MEMBRANE INTRODUCTION MASS SPECTROMETRY FOR THE ON-LINE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS

A Thesis

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By

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ABSTRACT

The analysis of water has acquired great significance in recent years. Volatile organic compounds (VOCs) have been detected in urban waters across the United States, including gasoline-related compounds such as toluene and water disinfection by-products such as chloroform. Some of these chemicals (benzene, chloroform, and toluene) are known or suspected mutagens, carcinogens, or teratogens, representing a risk to human health. Therefore, on-line analysis of water samples without time consuming extraction and purification is necessary. Membrane Introduction Mass Spectrometry (MIMS) has proven to be an efficient technique for the on-line analysis and continuous monitoring of various compounds from environmental samples. The purpose of this study was to construct a simple membrane inlet for the analysis of common VOCs in water and to determine the effects of membrane thickness, temperature and sample flow rate. Increasing the temperature and sample flow rate were found to shorten response times (lag-time and $t_{90\text{-}10}$) for the three analytes investigated, and to enhance signal intensity. Using a thinner membrane was found to improve signal intensity. The fastest lag-time response was 11.43 s for the three analytes investigated. This was obtained under at a temperature of 70 °C, and a sample flow rate of 5 mL/min, and a 0.010 in. silicone membrane. Response time, $t_{90\text{-}10}$, was most favorable at a 70 °C-membrane inlet temperature,

using a 0.5 mL/min-sample flow rate and a 0.10 in. thick silicone membrane (benzene: 28 s, toluene: 35.6 s, and chloroform: 43.19 s).

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LIST OF ABBREVIATIONS

A	amper
°C	degrees Celsius
CWA	Clean Water Act
DBPs	Disinfection by-products
EPA	Environmental Protection Agency
eV	electron Volts
g	gram(s)
GC	gas chromatography
h	hour(s)
HPLC	high performance liquid chromatography
IARC	International Agency for Research on Cancer
I.D.	internal diameter
L	liter(s)
m	milli
M	mega, molar
μ	micro
MCD	multiple concentration detection

MID	multiple ion detection
min	minute(s)
MIMS	membrane introduction mass spectrometry
MS	mass spectrometry, mass spectrometer
m/z	mass to charge ratio (MS)
Ω	ohm
ppb	parts per billion
ppm	parts per million
rt	room temperature
s	second(s)
SEM	secondary electron multiplier (detector)
V	Volt
VOCs	volatile organic compounds
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

Water is a necessary requisite for all organisms. Safe water is essential for a healthy life; thus the water quality has been an important issue for the last decades. All water contains natural impurities such as inorganic substances from the geological strata through which the water flows, sits and filters, and anthropogenic pollutants including microorganisms and chemicals. (Fawell and Nieuwenhuijsen 2003) There are a number of sources for water pollution but two general categories exist, point sources such as sewage and industrial waste and non-point sources such as agricultural runoff, and storm water drainage. (Lopes and Bender 1998; Fawell and Nieuwenhuijsen 2003)

More than 700 organic pollutants from sources including industrial and municipal discharges, rural and urban runoffs, natural decomposition of vegetable and animal matter have been identified in drinking water, along with water treatment by-products. (Lago *et al* 2003) The most common contaminants discharged by factories are solvents such as tri and tetrachloroethene and hydrocarbons, particularly from petroleum oils. (Fawell and Nieuwenhuijsen 2003) In a 1995 paper, 42 water quality reports submitted by the states in accordance with section 305(B) of the Clean Water Act of 1987 were reviewed. This review indicated that the eleven most frequently detected contaminants are nitrates, tri and tetrachloroethylene, volatile organic compounds (VOCs), arsenic, fluorides, 1,1,1-trichloroethane, barium, atrazine, 1,1-dichloroethylene, chlorides and bacteria. (Canter and Maness 1995)

Disinfection of water is the most important step in the drinking water treatment process to eliminate disease-causing organisms. Drinking water disinfection includes chemical oxidants, such as chlorine, ozone, chloroamines, iodine, chlorine dioxide, and UV-light. These oxidants are used also for remotion of chemical compounds or potential toxicants, being chlorine the most common oxidant. (Chaidou *et al* 1999) The reaction of chlorine with organic materials leads to the formation of halogenated disinfection by-products (DBPs) such as trihalomethanes, haloacetic acids, haloaldehydes, haloketones and haloacetonitriles among others. (Nikolau *et al* 1999)

