1991). Ochiai et al. (2003) investigated the stability of 58 VOCs in stainless steel canisters, and found that stable concentration for some components are dependent on the water content. Some of the components under investigation were very stable over a period of 14 days. The group of thiols was highly unstable and could not be found after more than 3 days of storage (Ochiai et al. 2003, Ochiai et al. 2002).

In addition to not having the above disadvantages, other advantages of in-situ analysis are the near real-time analysis and delivering immediate results from the analysis. Such methods allow a dynamic sampling strategy at lower cost and with reduced sample handling. Due to the fast response time, applications can include the monitoring of sites of chemical accidents or fires, allowing appropriate protection of the people dealing with, or being involved in an emergency situation. Further applications include defence applications where continuous monitoring can be performed on suspected sites during times of high risk of chemical attacks (Baykut, Franzen 1994). In a recent study, Alonso et al. (1999) compared sample adsorption and laboratory based GC analysis with the results from a portable GC and found the portable unit to provide valuable additional information to the lab-based method.

Laboratory based techniques, relying on collecting samples on adsorption traps or canisters, provide an average concentration over the time of loading the adsorbent trap or a snap shot of the concentration whilst filling the canister. Real time or near real time analysis in the field offers the potential to monitor changing VOC concentrations over time and allows the observation of high concentration peaks (like the personal exposure experiments described in section 5.1). It also allows situations to be better understood; for

example, for tracing the source of a leak. In-situ methods are also of advantage where the monitoring site is remote and monitoring results are needed faster than samples can be sent to the laboratory and analysed there (like air quality monitoring on the international space station described in section 5.4.1).

1.4. Current Technologies for the Measurement of VOCs

There are many different methods for analysing VOCs in air. Some of the methods use a chemical reaction with a solvent and subsequent analysis of the changes in the solvent. Other commonly used techniques monitor optical emissions from the chemical of interest when that chemical is reacting with another reagent gas, or the absorption of the sample when it is exposed to a specific radiation. VOCs can also be measured and identified by determining their molecular weight using mass spectrometric methods (Naumer, Heller 1990, Settle et al. 1997).

As highlighted, transportable equipment allowing in-situ analysis has distinct advantages over laboratory based techniques. As a result of this, the techniques discussed in this section have the potential to be taken into the field and to perform specific VOC analysis, leaving out technologies, used to measure a total VOC concentration. The techniques described are considered only in terms of basic working principles. The intention is to indicate the differences in the analytical methods rather than providing a comprehensive guidance for application. The advantages and disadvantages of the methods are also briefly discussed.

1.4.1. VOC Analysis by Gas Chromatography

Henry (1997) has reviewed studies investigating VOCs in ambient air. These studies have been completed almost exclusively with gas chromatograph (GC) or gas chromatograph with mass spectrometer (GC/MS) methods. Some recent studies, measuring VOCs, and performed with GC or GC/MS methods are: Escalas et al. (2003) investigating VOCs in a sewage treatment plant; Gordon et al. (2002) measuring VOCs in breath as bio markers for

active and passive smoking; Na, Kim (2001) investigating the seasonal characteristic of ambient VOCs concentrations in Seoul.

GC methods use the three stages of sampling, separating the sample into its constituent molecules and then detecting the separated constituents. Sampling is commonly undertaken by adsorption of the VOCs onto a solid material (EPA TO-1) or by pumping the air into special treated stainless steel canisters (EPA TO-14). The separation of the sample is performed in a gas chromatograph by injecting or desorbing the sample into a carrier gas stream (the mobile phase) that is led through a coated capillary column. Interactions between the sample and the column coating (the stationary phase) cause the individual compounds to require different times to travel through the column. In this way the individual compounds are separated and appear at the end of the column as single molecular peaks. The time taken for a sample to elute from the column depends on the compound, the column coating and length, the flow rate of carrier gas and the temperature of the column. The output of the column is monitored using a detector that is sensitive to a change in hydrocarbon concentration within the carrier gas stream. The detector will then report a chromatogram, which is a graph of measured hydrocarbon concentrations versus time. The areas underneath the reported peaks are used to calculate the concentration of a compound; the elution time is used to identify the compound. The schematic of such a system is shown in Figure 2.

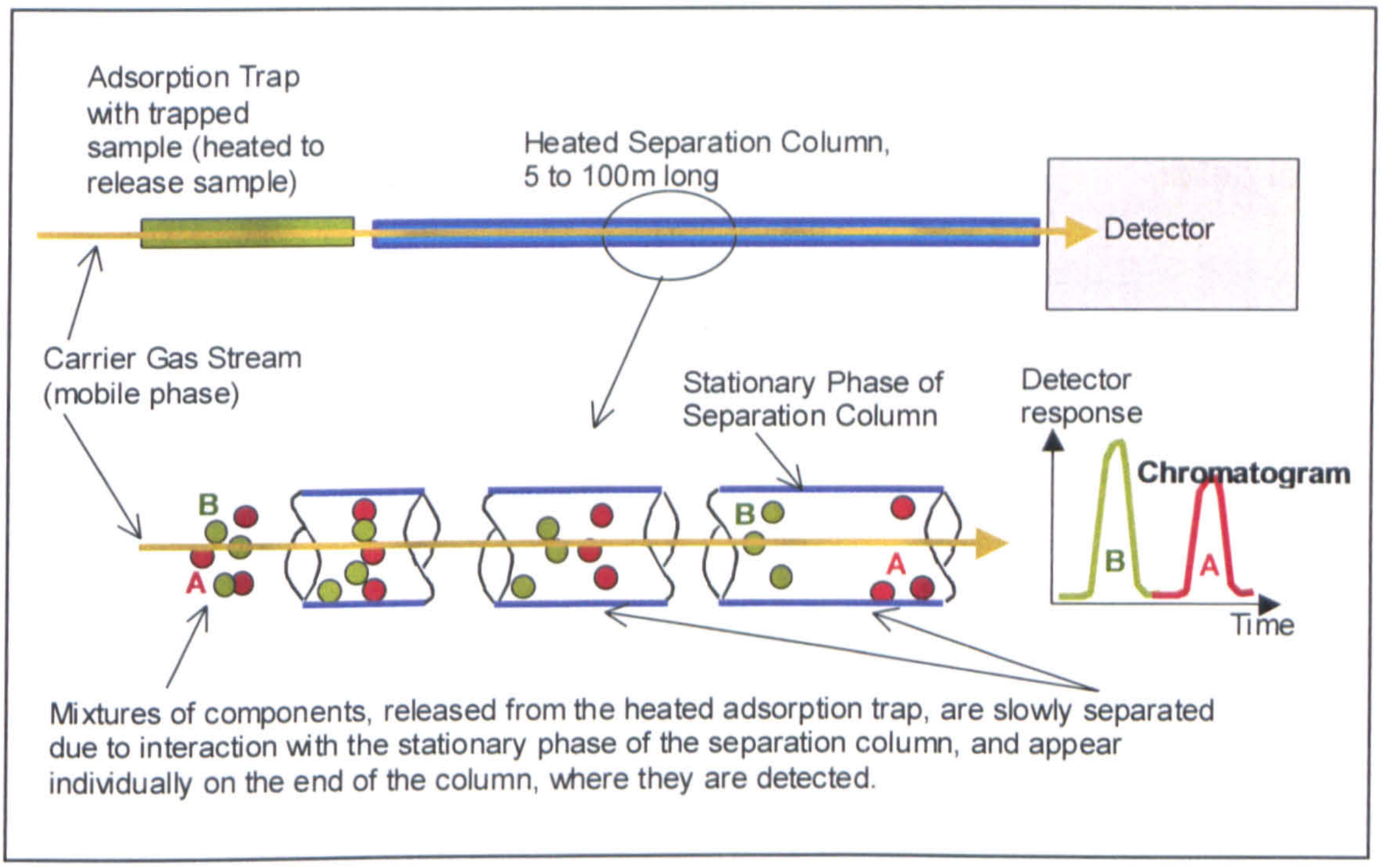

Figure 2: Schematic of Gas Chromatograph with thermal desorption

The different detectors that are used are flame ionisation, photo ionisation, electron capture or mass spectrometers. Detection of VOCs using this method can be performed down to the ppt concentrations, when having good separation and a highly sensitive detector (Berkley et al. 1991).

1.4.2. Ultra Violet or Visible Light (UV/VIS) Spectroscopy

This method enables the gases in a mixture to be analysed from their absorption spectra in the visible (wave length of 400 to 800nm) or ultraviolet spectral (200 to 400nm) regions. A light beam is passed through a sample of air. After a known path length, the absorption of the light source by the sample is measured. This absorption depends on the Beer Lambert's absorption law that states the relationship between the quantity of light absorbed and the number of molecules in the light path, and is caused by promoting electrons in the molecules from a ground to an excited state. A monochromator scans through the wave range of the light source and leads the filtered light to the detector. The detector therefore produces an absorption spectrum for the wave range of the light source. A computer then matches the information gained with a library of spectra and sensitivity factors, and identifies the chemicals and calculates their concentrations in the

sample. A schematic of this system is shown in Figure 3. Settle et al. (1997) and Naumer, Heller (1990) describe the working principles of this method in further detail.

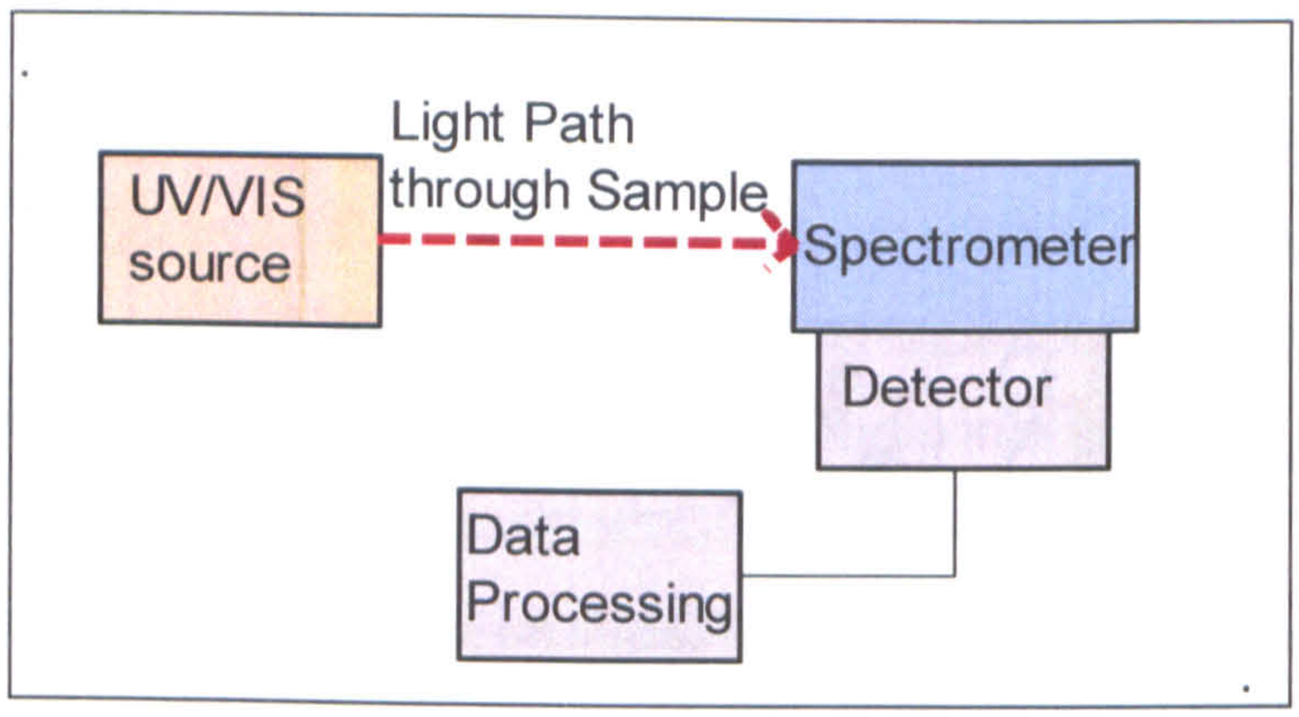

Figure 3: Principle of UV/VIS spectrometry

This method is available in portable analysers, but sensitivity is commonly limited by the length of the light path through the sample. To achieve higher sensitivity the light beam is reflected by mirrors and allowed to pass several times through a closed measurement cell to increase the path length. These closed path analysers are able to monitor a specific point or air parcel with concentrations typically in the ppm range. Better resolutions and lower detectable limits are achieved by instruments that use an open path of several hundred meters. Open path systems are suitable for measurement down to low ppb concentrations (OPSIS 1994, AIM 1996). One of the features of open path analysers is that they deliver an average of the concentration for the length of the path between source and receiver. Dependent on the application this can be an advantage or disadvantage. These open path instruments are portable in principle, but require lengthy setting up to achieve accurate orientation of the source and the receiver, and require mains power to operate. Open path instruments are commonly used for fence line monitoring on industrial sites or airports (Arvidsson 2002) and for long term air pollution studies (Agar et al. 2001). Open path UV monitors are recommended as technology by the European Union Network for the Implementation and Enforcement of Environmental Law (IMPEL), for the measurement of diffusive VOC emissions from industrial sites (IMPEL 2000).

1.4.3. Fourier Transformation Infra Red Spectroscopy (FTIR)

The basic working principle is the same as UV/VIS spectroscopy, as described in section 1.4.2. The main difference is that only the gases that have adsorption spectra in the infrared range can be measured with this system. During data acquisition, a gaseous sample is exposed to a scan over different wavelengths of infrared radiation. Some of the molecules hit by the light energy absorb the radiation, and this causes their expansion and contraction. This absorption of energy is then detected and plotted over the frequencies of the scan. The spectra are then evaluated by Fourier transformation and compared to library spectra. This technique is commonly used, but requires a closed measurement cell, therefore it is limited by the length of the measurement path and therefore in the concentrations that can be measured. This makes these instruments very suitable for applications requiring the measurement of VOCs at mid ppb to ppm level concentrations, as commonly found in stack gas measurements. Settle et al. (1997), Naumer, Heller (1990) and Armand, Tullin (2000) describe the working principles of this method in further detail.

Only gases that absorb light at a wavelength between 2.5-15.4μm can be analysed with this technology, and in the atmosphere the water peak is a problem over a significant section of these wavelengths (Armand, Tullin 2000). Detection thresholds are gas and path length dependent, but are typically in the range of 0.1 to 10ppm (AIM 1996). Some systems are supplied battery powered, but their power consumption of around 100W requires large battery capacity. Calibration is required only approximately every three months (AIM 1996). Honne (2000) describes the use of such a system for the air quality monitoring on the international space station and reports quantification limits between mid ppb to low ppm levels for various VOCs. Armand, Tullin (2000) describe the application of such an instrument for the measurement of unburned and burned combustion gases from a 12MW boiler at the Chalmers University in Sweden. Wright et al. (1995) describes FTIR measurements for continuous monitoring of the emissions of various VOCs from a cement manufacturing plant, reporting concentrations in the low ppm levels.

1.4.4. Mass Spectrometric Methods

Mass spectrometric methods (MS) are those which are able to measure the mass of molecules and produce a mass spectra dependent on the chemical. In most mass spectrometers, chemicals are ionised by either bombarding them with electrons, ionised molecules, lasers or ultra violet light. Once the sample molecules are ionised they are accelerated in an electric field. The beam of ions then is sent through a mass filter, before hitting an ion detector. Recording the ion current from the detector versus the setting of the mass filter results in a mass spectrum. The location of a mass peak in the mass spectrum is representative of the mass of the ion, and the area underneath this peak is representative for the number of ions at that specific mass (i.e. the concentration).

Current technologies for mass filters include quadrupole and magnetic sector spectrometers. The working principles of MS methods are explained in more detail in section 2.2.2. MS that work by using a mass filter have the disadvantage that most of the ion beam created is filtered out when the spectrometer is analysing one specific mass from the beam. As a result of this, more sample needs to be introduced in order to achieve a reasonable sensitivity for the VOC of interest. Time of flight mass spectrometers (TOFMS) overcome this disadvantage, by measuring all masses within an ion beam simultaneously, rather than one after the other, as happens with a mass filter. This results in a much higher sensitivity and, therefore, requires smaller samples being supplied to the spectrometer. The working principles of TOFMS analysers are described in detail in section 2.2.2.

These mass spectrometric methods rely on the ion beam that is created, not interfering with other gas molecules, and therefore they all work in a vacuum. This means that prior to analysis the sample has to be introduced into the vacuum system of the MS.

One can distinguish between direct and indirect sampling MS. A common feature of the sample inlets used, is the fact that the sample flow into the vacuum of the MS is adjusted to be low enough so that the vacuum pumps of

the system are able to maintain a vacuum level at which the instrument can operate. The most common indirect sampling MS is the GC/MS, mentioned in section 1.3 where the sample is first separated into clean chemical compounds by the GC and then introduced into the MS to identify the eluting chemicals according to their molecular masses.

Direct sampling mass spectrometers use mainly three different kinds of inlets (Wise, Guerin 1997).

a) Capillary restrictors, that allow all gases to enter the MS vacuum at a similar rate.
b) Membrane inlets, where the sample has to permeate through a selective polymer into the vacuum.
c) Atmospheric pressure ionisation and atmospheric sampling glow discharge ionisation, where the sample is ionised at atmospheric pressure and then introduced to the MS by means of an orifice and differential pumping.

Due to the high pumping requirements of the atmospheric pressure ionisation and atmospheric sampling glow discharge these two techniques (c) do not lend themselves to portable instrumentation. The capillary restrictor allows easy limiting of the sample flow to a low enough level to keep the pumping requirements of the vacuum system within levels that are acceptable for portable instrumentation. A big drawback of the capillary restrictor is that all the components in the sample are introduced at a very similar rate, which results in relatively high pressures of nitrogen, oxygen and water within the vacuum system. These high pressures, especially the water, can interfere with the MS and reduce sensitivity for the VOCs under investigation.

Membrane inlet MS (MIMS) limits the amount of sample that is led into the MS by forcing the sample to permeate through a thin polymer membrane, which in most cases is poly-dimethyl-siloxane (PDMS) (Johnson et al. 2000). The advantage of these membranes is that most VOCs will permeate through the membrane at a higher rate than nitrogen and water, thus resulting in enrichment (LaPack et al. 1994). Disadvantages compared with the other inlets are

the time delay caused by the permeation through the membrane. This time delay is dependent on the material, temperature and thickness of the membrane and is compound specific. The delay is typically in the order from a few seconds to minutes. Additionally the sensitivities for polar compounds and chemicals of a high molecular weight tends to be relatively low (LaPack et al. 1994)

Some of the recent studies using MIMS and reported in the literature include:

- Ketola et al. (1999) has investigated the analysis of volatile organic sulphur compounds;
- Ketola et al. (1997) has described the development of a MIMS for the analysis of air samples and investigates the solvents released from a paint shop;
- Virkki et al. (1995) has investigated the performance of a MIMS instrument for the measurement of VOCs in water;
- Cisper et al. (1995) have described a MIMS system being used for the measurement of VOCs with detection limits of ppt levels;
- Allen et al. (2001) have investigated the real time analysis of methanol in air and water by MIMS using different membrane materials.

1.5. The proposed portable system for monitoring of VOCs at low concentrations

As discussed in section 1.3 there is a need for a portable VOC monitor that is able to measure VOCs at low concentrations. The requirements of portable VOC monitors for environmental, personal exposure and industrial monitoring are:

- High sensitivity for a large range of VOCs in the low ppb levels, preferably even ppt levels.
- Low interference of the measurement with the air background matrix, especially high levels of moisture in the air.
- To be light enough to be carried by the operator, so as to be independent of vehicular access.

- To be battery operated for independence from mains power.
- To be rugged, which is a part of real portability, where the instrument easily might receive shocks whilst being carried to the site of analysis.
- Desirably to have the positive identification of a chemical in the sample, offered by MS.
- Low requirements of consumables.
- Fast analysis time.
- Safe to use.
- Able to be produced at a competitive price

It was felt that the current technologies for monitoring VOCs either do not have the required sensitivity of low ppb level detection, are very heavy or difficult to set up, or are very power thirsty. These disadvantages prevent them to be able to be adapted to fulfil the requirements of a field portable VOC monitor that is capable of low level VOC monitoring.

Gas chromatographs have a very high sensitivity, which makes them suitable to measure most of the VOCs down to ppt concentrations. A disadvantage is the relatively long analysis time required to collect the sample into a canister or onto an adsorbent trap (EPA TO-1, EPA TO-14) and to separate the different chemicals in the separation column. This results in an analysis often taking more than 30 minutes (EPA 1997) and commonly more than 1 hour (Hall 2003). Some manufacturers offer portable GC systems, allowing field analysis. One mobile GC/MS (Inficon Inc. Hapsite) system is known to be independent from power mains or a generator and is commercially available at the time of writing, and has been developed since this project started (Inficon 1996, EPA 1998). Power consumption for a GC/MS, due to the heating requirement of the GC and the vacuum pumping for the MS, is quite high and starts at around 200W and upwards (Inficon 1996, Chrompack 1995, Harris 2002). A second commercial transportable GC/MS system available is the Spectra Trak 625 from Viking Instruments. However, its weight of about 80kg and power consumption of 1000W (average) require a vehicle or trolley for transport and a generator or mains for operation (EPA 1997). Other disadvantages of GC systems are the requirement for compressed gases and high operating cost (EPA 1997, EPA 1998).

UV analysers are mainly used in permanent or semi-permanent fence line monitoring applications. This is because the setting up of the source and receiver of the UV light is a relatively lengthy procedure making them not suitable for portable operation. Additionally, the long measurement path required for low level VOC monitoring make them unsuitable for measurement of a time series of concentrations within a small space. This is also the case as their detection limits in mid to low ppb levels for many VOCs make them suitable for fence line emission monitoring.

FTIR spectrometers are commonly used in stack gas emission monitoring of VOCs and other air pollutants. These instruments are portable in principle, however the very sensitive mirrors within the measurement cell and the interferometer make them extremely sensitive to vibration and shock, and require lengthy re-calibration after transport (Horiba 2003). An advantage of these systems is the high stability of the calibration if the instrument is left stationary (Honne 2000).

Based on the different drawbacks of the current technologies for some applications that require portability combined with low detection limits, it was concluded that the above described membrane inlet, combined with a time-of-flight (TOF) mass spectrometer would provide a valuable addition to the existing VOC monitors. This instrument has the potential of near real-time continuous analysis at ppb concentrations for a large number of VOCs of concern. Other advantages of the system chosen are the low power consumption of the TOF mass spectrometer without the GC attachment, the low weight of the technology and the fact that no consumables are required for its operation. This provides a genuinely portable and mains independent instrument, opening up further applications, where both portability and low detection limits for VOCs are required. These applications could include spot checks of emissions, measurement of accidental release of chemicals, continuous personal exposure studies, or some of the applications discussed in Chapter 5, which investigate the use of this system further.

Many instruments that are offered as portable VOC monitors are mainly laboratory based instruments that were re-packaged and adapted in order to

be portable. In order to achieve the above mentioned requirements of a portable analyser every part of the proposed instrument was specifically designed for this instrument, always keeping weight, size and power consumption in mind, and hardly any standard components were used. The system and the decisions that led to that design are described in more detail in Chapter 2.

1.6. Aim of the Project and Structure of the Thesis

When starting the work, a portable MIMS technology demonstrator of the instrument described in this thesis, called a T-CAT, was already in existence and has been described by White et al. (1998). During the course of this PhD this instrument was reviewed and improved in order to be more robust, to have higher sensitivity and lower detection limits for common VOCs. Additionally, effort was devoted to improve the software and make the use of the instrument easier. The name of the "final" instrument was changed to the MS-200.

The aim of this research project was to investigate and improve the analytical performance of the system and demonstrate its suitability in various applications that could benefit from a portable low concentration VOC monitor.

In order to fulfil this aim, the following objectives were set out.

I. Investigate the general analytical performance of the instrument in laboratory experiments and feed back the findings into the design process.

II. Investigate the enhancements in detection and sensitivity provided by an adaptation to the MS-200, which was designed to improve these aspects.

III. Identify and select interesting applications, based on customer inquiries, investigate their requirements and test the MS-200 on these requirements, in particular analytical performance and portability.

IV. Discuss the results of the applications and the analytical performance, and identify the applications for which the MS-200 could be used.

V. Outline any further development of the instrument or its use that might be required to fully develop the use of the MS-200 in the applications identified.

The structure of the thesis is set out below. Chapter 2 describes the working principles of the MS-200 to allow an understanding of the instrument, and highlights some aspects of the design. The performance of the instrument within a laboratory environment is tested and discussed in Chapter 3. Chapter 4 describes a novel inlet system for the mass spectrometer, which enhances the sensitivity of the system for many VOCs, allowing the measurement of ppt level concentrations. Chapter 5 tested the performance of the instrument in different interesting applications. Each of the applications described is presented with an introduction to the specific requirements of the application; the method employed; the measurements performed; and the results obtained. Each application is a relatively independent study and therefore includes separate discussion and recommendation sections. The results of the over all work of the thesis are discussed in Chapter 6. Conclusions and recommendations for further work are presented in Chapter 7. An extensive set of appendices includes some further experiments, some detailed results on the applications chapter, and additional information on the instrument and the software used.

2. Design and Working Principles of the MS-200

The aim of this chapter is to describe the working principles of the MS-200. The chapter will describe the different parameters that influence the performance of the instrument when analysing a sample or using it for a specific application.

Most parts of the MS-200 are custom engineered to suit a portable mass spectrometer. The general physical working principles of many of these parts, however, are well understood and described elsewhere (Barrington 1963, Duckworth et al. 1990). This chapter will describe how existing technology has been used and adapted within the MS-200. Innovations and differences in design compared to other mass spectrometers will be highlighted. To help in understanding the design considerations of a specific part of the MS-200, an introduction to some physical principles will be provided. Where the principles are well understood supporting references are provided so as to avoid unnecessary background theory.

2.1. Design Considerations for the MS-200

As discussed in the previous chapter, it was seen that there is an advantage in, and therefore a potential market for, the in-situ analysis of VOCs using portable analytical instrumentation. Before deciding on the technical solutions of a portable instrument, one has to start with a description of the possible applications and environments encountered to understand what is needed. The next step is then to identify some of the key requirements of an in-situ VOC analyser. This thought process is symbolised in Figure 4, showing the ideal requirements for such a system.

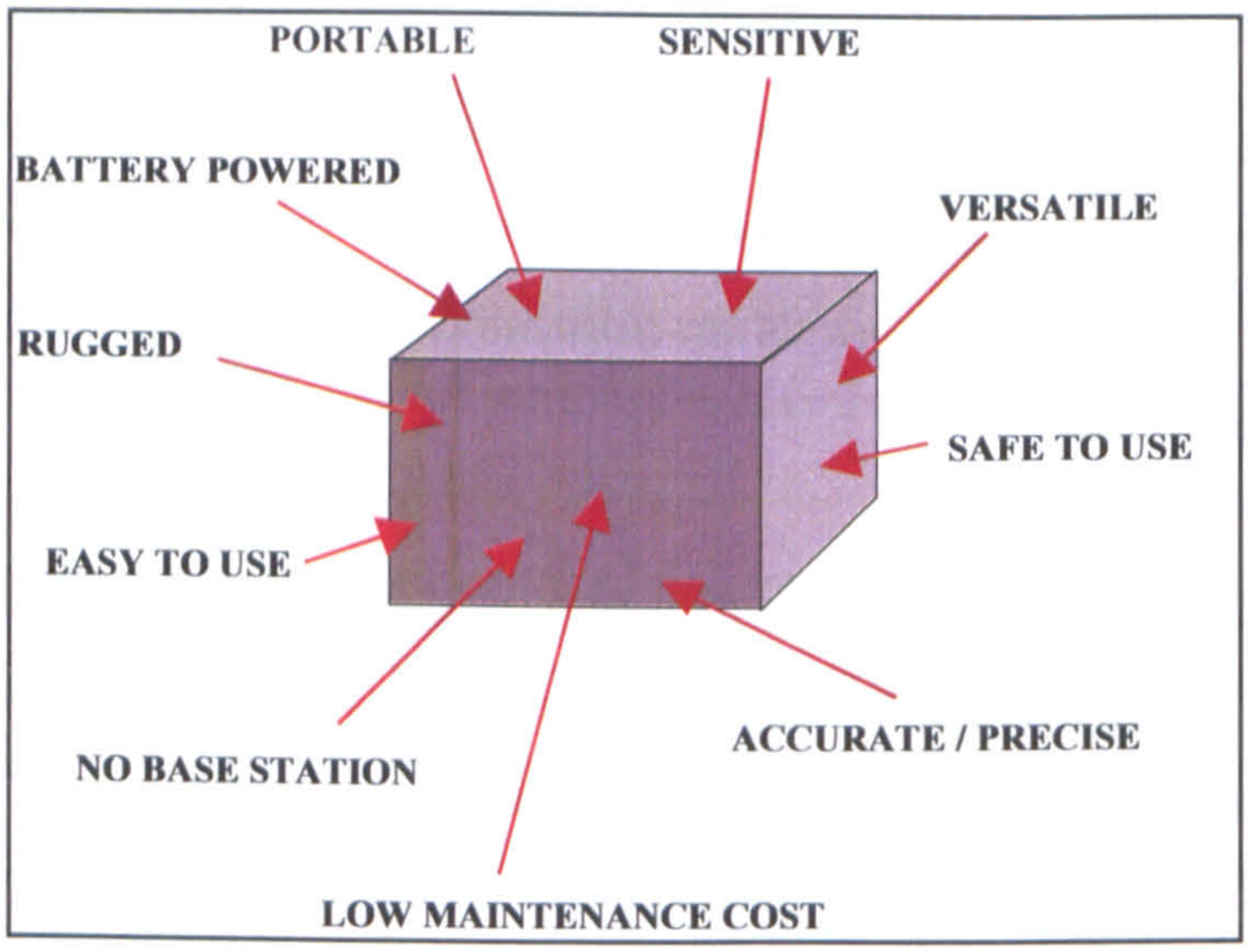

Figure 4: Key requirements of an in-situ VOC analyser

One of the early findings of the feasibility study conducted by Kore Technology and as discussed in section 1.5, was that the analytical technique used should be mass spectrometry (Kore 1995). This technique seems to offer significant advantages over other techniques like gas chromatograph (GC) or optical methods (see section 1.4). All but one of the other mass spectrometers (MS) currently available are rather large, heavy and power thirsty instruments. This seems contradictory to the aim of a portable instrument, but is not necessarily a feature of a mass spectrometer, as discussed in the following sections.

At the time Kore Technology made the decision to produce a portable mass spectrometer, there were already significant attempts in miniaturisation of existing technologies, however these were mainly one-off prototypes pointing into the right direction (Hemond 1991) (McDonald 1994), rather than commercially viable instruments. Since the MS-200 was developed another portable mass spectrometer is now available, the Hapsite GC/MS (Inficon 1996, EPA 1998). Other than portable instruments, there were various transportable mass spectrometers emerging onto the market. These instrument can be transported in the back of a car or a van and typically require large batteries or a generator to function (Meuzelaar et al. 1994, Wise et al 1995, EPA 1997). Therefore it is important to distinguished between transportable and portable systems.

At the time of writing this thesis, the following portable/transportable instruments (Table 1) were on the market. Note that all of these are gas chromatograph mass spectrometer (GC/MS) instruments. Currently the MS-200 is the only commercially available direct sampling portable MS on the market, known to the author.

Table 1: Portable/transportable GC/MS Systems (Harris 2002, EPA 1997)

Product	Manufacturer	Weight [kg]	Power [W]
CT-1128 GC-MS GC/MS	Constellation Technology Corp Largo, FL, USA	34	300
Hapsite GC/MS	Inficon East Syracuse NY, USA	16 + base station	200
Spectra Trak 672	Viking Instrument Corporation, Virginia USA	80	1000
EM 640 GC/MS	Bruker Instruments Billerica, MA, USA	60	600
MS-200	Kore Technology Ltd. Ely, UK	20	20 (aver.) 45 (peak)

As a result of the feasibility study into the requirements of an in-situ instrument and its commercial potential as summarised in the introduction (chapter 1.5), it was decided to build a membrane inlet mass spectrometer (MIMS). The advantage of such a system, compared to GC or GC/MS and to optical systems is discussed in Section 1.4 of the introduction. The different parts of the mass spectrometer, and decisions on the specific choice are described in the following sections of this thesis (sections 2.2 to 2.5). The resulting instrument, based upon the choices discussed below can be seen in Figure 5. The weight of the instrument is 20kg and the power consumption averages below 20W with a peak power requirement of 46W. Dimensions of the instrument are 531 x 328 x 213mm (w x d x h). Instrument control and data analysis is performed using a laptop computer.

Figure 5: The Kore Technology Transportable Mass Spectrometer MS-200

2.2. The Mass Spectrometer

As discussed in section 1.5, mass spectrometry is one of the most versatile and powerful analytical techniques available. The different variations of mass spectrometers and the ancillary equipment like gas chromatography (GC) and liquid chromatography (LC) allow a huge amount of different analytical tasks to be solved. In their different forms they can analyse gases, liquids, solids and solid surfaces. The mass spectra produced give valuable information on the chemical structure of the analyte, that can be used directly to identify the compound analysed. Their sensitivity, commonly down to the ppt range, can sometimes make them the only available tool for trace analysis.

A mass spectrometer is principally made up of a vacuum system, with an inlet for the sample, an ionisation source, mass separation, detection system control electronics and data analysis system. The principle parts and their interactions of the systems are shown in Figure 6.

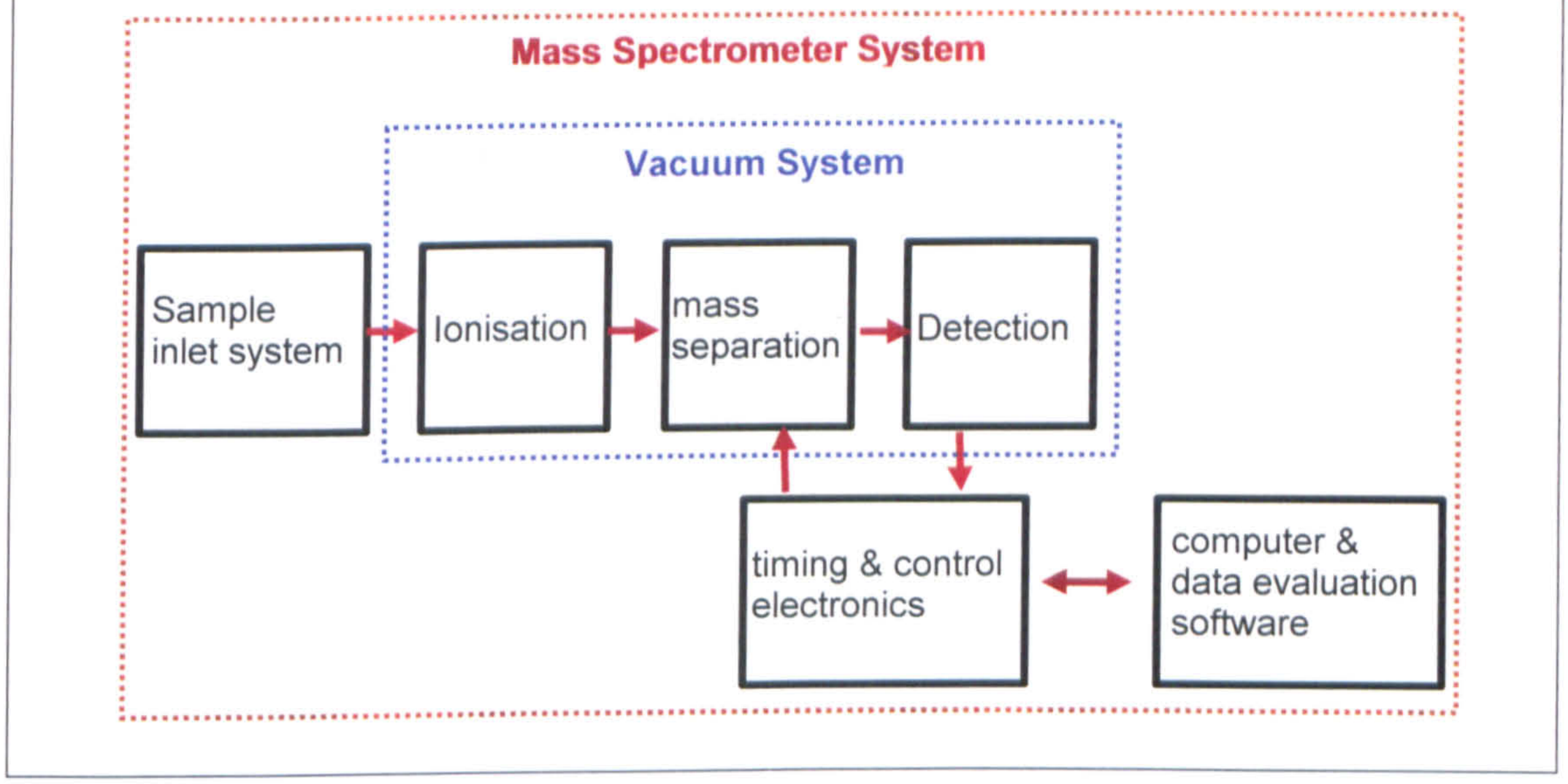

Figure 6: Block diagram of the different components of a mass spectrometer

The various components from the block diagram in Figure 6, which make up a mass spectrometer, are discussed in the following sections of this chapter.

2.2.1. Ionisation Source

Prior to measuring the mass of gas molecules introduced to the mass analyser they must be ionised. Ionisation produces charged molecules. This is in order to be able to manipulate the direction of travel of the gas molecules using electric and/or magnetic fields.

Ionisation relies on the removal or addition of electrons from the molecules (positive/negative ionisation). Ionisation can be achieved by various different techniques. The common methods used are electron bombardment ionisation, gas discharge, laser ionisation, chemical ionisation and photo ionisation. These different techniques are described and thoroughly discussed in the literature (Duckworth et al. 1990, Frauenhofer 2002).

The most commonly used technique for gaseous samples is electron impact ionisation. This is one of the most versatile ionisation techniques, as all gases present in the analyser chamber will be ionised (Duckworth et al. 1990). Resulting from this versatility, the technical simplicity, and the potential low power consumption, it was decided to design the MS-200 using an electron

impact ionisation source. Additional advantages are highlighted in following description of the ion source.

Electrons are produced by an electron-emitting filament, which is either made from a heated metal wire (commonly Tungsten), or by using a coating of compounds with low electron escape energy (e. g. yttrium, thorium) on a heated metal wire, which provides the electrons. For the ion source of the MS-200 the coated filament option was chosen, because this coating has the advantage of very low electron escape energy and therefore very low heating requirements. This allows the ion source to produce an ion current of a few hundred microamperes with a power consumption of less than 2 Watt.

The electron-emitting filament is held at a defined electrical potential below the rest of the Ionisation source, in order to accelerate emitted electrons to a specific kinetic energy. The most efficient ionisation energy for most components is between 70eV and 90eV [(Duckworth et al. 1990)]. To gain the maximum sensitivity, the electron-emitting filament in the MS-200 is at a potential of –70V, with respect to the rest of the ion source, therefore emitting electrons with energy of 70eV.

When an electron interacts with a gas molecule, it can introduce disturbances to the molecule so that it releases electrons, thus making it a positive charged ion. More commonly, the disturbance is sufficient to fragment the molecule into various fragment ions (dissociation) [(Duckworth et al. 1990)]. A simple case of ionisation is illustrated in Figure 7, where the molecule simply loses an electron and becomes positively charged. More typically a hit molecule will fragment, as shown in Figure 8. Fragmented ions can be either positive or negatively charged or in the majority of the cases are neutral, depending on the attachment of electrons to the different fragments. Whether fragmented molecules are ionised to create neutral, positive or negative ions is strongly dependent on the ionisation energy and the properties of the molecules. To be able to measure all of the results of the electron interacting with the molecule, sophisticated mass spectrometers allow a change in ionisation energy, and are able to switch between the analysis of positive and

negative ions in order to gain the maximum information about the analyte of interest.

Most alkanes, aromatic and chlorinated VOCs produce a good yield of positive ions and ion fragments, when ionised by 70eV electrons (Duckworth et al. 1990, NIST 1998). Therefore it was decided that it is sufficient for the MS-200 to only analyse positive ions. This reduces the number of components and, therefore, reduces cost and weight of the instrument.

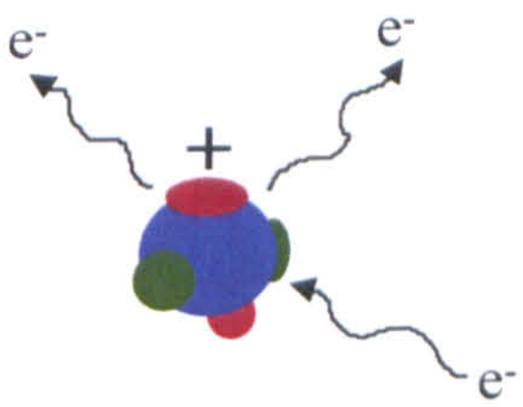

Figure 7: positive ionisation of molecule*

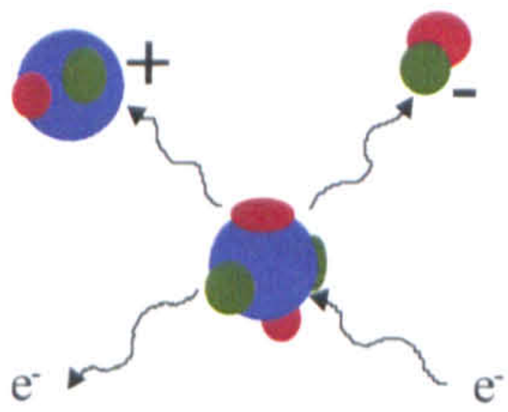

Figure 8: fragmentation of molecule*

** These pictures represent a simplistic view of a molecule with a base molecule (blue) that could be for example a benzene ring (C_6H_6) plus some groups attached to it (red and green), for example OH, Cl.*

The fragmentation patterns of a vast number of chemicals resulting from the commonly used 70eV electron impact ionisation are recorded and sorted into libraries of mass spectral patterns like in the NIST database (NIST98), which holds the positive ions fragmentation patterns of more than 100,000 compounds. Comparing observed spectra with spectra from a database allows the user to identify unknown chemicals in the sample and is one of the major advantages of mass spectrometers compared to other gas analysis techniques.

Common electron impact ionisation sources have an electron-emitting filament, behind a fine slot, through which electrons of a very narrow energy distribution pass. The electrons then ionise the sample stream that passes on the other side of the slot. This produces the continuous stream of ions (ion beam) that is required for magnetic sector or quadrupole instruments. However, the ion source of the MS-200 is a static ion source, where both the

gas molecules and created ions remain in the ionisation source. To get a sample pulse in the MS-200, an electrical field is applied to the source, and ions that are present in the source at this time are extracted into the mass analyser.

A picture of a three dimensional model of the source is shown in Figure 12. The electron-emitting filament is at a voltage of –70V. The back plate of the source is at a few millivolts below ground. The extract plate is also at ground potential. This way the source produces ions that are in an almost field-free region, which functions as ion storage. To extract ions from the source the extract plate is pulsed to approximately –400V, thus accelerating all positive ions from the source into the spectrometer. The filament is surrounded by the repellor, which is at a voltage of between –80V to –110V, depending on the specific tuning of the instrument. The repellor focuses the electrons emitted from the filament towards the centre of the ionisation source, increasing the number of electrons in the preferred ionisation region.

To increase the efficiency of ionisation, the ion source of the MS-200 was designed as an annular source with a relatively large ionisation area. Statistically having a large volume of gas through which electrons are passed results in a large chance of molecules being hit by electrons, and therefore being ionised. This design offers advantages over the normal point or line ionisation sources, which suffer from small volumes of ionised sample due to space charge saturation effects (Kore 1994).

2.2.2. Mass Analyser

The purpose of the mass analyser is to separate the ions, produced in the ion source, according to the mass to charge ratio (m/z)[1]. This allows the mass of the original molecule or a fragmentation ion to be calculated.

Separating ions by their mass to charge ratio (m/z) can be achieved by various methods. One of the oldest, and still very commonly used, is the

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[1] in the case of a single charged ion (z = 1) one can use atomic mass units (amu) instead

deflection of an ion beam in a magnetic field. In this case, an ion beam enters the magnetic field and is deflected onto a circular trajectory. The deflection of the beam is dependent on the speed of the ions, the mass and the magnetic field. Therefore if the ion velocity and the magnetic field remain constant, then only one specific mass of ions from the ion beam will reach the detector and be recorded. The molecules with other masses are filtered out and will miss the detector. As a result of this, magnetic sector instruments are commonly used in a scanning mode. A scanning mode is where either the input velocity of the ions or the magnetic field are continuously changed, and the ion current reaching the detector is recorded as a function of the magnetic field (Duckworth et al. 1990). This way a complete mass spectrum of different ions in the ion beam can be produced. The basic working principles of a magnetic sector instrument can be seen in Figure 9.

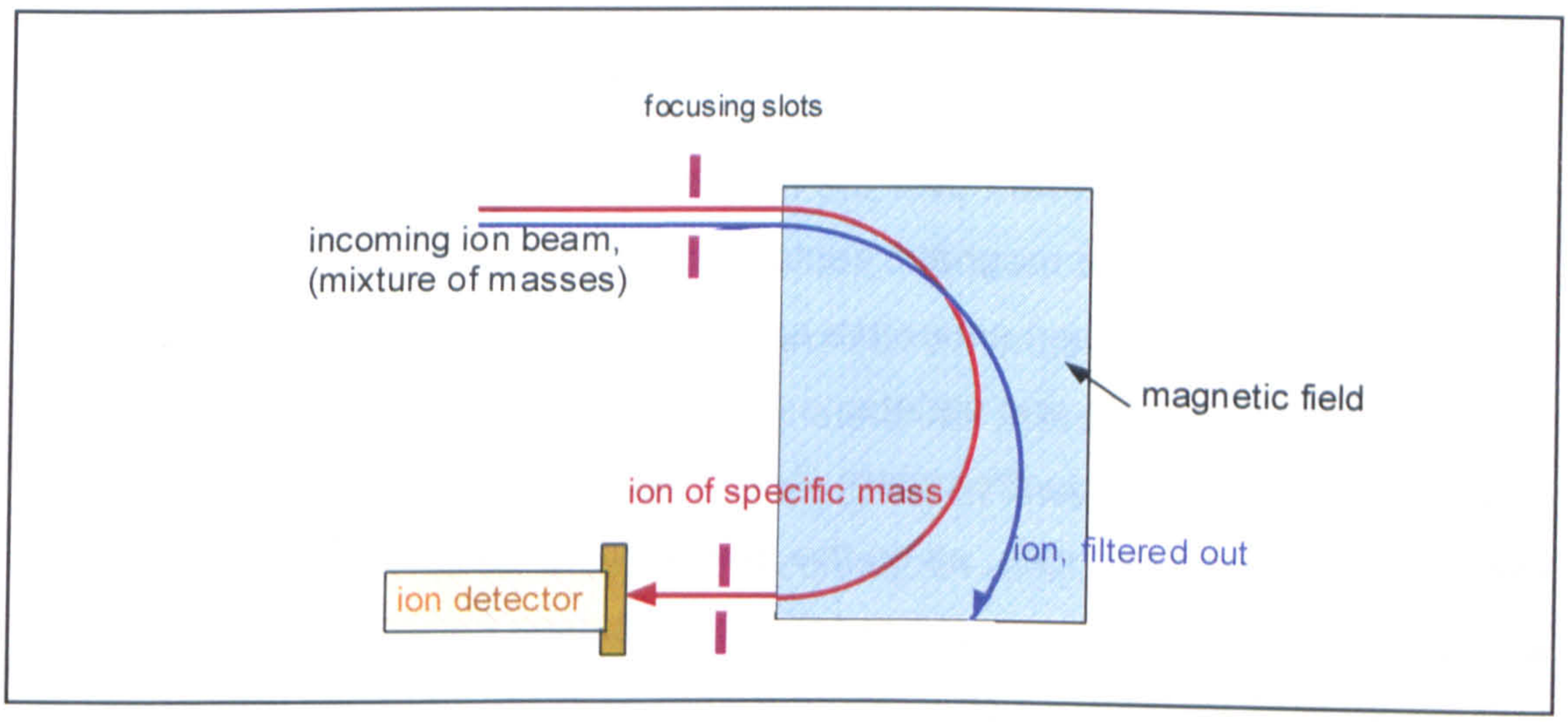

Figure 9: Principle of magnetic sector mass spectrometer

A disadvantage of these instruments is that sensitivity in the scanning mode is relatively poor due to the fact that most of the ions will miss the detector. Using the instrument in a single ion mode only can increase sensitivity. In this case the magnetic field is fixed, allowing the measurement of only one mass to charge ratio. A disadvantage here is that none of the other ions in the ion beam are analysed, so this is used in cases where identification is not the main concern, but high sensitivity is required.

The constant changing of the magnetic field in the scanning mode results in high power consumption. The above mentioned inefficiency in the scanning mode means that more of the sample will have to be introduced, ionised and pumped away in order to achieve reasonable sensitivity, which increases power consumption further. As a result of these constraints magnetic sector mass spectrometers typically have a minimum power consumption of a few hundreds Watts and are relatively heavy, making them unsuitable as portable instrumentation.

Further development of mass spectrometers came with the quadrupole instruments, designed in the early 1950s [Duckworth et al. 1990]. In these instruments the ion beam is passed through a high frequency electric field between four electrodes. Ions will move in a random path through this field. Depending on the frequency of the electromagnetic field only the path of one particular mass to charge ratio ions will be passed through the quadrupole and reach the detector. A detector on the exit point of the mass filter records the strength of the ion current over the frequency of the electromagnetic field [Duckworth et al. 1990]. Like the magnetic sector instruments, described above, these instruments are used either in a scanning or single ion counting mode. Quadrupole instruments and variations (ion-trap) are currently the most commonly used mass spectrometers. As in respect of portability they suffer similar power disadvantages, as do the magnetic instruments. Nevertheless, a quadrupole mass analyser was successfully chosen for the portable Hapsite GC/MS [Inficon02], which is another commercially available portable (rather than transportable) mass spectrometer on the market today.

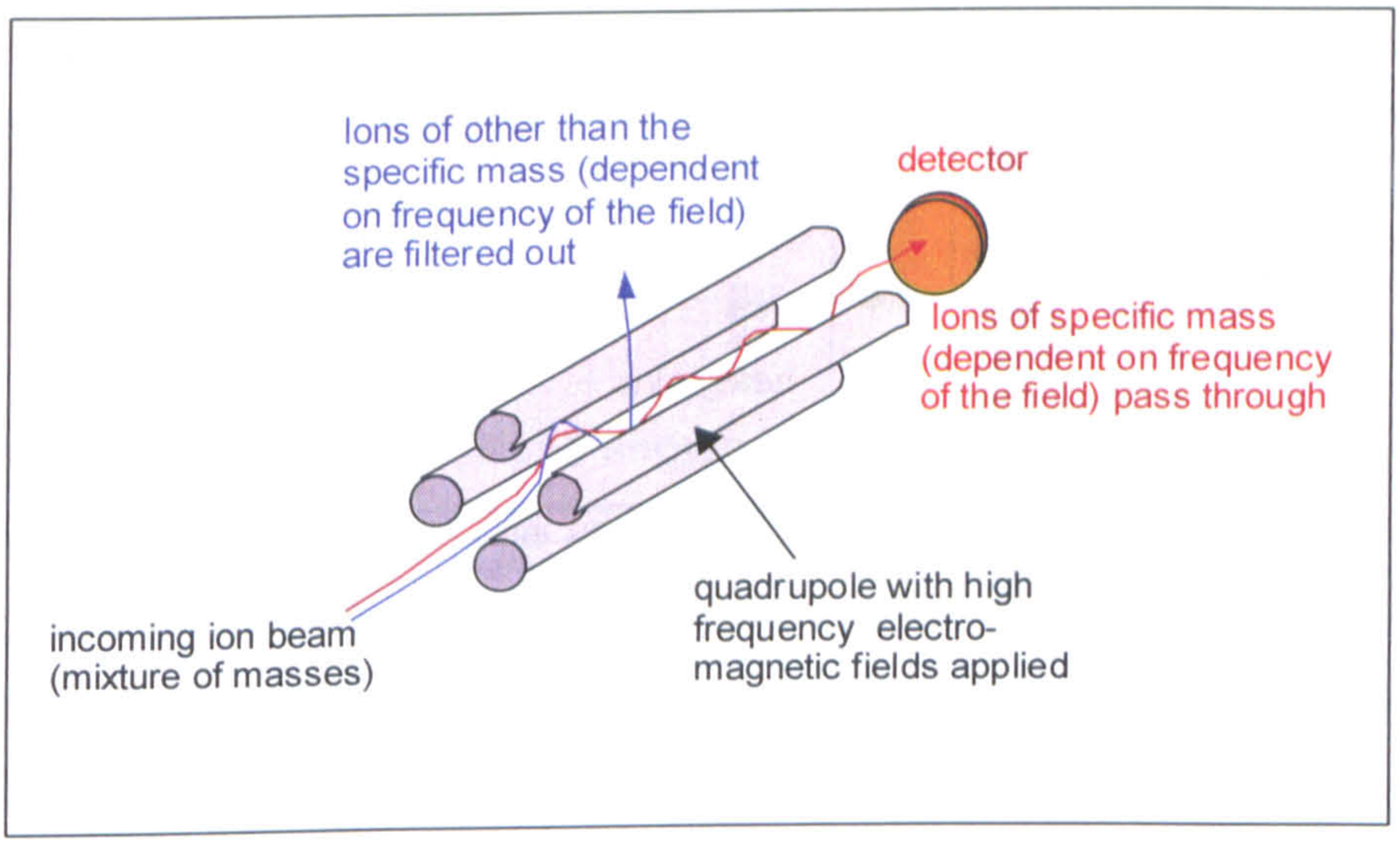

Figure 10: Schematic of a Quadrupole Mass Filter

It was decided that time-of-flight mass spectrometer (TOF or TOFMS) analysers would overcome some of the disadvantages. TOFMS were developed in the late 40s (Duckworth et al. 1990), but not very commonly used, until the development of high computing power to cope with the fast data rate produced.

The MS-200 incorporates a pulsed beam TOF. In pulsed TOF instruments, ions created in a source receive a short electrical pulse and are therefore accelerated into one direction forming a bundle of ions. This is different to the constant ion beams used in the other techniques, described earlier, and has the advantage of the source being at the same pressure than the rest of the analyser, requiring lower pumping and therefore saving power. After the acceleration the ion bundle flies through an acceleration free region (drift tube), before hitting a detector. All ions receive the same start energy given by the electrical pulse, received from the extractor and the potential slope created by the ion optics[2]. This results in ions with a higher m/z having a slower speed than lighter ions, and therefore taking more time to reach the detector. Mass separation is achieved by different flight times. The basic working principles of a TOF mass analyser are shown in Figure 11.

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[2] Despite the fact that all the ions receive the same energy from the ion optics, there are small variations in the energy spread when the acceleration pulse occurs. This is due to the direction of movement of a particular ion and the physical location within the source. How the spectrometer deals with this spread is explained later in this section.

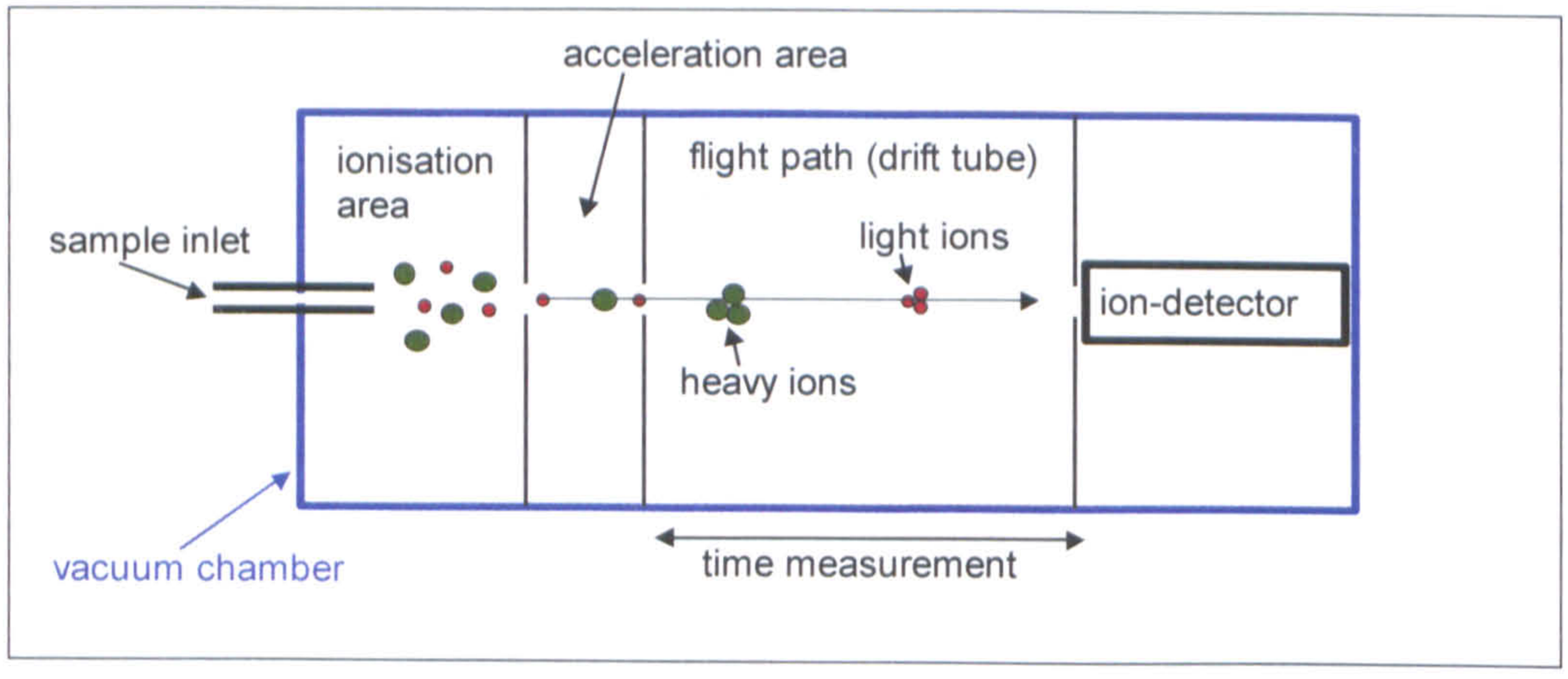

Figure 11: Working principle of a TOF analyser

The calculation for the mass of a molecule in a time of flight instrument is described by Equation 1.

$$m/z = t_0 + c_b * t^2$$

m/z = mass to charge ratio [g/(mole*e)]
t_0 = offset [g/(mole*e)]
c_b = instrument specific constant dependent on the length of the flight path, and the acceleration voltages [g/(mole*e*sec^2)]
t = flight time of an ion [sec]

Equation 1: Mass to Charge Ratio of an Ion, Depending on the Flight Time in a TOF Spectrometer

The geometry of a pulsed TOFMS is relatively simple, and the only voltage changed during analysis of a sample is the extract pulse for the pulsed source. Unlike in a magnetic sector instrument or a quadrupole the TOF analyser does not filter out (i.e. reject) any of the masses. This results in transmission rates (ratio of ions produced to ions actually arriving at the detector) for such types of mass analysers to be much higher than transmission rates of magnetic sector or quadrupole instruments, giving excellent sensitivity over the complete mass range. Transmission rates for TOF analysers are typically 60% to 80% of ions leaving the source (Vickerman, Briggs 2001). As a result of this, very little sample needs to be introduced into the analyser. The small amount of sample required to be introduced to the vacuum system, together with a source being at the same pressure than the rest of the analyser chamber results in very low pumping requirements to maintain ultra high vacuum (UHV).

TOFMS offers clear advantages over the other techniques described. These advantages are simplicity of the analyser and power supplies, lower weight and higher sensitivity. Therefore it was decided to use this technology in the MS-200.

As mentioned in section 2.2.1 and shown in Figure 12, the Kore TOFMS uses an annular ion source. The annular source arrangement results in the production of a ring shaped pulse of ions accelerated from the source into the spectrometer. In order to be able to use a detector with a relatively small active area, this ring is collapsed to a point by the time it has passed through the spectrometer. Collapsing the tube to a point is achieved by means of ion optics, bending the "beam" towards the central axis of the spectrometer by use of electrical fields. The geometry of the "Converging Annular Time of Flight Mass Spectrometer" is described in detail in a patent (Kore 1994) and is shown in Figure 12. The principal electric potential of the ion optics and the path of ions are shown in Figure 13.

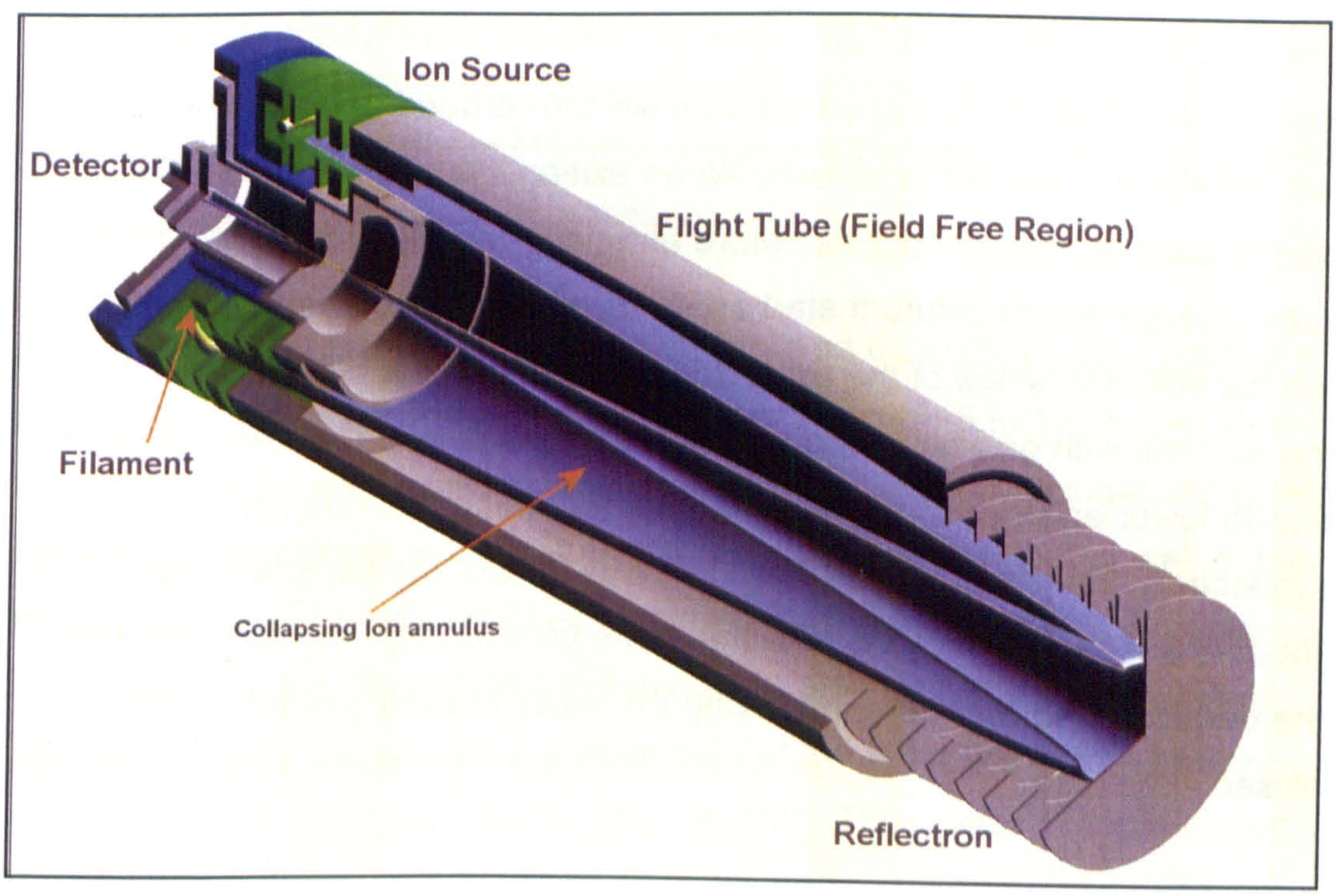

Figure 12: TOF geometry of the MS-200

As can be seen in Figure 12, rather than having a purely linear arrangement with the ion source in one line with the detector, Kore TOF analysers are equipped with a reflectron opposite the ion source. This reflectron has multiple uses. Firstly, it increases the length of the flight path for ions and therefore increases the resolving power of the spectrometer. Secondly, the reflectron allows focusing ions of the same mass, but with slightly different start energies (e. g. a variation of about ± 7.5% in start energy is focused so that the resulting mass peak has a width of about 0.2 to 0.3amu, measured at half the peak height). All ions produced in the source region will be extracted from the source by the same energy from the extract pulse. Thermal movement and the physical location of ions in the source prior to acceleration, result in different ions of the same mass having slightly different energies when entering the ion optics. This can result in a low mass resolving power for pulsed TOF analysers, which do not undertake further focusing of the ions.

Figure 13 shows that the reflectron, used in the MS-200 TOF, produces a slope in potential, which ions will 'climb up' until the point where all kinetic energy is absorbed. At this point the ions will turn around and accelerate down the slope in the potential field. When exiting the reflectron, ions will have the same kinetic energy as before entering the reflectron. Ions with a greater energy due to different start energies within the source therefore will climb the potential slope of the reflectron higher than ions of lower energy. By doing so, ions with greater energy will spend more time in the reflectron and ions with lower energy will spend less time. By tuning the slope (voltage) of the reflectron, this effect can be used to focus ions of the same m/z but with slight differences in energy, to take the same time through the spectrometer to the detector, and therefore improving the mass resolving power of the analyser.

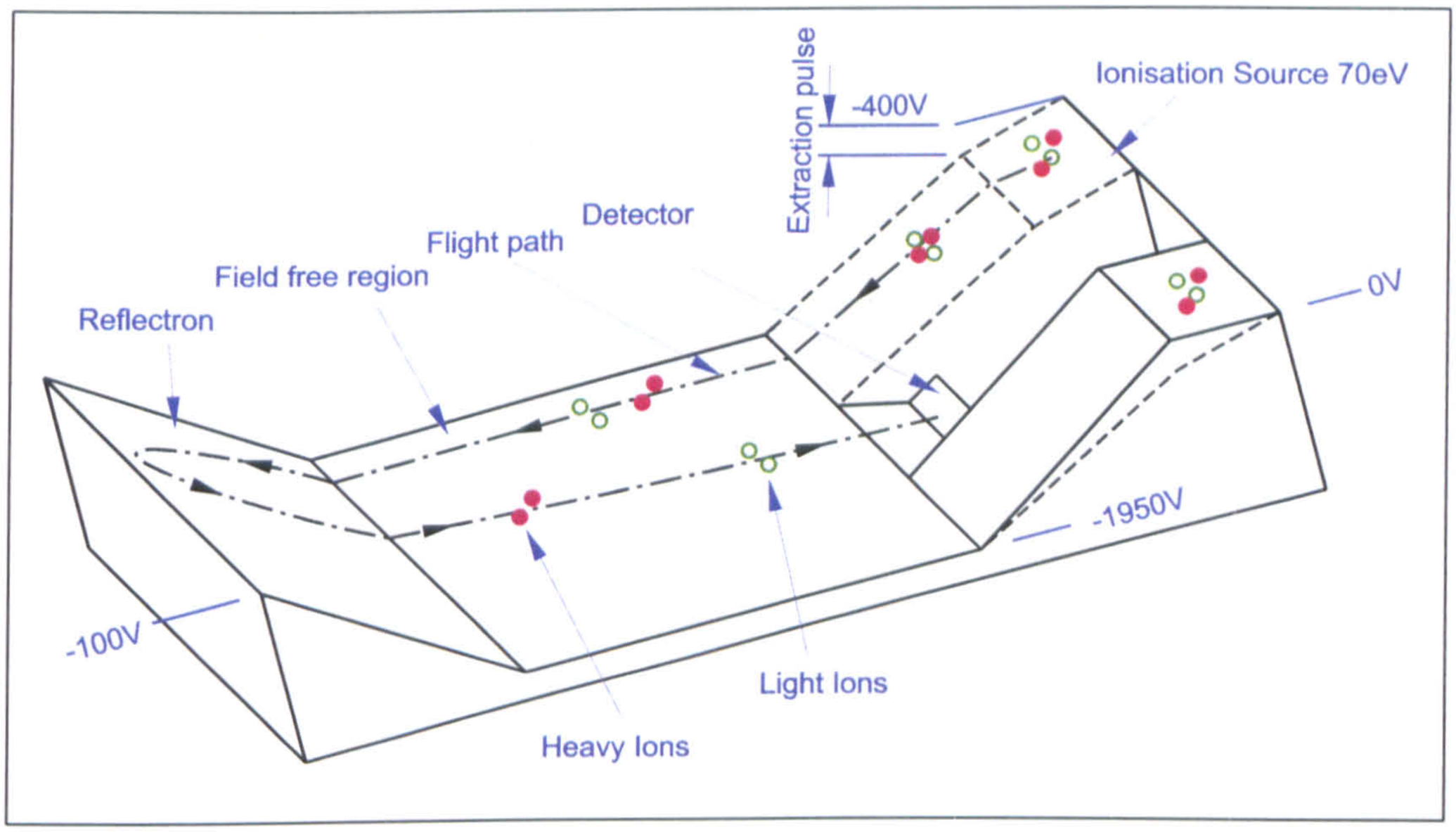

Figure 13: The potentials within the TOF analyser

2.2.3. Ion/Electron Detector

The purpose of a detector is to detect the arrival of a single ion, or the current produced by a stream of ions, and turn it into an electrical signal to be recorded. In the case of the MS-200, which is a pulsed TOFMS, the detector is used to record the arrival of individual ions.

Micro channel plates (MCP) are commonly used detectors, which consist of a bundle of fine glass tubes with a diameter of between 5 to 10μm that are internally coated with a secondary emissive layer (silicon dioxide). An electric field is applied along the tube. If an ion is incident on the coated wall of the glass tube, it will release multiple electrons from the secondary emissive layer. Those secondary electrons are accelerated due to the electric field, and when hitting the wall on the other side of the tube, will in turn release multiple electrons for each secondary electron. Thus, after multiple impacts, the electron current created will be high enough to be measured. The dynamic range for such a detector is typically 10^7, and output pulse width is approximately 1ns (Galileo 1997). The working principle of a channel plate detector is shown in Figure 14.