The World Health Organization (WHO) International Agency for Research on Cancer (IARC) evaluated more than 800 environmental agents from 1972 to 2002 classifying them into one of five groups according to the strength of the published scientific evidence for carcinogenicity. For instance, benzene was identified as carcinogenic, chloroform as possibly carcinogenic to humans (IARC 1987), and toluene was classified in group 3 (not classifiable as a carcinogen to humans). (IARC 1989) These three VOCs are recognized by the Environmental Protection Agency as potential contaminants in 38% of community water systems in the United States. (EPA 1997)

Identification of the sources of VOCs is a major step in protecting source water quality and prioritizing contaminant-control measures. The EPA has published methods for the analysis of organic pollutants in wastewater, drinking water and other water samples required by the Clean Water Act (CWA) regulations. (CFR 40, Part 136) The methods that are applicable for VOCs such as benzene, chloroform and toluene use either purge and trap gas chromatography (GC) (CFR 40) or isotope dilution gas chromatography-mass spectrometry (GC/MS). (CFR 40) While these methods provide reproducible data, they require a preconcentration step, making analysis time consuming. Ideal methods for water analysis are those, which permit handling of a large number of samples in a relatively short period of time.

In this thesis, results are presented for the analysis of aqueous mixtures of benzene-toluene-chloroform using Membrane Introduction Mass Spectrometry (MIMS), an analytical technique that introduces molecules from a liquid sample into the ionization chamber of a mass spectrometer by means of a membrane apparatus.

CHAPTER 2

MEMBRANE INTRODUCTION MASS SPECTROMETRY THEORY

Membrane Introduction Mass Spectrometry is an analytical method in which organic compounds are separated from water or air by a semi-permeable membrane (usually a silicone membrane) placed between the sample and the ion source of the mass spectrometer, Figure 2.1. (LaPack *et al* 1990; Bauer 1995; Srinivasan *et al* 1997; Ketola *et al* 2002)

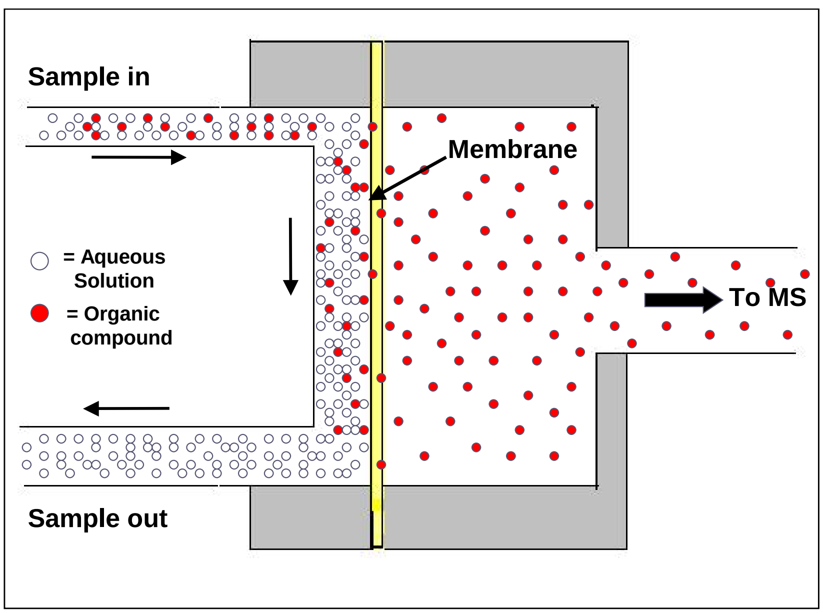


Figure 2.1: Schematic representation of a membrane introduction mass spectrometer. The water is circulated over the membrane and the analytes pass trough the membrane into the ionization chamber of the MS.

MIMS was introduced for the first time in 1963 when an inlet system was devised to follow the kinetics of photosynthesis, *in situ*, through measurements of oxygen and carbon dioxide dissolved in a liquid phase. (Hoch and Kok 1963) MIMS has been studied in different fields of application. Kinetic applications include the work of Calvo *et al* (1983) in which they measured the formation rates of ethyl-2-furoate in a α-chymotrypsin catalyzed transesterification reaction. (Calvo *et al* 1981) In a study by Augusti *et al* the suitability of MIMS to monitor complexation reactions between ß-cyclodextrina and a series of benzene derivatives in aqueous solutions was demonstrated. (Augusti *et al* 2003) MIMS has been used as a tool to investigate the mechanism, reaction intermediates, and kinetics of chloroform formation during the chlorination of simple organic molecules such as phenol, and di- and trihydroxybenzenes, which were modeling humic substances. (Rios *et al* 2000)

In MIMS, analytes are separated from an aqueous solution into the mass spectrometer by a three-step process called pervaporation. These steps are:

(1) The selective adsorption of the analyte onto the surface of the membrane,
(2) Selective diffusion of the analyte through the membrane under the force of a concentration gradient, and
(3) Desorption of the analyte from the membrane into the MS vacuum. (LaPack *et al* 1990)

The permeation process can be described by Fick's equation of diffusion; equation (2.1): (LaPack *et al* 1990)

$$I_m(x,t) = -AD\left\{\frac{\partial C_m(x,t)}{\partial x}\right\} \quad (2.1)$$

where $I_m(x,t)$ is the analyte flow inside the membrane (mol/s) with respect to analyte concentration, $C_m(x,t)$ (mol/cm^3), at a specific membrane depth x (cm) and time t (s). D is the diffusion coefficient (cm^2/s) of the diffusing substance (sample), the negative sign indicates that the diffusion proceeds from higher to lower concentration through a membrane of surface area A (cm^2). The flux is a positive quantity since the concentration gradient is negative in the direction of diffusion. Thus, according to equation 2.1, the analyte flow depends directly on the membrane surface area and the diffusion coefficient. Diffusivity is related to the molecular properties of the analyte and membrane and is driven by the membrane concentration gradient. (Chang 2000; Johnson *et al* 2000) The change of the analyte concentration within the membrane as a function of time is described by equation (2.2): (Srinivasan *et al* 1997)

$$\left\{\frac{\partial C_m(x,t)}{\partial t}\right\} = D\left\{\frac{\partial^2 C_m(x,t)}{\partial x^2}\right\} \quad (2.2)$$

Diffusion through the membrane is assumed to be the rate-determining process, while adsorption and desorption at the membrane surface are considered instantaneous. (LaPack *et al* 1990)

The introduction systems used can be divided in two groups: those in which the silicone membrane is mounted close to the ion source but outside the vacuum chamber, and hollow silicone fiber inlets or silicone capillaries mounted inside the vacuum chamber. (Lauritsen 1990; Johnson *et al* 2000) Improvements of these introduction systems have been investigated. Slivon and co-workers introduced pneumatic transport by purging with helium a single silicone rubber hollow fiber to carry the analyte from the membrane into the mass spectrometer. (Slivon *et al* 1991)

Some of the advantages offered by MIMS are: (1) speed (the typical analysis time ranges from 1 to 6 minutes with less than 1 mL of sample (Bauer 1995)), (2) sample pretreatments are not necessary, (3) the analysis cost per sample is low, (4) no solvents are required, and most importantly, (5) MIMS can be used for long-term continuous monitoring of environmental, biochemical and chemical processes. (Ketola *et al* 2002)

CHAPTER 3

MASS SPECTROMETRY OVERVIEW AND CONTROL EXPERIMENTS

Mass spectrometry, a powerful analytical technique in environmental sciences, has become an important tool in the acquisition of information about the composition and structure of organic compounds. MIMS, which was briefly described in the previous chapter, is one of the mass-spectrometric techniques used for the identification and measurement of organics in the environmental media.

The purpose of this chapter is two fold: (1) to describe the principles of a mass spectrometer (MS), and (2) to present the control results obtained with the mass spectrometer.

3.1 Mass spectrometry overview

The mass spectrometer is an instrument that serves for establishment of the molecular weight and structure, and identification of organic compounds and determination of the components of inorganic substances. The sample is volatilized within the spectrometer, and the gas-phase ions formed from it are separated according to their mass to charge (*m/z*) ratios, and are usually detected electrically. The ion currents corresponding to the different species are amplified and either displayed on an oscilloscope or a chart-recorder, or stored in a computer. (Constantin and Schnell 1990)

Various methods of ionization can be used depending on the physical state, volatility and thermal stability of the sample. Electron impact and photon impact are utilized for gaseous and liquid samples (liquid samples have to first be volatilized and then ionized). (Johnstone and Rose 1996; Harris 2002) In electron impact ionization, electrons are emitted from a hot filament and accelerated usually through a potential of 70 V before they interact with incoming sample molecules. This collision results in ionization of the sample. Some analyte molecules (M) absorb as much as 12-15 electron volts (eV) of energy in the collision, which is enough for ionization, Equation 3.1:

$$\underset{}{M} + \underset{70\text{ eV}}{e^-} \longrightarrow \underset{\text{ion}}{M^{+\cdot}} + \underset{55\text{ eV}}{e^-} + \underset{0.1\text{ eV}}{e^-} \qquad (3.1)$$

Several devices are available for separating ions with different *mass-to-charge* ratio. The separation of these ions according to their *m/z* ratios can be achieved in a number of ways with magnetic and electric fields alone or combined. Most of the basic differences between the various common types of mass spectrometers lie in the manner in which such fields are used to separate ions. The properties of quadrupole, ion trap, Fourier-transform, and time-of-flight analyzers are briefly explained:

1. Transmission Quadrupole mass spectrometer: it consists of four parallel metal rods to which are applied both a constant voltage and a radiofrequency oscillating voltage. The electric field deflects ions in complex trajectories as they migrate from the ionization chamber toward the detector, allowing only ions with one particular mass-to-charge ratio to reach the detector. (Harris 2002) Since The MS

analyzer used in the present thesis was a quadrupole, a detailed description of the analyzer can be found in Appendix A.