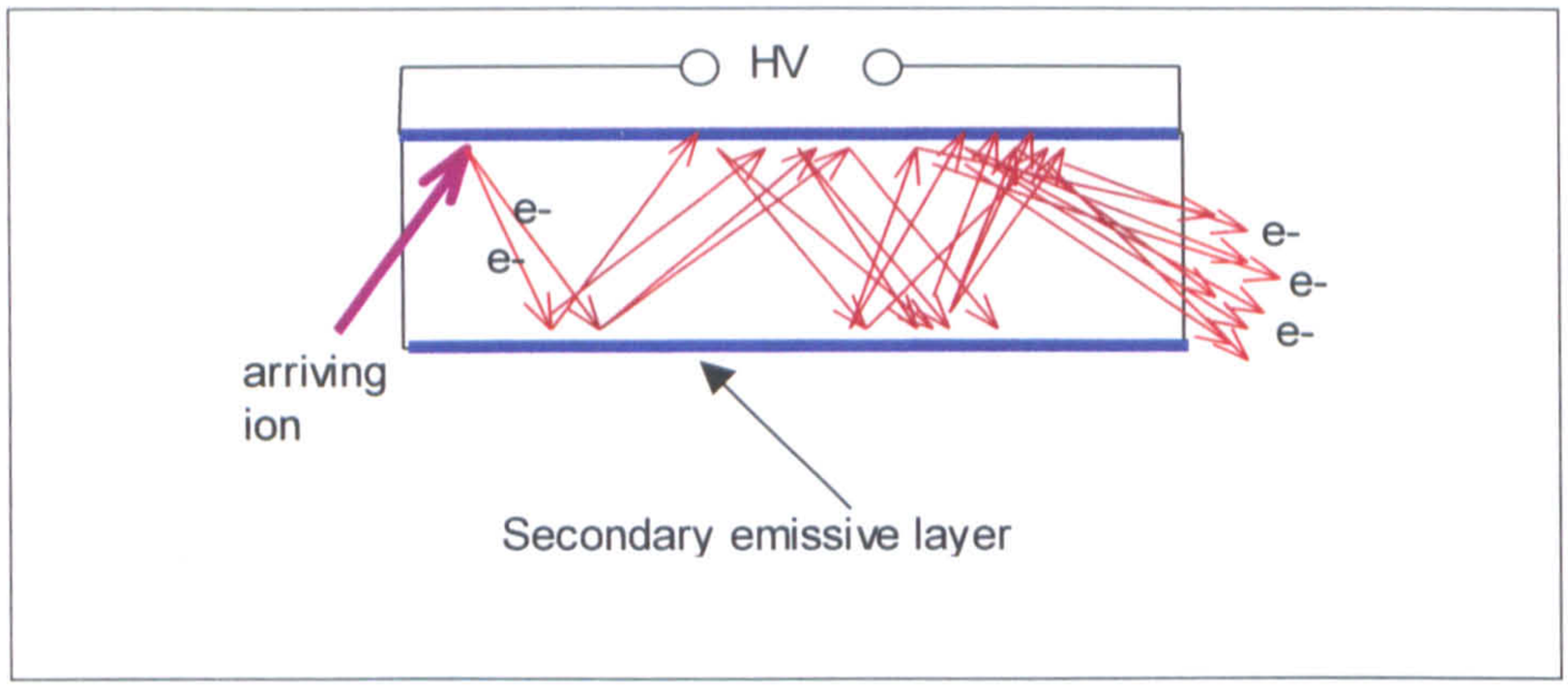

Figure 14: Working principle of a MCP

Other common detectors are faraday cups, which simply trap all ions from the ion beam in an analyser and record the current. This kind of detector is very robust, but not suitable for a pulsed source instrument where it must be able to record single ion hits, and not the intensity of an ion current.

The detector used for the MS-200 is a discrete dynode electron multiplier. In this detector type, the ion hits the coated cathode of the detector. Provided the impact speed of the ion is sufficient, this will release some electrons. Figure 15 shows that due to a difference of a few hundred volts between the different plates (dynodes) of the detector, those electrons are then accelerated towards the next dynode of the detector. When an electron hits the next dynode, it will release further multiple electrons. This effect cascades through the different dynodes of the detector until it produces a current that is sufficient in magnitude to be recorded by a pre-amplifier. The pre-amplifier converts the output pulses of the detector into an electrical signal, which is high enough to be processed.

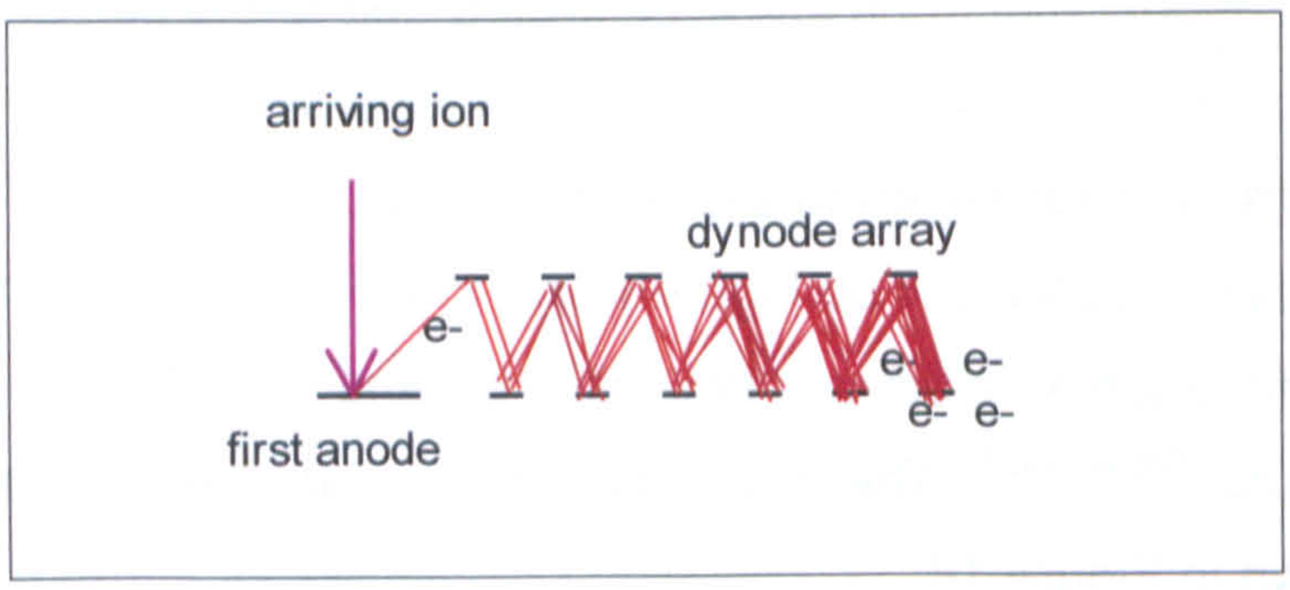

Figure 15: Schematic of electron multiplier detector (ETP)

The electron multiplying detector of the MS-200 has 20 dynodes with a typical gain of $1*10^8$ electrons produced per incoming ion (SGE 2002). Typical pulses produced by the detector of the MS-200 are between 10 and 200mV in height and have a width of about 5ns (SGE 2002). A typical output pulse of the detector was measured using a fast oscilloscope, and is shown in Figure 16.

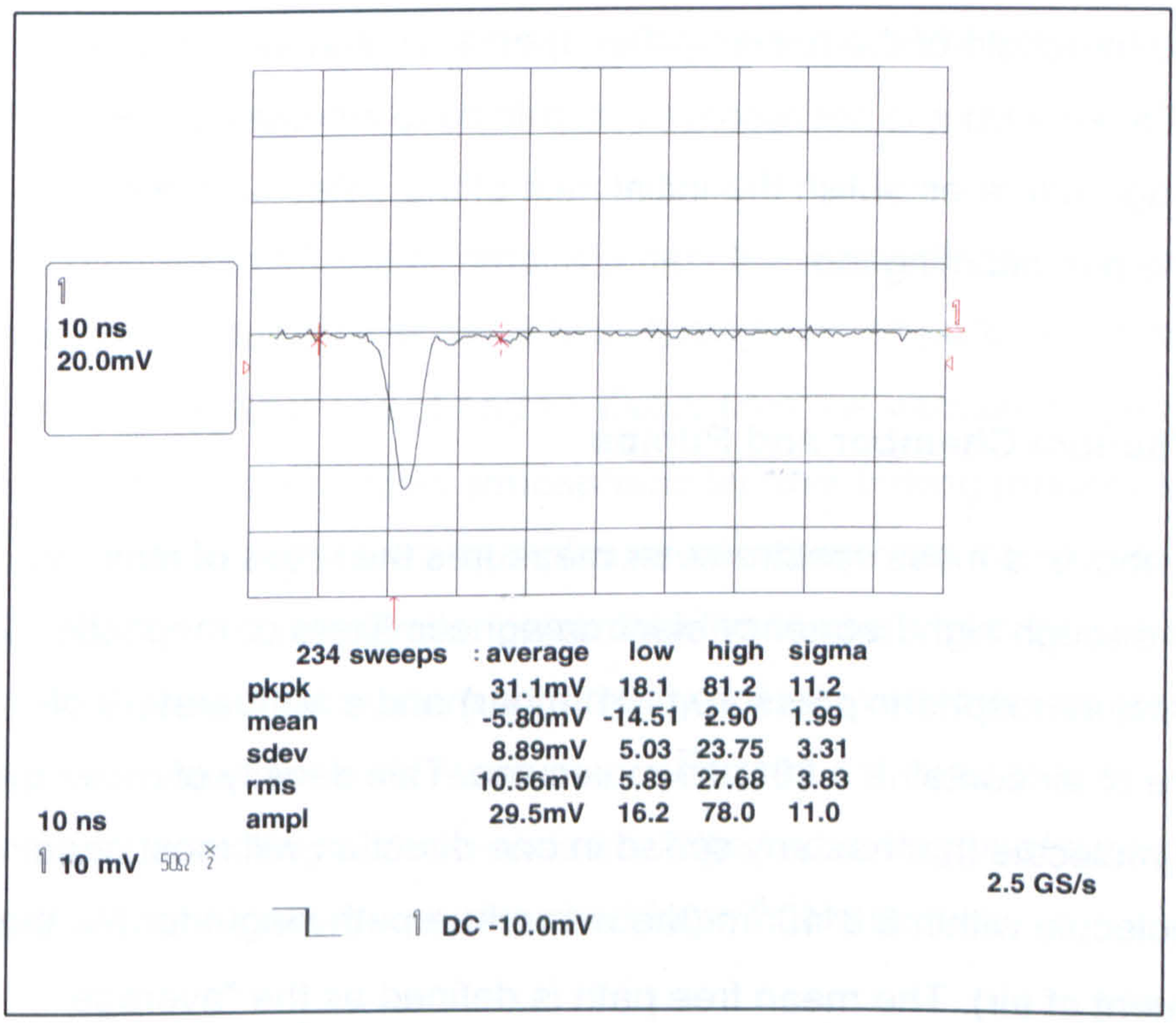

Figure 16 Output pulse of the detector

The advantage of an electron multiplier compared to a channel plate is the very short recovery time after a hit. After a detector is hit by an ion, it is temporarily "blinded" before it is ready to record the next arrival. Ions arriving within this blind time will not be recorded. Recovery time of the detector used is less than 30ns after a hit (SGE 2002).

A disadvantage of using an electron multiplier detector is that the arrival of two ions at the same time will only be recorded as one pulse. This, together with the recovery time causes loss of information. The limitations that this causes for the analysis will be discussed in Appendix 5 of this thesis.

For the electron multiplier to work a high voltage is needed between the different plates. The detector is supplied with a high voltage of –2.3kV. With use, the anode of the detector wears out, due to constant ion bombardment and contamination from cracked hydrocarbons and the output signal decreases (Cutter et al. 1994). The wear on the detector has to be carefully monitored, as this is one of the biggest influences in the change of sensitivity of the instrument. If a large proportion of the output peaks from the detector drop below the threshold of the pre-amplifier, then a significant proportion of the counts in the spectrum is not recorded. In this case increasing the excitation voltage will re-establish the initial gain of the detector of around $1*10^8$ electrons per incoming ion.

2.3. The Vacuum Chamber and Pumps

As described above, a mass spectrometer measures the mass of ions by passing them through high frequency electromagnetic filters or magnetic fields. At normal atmospheric pressure (1013mbar) and a temperature of 293K, one litre of air contains $2.88*10^{22}$ molecules. This density of molecules means that a molecule that has any speed in one direction will most certainly hit another molecule within $5.8*10^{-8}$m (the mean free path length for N_2, the major constituent of air). The mean free path is defined as the "average distance traversed by all the molecules between successive collisions with each other, or as the average of the distances traversed between successive collisions by the same molecule, in a given time" (Roth1990). As a result of this, mass spectrometers require vacuum where the density of air is lowered to a level at which the interference of the ions with the air molecules can be neglected. The principle set up of the mass analyser with the vacuum chamber and the vacuum pumps are shown in Figure 21.

The vacuum levels of the MS-200 are in the range of 10^{-7} to 10^{-9}mbar. At these pressures the mean free path of an ion is around 600m. The length of the flight path of an ion inside the MS-200 is approximately 50cm. Thus statistically, only one in 1200 ions from an accelerated ion parcel will not arrive at the detector because of collision with an air molecule. Of course due

to ion optics and focusing slots, a large proportion of the ions are actually likely to be filtered out before reaching the detector.

Achieving a vacuum at Ultra High Vacuum levels (UHV, below 10^{-7} mbar) is a quite challenging task. At these levels, leakage due to microscopic channels in the stainless steel crystal structure can cause problems (Corlett 2000). Organic materials from polymers will simply evaporate, due to a vapour pressure that is higher than the chamber pressure, and cause interference with the analysis.

Vacuum levels of 10^{-9}mbar require a high level cleanliness of internal parts of the vacuum system. To achieve this cleanliness, all parts are baked under vacuum at temperatures of 150°C. Every time the vacuum system of the spectrometer is exposed to atmospheric air, this baking procedure has to be repeated due to high levels of moisture adsorbed onto internal surfaces. To avoid this high maintenance, it was decided to use a permanently sealed vacuum system. This system is normally not allowed to reach pressures above 10^{-5}mbar, and as a result, the user does not need to spend too much care into maintaining a clean vacuum. Other advantages of a permanently sealed vacuum system are described later in this section.

The material chosen for the vacuum system is mainly stainless steel. The advantages of this material are easy availability, relatively low cost, well established manufacturing and processing, plus availability of reliable sealing techniques. The disadvantage is relatively high weight. Currently, the vacuum chamber plus the analyser weight around 4kg. Using aluminium could reduce this to approximately 2.5kg, but would add significantly to the cost of the system.

The material used for the ion optics assembly is macor, a vacuum compatible engineering ceramic, with excellent machining and electrical insulation properties. Other materials are oxygen-free copper and nickel for the cables, stainless steel for the electrodes and PTFE tubing for insulation purposes. The voltage feed throughs are made from nickel pins that are brazed into a glass disk, which is brazed onto the stainless steel. The system has three

flanges, one to fit the analyser assembly into the chamber, another to fit the detector, and the last one is for the gas inlet system.

The pumping requirements of the vacuum chamber are determined by the internal surface area of the chamber (because of the out-gassing) and the volume of sample required to achieve sufficient sensitivity for an application. For a relatively small chamber and a very sensitive mass analyser, the pumping requirement for the vacuum system of the MS-200 is about 2mbar*litre/second.

A very common pumping arrangement for a vacuum system is a turbo molecular pump together with a suitable backup pump. A turbo pump consists of a series of vanes. Those vanes spin at speeds of up to 80,000rpm, which pump the gases out of the vacuum system. Considerable effort has been made by manufacturers to miniaturise these pumps over the last few years. Small pumps with pumping speeds of a few mbar*litre/second are now available (Alcatel 2001).

The backup pump is required to start the turbo pump at around 10^{-3}mbar, as the turbo pump will not work at a vacuum of less than 10^{-3}mbar. With a suitable backup pump, a turbo pump has the capability to pump a system to a pressure of 10^{-10}mbar.

The major disadvantages of a turbo pump are the requirement for a backing pump to provide an initial pressure step from atmosphere to 10^{-3}mbar, and the vibration and shock sensitivity due to the fast spinning vanes. Power requirements are in the 50 to 100W region for the turbo pump and another 100 to 200W for the backup pump. These points set considerable constraints for the use of turbo pumps for portable vacuum equipment.

The MS-200 uses an ion pump to maintain the vacuum required for the mass analyser. An ion pump removes gas molecules by several physical and chemical processes. Molecules are ionised in a strong electromagnetic field and then pumped away through different processes described in Table 2.

Table 2: Different Pumping Processes of an Ion Pump (Barrington 1963)

• Gaseous ions collide with internal surfaces and adhere to them
• Gaseous ions dislodge and vaporise atoms of the electrodes on impact, and the metallic vapour traps some of the gas molecules when it condenses on the walls (called sputtering).
• Ions combine chemically with the walls and electrodes, or with sputtered electrode material

The pumping speed of this kind of pump is strongly dependent on the gas being pumped. Ion pumps have very good pumping speeds for organic components and are relatively good for nitrogen. On the other hand, it is known that noble gases are not pumped very efficiently [PHI 1999]. Relative pumping speeds for different gas species in an ion pump are shown in Table 3. To compensate to a certain extent for the difference in pumping speed for different chemicals, the pump is connected to the main vacuum system by means of a tube with a diameter that limits the conductance to about 2 litre/second. Therefore, despite the fact that the nominal pumping speed of the pump used is about 4 litres/second, the actual pumping speed is conductance limited by the tube, and therefore the difference in pumping speed for different components is neutralised up to a certain extent.

Table 3: Pumping speeds of an Ion pump dependent on the species (PHI 1999)

Gas Species	Pumping Speed (Percent of Rated Speed)
Hydrogen	160%
Carbon Dioxide	100%
Nitrogen	85%
Oxygen	70%
Water Vapour	100%
Helium	15%
Argon	20%
Light Hydrocarbons	90%

The lifetime of an ion pump is about 35,000 hours at pressures of 10^{-6}mbar (Varian 1993). This is equal to around 4 years. The MS-200 operates at pressures of less than 10^{-7}mbar and in stand-by mode pressures are typically less than 10^{-9}mbar. Therefore the lifetime of the ion pump in the MS-200 will be greater than 4 years.

As a result of using an ion pump (and cleanliness, as mentioned above) for the vacuum system of the MS-200, it was decided to never allow the vacuum chamber to come up to near atmospheric pressure. If this occurs the instrument has to be connected to a stationary vacuum system and pumped to 10^{-5}mbar, before the ion pump can maintain the vacuum. For this purpose the system is fitted with a 0.5 inch diameter copper tube through which the pumping takes place. After the pumping is completed, this tube is pinched off with a hydraulic ram. The cold weld of the copper creates a cheap and lightweight UHV vacuum seal at the pinch. If, for any reason the chamber needs venting to atmospheric pressure, this pinch off tube needs to be replaced and reconnection to the pumping system is required.

A major disadvantage of an ion pump is that the pressure in the vacuum chamber has to be in a region of 10^{-5}mbar before the pump is able to start pumping. This means an alternative mechanical pump is required to reach a pressure at which the ion pump will start. Ion pumps, however, have no moving parts and are, therefore, very rugged which makes them ideal for portable instrumentation.

An additional feature that makes an ion pump ideal for light weight and low cost vacuum system is the fact that the current drawn by the ion pump is proportional to the pressure in the vacuum system. Monitoring the ion pump current therefore allows monitoring of the pressure in the system, saving the cost and weight of a pressure sensor. The calibration curve for the ion pump used is shown in Figure 17 (VSS 1995).

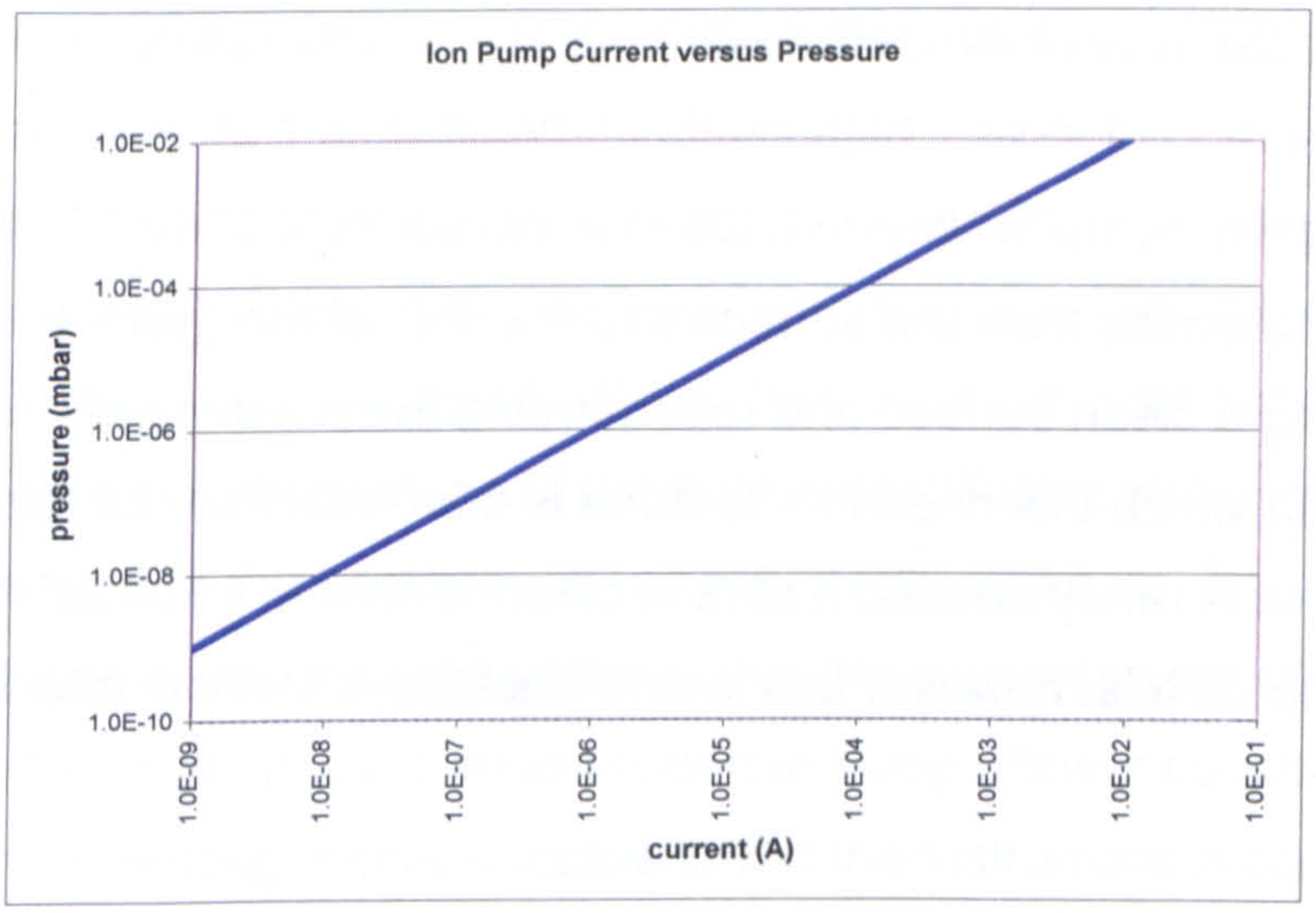

Figure 17: Ion pump current versus pressure of the MS-200 ion pump

If the instrument is deployed in the field and the battery has been used up, the instrument might be without power for several days or even weeks. In this case the ion pump will switch off. To have at least a limited amount of emergency pumping, a getter pump is included in the system. The getter pump will keep the pressure of the vacuum chamber at a level where the ion pump is able to start pumping once it is powered up again.

Getter pumps are very well understood and extensively used in applications like TV tubes, electronic valves and other commercial vacuum equipment. The getter pump used is made from a very fine powder made from 84% zinc and 16% aluminium (SAES 2000). This powder is coated onto a metal strip that is folded up and wrapped around a heater filament, as shown in Figure 18. Getter pumps are very effective at pumping all gases except for noble gases, which they will not pump at all (SAES 2000, SAES 2003).

Getter pumps can be operated either heated or at room temperature (cold pumping mode). In the cold pumping mode the getter pump works by the trapping of gas molecules onto the surface of the getter material. At elevated temperatures (over around 400°C) the pumping includes diffusion of the trapped chemicals into the getter material, increasing the pumping capacity. At room temperature this diffusion of trapped molecules from the surface into the bulk materials is insignificant (SAES 2003).

The pumping capacity of the getter pump, in the cold pumping mode, can be limited if it is exposed to very high levels of moisture or hydrocarbons. In this case, heating the pump for ten minutes to a temperature of 400°C helps the diffusion of molecules from the surface into the bulk of the getter material thus producing a clean surface and regenerating the pumping efficiency. The frequency with which this needs to be done is dependent on the use of the instrument, but is rarely needed if care is taken. There is a special function in the MS-200 to do this, however this is only possible when it is attached to mains power.

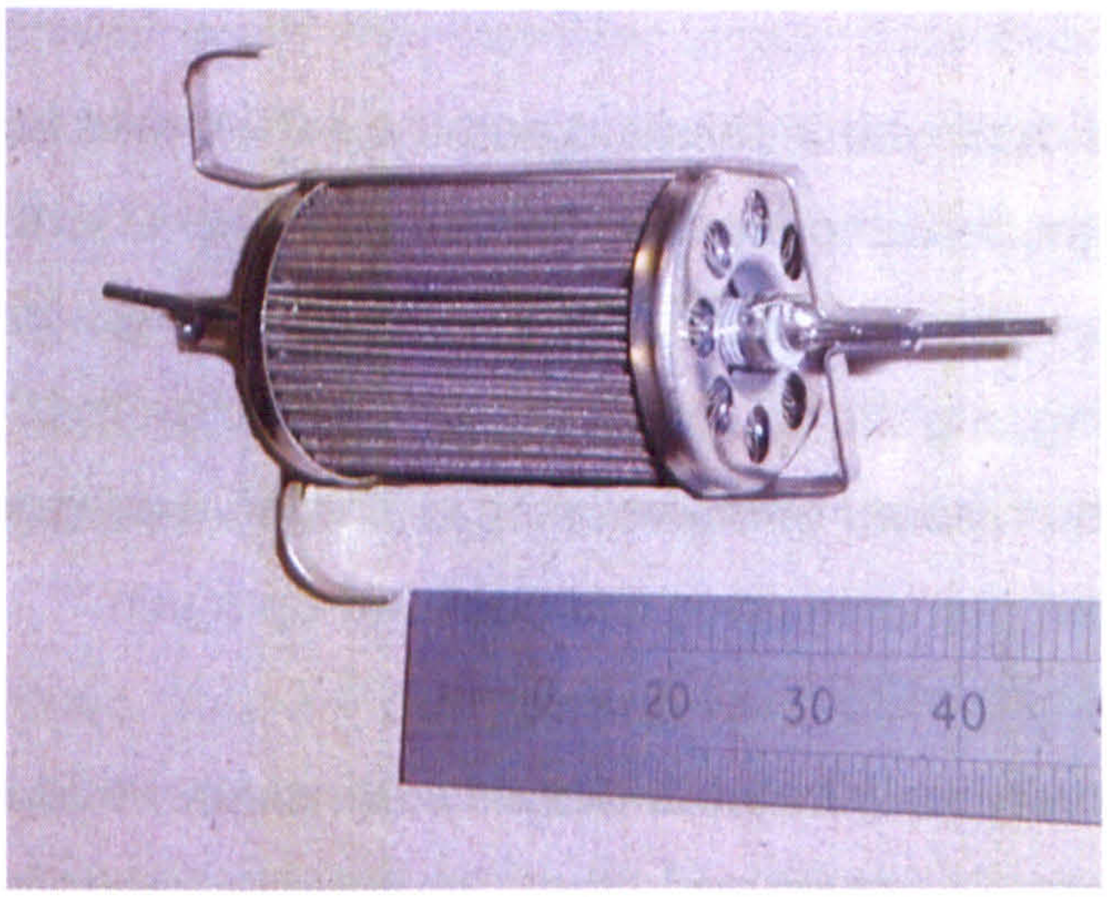

Figure 18: The SAES Getter Pump used In the MS-200

Operating the getter pump at room temperature obviously does have the advantage of powerless pumping. However, the pumping speed of the getter pump at room temperature is highly limited compared to pumping speeds at the standard operating temperature of 400°C. This should not be a problem, as the intended use of the getter pump is mainly for backup pumping during power fail situations, where a low pumping speed is sufficient. On the other side, the getter pump is always active and cannot be switched off. The slow pumping during cold operation causes the getter pump to act as a reservoir, collecting hydrocarbons from the vacuum system, which remain on the surface of the getter and can take a long time to diffuse into the bulk, as described above. During this time it is possible for these components to come off the surface again and contribute to the background of the vacuum system and, therefore, to the background of the mass spectra collected.

Under normal working conditions this is not too big a problem. However, the getter pump releasing components can cause problems when a high concentration exposure is followed by a measurement of very low concentrations. In this case the possible high background limits the detection limit of the instrument considerably. Given time, even at room temperatures, the hydrocarbons on the surface of the pump will diffuse into the material of the getter pump and the background will eventually clean up. To speed up the diffusion and clean up of the getter pump, the pump can be indirectly heated by a filament, which is fitted inside the pump. Power conservation means that this heating is only possible whilst the instrument is connected to a power supply.

2.4. The Gas Inlet System

The inlet system provides the pressure step from atmospheric pressure (normally around 1013mbar) to the vacuum of the analyser chamber at a working pressure of $2*10^{-7}$mbar. To achieve this, the inlet system has to restrict the flow of gases to such extent that the vacuum pumps of the analyser can sustain the required vacuum levels. This flow restriction can be achieved by different means. One is the restriction using a pinhole, allowing very little sample to enter the UHV region, but without discriminating for different components of the sample. A similar restriction can be achieved by a capillary, which normally has a larger diameter hole, but is longer, and therefore achieves similar restrictions as a pinhole. Both the pin-hole and the capillary allow all gases to enter the vacuum system at a very similar rate and, therefore, are suitable for indiscriminate analysis of components in a mass spectrometer.

A commonly used inlet system is a thin polymer membrane. The gaseous sample has to permeate through the membrane material in order to reach the high vacuum of the analyser chamber. Permeation can be described by a system whereby the analyte dissolves into the membrane material, followed by its diffusion through the membrane and then evaporation from the surface of the polymer membrane into the vacuum on the other side. The driving force behind this permeation process is a concentration gradient between the

high-pressure side and the low-pressure side of the membrane. Various publications discuss the permeation process through a polymer membrane (Sok, Berentsen 1992, Baltussen et al 1999, Dhingra 1998, Bhattacharya, Hwang 1997, Chandak et al 1998).

Permeation is dependent on the physical interaction between the membrane material and the analyte, and can be described by Equation 2 (LaPack et al. 1994). Some examples of permeation rates for different chemicals through a polydimethylsiloxane (PDMS) membrane consisting of 69wt% PDMS and 31wt% fumed silica, relative to nitrogen are given in Table 4.

$$P_i = D_i * S_i$$

P_i= Permeation of a component i through PDMS [$(cm^3*cm)/(s*cm^2*cmHg)$]
D_i= Diffusivity of a component i through PDMS [cm^2/s]
S_i= Solubility of a component i through PDMS [$(cm^3(STP))/(cm^3(membrane)*cmHg)$]

Equation 2: Permeation through a membrane (LaPack et al. 1994)

Table 4: Experimental Permeation Figures, relative to nitrogen, for a PDMS membrane at 25°C (LaPack et al. 1994)

Substance	Permeation relative to Nitrogen		Substance	Permeation relative to Nitrogen
Nitrogen	1		Chloromethane	69
Oxygen	1.9		Dichloromethane	350
Argon	1.9		Chloroform	430
Carbon Dioxide	12		Carbon Tetrachloride	430
Methane	4.6		Chloroethylene	57
Ethane	12		1,1,-Dichloroethylene	290
Propane	29		Trichloroethylen	640
Butane	36		Tetrachloroethylen	1600
Pentane	250		Bromomethane	68
Hexane	310		Dibromomethane	570
Heptane	790		Bromoform	2400
Benzene	460		Methanol	190
Toluene	960		Ethanol	390
Ethylbenzene	1500		1-propanol	460
			1-butanol	500

The membrane material chosen for the MS-200 is polydimethylsiloxane (PDMS). PDMS membrane material has the best over all permeation properties for organic hydrocarbons [Jonson 2000), (Pinnau 1994]. The membrane material chosen is "Sil-Tec", obtained from Technical Products, for the 0.002 inch and 0.005 inch thick material used for the outer and inner membranes of the inlet system.

Other possible membrane materials include polyethylene (PE), poly-tetraflouroethylene (PTFE), and variations of these materials with specific chemical properties designed to improve the permeation characteristics for a specific group of components [Pinnau 1994].

From Table 4 it can be seen that the permeation process varies with the different components that might be present in the sample. This effect is used to enrich the sample compared to nitrogen before entering the ultra high vacuum side (UHV) of the analyser. In the MS-200 this enrichment process is performed twice. A first membrane with a pressure step of one millibar is used for the initial enrichment stage. From the intermediate vacuum space there is a second membrane to the UHV of the vacuum chamber. This secondary enrichment has the same factor as the first membrane. From Table 4 it can be seen, for example, that benzene permeates through PDMS approximately 460 times more than nitrogen. This means that the ratio of benzene to nitrogen in the intermediate vacuum space is a factor of 460 higher than in the atmosphere. The same enrichment happens on the second membrane. As a result the over all enrichment factor for benzene is 211,600. The enrichment with each membrane varies widely for different compounds. This effect is quadratic due to the double membrane, and therefore the sensitivity of the MS-200 to a specific component is very strongly dependent on the compound to be analysed.

Figure 19 shows the principle of enrichment due to selective permeation. The background air is symbolised by the blue dots, the analyte by the red dots. At atmospheric pressure the majority of the sample is background with some analyte of interest in it. Taking a theoretical compound X with an enrichment factor of 100 and, assume a concentration of 100ppb in the atmosphere. The

first pressure step reduces the over all amount of gas molecules by a factor of around 1,000 (1mbar instead of 1,000mbar atmospheric pressure). The selective membrane however allows compound X to pass through at a rate of 100 times more than the nitrogen background, giving an analyte concentration of 10ppm. The second pressure step reduces the over all gas molecules by a factor of 10^8, but again increases the compound X by 100, resulting in an analyte concentration of 1,000ppm for the equilibrium state in the analyser chamber. As a result, while in the atmosphere there are only 10^{-7} mole of analyte in one mole of background air (nitrogen), in the analyser there are 10^{-3} mole of analyte within one mole of background.

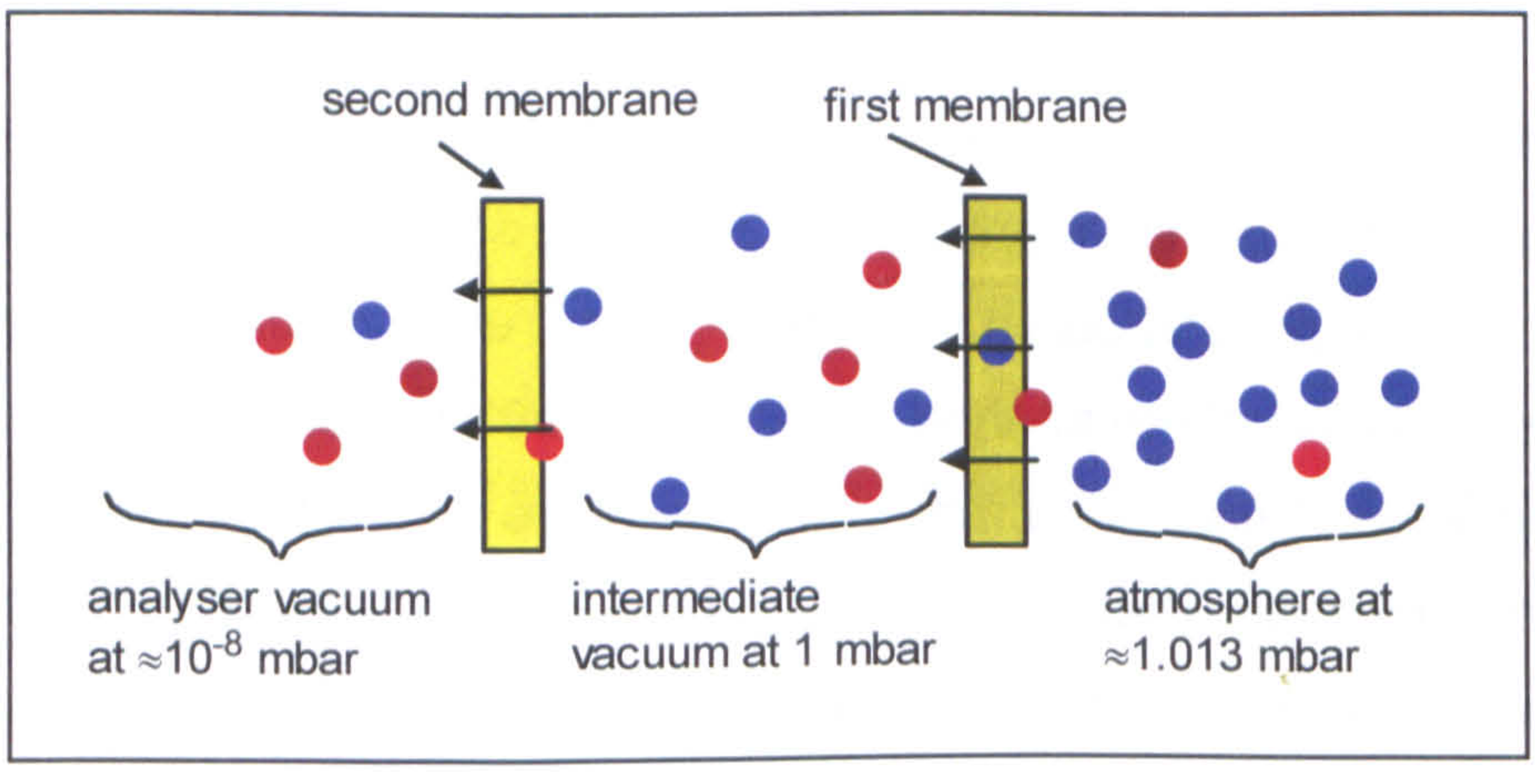

Figure 19: Principle of Permeation through the Double Membrane Inlet

In the MS-200, the intermediate vacuum step of around 1mbar is produced by means of a peristaltic pump, described later in this section. The second vacuum step employs the ion and getter pump to achieve UHV as described in section 2.3.

Permeation is a highly temperature dependent process (LaPack et al. 1994). Therefore, the inlet system with the two membranes is heated to a temperature of around 50°C with a measured precision of ± 0.1°C. The sample is led through a heated stainless steel tube in order to heat it to the same temperature as the inlet and, therefore, avoiding cooling of the outer membrane due to a cold sample stream.

The vacuum chamber including internal parts, the pumps and the inlet system is shown in Figure 20. Note that the chamber in this picture is wrapped in insulating materials to allow baking of the vacuum system if background levels are too high.

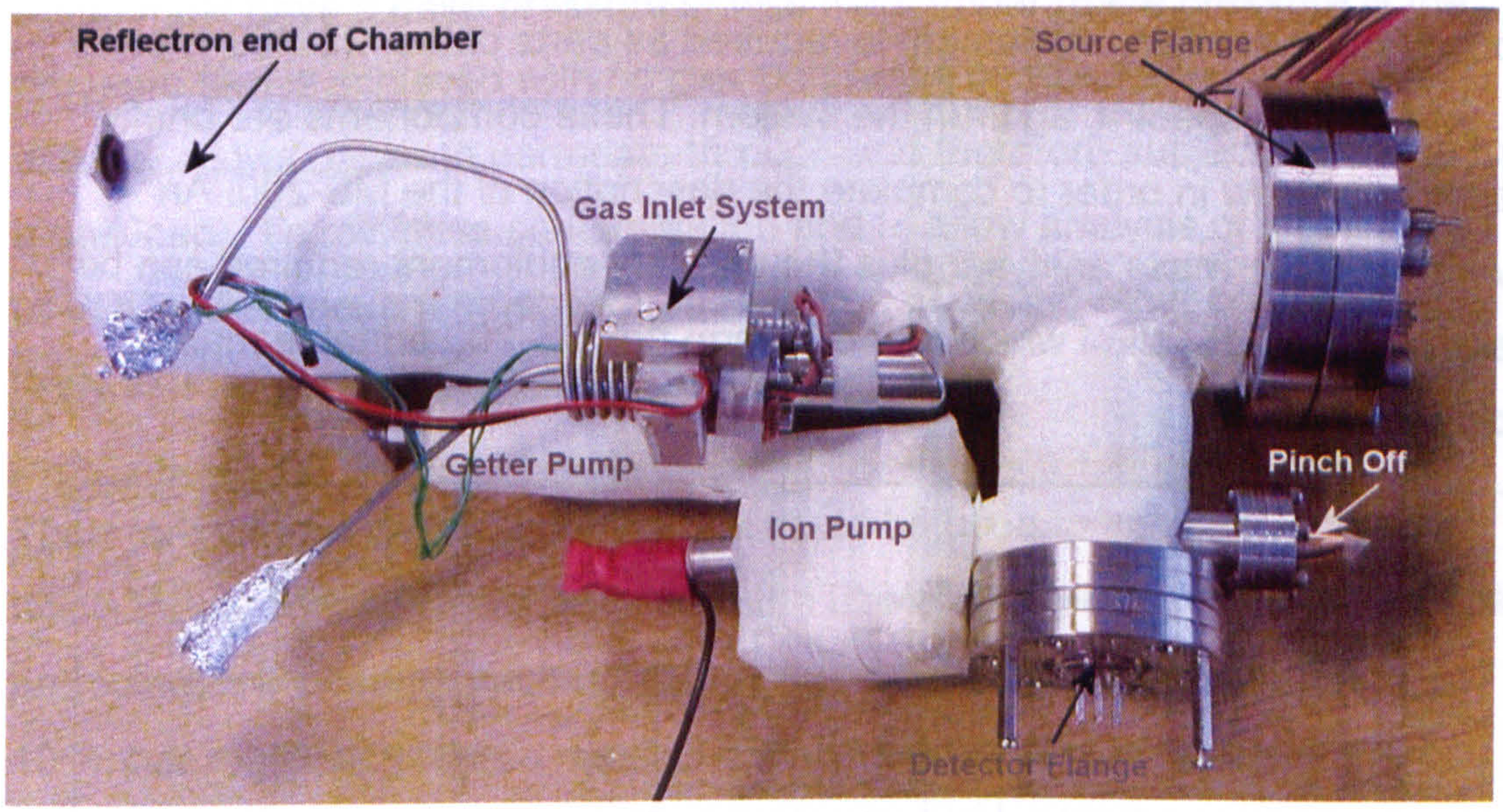

Figure 20: The analyser vacuum chamber of the MS-200.

2.5. Additional Equipment

In addition to the major components of a mass spectrometer mentioned above, some ancillary equipment is required as parts of the MS-200 in order to obtain mass spectra, and run the system. These components are briefly described below in order to complete the description of the MS-200. An overview of the mass analyser plus the ancillary equipment required can be seen in Figure 21, all of which together form the MS-200 portable mass spectrometer.

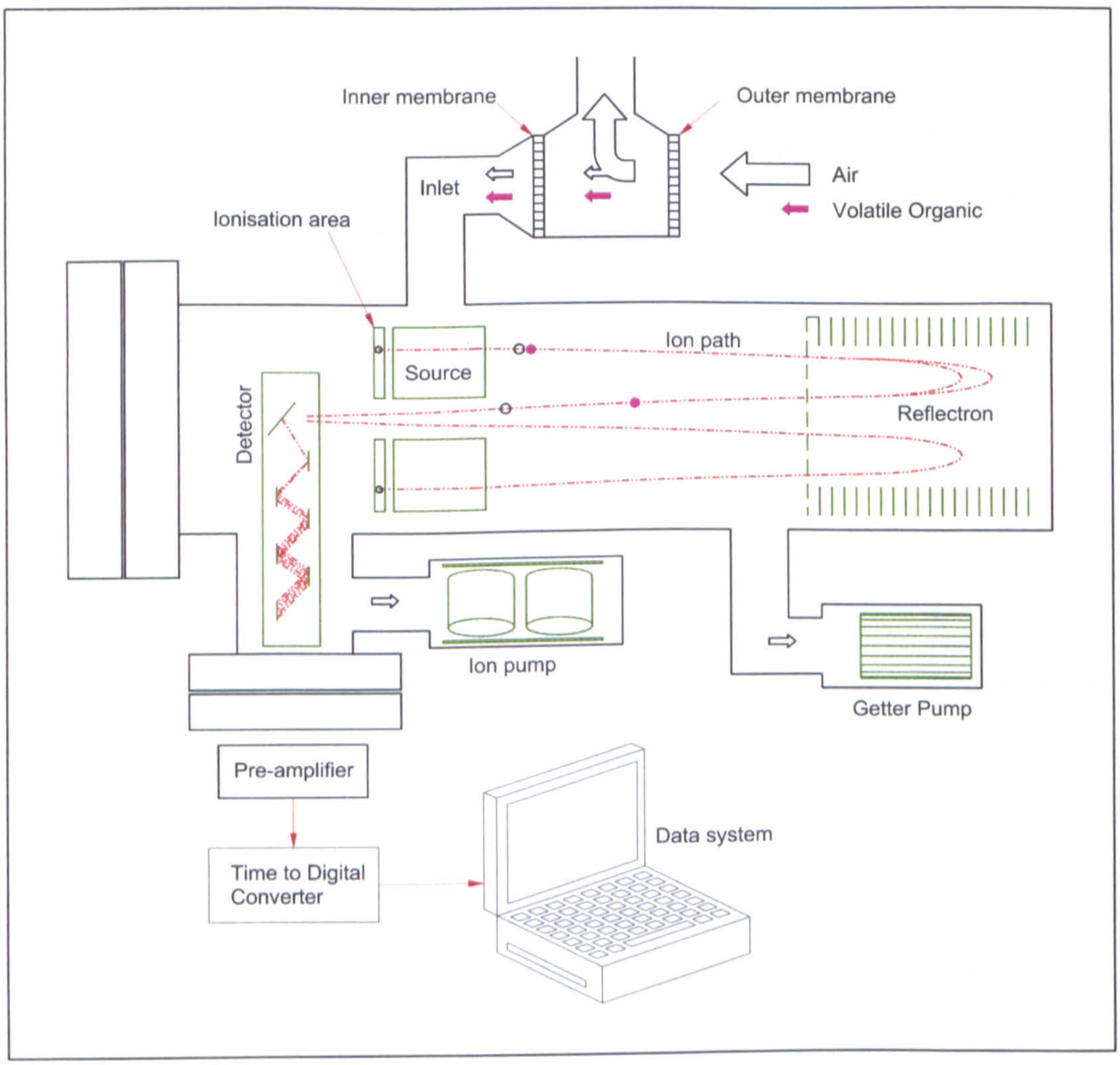

Figure 21: The mass analyser plus ancillary equipment

2.5.1. Intermediate Vacuum Pump

The double membrane concentrator inlet (described in section 2.4) of the MS-200 requires a vacuum of approximately 2mbar between the two membranes in order to work, which means that the intermediate vacuum pump must have a base pressure of less than 1mbar (base pressure is the pressure that is achieved with no gas load being pumped, the membrane actually allows gases to permeate through and therefore subject the pump to a gas load). To minimise contamination and to allow analysis of small traces of VOCs, this vacuum must be produced free of oil and other contamination, likely to interfere with the sample analysis.

There are various types of pumps that could be used to achieve vacuum levels below 1mbar. One possibility is the use of rotary pumps. These pumps are commonly used as back-up pumps to produce a pressure of around 10^{-3}mbar required for turbo molecular pumps to be able to start and then pump to pressures of below 10^{-10}mbar (as discussed in section 2.3). The disadvantage of rotary pumps is that the vacuum might be contaminated from oil that is used in the compression stage of the pump. However, when using a rotary pump together with a turbo molecular pump to achieve ultra high vacuum levels, oil contamination is of little concern as any oil will be on the low vacuum side of the system and is not able to pass the compression stages of the turbo pump and into the high vacuum side of the system. The major drawback of a rotary pump is that they are not available for battery operation and are not within the size and weight requirements needed for a portable system.

For these reasons it was decided to design a peristaltic pump that is able to pump a vacuum down to a base pressure of below 1mbar using the available battery power. A peristaltic pump consists of a flexible tube and two or more rollers, compressing the tube at various places, therefore trapping volumes of air in the pockets between the rollers. The rollers move along the tube, shifting the trapped air in direction of the outlet of the pump. As shown in Figure 22, the pump material has to be chosen to be flexible enough for the rollers to be able to compress the tube and form a seal. However, the tube

also has to be strong enough in order to expand against the pressure difference of one atmosphere. The pump used for the MS-200 has a tube coiled twice around a rotor with two rollers, resulting in air parcels being moved along the tube and, therefore, creating continuous pumping at a pumping speed of $0.002^{litre/sec}$.

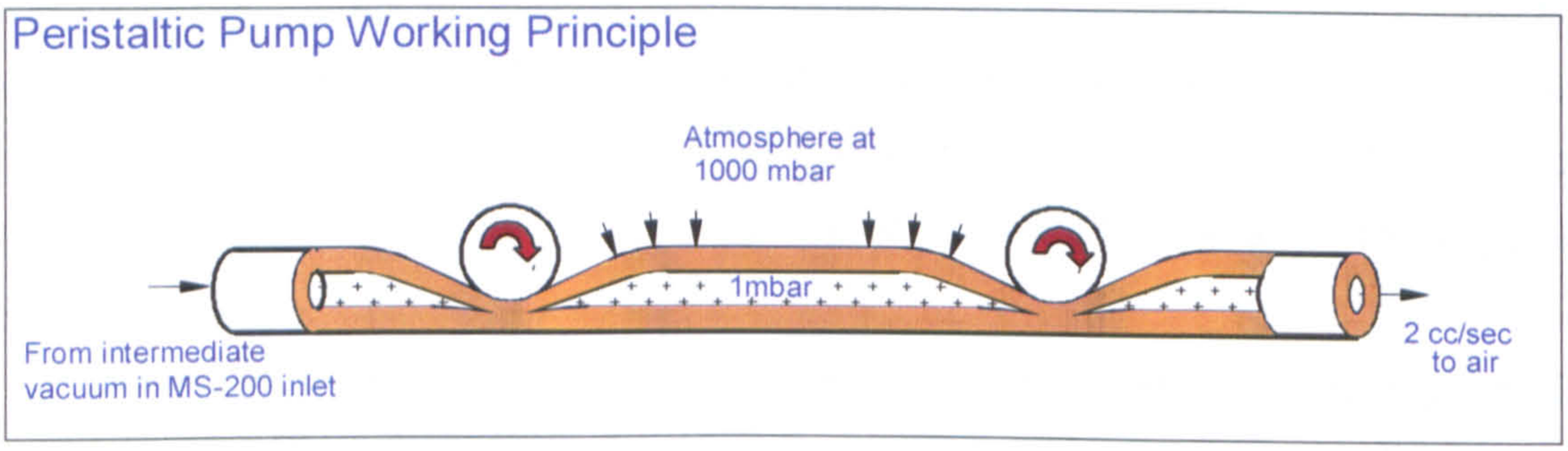

Figure 22: Working principle of a peristaltic pump

2.5.2. Pre-amplifier

The pre-amplifier converts the output pulse of the electron multiplier detector, (explained in section 2.2.3) into electrical impulses that are high enough to be registered by the counting electronics. It converts the typical output pulse of about 8mV to 100mV and a pulse width of 5ns shown in Figure 16 into very short pulses of 0.7V in height. In order to avoid noise pick-up, the pre-amplifier has a threshold setting of 8mV and therefore any signal below 8mV will not be amplified. To increase speed and to reduce electrical noise, the pre-amplifier sits directly on the detector flange of the analyser chamber.

2.5.3. Voltage Supplies and Controls

In order for the mass analyser to work, it requires a series of voltages. Firstly, there is a 12V to 3000V DC/DC converter that provides the high voltage for the ion pump. The current drawn by this converter, and therefore the ion pump, is metered and displayed on the front panel of the MS-200. As described in Section 2.3, the current drawn by the ion pump allows a direct reading of the pressure inside the vacuum system of the mass analyser.

Secondly, another 12V to 3000V DC/DC converter, supplies the high voltage for the electron multiplier detector. This high voltage supply also supplies a resistor chain, which at its different points supplies the ion optics with the required voltage. These voltages are (dependent on the individual tuning of the instrument) between approximately -80V for the back plate of the reflectron down to -1,950 V for the field free region (or drift tube), with some intermediate voltages for the ion optics used to accelerate and focus the ion beam. The electrical fields within the ion optics of the mass analyser are shown in Figure 13.

A third DC/DC converter supplies the -70V at which the filament is floating in respect to ground (in order to produce electrons of 70eV energy, described in section 2.2.1) and the approximately -90V to -110V for the repellor.

2.5.4. Extract Pulser

The extract pulser produces rectangular electrical pulses from 0V down to -400V each, with a pulse width of 3µs, in order to extract positively charged ions from the ionisation source. These pulses are supplied to the extract plate of the ion source of the MS-200. While the extract plate is at a voltage of 0V, the ions created in the ion source are exposed to an almost field free region, and are therefore stored within the ion source. At the moment the extract plate is switched to –400V, all positive ions are accelerated towards the extract plate through a fine mesh onto the next part of the spectrometer. There they are attracted by the next part of the ion optics, at a potential of –1,170V, which accelerates the ions away from the source region and through the mass analyser towards the detector. One such pulse is produced by the pulser every 20µs and therefore during a standard 10 seconds acquisition time about 500,000 extract cycles are performed.

2.5.5. Time to Digital Converter

The time to digital converter (TDC) is the link between the mass spectrometer hardware and the laptop computer. When performing a measurement, the operating software on the laptop sends a start signal to the TDC. The TDC then transmits a trigger signal to the pulser in order to release all the ions from the source and send them through the mass analyser. It then waits for the signal from the pre-amplifier to record the time between the release signal and each hit. This procedure is repeated at a frequency of 50kHz, and these measurements are stored as a histogram, which slowly builds up over the number of acceleration cycles within a measurement. The histogram splits the data into time slots of around 2ns. This information is then downloaded to the operating software on the laptop computer for further processing and data analysis. In the latest version of the instrument, the TDC also has an electronic interface that allows all of the spectrometer voltages and the inlet valve, as well as the peristaltic pump and the sample pump, to be controlled from the software of the laptop computer.

2.6. Data Acquisition

In order for the instrument to be able to perform the measurement of a sample, the instrument has to be switched on, the intermediate vacuum pressure has to be at 1mbar, and the inlet valve has to be opened.

The sample then continuously permeates through the first membrane into the intermediate vacuum space. From the intermediate vacuum space the sample permeates through the second membrane into the UHV of the analyser chamber. The molecules in the analyser chamber are continuously pumped away by the ion pump and the getter pump. An equilibrium representative of the sample will establish itself in the vacuum chamber, based on the selective permeation and the continuous pumping of molecules. This results in the composition of the molecules in the vacuum being directly representative of the composition of the sample supplied to the system (including the enrichment due to the membrane, described in section 2.4).

As described in section 2.2.1, the filament within the ionisation source of the analyser continuously emits electrons and ionises molecules within the source region. These ions, like the remainder of the analyser vacuum, are representative of the sample being supplied to the inlet of the MS-200.

During a measurement, the extract plate of the ion source (as shown in Figure 13) is switched from ground potential to –400V for the duration of 3µs. During this time all positive ionised molecules are accelerated out of the source towards the ion optics. All negative ions are accelerated towards the back plate of the source and are neutralised when they hit the back-plate of the source. The extracted positive ions are further accelerated through the ion optics, and are separated due to their mass. As described in section 2.5.5, the arrival times of the ions at the detector are recorded by the TDC and transformed into a mass spectrum by the software of the laptop.

In order for the ions arriving at the detector to be representative of the composition of ions in the source, multiple acceleration cycles are performed in each measurement in order to increase the dynamic range.

For example, if there was only one cycle the resulting spectrum would not be representative of the actual make up of ions in the ion source for the following reasons:

- Two hits of the detector at the same time will be recorded as only one arrival of an ion.
- An ion arriving at the detector during the blind time of the detector (section 2.2.3) would be missed out in the spectrum.
- An ion present in a very low concentration might be filtered out in the ion optics due to inefficiencies of the ion optics, or due to the ion having an unfortunate start position and start energy.

In addition, performing only one analysis cycle the instrument would have no dynamic range. Dynamic range is the difference between the smallest measurable peak and the largest measurable peak in a spectrum, and is required to display low as well as high concentrations. Having an analysis

length of only one cycle would mean that every mass could be either one or zero, resulting in a dynamic range of 1, and therefore not allow quantitative analysis.

For the above reasons, an analysis has to consist of multiple cycles to statistically compensate for the loss of information. A typical analysis run has a duration of 10 seconds during which approximately 500,000 analysis cycles are performed. A 10 seconds analysis (acquisition time) provides sufficient dynamic range in order to distinguish a peak with an area of around 50 counts from the background. The largest peaks in the spectrum will have a peak area of 500,000 counts. This results in a dynamic range of 10,000 for a 10 seconds acquisition.

When performing a sufficient number of cycles in order to have reasonable statistics, the height of a mass peak is directly proportional to the concentration of the chemical in the sample that has permeated into the vacuum system. This gives the system a linear response up to an upper limit of analyte concentration. Beyond the upper limit the height of the peak statistically no longer represents the concentration of the compound in the vacuum system - the system is saturated. When the linearity threshold is reached, there are too many ions reaching the detector, and statistically, there is a very large chance that during almost every cycle, multiple ions of this compound will arrive, either at the same time or within the blind spot of the detector, and are therefore not detected. This results in a loss of the quantitative information and the linearity of response. The linearity no longer can be assumed when the counts in a mass peak reaches about 2/3 of the number of cycles in the acquisition. The limit of linearity can be calculated by a shift in the relative abundance of a major mass peak in the spectrum compared to a minor mass peak.

During an acquisition, a snap shot of the molecular composition of the vacuum in the analyser chamber is taken. The vacuum in the analyser chamber is not a perfect representation of the sample (as assumed earlier). This is due to out-gassing of the chamber walls, and contamination from other internal components. This means that even with a sample of clean air

(or pure nitrogen) to the analyser there will be mass peaks of various components within the spectrum. The recorded spectrum from an analysis of a sample will, therefore, be the superposition of the sample supplied to the MS-200 and the components (contamination, residual gases) from within the analyser chamber.

In order to remove the interaction of the residual gases with the measurement of the sample, an analysis cycle should consist of the analysis of a clean air background, followed by the analysis of the sample. The clean air background should contain only the standard air peaks plus the residual gas peaks. The sample measurements should contain the standard air peaks, the residual gas peaks plus the sample peaks. As result of these two measurements, the software on the laptop then is able to subtract the background measurement from the measurement, resulting in a spectrum for the sample only.

2.7. Data Analysis

As described in section 2.5.5, the TDC stores a histogram of arrival times in bins of a bin width of 2ns. After an analysis cycle is finished, this information is sent to the lap-top computer for further processing. The initial information displays ion arrival intensity over arrival time and, therefore, is called the time spectrum (Figure 23). From this time spectrum the data processing software is able to calculate the ion intensity over the mass to charge ratio of the ions using Equation 1 (section 2.2.2). This plot is the mass spectrum, or sometimes called the raw mass spectrum of the analysis (see Figure 24) and is the basis for further data manipulation. The parameters t_0 and c_b in Equation 1 are calculated when performing a mass calibration during which the operator has to identify two mass peaks.

For further processing of the data, the raw mass spectrum is integrated by the operating software to calculate the area underneath each of the mass peaks. The resulting spectrum is displayed using bars with a height representing the area of the integrated peak. These bars are displayed for

each peak and are centred on integer mass numbers. This way of displaying a spectrum is called a “Stickplot” (shown in Figure 25).

Assuming a sample of a background has been taken, the software is able to calculate a background subtracted stickplot from the data. Like the stickplot, the areas of the peaks are displayed by bars where the height represent the area and hence the concentration of a particular chemical. The difference to the stickplot file is that this time the area of the background peak has been removed from the peak. This file is called the “Background Subtracted Stickplot”. The background subtracted stickplot is the basis for the software in order to determine what components are present, and at what concentration. The different ways this data can be assessed are described in the following section.

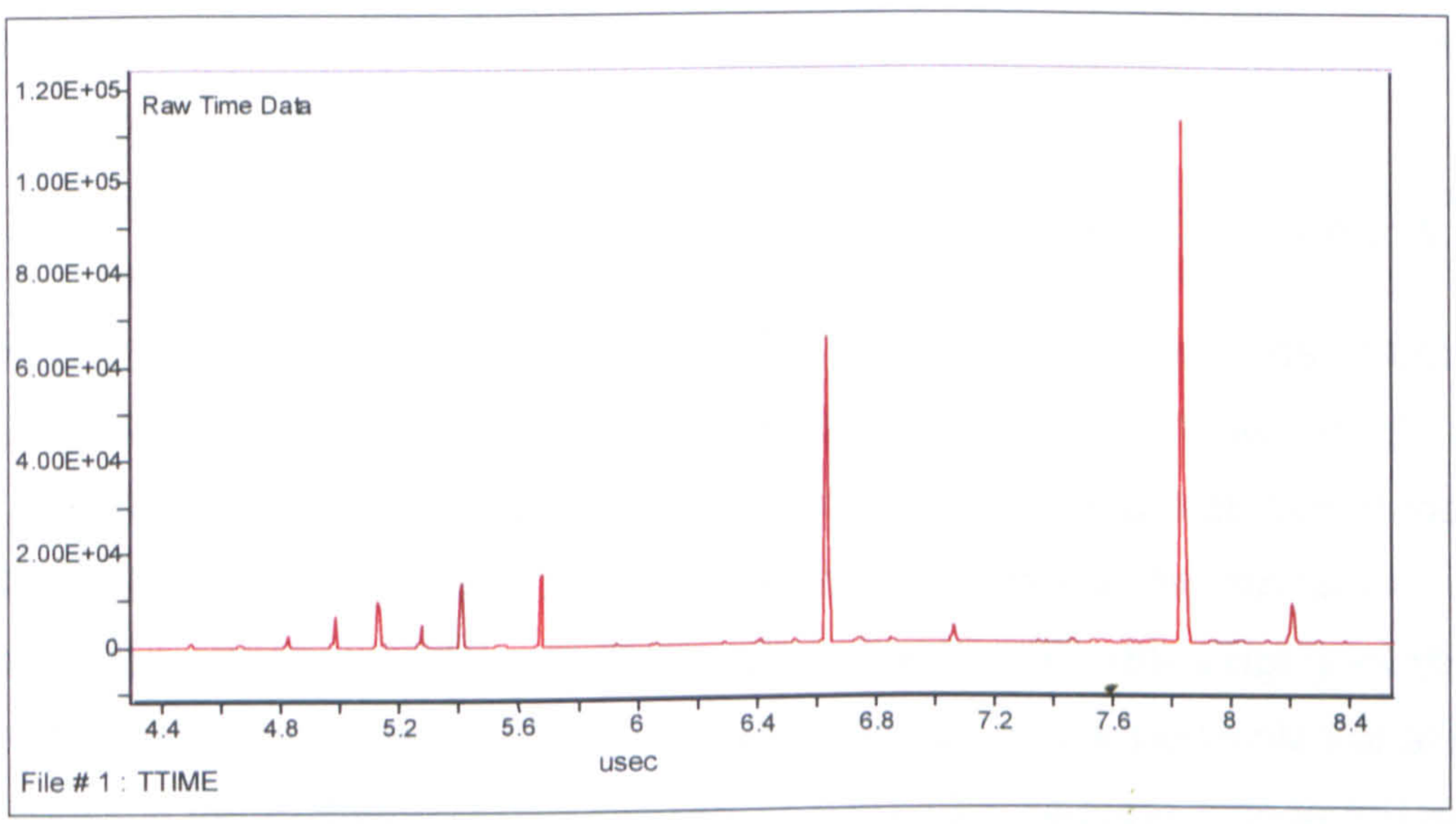

Figure 23: Time spectrum of the water, nitrogen, oxygen, argon and CO_2 peaks

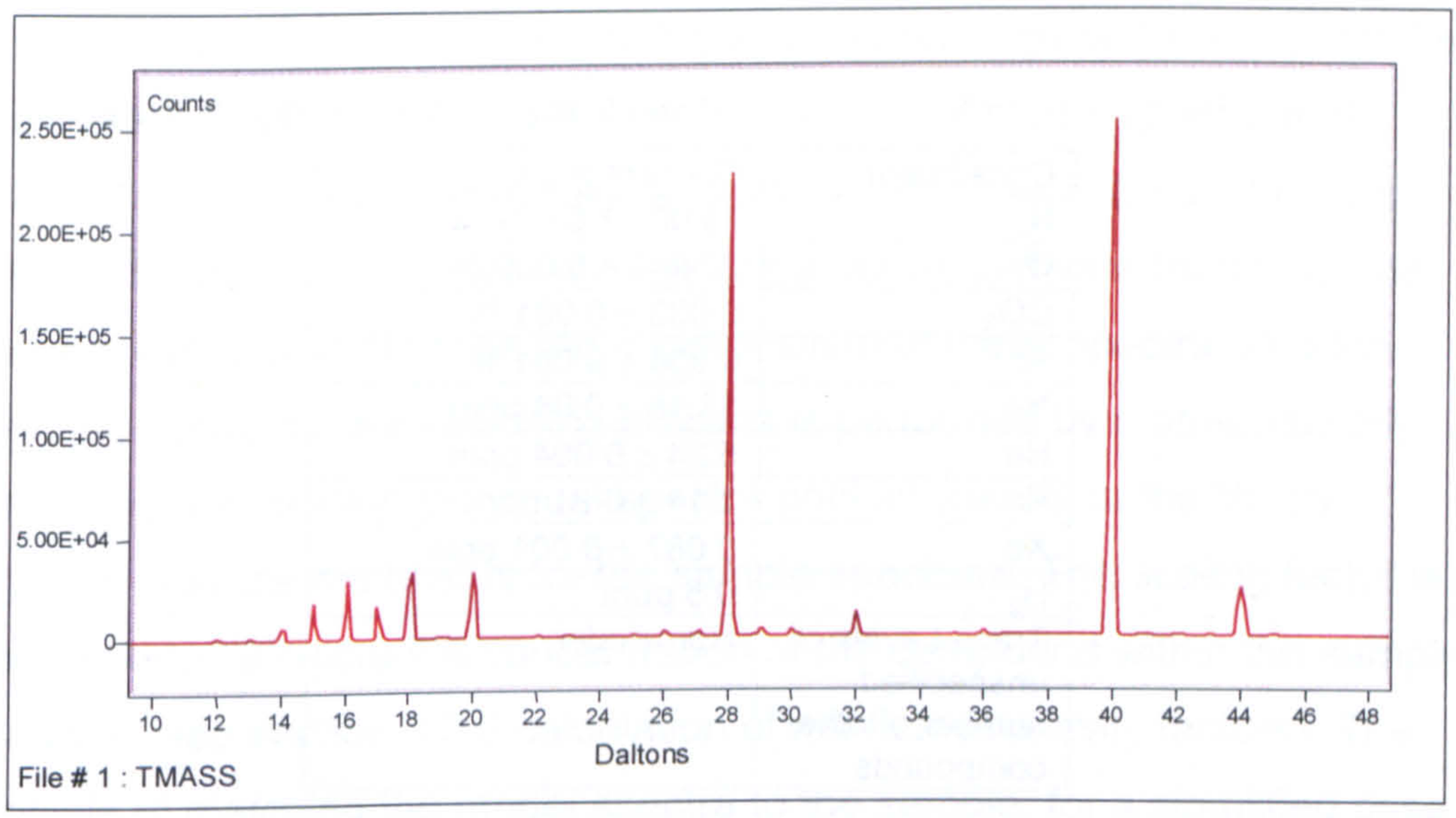

Figure 24: Raw mass spectrum of the water, nitrogen, oxygen, argon and CO_2 peaks

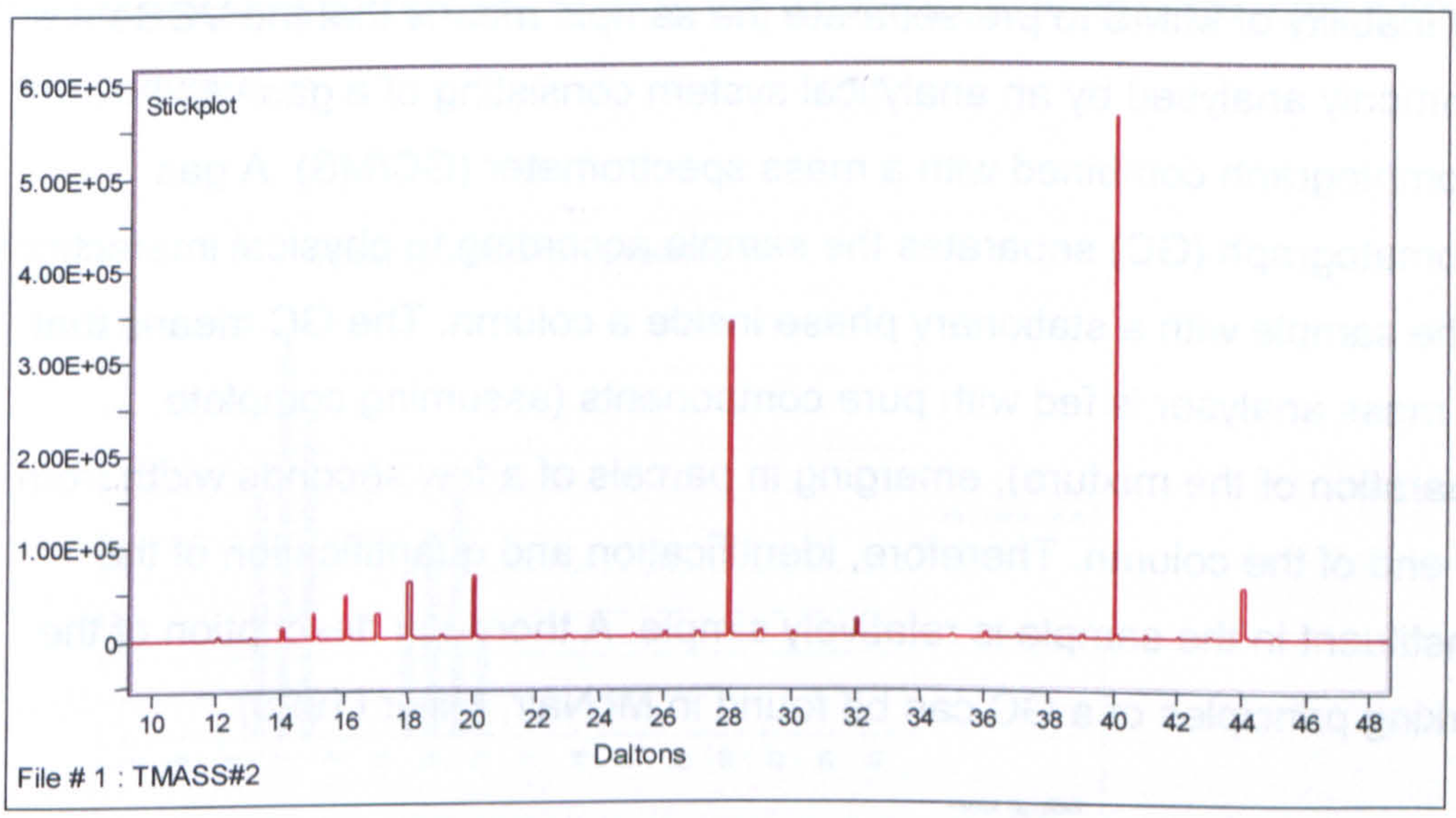

Figure 25: Stickplotted spectrum of the water, nitrogen, oxygen, argon and CO_2 peaks.

2.7.1. Implications of the Membrane Inlet Mass Spectrometry

Membrane inlet mass spectrometers (MIMS) have a speed advantage, compared to GC/MS, however, one of the major drawbacks of a MIMS, without using a GC, is the inability to pre-separate the sample prior to entering the mass analyser. This obviously would be of no disadvantage when analysing pure components one at a time, but a typical analysis is of one or more components in the sample. In addition the sample will contain at least the standard constituents of clean air, given in Table 5 together with the analyte(s) of concern.