2. Ion Trap mass spectrometer: this instrument stores ions in an evacuated cavity by applying appropriate electric fields and can then be made to eject them selectively according to their masses. (Johnstone and Rose 1996)
3. Time-of-Flight mass spectrometer: this instrument separates ions with the same kinetic energy but different *m/z*. It consists of a long, straight, evacuated tube with the source at one end and the detector. (Harris 2002)
4. Fourier-transform mass spectrometers: it, like ion trap, stores ions in a cavity, but by a different mechanism. In these instruments, ions are trapped in a high-vacuum chamber by crossed electric and magnetic fields. (Johnstone and Rose 1996)

There are four main ways of detecting ions and generating from them an electric current which is proportional to their abundance: by Secondary Electron Multiplier (SEM), scintillation counting and photomultiplier, Faraday cup or focal plane detectors. The SEM in most quadrupoles is a continuous dynode, which consists of a series of ten to twenty electrodes, Figure 3.1. Here, an ion exiting the mass filter is attracted to the negative potential of the mouth of the SEM. When the ion hits the surface of the SEMs it releases several electrons. These electrons are attracted to the more positive side of the SEM, and as they travel down the SEM releases additional electrons in collisions with the surface. Therefore, for every ion hitting the SEM, as many as one million electrons may be released, enhancing the signal. (Johnstone and Rose 1996; Foster 2002)

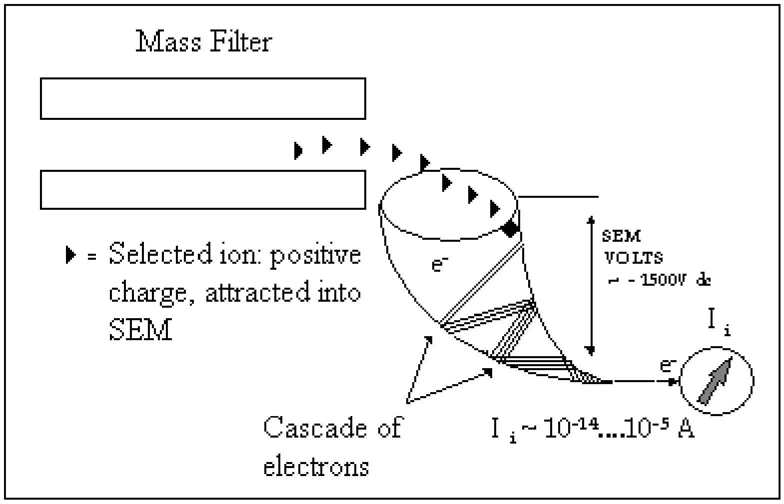


Figure 3.1: Schematic of a Secondary Electron Multiplier-continuous dynode. SEM is used to amplify the signal levels (currents) prior to the signal reaching the electrometer. Adapted from (Foster 2002).

The Faraday detector (Figure 3.2) is a simple plate that collects all ions that exit the mass filter. The ions are neutralized when they hit the plate by supplying a current through an electrometer. The magnitude of this current is determined by the number of ions hitting the plate per unit time, which in turn is related to the amount of gas in the ion source of that particular mass. (Foster 2002)

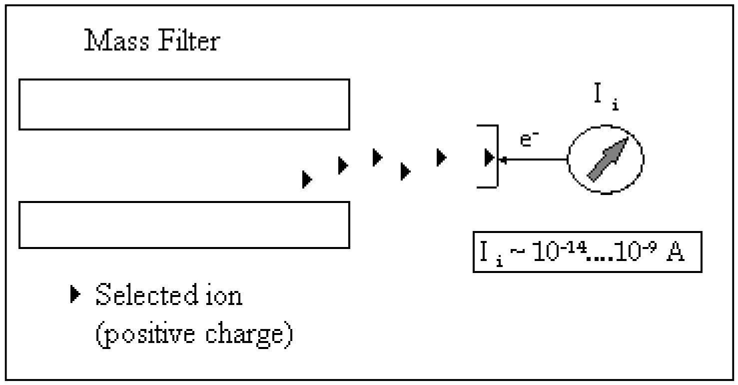


Figure 3.2: Schematic of a Faraday cup detector. The transducer is aligned so that ions exiting the analyzer strike the collector electrode. Adapted from (Foster 2002).