Table 5: Major Contents of Dry Air (Weast 1972)

Constituent	Concentration
N_2	78.084 ± 0.004 %
O_2	20.946 ± 0.002 %
CO_2	0.033 ± 0.001 %
Ar	0.934 ± 0.001 %
Ne	18.18 ± 0.04 ppm
He	5.24 ± 0.004 ppm
Kr	1.14 ± 0.01 ppm
Xe	0.087 ± 0.001 ppm
H_2	0.5 ppm
Trace Levels of unspecified number of other compounds	Remainder

The inability of MIMS to pre-separate the sample means that the VOCs are commonly analysed by an analytical system consisting of a gas chromatograph combined with a mass spectrometer (GC/MS). A gas chromatograph (GC) separates the sample according to physical interactions of the sample with a stationary phase inside a column. The GC means that the mass analyser is fed with pure components (assuming complete separation of the mixture), emerging in parcels of a few seconds width from the end of the column. Therefore, identification and quantification of the constituent in the sample is relatively simple. A thorough description of the working principles of a GC can be found in McNair, Miller (1998).

In the MS-200, this pre-separation step is missing, which results in all the constituents of the sample entering the mass analyser at the same time. The mass spectrum obtained, therefore, consists of a superposition of the individual mass spectra of the constituents in the sample.

As mentioned in section 2.2.1, each chemical when ionised with a fixed ionisation energy has a specific fragmentation pattern (see section 2.2.1). This fragmentation pattern is used to quantify the different chemicals in the sample by matching a list of fragmentation patterns (model spectra) with the spectrum obtained from the sample measured with the MS-200.

This method relies on the user having some knowledge of the sample to be analysed. In order to analyse a sample, a library of model spectra that includes all constituents that may be in the sample has to be built up and held on the laptop computer. The mixture analysis software then uses the model spectra, and matches the superposition of these spectra onto the sample spectrum. This matching process is performed by mathematically combining and scaling individual spectra until all spectra in the library together produce the best fit for the sample spectrum. The scaling factor is then used to calculate the concentration of the compound within the sample analysed (see section 3.2.6 calculation of relative sensitivity factors). The principle of matching the model spectra to the sample, for a simplified case of three components, is shown in Figure 26 to Figure 29, where Figure 29, shows the scaling factors (X, Y, Z) of the different model spectra, calculated by the software.

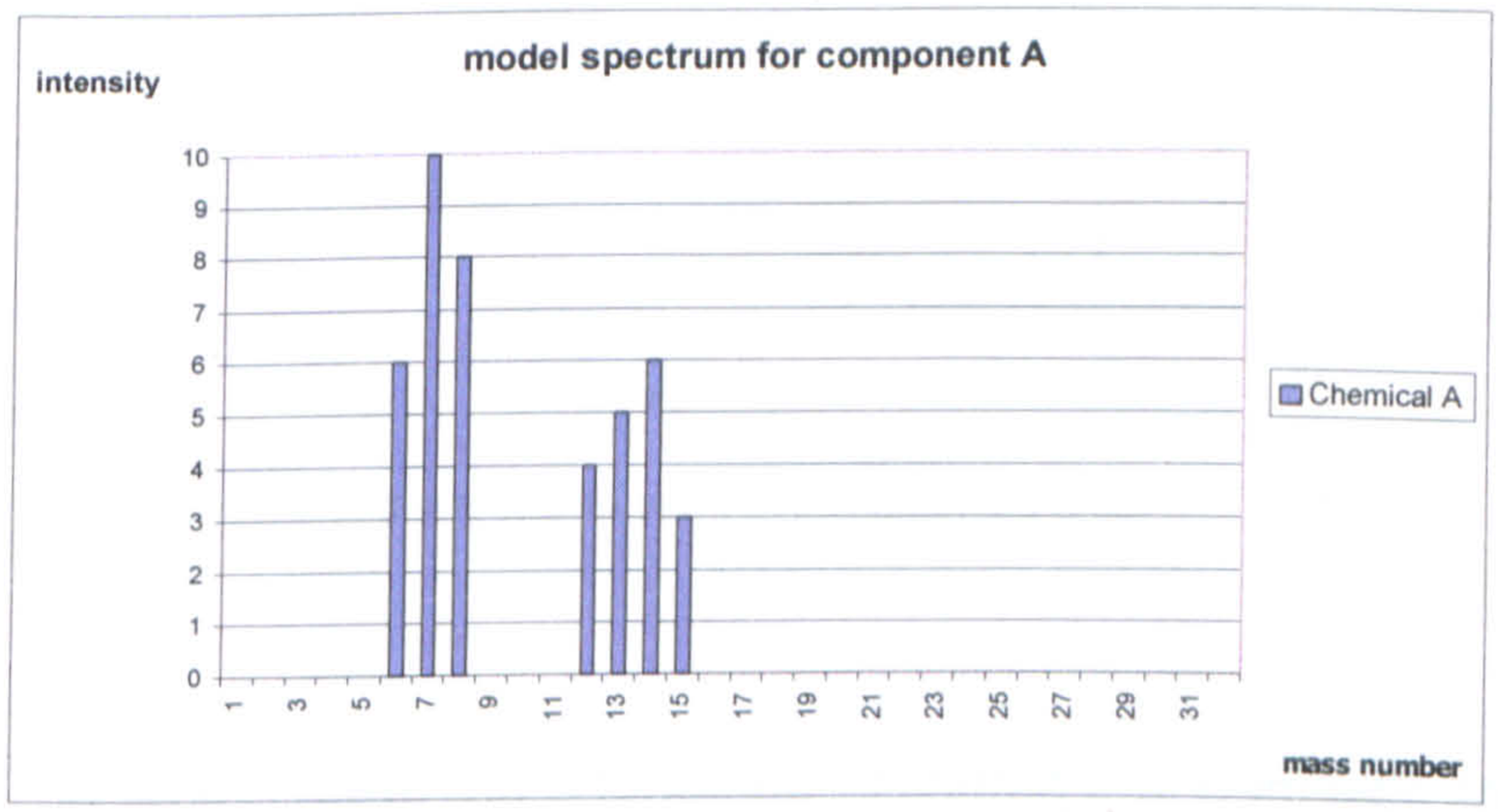

Figure 26: model spectrum of a chemical A

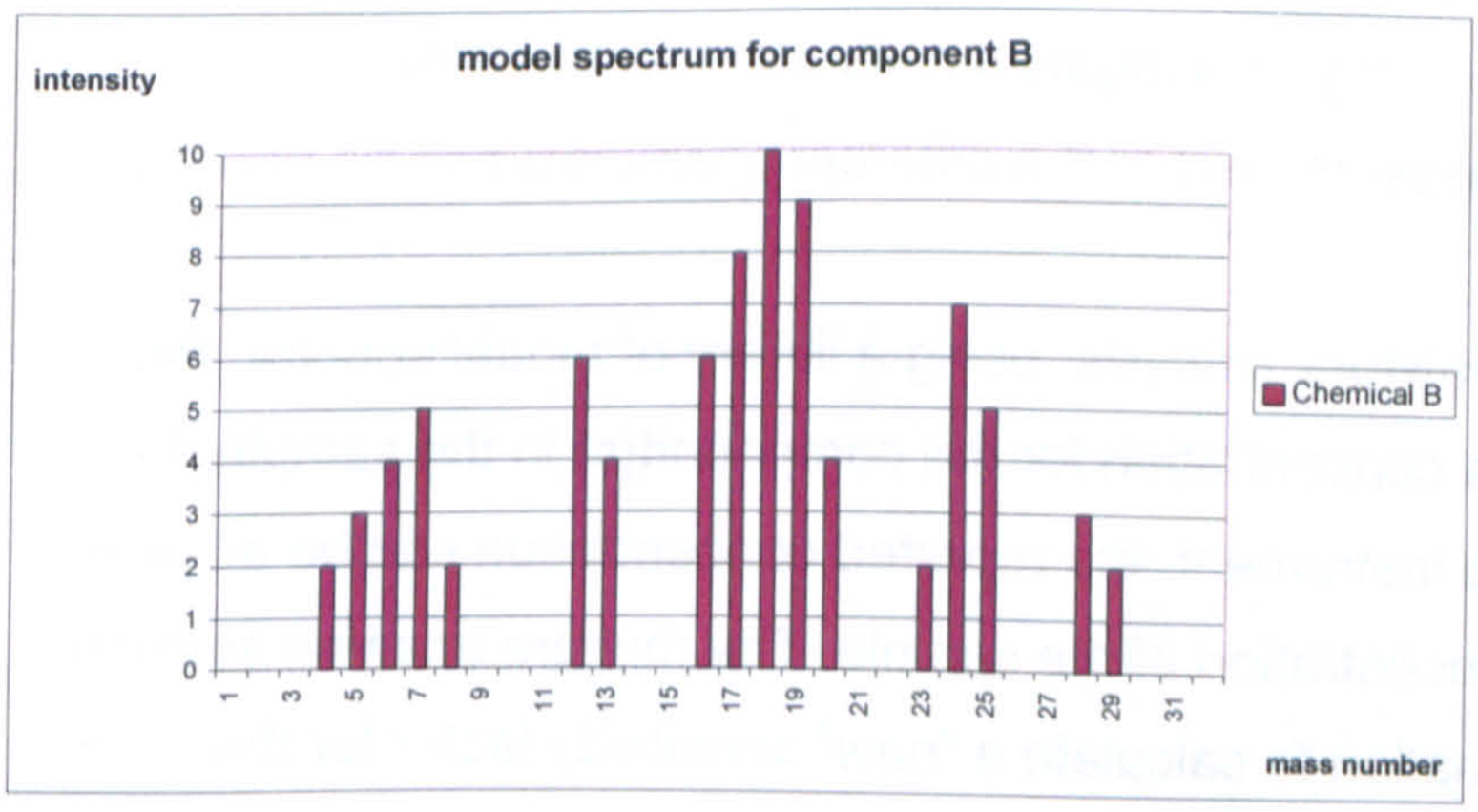

Figure 27: model spectrum of a chemical B

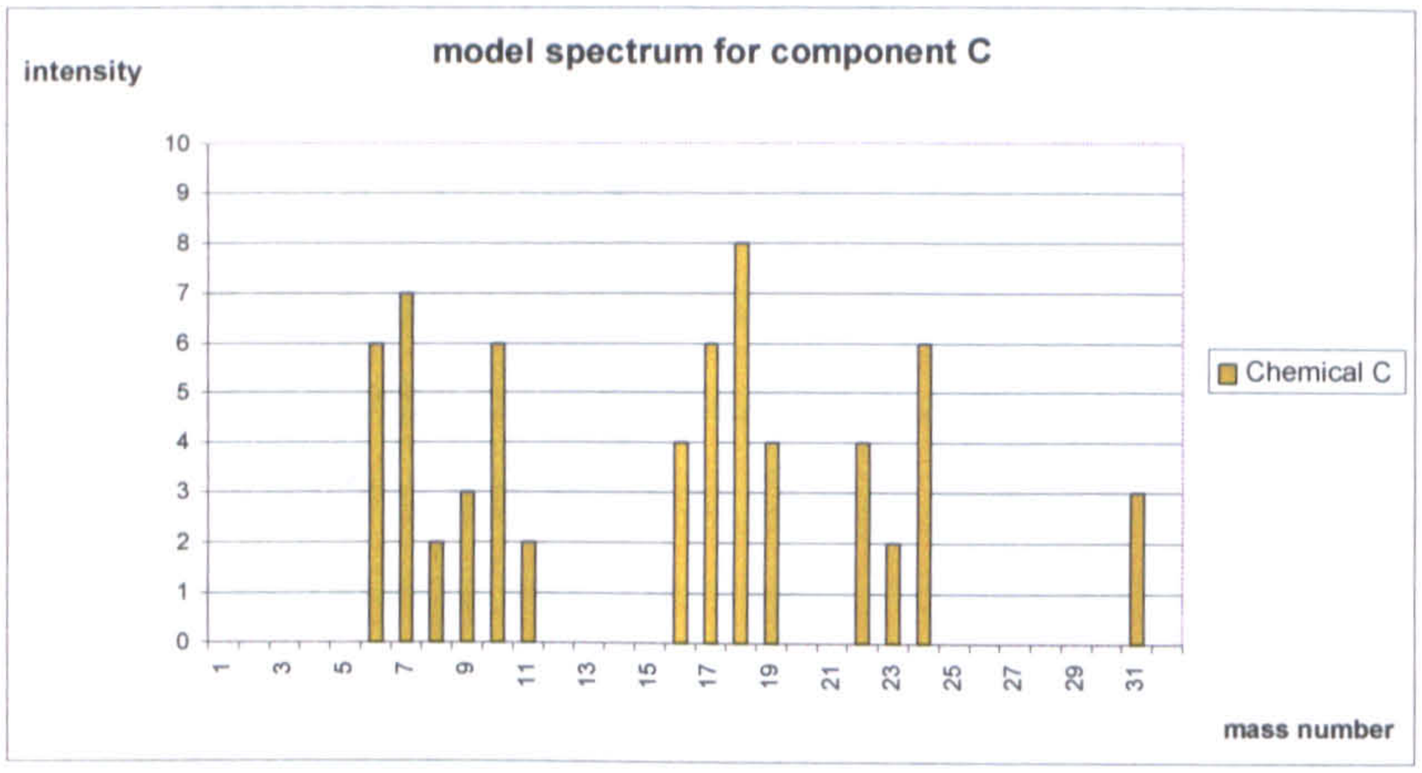

Figure 28: model spectrum of a chemical C

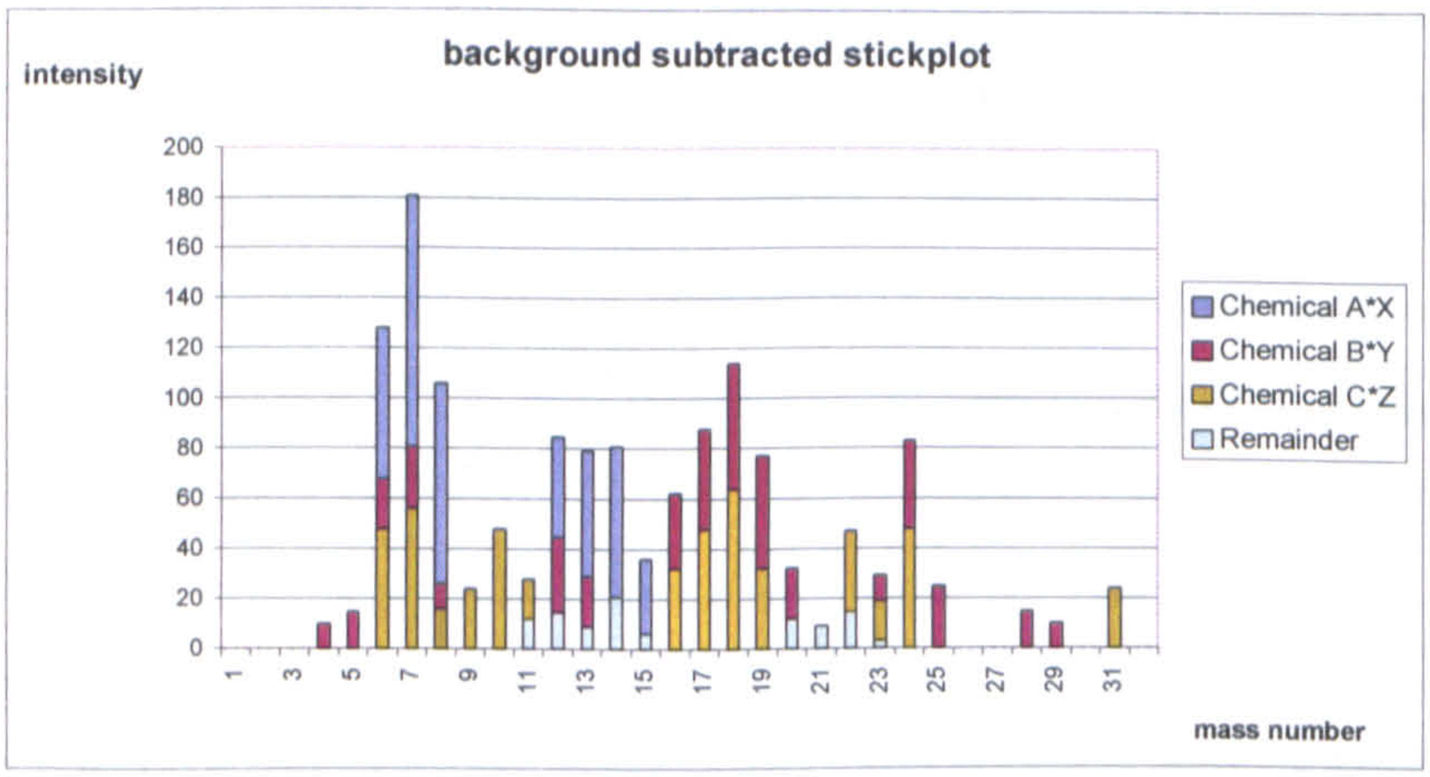

Figure 29: Matching of three Model Spectra to Real Sample

The number of counts assigned to a particular compound are proportional to the concentration of the compound (as mentioned in section 3.2.6, up to the linearity limit). By supplying a standard with a known concentration of a compound and performing an analysis a calibration for the different sensitivities of the measurement to the different chemicals can be performed.

When performing a mixture analysis, using a library of model spectra, the software will report a concentration for the compound(s) in the sample. In order to calibrate the instrument, the reported concentration can be adjusted to reflect the real concentration of the sample. The mixture analysis software then uses this information to calculate a “new” sensitivity factor for this compound. The sensitivity factor is then stored with the model spectrum file

of the specific compound, resulting in a calibration which is transferable between one library of components and another library, in case of a different mixture to be analysed.

Naturally the software will not be able to produce a perfect fit of the model spectra to the real sample. There will be always peaks that will not be assigned to any of the compounds. Additionally the best mathematical fit might not be fully represented by the sample spectrum. To allow the user to assess the correctness of the results, the mixture analysis will report a certainty to which it was able to match the model spectrum.

A more thorough description of the theory and working principles of the mixture analysis software are given in Appendix 4. Practical testing of the mixture analysis software is described in section 3.2.12.

3. Laboratory based performance test

The aim of this chapter is to analyse the performance of the MS-200 in a laboratory environment. This work forms an important part in preparing the instrument to be exposed to different applications with different requirements

The chapter outlines the operational parameters of the equipment including sensitivity, response time, temperature and moisture dependence. These investigations allow the instrument to be understood in terms of its merits and limitations, and therefore, enable it to be more effectively and appropriately used for real applications described in this thesis.

As a part of this chapter the MS-200 was compared to GC/MS analysis of two different samples. The two samples were prepared into passivated stainless steel canisters and independently analysed by Wyle Laboratories. They formed part of an investigation in the suitability of the MS-200 to be used as a volatile organic analyser (VOA) on the international space station (ISS). This application is discussed further in section 5.4.1. Some parts of this chapter are based around this comparison study. Other parts of this chapter were prompted by other applications for which the suitability of the instrument was investigated, discussed later in sections 5.1 to 5.4.

As the MS-200 can be used for the analysis of a wide group of volatile compounds in a variety of different applications, it is beyond the scope of this thesis to have a thorough investigation into all possible components. However this chapter describes the work performed for a range of chemicals that are representative for the group of VOCs that can be measured with the instrument. The measurements described here also enabled the merits and limitations of the instrument to be better understood for a range of chemicals. To achieve the objectives of this chapter the following points will be discussed in detail.

- Producing library of mass spectra for the chemicals of interest
- Analysing the response to a broad range of chemicals
- Linearity of the response

- Repeatability of a measurement (precision)
- Parameters that influence the response of the MS200 (speed, sensitivity)
- Confirming the performance of the mixture analysis software
- The influence of the libraries used on the mixture analysis results
- Detection limits for components
- Calibration drift of the instrument
- Comparison of the analytical results with other analytical techniques
- Simple evaluation of the performance of a new chemical

3.1. Equipment and Methods Used

This section describes the equipment used to produce and deliver a known concentration of a sample to the MS-200.

3.1.1. Cylinder Standards

For the major part of the following laboratory based performance test, a gas standard (as shown in Table 6) was obtained in a 5 litre pressurised cylinder from Scott Speciality Gases. The analytical accuracy of the analysis of the gas standard given by Scott is ± 10%. The standard does not contain any humidity.

Table 6 - Concentrations of the Calibration Standard

Component	concentration (±10%)
Methanol	493 ppb
Ethylacetate	200 ppb
2-Propanol	593 ppb
Xylene	396 ppb
Toluene	197 ppb
Dichloromethane	198 ppb
Trichloroethane	149 ppb
n-Hexane	297 ppb
Nitrogen	Balance

This standard was chosen to fulfil the requirements of a study, set out by Wyle Laboratories, performed for National Aeronautics and Space Administration of the US (NASA). It consists of representative compounds for a broad range of chemicals that might be present in a spacecraft environment [NASA 2000, NASA 2003], but also in other environments such as industrial and environmental monitoring applications.

The flow from the pressurised cylinder was regulated using a "model 13 series high purity, medium flow regulator" from Scott Speciality Gases.

For investigations on a single component and general instrument performance, additional standards of benzene were used (1190ppb and 1010ppb benzene in Nitrogen in a 10 litre pressurised bottle from BOC). The analytical accuracy is given by BOC as ±20%. The dilution gas used was Nitrogen from BOC UK, the purity was given by BOC as 99.999%.

3.1.2. Production of Standards by Sample Bag Injection

For some experiments it was chosen to produce a gas standard by injection of liquid volatiles into a metered nitrogen stream and collection in a tedlar® sample bag. This section describes the equipment and methods used and investigate the repeatability of the sample bag injection principle. This method was chosen for its simplicity, fast availability and low cost compared to the gas standard production, using permeation tubes or pressurised gases.

An injection port with a septum (a rubber seal that can be pierced by the needle of a syringe and will seal up again once the syringe is removed), similar to an injection port of a gas chromatograph, was used for the production of the gas standard. This port was heated to 80°C to allow fast evaporation of the injected volatiles. Using a flow meter, a flow of 2 l/min of nitrogen into the tedlar® bag was established. The setup for producing the standards is schematically shown in Figure 30. By knowing the injection volume, the flow and filling time the concentrations in the sample bag can be calculated, using Equation 3.

$$c = \frac{D * V_{inj} * V_{mol}}{M * V_{air}}$$

Where:
C = concentration of sample
[mole/mole, expressed as ppb (10^{-9}) or ppm (10^{-6})]
V_{bag} = Volume of Sample Bag [litre]
V_{mol} = Volume of 1 mole of gas at 20°C and
1013mbar = 22.4l/mol
V_{inj} = Liquid volume of injected sample [ml]
D = density of liquid sample [g/ml]
M = molecular weight of liquid sample [g/mole]

Equation 3:

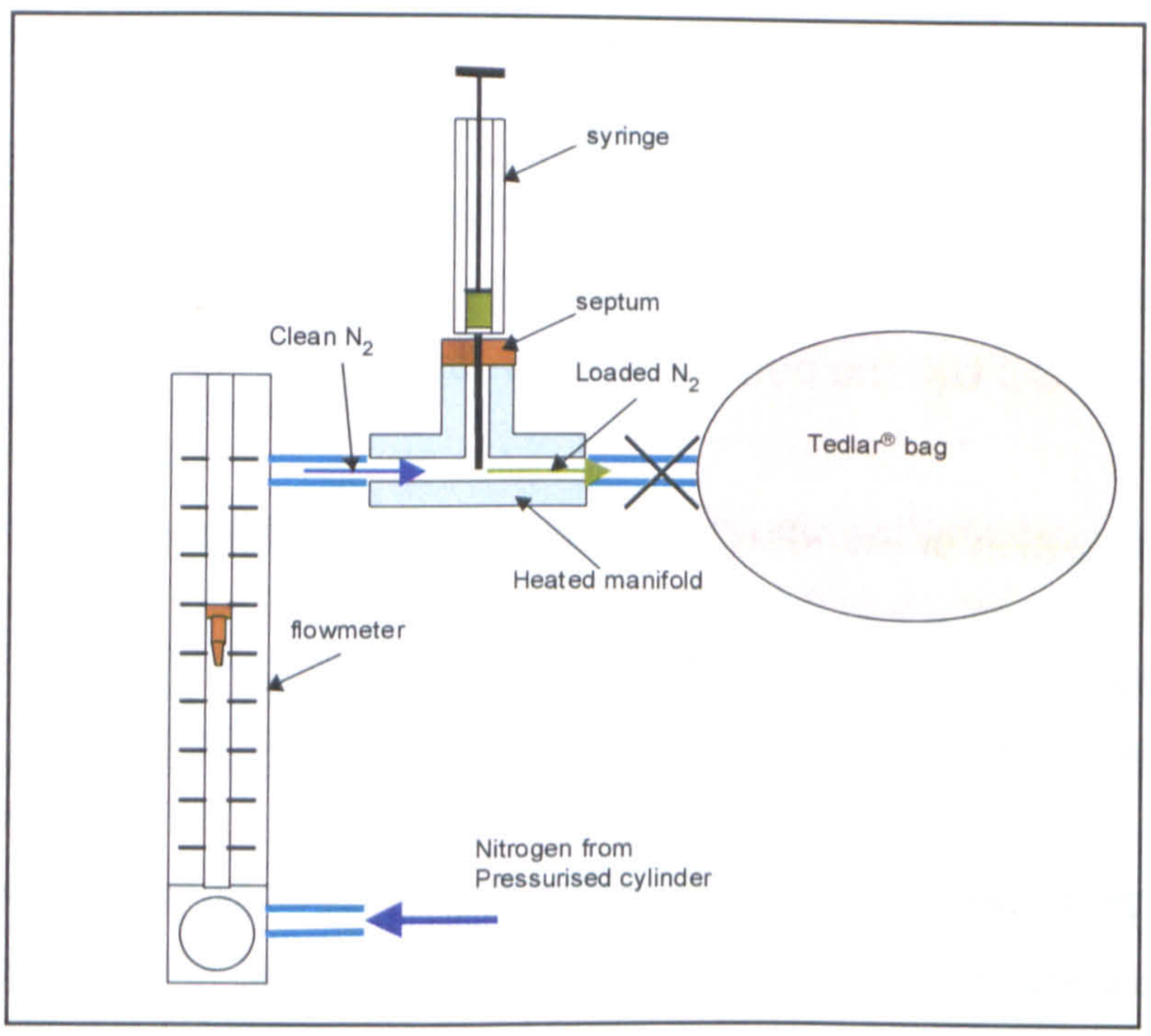

Figure 30: Principle of Sample Bag Injection

To simplify the production of low ppm concentrations and to reduce the error caused when injecting small volumes, the volatile mix can be produced as a solution in methanol (depending on the solubility of the volatile in methanol).

As an example, injecting 4µl of a VOC into 1ml of methanol and then injecting 0.5µl of this solution into a 10-litre nitrogen produces a concentration of approximately 1ppm for the VOC. Equation 3 shows that to calculate the exact concentration, atmospheric conditions, density and the molecular weight of the injected chemical have to be taken into account.

As discussed in section 3.2.7, the sensitivity of the MS-200 for methanol is very low and its mass peaks produced are below 33amu, which is lower than for most chemicals of interest. This means that there should be very little interference between the methanol and most chemicals of interest. However, this has to be individually checked for each chemical in the produced mixture.

The standards produced this way were found to have a precision of ± 20% for a concentration range from 1 to 3ppm. The experiments performed to determine the precision of this method are described in Appendix 1.

The gas and sample lines used were all routed in either copper for the dilution with nitrogen, or stainless steel for the pure and the diluted calibration standard. This was in order to avoid potential contamination or loss of sample due to surface interactions with polymer sampling lines. Stainless steel shows very little interaction with the sample for the majority of the chemicals used in this work.

An STEC "non-bleeding gas divider" with 20% increments from 0% to 100% was used to dilute the samples, where required. For some experiments the humidity of the analyte was measured using a Testo 605-H1 humidity meter, reading from 5 to 95% relative humidity with an accuracy of ± 3% relative humidity.

3.2. Characterisation of MS-200

As described in section 2.7.1 and Appendix 4, the mixture analysis software of the MS-200 relies on a library of model spectra. These model spectra are mathematically superimposed with the sample spectra to quantify the different component in the sample. Therefore the basis of a calibration is the availability of a library spectrum for a pure component. This library spectrum can be imported from an existing database of 70eV electron impact ionisation mass spectra like the NIST-database (NIST 1998) or can be produced by analysing a pure component using the MS-200.

Bearing the investigations of this section in mind it was possible to decide on the best method to obtain adequate sample spectra dependent on the specific need of an application.

3.2.1. Comparison of NIST and MS-200 (TOF) Mass Spectra

This section will evaluate the differences between mass spectra that are obtained using different mass spectrometer techniques. It is important to understand the differences in order to obtain meaningful results, depending on the application.

It is faster to produce a library using the spectra from the NIST database compared with producing MS-200 specific spectra. However, the relative abundance of fragment peaks in a mass spectrum can differ depending on what type of mass spectrometer is used. Most of the spectra in the NIST database are likely to have been obtained using quadrupole mass spectrometers. Therefore, spectra are likely to have slightly different relative abundance due to different mass dependent transmission rates of the different spectrometers. The difference between the mass spectrum for benzene obtained from the NIST database and one generated by the MS-200 is shown in Figure 31 in section 3.2.2.

3.2.2. Influence of a Small Variation in Ionisation Energy onto Fragmentation Pattern

The ionisation energy of the MS-200 was chosen to be 70ev, the same energy as used in the NIST database. As discussed in 3.2.1 this allows, within limits, the comparison of NIST spectra with MS-200 spectra.

Another reason for ionisation at 70ev is that the mixture analysis of the MS-200, as described in Appendix 4, relies on the information in the unique fragmentation pattern of a chemical ionised at 70eV. Fragmentation occurs when a molecule is hit by an electron and is ionised. In some cases an ion is hit in a way that it loses only an electron and, therefore, gains one positive charge. In other cases the impacting electron hits the molecule and actually fragments it into two or more charged fragment ions. The relative abundance

of the different fragment ions is constant for a chemical at a given kinetic energy of ionising electrons (NIST 1998).

The filament of the MS-200 requires a voltage of about 2V for it to get sufficiently hot to emit electrons (see section 2.2.1). If the centre of the filament is held at –70V, then the two ends are at –69V and –71V respectively. This results in electrons emitted with energies from 69eV to 71eV. Therefore, it needs to be investigated how much the spectral pattern will change when the ionisation energy is changed by a small amount, representing possible drift or tolerances from the 70V. In order to measure this, benzene spectra were measured at average ionisation energies of 66.5eV; 68.5eV and 70.5eV.

Figure 31 shows the fragmentation pattern for the three different ionisation energies of MS-200 spectra of benzene. In addition, the benzene spectrum from the NIST database is displayed. All the spectra are shown as being normalised to the 78amu mass peak, which is the major mass peak of the benzene spectrum.

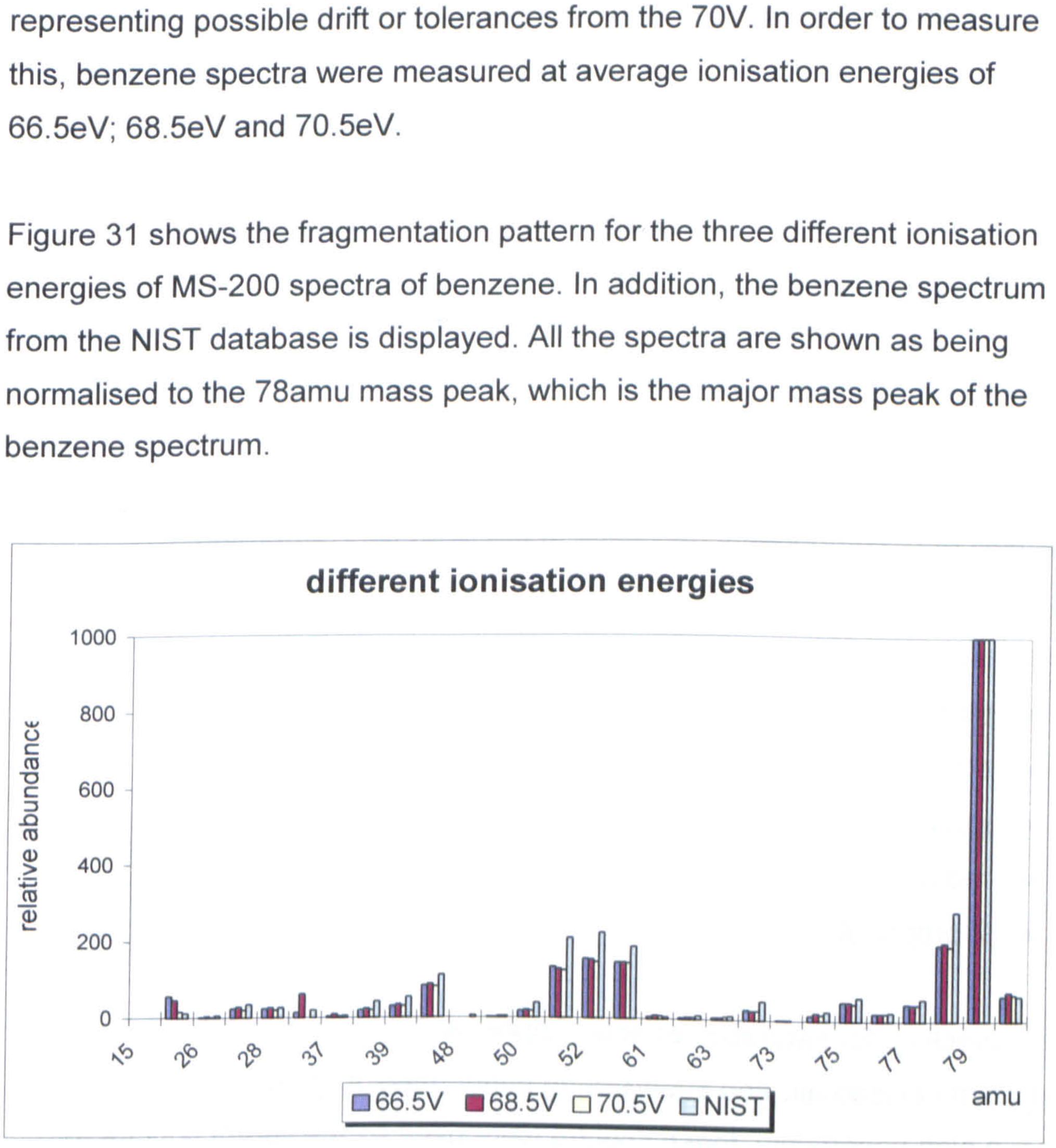

Figure 31: Difference of variation in ionisation energy

It can be seen that the differences between the MS-200 spectra at different ionisation energies are not significant. The fragment ions of the NIST spectrum show a higher relative abundance for the lower mass peaks. This partially confirms that TOF spectrometers have a higher transmission rate for the higher mass molecules than other mass spectrometric methods used. From the small variation in this experiment, it can be seen that if the MS-200 is used to identify unknowns in a background matrix, then NIST spectra can undoubtedly be used to match an unknown compound. However, if a mixture of components is to be analysed with the demand of a high level of accuracy, then it is advisable to use MS-200 produced spectra. It also can be seen that small differences in the ionisation energy do not change the fragmentation pattern significantly. This means that a spectrum obtained using an MS-200 should not change over time due to instrument drift.

3.2.3. Mass Spectra Used

Based upon the above investigations, it was decided to produce typical MS-200 TOF spectra for best analytical performance when measuring the calibration mix described in 3.1. An analysis of the headspace of the following pure components (available at the time) was performed:

- O-xylene
- n-hexane
- toluene
- ethylacetate
- ethanal
- methanol
- 2-propanol

After checking for saturation effects (Appendix 5) subtracting the background spectrum of clean air, and suppressing minor mass fragments and peaks that have a high uncertainty, these spectra were used as the library spectra for the mixture analysis software. An investigation on the production of library data is given in a publication by the National Institute of Standards "The Critical Evaluation of a Comprehensive Mass Spectral Library" (Ausloos et al. 1999).

In addition, the library spectra for dichloromethane and trichloroethane were imported from the NIST database. During other work described in this thesis, MS-200 library spectra were produced whenever feasible. If this was not possible, then NIST data was imported.

3.2.4. Initial Time Response on Supplied Standard

This experiment was undertaken to identify how the MS-200 responds over time, when supplied with the gas standard described in section 3.1, Table 6. A background was established, followed by a step change to 100% of the calibration mixture. A series of almost-continuous measurements were then performed to follow the response of the MS-200 over time. These consisted of 45 experiments each of 30 seconds acquisition, with 30 seconds delay between them. One data point per minute was produced.

The results are shown graphically in Figure 32. Tabulated data from the mixture analysis software are shown in Appendix 2.

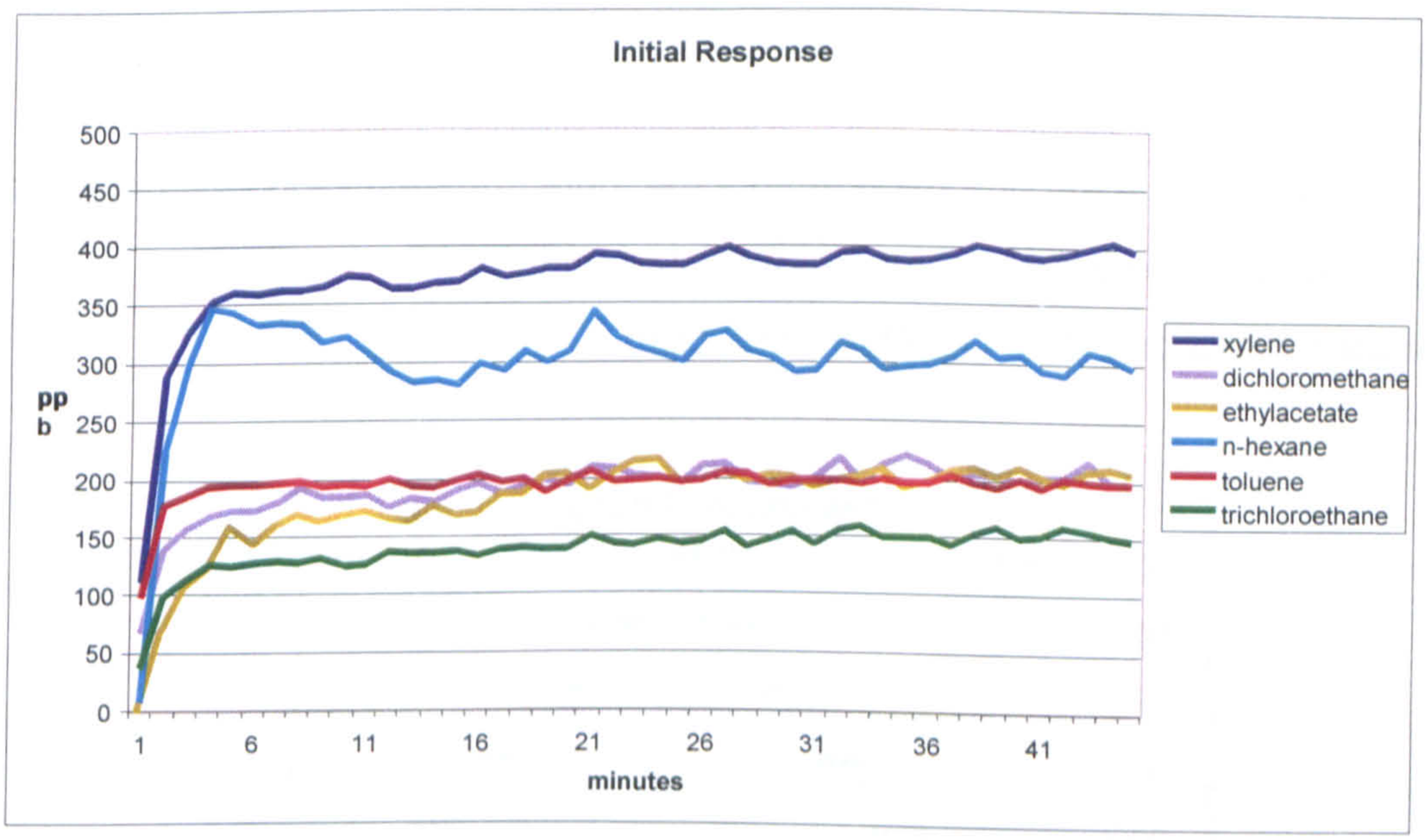

Figure 32: Medium Term Response of MS-200 on the Calibration Standard

These data show that after around 5 minutes, the measurement for xylene, dichloromethane, ethylacetate, n-hexane, toluene and trichloroethane reached a steady value, implying an equilibrium of adsorption effects, permeation through the membrane and pumping speed of the vacuum

pumps. The two alcohols do not record any counts, even after 45 minutes, showing that the sensitivity of the instrument is not sufficient to measure the low concentrations of the alcohol and, therefore, those curves are not displayed. From this experiment it was learned, that before performing a quantitative analysis the MS-200 must be allowed to equilibrate for a component specific time.

It can be seen that the response curves have a ripple and a slight up wards drift after five minutes. It was found out that this ripple was due to an instability of the temperature controller used to keep the inlet at a constant temperature of 45°C. This controller was later improved in order to be able to maintain the adjusted temperature to better than ± 0.1°C. This resulted in the ripple disappearing as can be seen in the results discussed in section 3.3.1

3.2.5. Linearity test

To allow calibration of the instrument, the linearity of the response has to be investigated. Therefore the response of the MS-200 to a series of step changes in the delivered gas concentration was measured. A series of 30 seconds experiments with a 30 seconds delay between them were performed. After every five experiments the input concentration was changed in 20% steps. The delivered input concentration in per cent of the gas standard described in 3.1 is shown in Figure 33:

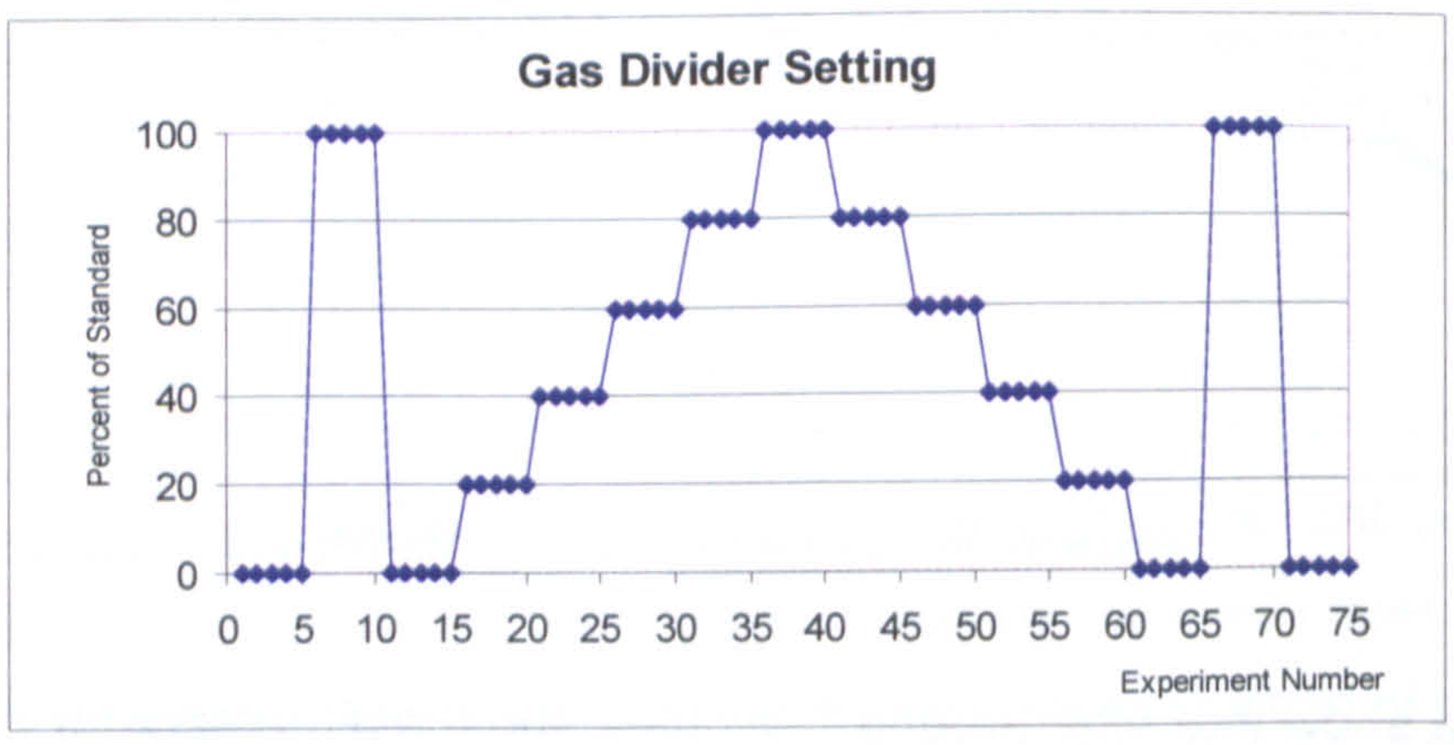

Figure 33: Input Concentration

Figure 34 to Figure 39 show the response of the MS-200 to step changes in the input concentrations. It can clearly be seen that there are components that have a response time in the one to two minutes range (0 to 90% step change), and therefore follow a step change very rapidly. Xylene has the fastest response time, which is below 2 minutes for a 90% step change. Other components have a slower response time. Ethylacetate seems to have the slowest response time of 8 to 10 minutes. There are various possible causes for this. It could be due to adsorption / desorption effects on the delivery line, or a lower diffusion coefficient through the membrane (LaPack et al. 1994)

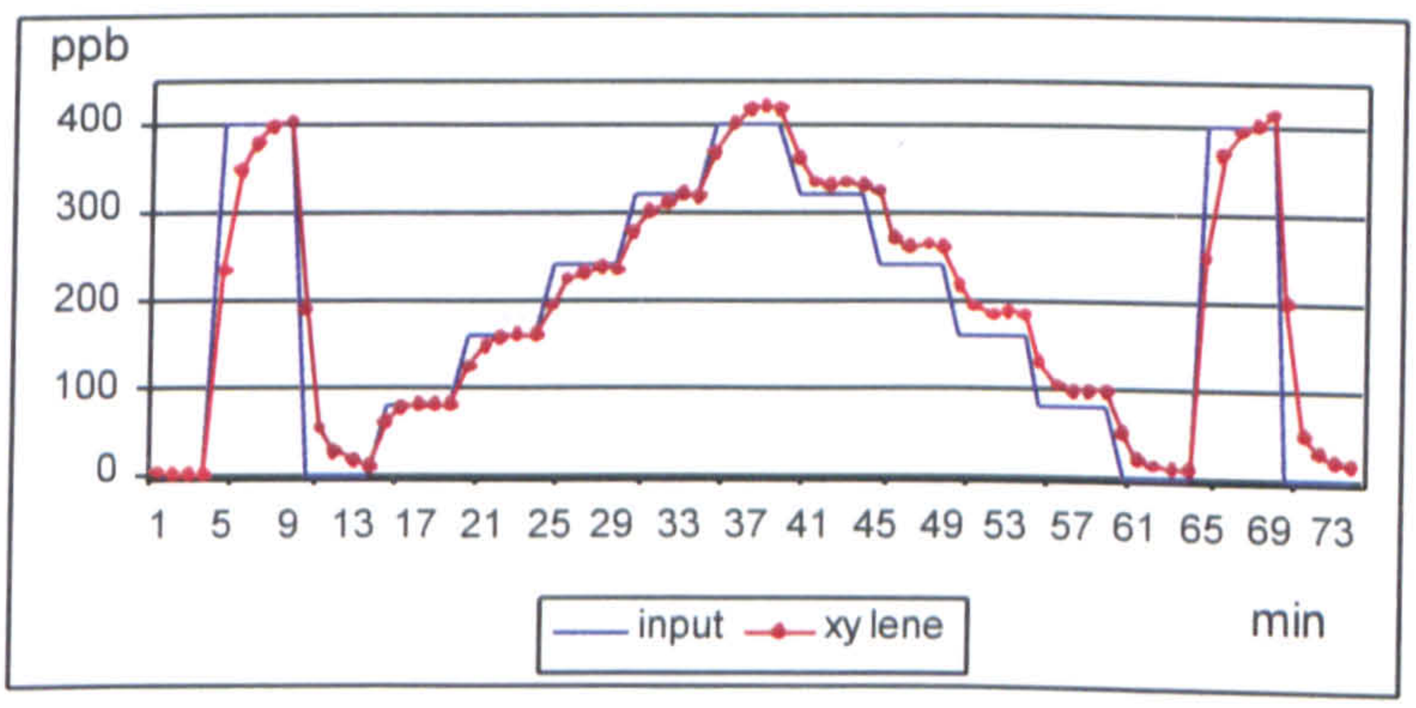

Figure 34: Response of MS-200 to step changes in the xylene concentrations.

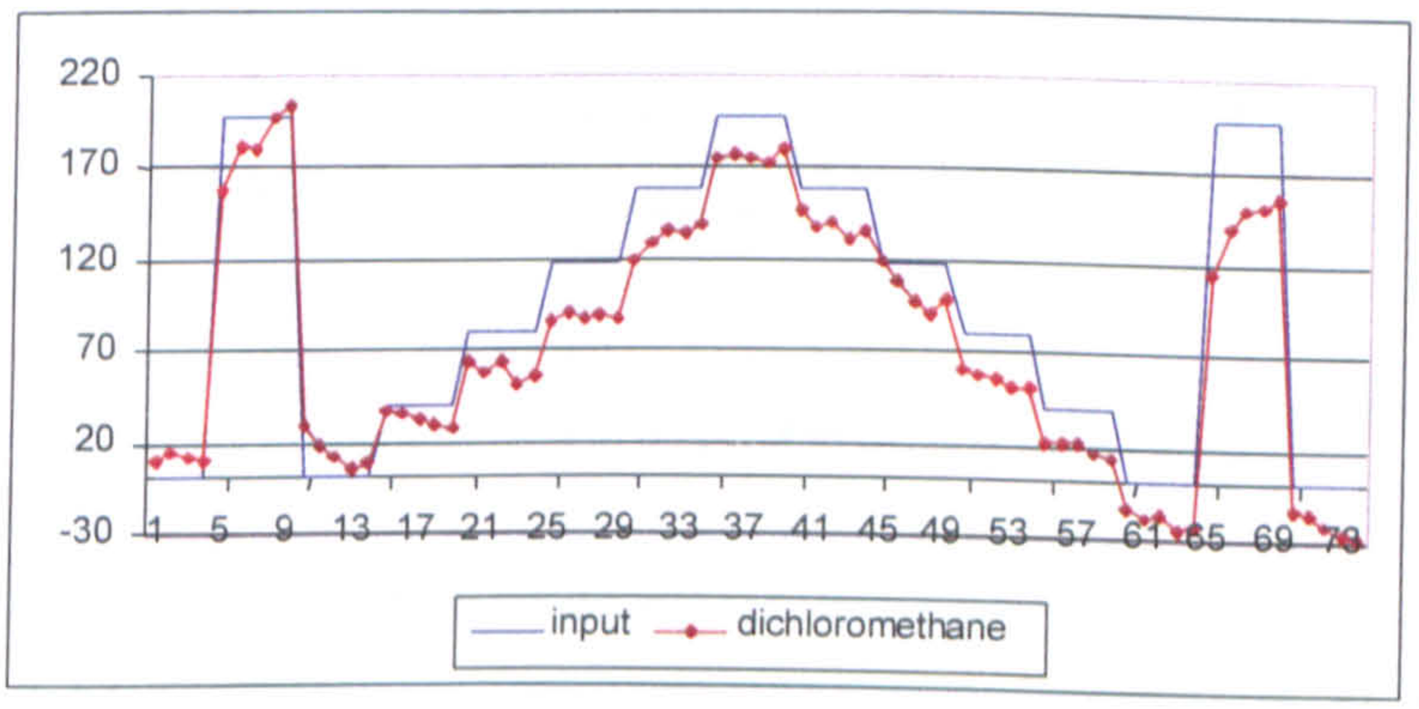

Figure 35: Response of MS-200 to step changes in the dichloromethane concentrations.

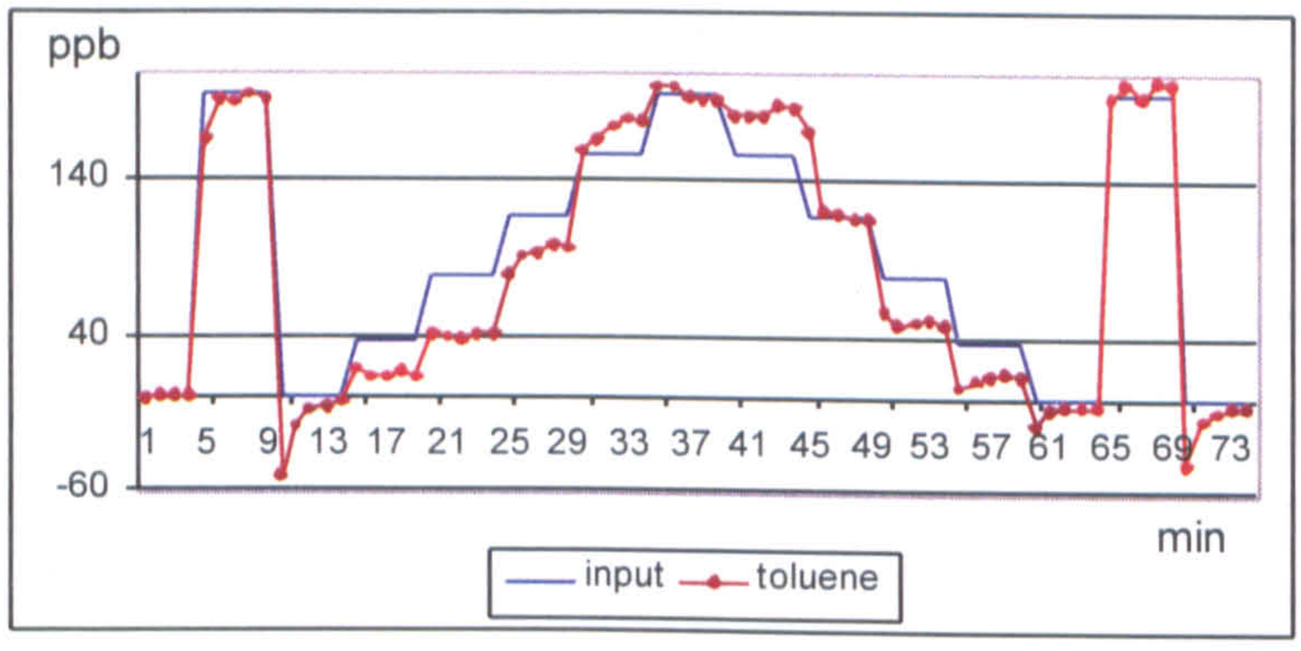

Figure 36: Response of MS-200 to step changes in the toluene concentrations.

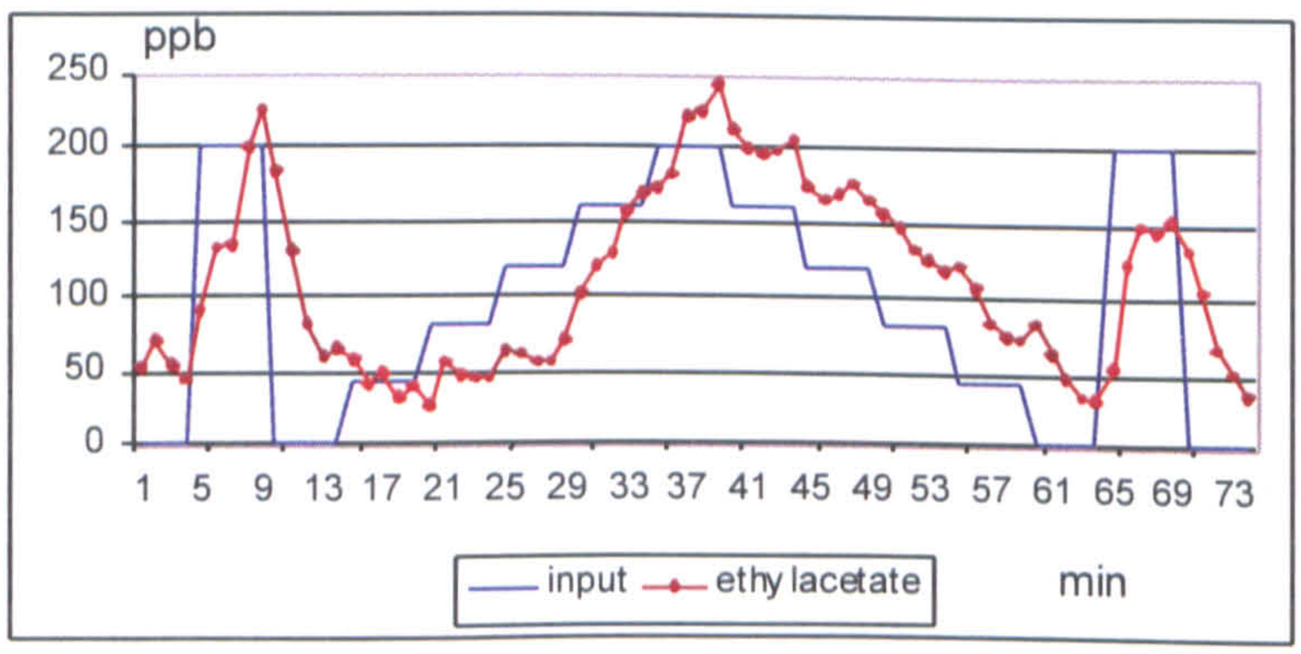

Figure 37: Response of MS-200 to step changes in the ethylacetate concentrations.

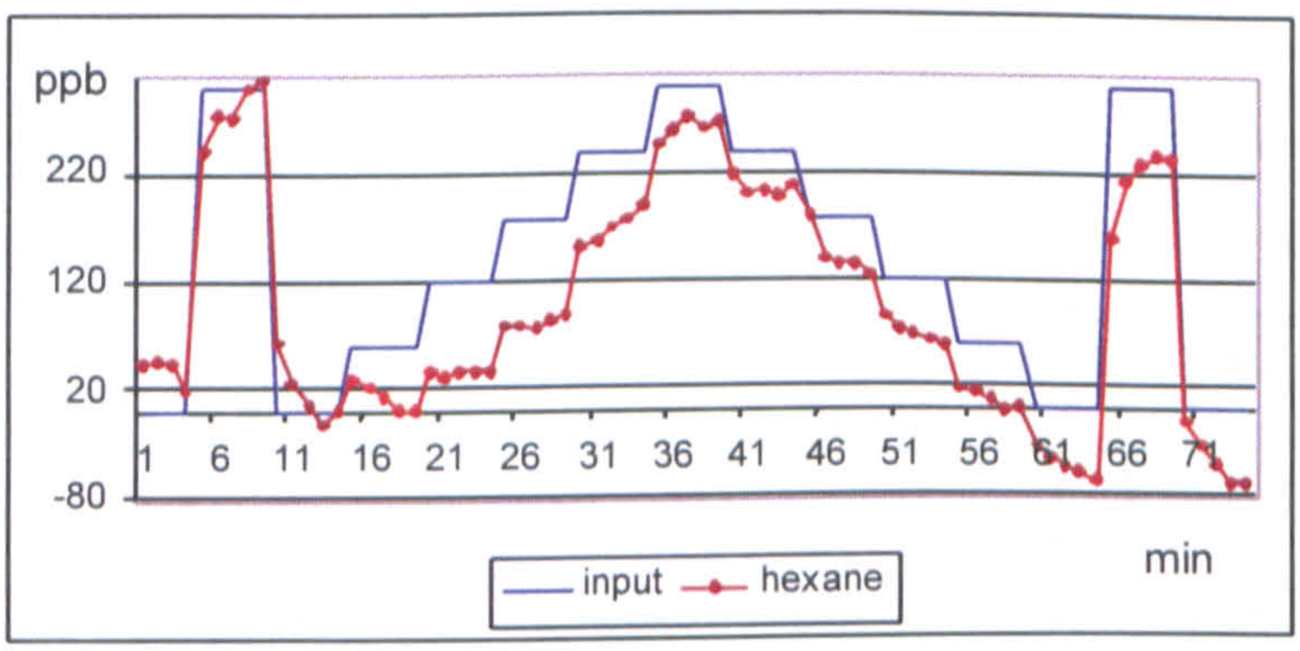

Figure 38: Response of MS-200 to step changes in the hexane concentrations.

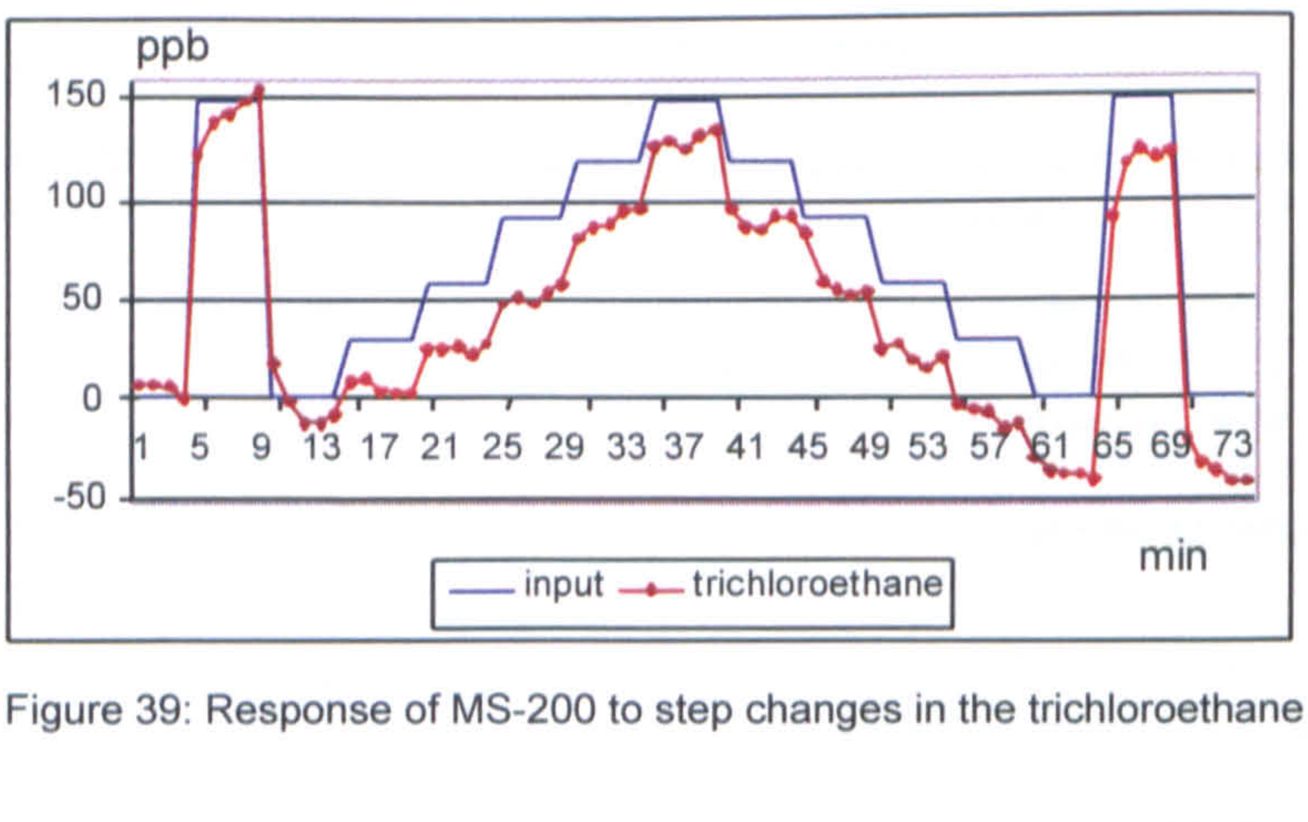

Figure 39: Response of MS-200 to step changes in the trichloroethane concentrations.

The linearity of the response to different concentrations was measured by analysing the o-xylene results and measuring the response after 20, 25, 30, 35 and 40 minutes, representing input of 20, 40, 60, 80 and 100% of the calibration standard. Xylene was chosen, as it reached equilibrium the fastest. The linearity test obviously relies on equilibrium being reached.

Figure 40 shows that the recorded response of the MS-200 is linear within 6% (relative to the response at 396ppb) for the calibration range between 80ppb and 396ppb for xylene. This indicates that a single point calibration for the components of interest can be performed. The working principles of the analyser suggest that the linearity for other components are within the same range, providing that equilibrium is reached.

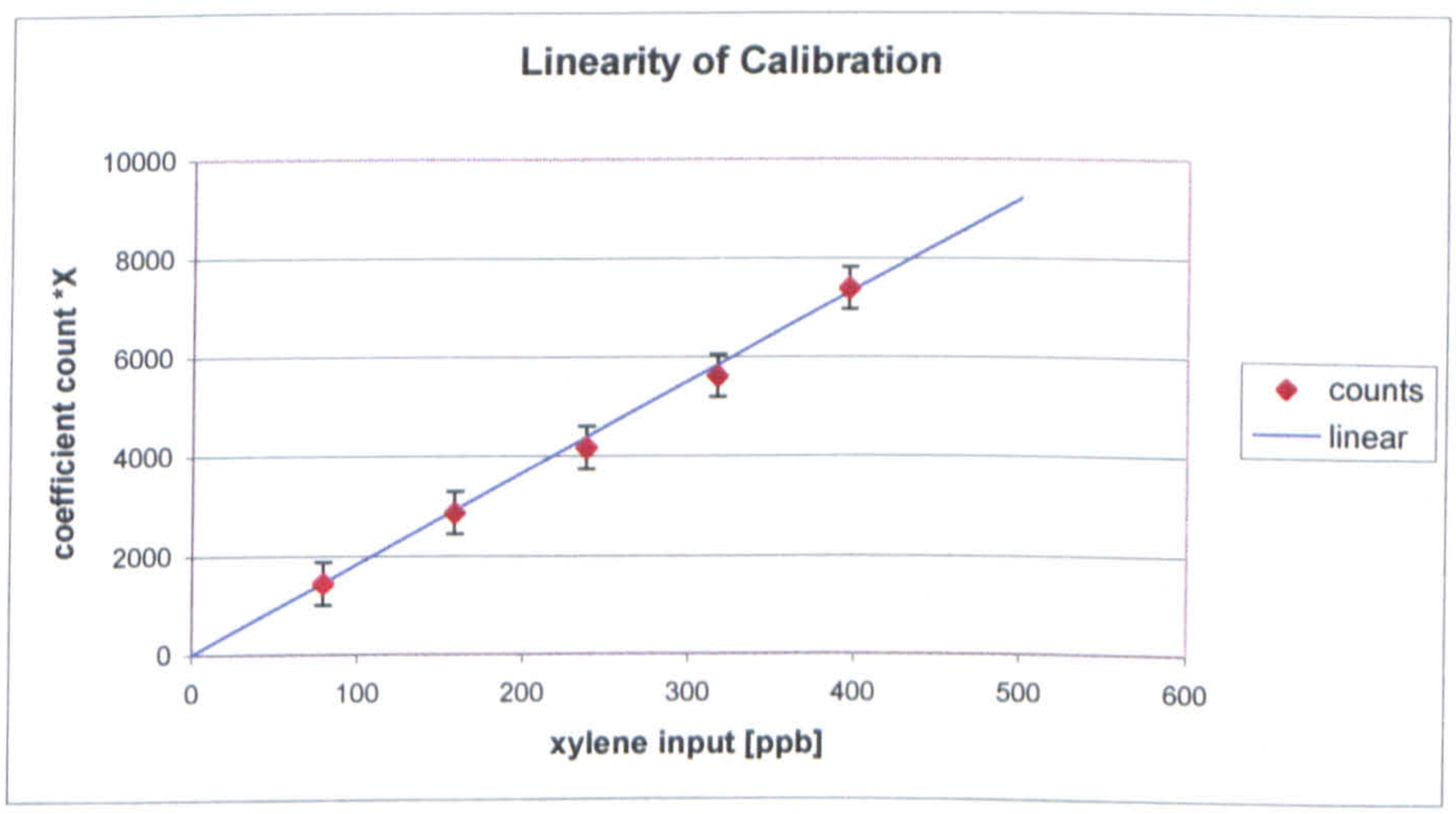

Figure 40: Linearity of xylene response

3.2.6. Relative Sensitivity Factors (RSF)

The sensitivity of the instrument is different for different chemicals as can be seen in Figure 33. This is due to several factors including differences in permeation rates through the membrane, ionisation cross section and pumping speed of the getter pump and ion pump for the different chemicals.

As the MS-200 uses a double membrane concentrator the difference in sensitivity due to different permeation rates is enhanced (as described in

section 2.4 of working principles). For example, if a component permeates 100 times more easily through the membrane than nitrogen, then the overall enrichment is 10,000 compared to nitrogen. If another component has a 60 times enrichment on a single membrane, then the overall enrichment is only 3,600 compared to nitrogen. Therefore, a calibration is needed to establish the relative sensitivity factor (RSF) for each chemical to be quantitatively analysed. After having proved that the response of the instrument is linear within 6%, a calibration can be performed.

A RSF for a component is measured by analysing a known concentration. By supplying the value for the concentration of the measured component, the software is able to calculate the RSF using Equation 4.

After the experiments described in section 3.2.4, it was possible to select a suitable time interval between applying the gas mixture and taking a calibration measurement. The data in Figure 32 shows that this can be done by allowing the instrument to equilibrate to a step change for 5 minutes.

As explained in detail in Appendix 4, the software calculates a concentration on the following basis:

$$\text{Concentration} = \text{Coefficient} / (\text{RSF} * \text{Cycles} * \text{Counts Per Cycle } N_2)$$

Where:

Coefficient	= number of counts assigned to chemical
Cycles:	=number of repeats of acceleration (50k per 1 second experiment)
Counts Per Cycle N_2	=A number representing the specific performance of instrument

Equation 4 - Calculation concentration

By using the gas standards (listed in Table 6), a calibration was performed and the RSF determined for the components in the calibration standard. This calibration was performed on the data in Figure 34 by first taking a spectrum of nitrogen as the background file, and then collecting a spectrum after five minutes to allow for equilibration.

Table 7 - Relative Sensitivity Factors for the Components (Dry Analysis).

Component	RSF	Estimated Uncertainty
Xylene	159,341	0.29%
Dichloromethane	10,878	1.4%
Ethylacetate	10,200	11%
n-Hexane	35,583	0.81%
Toluene	55,988	0.63%
Trichloroethane	9,600	1%

As described in Appendix 4 the estimated uncertainty is a measure of how confidently the mixture analysis software could match the model spectra to the sample. A low number indicates a low uncertainty in the measurement, a high number indicates a high uncertainty and therefore the RSF has to be taken with caution and in combination with estimated uncertainty. RSF for methanol and 2-propanol could not be calculated from the concentrations in the sample, as the mixture analysis does not record a positive coefficient for the concentration used. The detection limit for the alcohol seems to be considerably poorer than for the other components in the sample.

In addition to the influences on sensitivity discussed above whilst doing some of the applications experiments (section 5.4.6), it was observed that some chemicals (for example hydrogen sulphide, containing an S-H group or phosgene containing a double bound oxygen) could not be detected, even in the high ppm levels. This was despite the fact that permeation through the membrane should have been at an acceptable rate (LaPack et al. 1994). It is assumed that they adsorb onto the stainless steel surface inside the vacuum chamber of the mass spectrometer, resulting in a loss of sample, meaning that the component cannot be measured. Work by another research group (Ketola et al. 1997) reports measurements of volatile sulphur compounds using a single silicone membrane inlet magnetic sector mass spectrometer. This supports the thesis that the permeation through the membrane should be at an acceptable rate, and therefore if the sample would not adsorb it would be

possible to be measured by the MS-200. It was not reported if the spectrometer used for their work had an inert coating to prevent adsorption of components inside the vacuum chamber or not.

3.2.7. RSF for the alcohol

As discussed in section 3.2.6, the standard described in Table 6 did not contain 2-propanol and methanol in sufficiently high concentrations to measure the sensitivity of the MS-200 to these components. Therefore, it was decided to produce a high concentration of sample by injecting a known volume into a 10 litre 'Tedlar' bag of clean nitrogen and make a calibration based on this as a 'standard'. However, it has to be accepted that producing a standard this way will be rather approximate. Firstly, it is difficult to inject a small, precise volume of the liquid sample by using a syringe. Secondly, there is possible loss of sample due to adsorption effects onto the Tedlar bag. Thus the numbers that follow are intended only as a rough guide to the sensitivity of the MS-200 to the alcohol in its current configuration. The use of Tedlar bags for the production of a standard of known concentration is discussed in more detail in Appendix 1.

A sample of approximately 30ppm of 2propanol and methanol was produced, analysed and the RSF calculated. The results are shown in Table 8.

Table 8: RSF factors for the alcohol

Component	RSF	Estimated Uncertainty
Methanol (30ppm)	670	1.7%
2-Propanol (30ppm)	1,560	0.6%

Comparing these RSF to those for some of the other components, which are in the 100,000 range, shows how low the concentration factor of the membrane is for alcohol. However, they are still concentrated in relation to nitrogen, which has an RSF of 1.

3.2.8. Detection Limit and Quantification Limit

The detection limit of a component represents a threshold below which one can not reliably confirm the presence of an analyte in a sample. Knowing the detection limit therefore allows one to qualitatively state if an analyte is measurable in a sample or not.

When analysing clean air (often referred to as zero gas), an ideal instrument would report a concentration of zero for the component to be measured, as it is not present. In reality the measurement will be subject to some noise, and therefore the mixture analysis software might report the presence of an analyte in the sample. Depending on the confidence required, the detection limit is defined as a certain number of standard deviations (σ) of the results of multiple zero gas measurements. This means that if a signal is less than the detection limit, it might be due to the noise within the measurement rather than due to the presence of the analyte. In this thesis, the common definition of the detection limit being three times the standard deviation σ of the background reading is used (Keith 1983).

The noise measurement of multiple background readings follows statistically a normal distribution. Therefore at a signal height of $3 * \sigma$, there is a 95% certainty that a reported analyte is present in the sample rather than that the measurement is due to noise of the instrument. From this definition it can be seen that the detection limit is influenced by the background signal of the specific component and the sensitivity towards this component. A high background signal combined with a low sensitivity results in a poor detection limit and visa verse.

The quantification limit is the response height at which the qualitative expression of the detection limit can be safely turned into a qualitative analysis and report a concentration value of the analyte in the sample. Throughout this thesis, the quantification limit was defined to $10 * \sigma$. At that level, 99% of the reported results will be within ± 30% of the "true" concentration of the sample (Keith 1991).

The practical method of measuring σ is as follows: n+1 (where n = 30) consecutive background spectra of nitrogen are collected. Afterwards the standard is supplied and after allowing for equilibration, a spectrum is taken and a calibration performed. Then the background readings are analysed using the model library for the individual components, as described in section 3.2.3, and the sensitivity factors obtained from the calibration. Each of the nitrogen spectra is analysed using the preceding measurement as the background for the mixture analysis software. The standard deviation σ for each of the components are calculated from the n reported mixture analysis results.

Table 9 shows the calculated standard deviation for the components in the gas mixture in Table 6. Table 10 lists the detection limit (LDL) calculated as 3 * σ and the quantification limit (LQL) as 10 * σ. The detection limit for the alcohol is based on the crude calibration performed in 3.2.7, and therefore is only approximate.

Table 9 - Standard Deviation of the Background Reading for the Components (Dry Analysis)

Component	Standard deviation	Component	Standard deviation
Xylene	454 ppt	Toluene	851 ppt
Dichloromethane	5.4 ppb	Trichloroethane	3.2 ppb
Ethylacetate	26 ppb	Methanol	120 ppb
n-Hexane	6.4 ppb	2-Propanol	2 ppm

Table 10: Detection Limit and Quantification Limit for the Components

Component	LDL	LQL	Component	LDL	LQL
Xylene	1.4 ppb	4.5 ppb	Toluene	2.6 ppb	8.5 ppb
Dichloromethane	16.2 ppb	54 ppb	Trichloroethane	9.6 ppb	3.2 ppb
Ethylacetate	78 ppb	260 ppb	Methanol	360 ppb	1.2 ppm
n-Hexane	19.2 ppb	64 ppb	2-Propanol	6 ppm	20 ppm

A list of detection limits for further components measured during the work on this thesis can be found in Table 34 (section 6.2).

3.2.9. Stability of the Calibration

It is important to know the stability of a calibration if one is to employ the instrument for real applications. This allows an assessment of the time interval required between instrument calibrations to be made. The long-term stability of the dry calibration was measured by performing an analysis cycle some time later, using the RSF obtained earlier from the calibration done for section 3.2.5 (Figure 34). The time between the two analysis cycles was 7 weeks, in which time the instrument was occasionally used for different experiments.

Table 11 shows that the calibration stability over the seven weeks of the experiment was in the range of ± 20% for the components analysed.

Table 11 - Stability of the Calibration over 7 weeks

Component	Calibration 1	Analysis 2	Δ change
o-Xylene	396 ppb	384 ppb	- 12 ppb (-3%)
n-Hexane	297 ppb	265 ppb	- 32 ppb (-11%)
Toluene	197 ppb	229 ppb	+ 32 ppb (+16%)
Ethylacetate	200 ppb	161 ppb	- 39 ppb (-20%)
Dichloromethane	198 ppb	163 ppb	- 35 ppb (-18%)
Trichloroethane	149 ppb	144 ppb	- 5 ppb (-3%)

This stability experiment was performed under ideal circumstances, using dry nitrogen as background and a dry calibration standard. The work described in section 3.2.10 shows that the sensitivity of the instrument is dependent for some components more and for some less, on the humidity of the sample to be analysed. In a real application it has to be decided how often to re-calibrate the system. This decision will be highly influenced by the required accuracy and the concentration to be measured, as well as the humidity of the sample. Hence in practice the frequency of calibration could be hourly to monthly.

3.2.10.Humidified Calibration Gas

All the experiments described so far were done using a dry calibration standard for the components of interest, plus dilution using dry nitrogen. Most applications for which the instrument is intended involve the monitoring of VOCs in an ambient environment and hence will actually demand the analysis of humid samples. Therefore, the influence of humidity on the sensitivity and the calibration was investigated.

The way to humidify the gas standard in the pressurised cylinder is to use humidified nitrogen for the dilution. This was achieved by passing the nitrogen through a bottle containing de-mineralised water. The bottle had a bypass with a valve, so the amount of nitrogen that was passed through the humidifier, and therefore the overall humidity of the dilution nitrogen, could be adjusted within certain limits. The humidified nitrogen was then passed to the gas divider where it was mixed with the sample.

This arrangement did not allow the humidity and the concentrations to be changed independently of each other. It also limited the maximum humidity of the standard. For example, if the gas divider is adjusted to 60% and assuming the humidifier delivers nitrogen at 100% relative humidity, then the relative humidity of the mixture is 40%.

First a calibration was performed on the dry (< 5% relative humidity, which is below the measurement range of the humidity meter) sample to obtain a set of dry RSFs.

At each humidity level that could be set, two measurements were made in the normal way: first a background measurement using a mixture of clean dry nitrogen with humid nitrogen 'make-up' gas; second a sample measurement using the dry calibration standard from Table 6 with humid 'make-up' gas.

Each time the inlet gas was changed, time was allowed for a new equilibrium to be established. The waiting time should reduce adsorption / desorption effects in the calibration gas delivery system due to the different levels of humidity. The water in the sample is competing with the other chemicals that are adsorbed onto the surfaces of the sampling lines. Therefore, introducing humidity can result in the release of previously adsorbed components, which would alter the measurement.

Table 12 shows the relative change in the RSF for humid samples with respect to the dry calibration.

Table 12 - RSF dependent on relative humidity
(normalised to the dry calibration)

	Relative humidity				
	<5%	19%	26%	37%	49%
Component	**Normalised RSFs**				
Xylene-o	1	1.26	1.75	2.15	2.40
Hexane-n	1	0.86	1.63	2.71	2.61
Toluene	1	1.13	1.87	1.73	1.47
Ethylacetate	1	0.92	1.19	1.30	1.75
Dichloromethane	1	1.34	1.75	2.35	2.27
Trichloroethane	1	0.78	1.03	1.15	1.31

It can be seen that the increase in humidity causes a different increase in sensitivity for each of the components of interest. The cause for the apparent increase in sensitivity may be due to one of the following reasons:

I. Release of analyte absorbed in earlier experiments due to the presence of water vapour competing for absorption sites in the sampling lines (this implies that a complete equilibrium was not achieved).
II. Slower pumping speed for the analyte compounds due to the relatively high water vapour partial pressure in the analyser (remembering that the pumping is also partly an absorption process).
III. A change to the partition coefficient, or transport properties, across the membrane material due to water. Many such membranes have a solid phase filler in the polymer, which can affect the diffusion process

(LaPack et al. 94). It seems likely that absorption of large amounts of water onto this solid phase could speed up diffusion of the other components by preventing them from being held up in the solid phase.

An experiment to investigate adsorption / desorption effects within the calibration gas supply line, the inlet system and the vacuum system was performed. This experiment is described in Appendix 6 but some details are given below

In short, it was found that the more polar components in the standard, like the ethylacetate, have a tendency to adsorb onto the sampling lines and therefore might be released when humidity increases. However, the aromatic components were not affected by a change in humidity. Therefore the difference in RSF is likely to be from different pumping speeds or the membrane effects mentioned above.

From this we can see that it is important to have knowledge of the relative humidity of the sample. In most cases this uncertainty can be easily removed by drying the sample. An easy method found to dry a gas sample is a Nafion® dryer. The use of Nafion for drying moist air samples is extensively described in the US-EPA TO14 method. However, care has to be taken, as the Nafion® will not only remove water, it will also remove alcohols from the sample stream (Permapure 2002).

3.2.11.Sensitivity of Mixture Analysis Software to imperfect library

In order to have confidence in the final results of the MS-200 it is important to understand how sensitive the reported results are to the completeness of the library. This was investigated by introducing deliberate imperfections (missing components) in the library used. As explained in detail in Appendix 4 the mixture analysis algorithm will only produce the mathematically best result if the library is both complete and composed of spectra taken on the same instrument (to match the peak ratios as described in section 3.2.1). Therefore five different libraries were defined. Different components were removed or

added to the library and the change in the reported concentration for the different components, when analysing the same data set, was recorded.

The libraries used were as follows:

A) The complete library of components in the mix; o-xylene; n-hexane; toluene; dichloromethane; trichloroethane; ethylacetate; methanol; 2-propanol; plus the standard residual gas components (CO_2; O_2; H; H_2O; N_2; Ar) in a library.

B) Same as A, but leaving toluene out.

C) Same as A, but leaving xylene-o out.

D) Same as A, but adding benzene, trichloroethene, 1.1 dichloroethane.

E) Same as A, but leaving methanol and 2-propanol out.

The results are shown in Table 13. Library A was used to make the calibration, so this column shows only a remainder of the concentrations actually present and the mixture analysis reported standard deviation. The other columns show the deviations of the reported concentrations from the correct values, together with the reported estimated deviation.

Table 13 - Dependence of the MS 200 concentrations on the library used.
Numbers in brackets show the estimated standard deviation reported by the mixture analysis software.

Compound	A (calib.)	B	C	D	E
o-Xylene	396ppb (0.32%)	+16.9% (0.24%)	-	+55% (0.32%)	-0.3% (0.32%)
n-Hexane	297ppb (1.1%)	-1.1% (1.1%)	-1.1% (1.1%)	-0.3% (1.1%)	+1% (1.0%)
Toluene	197ppb (0.79%)	-	+253% (0.33%)	-79% (5.3%)	+1% (0.96%)
Dichloromethane	198ppb (2.0%)	+1% (2.0%)	+20% (1.5%)	+4% (1.9%)	-0.5% (2.0%)
Trichloroethane	149ppb	+2.6%	+2.6%	-4.7%	0%

	(1.5%)	(1.5%)	(1.5%)	(1.6%)	(1.5%)
Ethylacetate	200ppb (3.1%)	-12% (3.5%)	+20% (2.6%)	-6% (3.3%)	+10% (2.6%)

The results show variations in all but one case of between 1% and 55%. The most striking exception is for the reported toluene concentration in column C, when xylene has been omitted from the library and therefore the toluene is reported as 2.5 times the real concentration. Comparing the spectra of toluene and xylene it can be easily seen why this should be so, as toluene only has a couple of major peaks at 91 and 92amu plus another two peaks of more than 5% relative abundance, all of which overlap with xylene.

This investigation shows that for a quantitative analysis one should ensure that the library contains all model spectra of components present in the sample. In a well-defined application with a complete knowledge of the components present in a sample this should provide no problem. If there are any doubts about the precise composition of the sample, then it is advisable to reconstruct the best fit result produced by the mixture analysis software and compare it with the sample. Producing a best fit is an automated option in the mixture analysis software. From this it should be obvious if there is any additional chemical in the sample, like the xylene in case "C". The explanation on how a comparison of the reconstructed spectrum with the sample spectrum works can be found in Appendix 4.

3.2.12.Stability of Mixture Analysis Software

The aim of this section is to investigate the capability of the mixture analysis software to deconvolute and quantify a mixture of components from within the infinite possibilities of concentration ratios between different chemicals in a sample.

The method of having a multiple component gas mixture in a pressurised cylinder and a gas divider to adjust the concentration of this standard between 0% and 100% allows all the concentrations of the different

components to be changed with the same ratio. For example, the experiments described in section 3.2.5, where if the xylene concentration is halved by using the gas divider, then automatically all the other concentrations in the sample are halved as well. This means the multiple component analysis is only moving up and down on a single plane within a multidimensional space, rather than within the range of infinite possible concentration ratios between the different components occurring during measurements of unknown samples.

To test the software in a more realistic way, concentrations of single components in the mixture were changed without affecting the concentration of the other components. To achieve this by using gas standards in pressurised bottles would be rather complex and expensive. A sample preparation method that allows easy changes of single concentrations, is the injection of components of interest into a sample bag of known volume, as described in section 3.1.2. This method allows easy injection of an additional component, or increasing of the concentration of a specific component. The production of a gas mixture using sample bag injection, and the repeatability of the method are discussed in section 3.1.2 and Appendix 1 and is approximately ± 20%.

A stock solution of seven components of 4µl each in 1ml methanol was taken and injected at a volume of 0.5µl into a sample bag of 10 litre nitrogen. Initially this mixture was analysed in the normal way, then an additional amount of each of the seven compounds was added into the solution in order to increase the individual concentration, as shown in Table 15. The changed solution was used to prepare a gas standard for the next analysis. The initial concentration is calculated as described in section 3.1.2 and is shown in Table 14. As the experiments in this section evaluate relative changes in reported concentrations the accuracy of the initial concentration is not of concern. If the mixture analysis works satisfactorily, then all the unchanged concentrations will remain stable within the repeatability of the measurement of the MS-200, and the repeatability of the produced standard.

Table 14: Approximate Concentration in the Sample Bag
(with accuracy as discussed in section 3.1.2)

Component	Calculated Concentration in Sample Bag
Trans-1,2-dichloroethylene	1.28 ppm
1,1,1- trichloroethane	0.97 ppm
Trichloroethylene	1.08 ppm
Tetrachloroethylene	0.95 ppm
Benzene	1.08 ppm
Toluene	0.91 ppm
o-xylene	1.98 ppm
Methanol	30 ppm

In this way, multiple experiments with different components changing in concentration were performed. The pattern of experiments performed is shown in Table 15.

Table 15: Different steps of the experiment

Run No	Changed
1	4μl of all seven components in 1ml methanol
2	+ 4μl toluene
3	Repeat of 2
4	+ 4μl xylene
5	+ 4μl dichloroethylene
6	+ 4μl dichloroethylene
7	Repeat of 6
8	+4 μl trichloroethane
9	+4 μl trichloroethane
10	Repeat of 9
11	Repeat of 9 (on next day)

12	+4 µl trichloroethylene
13	+4 µl trichloroethylene
14	Repeat of 13

Figure 41 shows the reported counts for the different components analysed in the different experiments from Table 15. It was decided to normalise the results to the 166amu peak in order to compensate for the variation in the production of the concentrations in the different sample bags. The 166amu peak used is unique to tetrachloroethylene. Using tetrachloroethylene as the internal standard meant that its concentration was not changed during the experiment. The method of normalising the production of a mix of volatiles in a sample bag to an internal standard peak is described in Appendix 1. In an ideal situation it would be expected that none but the additional injected components change in the counts reported when performing a mixture analysis.

The results are displayed in Figure 41 and Table 16 and are discussed after these figures. Assessing the results of the experiments, in step two, the toluene goes up by some 18%, not double, as would be expected from doubling of the input concentration. Visually inspecting the spectrum leads to the conclusion that either the initial or the additional injection of Toluene into the solution was incorrect. More important for this experiment, the reported counts of the other components, especially the xylene, which shares the major mass peaks with toluene, seem to be almost unaffected.

In step three the toluene goes up by another 12% in respect to the second measurement. There should have been no change from the last step.

In step four, xylene is added, and the toluene keeps going up by another 8% to the previous step. The xylene only increases by 27%, instead of the expected doubling. The counts for trichloroethylene rise by 23% and the counts for benzene rise by 12% instead of both remaining constant as would be expected. The other components are unaffected. Some of the rise of the toluene concentration might be assigned to the fact that toluene has a rather

simple spectral pattern and shares both of its major mass peaks with xylene. The rise in trichloroethylene and benzene, however, can not be explained with similarities in mass spectra.

Step five and six each add 4µl of dichloroethylene into the stock solution. The reported counts for dichloroethylene are going up by 83% and 41% compared to counts from the previous run. All other components seem to be unaffected by the change.

Step seven should be the same than step six. The dichloroethylene rises by another 9%. The xylene drops by 7.4%. Everything else stays within the acceptable tolerance stable.

Step eight and nine each add 4µl of trichloroethane to the stock solution. The reported counts for trichloroethane rise by 43% and 38%.

Step ten appears stable within the known repeatability of the instrument.

Step eleven cannot be compared with step ten, as there was an overnight break in the experiment. However, other than the trichloroethane, all components remained the same concentration.

Step twelve and thirteen add 4µl of trichloroethylene to the stock solution. The trichloroethylene counts rise by 110% and 53%. Other than a further upward trend in the trichloroethane and the dichloroethylene counts in step 13 the reading was stable. Step fourteen should have been the same as thirteen and other than a drop in the dichloroethylene and the benzene, all reported counts remain the same.

Figure 41: Analysing changing concentrations (normalised to 166amu)

Table 16: Percentage change, compared to previous step, reported by mixture analysis (The steps at which the concentration of the chemical was actually changed are highlighted in grey)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
trichloroethylene	0	-2.6	1.7	1.7	-1.1	-0.3	6.2	0.1	-0.8	-1.2	-1.8	109.4	52.8	-1.0
o-xylene	0	3.4	3.8	26.5	0.4	3.2	-7.4	2.0	5.1	-1.3	3.3	-3.1	-7.1	11.0
t12dichloroethylene	0	2.5	-2.8	8.9	82.8	40.9	9.4	4.7	-9.6	2.2	0.4	0.2	15.9	-20.8
tetrachloroethylene	0	2.6	-1.1	0.1	-1.6	-0.3	1.7	0.3	0.7	-2.4	1.2	-3.3	2.4	0.9
Toluene	0	18.0	12.2	7.8	-0.4	-0.3	-2.5	-2.7	9.7	1.9	-3.2	0.4	-3.6	-3.1
Trichloroethane	0	-0.8	-2.2	23.4	-1.7	1.6	5.4	42.5	39.7	5.5	21.1	-2.0	9.2	-0.2
Benzene	0	-3.9	-2.0	12.1	-2.0	-5.6	4.7	0.0	-1.2	4.6	-7.7	4.2	7.3	-9.2

From this it can be seen that the mixture analysis software, in most cases, is able to de-convolute a complex multidimensional mixture. However, there are still some questions. Why are the toluene counts in step two and four and the trichloroethane counts between step nine and thirteen still rising when the concentration of the analyte has not changed? Also, where does the change in the dichloroethylene in step thirteen and fourteen come from? Most of the other changes are within the expected repeatability of the method of the gas standard production.

In order to investigate the cause of the unexplained drift of some components observed during the experiment, it was decided to first examine whether there are adsorption/desorption problems with the tedlar bag. The rise of

toluene could be explained by the fact that in earlier experiments some of the analyte was adsorbed onto the sample bag and, therefore, the measured concentration was reduced. In consecutive measurements this adsorption might have reach saturation and the concentration in the sample appears to rise. Therefore the sample bag was filled as before, but no stock solution was injected into the injection port. This "span" check was performed between step ten and eleven, and did not report any significant counts for any of the components of interest. If the tedlar® bag had adsorbed toluene and trichloroethane, but not have reached equilibrium, then a rise in the two components of concern would have been already observed during the repeatability experiments described in Appendix 1. Additionally, between each of the injections the syringe was flushed with methanol to prevent cross contamination of the different concentrations of the stock solution.

For diagnostic, and in simple cases like the measured mix, it is possible to analyse the mass spectra of the mixture visually. The major peak of trichloroethane at 97amu is mainly shared with trichloroethylene. The other seven components share the 97amu peak only as a minor fraction. The reported counts for trichloroethylene are very constant between step nine and eleven. This means it should be possible to use the height of the 97amu peak (as every thing else normalised to the 166amu peak) to check if the software is failing, or whether there was a real change in the trichloroethane concentration. Doing so, a genuine increase of 1.5% and 19% is observed.

As the software reported unexpected results, it was decided to visually inspect the mass spectra. This inspection suggested that the spectrometer measured a real rise in the concentration of concern. It is not clear what caused this rise. The different possible causes could be adsorption/ desorption effects in the sampling line, changing getter-pump speed, contamination of the VOC solution, or changes in permeation rate due to interference with the methanol (a similar effect as discussed in section 3.2.10 on the interference of humidity). It can be concluded from this that the unexpected rises observed in toluene and trichloroethane are more likely to be a result of the supplied gas standard or a change on the spectrometer response than a misinterpretation by the mixture analysis. To correct this, the

experiment should be repeated with a more reliable gas standard mix, which was not available due to the large cost of the seven standards that would be required.

Within the limitations of these experiments and by additionally inspecting the spectra visually it was shown that the mixture analysis will work for a multidimensional analytical problem. Despite the fact only seven components were used for the analysis, the experiments suggest that there should be sufficient space for introducing further components into the analysis. This is only a valid assumption as long as the mixture analysis works with a complete library of the components in the sample (discussed in section 3.2.11). Another limitation as discussed in Appendix 4 is that none of the sample spectra used is a linear superposition of the other spectra in the library. Such a compound has not got any unique peaks, which means the mixture analysis will not be able to assign any counts and therefore calculate its concentration.

3.3. Comparison Study

In collaboration with Wyle Laboratories of Houston (Texas USA) working for the NASA, it was decided to compare the analytical performance of the MS-200 against GC/MS analysis. The background of this work was to assess if the MS-200 would be suitable to be used as a second generation VOC analyser on the international space station (ISS). This application is discussed further in section 5.4.1.

The list of components from section 3.1 was chosen. These components represent the different groups of chemicals that are typically found in a spacecraft environment.

Two samples were prepared and analysed by GC/MS by Wyle. The sample contained some of the components from Table 6 at a concentration within the calibration range. Additionally, Wyle chose some other components to be introduced into the sample. After calibrating the MS-200 for the list of components in Table 6, the two samples were analysed. Only once the

MS-200 measurement had been reported to Wyle, was the author informed of the actual chemicals and concentrations in the two samples.

3.3.1. Calibration of the MS-200

Bearing in mind the effect of humidity discussed in section 3.2.10, it was decided that an attempt should be made to use calibration data taken from a humid rather than a dry sample. As the humidity was not known at this stage it was decided to perform a calibration at approximately 30% relative humidity. The selection of this humidity range was a trade-off between humidity levels encountered in a spacecraft environment, which are likely to be in the 80 to 100% range, and the limitation of the humidifier used. When performing this experiments the use of the Nafion dryer as described in section 3.2.10 was not available.

A background spectrum of nitrogen at 28% relative humidity was first collected, then the calibration standard was supplied at 60% concentration and a relative humidity of 28%. The calibration run consisted of 30 experiments of 30 seconds, with a delay of 30 seconds between them. Multiple calibration experiments were performed to check the stability and the equilibrium of the calibration mix. The library used for data processing is shown in Table 17. The full calibration run is shown in Figure 42.

Table 17: Library used for the analysis of the sample

o-xylene	Ethylacetate
n-hexane	Methanol
Toluene	Ethanal
Dichloromethane	2-propanol
Trichloroethane	CO_2; O_2; H; H_2O; N_2; Ar

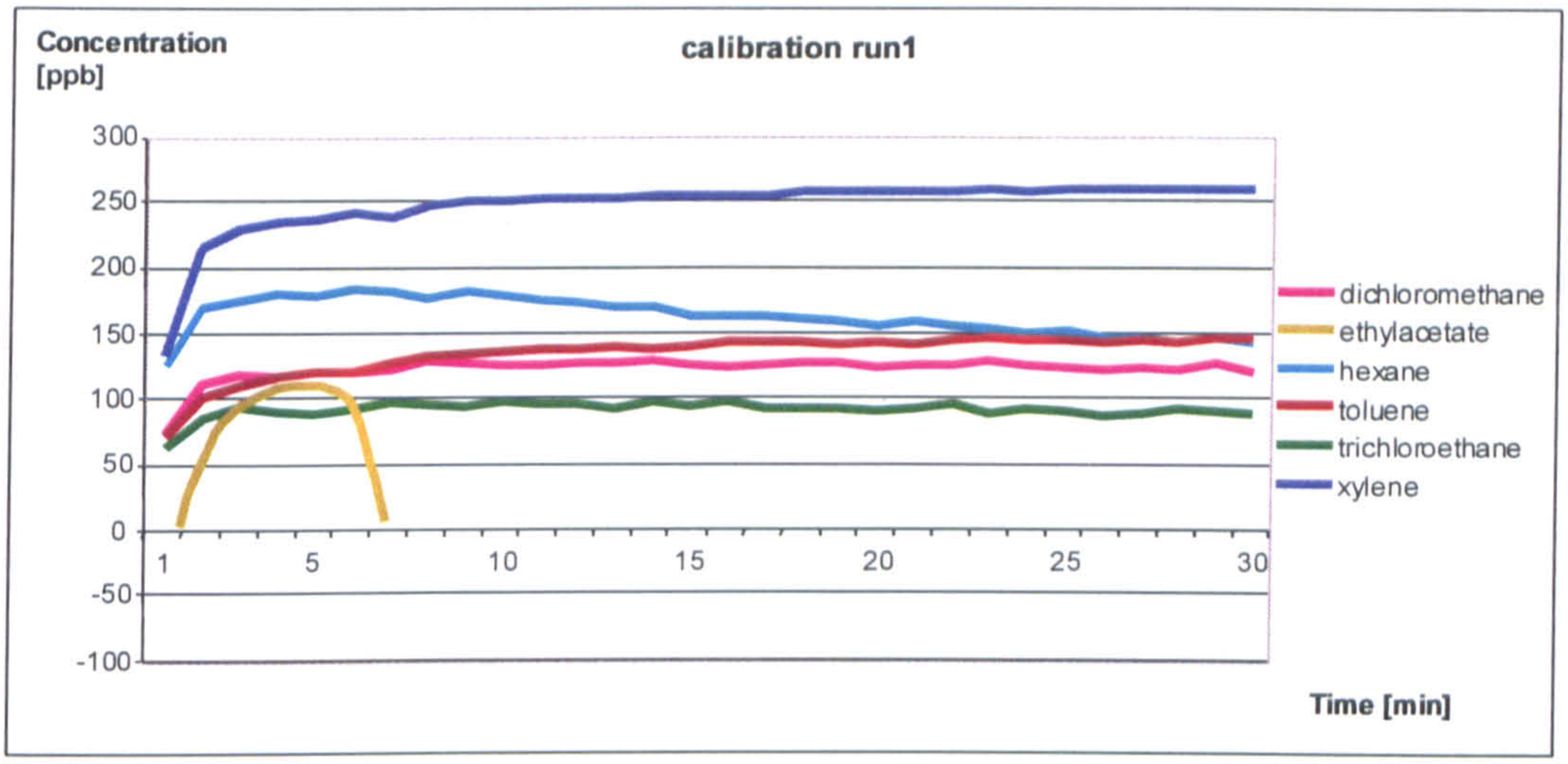

Figure 42 - calibration run for the analysis of challenge mixtures

All the responses for the components are acceptably stable, except for ethylacetate. The curve for ethylacetate follows a strange pattern. Comparing the curve for ethylacetate to Figure 32 produced earlier in the project suggests that the calibration standard was becoming unstable. The pressure in the calibration cylinder was down to approximately a 1/20th of the initial pressure, which could be the reason for the strange behaviour of the ethylacetate measurement. Therefore it was decided not to include the concentration for ethylacetate into the reported results.

Comparing the RSFs for this calibration run with the RSFs measured in section 3.2.10, (shown in Table 12) for the calibration at 26% relative humidity, we apparently see a large reduction in sensitivity for all components except ethylacetate. This could be caused by the detector reaching the end of its life and therefore the sensitivity of the instrument dropped.

Table 18 - Change of RSF between earlier Experiment and the final calibration run.

	RSF from 3.3.1
o-Xylene	592,616
Dichloromethane	19,809
Ethylacetate	34,102
n-Hexane	96,259
Toluene	216,534
Trichloroethane	33,952
Ethanal	No RSF could be determined

This calibration now allows analysis of the two samples of unknown composition and concentrations that were prepared and analysed by GC/MS analysis by Wyle Laboratories. Given the curves in Figure 42, it was decided that the data at 5 minutes would probably give the best calibration from this set.

3.3.2. Measurement of Comparison Mixture 1

After the calibration experiment, a period of approximately half an hour was allowed for the MS-200 to drop down to a stable base line. During this time nitrogen at 28% relative humidity was supplied to the system.

Before supplying mixture 1, a new background spectrum was established. After this the comparison mix 1 was connected to the sample inlet of the MS-200. Mix 1 was then analysed in the same way as the calibration run, with 30 second experiments, one per minute for 30 minutes. The results are shown in
Figure 43.

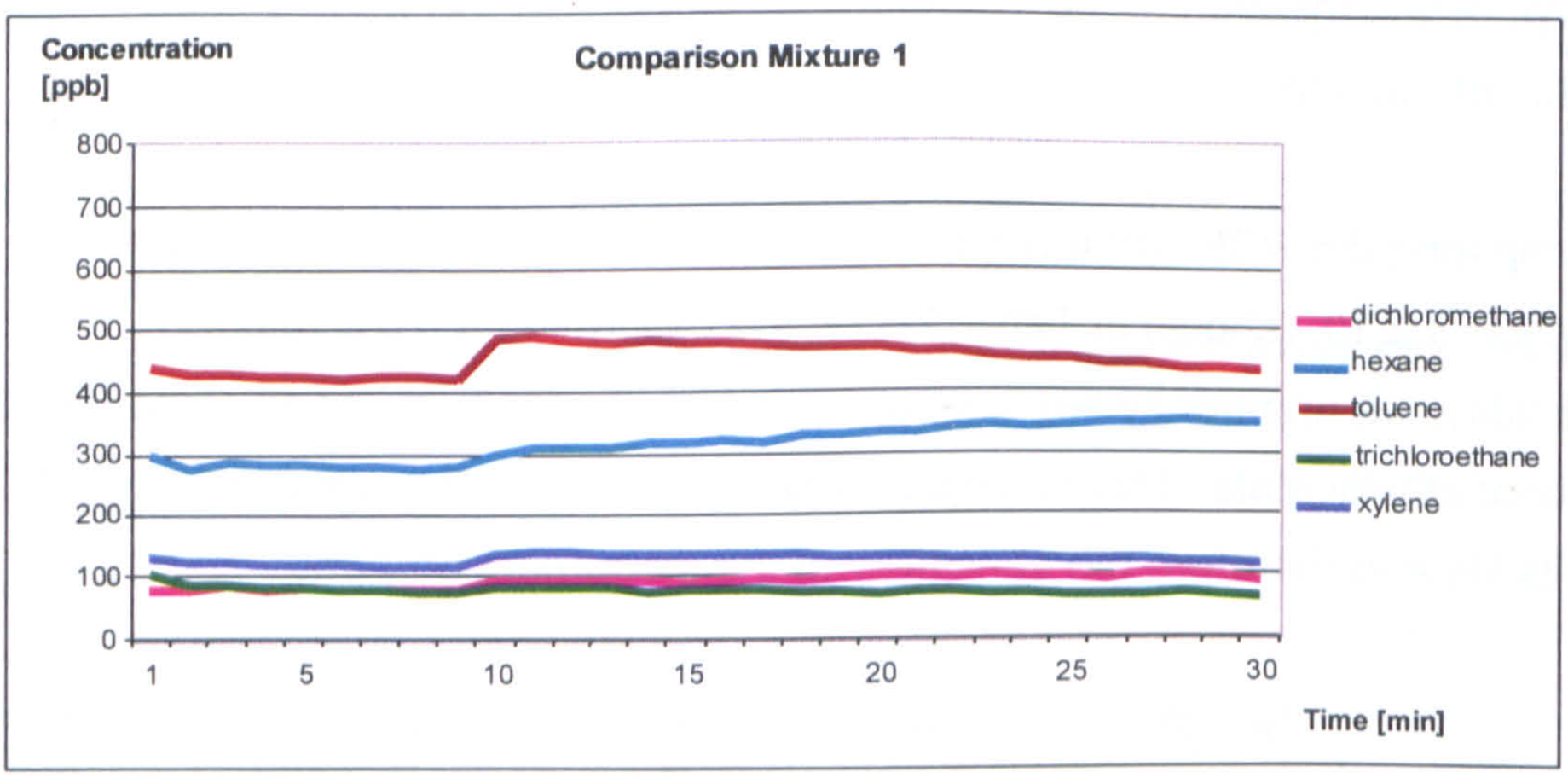

Figure 43 - Analysis of Comparison Mix 1, (calibration from this chapter)

The reported concentrations of the components follow a similar pattern to that observed during the calibration run. However, there is a strong rise for all of them at 10 minutes. This was due to the fact that during the first

10 minutes the flow of sample gas was slowly decaying, and at approximately 10 minutes the flow was re-adjusted. Therefore, the best analysis should probably be taken at around 15, 16 and 17 minutes to compensate for this adjustment. The concentrations reported from mixture 1 are shown in Table 19.

Table 19: Analysis of Mix 1

Values are calibrated as in 3.3.1 and the RSFs for alcohols are taken from 3.2.7
* BQL: Below Quantification Limit
+CNV: Calibration Not Valid

	15	16	17	minutes
Dichloromethane	89	95	99	ppb
Ethylacetate	+CNV	+CNV	+CNV	
n-Hexane	319	322	319	ppb
Toluene	479	478	477	ppb
Trichloroethane	78	79	79	ppb
o-Xylene	135	134	134	ppb
2-Propanol	11.9	12.3	13.6	ppm
Methanol	1.58	1.59	1.68	ppm
Ethanal	BQL*	BQL*	BQL*	

The alcohol concentrations are based on rather approximate RSF measurements as discussed in section 3.2.7. Ethanal values are below the quantification limit of the MS-200 and therefore no concentration could be calculated.

3.3.3. Measurement of Comparison Mixture 2

After waiting for another half an hour, the MS-200 was flushed with clean nitrogen at 28% relative humidity and comparison mix 2 was analysed in the same way as comparison mix 1. The results are shown in Figure 44.

The mixture analysis software consistently reported a concentration for toluene below the detection limit, together with a very high relative standard deviation, which suggests that there was no measurable toluene present in the standard. Hexane seemed to drift from 92ppb to 247ppb during the length of the experiment, assumed to be caused by a change in humidity, as discussed below.

During the measurement there was a slight increase in the relative humidity of the gas mix delivered by the cylinder, from 35% to 45% relative humidity. This could not be explained, but was also observed by other parties participating in the comparison study, analysing similar comparison mixes. As shown in section 3.2.10, this would influence the sensitivity of the MS-200. In this case, the data collected after 5 minutes was selected for the analysis to be consistent with the calibration run. This time there was a definite response for ethanal in the sample. As it was not possible to obtain an RSF for the ethanal, no concentrations are reported. The results are presented in Table 20, which therefore only reports the counts that the mixture analysis assigned to the ethanal. As described in section 3.2.6, the number of counts assigned to a component show a linear relationship with the concentration.

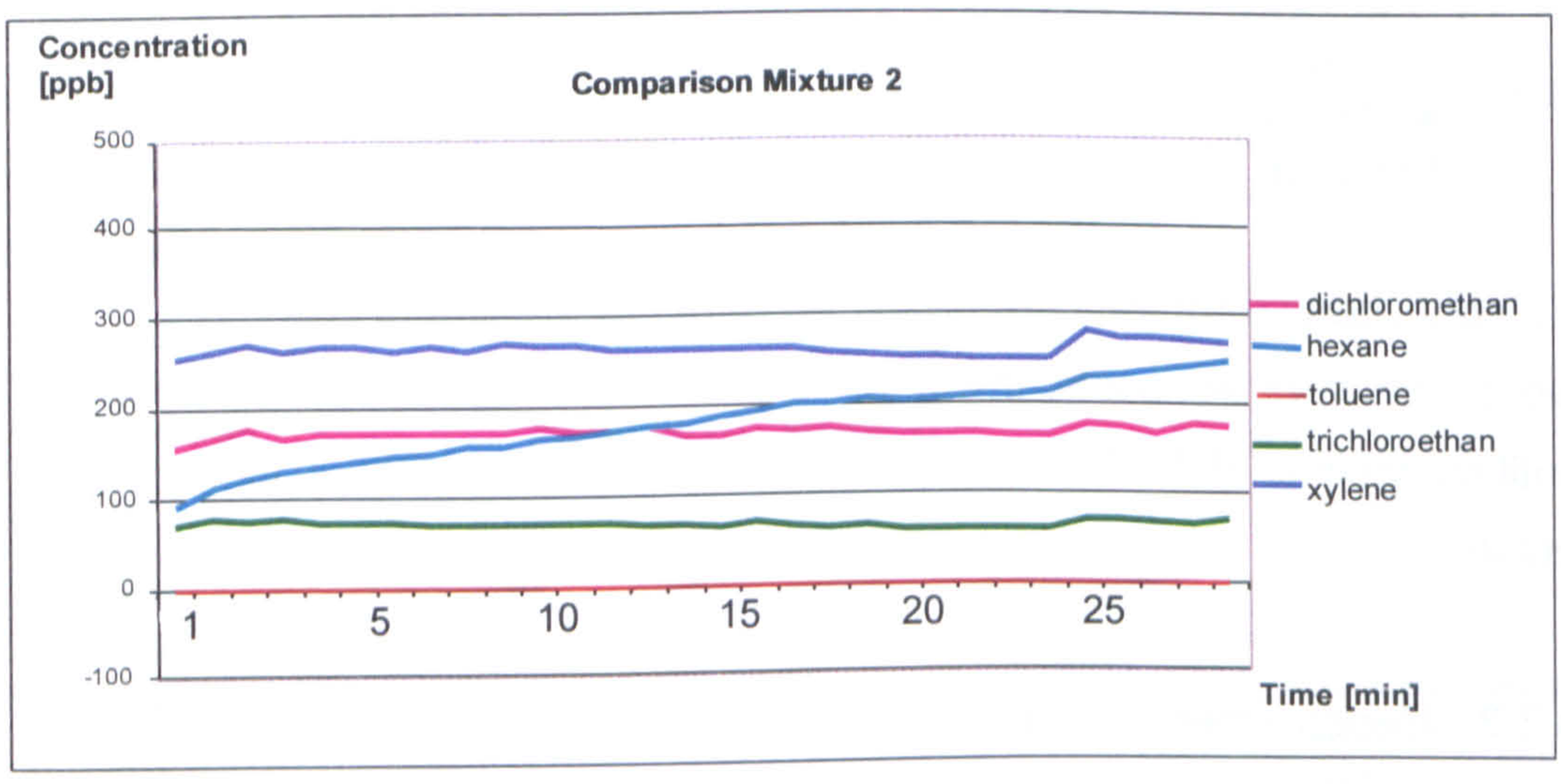

Figure 44 - Analysis of Mix 2, using the calibration from section 3.3.1

The concentrations reported by the MS-200 for mix 2 were:

Table 20: Analysis of Mix2

*CNV: Calibration not Valid

+BQL: Below Quantification Limit

Values are calibrated as In 3.3.1, and RSFs for alcohols are from section 3.2.7

	Data Collection Time (minutes)			
	5	6	7	
Dichloromethane	173	173	173	ppb
Ethylacetate	970	1117	1242	CNV*
n-Hexane	136	141	146	ppb
Toluene	BQL+	BQL+	BQL+	ppb
Trichloroethane	75	74	75	ppb
o-Xylene	268	268	266	ppb
2-Propanol	60	61.7	62.8	ppm
Methanol	511	623	765	ppb
Ethanal	759k	755k	751k	counts

Note that Ethanal could easily be detected in this sample with good statistics. A RSF value was not measured for Ethanal during this project so the counts have been reported instead of a concentration. If, for example, the RSF for Ethanal was similar to the alcohols (~1,000) this would imply a concentration of 100ppm.

The background subtracted mass spectrum and the reconstructed stick plot from the mixture analysis is shown in Appendix 8. By visually inspecting these spectra, it can be seen that both the mixtures contain peaks that are not included in the library. The same peaks were unaccounted for in both mixtures. This suggests that there were one or more additional compounds present in the mixtures. No attempt was made to identify these components, as this would have required knowledge of the conditions under which the samples were prepared.

3.3.4. Comparison to the "NASA" concentration

Only once the results of the measurements of the two mixes were reported, the expected concentrations measured by GC/MS, were revealed by Wyle. Table 21 shows the concentrations for the two mixes, as given by Wyle Laboratories, and compares them to the by the MS-200 reported values from section 3.3.2 and section 3.3.3.

As discussed in section 3.3.2 and section 3.3.3, the calibrations for the alcohols methanol and propanol are very coarse, and are strongly affected by the relative humidity of the sample and the calibration problems. Therefore, these values are quite far from the expected concentration. The same is valid for the ethyl acetate where calibration problems were encountered. Additionally, mix2 had a significantly different humidity, measured by the Testo humidity meter, than that reported by Wyle.

The other measured values were within acceptable limits, given the fact that two different analytical methods (GC/MS and MIMS) were used, and that most of the measured concentrations were below the theoretical quantification limits (Table 10) for the components with the MS-200. The accuracy of analysis of the comparison mixes are given with ± 10%, the calibration standard from section 3.1.1 used for the MS-200 was reported to within ± 10% and the actual accuracy of the MS-200 is in the range of ± 10%. This results in a theoretical accuracy for the total process of approximately ± 33%.

Table 21 – *Comparison of Kore to NASA Concentrations.*
Numbers highlighted in blue, means that the calibration was not reliable
x means no calibration was performed
y means that these components were in the mix, but not requested to be measured

	Comparison of Mix 1				Comparison of Mix 2		
COMPONENT	Wyle	Kore	Differ-ence		Wyle	Kore	Differ-ence
	ppb	ppb	ppb		ppb	ppb	ppb
Methanol	100	1580	1480		330	511	181
Ethyl Acetate	40	x	x		120	x	x
2-Propanol	700	11900	11700		94	60000	59906
Ethanal	220	x	x		150	759000	x
m-Xylene	100	135	35		310	268	-42
Toluene	370	479	109		40	0	-40
Dichloromethane	45	89	44		190	173	-17
1,1,1-trichloroethane	130	78	-52		28	75	47
Hexane	280	319	39		40	136	96
Acetone	140	y	y		270	y	y
Ethanol	380	y	y		900	y	y
Benzene	20	y	y		29	y	y
Octamethylcyclotetrasiloxane	600	y	y		700	y	y
Methane	101000	y	y		298000	y	y
Carbon Dioxide	0	y	y		8986000	y	y
Humidity	47%	43%			71%	42%	

3.4. Assessing Performance Parameters for Unknown Chemicals

As it is not possible to investigate the performance of the instrument to every chemical that might be encountered in an application, this section describes how the performance may be assessed for unknown or less known chemicals. In order to do so it is possible to take some simple and quick measurements and interpolate the performance of the instrument for a particular chemical based on the experience from the thorough investigation of other chemicals. The performance parameters of main interest are sensitivity, detection limit and the speed of response.

3.4.1. Assessing Sensitivity and Speed of Response for new chemicals

To measure the sensitivity and speed of a new component, a standard of a known concentration of the component in the 1 to 10ppm range should be introduced into the inlet of the MS-200. In most cases, a convenient way to

produce a known concentration is by injection of the liquid sample into a known volume of air or nitrogen in a sample bag, described in section 3.1.2.

After establishing a background spectrum of clean air or nitrogen, the sample is supplied to the spectrometer. Immediately after supplying the standard, a series of experiments need to be performed. For example, an experiment of 10 second measurement duration followed by 50 second delay. This will result in the measurement of one data point every minute. If the component under investigation is expected to have a high speed of response, the frequency of measurement can be increased to more than 1 datum per minute.

After the experiment, a plot of the area of the major mass peak[3] from the component over time is produced. The plot of the area over time normally follows an exponential curve towards a stable value. By analysing the curve it is possible to determine the time that is required for the peak area to reach 90% of the final values. Within the work of this thesis this is referred to as the delay time for the component of interest.

Figure 45 shows the response of the MS-200 for diethylether ($C_4H_{10}O$) which has the major mass peak at 31amu. The supplied standard was produced by injecting 1µl of diethylether into 5 litre nitrogen, which results in a concentration of approximately 78ppm. As described above, data points were collected at a frequency of 1 datum per minute.

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[3] The major mass peak within the mass spectrum of a component is not always the peak that corresponds to the molecular weight of the sample (like benzene that has a molecular weight of 78g/mole and the major mass peak at 78amu). Dependent on the break down pattern the major mass peak can be one of the break down products like in the example of diethylether, which has a molecular weight of 74g/mole and the major mass peak at 31amu. It is very difficult to asses the major mass peak of a component and therefore it is advised to consult a existing data bank of 70eV electron impact mass spectra like the NIST database.

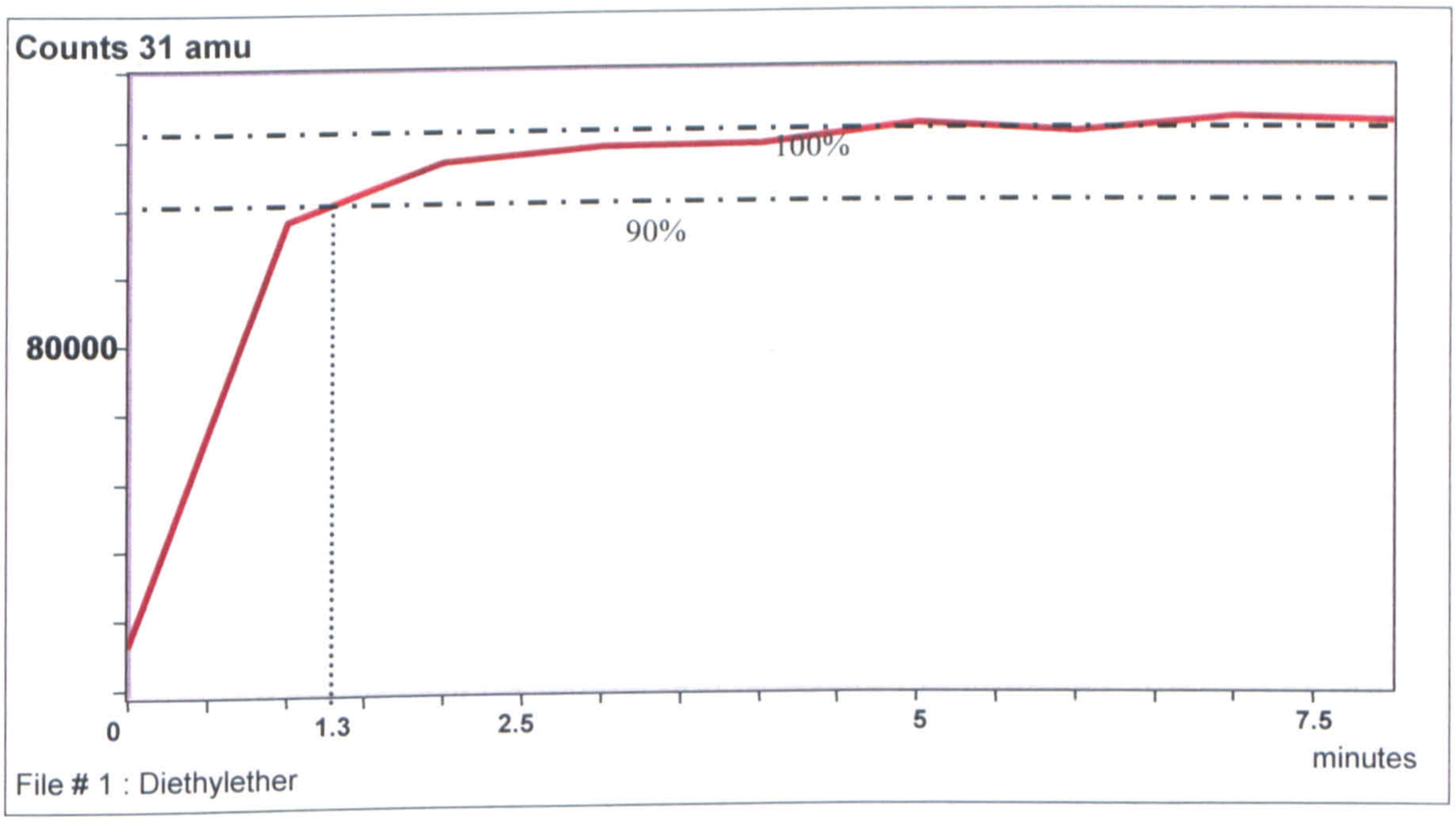

Figure 45: MS-200 Response to Diethylether

Using the area of a peak it is possible to estimate a value for the sensitivity of the MS-200 to the measured component[4].

$$S = \frac{A_S - A_B}{c}$$

S = Sensitivity [counts/ppb]
A_S = Area of the major mass peak at a stable response [counts]
A_B = Area of the major mass peak in the background [counts]
c = Concentration [ppb]

Equation 5: sensitivity estimation based on the major mass peak

[4] For example, dependent on the tuning of the instrument, the sensitivity for benzene is typically in a range from 40 to 70 counts /ppb in the peak at 78amu.

3.4.2. Assessing Detection and Quantification Limits for new chemicals

By analysing multiple clean background measurements, the mixture analysis will report different concentrations for each measurement for the component under investigation.

As discussed in section 3.2.8, the detection limit is defined as the point at which a sample signal clearly exceeds the noise of the background signal. If this threshold is exceeded, then, within an acceptable confidence, it can be stated that the compound is present in the sample and can be detected with the instrument. Determining the detection limit of an instrument therefore requires multiple measurements of a clean background and the calculation of the standard deviation of the results. As explained in section 3.2.8 the definition of detection limit used in this thesis is defined as $3 * \sigma$.

It is not always feasible to collect sufficient background measurements to perform a statistically significant analysis of the measured background noise. Therefore, as an alternative, the variation σ in the background noise can be estimated from the counting statistics of the background signal measured. As in section 3.4.1, the major mass peak of the component of interest is chosen to represent the variation σ of the background measurement. The calculation to estimate the standard deviation of the background, based on the major mass peak, is given in Equation 6.

$$\sigma = \frac{\sqrt{A_B}}{S}$$

σ = standard deviation of the background reading [ppb]
A_B = Counts of the major mass peak in the background [counts]
S = Sensitivity of components measured [counts/ppb]

Equation 6: Estimation of Detection Limit

It was found that the difference between the estimated detection limit and the full measurement of detection limit is typically only a few ppb. The difference between the estimate and the measurement is due to the fact that the full

measurement takes all peaks of the fragmentation pattern of a compound into account, however the estimation considers only the major mass peak. For components with a very simple mass spectrum, like for example methane, the estimation is very close to the full measurement. If it is a complex mass spectrum of a compound, then the estimation is less reliable. Additional caution in using this method has to be taken if the major mass peak of the component interferes with peaks from the background matrix.

The proposed method is a very useful tool for a fast estimation of some important parameters of a chemical under investigation. For precise determination, the full measurement of the parameters using the mixture analysis is required. The full measurement should be also performed if the component has a complex fragmentation pattern, peak interference with the background or if it is available as a mix only and not as a single component.

3.5. Conclusion - laboratory performance of the MS-200

This section has reviewed some of the performance specifications of the MS-200 that were discussed and measured in this chapter. The ability of the MS-200 to measure a large variety of chemical components, each of which causes a different response by the instrument, does not allow one to easily make general statements on the performance parameters. As a result, it was decided to measure performance parameters for different groups of chemicals. The following reported observations, therefore, are only guideline values that are valid for the reported groups of chemicals. With some experience the performance towards a specific, not yet fully investigated, compound can be estimated from comparison with parameters of similar compounds.

— Sensitivity

The sensitivity towards different chemicals can vary significantly. The major difference in sensitivity is caused by the different permeation rates of chemicals through the inlet membrane.

Relative sensitivity factors (RSF), as measured in section 3.2.6 and 3.2.7, can therefore vary from about 200,000 down to a few 100. This is compared to nitrogen having an RSF of 1. As found in this chapter, the MS-200 has poor sensitivity to low molecular weight polar components, such as alcohols, but very high sensitivity to aromatic and chlorinated hydrocarbons.

Independent of the problems of sample preparation and transfer to the MS-200 inlet, it was found that the sensitivity can be influenced by possible adsorption of compounds onto the inside of the vacuum chamber. Additionally it was found that there are possible interactions with humidity of the sample, especially when analysing polar components. The influence of humidity is explained in detail in section 3.2.10. Table 34 (section 6.2) lists the sensitivity for various compounds measured during the work on this thesis.

— Detection limit

The detection limit is determined by three main factors, sensitivity, the background signal for the component under investigation and possible interference with the matrix gas. Detailed description on definition and measurement of the detection limit is given in section 3.2.8, and section 3.4.2.

The detection limit of the MS-200 for different components can vary from 2ppb (3σ) for the xylenes to few ppm for alcohol and further to a few hundred ppm for some other components. For an extensive list of components and their detection limits that were measured during the work on this thesis, refer to Table 34 (section 6.2).

— Speed of Response:

Speed of response is a measure of how fast the instrument is able to follow a step change of the input concentration. It is important to know this time in order to allow for sufficient time before a quantitative measurement can be taken. Response time in this thesis is defined as the time required to reach

90% of the final value when performing a step change in concentration on the input.

The speed of response can vary from a few seconds for benzene to a few minutes for polar components like the alcohol methanol and propanol. Some examples for the speed of response can be taken from Figure 32 and Figure 34 to Figure 39 in sections 3.2.4 and 3.2.5. Additionally, where measured, Table 34 (section 6.2) lists approximate speed of response for some components.

Like for the sensitivity, it was found that the speed of response for low molecular weight polar alcohol, such as methanol and propanol, is strongly influenced by the moisture content of the sample. The response time will be faster with higher moisture content.

The different speed of response for different components can be used as additional information about a sample when attempting to identify unknown components by a mass spectral library search.

— Linearity

The measurement of the linearity of the instrument is described in section 3.2.5 and is given as ± 6% for xylene for the data set in Figure 34. As with the other parameters described in this section, there is a variation of the linearity dependent on the chemical measured. Most of the chemicals in this thesis that were thoroughly investigated produced a response that is linear within ± 10% for a range from approximately five times the detection limit to around 1000 times the detection limit.

As discussed in Appendix 5, linearity is no longer achieved once a single peak within the spectrum has reached saturation. This means that the measurement is not valid and should be repeated using a diluted sample.

— *Influence of moisture*

The influence of moisture within the sample on the sensitivity of the instrument depends on the chemical of interest. The influence of moisture can be as high as a doubling in sensitivity when moving from 0% to 50% relative humidity (section 3.2.10, Table 12). A very interesting observation for the polar low molecular weight alcohols methanol and propanol was that the speed of response for a step change was reduced from somewhere in the range of 8 minutes, down to less than 3 minutes with increasing humidity. This supports the theory that there is competition between the water and the sample for active sites within the membrane and therefore the permeation characteristics is changed.

The acquired knowledge has lead to the use of a NAFION® dryer to remove water from the sample. Unfortunately this dryer also affects some other chemicals that might be analysed. For example it will also remove the low molecular weight alcohol. Therefore using the dryer, the sample has to be assessed carefully and it has to be identified if some parts might be affected by the dryer.

The use of NAFION as a sample dryer is well understood and is described in the US EPA method TO14 (EPA 1996) that describes the measurement of VOCs in ambient air. A very thorough description of the working principles of NAFION and a list of the components that are removed or are affected can be obtained from the manufacturer of the equipment (Permapure 2002).

4. Sensitivity Enhancement for the MS-200 Using a Trap Evacuate Desorb (TED) Interface[5]

The MS-200 in its standard set-up uses a double membrane pre-concentrator as a sample inlet to the mass analyser. As can be seen from chapter 3 of this thesis, this inlet system is very suitable for the analysis of aromatic and chlorinated hydrocarbons and other selected volatile organic compounds (VOCs). With the double membrane inlet, analysis can be performed semi-continuously down to low ppb levels. A drawback of the system is that the detection and the sensitivity of the measurement depend on the ability of a component to permeate through the membrane. In the case of polar or oily components this limits the detection to ppm levels (section 3.2.7). Also for VOCs that have detection limits in the low ppb levels, some applications would benefit from the detection limit being lowered even further into the mid to low ppt levels.

It was proposed that a further pre-concentration of the sample onto a adsorption trap, like those used in thermal desorption systems for gas chromatographic (GC) analysis (Nuber 1994), might improve the detection limit of the MS-200 for VOCs.

An ideal adsorption trap will selectively collect traces of VOCs from a sample stream that is passed through the trap, but will not collect any of the major compounds in the air (N_2, O_2, CO_2, H_2O). In this way the trap material will filter out and hold onto traces of VOCs, building up sufficient quantity of trace contaminants to allow later analysis. One of the methods to remove the collected VOCs from the adsorbent is by washing the trap material with a solvent, and this solvent is then analysed for its VOC content. A more common method of desorption is removal of the VOCs by heating the trap material, releasing the analyte into a gas stream which is then passed through a gas chromatograph and analysed (Sanchez, Sacks 2003, Lord et al. 2002, Phillips et al. 1999a)

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[5] The TED interface was patented by Kore Technology in 2002.

As opposed to the two usual methods described above, it was proposed to thermally desorb the trap by using pressure lower than that of the ambient value. This increases the initial concentrating effect of the trap, achieved by sampling the trace levels from a large volume of air. Evacuating the tube to 1 mbar before desorption, rather than at atmospheric pressure (1013mbar), results theoretically in a further concentration factor of 1013, relative to air (mainly N_2 and O_2) molecules. This novel method seems particularly suitable for the membrane inlet of the MS-200, as it uses a pressure step down to 1 mbar across a first membrane, before a final pressure step across the second membrane into the ultra high vacuum (UHV) of the analyser chamber (see section 2.4).

As described in section 2.4, the standard membrane concentrator of the MS-200 results in an enrichment of benzene at a factor of around 100 per membrane (LaPack et al. 1994). Using the TED results in the lack of the enrichment of the first membrane (which is omitted for desorption experiments) but which is more than compensated by evacuation of the desorption space and the enrichment of a large sample volume onto the trap.

4.1. The Desorption Interface

In order to conduct the experiments planned within this PhD, a special interface was needed. This interface must allow an adsorption tube to be fitted so that it can be exposed directly to the intermediate vacuum of the MS-200 inlet system. It then must be able to be heated up, causing desorption of VOCs from the trap material.

The interface developed consists of two main parts, an evacuation interface, as described in section 4.1.1 below, and a desorption oven. The desorption oven is designed to allow an increasing temperature and therefore enabling the thermal desorption of the analytes from the trap, and is described further in section 4.1.2. This system, consisting of an evacuation interface together with a desorption oven will be referred to as the Trap Evacuate Desorb (TED) interface.

4.1.1. The Evacuation Interface

The new system must allow the sample to be passed into the vacuum of the MS-200 analyser chamber. To allow this, a special interface was machined from stainless steel. Figure 46 shows this interface, which replaces the standard outer membrane holder and outer membrane so that the adsorption tubes can be fitted to the MS-200. The tubes are sealed onto the interface by means of a 1/4" Swagelock fitting welded onto the interface. In order to avoid memory effects from polymer seals, it was decided to use graphite ferrules for the Swagelock fitting and seal the interface to the existing inlet by means of a gasket made from indium wire.

The evacuation of the air from the space created between the adsorption trap and the inner membrane of the analyser was done using the peristaltic pump, which is normally used to evacuate the pressure step between the outer and the inner membrane in the double membrane configuration of the MS-200. This way, the trapped VOCs will be desorbed into a vacuum of about 1 to 2mbar before permeating through the inner membrane into the ultra high vacuum (UHV) of the analyser chamber to be analysed.

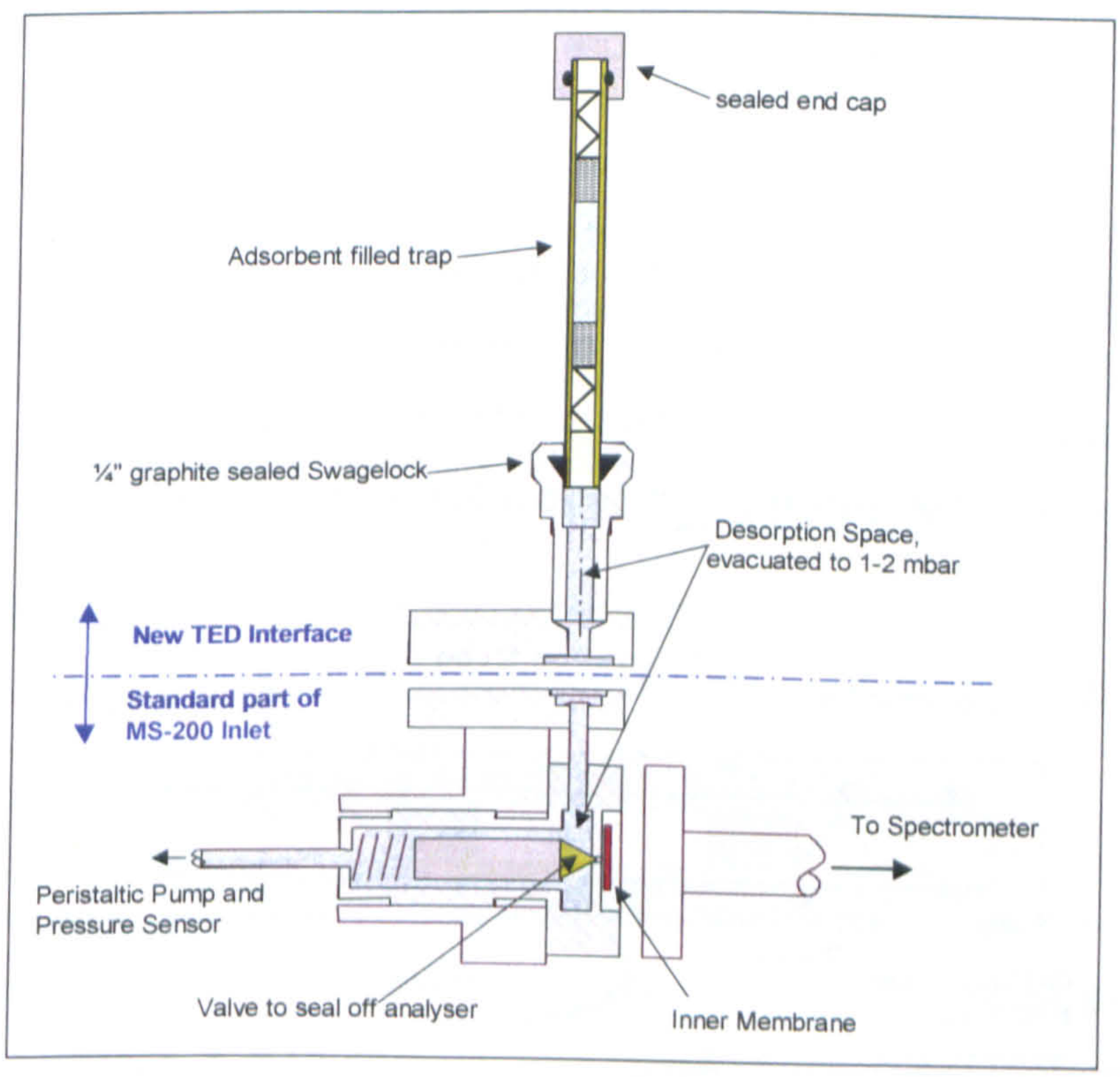

Figure 46: Schematic of the MS-200 TED Option

4.1.2. The desorption oven

To allow thermal desorption using the evacuation interface described above, the adsorbent trap needs to be heated to a temperature of between 100 to 300°C. The desorption temperature is dependent on the trap material chosen and the analyte to be desorbed. To keep analysis time short, and to avoid dilution of the sample due to permeation of the sample into the analyser, this heating should be achieved relatively rapid. To allow monitoring of the temperature the heater should be fitted with a temperature sensor, recording a temperature that is representative for the temperature of the trap material inside the trap tube. This heater should slide easily over the trap, to allow changing of the adsorbent trap, but fit tightly enough in order to provide good heat transfer to the tube.

Figure 47 shows the design of a micro-furnace, or desorption oven. This oven fits around the adsorption trap and includes the heater and temperature sensor.

Heating is achieved by applying a voltage to a nickel wire, supported in a cylinder of a high temperature ceramic. A thermocouple is placed inside the heater, on a location where temperature reading is representative of the temperature inside the trap material.

The heater is tailored to suit the commonly used glass or stainless steel adsorption tubes of 6.35mm diameter and 90mm length. By sliding the tubes into the heater, tubes can be changed quickly and easily. This oven is capable of heating the adsorption tube to a temperature of 450°C.

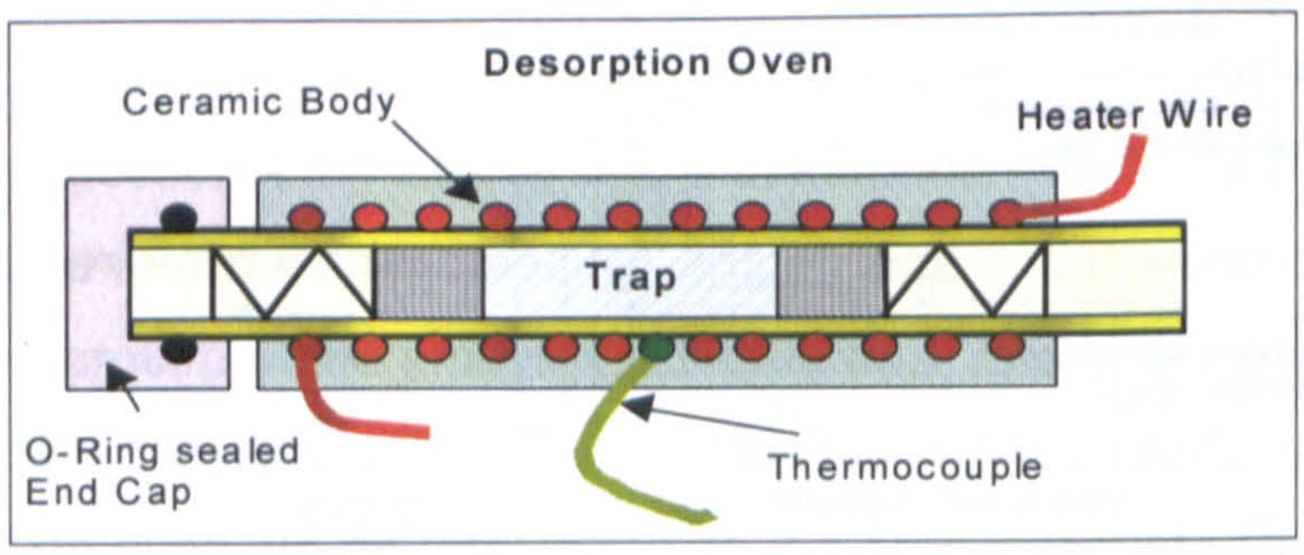

Figure 47 The desorption oven

The temperature of the heater is controlled using a commercially available temperature controller together with a 24V switch-mode power supply and a power regulator. The controller is programmable to change the temperature in a slow ramp, or to perform a step change of temperature. In order to speed up the cooling of the tube, a fan cooler is installed next to the heater and is switched on and off from the controller.

At full power, the heater requires about 60 seconds to follow a step change of the controller from 30°C to 200°C. The temperature of the adsorbent was measured with a thermocouple introduced into the centre of the adsorbent material. The deviation of the temperature of the adsorbent to the one reported by the thermocouple placed inside the heater is less than 20°C during the heating ramp. This difference reduces to a few °C once the final temperature is reached.

4.2. The Adsorbent Material and Defining Breakthrough Volume

Choosing the right adsorbent for the chemicals that are to be analysed is an important step in the production of the adsorbent trap. An ideal adsorption trap will selectively collect traces of VOCs from a sample that is passed through the trap, but will not collect any of the major compounds in the air (N_2, O_2, CO_2, H_2O). Adsorption traps contain resins with a large surface area to volume ratio, that have a high affinity to adsorb the chemicals that are passed through them. Different trap materials have differences in their affinity for lighter or heavier VOCs (i.e. the larger or smaller number of carbon atoms in the molecule). Affinity is also highly temperature dependent, and decreases with increasing temperature. Therefore a trap material should be chosen to suit the range of VOCs to be analysed. A manufacturer of various adsorbent materials gives a good description of the selection of adsorbent resins (SIS 2002b).

Affinity of an adsorbent to a VOC or other chemical to be collected can be described by means of the breakthrough volume (Jones et al. 1996). Scientific Instrument Services, a manufacturer of a range of adsorbent materials defines the breakthrough volume as the volume of carrier gas that will purge

an analyte through one gram of adsorbent resin in a desorption tube at a specific temperature (SIS 2002e) (Jones et al. 1996).

The measurement of breakthrough volume is performed by an injection of a liquid sample into one end of the adsorbent. The amount of air that is needed for the component to be purged through the adsorbent volume and to appear at the other end is measured. The breakthrough volume of the adsorbent trap is then defined by Equation 7 (SIS 2002a):

$$B_V = R_T * F / W_A$$

Where:
B_V = Breakthrough Volume (litre/gram)
R_T = Retention Time (seconds)
F = Flow Rate (litre/seconds)
W_A = Weight of the Adsorbent (gram)

Equation 7

Breakthrough volume is normally given as litre per gram, or litre of sample for the specific trap used.

This means that once the breakthrough volume of an adsorption trap is reached, the collected VOCs will leak out of the exit of the tube. The concentration of the analyte of interest in air has to be calculated from the amount of analyte on the trap and the volume of air pumped through the trap. Up to the point where the breakthrough volume is reached this relationship is linear. Once the breakthrough volume is exceeded this linear relationship breaks down, and the amount of analyte on the trap is no longer representative for the concentration of an analyte in the sampled air. As a result of this, it should be ensured that the breakthrough volume of the chosen trap material and the analyte of interest is sufficiently high to be able to collect as much material onto the trap as is needed to perform a meaningful analysis afterwards.

For these initial experiments the adsorbent used was Tenax TA® (Tenax). It is a porous polymer resin and was specially designed for the trapping of volatiles and semi-volatiles in gaseous form. Tenax has a low affinity for

nitrogen and water, which allows the removal of water from the sample prior to analysis. The most extensive study of breakthrough volumes for different compounds, at different temperatures is given by the manufacturer of Tenax, who describes the breakthrough volume of Tenax for up to 16 temperatures between 0°C to 300°C for some 200 components (SIS 2002d). These physical and chemical properties of Tenax make it a widely used adsorbent material for VOC analysis (Lu, Zeller 2001, EPA 1996) and was therefore chosen for the initial thermal desorption experiments. Another commonly used adsorbent material is activated carbon (Pfeffer et al. 1995, Qin et al. 1997, Zabiegala et al. 2003), but the need for very high desorption temperatures makes it less suitable for the proposed experiments.