3.2 Mass Spectrometer Control Experiments

3.2.1 Instrumentation and Software

Before the MIMS experiments, the abilities of the Mass Spectrometer (MS) software and ideal operating conditions were determined. The MS used in these experiments was a Quadrupole MS, Omnistar GSD 300 O (Pfeiffer Vacuum, D-35614 Asslar) equipped with a Faraday cup and an SEM (channeltron™) detector. Balzers Quadstar 200 (QMS 200) software (Pfeiffer Vacuum) was used for collecting and displaying data. Four different types of measurements can be done with the Balzers Quadstar 200, (1) Scan Analog Mode is a continuous measurement of the ion current as a function of *m/z*. The spectrum is represented by a curve across the chosen *m/z* range. (2) In Scan Bargraph Mode only the maximum peak intensities and the corresponding *m/z* numbers are collected. The peaks are represented as bar lines over the corresponding *m/z*. (3) In Multiple Ion Detection (MID) Mode measurements on defined *m/z* are measured, the measured intensities can be displayed as a table, a bargraph, or as a function of time. (4) The Multiple Concentration Detection (MCD) Mode provides concentration measurements on one or several predefined *m/z* via calibration factors. (Balzers Quadstar 422 User's Guide 2001)

Air spectra were obtained using the Scan Analog, Scan Bargraph and MID modes. The spectra were obtained by electron ionization at 70eV and the following EI fragment ions were used to monitor the air in the MID mode: N^+ (*m/z* 14), O^+ (*m/z* 16), H_2O^+ (*m/z* 18), N_2^+ (*m/z* 28), O_2^+ (*m/z* 32), Ar^+ (*m/z* 40), CO_2^+ (*m/z* 44). The experiments were made with an electron emission current of 1.0 mA. All air measurements were carried out with an operating voltage of the SEM at 1200 V. Measuring time per amu for scan measurements was 1 second. The threshold intensity set in order to display the peaks was 1×10^{-15} A. The spectral resolution (R) of the MS spectra was 50. Resolution is defined as, Equation 3.2:

$$R = m / \Delta m \qquad (3.2)$$

where m is the ion mass and Δm is the difference in mass between two resolvable peaks in a mass spectrum.

The QMS 200 determines all necessary correction values to eliminate offsets of the measured signal from the SEM. For this, the ion current is measured under a mass previously specified (5.5amu). This QMS offset calibration is performed before obtaining each spectrum. Since the first objective of this study was to assure an adequate manipulation and understanding of the MS, air Scan Analog spectra were run before and after performing the QMS offset calibration.

3.2.2 Sample Preparation and Control Experiments

MS spectra of air and neat (pure) organic compounds were acquired as control spectra to compare with MIMS spectra. Air was directly obtained through the MS capillary (37 in. (94 cm) long and 1/16 in. (1.58 mm) I.D. stainless steel) from the lab. The MS capillary is connected to the MS via a valve block. These valves are opened in the software by choosing MANUAL > DI/DO and choosing DO#1. Once the valves are opened, the gas at the end of the capillary is drawn into the MS in about 0.5 seconds. A good way to test the response is to set up an air MID measurement and breath over the end of the capillary, the *m/z* 44 should increase due to the CO_2.

Neat organic compounds were placed individually/mixed in tight glass septa bottles, which had been previously cleaned by thoroughly washing them with nanopure deionized water (18.3 MΩ·cm) and allowing them to air dry. The headspace gas was transferred to the MS capillary by means of a collection needle arrangement. In this set up, a 1/16 in. (1.58 mm) stainless steel needle was inserted directly into the septa bottles. The short length of the needle insured that the needle was not submerged into the sample. The needle was connected to a 1 in. (2.54 cm) long 1/8 in. (3.18 mm) stainless steel tubing via a 1/16 in. (1.58 mm) to 1/8 in. (3.18 mm) reducing coupling. This tubing was connected to the MS capillary with a similar reducing coupling, Figure 3.3. Thus, the headspace gas is transferred to the MS once the valves are open. The MS capillary in all the experiments was heated to 180°C to avoid condensation of the sample. Since the spectra of the analytes of interest have peaks in common, the cleanliness of the needle set up and the MS capillary in between individual samples was crucial. Each part of the needle system was handled with powder-free nitrile gloves during assembly and disassembly. All the parts were cleaned by sonication in a solution of acetone- nanopure deionized water (18.3MΩ·cm) (50%-50% v/v) for fifteen minutes, followed by sonication in nanopure deionized water (18.3MΩ·cm) for fifteen minutes. After sonication, the needle set up components were placed in an oven at approximately 120°C for 3 hours. The MS capillary and the MS were cleaned in between samples by baking the instrument out at 180 °C for 15 minutes with the MS capillary open to the atmosphere.

In order to verify that the analytes of interest could be detected, benzene, toluene and chloroform spectra were acquired by Scan Analog, Scan Bargraph, and MID modes. The same conditions were used (SEM of 1200 V, 1 s of measuring time, 1×10^{-15} A threshold intensity, and spectral resolution of 50), except the ionization, increased to 90 eV since no fragmentation was observed for any of these organic compounds at 70 eV. The mass spectra for air measurements were acquired within an *m/z* range of 1-50 amu, while the *m/z* range for the organics was 1-100 amu (benzene and toluene) and 1-130 amu (chloroform). Since MIMS experiments were performed using benzene-chloroform-toluene aqueous mixtures, the response for a neat mixture of the three organics as function of time to the MS was acquired by MID mode (MS-MID). Neat solution mixtures were prepared by delivering volumes equal to 1.00 g of each compound in a glass septa vial. The headspace was analyzed by MID mode as explained above. The SEM detector was set to 1500 V since it was a neat organic mixture.

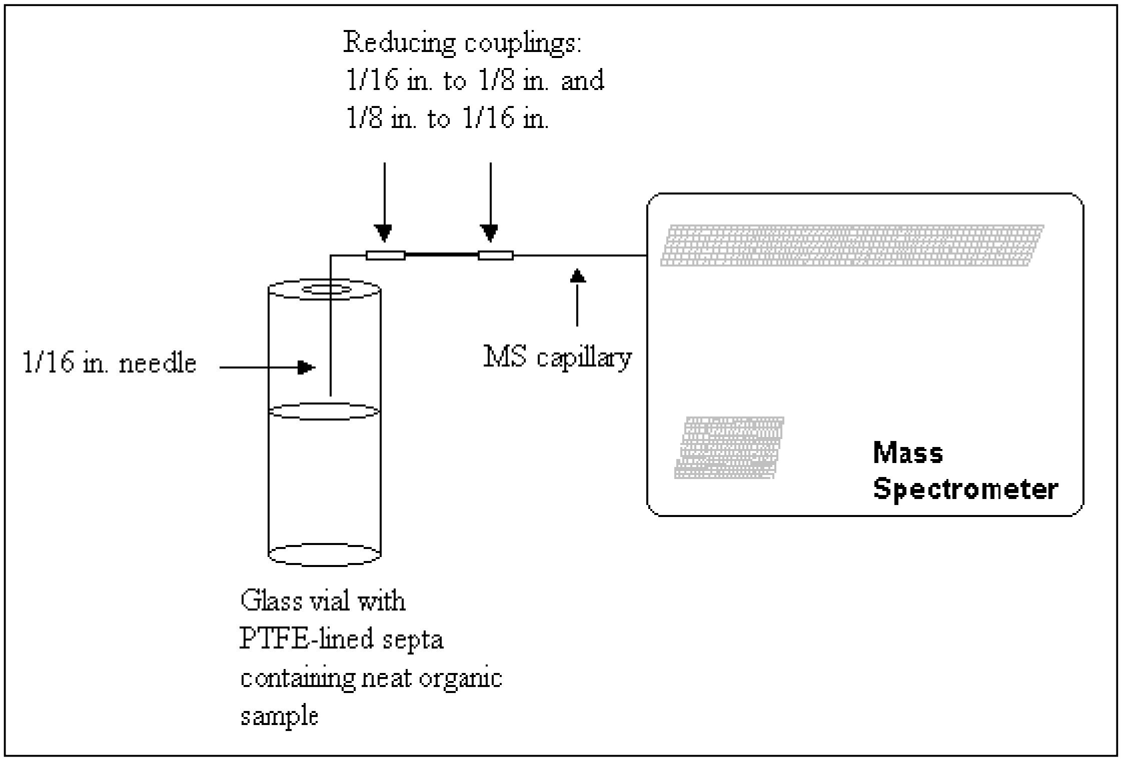


Figure 3.3: Detailed schematic of the inlet system for pure organic compounds. Components not to scale.

3.2.3 Results and discussion

As mentioned above, air spectra were taken before attempting any other experiment, to ensure an adequate manipulation of both the MS and the QMS 200 software. The purpose of the first set of experiments was to compare air spectra before and after the offset calibration. The baseline of the spectra was moved to zero by turning the ON calibration on, as is illustrated in Figure 3.4. Both spectra show all the characteristic fragment ions (Table 3.1). It is important to mention that the intensity of the peaks was graphed using a logarithmic scale in order to observe fragment ions such as those from CO_2 and Ar, whose concentration are 0.037 % and 0.93 % volume in dry air, respectively, (Barry and Chorley 2003) Figure 3.4.