4.3. Adsorption Tubes

The adsorbent tubes used for the initial experiments are silicate glass tubes with an external diameter of 6.35mm, internal diameter of 4mm and a length of 90mm. These tubes were filled with approximately 125mm^3 of Tenax TA® (around 31mg of material). The adsorption material was held in place with a plug of glass wool on either end. Additionally a retaining spring made of nickel wire was introduced to retain the glass wool to avoid losing the packing when sudden changes in pressure occur. A schematic of the tubes is shown in Figure 48.

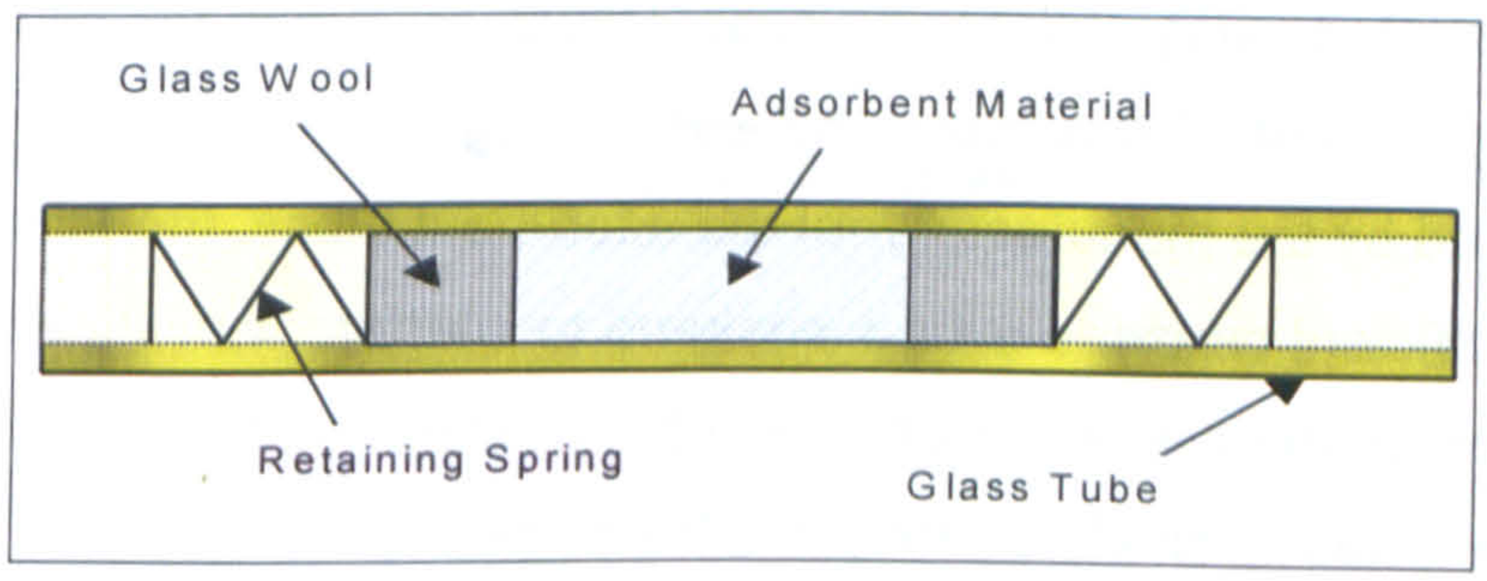

Figure 48 Schematic of the Adsorption Tube

4.4. Cleaning the Adsorbent Tube

Prior to use, the adsorbent in the adsorbent tube has to be cleaned to remove all traces of adsorbed matter from previous experiments. To achieve this the tube was fitted into the desorption oven and heated to 250°C. A flow of 200ml/min of dry nitrogen was passed through the tube. At this temperature the breakthrough volume for benzene is reduced from 70 at 20°C to 0.001 litre per gram of adsorbent (SIS02d). As the trap used contains about 31mg of adsorbent resin, this relates to a breakthrough volume of 0.31µl of nitrogen. Purging the tube for five minutes, 1000ml of nitrogen are passed through the trap, which is sufficient to clean out benzene and most of the higher boiling point components.

For the initial conditioning of the adsorbent material, the guidelines were followed which require purging the tube with 10 to 50ml/min of high purity (less than 1ppm oxygen) gas. Then after 10 minutes, to ramp the temperature at a rate of 4 to 10°/min to approximately 25 to 50°C higher than the maximum desorption temperature that will be used later in the experiment. The trap tube should be left for two to three hours at this elevated temperature. Cooling to ambient temperature should be done within a few minutes without any gas flow, to prevent new trapping of trace amounts of volatile from the gas stream (SIS 2002d).

In order to avoid diffusion of VOCs from the ambient air into the tube the tubes were sealed using airtight end caps. However, during the course of the following experiments it was found that even using the end caps supplied and recommended by the manufacturer of the adsorbent tubes, the tubes adsorbed sufficient benzene over a weekend to interfere with experiments. Therefore the strategy was to clean the tube, as described earlier, before using it after it has been stored for more than one day.

4.5. Defining Sensitivity and Detection Limit Calculations used for the Thermal Desorption Experiments

Expressing the performance of the MS-200 the two expressions "Sensitivity" and "Detection Limit" are commonly used. The sensitivity and detection limit calculations for the double membrane inlet are described in detail in sections 3.2.6 and 3.2.8.

Using the standard double membrane pre-concentrator, the concentration inside the vacuum system is directly linked to the concentration of the sample gas on the outside of the membrane. Therefore the measurement results of the MS-200 can be directly related to a concentration in the sample gas stream. When using adsorbent traps, a specific volume of a sample is passed through the trap, and volatile compounds (dependent on the trap material) are trapped. This results in the amount of sample collected being dependent not only on the concentration in the sample stream, but also on the sampling volume. Therefore when using adsorbent tubes, the sensitivity and detection limit calculation from sections 3.2.6 and 3.2.8 are unsuitable. The following sections 4.5.1 and 4.5.2 detail the sensitivity and detection limit calculations that are suitable for use with adsorption tubes.

4.5.1. Sensitivity Using Adsorbent Tubes and the TED

It was decided to express the sensitivity using adsorbent tubes relative to the number of molecules, or the weight, of sample on the trap. This results in an expression of the sensitivity as counts per mole or counts per nano-gram of sample, rather than the counts per ppb as expressed when using the double membrane concentrator.

The sensitivity of the trap, S_{trap}, will be expressed as counts per mole or nano-gram, as shown in the following equation (Equation 8).

$$S_{Trap} = \frac{Counts_S - Counts_B}{amount\_trapped}$$

$Counts_S$	= Counts in the major mass peak of the chemical under investigation.
$Counts_B$	= Counts in the background reading of major mass peak of the chemical under investigation.
amount_trapped	= Amount of sample trapped [mole, or ng]
S_{Trap}	= Sensitivity using TED [counts / mole, or counts / ng]

Equation 8:

In order to aid comparison it is an advantage to be able to relate the sensitivity of the TED interface directly to the sensitivity of the double membrane inlet of the MS-200. To do this, the new sensitivity of the TED compared to the double membrane inlet, S_{AT}, will be expressed as counts per ppb per ml. This is shown in Equation 9.

$$S_{AT} = \frac{Counts_S - Counts_B}{Concentration * SampleVolume}$$

S_{AT}	= Sensitivity [counts / (ppb ml)]
Concentration	= Concentration of the Sample [ppb]
Sample Volume	= Volume of sample purged through trap [ml]

Equation 9:

As in the sensitivity calculation for the double membrane inlet, described in section 3.2.6, the sensitivity calculation for the adsorption tubes is limited by the linear response of the analyser. In addition to the equations above, the breakthrough volume of the adsorbent trap, described in section 4.2 has to be considered.

Assuming the analyser is not saturated and the breakthrough volume of the trap is not reached, the sensitivity of the TED can be expressed directly to the concentration of the sample. In this case:

$$S_{TED} = S_{AT} * SampleVolume$$

S_{TED} = Sensitivity [counts / ppb]

Equation 10:

4.5.2. Theoretical Detection Limit for Adsorbent Tubes

The detection limit defines the point from which a signal measured from a sample is considered not to be just caused by a variation in the background measurement - i.e. noise. The detection limit is defined as the concentration at which the signal of the sample is three times the statistical variation σ in the background noise (Keith 1983, EPA 1996).

The estimation of the detection limit for the double membrane inlet, described in section 3.2.8, assumes that the variation in background measurement, performed by the MS-200 is mainly due to the variation caused by counting statistics. For the TED, the same relationship can be assumed - provided the adsorption tubes used to measure the background are cleaned to the same level. The theoretical detection limit for the TED, σ_{TED} can then be calculated by using Equation 11.

$$\sigma_{TED} = \frac{\sqrt{Counts_B}}{S_{TED}}$$

σ_{TED} = Theoretical Detection Limit [ppb]

Equation 11:

4.6. Experimental Work

The following sections describe the experimental work used to test the working principles of the TED inlet system.

4.6.1. Methodology used in this section

The trap tubes were filled with various amounts of benzene from a 1ppm gas cylinder (from Scott Speciality Gases), diluted, using a gas divider (from STEC) and nitrogen. The amount of gas introduced was metered with a stopwatch and a soap film flow meter. The analysis procedure when using the TED was to first seal the tube onto the special inlet, as shown in Figure 46, and then evacuate the desorption space to a pressure of approximately 1mbar. The evacuation pump was then switched off and the inlet to the MS-200 opened, in order to expose the desorption space to the inner membrane and allow permeation of the sample into the vacuum of the analyser chamber. In the next step, the adsorption tube was heated in a step change to 200°C, desorbing the chemical of interest, before taking a spectrum in order to measure the instrument response to the chemicals on the adsorption trap.

4.6.2. Initial assessment of the impact of the TED on sensitivity

As an initial experiment a tube was cleaned and analysed as described in section 4.4. This supplies the background measurement. Next, the tube was loaded with 200ppb benzene. This was done for 5 minutes at a flow rate of 200ml/min, resulting in a sample volume of one litre. The tube was analysed in the same manner as the background.

The background reading reported 14,150 counts at 78amu, which is the major mass peak of benzene. The analysis of the sample resulted in 830,000 counts at 78amu. In this experiment the 78amu peak actually saturated – this means there was too much benzene in the sample. Under

conditions of saturation the instrument response is no longer linear. Saturation effects of the mass spectrum are described in detail in Appendix 5. The mass spectra collected can be found in Appendix 9.

The saturation of the benzene peak suggests that the TED is very sensitive. In order to evaluate the real gain in concentration, it was decided to repeat the experiment, but with reduced sample volume of the benzene standard onto the trap. This experiment is described in the following section.

4.6.3. Second assessment of the impact of the TED

In order to get a better idea about the sensitivity of the TED it was decided that for the next experiment the tube was loaded with only 10ml of 200ppb benzene. This should ensure that the response is not saturated and therefore the measurement can be used to calculate the actual sensitivity and detection limit of the TED.

The measured background for this measurement reported 26,125 counts, and the measurement of the sample reported 84,210 counts at 78amu. The mass spectra collected can be found in Appendix 9. Table 22 shows the results of this experiment, calculated as described in section 4.5.

Table 22: Results for experiments in section 4.6.3

TED	MS-200*	Factor of Improvement
$S_{TED} = 280^{counts}/_{ppb}$	$S = 61^{counts}/_{ppb}$	4.6
$\sigma_{TED} = 580ppt$	$\sigma_{Theor} = 2.3ppb$	4.0

* The values for the MS-200 were measured previous to the TED experiments and were calculated as described in section 3.4.

These results are very promising as they show a clear improvement in sensitivity and detection limit, when using the TED. Significant improvement can be achieved already with a sampling volume as low as 10ml.

4.6.4. More accurate assessment of the TED

For the above experiments the concentration at which the instrument was calibrated was two orders of magnitude higher than the detection limit. To substantiate the sensitivity of the instrument further experiments were conducted with a benzene concentration that was closer to the actual detection limit. For a preliminary experiment, a tedlar bag was filled with 200ml of benzene at 200ppb that was then diluted with 800ml of nitrogen. This produced a 20ppb sample.

After analysing a new background, the adsorption trap was filled using 10ml sample of 20ppb benzene and analysed. Background measurement was 8,975 counts at 78amu; Appendix 9. Table 23 shows the results of this experiment, calculated as described in section 4.5.

Table 23: Results for experiments in section 4.6.4

TED	MS-200*	Factor of Improvement
$S_{TED} = 470^{counts}/_{ppb}$	$S = 61^{counts}/_{ppb}$	7.7
$\sigma_{TED} = 200ppt$	$\sigma_{Theor} = 2.3ppb$	11.5

These experiments suggest an even better performance of the TED than the ones found in section 4.6.3. Dilution of the initial benzene standard, using gas-tight syringes and tedlar bags as used in this experiment introduces some unknown factors, such as adsorption of sample and the uncertain accuracy of the syringes, into the process. It is believed that the production of even lower standards for benzene using this method is too unreliable and therefore it was decided not to produce and measure a benzene concentration below the 20ppb used, until a better method for the production of low levels of benzene is identified.

4.6.5. Using the TED with moist samples

Many possible applications require the measurement of VOCs in water or soil. In both cases the analyser has to deal with very moist samples. This was therefore assessed and details are given below.

A sample of 1 litre of water was spiked with 10µl of benzene, producing a concentration of 10ppm of benzene in water. From this an aliquot of 5ml was taken to which another 495ml of water were added, producing 0.5l of 100ppb benzene in water. This 100ppb standard was filled into a 1-litre sample flask. After 30 minutes in order to allow for equilibration, 100ml of headspace above the water standard was sampled onto a cleaned adsorption tube. Without any further processing the sample collected onto the adsorption tube was desorbed into the spectrometer. The water peaks in the spectrum reached saturation. This in itself could cause problems with the quantification of the results for other components. In section 3.2.10 it was shown that the amount of water in the sample would influence the relative sensitivity factors (RSF) for some components. In addition, the huge amount of water made it difficult to maintain the intermediate vacuum at the required level of 1mbar. The result was that the overall permeation rate through the inner membrane of the inlet system was so high that the vacuum pumps (section 2.3) was unable to maintain the vacuum of the analyser within its operation level of below $1*10^{-7}$mbar.

The benzene peak also saturated in the experiment, so it was decided to reduce the sampling volume and therefore reduce the amount of sample introduced into the analyser. This should ensure that the benzene peaks are not saturated, allowing quantitative analysis. This time only 50ml of headspace was sampled.

This time the tube was further conditioned, before analysis. The differential breakthrough volume of benzene and water was used to remove the water. The breakthrough volume of the 31mg Tenax trap at 20°C for benzene is 2.17 litres and for water it is only 2ml. This differential meant that after sampling the trap was purged using 20ml of dry nitrogen, which was sufficient to exceed the breakthrough volume for the water, and therefore purging the water from the trap, without exceeding the breakthrough for the benzene, which would result in a sample loss.

The pressure in the intermediate vacuum space could also be held at an acceptable level during desorption. In addition, the spectrometer did not

record a saturation of the mass peaks that were associated with the water in the sample.

The background reported 13,967 counts for the major mass peak of benzene at 78amu peak. The measurement of the sample reported 443,904 counts. These spectra are shown in Appendix 9. Again above 300,000 counts, the peak is assumed to be saturated and linearity could no longer be assumed. However, it was still possible to estimate the sensitivity and detection limit, with the note that the actual sensitivity and detection limit will probably be better than the one calculated, based on the above results.

Therefore the sensitivity calculates to better than $2150^{counts}/_{ppb}$ for benzene in water. The detection limit of benzene in water equals to 54ppt.

4.7. Discussion

The experiments described were all done on laboratory prepared samples and were only of a preliminary nature. These experiments demonstrate that using the trap evacuate desorb system without the outer membrane offers very high sensitivity and low detection limits compared to the double membrane inlet described in section 2.4. Missing out the concentrating power of the outer membrane is easily compensated by the greater concentrating factor of the adsorption tube together with the evacuation to $^1/_{1000}{}^{th}$ of an atmosphere.

Some problems were expected when evacuating the trapping material to 1mbar. However, other than the problem of background contamination, assumed to be caused from the bulk of the adsorbent resin, described in section 4.4, no other problems were observed. This suggests that the TED could be a useful addition or replacement to the MS-200 double membrane concentrator to handle applications that require higher sensitivity and lower detection limits than the ones offered by the standard double membrane inlet of the MS-200.

However, the enhancement in sensitivity does come with a price. Using adsorption tubes, the MS-200 looses the ability for semi-continuous measurements. Using the double membrane concentrator the MS-200 can measure a time series of a changing sample concentration with a data point every ten seconds, or measure a new sample every 2 to 5 minutes. This results in the ability to measure between 12 to 30 samples per hour. Using the TED a measurement cycle takes about 10 to 15 minutes and therefore only four to six data points per hour can be collected. This makes the TED unsuitable for some applications, where speed of analysis is of concern.

The significant difference in the results from 4.6.3 compared to those reported in paragraph 4.6.4. show that there are still some repeatability problems, either caused by an unreliable production of low concentration samples, and / or in the cleaning and loading of the trap.

4.8. Future Work

All the work so far was done using simulated samples of benzene in nitrogen or water. Benzene is a good representative chemical for aromatic hydrocarbons, and the performance of the MS-200 for benzene is well understood. With the above experiments it was demonstrated that the TED has the potential to push the detection limit of the MS-200 for the aromatic and probably also the chlorinated hydrocarbons from the low ppb into the low ppt range. The results presented here would be more robust if confirmed in some more detailed experiments, for example, producing and analysing a low concentration mixture of some components of interest.

The other interesting question that should be addressed in future work is whether the TED will improve the performance of the MS-200 on chemical species that are currently difficult to analyse. Components that might be of interest include: polar components like alcohols, high molecular mass and "sticky" components like certain oils or explosives as they have fairly poor performance using the double membrane inlet of the MS-200.

Investigating the lack of repeatability is an important part of any future work, as this will determine how useful and reliable the TED system is.

Another experiment that should be conducted is whether the TED could be used for some sort of pre-separation of complex mixtures. Different volatile components might desorb from the Tenax at different temperatures. Therefore ramping the temperature slowly up to the maximum temperature, whilst analysing the chemicals that are being desorbed, might result in some separation of a complex sample. This would be advantageous in assisting the mixture analysis software when trying to analyse complex samples.

With the adsorption tube giving a concentration factor of over 1,000 times, the next logical step would be to investigate the detection of components that have difficulties to pass through the PDMS membrane material by replacing the inner membrane with a pin-hole. In the current set up of the TED, the desorbed chemicals will still have to be able to permeate through the inner membrane between the desorption space and the vacuum of the analyser chamber. Replacing the inner membrane should certainly be helpful with the polar components. However, due to its low breakthrough volumes for polar components, the trapping material may also need to be changed, as Tenax TA® might not be the right trapping material for these and a trapping material offering higher breakthrough volumes for polar compounds should be chosen.

It should also be investigated how much of the sample, especially the high vapour pressure chemicals, is lost in the initial pumping down to 1mbar process. This loss is likely to be a function of the vapour pressure of the component and the adsorption material used, and may be the cause of some of the repeatability issues found.

A further aspect that should be studied is the suitability of trapping materials for different groups of chemical compounds. For this experiments Tenax TA® was used because it has been shown in many studies that it works well for benzene. However other materials might be more useful for the trap evacuate desorption, particularly for other chemicals of interest. These

materials might include molecular sieve, silica gel, activated carbon, Carbosieve®, Tenax GR® and others.

5. Applications of the MS-200

This chapter will describe some of the applications work that was undertaken using the MS-200. Each of the applications will have a short introduction and a section discussing the requirements on the analytical performance of the instrument. Each of the applications will also describe the experimental work, highlight and discuss the results and will include a conclusion and section with recommendations for further work.

5.1. Operator Exposure to Benzene during Refuelling of Petrol Vehicles

Benzene has long been of concern to health and is assumed to be a human carcinogen if exposed over a extended period (WHO 1997). Ambient concentrations are significantly reducing, and it is unlikely that in the UK, the national air quality objectives or the European Union (EU) limit values of 5μg/m^3 (about 1.5ppb) annual mean by 2010, will be exceeded in rural, urban or even roadside locations (Stedman 1999). However, there is still concern about the level of benzene concentrations where petrol is handled or stored (2001/81/EC, Jones 2000, CONCAWE 1999, DEFRA 2001, DEFRA 2002).

The UK has already introduced stage 1 vapour recovery requirements for the larger petrol stations, which requires the recovery of vapours from petrol storage tanks. Petrol stations are also required to register as a regulated part B industrial process, starting with the largest petrol stations (more than 2,000m^3 per year)[6]. The UK government has recently consulted on introducing stage II vapour recovery (DEFRA 2002), which requires the recovery of vapours when refuelling a vehicle. Once fully implemented, stage II vapour recovery is estimated to reduce benzene emissions from petrol stations by between 13 to 17 kilotonnes per year (DEFRA 2002).

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[6] Industrial processes are regulated where there is a risk of emission to air, water or land. Part B processes are the smaller sized processes, and are regulated by the local authority (Sadler 2002).

CONCAWE (Conservation of Clean Air and Water in Europe, the oil companies' European organisation for Environmental and Health Protection) has investigated the total benzene exposure of individuals during a typical day (CONCAVE 1999). It compares typical total daily-absorbed doses of benzene for drivers and non-drivers. The report claims that an average person living and driving a car in a city absorbs a daily dose of about 270μg of benzene. This number is calculated based on ambient exposure to benzene, indoor exposure, exposure due to active/passive smoking, ingestion of benzene and contact with skin. A similar person who is a non-driver would absorb about 240μg of benzene over a day. Furthermore the report claims that after introducing stage-two vapour recovery, the daily absorption for the city person driving a car would drop to 255μg. These numbers are based on the assumption that a motorist refuels his/her car once a week with a total exposure of 1ppm for five minutes without stage-two vapour recovery. Stage-two vapour recovery is assumed to reduce the benzene concentration in the breathing zone to 200ppb.

Jones (2000) describes a study of 18 petrol stations, where diffusion tubes were installed at about 3m height, and at a distance of 10 to 100m from the petrol station. Tubes were exposed for 14 days and analysed for their benzene content. He reports average ambient concentrations of between 0.5 to 5ppb (Jones 2000).

In order to estimate the personal exposure to benzene, Harrison (1998) suggests using static samplers placed in microenvironments and modelling of personal exposure based on time a person spends in the different locations. However, portable real-time sampling would allow actual exposures to be measured when and where it happens.

Most of the non-workplace regulation for air quality is based on ambient concentrations, and the control procedures are based on reducing emissions. As a result of health concerns of air pollutants such as benzene, air quality research is now focusing more on personal exposure. The following sections report on a study to demonstrate the suitability of the MS-200 to measure personal exposure to benzene in petrol station environments.

The high sensitivity to benzene and the semi-continuous analysis capability offer the potential to monitor exactly at what stage during the refuelling process highest exposure is expected.

5.1.1. Methodology Used for these Experiments

As the concentrations expected for these experiments are in the ppb to low ppm levels, the MS-200 was used in its standard double membrane configuration, which also allows near real-time measurements (section 2.5). The instrument was switched on at least 1 hour previous to starting the measurement to ensure that the instrument was fully warmed up and that the measurement of low concentrations would be stable before the experiment.

During warming up, the instrument was supplied with laboratory air, which was first passed over an activated charcoal trap (activated charcoal from Sigma Aldrich) to remove background VOCs from the air. The VOC trap was followed by a nafion dryer (Perma Pure Inc. Model DM-060-24) in order to remove moisture from the air.

The air was drawn through the charcoal filter and the nafion dryer and then passed over the outer membrane of the instrument by means of the in-built sample pump of the MS-200. The flow rate of the pump was approximately 150ml per minute.

The instrument was then set up to acquire a ten-second measurement, followed by a twenty-second wait. This resulted in a data point being collected once every half minute. The measurement was started about 5 minutes before the charcoal filter was removed and the instrument was taken to the car. Once the charcoal filter was removed, a 1.5m long, 1/8" diameter PTFE hose was connected to the nafion dryer to enable the sample to be collected from the breathing region of the driver and passed through the nafion dryer into the MS-200.

Throughout the experiment the sample hose was held within 10cm of the mouth of the driver. This ensured that the sampled air was representative of

the air that the driver would breath in. The petrol station chosen was a large (above 2,000m^3 per year) petrol station, located on the crossroad of two major A-roads about 2km drive from the laboratory. The vehicle was filled up with 98octane, unleaded petrol.

Measurements were taken from the start of the drive to the petrol station, throughout refuelling and during the drive back. Depending on the traffic and the availability of the pump, measurement cycles had different length, ranging from 20 to 30 minutes. During the driving, the ventilation of the car was switched to the lowest level, but not off. During refuelling the drivers door was left open.

Once back at the laboratory the instrument was once again hooked up to the charcoal filter in order to measure any potential shift in the background base line. This was followed by a calibration using a benzene standard of 990ppb. The calibration was performed at the end of the measurement in order not to disturb the warm-up of the instrument that would be given by connecting the benzene in nitrogen standard.

5.1.2. Experiments and Results

Measurements were taken on four separate days, around a week apart during June and July 2003 on a petrol station near a major UK A-road, but in a rural setting. Measurements were taken around midday, with traffic and use of the petrol station estimated to be of a similar level. The weather conditions on all four days were similar, with temperatures of about 27°C to 30°C, sunshine or slight cloud coverage, although with differing winds. While refuelling, the cars are parked facing roughly north. The petrol station has eight pumps in two rows. The north west pump was always used for these experiments. Approximate set up of the petrol station is shown in Figure 49. The wind direction on measurements 1, 3, 4 was from south to north, and wind speed was estimated to be about 5km/h. During measurement 2 the wind direction was from north to south, and the wind speed was estimated to be about 10 to 15km/h. During measurements 1 to 3 the tank was nearly empty before filling up, and about 45 litres of petrol were refuelled. In

measurement four only about 25 litres of petrol were refuelled. The values for the different days (measurements) are shown in Table 24.

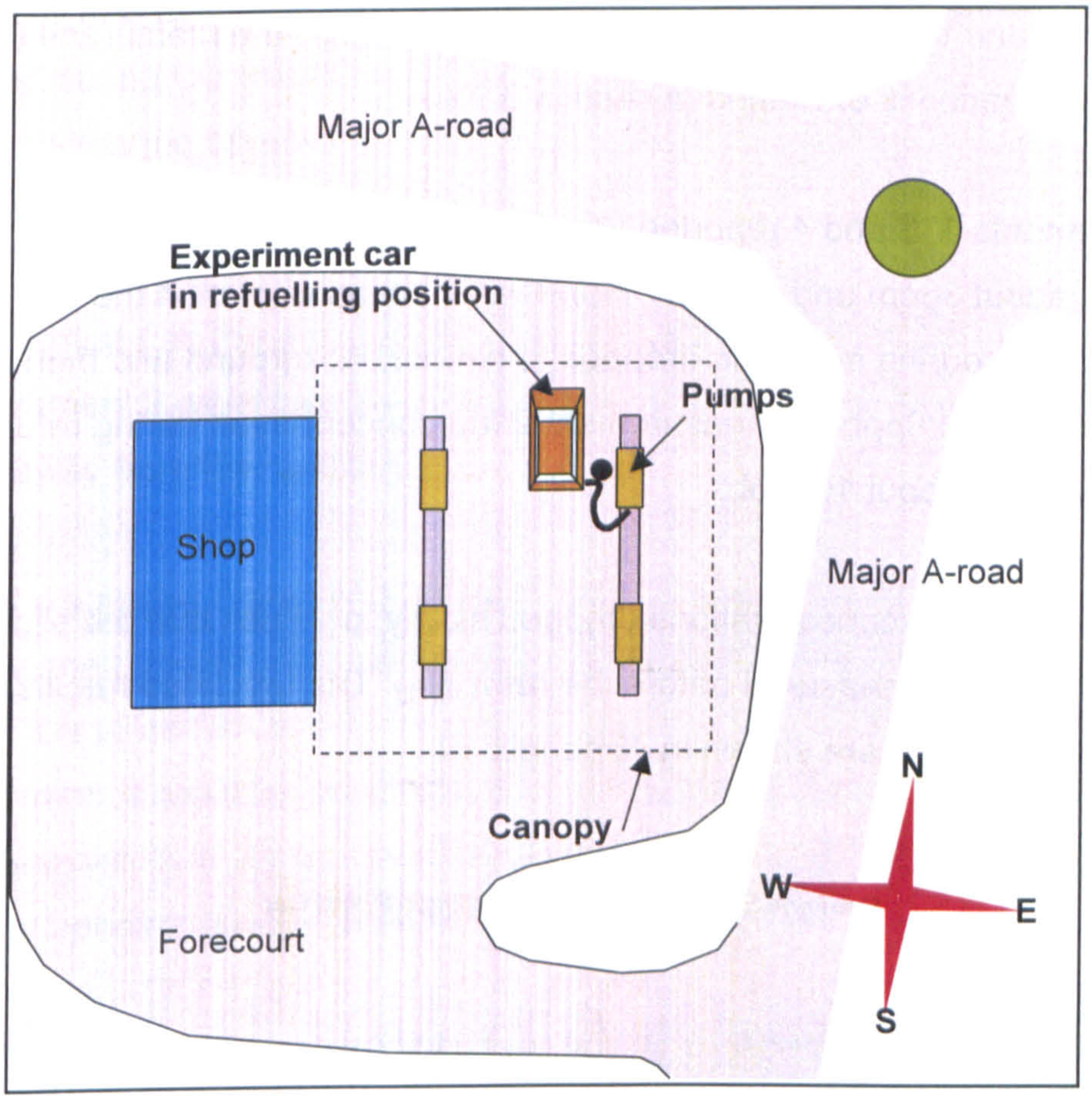


Figure 49: Approximate Set up of Petrol Station

Table 24: Experimental Conditions when Refuelling

Measurement Number	Wind Direction	Estimated Wind Speed	Amount of petrol tanked
1	South to North	5km/h	44.5
2	North to South	10 to 15km/h	46.2
3	South to North	5km/h	42.8
4	South to North	5km/h	25.3

The benzene concentrations measured during the experiment are shown in Figure 50. In order to aid visualisation the different measurements in Figure 50 were superimposed to synchronise to the start of refuelling. During the drive to the petrol station the measured concentrations inside the car were near the quantification limit of the MS-200 for benzene. The quantification limit is about 35ppb for benzene and is explained in section 3.2.8. Therefore it was decided to include only about five minutes before the refuelling started and about five minutes after refuelling finished.

In all cases refuelling took about 2 to 3 minutes. The response of the MS-200 is delayed by about 30 to 60 seconds by the long sampling line used in this experiment and the permeation of the benzene through the membrane (delay due to permeation is explained in section 3.2.4).

Measurements 1, 3 and 4 reported very similar concentrations, peaking between about 3ppm and 4.2ppm. However, in measurement 4 the concentration during refuelling dropped to almost background and then rises again to about 820ppb. In measurement 2 the concentration during refuelling peaked at only about 100ppb.

After refuelling the concentrations dropped slowly to values that are slightly higher than those measured before the refuelling. The tabulated results of the four measurements are shown in Appendix 10.

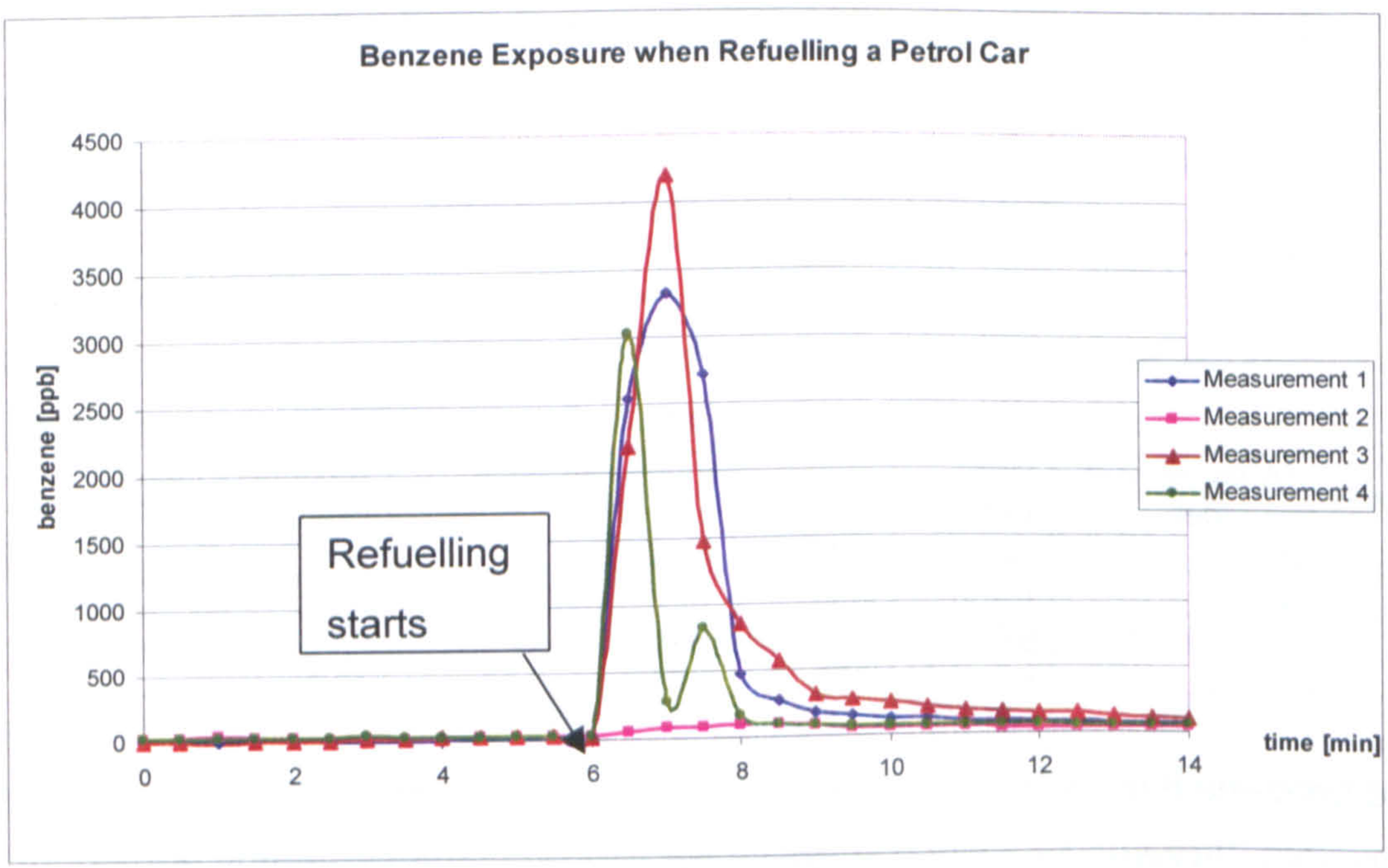


Figure 50: Benzene measurement during four refuelling cycles

5.1.3. Discussion

The delay and dynamics of the MS-200 means that the concentrations reported during the refuelling will take some time before rising to the concentration the operator is exposed to. Similarly, the drop in concentration is subject to a delay.

It is assumed that the much lower concentrations measured during measurement 2 were caused by the relatively strong wind blowing the petrol fumes away from the operator.

It is not a surprise that during measurement 4, where the tank was filled only halfway, the concentration measured is lower and the length of the exposure is less. It is uncertain where the second peak exposure after the initial peak comes from. It could be caused by the wind being in the right direction to blow benzene from another vehicle refuelling on the opposite pump or by the operator bending down in order to replace the filler cap.

The measurements taken suggest that during a standard refuelling, without strong wind conditions like in measurement 2, the operator is exposed to benzene concentrations of about 3 to 4ppm for a duration of about 3 minutes. This is quite different from the average of 1ppm for five minutes (CONCAWE 1999), mentioned in the introduction. These are however limited measurements and a more in depth study would be required to reach firm conclusions.

After the refuelling was finished, the benzene concentration in the car dropped to concentrations slightly above the background levels that were measured before the refuelling. Connecting the MS-200 to the charcoal VOC filter back in the laboratory and taking further measurements has shown that the background level of a clean air sample had also risen slightly, compared to before the experiment.

It is assumed that this rise in background is caused by memory effects of the MS-200 due to the relatively high exposure to benzene during the refuelling.

In case of measurement 3, the background check after the experiment reported benzene of a concentrations of 65ppb, suggesting that the instrument response over the experiment has shifted by about 65ppb. This results in an over reporting of the real benzene concentration. This over reporting is significant for the lower concentrations measured in the car after refuelling, making these measurements more difficult to interpret. However, at the peak exposure during the refuelling this shift only represents a measurement error of about 1.5%.

Adding the quantification limit of about 35ppb (see section 3.2.8), means that measurements after the refuelling that are below 100ppb are below the quantification limit and therefore should not be taken into account when quantifying the over all exposure. This suggests that it takes about another two minutes after refuelling before the benzene concentrations in the car drop to levels before the refuelling.

The above experiments demonstrate that this methodology can be used to estimate an annual average exposure due to refuelling a petrol car. However, more detailed measurements would be required for a period that was representative of the exposure patterns of any individual. On the basis of the present work a crude estimate can be made of the annual exposure level. If it is assumed that an average car driver refuels his/her car about once per week, and the exposure is about 2.6ppm for the duration of 3 minutes (the average of the four experiments), then this implies an annual average of about 0.75ppb (see footnote[7] for calculation), caused by refuelling from a petrol car.

[7] Assuming 52 refuelling cycles of 3 minutes at 2.6ppm = 429ppm*min; one year = 525,600 minutes; therefore average over one year = 429ppm*min / 525,600minutes = 0.75ppb

5.1.4. Conclusion

These measurements show that the MS-200 is very effective at measuring quasi-real time exposure levels providing greatly improved information over a simple average, measured when using diffusive adsorbent tube samplers.

For some specific investigations it might be of scientific interest to be able to measure exposure in 'real time' as it happens. For example, where concentrations or dispersion are studied to improve understanding of a model or a situation, or where there is both a long term average concentration level connected with the long term exposure problems, and a short term exposure limit concerned with directly harmful effects of the pollutant.

Previous chapters (chapter 3) have proved that the MS-200 is able to reliably measure the real time concentrations of benzene This experiment has shown that it is able to measure the exposure of a car driver when refuelling his/her car. However, in order to produce a more reliable estimate of the typical exposure of a car driver during refuelling, further measurements at different petrol station, during different wind and weather conditions and for different vehicles, using different fuels, should be taken.

The memory effect of the MS-200 when exposed to the high concentrations that were measured during these investigations does not significantly influence the measurement during high exposure times. However, it reduces the ability of the instrument to reliably quantify low levels of benzene concentrations that might be found in the car for some time after the refuelling. One way to reduce the exposure of the instrument to the high concentrations during the refuelling would be for example to use a sample dilution. This would benefit the quantification of the after-effects of refuelling, when concentrations below 100ppb are to be measured. An alternative would be to measure the after-effects of refuelling in a separate experiment, where the instrument was not subjected to high concentrations directly beforehand.

As a crude estimate the average exposure from refuelling was calculated in section 5.1.3, to be about 0.75ppb/year. Although a considerably more in

depth study would have to be undertaken to make any firm conclusions it is interesting to speculate on the implications of this result. It does seem to imply that a reduction of ambient benzene concentrations below the proposed 1ppb annual mean may have limited impact unless peak exposures, such as during refuelling, are significantly reduced.

5.2. Arson Investigations

Investigation into arson is a daily routine for many fire brigades around the world. To identify if a fire was accidental, or if the fire was started on purpose arson investigators use burn patterns, dogs trained to smell accelerants, or their own sense of smell. These techniques are good for initial screening, but often do not stand up to legal scrutiny, where more scientific facts are requested. In order to gain more information and understanding of the causes of the arson incident, samples of debris from the suspected sites are normally taken and sent to forensic science laboratories. Samples are subject to various analyses including analysis for organic compounds. In this case the samples are thermally desorbed and the released vapours are analysed, usually using gas chromatographic (GC) techniques. The current instrument offers a fast and reliable method for in-situ analysis to identify the presence of accelerants at the site without having to undergo additional, and hence time consuming, laboratory analyses.

5.2.1. Introduction

It is commonly assumed that the highly volatile accelerants, like petrol, would burn out completely during a fire. However, traces of fuels often remain, even after an intense fire. These remains can be collected and analysed (Bertsch 1996). The same source states that by using a gas chromatograph (GC) setup it is still possible to classify hydrocarbon distillates, used as accelerants, even after as much as 90% has been evaporated due to the fire.

A handbook published by the Federal Emergency Management Agency United States Fire Administration (FA 127 1993) describes the use of catalytic combustion detectors, photo ionization detectors, flame ionisation detectors

and accelerant detection dogs in cases of arson. These field techniques are primarily used to identify locations with a high concentration of volatile vapors. Debris samples are then collected from the suspected locations and sent to the forensic laboratory.

One of the big challenges when analysing headspace (the vapours that are coming off a sample) of fire debris for accelerants, is the problem of interference from naturally present compounds, which are themselves derived from petroleum products. The most promising way to deal with these very complex samples is the use of GC/MS methods, which first separates the different compounds using the GC and then identifying them with the MS (Bertsch 1996). In a discussion for further advances, Bertsch (1996) mentions the potential advantages of field portable equipment that are easy to use and require little user interaction to identify an accelerant.

Cafe (1993) describes the use of a portable gas chromatograph (GC) which has sufficient sensitivity for arson analysis, but of which the resolving power of the short separation column used was limited. This meant that the sample still had to be sent to the forensic science laboratory in order to perform scientific indisputable analysis

The following sections describe an application of the MS-200 instrument for arson investigation in collaboration with Strathclyde Fire Brigade (SFB). The SFB had identified the need for an easy to use, portable arson detector to be used in-situ as soon as a fire is extinguished, and the location is safe to be entered by a fire investigator. The aim was to assess if the use of the MS-200 could speed up the detection of cases of arson (referred to as fire raising in Scotland) and, therefore, allow faster identification of suspects. As the MS-200 uses mass spectra data to positively identify a potential accelerant, the method might have the potential to find acceptability in the legal courts.

5.2.2. Experimental Methodology Used

— Initial Experiments with Simple Samples

In order to assess the suitability of the MS-200 it was decided to test the performance of the instrument first with some simple samples with low background interference, and then with more complex samples within a potentially interfering matrix.

For the initial experiments our collaborator produced 10 different samples in polystyrene bags. Four of the samples (B, C, D and F) contained commonly used accelerants (petrol, surgical spirit, Shell Sol-T and methylated spirit respectively) on sawdust. Sample bag A was an empty control sample. Five samples (E, G, N, Q, and W) were filled with debris of sawdust, lit using the accelerants and extinguished with water after burning for 5 minutes.

The three aims of these initial experiments were:

- Identify if the MS-200 is able to distinguish different accelerants by analysing the headspace of the pure sample.
- See if the concentration of accelerant in the simulated debris samples are sufficiently high for the MS-200 to detect.
- Match the analysis of the pure accelerants to the different samples of simulated fire debris.

For analysis a background reading was taken by supplying room air to the MS-200. After the background was recorded the sample bags were pierced and a PTFE sample line was introduced into the headspace of the sample bag. After waiting for five minutes for the instrument to equilibrate to the sample, an acquisition was performed. The spectra gathered were compared visually to identify re-occurring patterns in the mass peaks from the pure components and the debris samples.

— Experiment Using More Complex Samples

The next step in the experiments was to simulate some more realistic samples. This was done by burning 5cm by 5cm foam backed carpet samples using different accelerants, as described below. The samples were left burning for about 10 minutes, by which stage the flames were almost burned down. The remaining burn was extinguished with water, and the burned carpet samples were placed into sample bags. Analysis using the MS-200 was performed in the same way as with the sawdust samples. The difference this time was that a library entry for the different accelerants had already been produced and that the carpet samples were analysed using the MS-200 mixture analysis software. The software in this case was only used in order to match the sample to the library entry and calculate a confidence on how well the library entry could be fitted to the sample spectra. These experiments were purely concerned with identification, and therefore no calibration was performed in order to calculate concentrations of the potential accelerant.

The accelerants used were petrol, diesel (petrol station), methylated spirit (Bird Brand, Jones Ltd Downham Market UK) and Cellulose Thinners (Automotive Chemicals Ltd. Bury Lancashire, UK), and a library entry was produced for each.

The following experiments were performed on the carpet samples:

A) A sample bag was sealed with a sample of clean, background air one day before analysis.
B) An unburned control carpet sample was placed into a sample bag.
C) A carpet sample that was burned using a blow torch rather than with any liquid accelerant.
D) Petrol was used as accelerant.
E) Cellulose thinner was used as an accelerant.

— Experiment Using A Real Sample

In the follow-up experiment, we received a heavily burned carpet sample of about 5 by 10cm from a real fire incident where arson was suspected. This sample was analysed like the sawdust samples and the patterns of the different accelerants were matched manually as the previous experiments shown that this proved more reliable than matching using the mixture analysis software.

5.2.3. Results and Discussion

— Initial Experiments with Simple Samples

The concentration of accelerant in the sample bags was more than sufficient to produce good mass spectra of the components. The stickplotted (stickplot represents the raw mass peak for each integer mass unit) spectrum for Shell Sol-T is shown in Figure 51. The other spectra from these experiments are shown in Appendix 11.

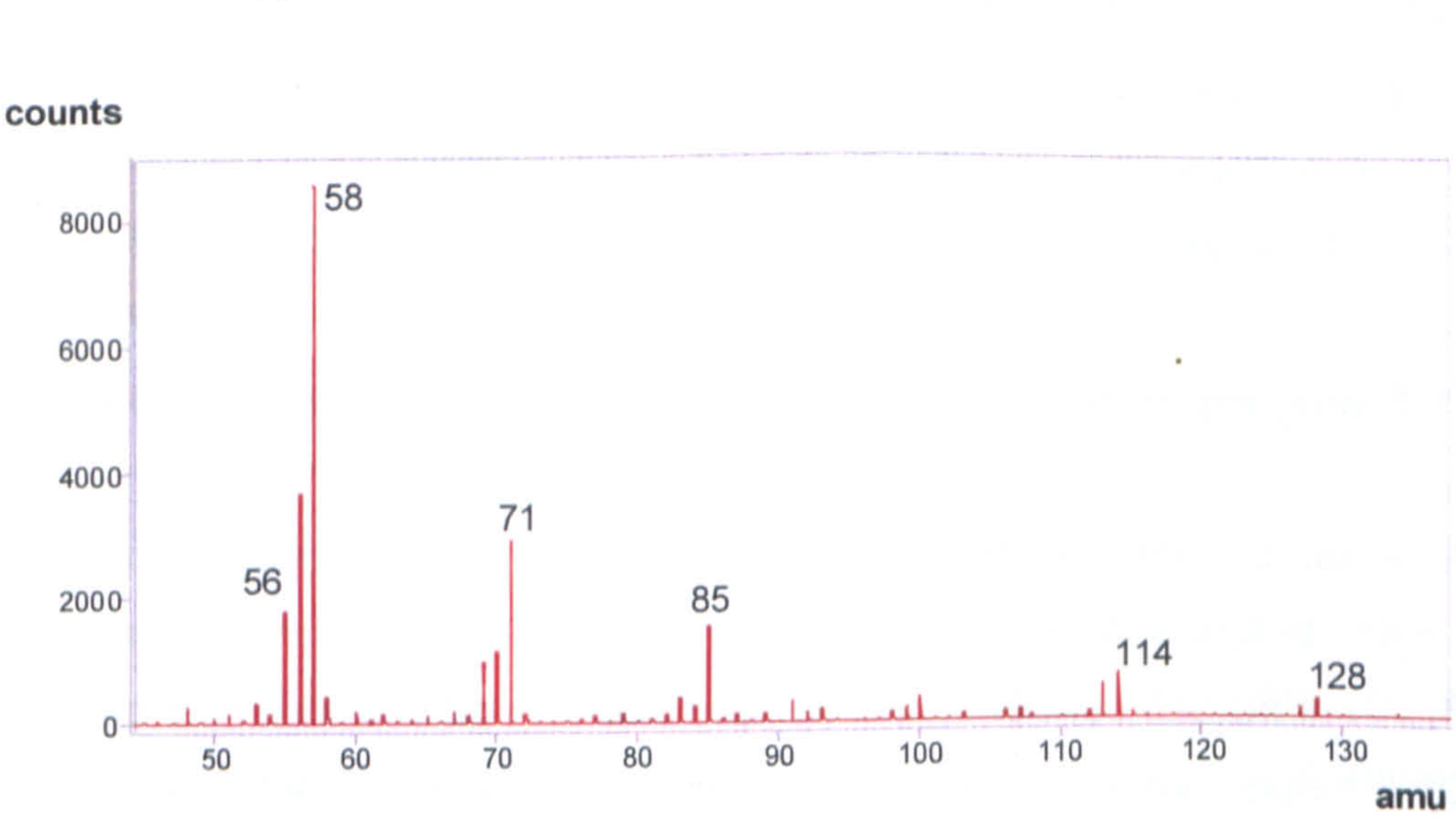


Figure 51: Sample Spectrum of Shell Sol-T

Sample N showed a dominant pattern that fitted Shell Sol-T. Peaks at 55, 56, 57amu; 69, 70, 71amu; 85amu and 111, 112amu show sufficient fit to identify it.

Sample W shows the same patterns as methylated spirit. Peaks at 63, 65, 67, 69, 70, 71amu; 91amu; 105, 107amu and 120amu produce a good fit.

Petrol and surgical spirit produce very similar (if not identical) patterns, and therefore distinguishing between these two was difficult. The only difference identified was a slight difference in the relative size of the peaks at 92, 93, 94amu, and a peak at 121amu which appears in petrol but not in surgical spirit. Those slight differences are probably not sufficient enough to reliably distinguish between them.

The petrol and surgical spirit pattern fits to samples E, G and Q. Samples G and Q have the peak at 121amu, which could suggest that they originate from petrol rather than from the surgical spirit.

The control sample bag A had significant peaks at 91, 92, 93amu and 105, 106, 107amu. The main peaks at 91amu and 106amu are typical for xylene The peaks at 91, 92amu suggest additional Toluene contamination.

Table 25 gives a summary of the MS-200 analysis of the samples in the initial experiment.

Table 25: Summary of Analysis in Initial Experiment

Sample	**MS-200 anaylsis result by visual comparison of spectra**	**Qualitative certainty of identification**
N	Shell Sol-T	Very confident
W	Methylated spirit	Good fit
E	Petrol	Could also be surgical spirit
G	Surgical spirit	Could also be petrol
Q	Surgical spirit	Could also be petrol
A	Xylene with Toluene contamination	Very confident, potential quality problem with the sample bags

All of the simulated sawdust and accelerant sample matches were later confirmed by Strathclyde fire brigade. Therefore it was decided to move on and perform some the more realistic follow-up tests, using different accelerants to burn foam backed carpets. This time patterns were compared using the mixture analysis software of the MS-200.

— Experiment Using More Complex Samples

This included the headspace analysis of samples of carpet with and without accelerant, described in section 5.2.2. The following results were found:

A) The spectrum of the empty sample bag did not record peaks that were significantly different to a clean air sample. Therefore it can be concluded that the sample bags will not interfere with the sample.
B) The spectra for the control carpet sample shows clear but very small peaks at 63, 65, 77, 91, 92, 105, 106amu. This is certainly one or more of the isomers of xylene and toluene.
C) Comparing the carpet sample visually with the other spectra, less and much smaller peaks were observed, showing that VOCs released by the burning of the carpet by itself should not add significantly to the measurement. However, there are peaks that indicate the presence of xylene. Results are presented in Table 26.
D) This sample showed significant peaks. The results are presented in Table 26.
E) This sample showed significant peaks. The results are presented in Table 26.

Sample A and B produced such low response or clear peaks that no mixture analysis was performed. Samples C, D and E were analysed using the mixture analysis software of the MS-200. Table 26 shows the reported confidence of the mixture analysis software on how well the different library entries could be matched to the sample spectra. The smaller the reported number the better the fit and therefore the higher the confidence that the library entry is present in the sample.

Table 26: Reported Mixture Analysis Confidence for the different Accelerants

	Petrol	Methylated spirit	diesel	cellulose thinner
Sample C (no accelerant)	2.1	3.5	6.3	17
Sample D (petrol)	0.16	0.19	2.2	4.3
Sample E (cellulose thinner)	0.18	0.35	1.9	0.92

From the results in Table 26, it can be seen that none of the four library files report a good match on sample C. Although it is at very low levels, sample C still reports a peak at almost every mass. This means that the software will be able to fit the library files, however the confidence is fairly low. Sample D clearly reports very good fit for petrol and methylated spirit. As discussed above, petrol and methylated spirit produce fairly similar mass spectral patterns and therefore it is not surprising that both report similar good fit to the petrol burned sample. Sample E reports a good fit for the cellulose thinner, however it reports an even better fit for petrol and methylated spirit. From this it can be seen that the mixture analysis software of the MS-200 has problems in reliably distinguishing between some of the commonly used accelerants. This is especially true for the most common accelerants that consist of a large range of hydrocarbons. In the case of the carpet samples, it can also be assumed that the burning of the carpet together with an accelerant will release many of the hydrocarbons that are bound in the synthetic materials from the carpet and the foam backing, resulting in the other peaks found and interfering with the analysis.

— *Experiment Using A Real Sample*

This more detailed experiment analysed the heavily burned carpet sample of about 5 by 10cm from a real fire incident. A headspace from the sample bag was taken, and analysed using the MS-200. The resulting spectrum was visually compared to the model spectra produced. It was decided that the spectra from petrol and the surgical spirit have visually the most similarity to the sample spectrum. However, a peak at 121amu suggests that the accelerant used is more likely to be petrol. This result was reported back to the fire investigator and later confirmed by GC/MS analysis from the forensic laboratory.

5.2.4. Conclusions and Recommendations for Further Work

The results of the first experiments were very promising. Despite the fact that the spectra for petrol and surgical spirit appeared very similar, it was possible to visually identify all of the samples correctly. This was successfully performed when comparing different known model spectra with unknown spectra from the simulated fire debris. Of course the task of visual comparison was made easier by the fact that the simulated fire debris caused very little interference with the spectra created by the accelerant. In real life situations, where a library of more than four potential accelerants will have to be matched to samples with various degrees of interference from chemicals naturally present at the site of the fire, these visual inspections may become relatively complex.

The second experiment has shown that the general use software is not yet ideally suited to automatically perform the task to identify the use of accelerants, such as petrol, surgical spirit, methylated spirit and other flammable hydrocarbon mixtures. However, it is believed that the main working principles of the mixture analysis software as described in section 2.7.1 can also work for the arson application. Hence additional work on creating suitable model spectra for the different accelerants, and defining the confidence thresholds above which identification of an accelerant can be confirmed, needs to be performed. Potentially, model spectra representative of the sample environment that is likely to be found by the arson investigators (such as , carpet, wood and PVC flooring) could be included into the MS-200 library. Despite the fact that the software used during the second sets of experiments was not ideally tuned, there is a noticeable trend, showing the presence of accelerant compared to the lack of an accelerant, which may be used as a screening tool.

The results of the third experiments are again very promising. Having been able to identify petrol as an accelerant on a debris sample from a real arson incident suggests the following. Firstly, the remaining concentrations of hydrocarbons from an accelerant, even after it has been burned for quite some time, can be still high enough for detection with the MS-200. Secondly,

the interference from this specific carpet was relatively low and therefore the peak patterns, described above, that are associated with the petrol spectrum, were still clearly visible. Confirmation of the results by independent analysis by a forensic science laboratory supported the conclusion that the MS-200 could be a useful tool in the arson investigation. Of course, further work is needed to confirm the results. For example, many more samples on different background materials, with different accelerants, different fire temperatures and different degrees of interference from paints, fabrics and other hydrocarbon-based products will need to be analysed.

From the viewpoint of fire investigators initially the visual comparison of model spectra and sample spectra would be the preferred method, as showing raw mass data and explaining the differences seems to have a stronger acceptance at a legal court. However, for the data to stand up in court the arson investigator will have to develop expert knowledge on the MS-200, having performed the supporting work described above. At a later stage this expert knowledge could be used to create automated software routines that could be used to identify patterns and compare them with a library of patterns.

An advantage of the membrane inlet of the MS-200 compared to suggested portable GCs is the speed of analysis, as it allows potentially up to 10 measurements to be taken per hour. In very simple cases like the Shell Sol-T the MS-200 also offers the potential to identify an unexpected accelerant by comparing the spectrum to a library of 70 electron volt impact mass spectra, like the NIST database, containing mass spectra of over 100,000 chemicals.

The expected concentrations in arson investigation could potentially range from low ppb to very high ppm levels. With the high sensitivity achieved by the MS-200, the low ppb levels will be relatively easy to analyse, however the high ppm levels will very likely cause saturation on various mass peaks which could heavily interfere with any pattern recognition. In some cases where the concentrations are very high, the inrush of hydrocarbons into the analyser chamber might result in the ion pump being unable to maintain the ultra high vacuum in the mass analyser chamber required for the instrument to work,

and result in potential damage to the analyser. Therefore, the arson investigation requires an adjustable sample dilution to adjust the sample concentration onto the analyser. This can be achieved first by using dilution when analysing suspected debris, and if the signal is not sufficient, by changing over and analysing undiluted sample to confirm if accelerant is present or not. Further work on the arson investigation is currently been undertaken by the fire brigades of Rome and Venice (Italy) that have obtained the MS-200 instrument.

5.3. Breath Analysis

5.3.1. What is breath analysis?

Diagnosing various diseases by means of the smell (i.e. the chemical content) of expelled breath is an ancient method. Breath tests have been used since the time of Hippocrates, when he used the smell of acetone on the breath to identify patients with uncontrolled diabetes. These early methods relied on the physician to smell some basic chemicals with very distinctive flavours. The need to identify components in breath that might not have such distinctive flavours was identified as far back as 200 years ago when Lavoisier bubbled exhaled breath through a solution that caused a visible precipitate when reacting with the expelled CO_2. With these experiments he identifying that the metabolism produces CO_2 when "burning" food. In the second half of the 19th century, Nebelthau bubbled exhaled breath through an alkaline iodine trap and observed a rapid colour change if acetone, indicating diabetes was present. (Phillips et al. 2000a). Nowadays one is aware that exhaled breath does not only consist of the major components of the inhaled air, plus water from the body and CO2 from the metabolism. It is known that breath also contains a huge number of chemical compounds that are caused by chemical processes within the body.

The latest developments in analytical methods, which allow the detection of sub-ppb concentrations of volatile organic compounds (VOCs) in air, have given new momentum to the research into links between various diseases and the chemical contents of exhaled breath. Breath contains valuable information because only a slender barrier separates the air in the alveoli of the lung from the blood in the capillaries (Phillips et al. 2000a).

The major VOCs in breath of healthy individuals are isoprene (12 to 580 ppb), acetone (1.2-1880 ppb), ethanol (13-1000ppb) and methanol (160-2000 ppb). These are present as the result of normal metabolic processes (Lord et al. 2002).

Phillips et al. (1999b) identified 22 different VOCs from exhaled breath - predominately alkanes and alkane derivatives and benzene derivatives, that were found at different levels in patients with and without lung cancer. The study highlights the possibility that carcinogenic cells have higher oxygen free radical production than healthy cells. These oxygen free radicals convert polyunsaturated fatty acids into volatile alkanes that are excreted in the breath, which can be measured. The described chemical process is referred to as oxidative stress [(Phillips et al. 1999b)].

Phillips et al. (1994) suggests that the commonly used markers, ethane and pentane, are not sufficient to monitor oxidative stress. He proposes that one should monitor various VOCs and calculate an alveolar gradient. The alveolar gradient is the difference in concentration of a specific chemical between the inhaled and the exhaled air. It varies with the difference between the rate of synthesis - production in the body and passing on into the breath - of a VOC and its rate of clearance -absorption from the breath into the body. If the alveolar gradient is positive, then the rate of synthesis of a VOC is bigger than its absorption and vice versa.

In a study of 50 normal people more than 200 C_4 to C_{20} VOCs were observed in most breath samples, and more than 3,000 different VOCs were observed in one or a few samples. Phillips et al. (1994) found that it was sufficient to only measure the abundance of a compound relative to a known concentration of an internal standard injected into the sample. He also suggests that the best way to deal with the contamination of breath by background air is by analysing the ambient air and subtracting this background from the breath sample. This way it is possible to calculate the alveolar gradient. His paper also lists the 50 most commonly found VOCs with positive and the 50 most common ones with negative alveolar gradient, which were identified within the study [(Phillips et al. 1999a)].

Oxidative stress can be an indicator in breast cancer, lung cancer, rheumatoid arthritis, heart transplant rejection, acute myocardial infarction, schizophrenia and bronchial asthma [(Phillips 1992a, Humad et al. 1988, Olopade et al. 1997)].

Other studies have investigated the correlation between schizophrenia and the level of CS_2 and pentane in breath (Phillips 1992b, Phillips et al. 1993).

Lindstrom, Pleil (2002) and Pleil, Lindstrom (1997) describe the use of breath testing for exposure assessment studies involving VOCs. Some of the investigations include: an assessment of exposures related to the residential use of contaminated groundwater, exposure to gasoline and fuel additives at self-service petrol stations, exposure of swimmers to trihalomethanes, and occupational exposure to jet fuel vapours (Lindstrom, Pleil 2002, Pleil, Lindstrom 1997).

Breath tests are not only useful for health care monitoring. The most commonly known form of breath analysis is the 'breathalyser' alcohol tester where those suspected of driving a car while over the alcohol limit have to breathe into a tube where a chemical reactant changes colour if ethanol is present. Breath testing can be of use in drug monitoring. Most prescribed and illicit drugs have low molecular weights, and might have sufficient vapour pressure at body temperature, so that they or their metabolites are exchanged into alveolar air in measurable quantities. This means that breath testing could potentially be used to easily identify drug abuse or monitor the level of a prescribed drug in the body (Phillips 1992a).

We were invited to participate in current research programmes by Adenbrooks hospital in Cambridge, conducting research into the use of breath analysis to identify markers that allow diagnosis of irritable bowl syndrome and from the Department of Medicine at the Medical Centre of Richmond, New York. The second institute is interested in the use of breath test as a screening tool for early detection of various diseases, ranging from lung cancer to schizophrenia. Both institutes expressed an interest in having a fast, non-laboratory based technology to measure breath samples more efficiently and cost effectively, which would also increase the number of samples that could be taken.

5.3.2. Analytical Requirements for Breath Analysis

This section describes the methods and results of a study to evaluate the application of the MS-200 to detect various VOC markers in human breath. In order to prove that it is a useful analytical technique we decided to evaluate the performance of the instrument to the following 9 alkanes given in Table 27 that were identified as markers in breath testing, with a strong correlation with the occurrence of lung cancer [Phillips et al. 1999b].

Table 27: Breath Markers for Identification of Lung Cancer

Name	Chemical Equation
Butane	C_4H_{10}
Pentane	C_5H_{12}
Heptane	C_7H_{16}
Hexane, 2-methyl	C_7H_{16}
Hexane, 3-methyl	C_7H_{16}
Octane, 4-methyl	C_9H_{20}
Decane, 5-methyl	C11H24
Tridecane, 3-methyl	C14H30
Tridecane, 7-methyl	C14H30

The standard method to analyse breath samples used by current studies is the collection of exhaled breath onto an adsorbent trap followed by thermal desorption and GC, or GC/MS analysis [Sanchez, Sacks 2003, Phillips2000a, Lord et al. 2002, Lindstrom, Pleil 2002]. The references suggest that the expected concentration for the selected markers will be in the very low ppb to ppt levels. It was therefore decided to initially determine the detection limit of an MS-200 using the standard double membrane inlet described in section 2.4 of this thesis. This was followed by investigating the improvement of the detection limit and sensitivity of the instrument using the novel trap evacuate desorb (TED) interface as described in Chapter 4, and also using the same trap tube technology as the "standard" methods used so far – I. e. thermal desorption GC/MS analysis.

As discussed in section 3.5, the permeation through the silicone membrane used in the MS-200 is the limiting factor for most chemicals to be measured. In a study, Lord et al. (2002) report on a breath sampler that uses silicone membranes as a moisture barrier. He explains that the silicone membranes used are of similar nature to the non-polar lipid bilayer cell membrane of the alveoli, across which many compounds must travel in the body in order to be expired in the breath. Most polar and non-volatile compounds are excreted by the kidneys, which results in the breath consisting of mainly non-polar and volatile compounds [Lord et al. 2002]. As the MS-200 measures non-polar and volatile compounds well, this allows us to estimate that the MS-200 in its current form has potential to be used in breath analysis, especially when using the TED interface.

5.3.3. Methodology

From the measurements performed in chapter 3 it is known that the standard double membrane inlet does not offer sufficient performance to measure the concentrations discussed in section 5.3.2. However, the TED, introduced in chapter 4 offers the potential to detect and measure the components at sufficiently low concentrations.

In order to assess the suitability of the MS-200 for each of the individual nine markers identified in section 5.3.2, it was decided to initially measure the sensitivity and detection limits using the standard double membrane inlet and then again using the TED. This initial work was then followed by the analysis of some real breath samples in order to confirm that the MS-200 is able to identify different VOCs within a real and complex breath sample.

— Production of Samples

Various concentrations of the markers were produced by either liquid injection of the sample (obtained from Sigma Aldrich) into tedlar bags of known volumes and filled with nitrogen (from BOC UK). The nitrogen gas was purified by passing it through a filter of activated carbon (also from Sigma Aldrich). Further dilutions were produced by taking a sample from the

first tedlar bag, using a gas tight syringe (from Hamilton, Switzerland) and injecting it into a second bag.

Later in the study, primary standards were obtained as pure components in nitrogen, supplied in pressurised cylinders (from Spectra Gas). Dilution was performed using the method described above, by taking a sample using a gas tight syringe, and diluting it into a tedlar bag. A standard for tridecane-7-methyl could neither be produced nor purchased. Therefore this preliminary study will concentrate onto the analytical performance of the first eight components from Table 27.

— Sensitivity and Detection Limit for Double Membrane Inlet

The initial work, which recorded the sensitivity of the standard double membrane inlet of the MS-200 was performed using the methodology described in section 3.1. This consisted of first recording a nitrogen background, and then attaching a tedlar bag with the chemical of interest onto the inlet and drawing the sample across the outer membrane by means of the in-built, approximately 100 $^{ml}/_{min}$, sample pump.

— Sensitivity and Detection Limit for TED

For the experiments using the TED, pressurised cylinders with approximately 1ppm of the alkane in nitrogen were used due to its higher sensitivity. Table 28 lists the concentrations of the samples in the pressurised cylinders. The concentrations stated by the manufacturer are measured by GC, using traceable standards and are within ± 10%.

Table 28: Concentration of standards used

Butane	990 ppb
Pentane	1005 ppb
Heptane	1010 ppb
Hexane, 2-methyl	985 ppb
Hexane, 3-methyl	1005 ppb
Octane, 4-methyl	975 ppb
Decane, 5-methyl (undecane)	995 ppb
Tridecane, 3-methyl	not available
Tridecane, 7-methyl	not available

Adsorbent traps, used in the later parts for this study were filled with approximately 200 mg of Tenax TA (from Markes International). Before their initial use the tubes were conditioned with respect to the manufacturers information. Between use the tubes were re-conditioned at 300°C for about 15 to 20 minutes with a flow of nitrogen of about 200 $^{ml}/_{min}$.

Tenax TA offers the great advantage that it has very small breakthrough volumes for water. This allows purging of the water from the trap in the later phases where very moist breath samples might be collected.

The gaseous samples in the tedlar bags were connected to the adsorption using a 30 mm long PTFE pipe and a 1/4" stainless steel union (from Swagelock). The amount of sample that was passed through the adsorbent trap was accurately metered using a 50 ml capacity soap film flow meter (from Sigma Aldrich).

When loading the adsorbent trap, it is important to carefully evaluate the breakthrough volume of the trap. The breakthrough volume is dependent on the trap material and quantity, the chemical to be trapped and the temperature of the trap. Breakthrough volumes for the tracers with the trap used are given in Table 29. The breakthrough volumes were obtained from the manufacturer of the adsorbent traps (SIS 2002d). If the volume of air that is passed through the trap exceeds the breakthrough volume, then the trap will release some of the sample again, and sample loss will occur. The breakthrough volume is discussed in detail in section 4.2.

Table 29: Breakthrough Volumes for the Tracer Compounds

	Breakthrough Volume for a 200 mg Tenax-TA trap [litre at 20°C]
Butane	0.160
Pentane	1
Heptane	20
Hexane, 2-methyl	20
Hexane, 3-methyl	20
Octane, 4-methyl	500
Decane, 5-methyl	2.520
Tridecane, 3-methyl	60.000
Tridecane, 7-methyl	60.000

Analysis of the tubes was then performed in the following way using the TED interface, to investigate the impact of the improved sensitivity. First, the freshly conditioned tube was connected to the TED interface of the MS-200. The tube was then evacuated using the peristaltic pump of the MS-200. Pumping is stopped when the pressure drops to less than 2 mbar and the evacuated region is sealed off. At this stage, the heater is switched on and the adsorption tube is heated to 250° C in order to desorb the analyte into the evacuated desorption space. Once the desorption temperature is reached (which takes about 60 seconds) the inlet valve to the mass analyser is opened, allowing the analytes in the intermediate vacuum space to permeate through the inner membrane of the inlet system into the vacuum of the mass analyser. Allowing two minutes for the sample to equilibrate, a ten second measurement of the analyte in the mass analyser was taken.

This recorded a background measurement for this specific tube. After cooling down, the tube was loaded with the analyte of interest and the analysis was repeated as in the background measurement, this time recording the response to a specific loading of the tube.

— *Analysis of a Real Breath Sample*

Phillips (1997) describes a microprocessor controlled breath sampler that ensures that only alveolar breath is collected and the majority of the dead volume breath is excluded from the adsorbent trap. The sample is collected onto an adsorbent trap.

For this part of the study it was decided to use a simple but also very efficient method to collect alveolar breath samples. Exhaled breath was sampled by first breathing normally and then stopping breathing for about 30 seconds, followed by exhaling most of the held breath through a breath sampler of 0.125 litre volume (Biovoc from Markes International). This breath sampler allows the air to escape and retains only the last 0.125 ml of air from the breath. The sampler can then be sealed off, an adsorption tube connected to the sampler, and the content of the sampler is pushed into the tube by means of an internal plunger, similar to a syringe. This way only the last part of

exhalation, which mainly should consist of alveolar air, is retained in the breath sampler and transferred to the adsorption tube.

In order to remove the high moisture content of the alveolar breath a nafion® dryer (Perma Pure Inc. Model DM-060-24) was fitted between the sample bag and the adsorption trap, during loading of the trap.

5.3.4. Experimental Work and Results

Initially the sensitivity and detection limit of the MS-200 for the alkanes was measured. As it was not possible to purchase decane-5-methyl it was substituted by undecane, having the same molecular weight and number of carbon and hydrogen, it was expected to have a similar sensitivity.

— Sensitivity and Detection Limit for Double Membrane Inlet

When measuring the sensitivity and detection limit for the components with the double membrane, samples of 1 ppm and 16 ppm were produced by injecting of the liquid or gaseous alkane into a tedlar bag. The results of these experiments are shown in Table 30.

— Sensitivity and Detection Limit for TED

The TED experiments were performed with the samples from the gas cylinders diluted to 10 ppb. From this diluted sample of each of the alkanes 0.5 litres were loaded onto each of the adsorption tubes and analysed as described in section 5.3.3.