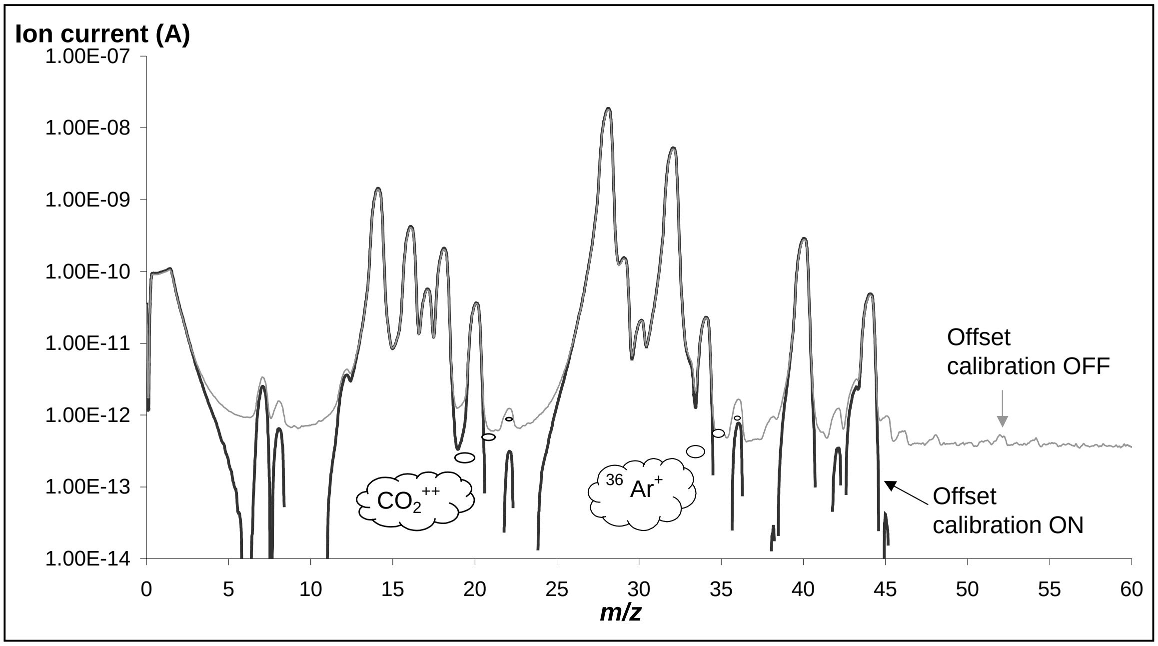


Figure 3.4: Air Scan Analog spectrum with offset calibration ON and OFF.

Two differences can be observed for the spectrum baseline: (1) the baseline is on zero when the offset calibration is ON, and (2) the baseline is non zero when the offset calibration is OFF, small "peaks" are observed in the range of *m/z* 46-54, which do not appear when the offset calibration is ON (Scan Analog mode) or in the Scan Bargraph mode. These peaks are attributed to the offsets of the amplifier (noise).

m/z	Key fragment	Possible parent molecule
1	H^+	H_2O
2	H_2^+	H_2
7	N^{++}	N_2
8	O^{++}	O_2
12	C^+	CO_2
14	N^+	N_2
15	$^{15}N^+$	N_2
16	O^+	O_2 and H
17	OH^+	H_2O
18	OH_2^+	H_2O
19	$^{18}OH^+$	H_2O
	$^{38}Ar^{++}$	Ar
20	Ar^{++}	Ar
22	CO_2^{++}	CO_2
28	N_2^+	N_2
29	$^{15}N^{14}N^+$	N_2
30	$^{15}N_2^+$	N_2
32	O_2^+	O_2
33	$^{17}O^{16}O^+$	O_2
34	$^{18}O^{16}O^+$	O_2
36	$^{36}Ar^+$	Ar
	$^{18}O_2^+$	O_2
38	$^{38}Ar^+$	Ar
40	$^{40}Ar^+$	Ar
42	$C_3H_6^+$	alkane
44	CO_2^+	CO_2
45	$^{13}CO_2^+$	CO_2

Table 3.1: Air ion fragments by NIST (including several isotopes).