Table 30 shows the result of the measurements for the alkanes, using the TED interface and the double membrane inlet. In order to simplify the comparison between the two methods, it was chosen to display the detection limit for the TED based on the sample volume of 0.5 litre, which allows expressing the detection limit in ppb equivalent rather than in µg of sample on the trap. For a further explanation of the conversion undertaken, see section 4.5.2.

The results of Table 30 are also presented graphically in Figure 52. The dark blue line shows the detection limit for the alkanes using the standard membrane inlet of the MS-200. The dark red line shows the improvement that was achieved using the TED with a sampling volume of 0.5 litre. This sample volume was chosen in order to have sufficient loading of the alkanes on the trap and therefore produce a reasonable signal when measuring with the TED. From this signal the sensitivity is calculated (see section 4.5.1) for the majority of the nine alkanes. Choosing this sample volume meant that butane will have reached its breakthrough volume, and therefore the values that are recorded are likely to be slightly higher if the breakthrough volume were increased by cooling the trap during sampling.

The detection limit of the TED method is currently limited mainly by the variations in the counts of the background measurement and not by the sensitivity of the analyte. However, the background measurement in this method is independent of the sampling volume, and therefore, chemical loading onto the trap. This allows an estimation of the detection limit improvement for higher sampling volumes by using the assumption that the sensitivity is linear to the loading of the tube, which again is linear to the sample volume. This assumption is valid up to a point where the analyte reaches its breakthrough volume on the trap, and sample loss occurs. For Figure 52 this means that the 2 litre estimated TED detection limits (green line) are over estimated for the two lightest alkanes as breakthrough of the trap occurs after 0.16 litre for butane and 1 litre for pentane. For the remaining compounds the sample volume could be increased to 20 litres for Heptane, Hexane-2-methyl and hexane-3-methyl without loss of sample. The remaining four have breakthrough volumes in excess of 500 litres and therefore the detection limit for them could be improved significantly, simply by sampling for longer.

Table 30: Detection Limit and Sensitivity Comparison between double membrane and TED

Substances	Double membrane			TED			Ref. Mass
	Sensitivity counts/ppb	Detection limit 3*Sigma ppb	Backgr. counts	Sensitivity counts/ppb	Detection limit 0.5 litre 3*Sigma [ppb]	Backgr. counts	
Butane	0.41	207.3	803	30.4	3.12	1017	58
Pentane	0.72	82.2	389	186.3	0.84	2667	72
Heptane	3.5	8.7	102	855.7	0.126	1269	100
Hexane, 2-methyl	7.6	9.3	565	984.8	0.135	1958	85
Hexane, 3-methyl	9.7	10.5	1130	1170.7	0.12	2223	71
Octane, 4-methyl	50.3	0.93	241	1261	0.069	869	85
Decane, 5-methyl	12	8.4	1130	99.9	1.08	1296	71
Tridecane, 3-methyl	0.16	300	256				85
Tridecane, 7-mehyl							112

Figure 52: Detection Limit and Sensitivity Comparison between double membrane and TED

— *Analysis of a Real Breath Sample*

After these initial experiments it was decided to investigate if compounds could be identified within a real breath sample, using two different methods available in our laboratory. Therefore a breath sample was collected from a test person, using the above mentioned method, and 0.5 litres of alveolar breath were passed through the nafion dryer onto an adsorption tube. The same was done for a sample of background air onto a second tube. Two sets of sample and background tubes were produced in this way, and one set of these tubes were analysed using the "standard" GC/MS method, and the other set was analysed using the TED interface on an MS-200.

Analysis of the first set of tubes, using the GC/MS method revealed 41 significant peaks in the breath sample, each representing a compound that can be detected with the GC/MS method used. The following table (Table 31) shows the major peaks - compounds - in the breath sample from the GC/MS analysis. The area given for a peak is the area of the sample peak reduced by the area of the background peak.

The second set of tubes was analysed by using the TED. A mixture analysis library was built using the 21 major compounds that were identified by the measurements taken with the GC/MS system (Table 31) and the sample was analysed. The use and working principles of the mixture analysis software of the MS-200 is extensively described in Appendix 4 of this thesis.

The results of the two measurements, using the GC and the TED systems are difficult to compare without having a calibration for the different compounds for each of the two systems. This is due to the fact that the two methods have very different sensitivity for different compounds. Therefore, a compound at a specific concentration and with a high sensitivity in one method might produce a very large response (peak), whereby the same compound measured with the other method compound might have a low sensitivity, resulting in a low peak. As discussed in section 5.3.1, the methods given in the literature for breath analysis use the relative abundance of GC peaks to map the markers for disease, not the absolute concentrations

of chemicals. As the GC/MS will have different sensitivities to different chemicals than the TED, the relative abundance patterns given in the literature found so far cannot be directly transferred between the two techniques.

For this reason it was decided to report the confidence for each of the compounds that were found by the MS-200 mixture analysis software. The confidence level allows an estimate of how confident the mixture analysis is that the component was identified correctly in the sample spectrum. The smaller the number given, the higher the confidence. From previous experience with the software, a confidence of lower than 5 is a fairly good fit. Between 5 and 10 the fit is not too good. A number of more than 10 means that it is unlikely that the compound was detected by the MS-200. A more detailed description on how the software calculates the confidence level is explained in Appendix 4.

Table 31: Major Compounds in Breath Sample by GC/MS

Compound	Peak Area (counts) GC/MS	Counts (counts) MS-200	Confidence % MS-200
Alanine	47,368	-22	2.8
Isobutane	280	14	2.8
oxalic acid	799	2	4.5
2 methyl 1,3 butadiene	45,265	55	0.3
Acetone	43,678	1	31.9
2 propanol	-16,277	-3	4.7
Benzene	-19	6,897	2.8
1,2 dimethyl cyclopentane	96	12	1.6
3 methyl hexane	781	10	3.3
methylcyclohexane	1,877	13	0.9
Toluene	3,599	52,223	1.0
Hexanal	-32	7	2.7
ethylbenzene	-37	0	489.3
p xylene	-253	-1,334	117.7
3 carene	-41	-1	11.5
Tetradecane	7	4	3.1
1,3,5 trimethyl benzene	-258	-1	10.1
d limonene	113	2	6.6
2,6 dimethyl heptadecane	-9	2	5.9
Phenol	37	1	8.8
Heptanal	-78	3	5.6

The MS-200 is known to have very low sensitivity (see Table 34, section 6.2) to some of the components in Table 31. This will particularly affect the lower molecular weight and polar low molecular weight components that will not easily permeate through the silicone membrane used in the inlet of the MS-200. Even when replacing the double membrane inlet with the TED, the components still have to pass through the inner membrane that separates the desorption space from the ultra high vacuum side of the analyser chamber. Therefore it is not surprising that the MS-200 does not report a high concentration for example for alanine and iso-butane. All the compounds from the GC/MS run were found by the MS-200 mixture analysis software reporting a reasonable confidence, with the exception of acetone, ethylbenzene, p-xylene, 3-carene and 1,3,5 trimethyl benzene.

The MS-200 software has the capability of calculating the best-fit spectrum, which it creates by superposition of all the model spectra in the mixture analysis software (see section 2.7.1). Figure 53 shows the best fit the mixture analysis could produce (red) and the spectrum of the breath sample taken (blue). There is clearly a very good agreement. However, this comparison also shows that there are some of the peaks in the breath spectrum that are not covered by any peak from compounds in the library. This suggests that the MS-200 has detected additional chemicals in the breath that were not detected using the GC/MS method, based on which the library of compounds was created.

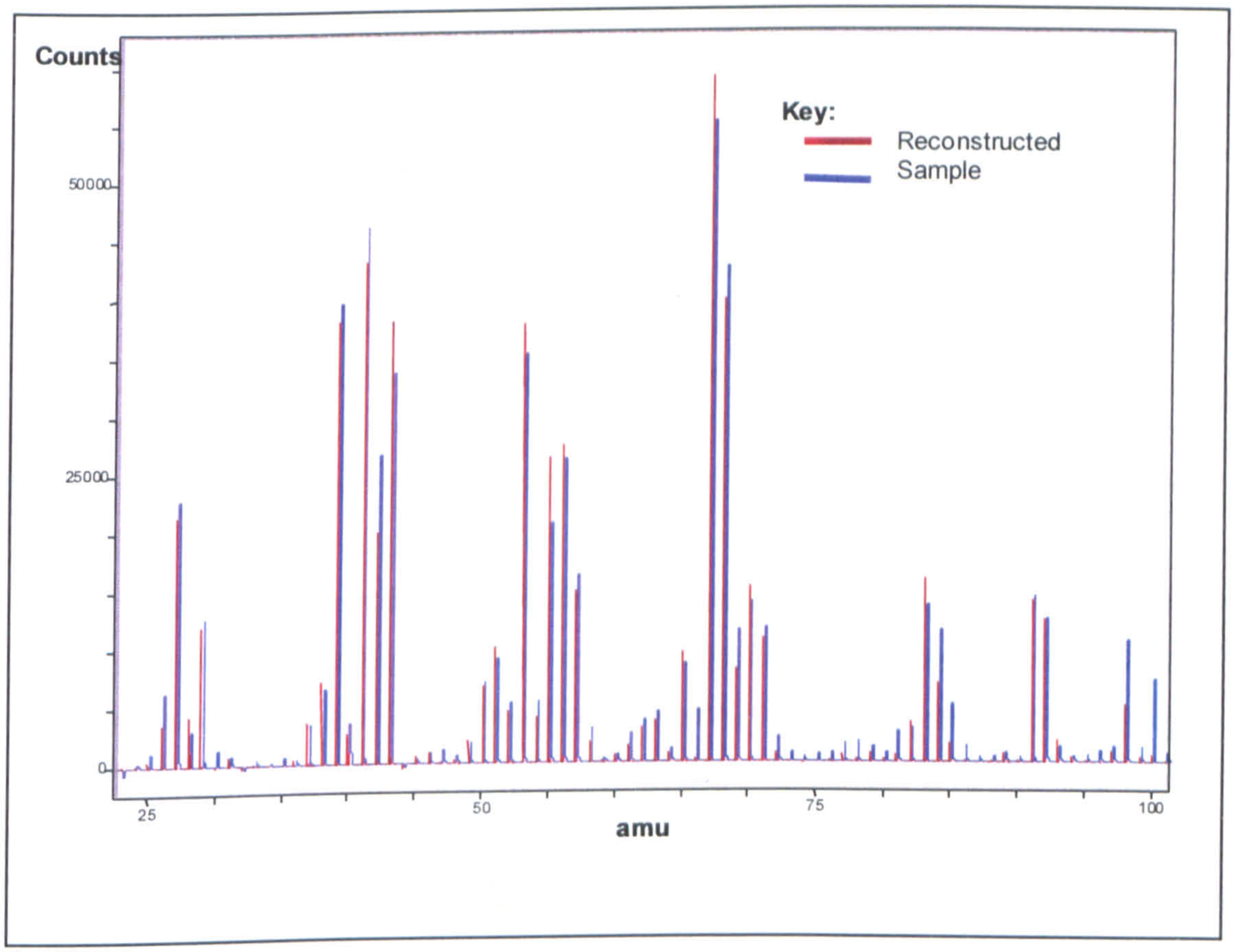


Figure 53: Fit of model spectrum to breath sample

5.3.5. Discussion and Further Work

— The Adsorbent Material Used

Using both the MS-200 and TED, it was found that the background reading of some of the adsorbent tubes was still relatively high, despite the fact that the recommended cleaning procedure was followed. It was also found that analysing tubes within a few hours of cleaning resulted in much lower background readings than tubes that were stored for some time - e. g. over night. This was despite the fact that tubes were stored with end caps with PTFE seals, providing very good seals, as recommended by the manufacturer of the tubes. Therefore, it is assumed that this background consists of compounds that are within the adsorbent, that slowly diffuse into the outer layers of the bulk material and are therefore desorbed when the sample is taken. It is assumed that an adsorbent where either the bulk can be cleaned more thoroughly, or that does not collect chemicals in its bulk

would be more effective for use with the TED - while having sufficient affinity for the chemicals of concern in breath analysis. A preferable adsorbent material would also be one that is possible to be evacuated to 1 mbar. The use of adsorbents in the TED is quite different from the normal use of commercial adsorbents and therefore no reports or previous investigations into this problem could be found in the literature. Future work should concentrate of identifying such an alternative adsorbent material.

— Spectra Deconvolution

In this specific application, the challenge will be that the spectra for the 9 alkanes under investigation do in some cases overlap heavily in their fragmentation pattern. Currently the mixture analysis of the MS-200 is tuned for general use and therefore might have problems to reliably distinguish these 9 alkanes from each other. Future work will have to include very careful data modelling and the production of very precise model spectra to improve the MS-200's ability to identify the individual alkanes in a sample of very similar alkanes. In order to assess the analytical performance of the TED for breath analysis, rather than the software it was decided that this initial investigation looked at each of the alkanes separately. Investigating the nine alkanes and the real breath sample it was found that the TED has sufficient sensitivity and a low enough detection limit in order to measure a considerable number of the components that might be found in human breath.

In order to overcome the deconvolution of the nine alkanes markers changes to the hardware could make the deconvolution by the software easier. During the work in these investigations it was noticed that the different alkanes desorb from the trap at temperatures between about 70°C for the low breakthrough volume, up to about 200°C for the higher breakthrough volume components. This suggests that there might be a chance to aid the software deconvolution of the alkanes by releasing the alkanes from the trap at different times - i.e. different temperatures - resulting in a separation of the compounds that would aid the software. This separation will unlikely be as good and as complete as the separation from an GC, however it still might

reduce the problem for the mixture analysis software from 9 alkanes to two or three alkanes at a time.

— *Analysis of the Real Breath Sample*

The comparison of the MS-200 and the GC/MS analysis of breath samples taken from the same person do show that the TED has sufficient sensitivity to detect most of the compounds that are detected by the GC/MS. However, it was found that the two measurements cannot be related directly, due to the quite significant difference in sensitivity of the two methods for different compounds. For example the MS-200 has very poor sensitivity for the low molecular weight and polar acetone, where the GC/MS method seems to have a very high sensitivity. Therefore, if findings of a study performed with GC/MS methods are to be related to the TED method, the GC/MS work needs to be calibrated. This allows comparison of concentrations for the individual compounds (markers), rather than expressing it as a relative instrument response.

Another question that arises, independent of the analysis of the adsorption traps, is the validation of which VOCs in the breath are caused by a person's metabolism, and which could be adsorbed into the body from other sources and are slowly released, influencing the breath test. In another brief experiment performed using the GC/MS a co-worker found that her breath 15 minutes after re-fuelling her petrol car still contained considerable amounts of VOCs that were not present in the control sample, which was taken a few minutes before the visit to the petrol station. Performing breath analysis before the body was able to clear out chemicals from a previous high level exposure therefore could potentially lead to wrong conclusions. In clinical use, this may mean that in practice the patient would need to be in a controlled atmosphere (e.g. within the clinic) for a set time before the breath sample was taken.

5.3.6. Conclusion

Breath analysis is an exciting and emerging field in medical care. A considerable number of research groups are focusing onto the basic research on which components can be found in breath, and how to relate the complex concentration patterns to different processes and diseases within the body. This work relies mainly onto GC/MS analysis of breath samples.

This pilot study has shown that both in a simulated, and fairly realistic scenario, a technology based on the MS-200 and TED has the potential to compete with the thermal desorption GC, GC/MS-methods, used when analysing adsorption tubes from breath samples for known markers. It was also identified that in order to transfer knowledge about breath markers from the GC/MS methods to the MS-200 analysis of samples a considerable additional effort will have to be made. This effort includes measuring quantitatively the sensitivity of the two systems and translating the instrument responses into concentrations of marker in the breath or a loading of the marker on the sample tube.

GC/MS analysis of a breath sample is very slow and the analysis cost for each sample are relatively high. With the MS-200, one analysis cycle of taking a background reading plus analysing a sample tube is in the order of about 15 minutes. This compares to an analysis cycle of about 2 hours for the analysis of a background tube and a sample tube when using GC techniques. The time disadvantage of GC comes with the advantage of an enormous discriminating power and the clear ability to identify unknown compounds in the breath at trace levels, never achieved by an MS-200 and TED in its current form. This makes the GC based methods superior in the research for breath markers.

On the other hand, once research has identified specific markers for a disease under investigation, and established the connection between the concentration of the various markers, then the lack of discriminating power of the MS-200 can be overcome by focusing the analysis of breath samples simply on the markers identified in the GC/MS work.

The sensitivity of the TED is, for many components, comparable to currently used methods and therefore does not require large volumes of breath samples, which in some cases might be difficult if, not impossible, to obtain.

The future developments, particularly on the deconvolution issues, discussed above will further improve the ability of the MS-200 to be used in breath analysis. However, for some chemicals this may be a remaining issue even after improvements, and may mean that some types of breath analysis where the chemicals of interest can be more easily convoluted by the MS-200 may be more appropriate for the use of the MS-200 than others.

The MS-200 with the TED interface and software that is more tailored to the need of the breath analysis therefore has the potential to offer a fast, easy to use and therefore cheap way for breath analysis. The portability of the instrument and the potential to speed up analysis even further could result in mass screening of large populations, similar to early mass screening for tuberculosis using mobile x-ray instruments.

5.4. Other Applications

This chapter will briefly discuss various other applications for which the MS-200 was used or evaluated during the work on this PhD thesis.

- Air Quality Monitoring on the International Space Station
- Analysis of Contamination on Chemical Protection Suits
- MS-200 as "Artificial Nose" in the Food Industry
- Further Applications Investigated by Collaborators
- Applications where the MS-200 did not have Sufficient Sensitivity

Each of the sections below will briefly introduce each application, explain some of the work that was done and discuss the results. The following sections should be seen to indicate other potential uses of the MS-200 and are not meant to provide an in depth treatment

5.4.1. Air Quality Monitoring on the International Space Station (ISS)

The following section describes an application as a result of collaboration with Wyle Laboratories, working for NASA. The aim was to evaluate the potential use of the MS-200 as a second-generation-volatile-organic air (VOA) monitor on the ISS.

As astronauts are spending longer periods in spacecraft, it is getting increasingly important to monitor the air they breathe. Air samples from spacecraft are commonly collected in stainless steel canisters and brought back on earth for subsequent analysis. The GC/MS analysis generally used reveals over 100 compounds (NASA 2003). NASA scientists have prepared a priority list of compounds (NASA 2000) and are currently looking into a possibility to monitor these priority compounds directly inside the ISS.

Comparing the suitability of different analysis techniques, the MS-200 was evaluated together with two Fourier-transformation-infra-red analysers (FTIR) and a gas chromatograph ion mobility spectrometer (GC/IMS) for the

analysis of the priority list of compounds. The experimental work for this study is described in detail in chapter 3, the laboratory based performance tests. These assessed the response time, detection limit, repeatability and long term stability of the measurement of the instrument. Results of this work are discussed in detail in chapter 3. The key results are shown in Table 21 (section 3.3.4). These results have been submitted to NASA and are currently being evaluated.

5.4.2. Exposure to cigarette smoke

We were contacted by the Building Science Research Industrial Associates (BSRIA), who were conducting independent research into the efficiency of air cleaners used to minimise cigarette smoke related air pollution in public houses. Current measurements of efficiency concentrate on the particulate emission from cigarette smoke. One of the major volatile organic emissions from cigarettes is toluene, and it was investigated whether the MS-200 is able to analyse toluene concentrations inside a test chamber, and could therefore be used to monitor concentrations of cigarette smoke.

The test chamber had a volume of 57m^3 and was fitted with a commonly used electrostatic air cleaner, designed to remove particulate contamination from the air. The chamber was fitted with a device that lit five cigarettes, and expelled the smoke into the test chamber. The toluene concentrations in the chamber were monitored, alongside the current particulate monitor whilst the air cleaner was operating. The results are shown in Figure 54.

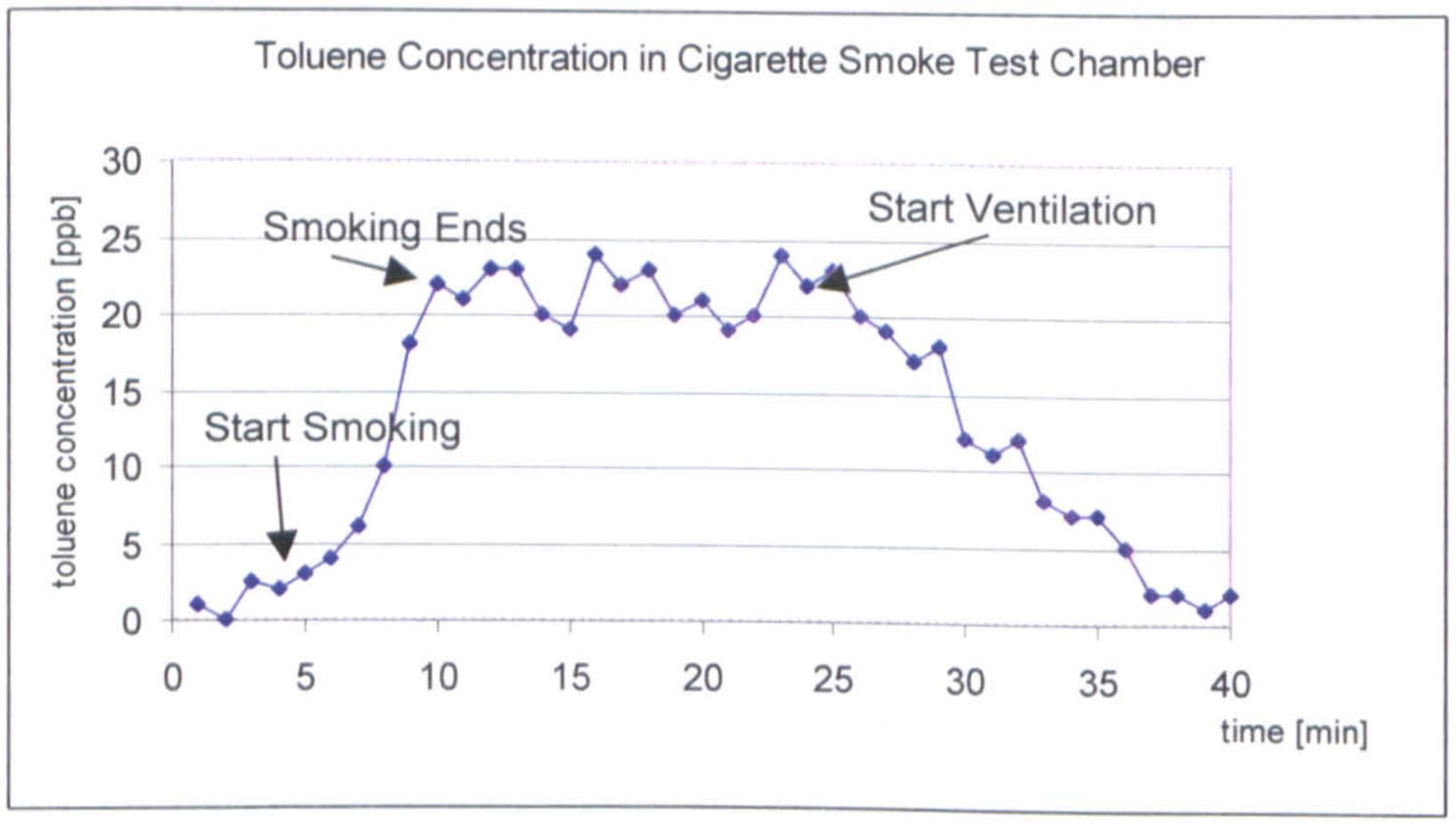


Figure 54, Toluene Concentration in Cigarette Smoke Test Chamber

The particulate monitor measured a strong rise in particulate concentration during the first five minutes, after which time concentrations reduced as the particulate were successfully removed by the air cleaner. The MS-200 reported a rise of the toluene concentration over the first five minutes and then reported a constant concentration of toluene of about 20ppb throughout the experiment. Toluene concentrations only dropped once the door of the chamber was opened and the air inside the chamber was exchanged.

The preliminary nature of this experiment meant that there was no possibility to change the air cleaner from one designed to deal with particulate, to one that would deal with VOC contamination either in addition, or replacement to, the particulate cleaning. However, the MS-200 was able to monitor a rise in toluene concentrations once the cigarettes were lit and later a drop in toluene concentration once the air in the chamber was exchanged. This allows us to conclude that it would be able to monitor the change in toluene concentration if the air would be cleaned rather than exchanged.

This initial experiment suggests that the MS-200 has the capability to monitor toluene concentrations as a marker for the air quality in pubs. The portability of the system would allow spot checks in pubs to confirm that the cleaning system is working efficiently and that maintenance schedules of air cleaning equipment are adhered to. This initial experiment should be followed by an

experiment confirming that the MS-200 is able to report the toluene concentrations over a period, when using VOC removing air filters.

5.4.3. Analysing Contamination on Chemical Protection Suits

Chemical protection suits are used to protect personnel working in chemical manufacturing situations or during clean up operations. When using such suits, various issues arise. Is the cleaning of the suits efficient enough to remove contaminating chemicals? Is the protective layer of the suit still working and do chemicals permeate through to the inside?

In industrial clean up procedures, suits are extremely well monitored and it is known exactly which chemical(s) the suit was exposed to, and for how long. However, in emergency clean up situations, one often does not know to what kind of chemicals the suit was exposed.

The MS-200 was tested to investigate if it could offer a fast and cost effective method to analyse contamination on protective suits. In an initial experiment, suits sent back to the manufacturer for repair work were investigated for contamination. These suits were stored in sealed plastic bags. First a background reading of ambient air was taken, then the sample line of the MS-200 was introduced into the storage bags, and after five minutes, an analysis was taken.

From the ten storage bags that were analysed, two suits were found to have contamination that could be detected by the MS-200. In both cases the contamination was from a single chemical and therefore it was possible to compare the mass spectra to library of mass spectra and identify the chemical. The chemicals were identified as tetrachloroethylene and toluene. The analysis of the ten suits took about 1.5 hours.

Motivated by the positive results from the initial test, it was decided to select a list of representative compounds from a list of the most common chemicals that the suits are used for. Standards were produced by injection of the liquid chemical into Tedlar bags, filled with clean nitrogen. It was then tested

whether the MS-200 was able to detect these compounds at ppm level concentrations. The results are displayed in Table 32.

Table 32: Sensitivity and Detection Limit

Compound	Sensitivity*	Detection Limit**
Dimethylformamide	3750	30 ppb
Acetonitrile	2102	600 ppb
n-Heptane	128 000	< 10 ppb
Tetrahydrofuran	10 400	70 ppb
Diethylamine	625	400 ppb
Carbondisulfide	23 500	< 5 ppb
Nitrobenzene	99 000	< 5 ppb
Bromine	7	15 ppm
Dibromomethane	37 500	< 5 ppb
Diethylether	1 400	150 ppb
Pyridine	53 900	< 5 ppb
Diethylenglycol	34	15 ppm
Pentanol	22 300	20 ppb

*Compared to nitrogen having a sensitivity of 1.

**Estimated from the sensitivity and the statistical noise of the background spectrum for the component of concern. Calculated as 3*σ of the background noise.

In a final experiment, the MS-200 was taken into a chemical factory and suits were analysed for contamination inside the suit itself. In this case, all the suits were cleaned and hung up to air and dried, as per the normal procedure. Samples of air from the inside of the suits were analysed to identify if personnel could potentially be exposed to chemicals when using the suit for the next operation. Analysis was performed as above, by taking a background reading from the ambient air, and then the sample line of the MS-200 was introduced to the inside of the suit and after equilibrium time, an analysis was performed. Eleven suits, randomly chosen, were analysed this way. For some suits, the MS-200 reported the presence of a chemical inside the suit. The reported peaks were analysed 'blind' using the NIST database. A library search suggested that the unknown compound could be "Limonene". It was then confirmed that limonene is the major constituent of the cleaning agent used when decontaminating the suits. The MS-200 mass spectrum sampled can be seen in Figure 55.

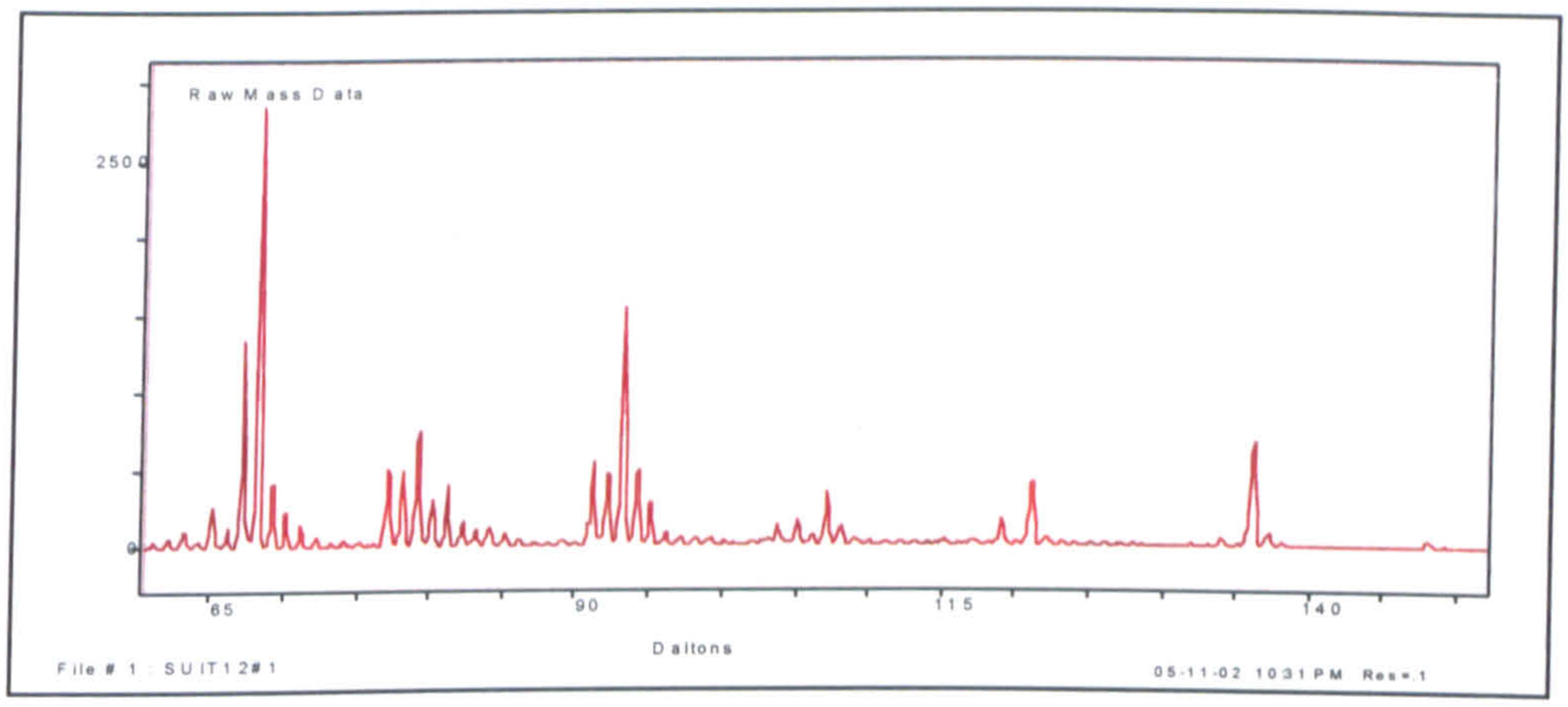


Figure 55: MS-200 mass spectrum for limonene

The result of the NIST search was fed back into the MS-200 and a 'mixture analysis' was performed. The MS-200 mixture analysis reported a very good fit for limonene, thus confirming the NIST search result.

Limonene residues were found on 7 out of the 11 suits analysed, at various levels. No other contamination could be identified, thus confirming the effectiveness of the cleaning process for the chemicals handled, within the detection sensitivity of the instrument mentioned above.

From this work, it was demonstrated that the MS-200 has the potential to offer a fast method to identify the presence of various chemicals during in-situ measurements. However, care will have to be taken, as the sensitivity of the MS-200 for some chemicals is very poor. Therefore detecting no chemicals within a suit only confirms that there are no chemicals to which the MS-200 has reasonable sensitivity, but it does not give the suit a clean bill from all contamination.

5.4.4. MS-200 as "Artificial Nose" in the Food Industry

Flavour analysis in the food industry is commonly undertaken using expert panels to analyse different flavours with the human nose. These panels are expensive, subjective and suffer from the fact that only few samples can be analysed before the panel members require a break. Therefore, it would be useful for the food industry to have alternative sensors that could potentially replace the expert panel. These sensors are commonly referred to as "artificial noses".

Current technologies rely mainly on an array of sensors that are coated with different chemicals. These coatings will react with different components of the flavour that is produced by the food to be analysed. Sensors measure these reactions by different physical principles, such as the change in electrical conductivity or resonance frequency of the sensor. These arrays of sensors are "trained" using known samples, and the response of each of the sensors in the array is mapped. Later analysis compares the response to the training samples in order to identify if the sample is within the required limits or not. The disadvantage of these sensor arrays is the sensitivity to moisture and the limited lifetime of the array. If the array needs replacing, due to relatively large tolerances in the coatings, a completely new training session will have to be performed, which is time consuming and expensive.

Some of the latest artificial noses use mass spectrometer based technologies. These technologies are believed to overcome the re-training problem of the sensor arrays, and are potentially more flexible towards different tasks.

Initially preliminary tests were performed on different food samples to see if the MS-200 could measure some of the chemicals in food flavours. Samples analysed were peppermint tea, two different sorts of coffee, and some shrimps that were two days old.

Analysis was performed in a way that first a sample of background air was analysed, followed by supplying the head space of the sample to the MS-200, waiting for 5 minutes to allow equilibration, followed by data acquisition.

The first sample to be analysed was the air inside a freshly opened box of dried peppermint tea bags. The sample spectrum between 45 and 170amu is displayed in Figure 56. No peaks from the background spectrum interfere in the mass range displayed and therefore it was decided not to show the background. The spectrum shows very clear peaks, caused by the peppermint sample.

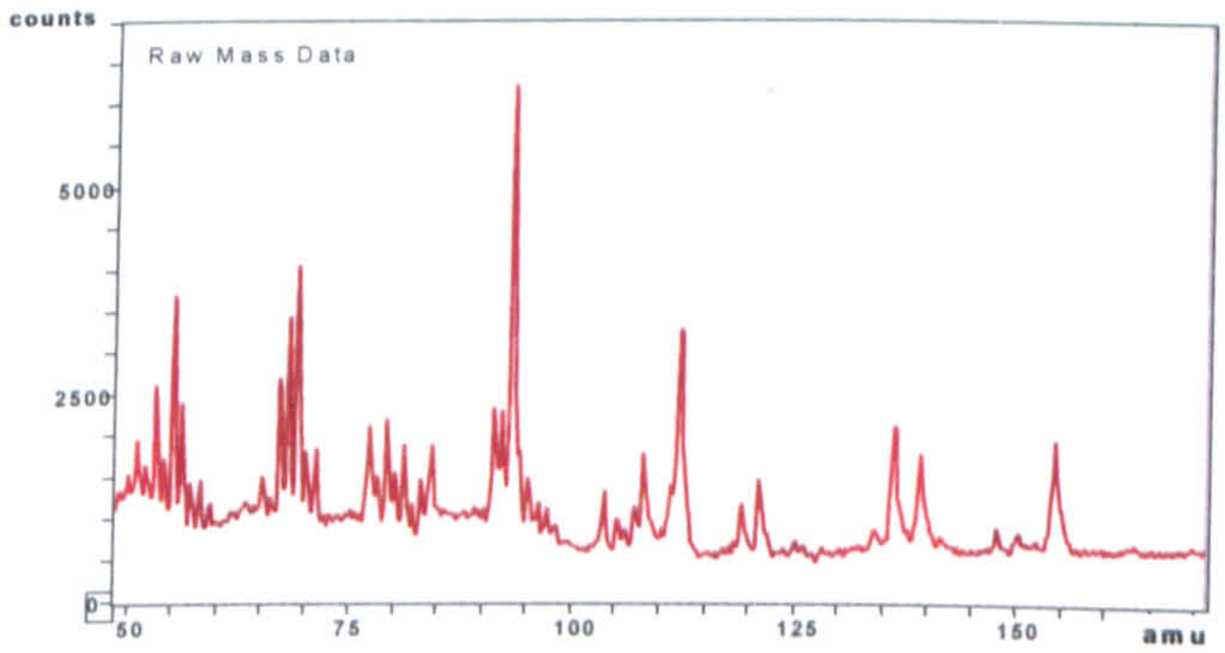
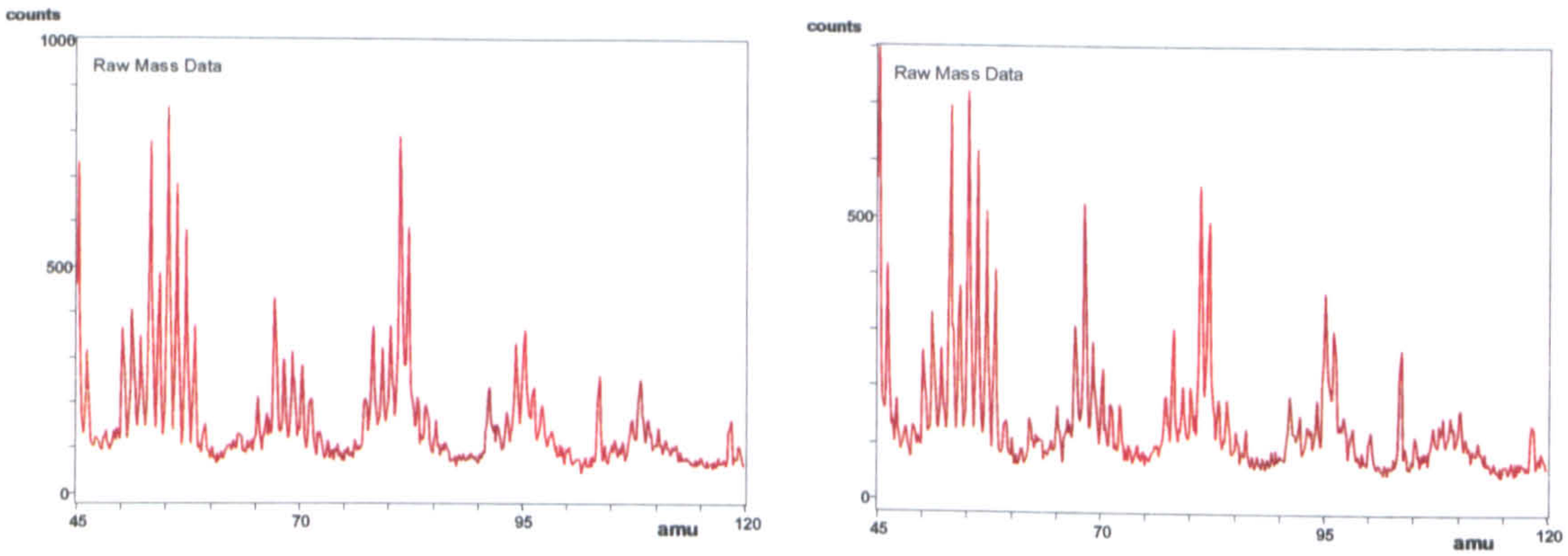


Figure 56: MS-200 Spectrum for Peppermint Tea

The second experiment was performed to see if we could distinguish between different samples, but of the same type. Therefore, two different sorts of coffee were chosen for these tests. One of which was "Tesco Kenyan Coffee", the second was "Tesco Espresso". The acquired mass spectra are shown in Figure 57, the Kenyan Coffee on the left and the Espresso on the right.

At first glance, the two spectra look very similar. However, there are differences in the patterns of the group of peaks between 65 and 70amu, those around 80amu and around 108amu.



Kenyan Coffee

Espresso Coffee

Figure 57: MS-200 Spectra for two different Coffees

The next analysis of the two days old shrimps was chosen and as it had high moisture content, it would provide a contrast to the previous analysis of dry samples. The resulting mass spectrum of the shrimp is shown in Figure 58. Like with the other samples, there are some very clear peaks resulting from the shrimp. One can clearly see a group of peaks appearing between 45 and 70amu. There are also significant peaks at 94, 104 and 119amu.

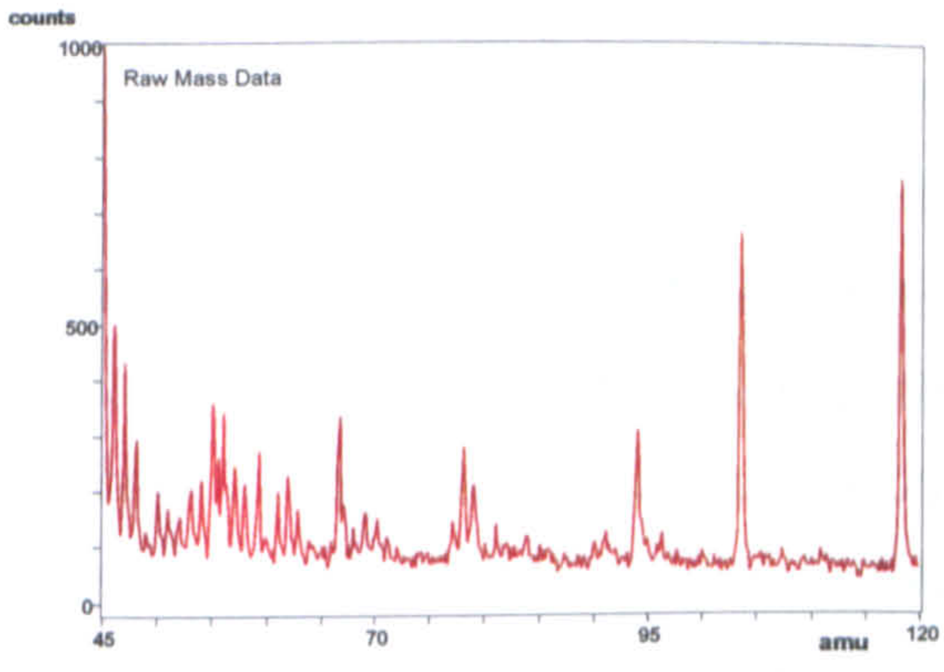


Figure 58: MS-200 Spectrum of Two Day Old Shrimps

These preliminary experiments show that the MS-200 has the potential to measure mass spectra of a wide range of flavours in foods and therefore might have an application in the food industry. In order for the MS-200 to be used for this application, a considerable number of samples will have to be analysed and investigated, to ensure that the spectra were consistent, and to get a library of spectra. This further investigation would lead to an understanding of how the mass spectrum of a flavour changes with the

quality of the product. This knowledge would need to be transferred into a software algorithm, allowing automated evaluation of the results.

5.4.5. Further Applications Investigated by Collaborators

Other researchers or users who are working with the MS-200 are using the instrument for the following applications:

I. Japanese collaborators are undertaking soil gas monitoring, where environmental legislation requires a list of 11 chlorinated hydrocarbons to be monitored on brown field industrial sites.

II. The Desert Research Institute in Nevada is undertaking measurement of the BTX exposure of drivers in various driving situations, including petrol refuelling and cars parked in garages that are part of the house. This study is sponsored by the Environmental Protection Agency of the USA and the American Petroleum Institute.

5.4.6. Applications where the MS-200 did not had Sufficient Sensitivity

The list of applications that were under investigation during the work on this PhD would not be complete if applications where the sensitivity of the MS-200 was not sufficient were not mentioned. Here are three of these that were tried during the course of this PhD.

— *Industrial monitoring of Phosgene*

Phosgene is an intermediate product in the chemical industry and is used for example as the basis for many polymers, such as polyurethane foam. Annually, approximately 3×10^9kg of phosgene are used worldwide. Phosgene is highly poisonous and current monitors are unsatisfactory. Monitors for air include ultraviolet spectrophotometry, gas chromatography, infrared spectrophotometry, automated colorimetry and paper tape monitors containing 4-(4-nitrobenzyl)-pyridine and *n*-benzylaniline. We were addressed by one of the biggest chemical manufacturers in Europe to find

out if the MS-200 would be able to measure phosgene at levels below 400ppb.

The MS-200 was used in its standard operating mode, and a background spectrum of clean nitrogen was collected. Phosgene was then supplied at a concentration of 400ppb. Even after 15 minutes, the MS-200 did not report any signal for phosgene.

Information from a silicone manufacturer has shown that phosgene has reasonable permeation through silicone membranes, as used in the MS-200. However, due to phosgene's double bound oxygen it will have a very strong tendency to adsorb onto the stainless steel surfaces inside the vacuum chamber of the mass analyser. This results in the entire sample being lost before it can be ionised and analysed.

Potential solutions would be to passivate the internal surfaces of the MS-200 using a passivation process like "silcosteel", which is a glassy coating onto the stainless steel. Another alternative is to operate the mass analyser of the MS-200 at an elevated temperature. Both possible solutions will need further investigations, as the electrical properties of silcosteel are not fully understood and the heating of the analyser chamber will lead to an increased background signal, due to outgassing of the stainless steel.

— Hydrogen sulphide from car exhausts

Modern cars using catalytic converters are known to emit hydrogen sulphide. As a result of interest from a major European car manufacturer it was decided to investigate if the MS-200 could be used to measure hydrogen sulphide emissions during different driving conditions.

The MS-200 was used in its standard mode, and a background spectrum of clean nitrogen was supplied. This was followed by a gas standard containing various combustion products, including hydrogen sulphide at a concentration of a nominal 10ppm.

The MS-200 did not report any response for the hydrogen sulphide, even after waiting for 20 minutes to allow permeation through the membrane. As with the phosgene measurement, it is assumed that the hydrogen sulphide permeates relatively easily through the membrane. However due to the double bound sulphur, the hydrogen sulphide molecule is strongly electronegative, and therefore adsorbs onto the stainless steel walls of the vacuum chamber. The potential solutions again, are passivation of the vacuum chamber or heating of the chamber.

— Measurement of Inorganic components

A common request for the MS-200 is for the measurement of inorganic compounds in the atmosphere. In principal, the MS-200 is able to measure these compounds. However, despite the very high vacuum of about 10^{-6} Pascal, the majority of the compounds inside the vacuum chamber are the major constituents of air (nitrogen, water, carbon dioxide, oxygen and argon. Many of the inorganic compounds however, have mass patterns that interfere strongly with the mass peaks from the air background that are present in such a concentration that they are saturated. Once saturation is reached, quantitative analysis is no longer possible (more information on saturation, see Appendix 5).

6. General Discussion

This chapter revisits and adds to the discussions in the previous chapters of this thesis. It brings together many of the issues found during the course of the work on this thesis, and covers issues that cross chapters, allowing a broader discussion than is possible in each of the previous chapters. Many of the issues here are taken forward in the next conclusions chapter, together with issues raised elsewhere in the thesis.

6.1. General Approach for the Experimental Work

The laboratory based performance tests were designed as to give as a broad an understanding of the instrument as possible. Chemicals investigated in this part of the work were chosen to represent a range of different groups of chemicals that might be of interest in different applications. The major part of this work was based around an application request from customers. In the same manner, every application discussed in chapter 5 is based on a real situation relevant to industry or research institutes where the MS-200 could be used. This means that the applications selected were representative of real world analytical tasks and problems, rather than simply theoretical challenges.

6.2. General Performance of the MS-200

The MS-200 is different to all other commonly used mass spectrometers that are built to perform VOC analysis in air known to the author. As a result of this, the evaluation of the performance of the spectrometer was more detailed than if the instrument would have been a variation of well understood systems. An overview of some of the findings from the laboratory performance work described in chapter 3 are listed in Table 33, and summarise the kinds of responses and sensitivities of the MS-200.

Table 33: Extract of results from chapter 3

	Time response [min]	Linear [%]	Sensitivity Factor [relative to nitrogen being 5]*	Detection Limit (for 3σ) [ppb]	7 week stability of calibration [%]*	Influence of Moisture from 0 to 50% onto RSF Normalised to 1 when dry
o-xylene	< 5	< 6	159,341	1.4	-3	2.40
n-hexane	< 5	-	35,583	19.2	-11	2.61
Toluene	< 5	-	55,988	2.6	+16	1.47
Ethylacetate	< 5	-	10,200	78	-20	1.75
Methanol	10	-	670	6000	-	-
Propanol	10	-	1,550	360	-	-
Dichloroethane	< 5	-	10,878	16.2	-18	2.27
Trichloroethane	< 5	-	9,600	9.6	-3	1.31
See section	3.2.4	3.2.5	3.2.6 & 3.2.7	3.2.8	3.2.9	3.2.10

*This data was averaged over 5 measurements taken on the same days.

From this table it is clear that the instrument has quite different sensitivities and detection limits for different chemicals. This means that a performance described for the instrument is only valid if it is considered together with the chemical for which this performance was measured. For a different chemical the performance will be different.

In addition to the chemicals more thoroughly investigated described in the laboratory based performance test, the MS-200 was evaluated on some basic performance parameters like sensitivity and detection limit for a large list of compounds. The list of compounds that were additionally investigated originated from other potential applications for the MS-200 investigated during the work, but have not been described in this thesis. It is expected that this range of applications, and the hence the list of chemicals that have been analysed, will be expanded in the future. The sensitivity and detection limit of these chemicals, shown in Table 34, provide important information on the performance of the instrument, and give a guide when estimating potential performance of the instrument to compounds not previously measured.

Table 34: Sensitivity and Detection Limit of MS-200 for various compounds

Chemical Name	RSF From Mixture analysis	Sensitivity From MMP	Detection Limit (3*sigma)	Basis of Calculation	Response Time to Reach 90% of step change
1,3-butadiene	11,435	1.3 c/ppb	35 ppb	mix analysis	
2-propanol		1 c/ppb	6,000 ppb	mix analysis	
Acetonitrile	1,379	1.7 c/ppb	180 ppb	mix analysis	
Acetylene		#	#		
Benzene	44,000	40-80 c/ppb	4.5 ppb	mix analysis	180 sec
Bromine		0.003 c/ppb	14,000 ppb	MMP variation	300 sec
Camphor		25 c/ppb	15 ppb	mix analysis	
Carbondisulfide		23 c/ppb	3 ppb	MMP variation	20 sec
Carvone		15 c/ppb	30 ppb	mix analysis	
Dibromomethane		37 c/ppb	1.5 ppb	MMP variation	20 sec
Dichloromethane		6 c/ppb	20 ppb	mix analysis	
Diethylamine	1,675	1.5 c/ppb	265 ppb	mix analysis	
Diethyleneglycol	33	0.034 c/ppb	11,000 ppb	mix analysis	20 sec
Diethylether	3,372	1.4 c/ppb	80 ppb	mix analysis	20 sec
Dimethylformamide	.	3.8 c/ppb	30 ppb	MMP variation	10 min
Ethane		#			
Ethanol		0.6 c/ppb	1 ppm	MMP variation	7 - 8 min
Ethylacetate		50 c/ppb	50 ppb	MMP variation	
Ethylendiamine		#	#		
Ethylene	28,671	3 c/ppb	56 ppb	mix analysis	
Eucalyptol		25 c/ppb	6 ppb	mix analysis	
Formaldehyde		#	#		
Hydrogensulfide		#	#		
Isobutylene	15,705	1.7 c/ppb	90 ppb	mix analysis	
Isopropanol		2.4 c/ppb	150 ppb	MMP variation	7 min
Limonene		1 c/ppb	300 ppb	mix analysis	
Menthol		15 c/ppb	50 ppb	mix analysis	
Methane	13,083	1.5 c/ppb	780 ppb	mix analysis	
Methanol		0.5 c/ppb	400 ppb	mix analysis	
Methylacetylene	40,369	4.4 c/ppb	23 ppb	mix analysis	
MTBE	3,554	2.5 c/ppb	63 ppb	mix analysis	10 min
n-Heptane	83,414	128 c/ppb	14 ppb	mix analysis	40 sec
n-hexane		20 c/ppb	20 ppb	mix analysis	
Nitrobenzene		99 c/ppb	2 ppb	MMP variation	20 sec
Octamethylcyclotetrasiloxane		80 c/ppb	6 ppb	MMP variation	
Pentanol		21 c/ppb	33 ppb	MMP variation	200 sec
Pentene	2781	3 c/ppb	260 ppb	mix analysis	

Phosgene		#	#		
Propylene		#	#		
Pyridine		58 c/ppb	4 ppb	MMP variation	140 sec
Sulphur Dioxide		0.012 c/ppb	####	MMP variation	10 min
Tetrachloroethylene		65 c/ppb	600 ppt	MMP variation	20 sec
Tetrahydrofurane	14,488	11 c/ppb	35 ppb	mix analysis	1.5 min
Thymol		25 c/ppb	5 ppb	mix analysis	
Toluene	1,320,000	48 c/ppb	750 ppt	mix analysis	
trans1,2,dichloroethylene		5.6 c/ppb	6 ppb	MMP variation	
Trichloroethane		3 c/ppb	30 ppb	MMP variation	
Trichloroethylene		15 c/ppb	8 ppb	MMP variation	
Triethanolamine		#	#		
Xylene		100 c/ppb	2.5 ppb	mix analysis	
Methyl Mercaptane		#			

Key:

MMP	= Major Mass Peak method, described in section 3.4.1
RSF	= Relative Sensitivity Factor, described in section 3.2.6
Mix analysis	= Detection limit was calculated as described in section 3.2.8
MMP variation	= Detection limit was calculated as described in section 3.4.2
#	= Value could not be determined, normally because the sensitivity was not sufficient.

Note: *The values that are given in this table can vary from the ones that are discussed in other parts of the PhD. This is because values were measured over a time scale of about 5 years, using different instruments with different sensitivities. The results here are the most recent at the time of writing.*

From the experience gained during the work and from the sensitivity measurements shown in Table 34, the likely sensitivity of the MS-200 depends on the molecular weight and the polarity of a compound, and can be approximately represented by Figure 59. This can be expressed by a simple diagrammatic representation, resulting mainly from experience gained in real applications. This approximation helps when estimating the sensitivity of the MS-200 to a compound not previously measured.

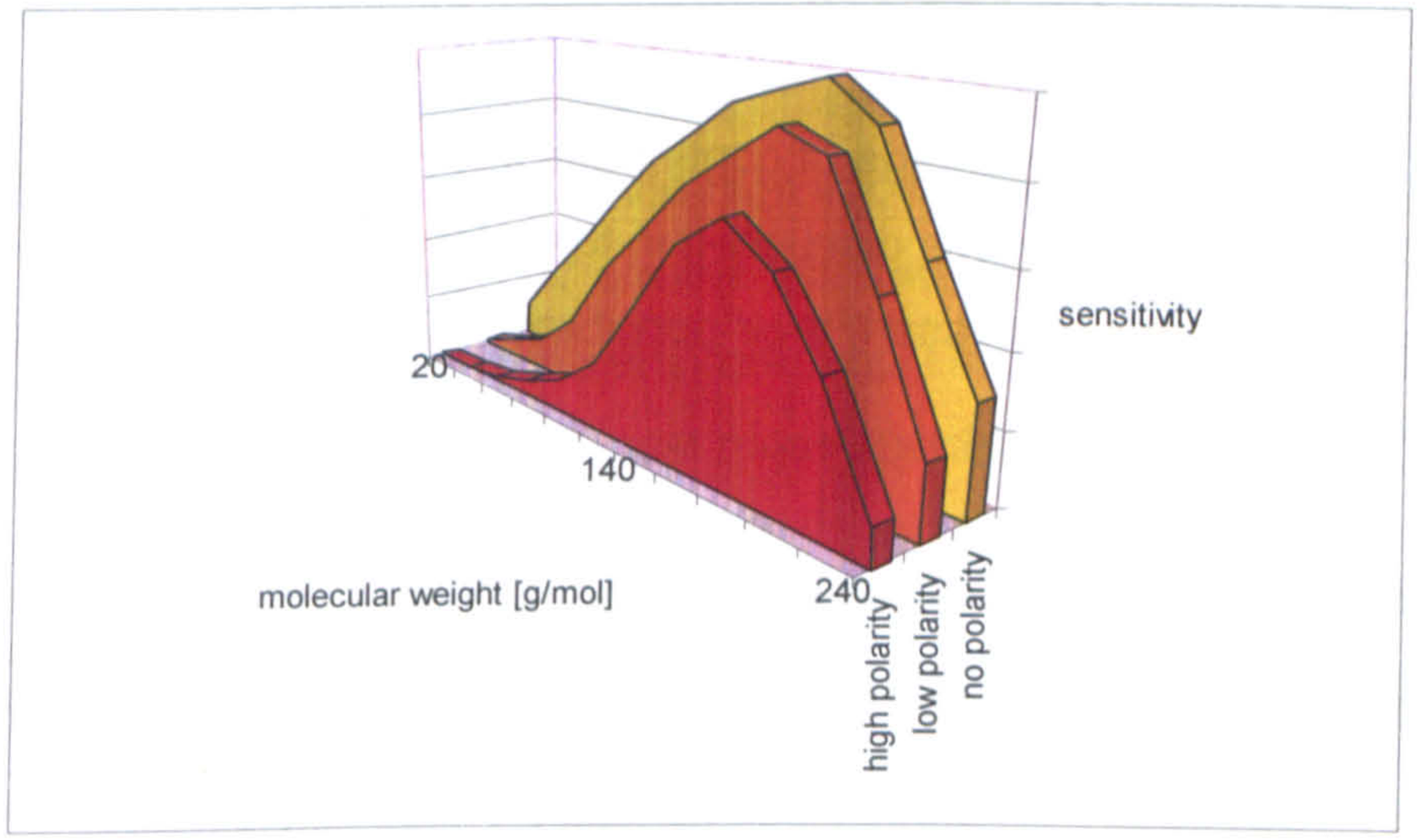


Figure 59: Approximation of sensitivity of MS-200 based on physical properties of the analyte

Figure 59 does not consider the electronegativity of a compound. High electronegativity will cause the compound to adsorb onto the stainless steel of the analyser system, and therefore independent of its permeation rates through the silicon membrane, the compound will have a very poor sensitivity. A good example for this is the sensitivity for phosgene, with a molecular weight of 98 and no polarity, which referring to the chart should be reasonably high, but reported no signal at a concentration of 400ppb (see section 5.4.6).

During the evaluation of the trap evacuate desorb inlet (TED, chapter 4), and its application in the breath analysis described in section 5.3, it was found that the detection limit of the MS-200 could be enhanced by at least two orders of magnitude for many of the compounds under investigation. No reason can be seen why a similar enhancement in sensitivity and detection limit could not be achieved for all of the compounds in Table 34, provided that they have reasonable adsorption and desorption efficiencies for the trap material used.

6.3. Advantages of the MS-200

The MS-200 offers the advantage of continuous low ppb level monitoring for many VOCs. Other techniques discussed in the introduction (section 1.4) allow this. However as discussed, their portability is limited by weight and/or power consumption.

Other than the use of electricity at a peak consumption of 45W and an average of 20W there are no further requirements to operate the MS-200. This low power consumption allows the instrument to be operated from a battery, or potentially a small solar panel or fuel cell. The closed vacuum system and the power-less emergency pumping provided by the getter pump (section 2.3) means that the vacuum required to operate the mass analyser will not be compromised by any loss of power. This gives the MS-200 a huge advantage over other transportable instruments available shown in Table 1 (section 2.1), when being deployed in situations were supply of consumables or return to a mains power supply are limited. Such applications could include the air quality monitoring on the international space station or its deployment for the detection of chemical warfare agents during a military conflict.

An additional advantage of the MS-200 compared to the other instruments, highlighted in Table 1, is the low weight of 20kg. The Hapsite GC/MS has a lower weight, however it requires an additional base station of about 24kg recommended for start up of the instrument [(EPA 1998)]. Again this results in advantages for the MS-200 when employing the instrument in situations where it is difficult to return to a base station in between measurements.

All the other systems mentioned in Table 1 use mechanical vacuum pumps (in the case of the Hapsite aided by a non-evaporative getter pump, which needs replacing about every 30 days [(EPA 1998)]). These vacuum pumps are very sensitive to shock and vibrations [(Corlett 2000)]. Losing power when using mechanical vacuum pumps results in loss of vacuum within the mass analyser. This loss of vacuum is likely to cause contamination and a lengthy start up procedure in order to achieve the vacuum pressures required to operate the instruments. The ion and getter pumps used in the MS-200 have

no moving parts and are therefore extremely rugged and require no maintenance, and do not result in a loss of vacuum when the instrument is not powered. Other advantages of the high vacuum levels and the sealed vacuum employed in the MS-200 are the fact that the filament of the electron source is operated in a very clean environment. This means that the problem of filament poisoning, common to most mass spectrometers, does not occur in the MS-200.

Using mass spectrometry with a 70eV electron impact ionisation source provides the potential to identify unknown chemicals with acceptable certainty by comparing the mass spectral finger print of the unknown chemical with a database of spectra (NIST 1998). This is a significant advantage over GC or many optical VOC monitoring methods which do not offer the positive identification of a chemical compound by comparison to unique mass spectral patterns.

Comparing the MS-200 with its closest commercial rivals, the transportable and portable GC/MS instruments shown in Table 1 (section 2.1), the MS-200 is the lightest instrument. The 20kg for the MS-200 is half as much as the next competitor, the Hapsite, which together with its base station weights about 40kg (EPA 1998) and the Constellation CT 1128 at 36kg. At a sales price of £30,000 the MS-200 is winner also on the cost (crucial for the 'real' world commercial success of an instrument), with the Hapsite at about £70,000 being second and the Spectra Trak at about £100,000 being third. No prices for the Brucker EM 640 and the Constellation CT 1128 are known, but due to their capabilities and design are assumed to be higher than for the MS-200.

6.4. Limitations of the current MS-200

When dealing with very complex samples, for example the headspace of petrol, the membrane inlet of the MS-200 will allow all components to pass into the mass analyser at the same time. In order to identify and quantify the different components of such a mixture the MS-200 employs a mixture analysis software. This approach has limitations in the number of compounds that can be identified and quantified within a single sample. GC/MS

technologies do have the advantage of first separating complex mixtures into individual compounds, before introducing them into the MS for identification and quantification. However as suggested in the future work on the TED, further investigations may enable the TED to be used as a simple pre-separation potentially reducing this problem (although at the expense of continuous analysis which is not possible with the TED).

The PDMS membranes used in the MS-200 inlet system provides excellent permeation characteristics for many VOCs, for example aromatic and chlorinated hydrocarbons, allowing detection limits of very low ppb to even ppt levels. However, the permeation characteristics of these membranes to low molecular weight, polar components, such as the alcohol methanol and propanol are not as good and therefore such components do have detection limits only in the low ppm to high ppb levels.

The design of the analyser vacuum relies on very small amounts of samples being introduced to the system. Most analysers introduce the samples as a stream of gas that is passed through the ionisation source, and so avoiding contact with the internal surfaces through adsorption. However the membrane inlet of the MS-200 only allows the permeation of individual molecules into the vacuum system, which arrive there with a low, non-specific kinetic energy, and move freely within the vacuum and disperse uniformly due to molecular movements. The low molecular density of the vacuum means that every molecule is likely to impact onto an internal surface of the analyser chamber. For most molecules this is not a problem, as they will simply bounce off the surface and thus freely fill the space available. However, for some molecules with a tendency to adsorb strongly onto stainless steel surfaces this provides a problem. In these cases, all the molecules will adsorb onto an internal surface before reaching the ionisation area of the analyser, and will get lost before ionisation and analysis can be performed, resulting in a very low, or no sensitivity. Examples for these limitations are the measurement of H_2S and phosgene, reported in section 5.4.6.

Having the advantage of the sealed vacuum system, which is not affected by power failures, does come also with a limitation. Replacing the detector or any other part within the vacuum chamber results in a vent to the vacuum. As described in section 2.3, this vent means that the system has to be brought to a pumping station and pumped to vacuum levels where the ion pump can take over pumping, making a detector change time consuming and expensive.

The getter pump, which is employed as a contingency back up pump when the instrument is turned off or during power failure, has proven to be a successful approach. However, if the instrument is exposed to samples with high levels of moisture or very high concentrations, then the pump will saturate its surfaces, due to adsorption of too many molecules, leading to a change in its pumping speed. This causes a drift in the chamber pressure and therefore a drift in sensitivity, and means that the calibration is no longer valid and the results of the instrument are unreliable. Given some time this process reverses as the adsorbed molecules slowly diffuse into the getter material, and the instrument returns to its previous sensitivity. If care is taken to supply only dry and low concentration samples to the analyser this drift in sensitivity is not observed.

In order to reduce the size and weight of the instrument it was decided to allow only the measurement of the positive ions created in the ion source. For the measurements of most VOCs this is not a disadvantage, as the positive ionisation of theses compounds is very common. However, for some compounds, which produce mainly negative ions when fragmented, being able to analyse the negative ions would result in a higher sensitivity of the measurement (Ylnon, Zitrin 1996).

6.5. Deployment Issues

Deployment issues in the handling of the instrument do not differ significantly from handling any other similar scientific instrument. For example, one should avoid steep temperature changes, and extremes of temperatures, as well as exposure to strong shocks or heavy vibrations. However, a few issues should be borne in mind when using the MS-200.

The disadvantages discussed above, of not having the pre-separation that exists in a GC/MS system, is that the software will have to perform a de-convolution of the different compounds in the sample. This is similar to UV and FTIR spectrometers, where the superposition of different adsorption spectra are analysed. This results in the fact that the user must have some knowledge about the components that are in a sample in order to perform quantitative analysis.

Another issue is that under most circumstances the MS-200 should be used on dry samples only in order to avoid high moisture problems with the analyser chamber. Drying the sample is easily performed using a Nafion® dryer. However one has to be aware of the working principles of this dryer and how it affects certain chemicals from a sample. For example, not only water is removed, but also low molecular weight alcohols. Additionally some other compounds undergo chemical changes when in contact with the dryer. The use of these dryers and how samples are affected is thoroughly described by the manufacturer [(Permapure 2002)]. Whilst not in use, and whilst the lid of the instrument is closed, the MS-200 is water tight to IP66 standard (can cope with spray water). However, during operation the instrument lid needs to be open at which stage the instrument should not be exposed to rain or any other liquids or significant levels of dust.

6.6. New / Potential Applications Possibilities with the MS-200

There are several applications undertaken as part of this thesis that would not have been possible to measure by any other commercial VOC analytical system. For example, the measurement of benzene exposure during refuelling of a petrol vehicle (described in section 5.1). These exposure studies are commonly performed by adsorption tube measurements, which report a time averaged exposure, followed by careful modelling of the estimated exposure during the refuelling cycle [CONCAWE 1999, DEFRA 2002]. The MS-200 has clearly measured the exposure where and as it happened, therefore potentially removing all the uncertainties involved when employing models for the calculation of personal exposure. This results in the portable MIMS technology having the potential to replace the current modelling methodologies for this purpose, or alternatively to provide valuable information to confirm the validity of a model. The portability, sensitivity and continuous measurement of the MS-200 were key in this application.

Analysing potential contamination of protective suits (described in section 5.4.3) was another application field that at the speed and sensitivity it was performed would not have been possible with any other commercially available system. Being able to identify unknown contamination on protective suits within a few minutes provides a cheap alternative to pre-concentration of the sampled air onto adsorption tubes and lengthy GC/MS analysis. The portability and speed of the MS-200 again is a key advantage in emergency situations where fast identification of contamination, either on protective suits, or at sites of chemical spills / attacks is required.

Other applications, where the real portability, mains independence and speed of analysis is of advantage include on the spot check of whether industries are conforming to agreed emission values. An operator can walk along the boundaries of a plant, taking a continuous profile of concentrations of VOCs to check this. In a similar manner, the instrument has the potential to be used for on the spot check in manufacturing plants, to check if air-cleaning equipment to remove VOCs from an industrial process is maintained and working properly. The same spot check could potentially be employed to

monitor functionality of air cleaning equipment used in pubs to remove carcinogenic VOCs from cigarette smoke, potentially reducing the exposure of non-smoking visitors. This application is currently pursued together with a manufacturer of such air cleaning equipment.

The above examples are only few of the examples that were discussed with potential users of this technology and do not represent a complete list. Like with many different methods, further uses are identified once an analytical method is available that makes this use of interest. A recent example of this involves that analysis of a product spiked with a tracer, allowing on the spot checks if the product at a sales outlet is genuine or a replica undercutting their markets.

7. Conclusions and Recommendations

During the work on this thesis, the MS-200 has moved from a technology demonstrator (initially called T-CAT), to be a rugged, reliable and technically advanced instrument. At the time of writing, 45 instruments have been produced and sold world-wide. The distribution of instruments spans Japan, Korea, Kazakhstan, Europe to the US. The applications that the MS-200 is used for are diverse and include: environmental soil gas analysis; arson investigation; national security measures; soil contamination on rocket launching sites; environmental monitoring in industry and research; breath analysis, and potentially air quality monitoring in submarines and the international space station. This list is not exclusive, and new interesting applications are continually being added as they are investigated.

The thesis describes the design of the instrument and the investigation into its analytical performance. The results of this work show that the MS-200 is a robust and reliable portable mass spectrometer. It is particularly suited to measuring volatile organic compounds (VOCs) down to ppb levels, and with the TED adapter down to ppt levels. It has been tested with traditional methods such as the GC/MS system and proven to provide reliable results.

7.1. Conclusions

At the beginning of this thesis, five objectives were set out (see section 1.6). The structure of the thesis followed these objectives, and the discussion below looks at how these objectives were met. This should be seen in conjunction with the specific discussions in each section, as the issues raised there are not repeated here.

During the work, the performance of the instrument was tested and the results of these tests were fed back into the design process of the MS-200. Specific improvements that were achieved during the course of this PhD, above the general work on making the instrument more rugged and hence improved the portability, included addressing the following major points:

- Permeation through silicone membranes is highly temperature dependent, and the initial instrument had the membrane inlet at room temperature. Changing to a temperature controlled membrane inlet meant that permeation through the membrane was very stable and therefore improved the analytical stability significantly.

- Sensitivity, detection limits and mass resolution of the technology demonstrator were in the region of 5 counts/ppb and detection limits of 30ppb for benzene (calculated after the method described in section 3.4). Current instruments commonly achieve a sensitivity of 50 to 80 counts/ppb for benzene with detection limits of about 2ppb. Most of this improvement was achieved by design changes to the ionisation source, as well as a different tuning approach[8], developed during the work.

- The interface between the instrument and the laptop computer was improved. The interface now allows automatic control of most switches and operation of the instrument, making it easier to use and even allows remote operation.

Some other improvements to the MS-200 that were triggered specifically by the work on this thesis were:

- The development of a different approach when performing background subtraction of a mass spectrum, reducing errors during this mathematical process and therefore helping in improving the analytical precision and enabling lower detection limits to be achieved.

- Including a possibility to bake the getter pump of the instrument during instrument maintenance. This is helpful to reduce background contamination of the measurement, and again is a requirement to achieve lower detection limits.

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[8] The ion optics has certain tolerances, and therefore the voltages required for each instrument are different. These voltages are "tuned" to produce the best performance.

- Another additional maintenance option included was being able to automatically switch all parts of the electron source to ground potential. This results in the electrons from the electron-emitting filament impacting the surfaces of the ionisation source, and releasing the molecules that have been adsorbed onto these surfaces. This is useful to clean up internal surfaces of the source and therefore reduces background contamination.

Many more, although sometimes minor, changes to the instrument were made during the program. All of these helped towards the MS-200 being a truly portable VOC analyser with good analytical performance, high sensitivity and low detection limits. Some of the experiments within this thesis were undertaken with different versions of the instruments at different stages of its development and incorporating improvements as they were identified. During the course of this research work, the true portability of the instrument has been demonstrated by taking it in a car, on aeroplanes and even on trains. As an example, its advantage of being independent from mains power with automated analysis allowed it to be installed in a car, taking measurements whilst driving, needing no care other than the safe securing of the instrument on the rear seat.

Further enhancement in sensitivity and detection limits were achieved with the trap evacuate desorb interface (TED). The TED described is a fairly new development, and no reports of such a technique being used before were found in any literature, and it is now being patented. It was shown that this new interface technology has the potential to increase the detection limits by two orders of magnitude, into the low ppt range. The viability of this approach to real applications has been demonstrated with experiments within the applications described in the thesis. The combination of a commonly used technology (the pre-concentration of a sample onto an adsorbent trap) together with the vacuum desorption of the sample, offers distinct benefits. These range from the possibility to deal with very moist samples, to analysis of contaminated samples at very high sensitivity. Although the TED offers considerable advantages, there are also some disadvantages. The main

disadvantage is the loss of semi-continuous analysis, possible when using the double membrane concentrator. The findings of the work on the TED have been fed back into the next design cycle, which will be followed by a commercial launch of this new inlet in the next few months.

Seven interesting applications were selected, based on real world problems and are described in this thesis. For most of these applications, the performance of the instrument was first tested for some model samples, and then followed by further testing on more realistic samples and employment in the field. For example in the arson investigation, where the instrument was initially tested on sawdust samples burned using different accelerants. This was followed by more realistic measurements on burned carpet samples, and finally the analysis of a debris sample from a real fire incident. A similar approach was taken in the work describing the breath analysis, the protective suit application and the personal exposure measurements to benzene whilst refuelling a petrol car.

The various applications undertaken during this study have allowed the potential of the MS200 to be investigated. Following from this, the major potential of the instrument is seen in the study of personal exposure, the breath analysis and the arson investigation, combined with chemical spills/attacks emergency situations. This is because these applications seem to offer high commercial value and the MS-200 is believed to be able to be employed into these applications without major changes to the instrument.

From the discussion above, it can be seen that the objectives of the PhD have been achieved. In addition, the instrument was tested on an extensive list of compounds (Table 34, section 6.2). The applications described, plus the list of sensitivity and detection limits, should help in an easy assessment of further applications as they arise.

7.2. Recommendations for Future Work

Some issues identified during this thesis could benefit from further investigation and might lead to additional improvements of the instrument and its analytical performance. The different fields that should be investigated are the inlet system, the vacuum system, the ionisation source, the software and some general points. The further work that is suggested from the work in this thesis is described in more detail in the following section.

7.2.1. Further Work on the Sample Inlet System

In its current form, the membrane inlet does not separate the different components within complex samples, but allows all components into the analyser at the same time. Resolving the concentrations of different compounds is the task of the mixture analysis software, which relies on prior knowledge of model spectra for each compound in the mixture. As shown, this works well, as long as all components in the sample are known, but introduces a large error for each additional compound in the sample not identified prior to analysis. This limits the instrument's application to those areas where the content of a sample is known, or where only one unknown compound in an otherwise known sample matrix needs to be identified. In order to deal with complex samples containing unknown compounds, and improving the possible identification of unknown compounds, the instrument would benefit from some pre-separation of the sample, which would potentially remove some of the complexity. Therefore, it should be investigated whether the TED interface could be used as a simple pre-separator, by slowly heating up the trap tube, and desorbing the samples at times dependent on their affinity for the trap material. Although this may not produce a clear separation, as on a properly tuned gas chromatographic separation column, it might be sufficient in some applications to reduce the complexity to a level where the mixture analysis software can deconvolute the sample.

In order to achieve the full capability of GC/MS analysis it should be investigated if the instrument could be fitted with a GC, without compromising too much on weight, power consumption, speed of analysis and portability.

The TED described in this thesis could benefit from further investigations into the suitability and cleanliness of the adsorbent materials used. Cleaner adsorbents could reduce the background reading when using a TED, and therefore might reduce the detection limits even further than the low ppt level reported. The adsorbent material currently used in the TED were found not to be ideal for some of the applications, and further work should investigate alternative materials.

During the analysis of heavier molecular weight components, the time delay of the compound through the semi-permeable membrane started to slow down analysis. This delay time is mainly dependent on the thickness and the temperature of the membrane that are used. This can be improved by reducing the thickness or by elevating the temperature of the membrane.

Currently available sheet membranes of polydimethylsiloxane (PDMS) are commercially available only to a minimum thickness of 0.025mm. Preliminary tests, though not reported in this PhD, have shown that it is possible to produce thinner membranes by spin coating liquid PDMS onto a copper support. This copper support has a specified number of holes drilled in it, to ensure the overall permeation of gases is about 2mbar*litre/second, whilst still providing sufficient support for the membrane to sustain the forces caused by full atmospheric pressure. These membranes are hoped to reduce the permeation time for heavier molecular weight components significantly. Future work should include an investigation into the minimum thickness of membrane that can be produced reliably, without the risk of creating pinholes. As we are able to produce membranes in-house, it should also be investigated whether membrane materials could be functionalised, similar to the coatings of GC separation columns, potentially improving the permeation for polar compounds and increasing sensitivity for their analysis.

The current set up of the MS-200 has a temperature limitation of about 80°C for the inlet system, which holds the membranes. Speeding up the permeation of heavier components could also be achieved by re-designing the inlet system, allowing higher temperatures on the membranes. Higher temperatures would also benefit the cleaning up of the inlet after being exposed to high concentrations of "sticky" components, which potentially cause high background readings during analysis of clean background. However, one has to be aware that increasing the temperature of the silicone membrane will reduce the selectivity for some compounds (such as the organics like benzene and xylene) and, therefore, reduce the sensitivity for these compounds.

Another issue on the inlet system, potentially causing high background readings when supplying clean air, is the fact that the current inlet valve uses a polymer seal to protect the vacuum system of the analyser from the environment whilst it is not in use. Replacing this sealing technology with a metal sealing technology could further reduce the background reading, as the polymer seal has the tendency to adsorb components and release them slowly, causing contamination. This would, therefore, potentially improve the detection limit for some compounds that are currently limited by the height of background signal.

Some applications commonly need to measure very high concentrations of sample, followed by low concentrations. Memory effects from the high concentrations will require some waiting time before the background measurement is sufficiently clean to analyse the low concentration samples. These applications, like the arson investigation, could benefit from a sample dilution fitted into the sample inlet line, allowing the selection of pure, or diluted, sample to avoid high concentrations in the analyser.

7.2.2. Further Work on the Vacuum System

It was found that some compounds, mainly those that contain double bound oxygen groups or double bound sulphur in their molecule structure, have low sensitivity. These components are believed to have a tendency to adsorb

onto stainless steel surfaces which could result in part or all of the sample adsorbing onto the inner surfaces of the analyser chamber. Future investigations should include ways to understand and minimise such potential adsorption effects, potentially by applying a passivating coating - i.e. one that has less tendency to adsorb chemicals - onto the surfaces. The current method for passivating stainless steel to minimise the adsorption of sulphur compounds is to coat the stainless steel surface with a thin silica glass layer. In order for such a passivating layer not to influence the ion optics of the analyser negatively, it would have to be a good electrical conductor, to prevent charging which would disturb the electric fields. The electrical properties of the glass coating are not understood yet, and therefore it may not be able to be used on the MS-200, and another passivation technique may have to be found.

7.2.3. Further Work on the Ionisation Source

The ion source of the MS-200 creates neutral and positive as well as negative ions. However, only the positive ions are currently accelerated, guided through the ion optics and detected. Some samples with heavier molecular weights are known to have a higher tendency to form negative ions when ionised by electron bombardment, due to electron attachment. For these chemicals, it would be beneficial if the polarity of the extract pulser and the ion optics could be reversed, allowing the analysis of negative ions. It should be investigated if reversing polarities can be achieved without compromising the portability of the system.

Ionising larger molecules by electron impact can result in relatively heavy fragmentation of these compounds. Heavy fragmentation will reduce signal on individual peaks, and adversely affect the detection limit. In these cases, it would be beneficial if the instrument could use a softer ionisation, like an UV ionisation source, ionising the sample with low energy photons. The use of UV ionisation has been raised as a possibility for a specific applications and is currently being investigated.

7.2.4. Further Work on Software Issues

The software currently used to analyse the spectra produced by the MS-200 is intended for research. This software has many built in features, such as the mixture analysis routine, including a pre-defined set of model spectra for the compounds under investigation, auto processing a number of spectra to avoid laborious repetitive tasks, and many more features. This software is an excellent tool for developing applications, and defining the analysis parameters required. However, once an application is investigated, the software would benefit from tailoring to the specific needs for this application, thus easing the analytical task for the operator. This has been demonstrated for the Japanese soil market, where a specific software and user interface has been produced, tailoring the system for the specific task.

7.2.5. General Points of Further Work

Future work should also include the aim of specifying the sensitivity, detection limit and delay time for a larger list of components than those investigated so far. This will help to improve the understanding of the analytical performance, and would allow better estimation of performance of the measurement of compounds not previously measured.

Summing up, the membrane inlet mass spectrometer, as described, will not be able to replace or compete with the versatility of a GC/MS system, which has established itself as the industry and research standard for VOC analysis. However, there are a huge sub-section of applications, some of which were investigated and discussed here, for which the GC/MS analysis is too sophisticated, takes too long and is too expensive. These are the niches for a membrane inlet mass spectrometer, or the TED, which allows fast and quantitative analysis of VOCs with potentially similar sensitivity to the GC/MS. Some of the suggested points for future work will help to improve the analytical performance and therefore increase the number of applications where the use of the MS-200 system or the TED could be of benefit.

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Appendix 1. Production of a VOC mixture by sample bag Injection

A set of experiments was performed to determine the repeatability of the gas standard production using sample bag injection method explained in section 3.1.2.

Metering of small volumes of a VOC, using a syringe is difficult, and the introduced error can be relatively large compared to the injection volume. In order to be able to produce a mixture of components in the 1 to 3ppm concentration range, a solution of the VOCs of interest was produced. 4µl of each of the volatile in Table 35 were injected into 1ml of methanol. Then 0.5µl of the stock solution was injected through a heated injection port into a 10 litre nitrogen sample bag. The calculated concentration of the VOCs in the sample bag is reported in Table 35.

The sample was analysed by the MS-200 in the normal way, by first analysing a background signal, then supplying the gas standard from the sample bag, waiting for five minutes and then perform a measurement.

Table 35: Components and Approximate Concentration in the Sample Bag

Component	Calculated Concentration in Sample Bag
Trans-1,2-dichloroethylene	1.28 ppm
1,1,1- trichloroethane	0.97 ppm
Trichloroethylene	1.08 ppm
Tetrachloroethylene	0.95 ppm
Benzene	1.08 ppm
Toluene	0.91 ppm
o-xylene	1.98 ppm
Methanol	30 ppm

To test the repeatability of the method, the production of the standard was repeated five times by injecting 0.5µl of the solution into the sample bag and performing an analysis.

Table 36 shows the mixture analysis assigned counts for each VOC in the different sample bags. The numbers show that there is a variation of up to ± 20% around the average result. This is a higher variation than is expected

from the repeatability of the instrument. Therefore it appears that even using a solution of the analyte in methanol (which allows larger injection volumes) injection of a precise volume appears difficult.

Table 36: Sample bag injection without normalisation

	1	2	3	4	5
Toluene	483457	622184	551308	629475	444432
trans-1,2-dichloroethylene	311511	377168	312457	330501	274004
Tetrachloroethylene	1.25E+06	1.60E+06	1.45E+06	1.61E+06	1.17E+06
Benzene	472337	533722	500554	540549	434401
1,1,1-trichloroethane	1.11E+06	1.18E+06	1.16E+06	1.24E+06	1.02E+06
Trichloroethylene	643305	794730	716346	770254	621564

To improve the repeatability, it is proposed to normalise the injection volume to a chosen mass peak of one of the components in the mix. For the following figure the results were normalised to the 78amu peak. Normalisation adjusts all concentration calculated by the mixture analysis software to the height of the chosen internal standard peak. Stretching or compressing all concentrations with the same factor as the change in the peak, to which the spectrum is normalised, should result into the removal of the uncertainties in the production of a standard in the sample bag.

To test the proposed normalisation method, a sixth sample bag was deliberately injected with 0.8µl instead of the 0.5µl in the other 5 samples.

Figure 60 shows the mixture analysis assigned total counts for the different components normalised to the area of the 78amu peak. The variation of each of the measurements from the average has improved to better than ±10%.

Table 37: Sample bag injection with normalisation

	1	2	3	4	5	6
Toluene	483457	541566	511122	538797	477916	539106
Trans-1,2-dichloroethylene	311511	328297	289681	282891	294648	302125
Tetrachloroethylene	1250000	1392683	1344306	1378073	1258149	1375453
Benzene	472337	464566	464067	462681	467129	458120
1,1,1-trichloroethane	1110000	1027104	1075445	1061373	1096848	1024060
Trichloroethylene	643305	691754	664130	659296	668394	675513

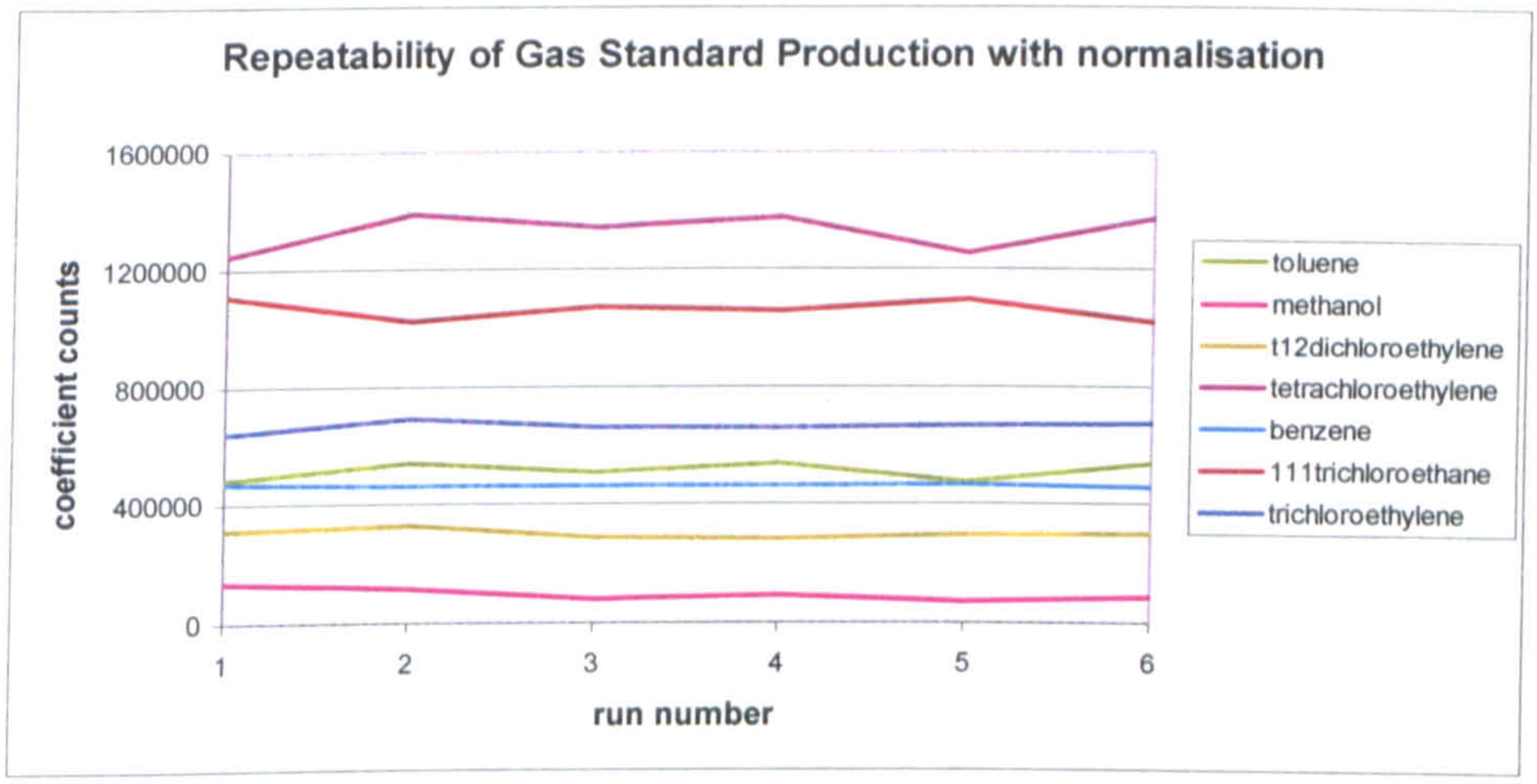


Figure 60: "Repeatability of Gas Standard including normalisation to the 78 amu peak"

From this experiments it can be seen that normalisation improves the precision of the sample bag injection to better than ±10%. Dependent on the experiments performed, one has to decide if this method produces reliable results. Certainly for a fast estimate of the performance of the MS-200 for a previously unspecified chemical the method is sufficient.

Appendix 2. Mixture Analysis Results for Initial Response Experiments

Concentrations in ppb, calibration on background and run number 45

Run (min)	o-xylene (ppb)	dichloro-methane (ppb)	ethyl-acetate (ppb)	n-hexane (ppb)	Toluene (ppb)	trichloro-ethane (ppb)
1	112	67	-131	7	97	37
2	289	139	-21	226	178	99
3	329	158	43	302	186	114
4	354	169	68	347	194	127
5	361	172	125	344	195	125
6	359	174	100	334	196	128
7	363	181	127	335	197	130
8	363	193	142	333	199	128
9	366	185	133	318	195	131
10	375	185	140	323	197	125
11	374	188	146	309	194	126
12	364	176	137	294	201	137
13	365	184	134	285	194	137
14	368	181	153	286	193	137
15	370	190	141	282	199	138
16	381	196	144	299	204	133
17	374	188	170	293	198	139
18	377	194	169	311	200	140
19	381	199	196	301	188	139
20	382	195	198	311	199	139
21	393	210	177	343	206	150
22	392	209	198	322	197	143
23	386	203	215	313	199	142
24	384	201	216	307	200	147
25	384	197	187	302	198	144
26	392	212	189	323	200	146
27	399	212	200	328	206	154
28	390	197	189	310	203	141
29	386	197	197	303	194	147
30	384	193	193	292	200	155
31	385	201	180	292	200	143
32	396	217	189	317	199	156
33	397	197	196	310	197	158
34	389	213	205	296	201	150
35	387	221	180	298	197	151
36	389	213	188	299	198	150
37	394	202	204	306	204	143
38	402	205	207	319	198	153
39	398	204	196	306	193	159
40	392	200	207	306	202	149
41	391	203	194	294	194	151
42	393	203	186	291	202	159
43	399	217	205	310	200	156
44	405	200	206	306	198	152
45	396	198	200	297	197	149

Appendix 3. Response on Step Changes on Input

run	input	Xylene measured	input	Hexane measured	input	Trichloro-Ethane measured	input	Di-chloro-methane measure	input	Toluene measured	input	Ethyl-acetate measured
2	0	2.2	0	45.8	0	8.1	0	10.4	0	-0.4	0	53.7
3	0	1.0	0	48.2	0	7.6	0	14.2	0	1.0	0	70.4
4	0	1.5	0	45.5	0	6.4	0	12.0	0	0.7	0	54.5
5	0	0.0	0	17.0	0	0.2	0	9.3	0	0.7	0	44.0
6	396	233.3	297	238.8	149	122.6	198	157.8	197	166.8	200	90.8
7	396	346.8	297	273.2	149	139.0	198	181.6	197	193.1	200	132.8
8	396	377.0	297	270.9	149	142.2	198	179.9	197	191.8	200	134.5
9	396	396.0	297	297.0	149	149.0	198	198.0	197	197.0	200	200.0
10	396	402.3	297	305.1	149	154.5	198	203.7	197	193.0	200	226.8
11	0	191.4	0	65.3	0	18.6	0	28.8	0	-51.7	0	184.9
12	0	53.6	0	27.4	0	-1.8	0	18.0	0	-19.1	0	131.5
13	0	26.4	0	6.0	0	-11.9	0	10.6	0	-8.7	0	83.0
14	0	16.2	0	-12.8	0	-12.1	0	5.5	0	-6.0	0	60.6
15	0	11.1	0	-1.0	0	-8.6	0	8.1	0	-2.1	0	65.7
16	79.2	59.6	59.4	28.8	29.8	9.3	39.6	36.5	39.4	19.7	40	59.2
17	79.2	79.1	59.4	21.6	29.8	10.4	39.6	35.9	39.4	13.8	40	41.0
18	79.2	82.5	59.4	13.6	29.8	3.4	39.6	31.9	39.4	14.4	40	49.9
19	79.2	83.3	59.4	-0.9	29.8	2.3	39.6	28.7	39.4	17.0	40	31.0
20	79.2	82.0	59.4	0.3	29.8	2.0	39.6	27.0	39.4	14.1	40	38.8
21	158.4	124.5	118.8	38.3	59.6	25.8	79.2	63.2	78.8	42.9	80	26.3
22	158.4	150.3	118.8	33.3	59.6	25.9	79.2	57.4	78.8	40.4	80	55.9
23	158.4	158.8	118.8	36.3	59.6	26.1	79.2	63.4	78.8	38.8	80	47.8
24	158.4	163.3	118.8	36.7	59.6	22.7	79.2	52.0	78.8	42.1	80	44.9
25	158.4	162.2	118.8	38.0	59.6	28.2	79.2	56.7	78.8	41.8	80	46.4
26	237.6	196.4	178.2	81.0	89.4	48.8	118.8	86.5	118.2	79.4	120	64.0
27	237.6	225.5	178.2	79.1	89.4	50.5	118.8	91.4	118.2	92.3	120	61.3
28	237.6	232.1	178.2	78.7	89.4	48.6	118.8	88.5	118.2	94.4	120	57.4
29	237.6	239.7	178.2	85.1	89.4	54.3	118.8	90.2	118.2	99.2	120	56.9
30	237.6	235.8	178.2	90.2	89.4	57.5	118.8	88.2	118.2	97.7	120	71.8
31	316.8	277.9	237.6	152.1	119.2	80.5	158.4	120.0	157.6	159.2	160	102.2
32	316.8	301.2	237.6	156.7	119.2	85.5	158.4	129.5	157.6	166.1	160	119.6
33	316.8	310.6	237.6	169.7	119.2	87.2	158.4	136.3	157.6	175.6	160	130.4
34	316.8	321.0	237.6	177.8	119.2	94.3	158.4	133.6	157.6	180.2	160	156.6
35	316.8	317.2	237.6	190.9	119.2	95.7	158.4	138.4	157.6	179.7	160	170.0
36	396	367.9	297	245.0	149	126.7	198	175.6	197	201.9	200	173.9
37	396	399.3	297	258.0	149	129.1	198	177.0	197	201.1	200	183.2
38	396	416.0	297	269.8	149	124.9	198	176.2	197	193.7	200	222.4
39	396	421.8	297	259.8	149	131.7	198	172.2	197	193.2	200	226.6
40	396	417.5	297	264.6	149	134.7	198	180.0	197	192.1	200	245.4
41	316.8	361.6	237.6	217.2	119.2	95.6	158.4	146.5	157.6	182.2	160	214.0
42	316.8	332.8	237.6	199.1	119.2	85.8	158.4	137.2	157.6	182.3	160	200.8
43	316.8	331.3	237.6	203.3	119.2	84.9	158.4	140.2	157.6	183.0	160	197.7
44	316.8	335.3	237.6	196.4	119.2	91.0	158.4	131.0	157.6	189.0	160	198.4

45	316.8	329.5	237.6	207.5	119.2	91.2	158.4	135.7	157.6	187.6	160	206.6
46	237.6	325.6	178.2	180.7	89.4	83.6	118.8	119.7	118.2	171.3	120	174.5
47	237.6	272.3	178.2	141.1	89.4	59.7	118.8	107.8	118.2	121.8	120	166.3
48	237.6	262.4	178.2	135.2	89.4	54.4	118.8	98.0	118.2	119.4	120	169.6
49	237.6	263.8	178.2	135.2	89.4	52.7	118.8	91.3	118.2	117.3	120	176.3
50	237.6	259.9	178.2	125.7	89.4	53.9	118.8	98.9	118.2	116.3	120	166.4
51	158.4	219.2	118.8	86.9	59.6	26.0	79.2	61.0	78.8	57.7	80	156.1
52	158.4	193.9	118.8	76.1	59.6	27.4	79.2	58.4	78.8	48.3	80	148.6
53	158.4	186.3	118.8	70.1	59.6	20.2	79.2	56.7	78.8	50.3	80	133.5
54	158.4	187.7	118.8	65.6	59.6	15.5	79.2	51.6	78.8	52.8	80	126.5
55	158.4	186.3	118.8	61.1	59.6	21.5	79.2	51.3	78.8	48.4	80	118.3
56	79.2	131.7	59.4	16.9	29.8	-2.6	39.6	20.9	39.4	8.2	40	122.8
57	79.2	104.6	59.4	14.5	29.8	-5.5	39.6	21.4	39.4	13.5	40	107.1
58	79.2	98.7	59.4	6.3	29.8	-6.3	39.6	21.0	39.4	15.7	40	84.1
59	79.2	97.7	59.4	-2.5	29.8	-14.5	39.6	16.0	39.4	17.4	40	74.2
60	79.2	98.1	59.4	1.2	29.8	-12.5	39.6	13.6	39.4	16.1	40	72.5
61	0	49.8	0	-35.4	0	-29.3	0	-13.3	0	-17.1	0	84.4
62	0	18.5	0	-48.5	0	-36.4	0	-18.5	0	-6.0	0	63.0
63	0	13.5	0	-56.1	0	-37.3	0	-17.9	0	-5.1	0	48.2
64	0	10.7	0	-60.3	0	-37.9	0	-24.9	0	-4.7	0	32.5
65	0	9.5	0	-67.8	0	-40.6	0	-23.9	0	-4.2	0	30.9
66	396	250.7	297	161.2	149	89.6	198	115.6	197	194.3	200	54.1
67	396	367.2	297	211.3	149	117.1	198	140.0	197	202.6	200	123.5
68	396	394.0	297	227.3	149	124.1	198	150.4	197	195.2	200	149.7
69	396	400.6	297	235.2	149	119.8	198	151.1	197	204.5	200	145.3
70	396	413.9	297	231.7	149	122.2	198	155.6	197	202.7	200	154.2
71	0	202.0	0	-11.8	0	-20.0	0	-13.6	0	-42.0	0	133.5
72	0	51.1	0	-34.5	0	-33.0	0	-16.3	0	-13.6	0	105.1
73	0	28.2	0	-52.1	0	-36.8	0	-22.8	0	-7.3	0	68.2
74	0	18.6	0	-69.3	0	-41.9	0	-26.5	0	-4.5	0	51.4
75	0	15.1	0	-70.4	0	-42.1	0	-28.4	0	-4.2	0	34.3

Appendix 4. Data Reduction.

Internal Report from Kore Technology written by Dr Stephen Mullock

Data Reduction Performed by MS-200 Operating Software

Strictly speaking the starting point for the data processing is a histogram of arrival times that has been built up during the acquisition task. However, a view of the data on a time axis is so rarely useful that normally the conversion to a histogram expressed as a function of ion mass (actually mass to charge ratio) is made at the same time that the data is collected. In this case the time histogram is discarded and the apparent starting point for the data reduction is a raw mass histogram. All bins in this histogram have the same width (typically 0.1 Daltons) and the value in each bin is a count of ions that arrived in that mass range during the experiment.

Given library data describing the response of the MS-200 to known concentrations of all compounds that are present in the sample, and under suitable experimental conditions, the software can reduce this "raw mass" data in a series of stages to a simple table of compound concentrations. A clear understanding of this process is necessary to assess whether the data from a particular application or experiment will give good results. Also it is most helpful for extracting meaning from processed results in non-ideal situations.

As the data reduction proceeds, the original raw mass spectrum and intermediate results, are retained in the data file. This means that data processing options may be changed and the data re-analysed as many times as desired. This can be useful in some circumstances, particularly when new applications are addressed. For example, a first analysis may indicate the presence of an additional compound not anticipated in the mixture analysis library used. It is an easy matter to add a model spectrum for the additional compound to the library and re-analyse the data.

Mass peak integration ("Stick-plotting")

Given that the MS-200 has rather modest mass resolution, most of the sample information available in the raw data is contained in the peak areas (total counts) at each integer mass. A set of numbers denoting intensity at integer mass values is also the format used for most 'fingerprint' type libraries, for example, the NIST mass spectra database. Therefore the first step in the data reduction is to detect the position of all mass peaks, integrate them, and produce a 'stick-plot'.

Actually the MS-200 software also makes an estimate of the uncertainty (expressed as an estimate of the standard deviation) in the intensity value at each integer mass position. Thus the MS-200 stick plot format holds two numbers for each integer mass position. The uncertainty values are needed in order to make an estimate of the uncertainty in any processed data derived from the stick-plot in later operations.

The uncertainty estimate is currently quite simple-minded, being based on the "shot noise" expected from a counting system, plus a rather arbitrarily chosen estimate of the inherent repeatability of a typical spectrometer (actually an adjustable parameter held in the ms200.ini file). Thus the final uncertainty values reported in the mixture analysis (see below) are approximate.

Background subtraction

Unfortunately not all the ions recorded during the experiment derive from the sample gas in use at the time. For example, there is some history effect in the inlet that depends on the identity and concentrations of other gases recently analysed. In particular, 'sticky' analytes that have been present at high concentrations may linger for some time in small quantities. Also there are residual gas species in the mass spectrometer vacuum, even when the inlet is closed. These result primarily from slow desorption of molecules from the surface and near surface of the mass spectrometer parts.

Fortunately, it is usually fairly easy to measure the background signal first and then subtract this from the signal obtained from the sample gas. To achieve the best detection limit, the 'background' experiment should be as similar as possible to the measurement of the sample gas in all respects expect the presence of trace gases of interest. This is usually achieved in practice, for the MS-200, by running the sample gas itself - often ambient air - through a built-in activated carbon filter. This removes all the gases of interest, leaving only the matrix gases to be measured as the 'background' data. Depending on circumstances and the detection limit required, other methods could be used. For example, during laboratory calibration, clean gas from a cylinder is usually used.

There is more than one way to combine the background data with the sample data to compensate for the background signal. The method most often in use with MS-200 (as set in ms200.ini, [Background subtraction], Method=Raw) is to create a background compensated stick-plot by performing a subtraction using the raw mass traces of both sample and background experiments directly. This data is included in the sample data-file along with the 'raw mass 'and 'stick-plot' traces. An explanation of why it is done this way and is not simply the difference between the two stick plots is beyond the scope of this document. Suffice to say that the two results should be approximately the same.

Like the plain stick-plot trace, the subtracted stick-plot contains calculated estimates for the standard deviation in the intensity at each mass value. Due to noise and drift, the background subtracted stick-plot may contain negative peaks and small peaks where the relative uncertainty is very high. This data needs to be retained because it is the starting point for the mixture analysis (see below). However for more convenient viewing by an operator, or as a step towards creating a new library file, the background subtracted stick-plot may be further processed with a user-entered uncertainty threshold to yield a 'censored' stick-plot. In this trace all the negative peaks and all peaks with excessive uncertainties are discarded leaving a clear view of the interesting peaks in the sample gas.

Mixture analysis

To a good approximation the response of the MS-200 is linear, even when a mixture of trace compounds is present in the sample gas. The relatively low source pressure used in MS-200 eliminates any interaction between different compounds. This makes it possible to perform a mixture analysis by a relatively simple 'least squares' fit method.

First a library is specified in the form of list of library data files. Each library file contains an ideal mass spectrum for a single compound, normalised so that the total of the intensities in the spectrum equals one. Each library file also contains a relative sensitivity factor (RSF) indicating how many counts would be expected at a given concentration compared to the counts that would be obtained from nitrogen (that is to say the RSF for N_2 gas is roughly 1 assuming the variable *CountsPerCycleN2* is correctly set - see below).

The mixture analysis algorithm normally performs a fit using the sample data file 'background subtracted' stick-plot (specified in ms200.ini by [Mixture analysis] Background method=Subtract). The fit is made by calculating a set of coefficients, each being a multiplier for a library file, such that the weighted sum of library files is the closest possible match to the sample data. Because the library files have been normalised to a total intensity of one, each coefficient can be interpreted as the total counts, across all mass peaks, arising from the presence of the corresponding library compound.

Calculating concentration

In order to calculate a concentration in ppm or ppb the RSFs are required. The concentration is then calculated thus:

$$Concentration = \frac{coefficient}{RSF \times Cycles \times CountsPerCycleN2}$$

Alternatively this can be viewed as a definition of the RSF as used in MS-200. Here *Cycles* refers to the number of ion extraction pulses in the

experiment and *CountsPerCycleN2* is a constant, set according to the sensitivity of a particular spectrometer. To obtain the correct RSF, a calibration experiment must be performed, in which a known concentration of the compound of interest is present. The user enters this concentration and the library data file's RSF is adjusted accordingly.

Noisy or negative values

As well as calculating the set of coefficients that gives the best fit, the mixture analysis algorithm uses the estimated standard deviations available with the background subtracted stick-plot data, to calculate corresponding standard deviations for the coefficients. These are listed, along with the concentration values, as a percentage standard deviation to indicate the confidence in the fit result for each compound. Thus, a small reported concentration together with a large percentage standard deviation indicates that the compound in question was not detected at a level significant relative to the estimated noise. A longer experiment may improve the relative standard deviation, if more counts, and therefore better statistics, are achieved for that compound.

It is perfectly possible, and mathematically quite proper, for the best fit coefficient to be negative. Either the relative uncertainty will be high, indicating simply that the compound was not detected in a statistically significant amount, or a negative coefficient indicates that the concentration genuinely dropped between the background experiment and the sample experiment.

The library should be complete

It should be noted that the best fit will only yield the right results if all the compounds present in the sample are represented in the library. Put another way, if a compound is present in the sample, but not in the library, then not only will there be no information on the concentration of that compound, but also the reported concentrations for the other compounds in the library will be distorted. Although this is true mathematically, and there exist other much more complex methods for trying to deal with the problem, in practice, the

mass spectral data is so mathematically 'nice' that the distortions are usually relatively modest. This is because the overlap between mass spectra for different compounds is usually 'modest'. However the hazard should be borne in mind as the distortion can be large in special cases.

Checking the fit

A pseudo mass spectrum may be constructed from the best bit coefficients for comparison by eye with the sample spectrum. This is usually best done by overlaying them. Compounds present in the sample that weren't in the library can then, generally, be readily seen and often identified, using a mass spectral library search (e.g. NIST database). Once identified, they can be added to the library and the analysis performed again for an improved result.

Obtaining the library files

Clearly it is very important that the library spectra themselves are correct. The best quantification will be achieved if the library spectra are derived from data taken with an MS-200. This is because spectra taken on different mass spectrometers tend to have different peak ratios. However, it is still possible to get useful approximate results using library spectra that have been derived from other instruments. In particular this means that, for example, NIST library spectra can be used to create library files.

Note also that the measurement of RSFs may be done for *several components in one experiment.* That is to say, the calibration run may be performed on a *mixture* of compounds. Calibrated standards are expensive and this can therefore lead to a great saving in both time and money. The peaks ratios for a given pure compound can be created from sample gas in which the exact concentration is not known. For example, a quick headspace measurement with enough concentration to give good statistics can give the peak ratios for the pure compound, whilst the RSF is derived from another experiment on a commercial calibrated standard mixture.

If NIST library spectra for the pure compounds give acceptable fits then it is not necessary to prepare single compound calibration gases at all, they can simply be taken from the library. This can lead to a further savings in time and resources. Often this is sufficient for a quick look at a new application or to deal with a compound found unexpectedly for which a pure spectra has not yet been prepared.

Appendix 5. Saturation Effects

This appendix details saturation effects within a mass spectra. When saturation occurs, then the response of the MS-200 to a changing input concentration is no longer linear. As described in section 3.2.11, the mixture analysis of the MS-200 relies on the comparison to a model spectrum of the analyte. In cases of saturation this model spectrum is no longer representative for the measured response and therefore quantitative, and in extreme cases qualitative analysis can no longer be performed. Therefore it is crucial that the principles of saturation are understood and that in cases that appear to be showing effects of saturation the mass spectrum is inspected.

During a typical ten second acquisition time, the TOF analyser of the MS-200 performs around 500,000 analysis cycles (the precise number is dependent on the mass range setting of the software). Ions are permanently created within the source region, which is virtually field free. In every twenty microseconds the extractor is pulsed for 3 microseconds from near ground to minus 400 Volts. This extracts the ions, created in the source region and accelerates them through the ion optics towards the detector. The detector records the hits and delivers a signal to the timing electronics. The timing electronics measures the arrival time of ions with a time resolution of 2 nanoseconds and stores the information in mass bins of 0.1amu bin width.

The detector is operated in the ion counting mode. This means, that if an ion hits the detector, the timing electronics (TDC) receives one electrical impulse. If two ions arrive at the same time they will be recorded as only one event. Additionally, after a detector recorded a hit from an ion, it requires a few nanoseconds to recover from the hit and to be ready to record the next ion arrival. This means that ions arriving within the recovery time will not be recorded.

For example, in a simple case, where the source contains two N_2 ions with a m/z of 28amu plus an ion at m/z 40 and one at m/z 40.1. In this case, the mass spectrum would report only one count at 28amu and one count at

40amu. The second count at 28amu is lost due to the ability of the detector to report only one hit at the time. The hit at 40.1amu is lost due to the recovery time of the detector. For this reason a typical experiment consists of 500,000 cycles in order to obtain an adequate statistical distribution.

In a normal situation, the mass spectrum represents the concentrations of the different ions (including fragmentation ions) within the ionisation source of the spectrometer. This means that if a particular concentration of a component is increased, the mass pattern corresponding to the component increases at the same ratio. Once the concentration of analyte measured is so high that saturation is reached, the number of double hits on the detector, that are counted as one event, reach a level at which the statistical distribution is no longer valid. Saturation also happens when the number of ions that reach the detector during a recovery time window and are therefore not counted. As a result of this an increase or decrease in concentration of the analyte in a sample is no longer represented by an according change in the mass spectrum measured and linearity of the response is no longer valid.

From experience, saturation occurs when the area (counts) of a single mass peak of the component of interest is reaching around 60% of the number of cycles of an experiment. In a normal 500,000 cycles experiment the area of a mass peak should not exceed 300,000 counts.

Saturation can occur for individual peaks in the spectrum, and therefore not all parts of the spectrum may be saturated. This fact can be used to calculate the point at which saturation due to a too high input concentration of an analyte occurs. As described in section 3.2.1, the ratios between the different peaks of the mass pattern of a component are constant. Therefore when a component is saturated, the comparison between the size of the major mass peak and the ratio of a minor peak of the same compound will change and therefore can be an indication for the amount of saturation.

For example, in a 46ppm heptane spectrum the major mass peak at m/z 43 is reported with 484,000 counts. The peak at 55amu is reported with 176,000 counts. The NIST mass spectral database gives the 55amu peak to be

approximately 12% of the 43amu peak. Therefore the 43amu peak should theoretically have a height of 1,467,000 counts, resulting in a saturation of about 300%. So generally heptane can only be measured up to a concentration of approximately 12ppm without saturation occurring.

Appendix 6. Adsorption / Desorption Effects

As mentioned in 3.2.10, it was decided to investigate the adsorption / desorption effects of the sample onto the walls of the stainless steel tubing supplying the sample to the membrane, in the membrane, the intermediate vacuum space, the inner membrane and the vacuum system itself.

A similar experiment to the initial dry experiment was performed. This time the standard was humidified to approximately 28% relative humidity. The sequence of states is indicated in Figure 61 showing the results.

State	
1	Clean, humidified (28% rel.) background
2	60% concentration selected, humidified (28% rel.) calibration standard
3	Inlet valve shut

Closing the inlet valve leaves only the inner membrane plus the high vacuum space of the analyser chamber for adsorption / desorption effects. Whereas in case 1 the complete inlet system plus the high vacuum of the analyser chamber can contribute to adsorption / desorption effects.

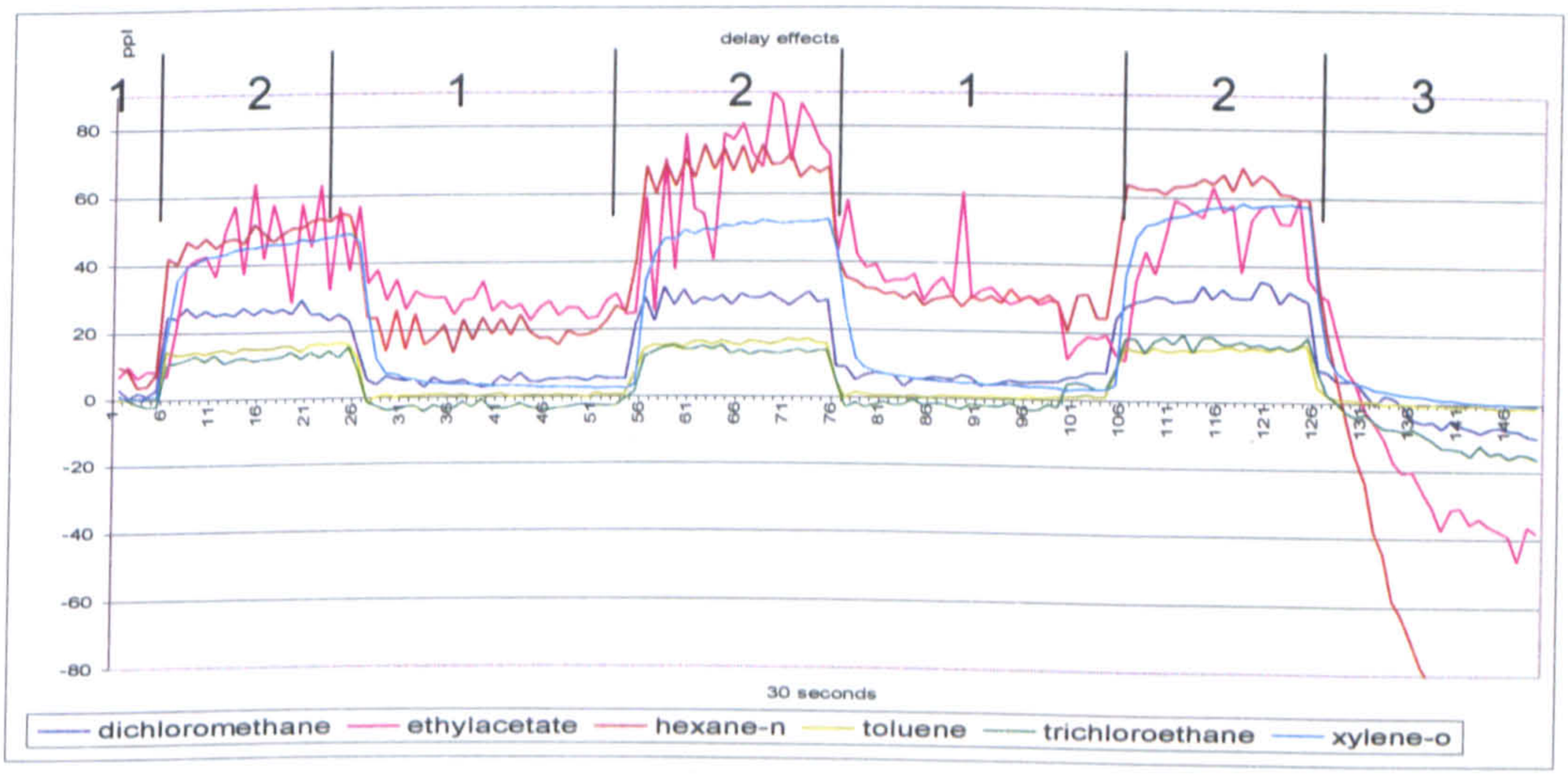


Figure 61 - Investigating the source of the adsorption / desorption effects in the MS-200

This graph shows that dichloromethane, toluene, trichloroethane and o-xylene follow the step changes on the input within one to two minutes in both directions. Therefore it can be concluded that there are no major adsorption / desorption effects, affecting those components.

However, hexane and ethylacetate do not recover after the first peak and climb higher on the second peak, after which they do not come back to their background values. After the third peak when the inlet valve of the MS-200 is switched off, all of the samples decay to the background level within one to two minutes. Further, ethylacetate and n-hexane drop below the background concentration used, which shows that there was still some remaining from a previous experiment when the background reading was obtained.

This preliminary experiment suggests that the major part of the adsorption / desorption effects occur in the sample supply and intermediate vacuum space side of the spectrometer and that the high vacuum side, including the second membrane, does not contribute to those effects significantly.

Appendix 7. Results from the Comparison Study

Results for the analysis of challenge mix 1.
Assuming the RSF calibrated in 3.3.1

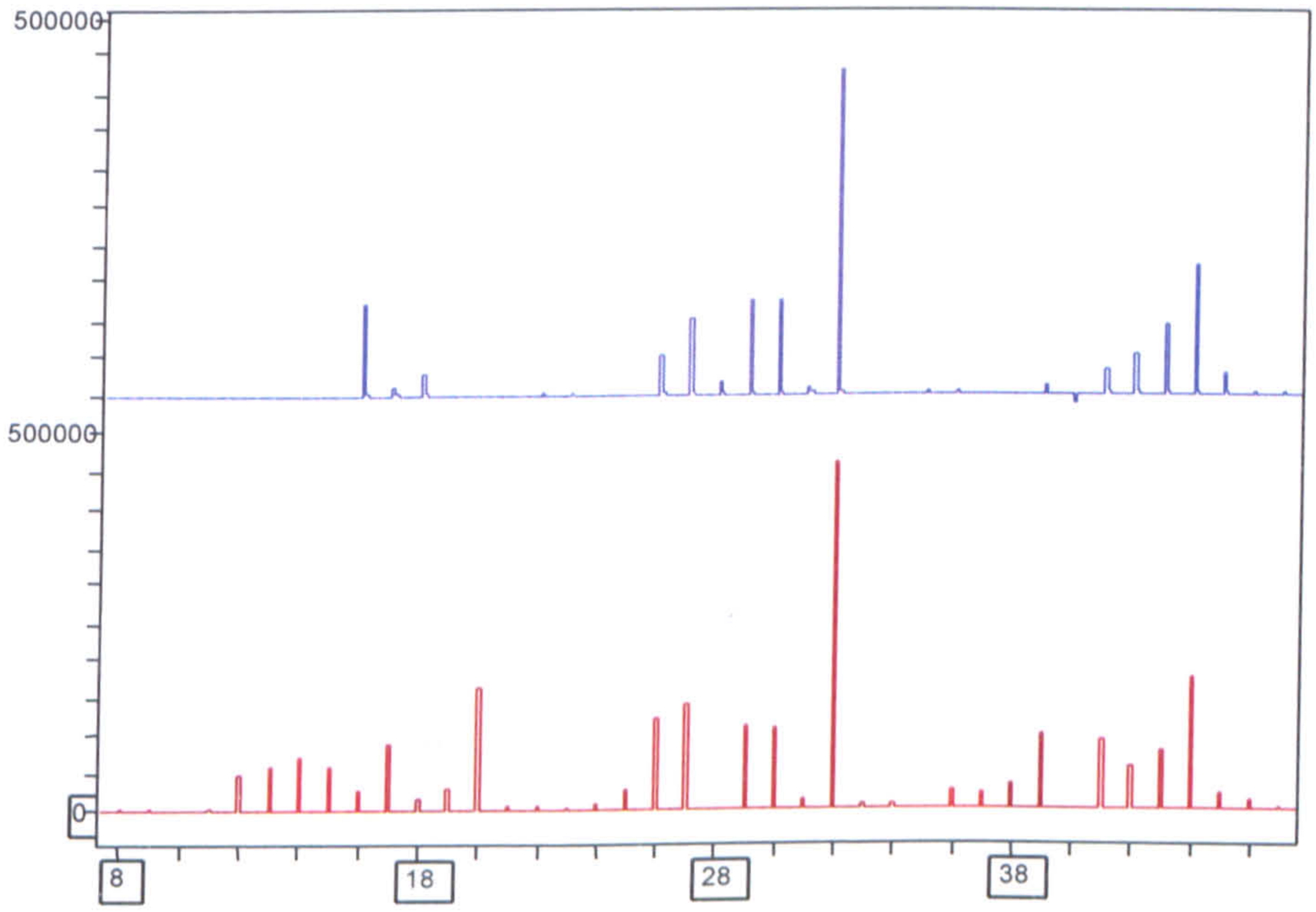
min	Dichloro-methane	Ethyl-acetate	hexane	toluen	Tri-chloro-ethane	xylene	2-propanol	methanol	ethana
1	80	428	300	440	104	132	-1382	549	0
2	78	531	279	429	86	123	-61	822	0
3	85	719	289	431	85	123	3199	1041	0
4	80	799	285	428	82	119	4544	1067	0
5	82	862	285	426	83	119	5134	1105	0
6	78	895	283	424	79	118	5163	1192	0
7	78	941	283	427	78	117	6615	1254	0
8	81	978	278	425	74	117	6460	1161	0
9	80	1054	279	424	74	116	7675	1324	0
10	92	1131	302	487	82	135	6576	1356	0
11	94	1166	311	489	84	137	8067	1394	0
12	95	1272	310	484	82	137	9152	1196	0
13	94	1366	311	480	81	137	10410	1525	0
14	95	1461	317	484	77	136	11815	1581	0
15	89	1541	319	479	78	135	11894	1583	0
16	95	1648	322	478	79	134	12304	1590	0
17	99	1750	319	477	79	134	13590	1684	0
18	96	1845	328	473	76	133	13571	1725	0
19	99	1929	328	470	76	132	14816	1888	0
20	100	2049	335	470	72	132	15937	1767	0
21	100	2146	334	464	76	130	16617	1892	0
22	99	2261	341	466	74	129	17845	1894	0
23	102	2366	343	458	73	128	19222	2065	0
24	100	2472	342	453	73	126	19590	2232	0
25	100	2550	345	453	70	125	21134	2174	0
26	93	2642	348	447	68	124	21090	2180	0
27	101	2724	347	444	69	123	21917	2193	0
28	103	2803	353	439	70	121	22510	2316	0
29	97	2880	349	436	68	119	22839	2303	0
30	91	2934	349	432	65	118	23592	2335	0

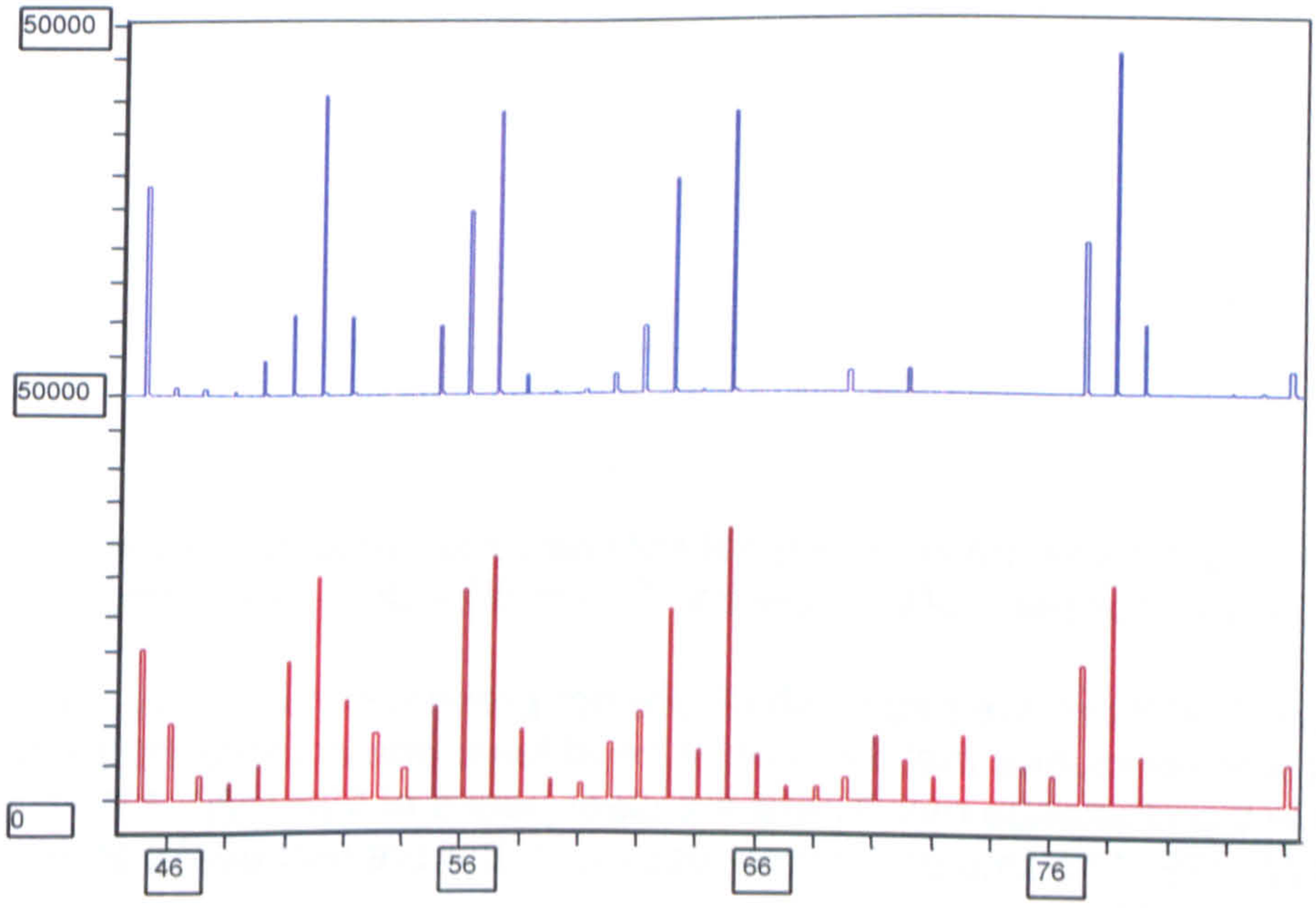
Results of the analysis of challenge mix2.
Assuming the RSF calibrated in 3.3.1
Ethanal assuming a RSF of 1000

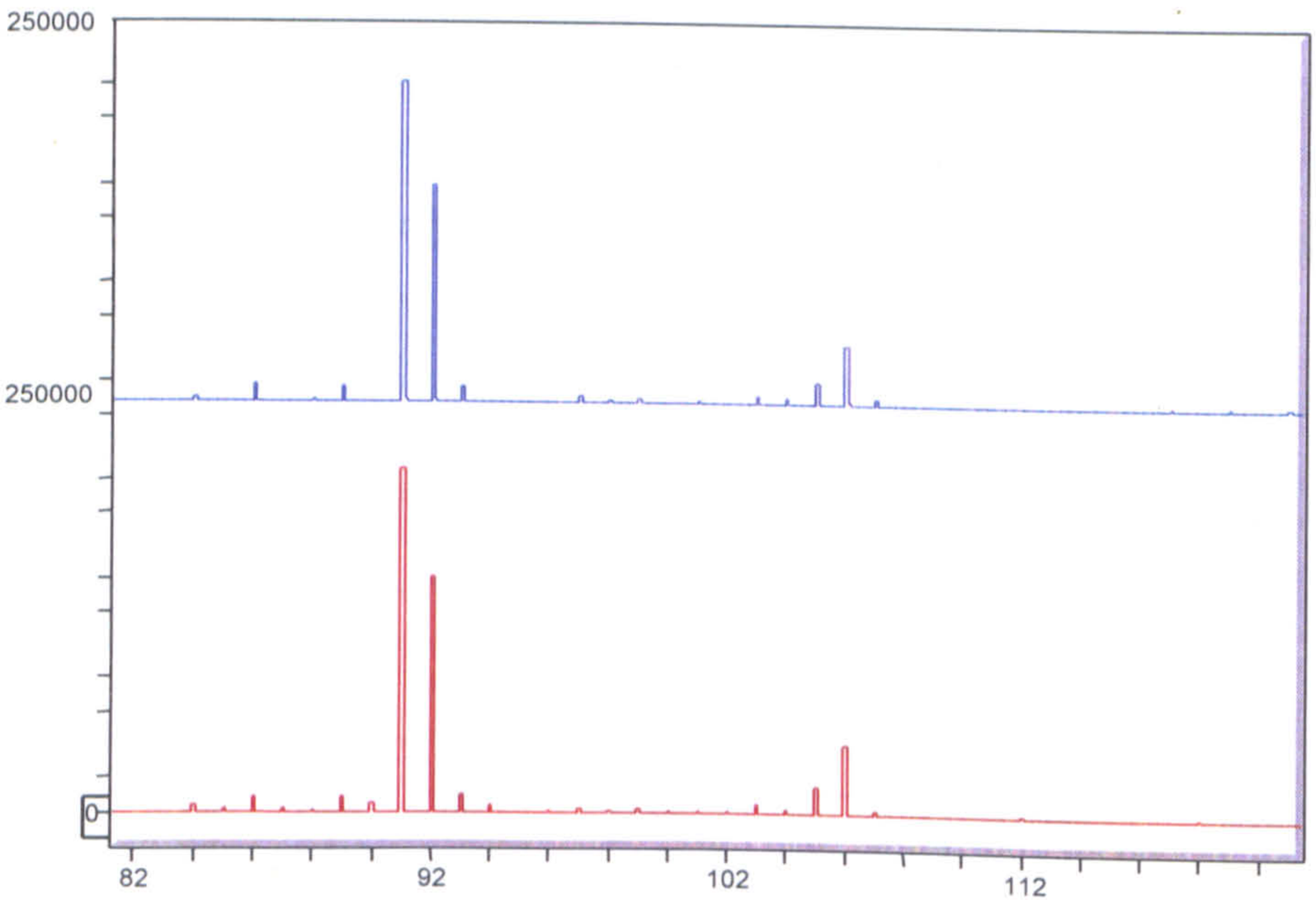
min	Dichloro-methane	Ethyl-acetate	hexane	toluen	Tri-chloro-ethane	xylene	2-propanol	methanol	ethanal
1	158	32	92	0	70	257	43140	-518.3	103759
2	166	429	113	0	79	264	51639	11.6	104521
3	176	632	124	0	76	270	55471	235.5	104119
4	169	813	131	0	78	266	57822	342.3	103879
5	173	970	136	0	75	268	60003	510.5	101332
6	173	1117	141	0	74	268	61651	623.4	100728
7	173	1242	146	0	75	266	62790	765.3	100187
8	172	1359	150	0	71	268	63594	758.6	97295
9	172	1471	158	0	71	266	65662	842.1	96306
10	173	1609	159	0	71	270	67113	1072.2	95785
11	176	1723	164	0	71	268	68229	1294.9	94115
12	172	1831	166	0	72	268	69143	1268.3	92013
13	173	1951	173	0	71	266	69836	1260.0	90221
14	179	2088	177	0	68	266	71139	1342.6	89487
15	168	2188	181	0	67	264	72576	1495.6	86783
16	169	2348	190	0	66	264	74280	1609.3	85463
17	174	2512	193	0	71	264	75401	1603.5	82805
18	172	2605	201	0	66	264	75531	1690.9	80203
19	174	2697	202	0	64	259	76905	1812.2	79635
20	171	2782	206	0	65	257	76311	1687.5	78071
21	167	2848	203	0	62	255	78055	1794.6	76505
22	166	2914	206	0	62	255	78394	1855.6	74029
23	167	3005	211	0	63	252	78463	1904.8	73075
24	164	3048	210	0	61	252	78960	1829.1	71363
25	164	3109	214	0	60	250	79264	1974.8	71050
26	178	3176	232	0	71	282	80861	1981.1	70029
27	175	3238	234	0	73	275	81166	2112.4	69389
28	169	3333	238	0	67	273	83384	2125.7	68730
29	177	3396	242	0	67	270	82986	2163.7	68597
30	175	3459	247	0	70	268	83435	2201.8	68652

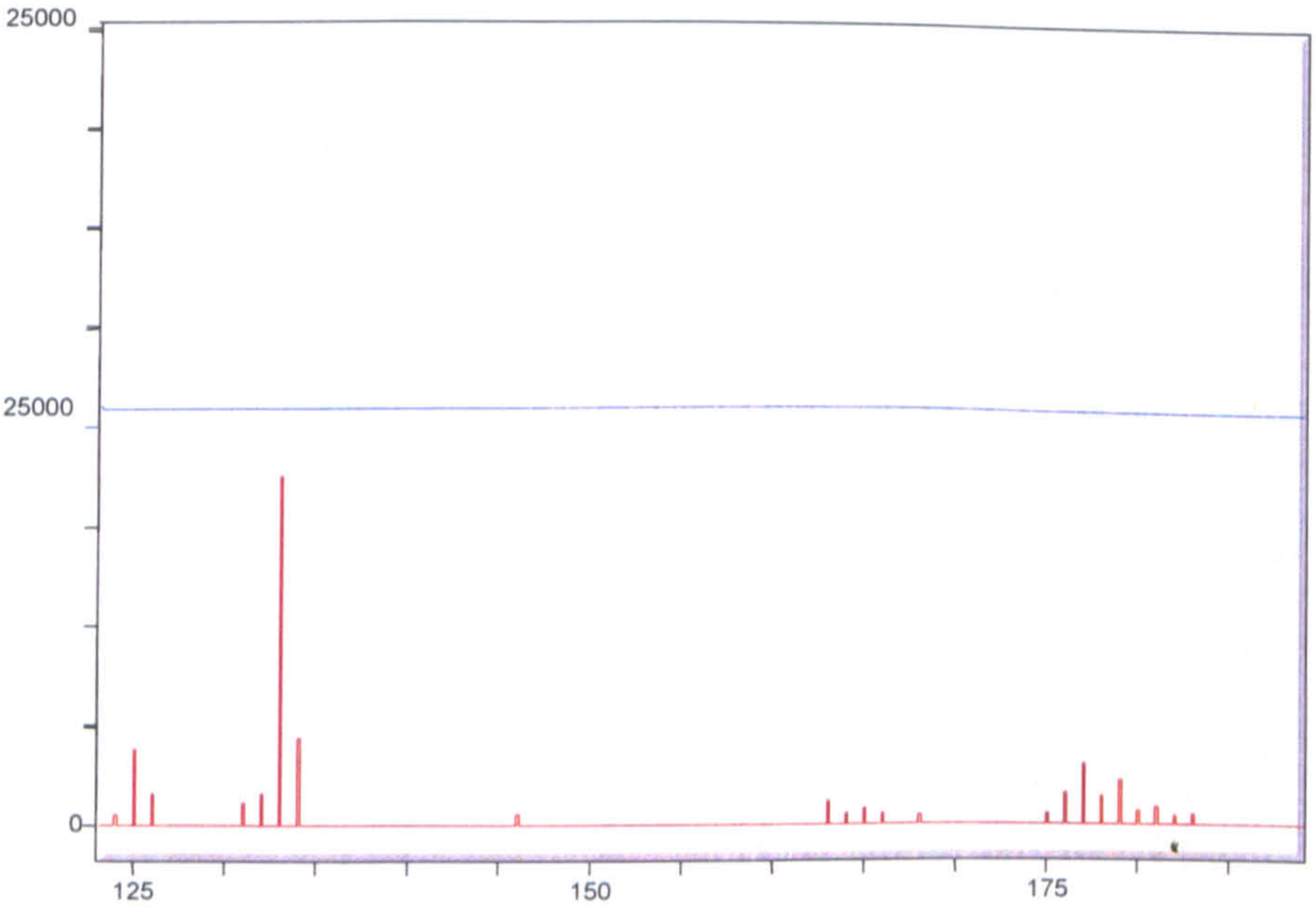
Appendix 8. Spectra from Comparison Study

The following graphs compare the experimental data from mix2 with the mixture analysis fit. Red traces display background subtracted sample. The blue trace on top shows the reconstructed fit from the mixture analysis on the sample. For clearer display it was decided to break the trace up into windows of approximately 50 amu width and a varying scale on the y-axis.









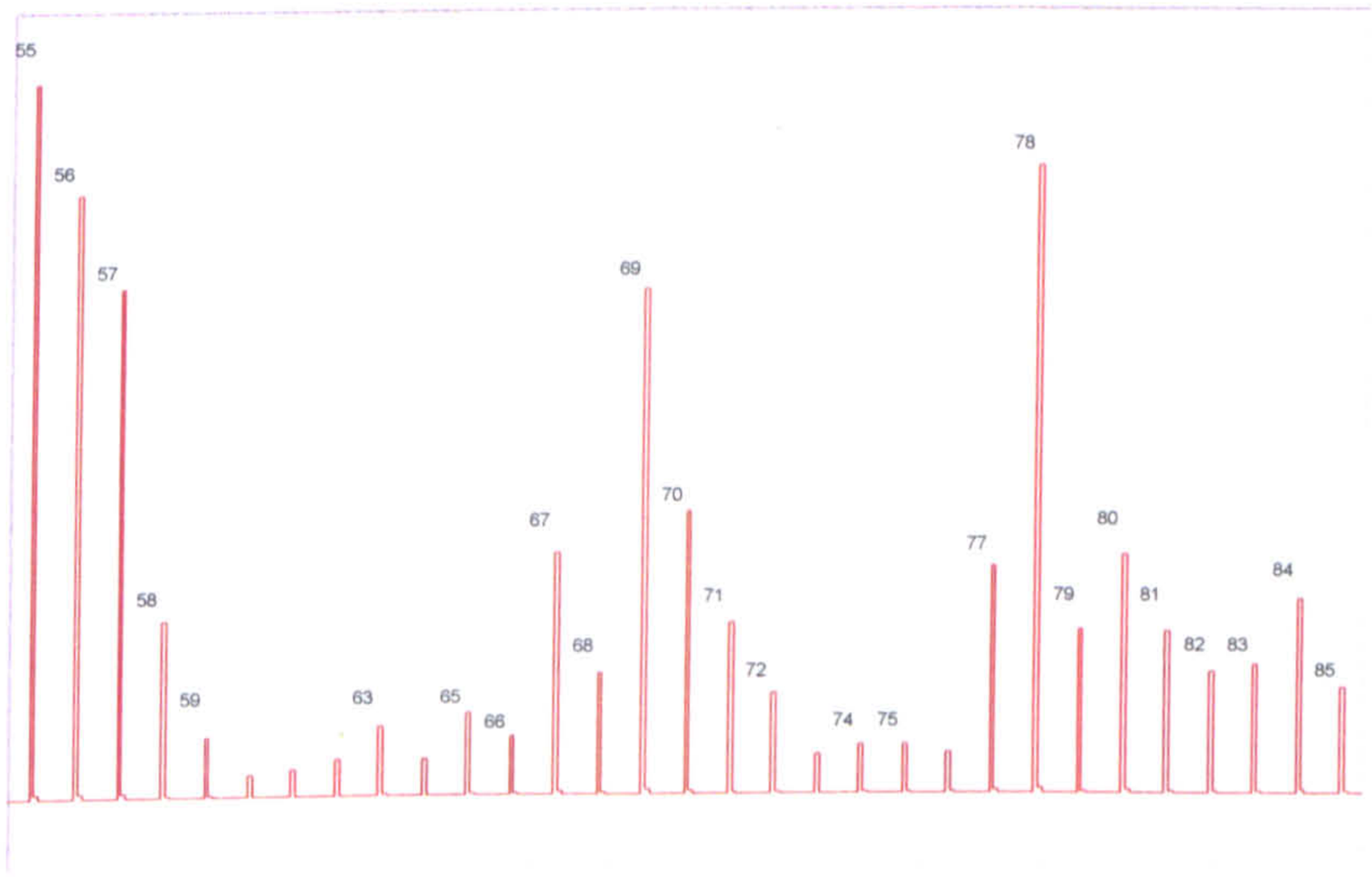
When examining the spectra in its original software it is easier to display differences by superposition of the spectra. This is difficult to export into a report

It can be seen that there are peaks which are not present in the library used Therefore it was concluded that there must be at least one or more additional component in the challenge mix. There are clear peaks at 125, 126, 133, 134, 176, 177, 178, 179 amu plus some less clear, but present peaks at 26, 39, 70, 73, 85, 94, 118 amu.

Appendix 9. Spectra from the initial TED experiments in Chapter 4

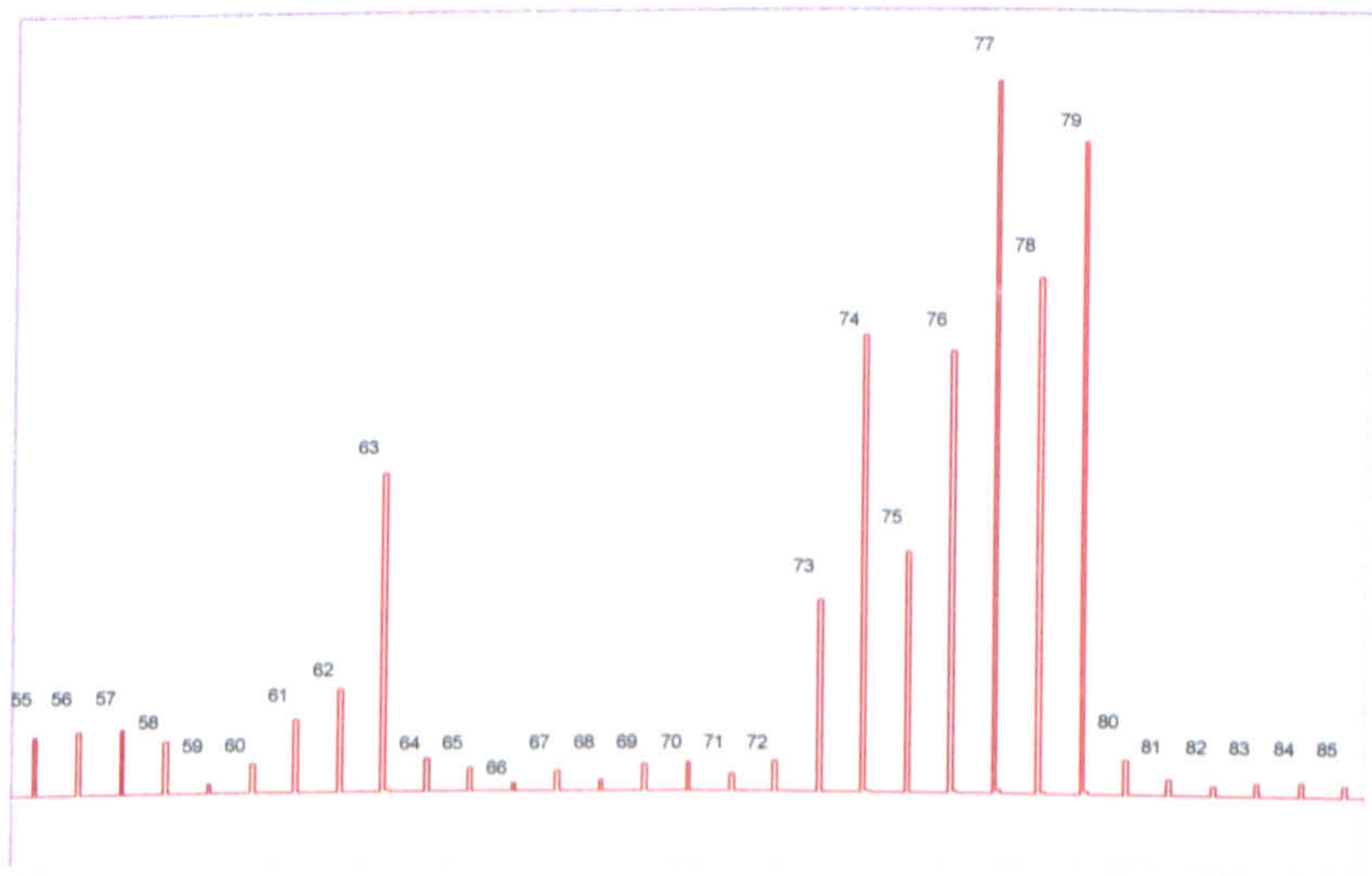
- Stickplotted background measurement from section 4.7.2, Initial assessment of the impact of the TED on sensitivity

*Displayed is the interesting mass range from 55 to 85 amu



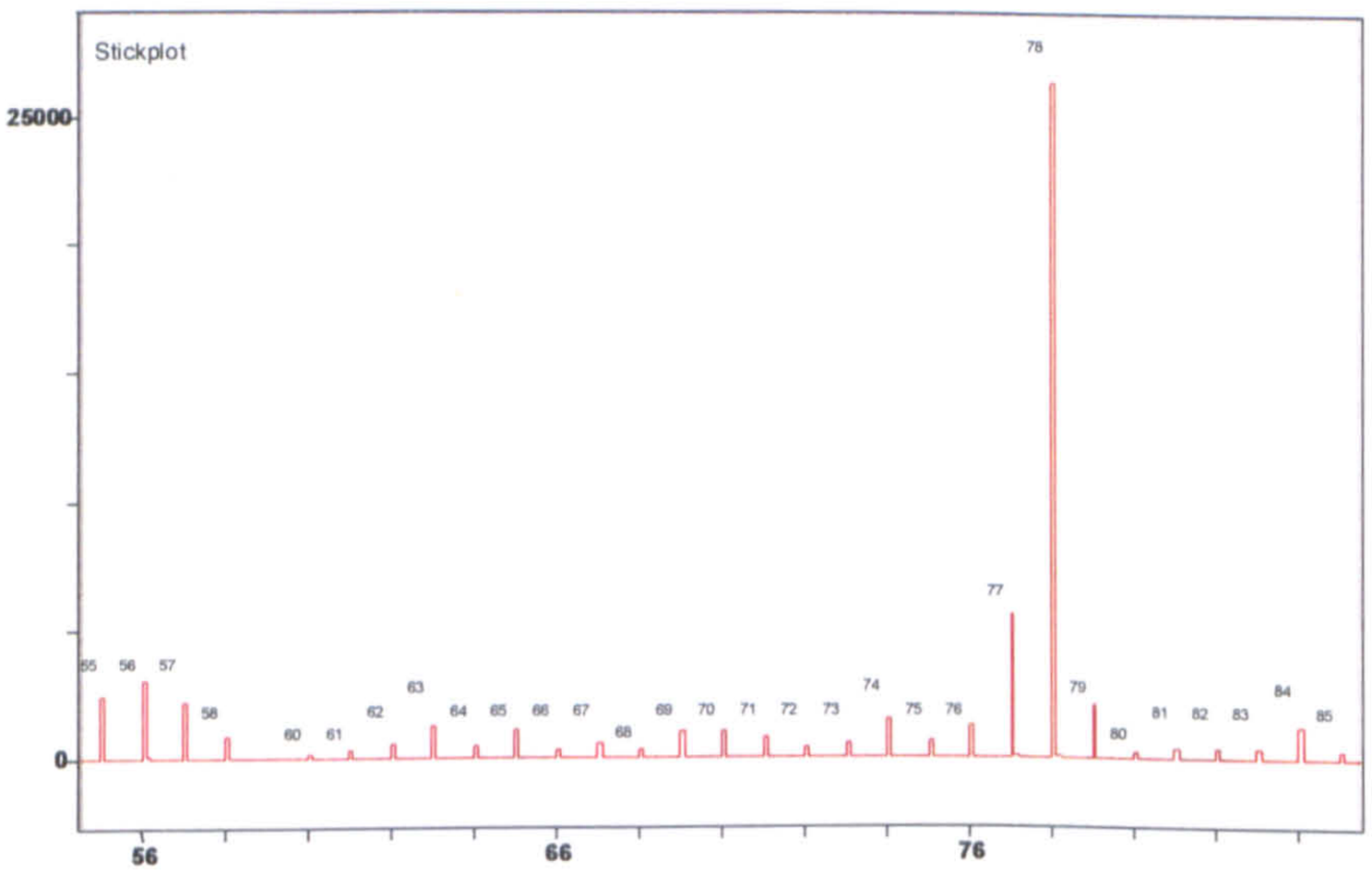
- Stickplotted sample measurement from section 4.7.2, Initial assessment of the impact of the TED on sensitivity

*Displayed is the interesting mass range from 55 to 85 amu



- Stickplotted background measurement from section 4.7.3, Second assessment of the impact of the TED

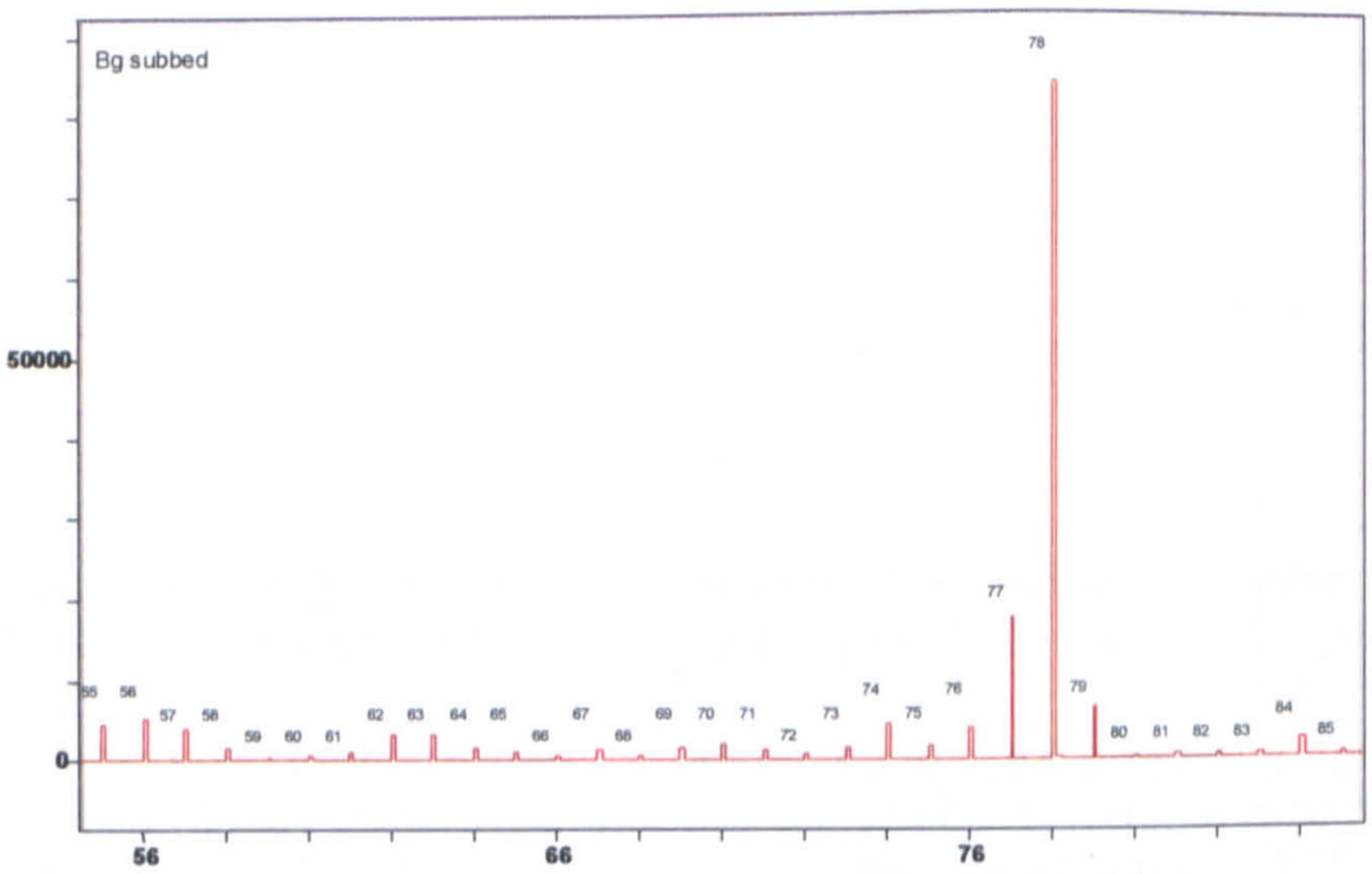
*Displayed is the interesting mass range from 55 to 85 amu



File # 1 : D SUCKD E S9#2

- Stickplotted sample measurement from section 4.7.3, Second assessment of the impact of the TED

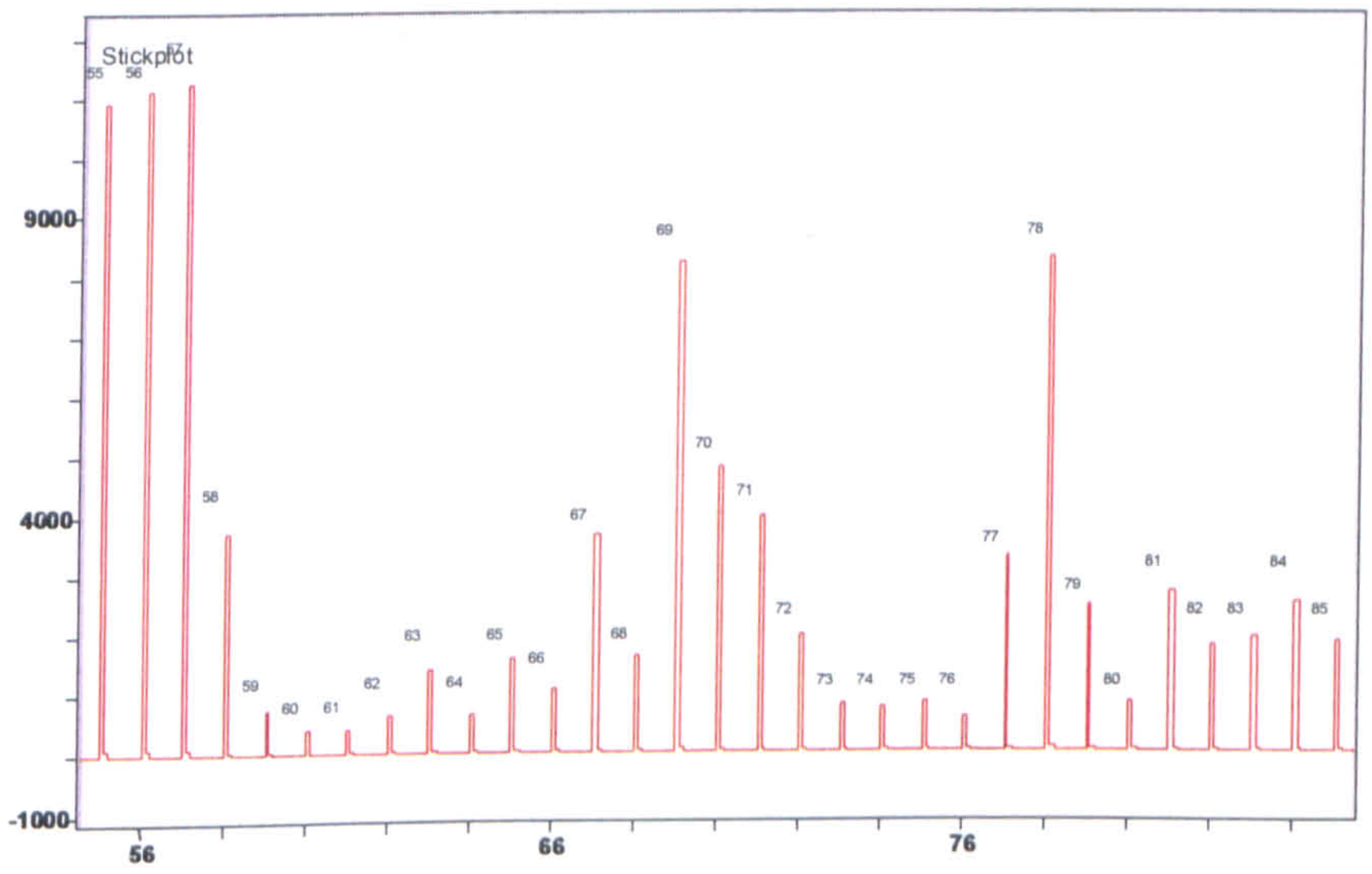
*Displayed is the interesting mass range from 55 to 85 amu



File # 1 : D SUCKD E S29#3

- Stickplotted background measurement from section 4.7.4, More accurate assessment of the TED

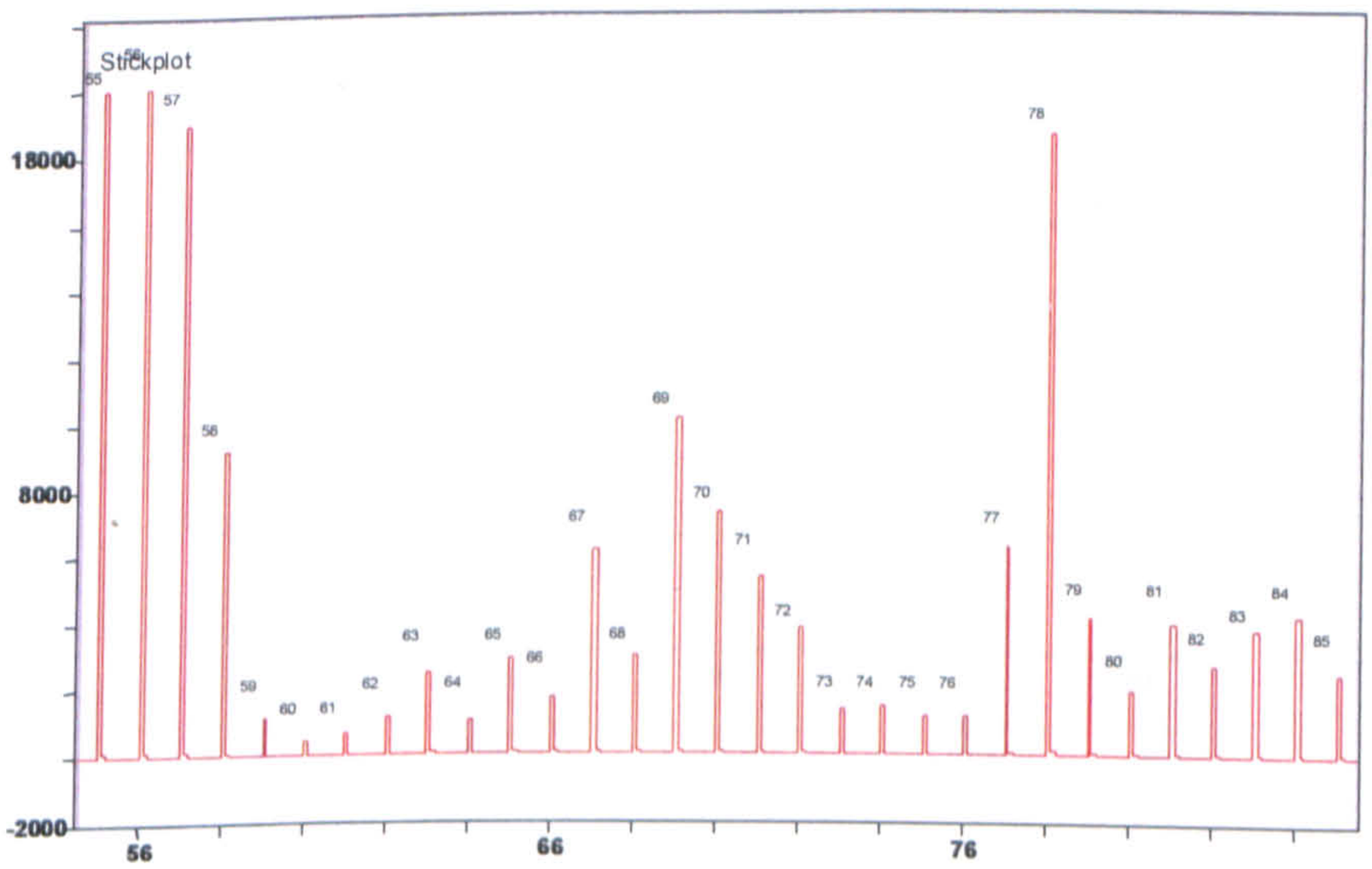
*Displayed is the interesting mass range from 55 to 85 amu



File # 1 : BSUC KD ES 10#2

- Stickplotted sample measurement from section 4.7.4, More accurate assessment of the TED

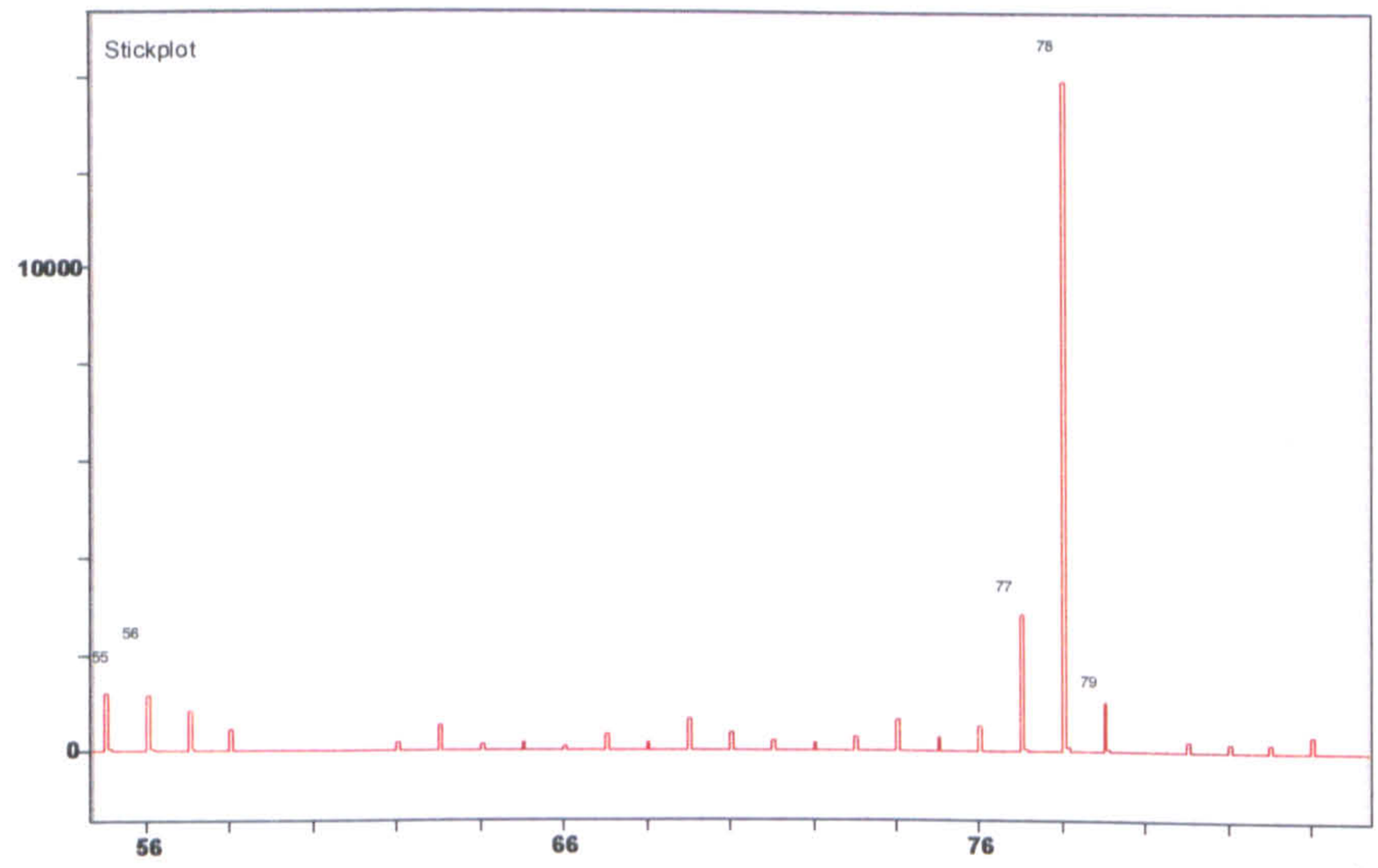
*Displayed is the interesting mass range from 55 to 85 amu



File # 1 : BSUC KD ES 40#2

- Stickplotted background measurement from section 4.7.5, Using the TED with moist samples

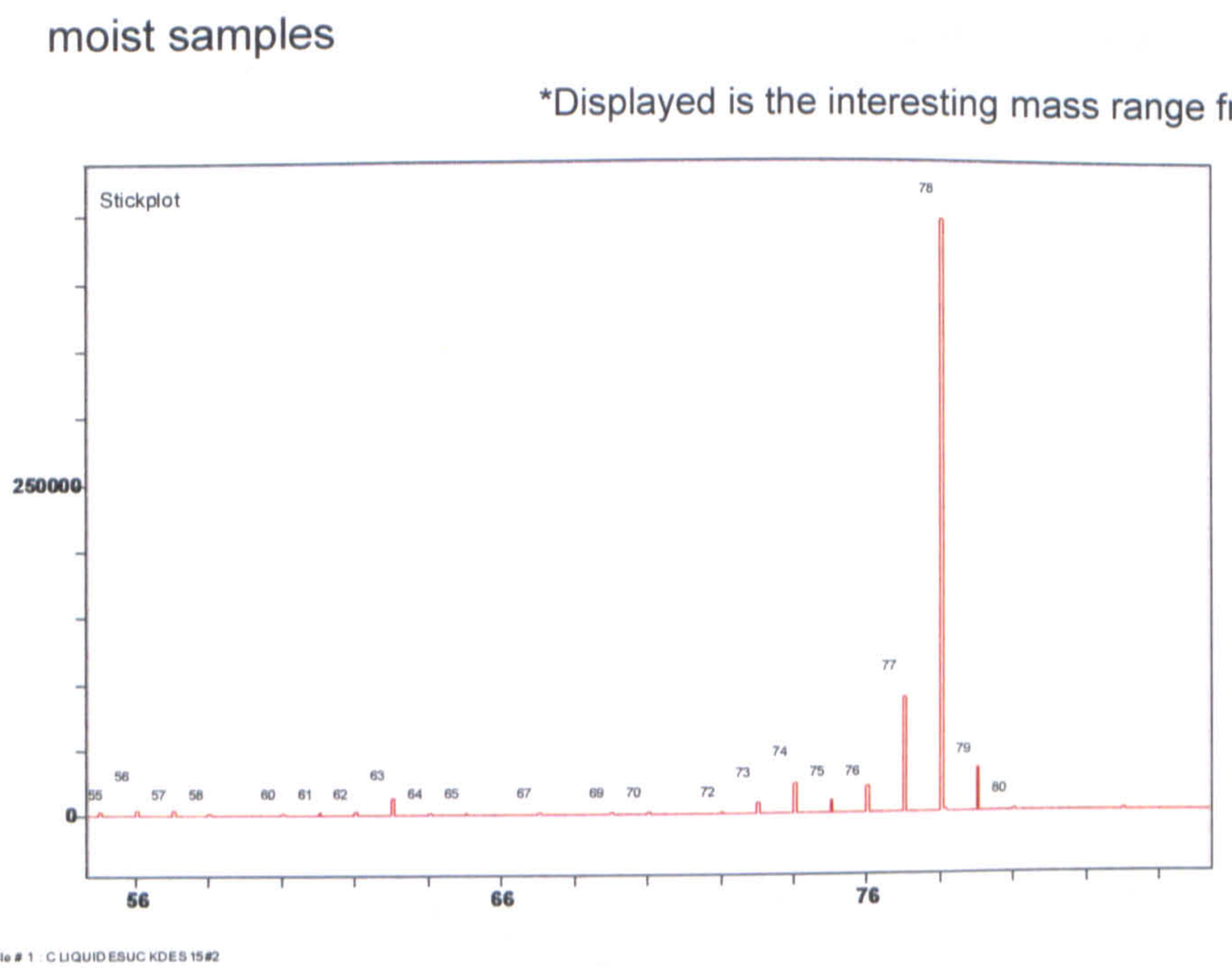
*Displayed is the interesting mass range from 55 to 85 amu



File # 1 : C LIQUID ESUC KDES 1#2

- Stickplotted sample measurement from section 4.7.5, Using the TED with moist samples

*Displayed is the interesting mass range from 55 to 85 amu



File # 1 : C LIQUID ESUC KDES 15#2

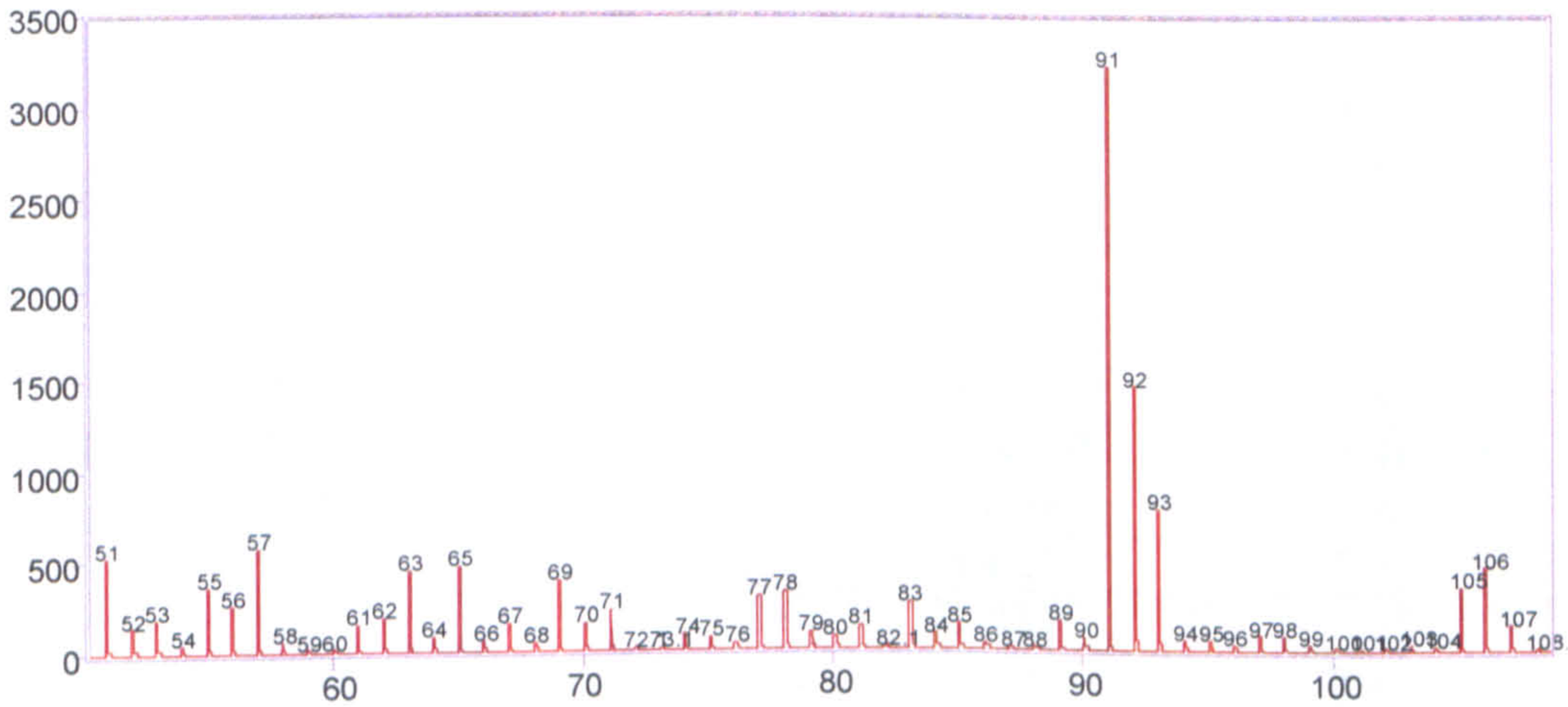
Appendix 10. Results, Personal Exposure Refuelling a Car

	21/07/03	14/08/03	21/08/03	27/08/03
Time [min]	Benzene [ppb]	Benzene [ppb]	Benzene [ppb]	Benzene [ppb]
0		24.3	-2.6	28.4
0.5	3.3	27.4	-5.4	32.1
1	0.4	34.1	-7.1	29.8
1.5	2.4	28.7	-5.6	21.2
2	1.2	28.0	-2.3	28.9
2.5	2.5	20.2	0.0	30.6
3	2.6	20.7	9.7	35.7
3.5	1.9	19.2	19.0	32.4
4	3.5	19.4	24.4	31.7
4.5	6.8	21.0	23.2	28.9
5	8.7	31.4	20.4	27.4
5.5	7.5	33.7	21.0	29.7
6	11.2	31.0	20.0	29.6
6.5	2534.5	57.7	2185.0	3020.5
7	3319.8	76.6	4207.2	274.5
7.5	2718.6	85.2	1467.2	823.6
8	468.0	99.9	852.3	165.9
8.5	264.8	98.0	573.2	97.2
9	178.8	76.1	315.9	78.6
9.5	154.0	58.0	273.6	69.9
10	126.5	52.2	240.9	65.8
10.5	117.5	53.7	202.5	69.4
11	97.6	50.0	177.5	64.2
11.5	87.9	44.3	161.0	62.9
12	81.2	42.3	150.8	60.9
12.5	75.6	40.4	146.9	55.3
13	69.5	43.6	127.4	54.2
13.5	65.0	44.0	105.0	53.1
14	60.9	42.4	100.8	48.3

Appendix 11. Sample Spectra from Arson Investigation

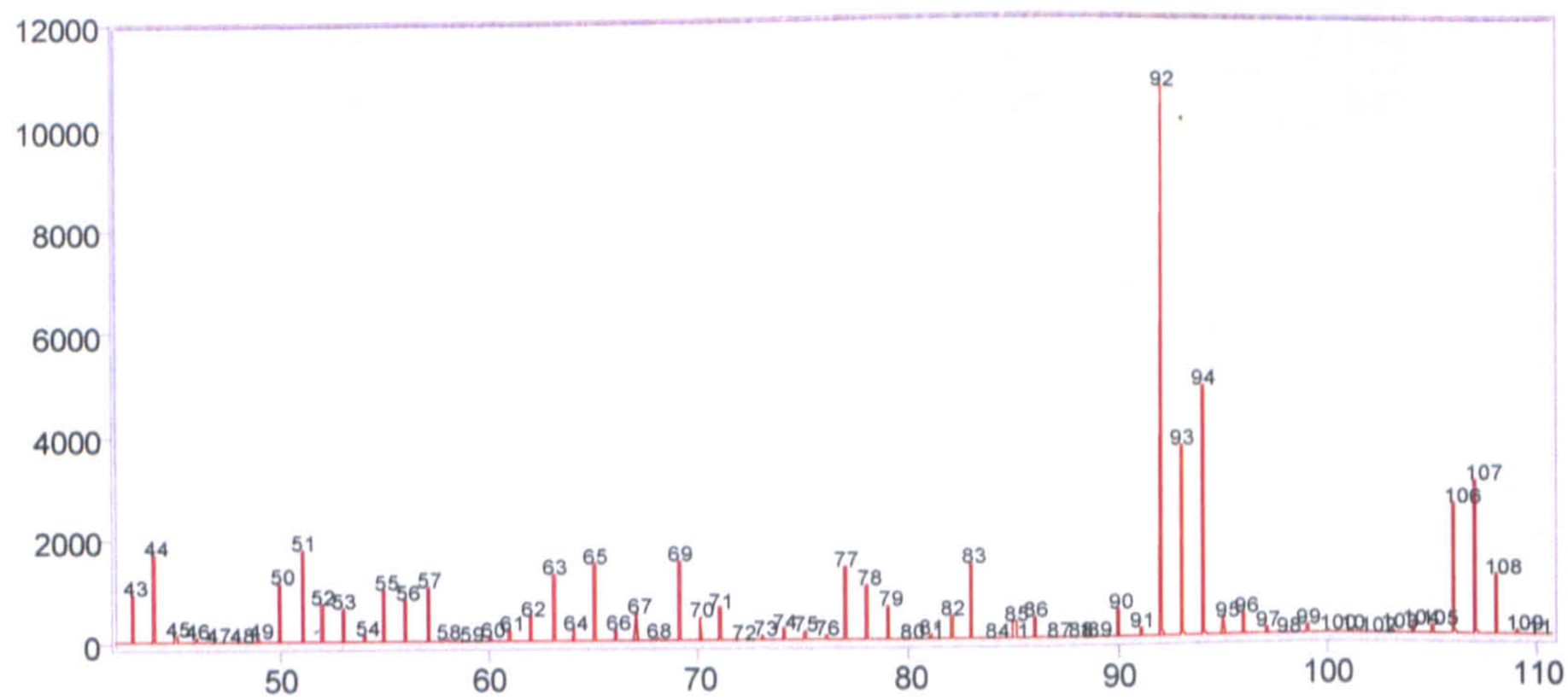
Results of the initial experiments on investigation into arson. The different spectra are displayed in the stickplotted mode, were each peak height represents the integrated area of the mass peak at a specific integer mass. The background spectra are only displayed if the peaks in the background spectrum were significantly enough in order to interfere with the sample spectrum.

Sample A (empty control sample bag)



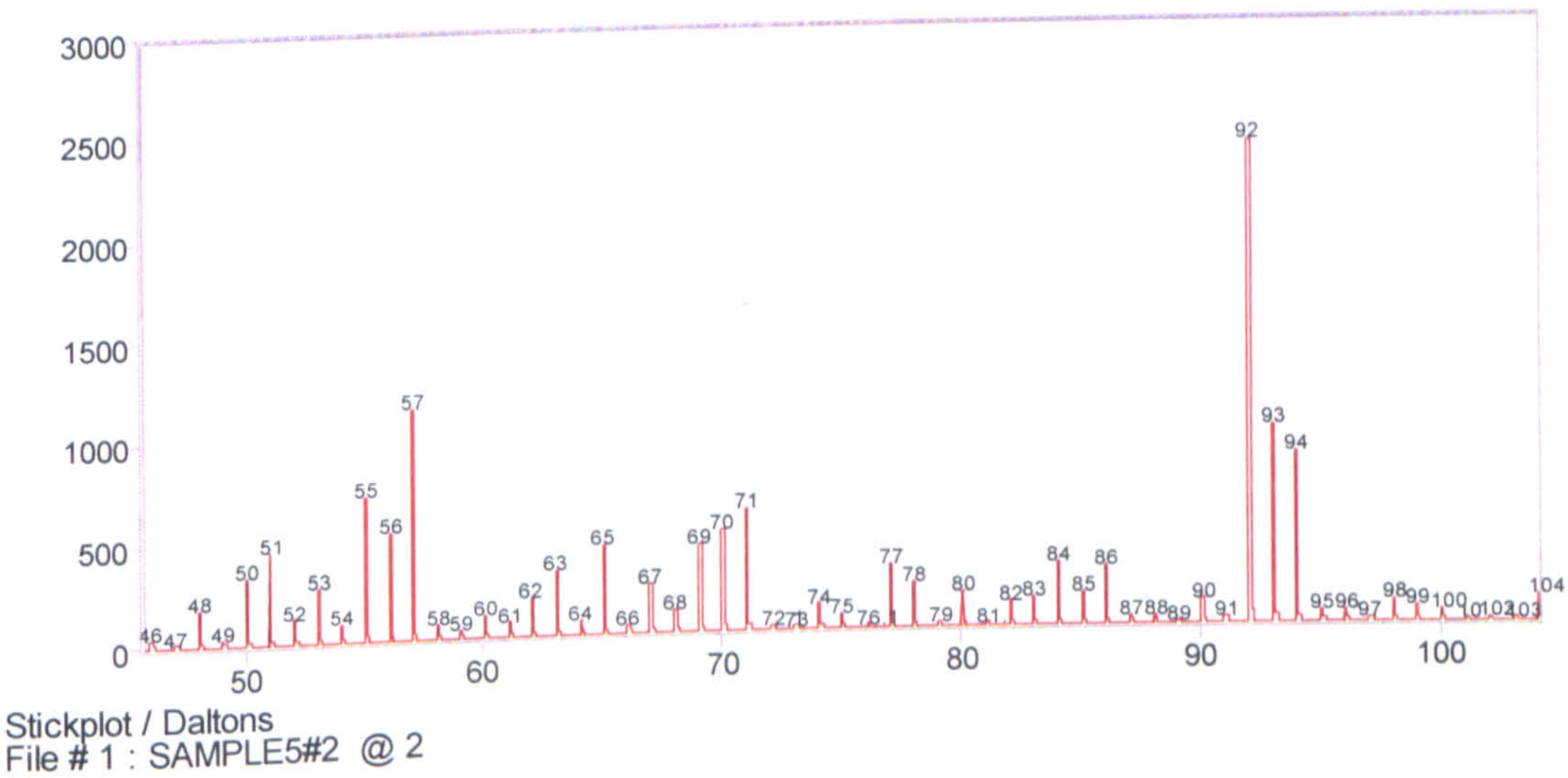
Stickplot / Daltons
File # 1 : SAMPLE3#2 @ 2

Sample B (petrol sample)

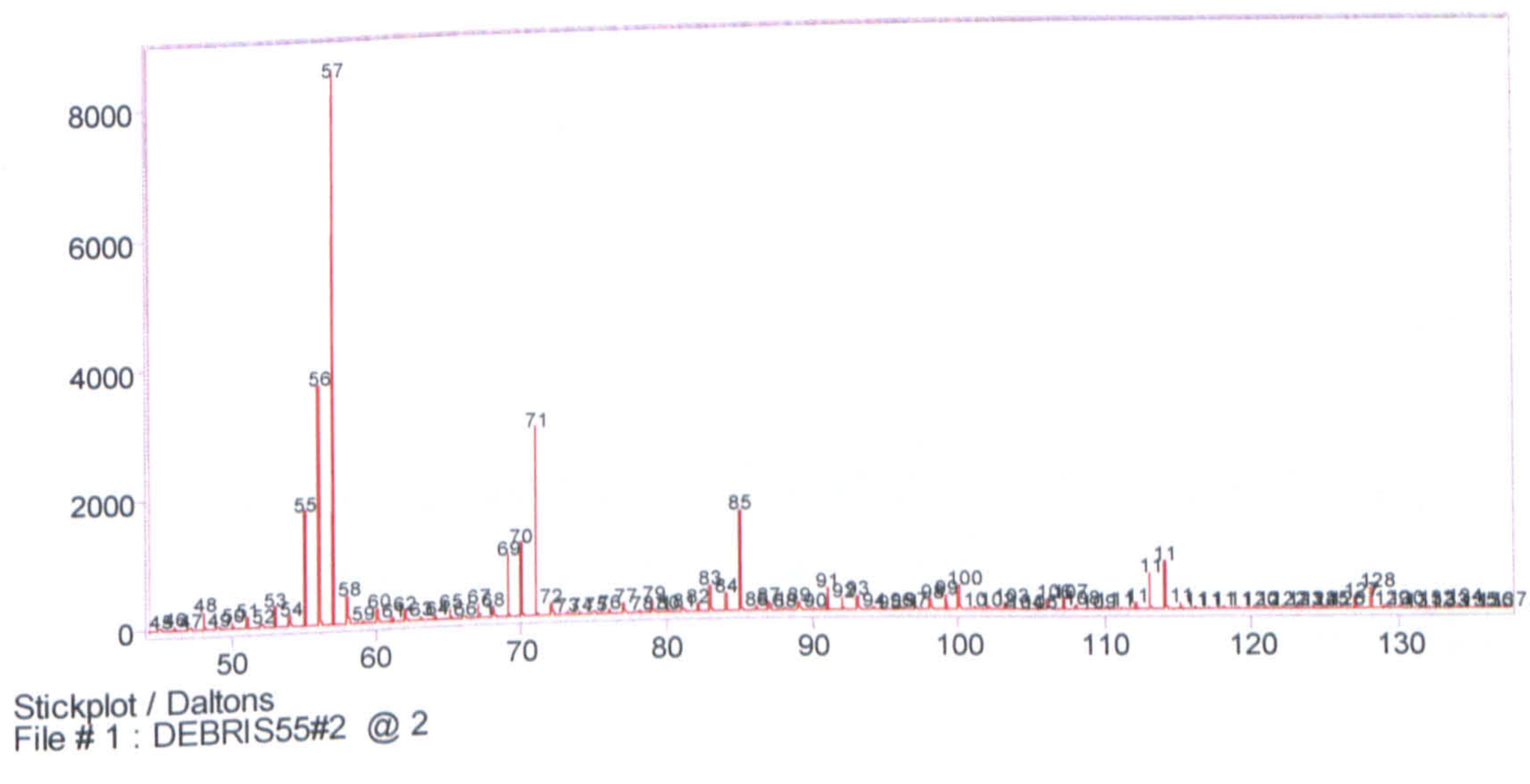


Stickplot / Daltons
File # 1 : DEBRIS52#2 @ 2

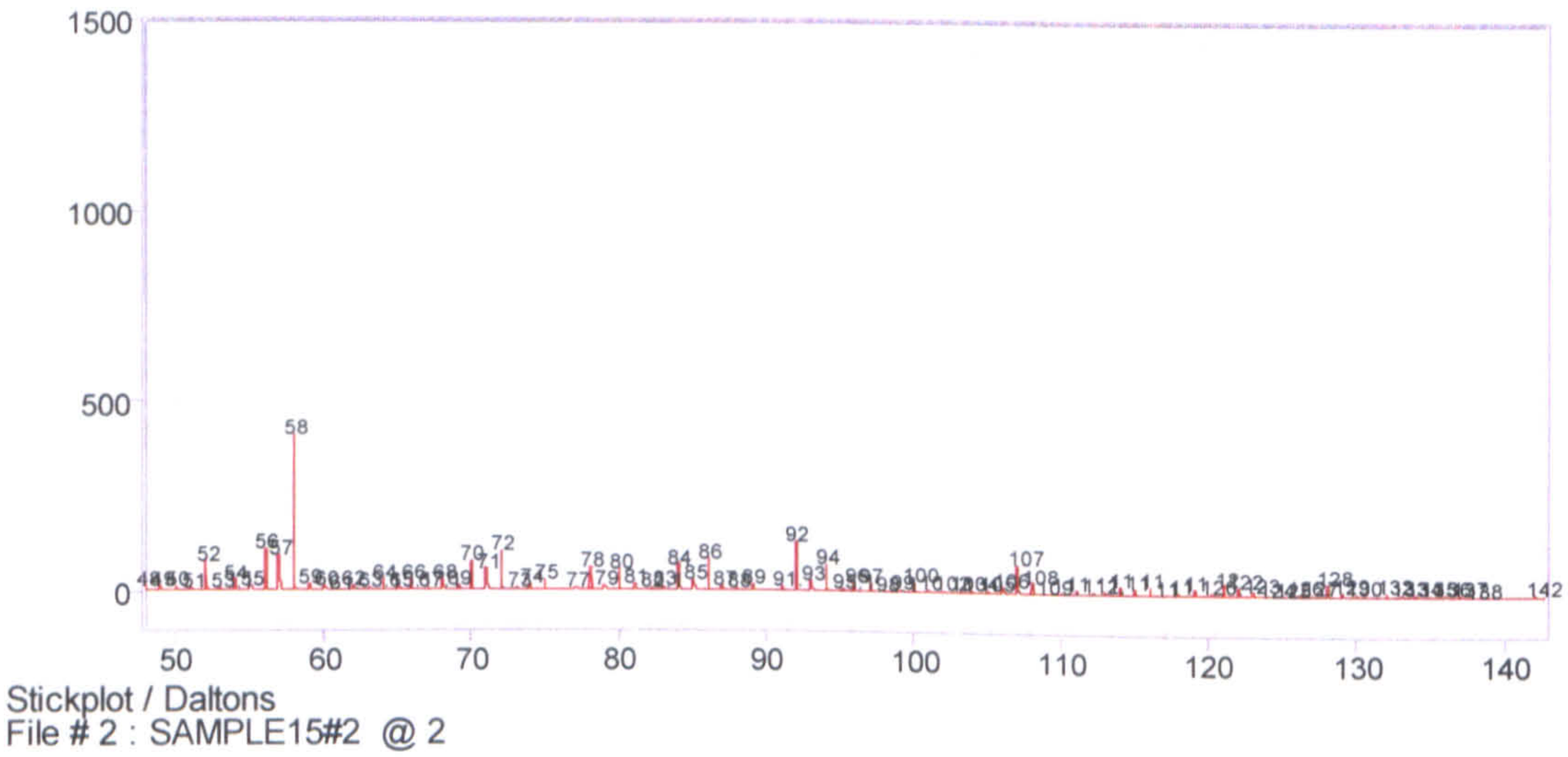
Sample C (surgical spirit)



Sample D (Shell Sol-T)

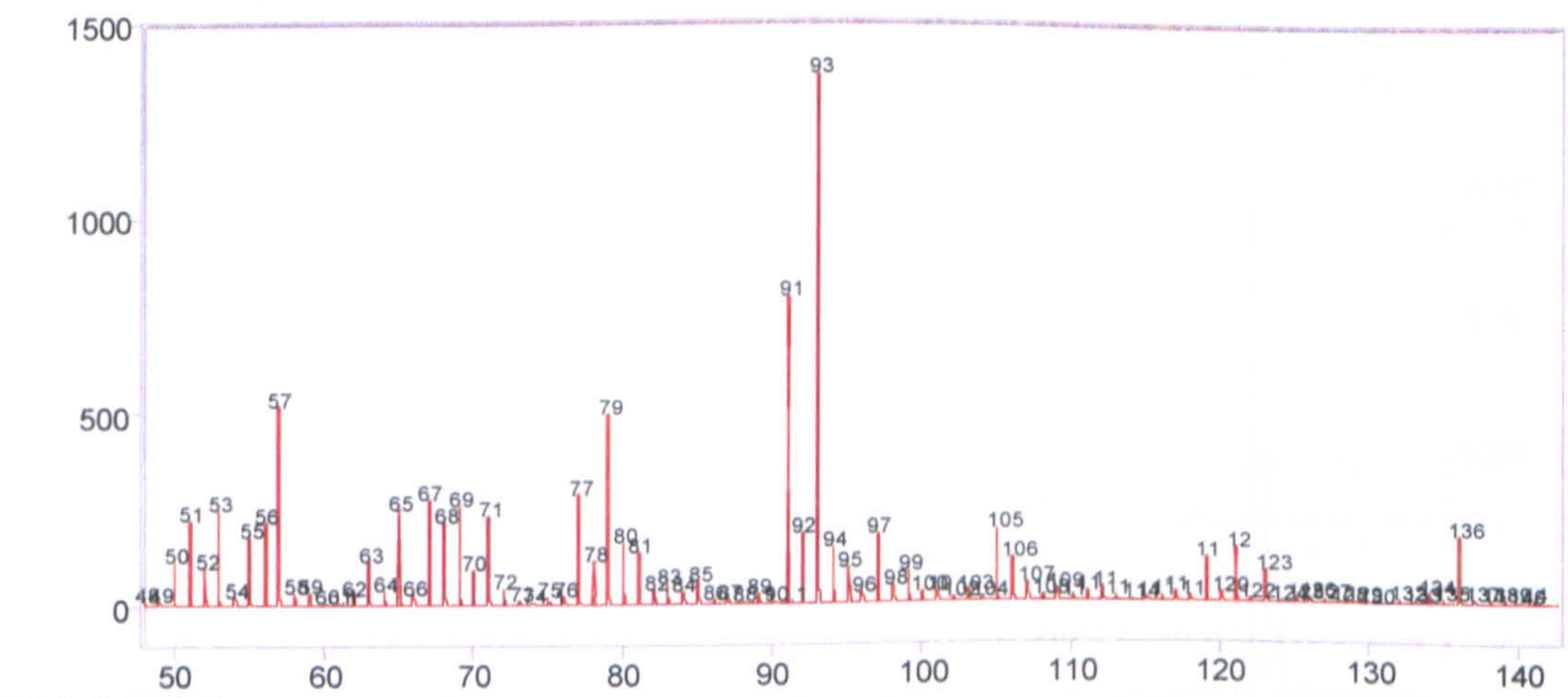


Background E



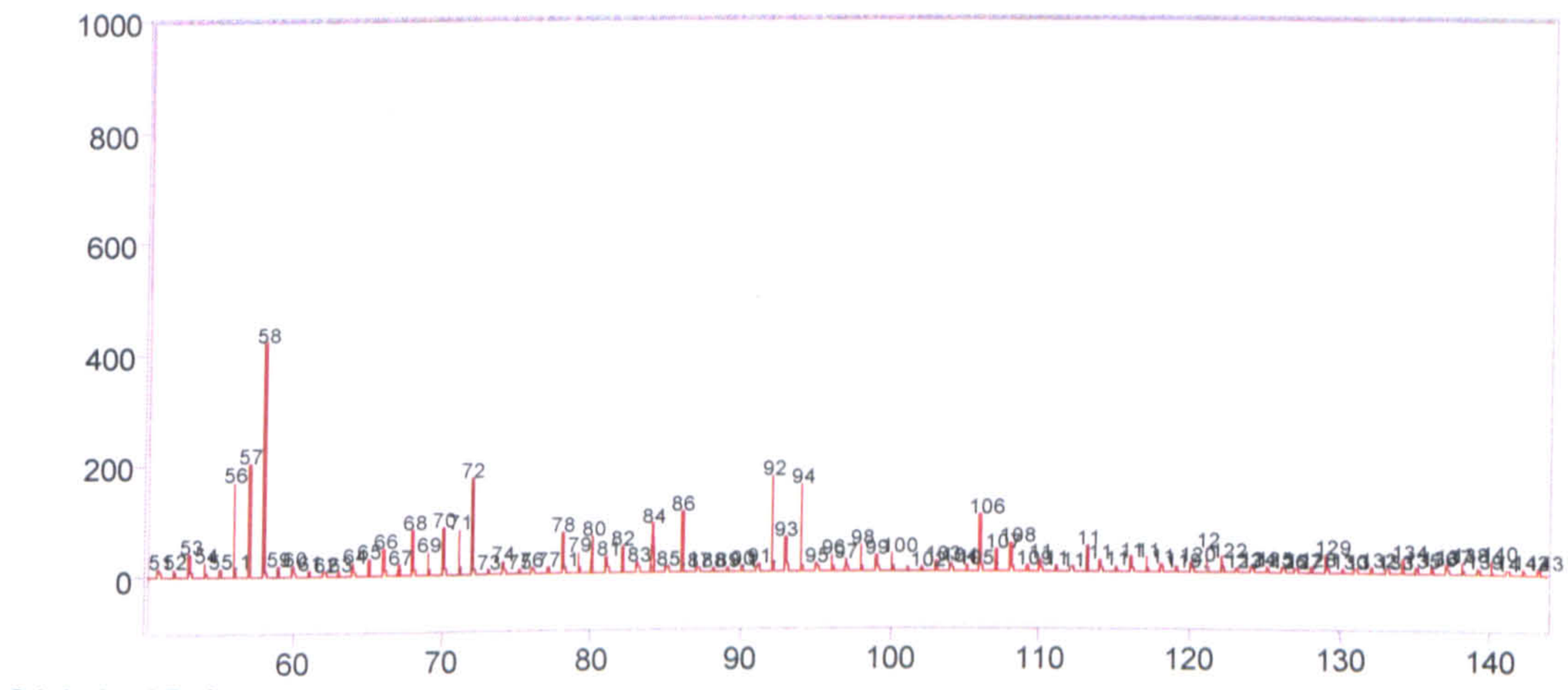
Stickplot / Daltons
File # 2 : SAMPLE15#2 @ 2

Sample E



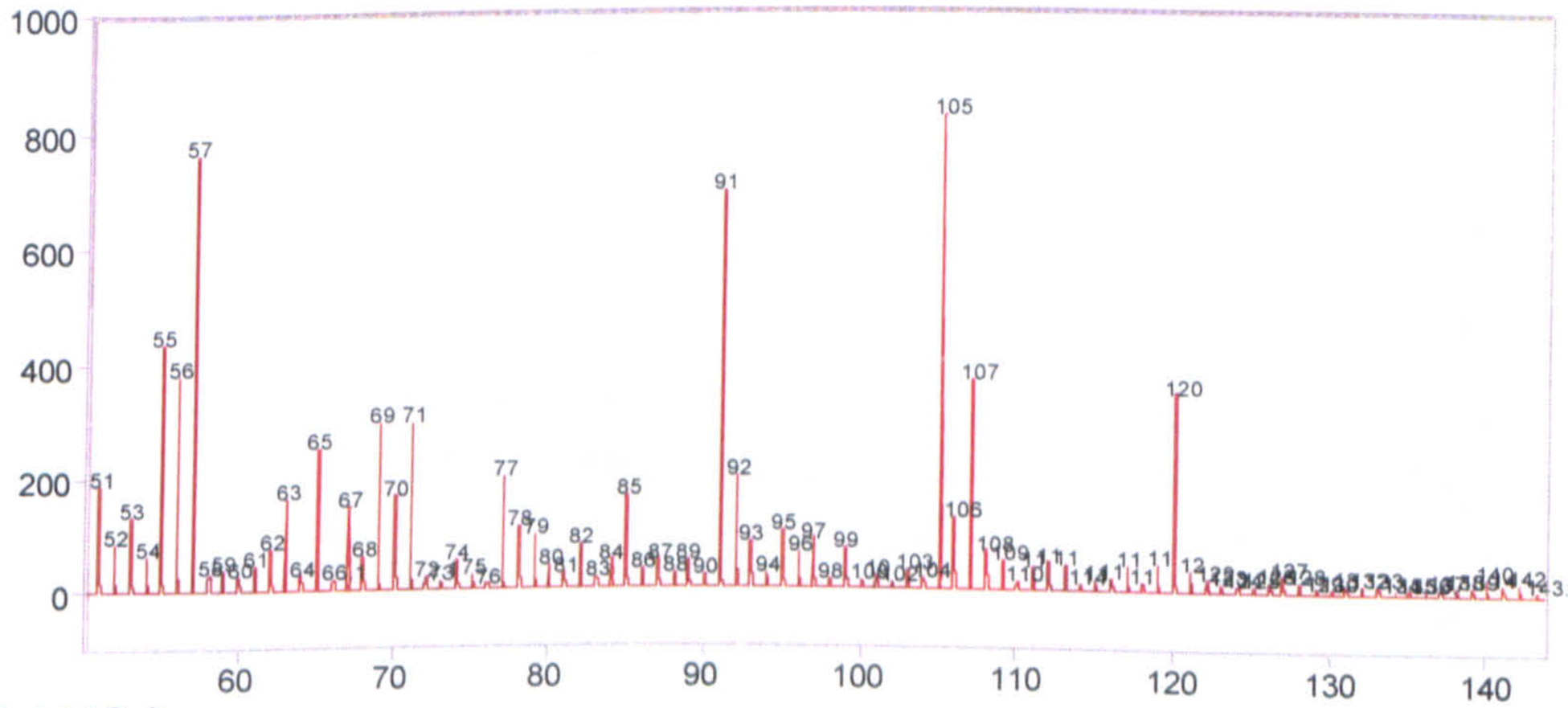
Stickplot / Daltons
File # 1 : SAMPLE16#2 @ 2

Background F



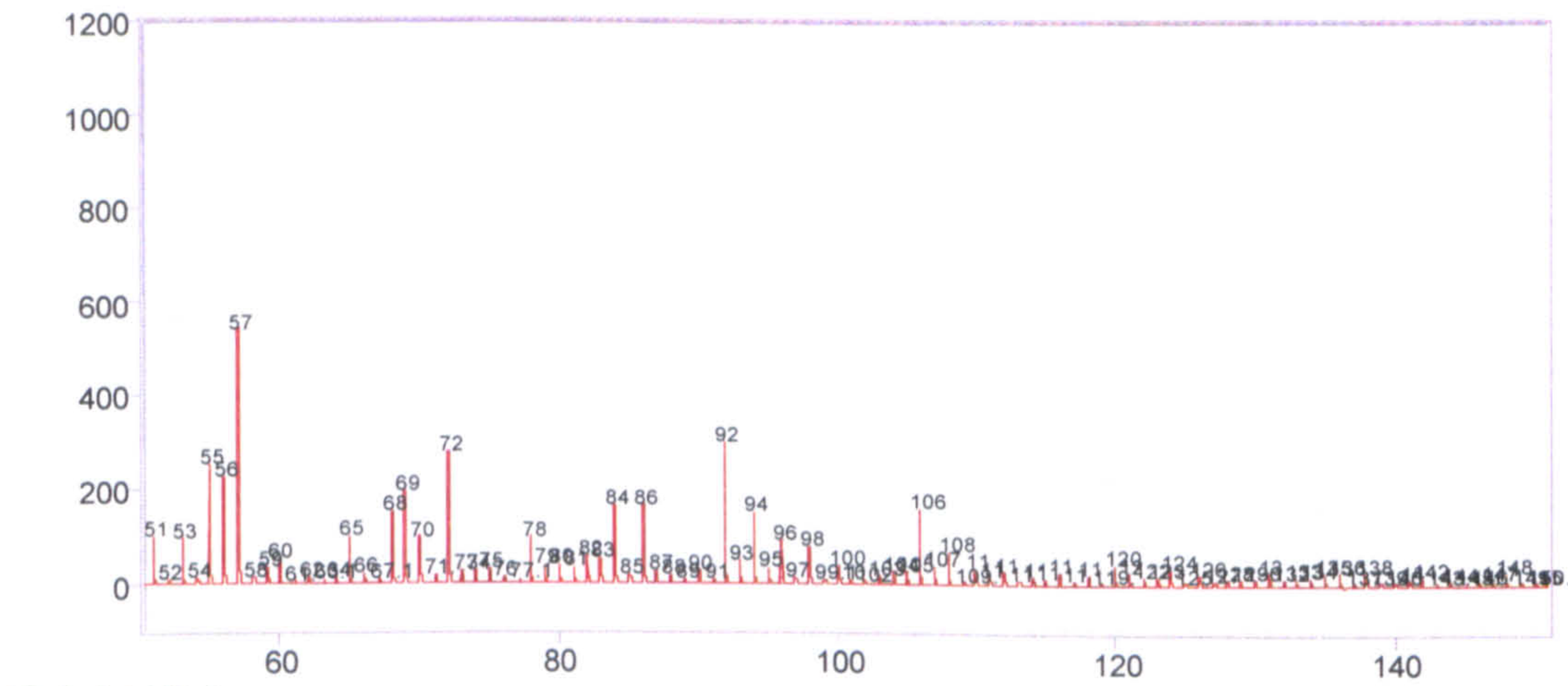
Stickplot / Daltons
File # 2 : SAMPLE18#2 @ 2

Sample F (methylated spirit)

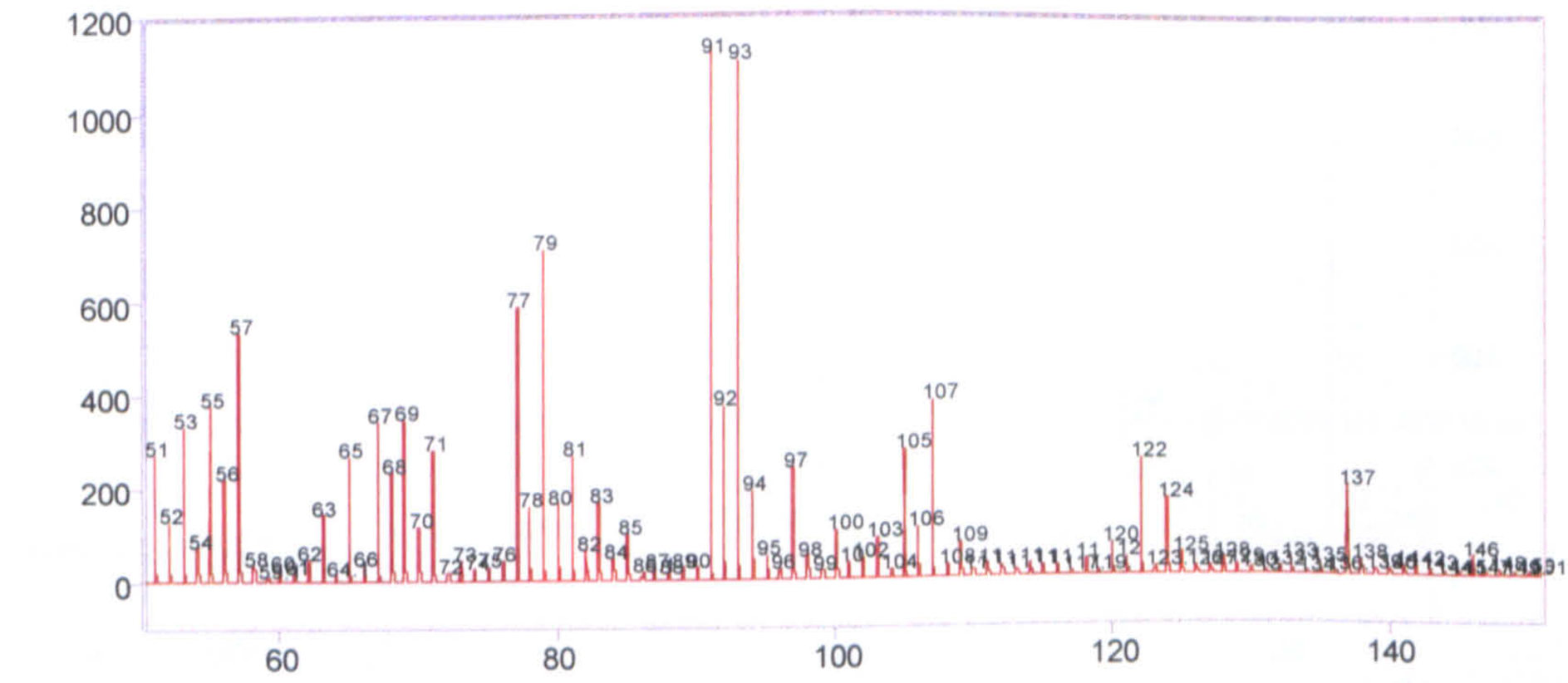


Stickplot / Daltons
File # 1 : SAMPLE19#2 @ 2

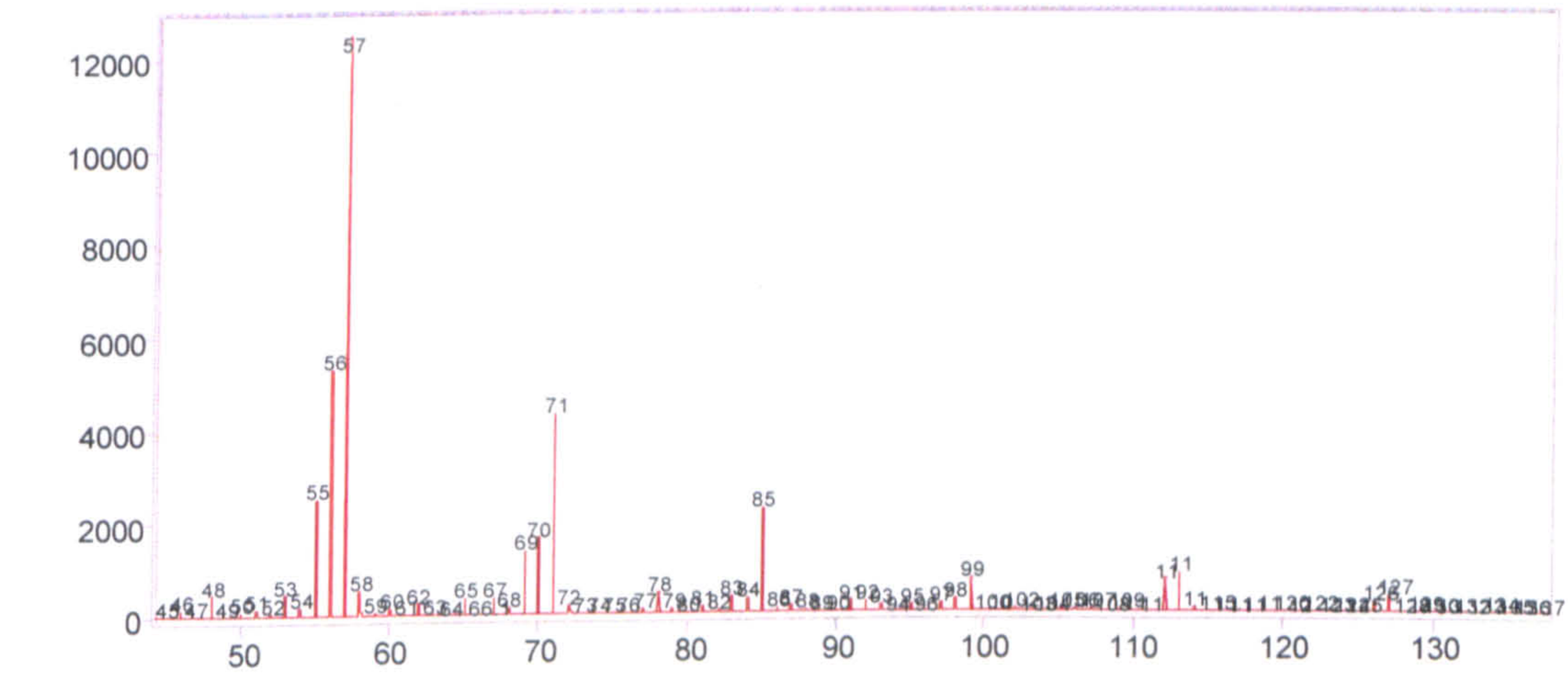
Background G



Sample G

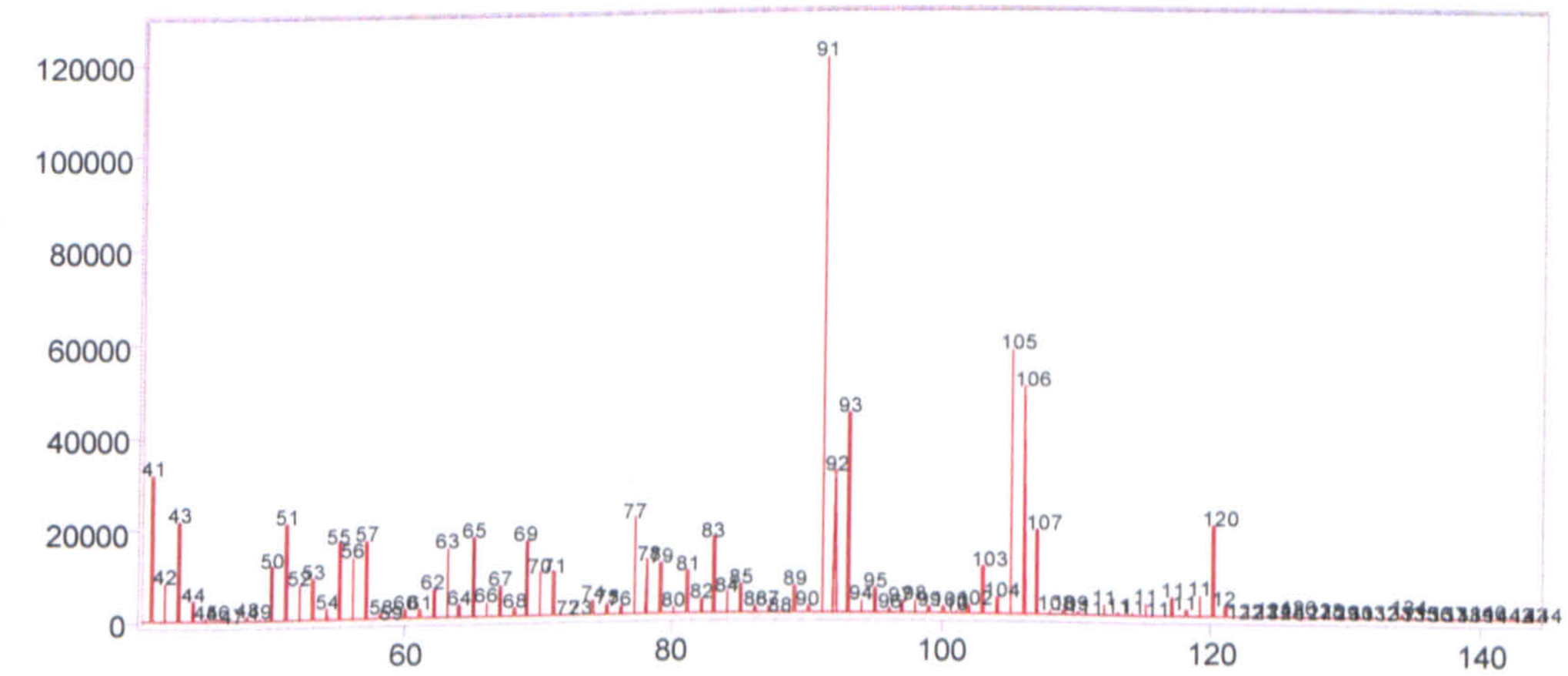


Sample N



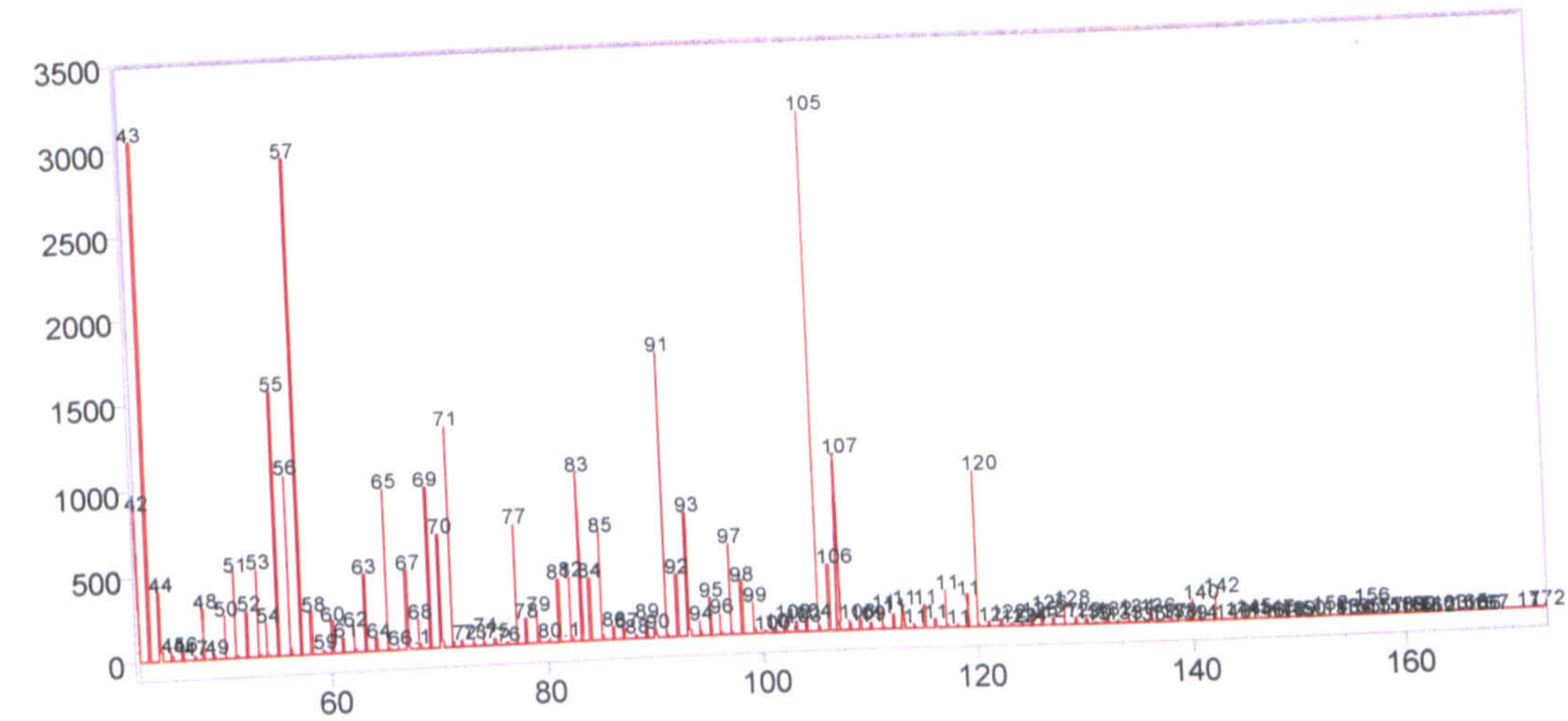
Stickplot / Daltons
File # 1 : DEBRIS58#2 @ 2

Sample Q



Stickplot / Daltons
File # 1 : DEBRIS60#2 @ 2

Sample W



Stickplot / Daltons
File # 1 : SAMPLE34#2 @ 2