The relative intensity and ion current of the peaks obtained by using Scan Bargraph are compared and shown in Figures 3.5 and 3.6, respectively. Relative intensity plots are obtained from ion current spectra as follows: the most intense peak in the spectrum is termed the base peak and all others are reported relative to its intensity. Nitrogen (*m/z* 28 and 14), oxygen (*m/z* 32 and 16), water (*m/z* 18), argon (*m/z* 40) and carbon dioxide (*m/z* 44) main fragment ions are clearly seen in Figure 3.5. The other formed ions are observed only when a logarithmic scale is used (Figure 3.6). Despite this difference, the most abundant components of air were detected by means of this MS, from nitrogen, which is about 78% of air to carbon dioxide, which represents 0.03% of air composition (Barry and Chorley 2003). The difference between Scan Analog and Scan Bargraph modes is explained below. Scan Analog takes 32 data points per mass, therefore, it is used as a diagnostic scan, performed to see the peak position, peak shape and resolution. In Scan Bargraph mode, only the maximum peak intensities and the corresponding mass numbers are collected. This is done by a peak detection integrated in the QMS, meaning 32x less data points. This reduces the data to just one point per mass. (Balzers Quadstar 422 User's Guide 2001)

Air components intensity as a function of time was acquired with the MID mode, Figure 3.7, shows the response of the system when the end of the capillary was breathed over. The intensity of the CO_2^+ signal increased immediately after exhaling. This mode for acquiring data is a good choice for monitoring changes in samples as a function of time.

To investigate the performance of both, Faraday cup and Secondary Electron Multiplier detectors, air spectra were obtained in Scan Analog and Scan Bargraph modes,

Figure 3.8 and 3.9, respectively. Electron multiplier detectors such as SEM increase the intensity of the signal, whereas the Faraday cup detector allows for a direct measurement of the charges that reach them. (de Hoffmann and Stroobant 2001) This difference is illustrated in both figures, in which the peak intensities of the Faraday cup spectra are one order of magnitude lower than the intensities of the SEM spectra. The fragment ions *m/z* 8, 22, 36, 38 and 42 have intensities less than 1 X 10^{-11}A and are not detected when the Faraday cup is used. Thus, the Faraday detector is selected for high intensity signals, while the SEM detector is used for low intensity signals.

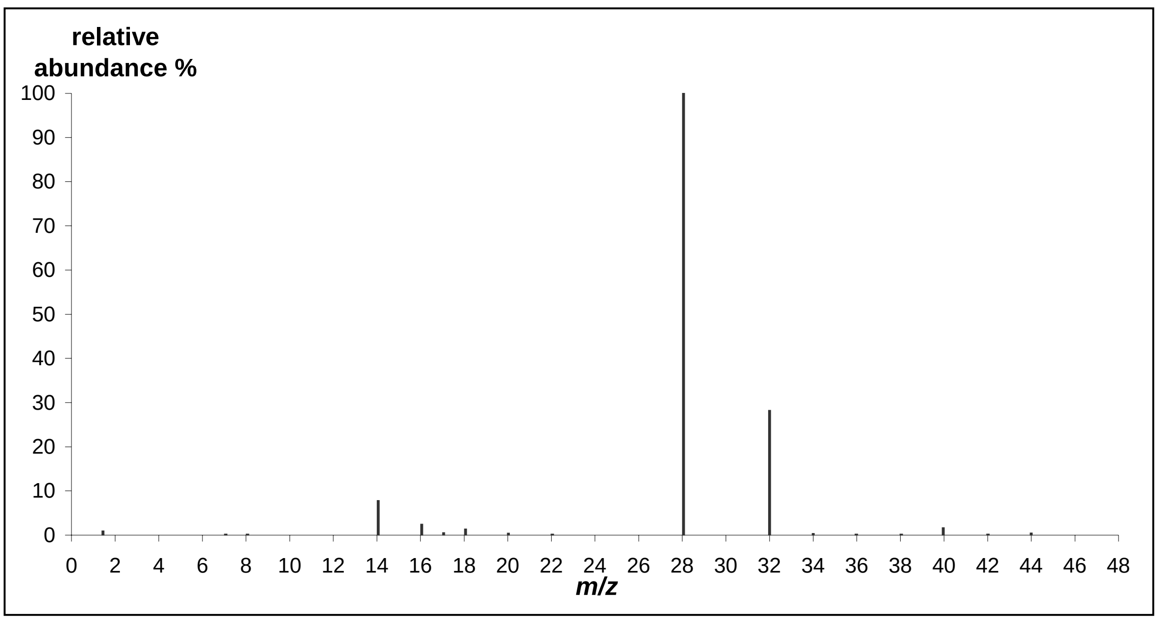


Figure 3.5: Air Scan Bargraph spectrum, intensity of peaks represented as relative abundance.

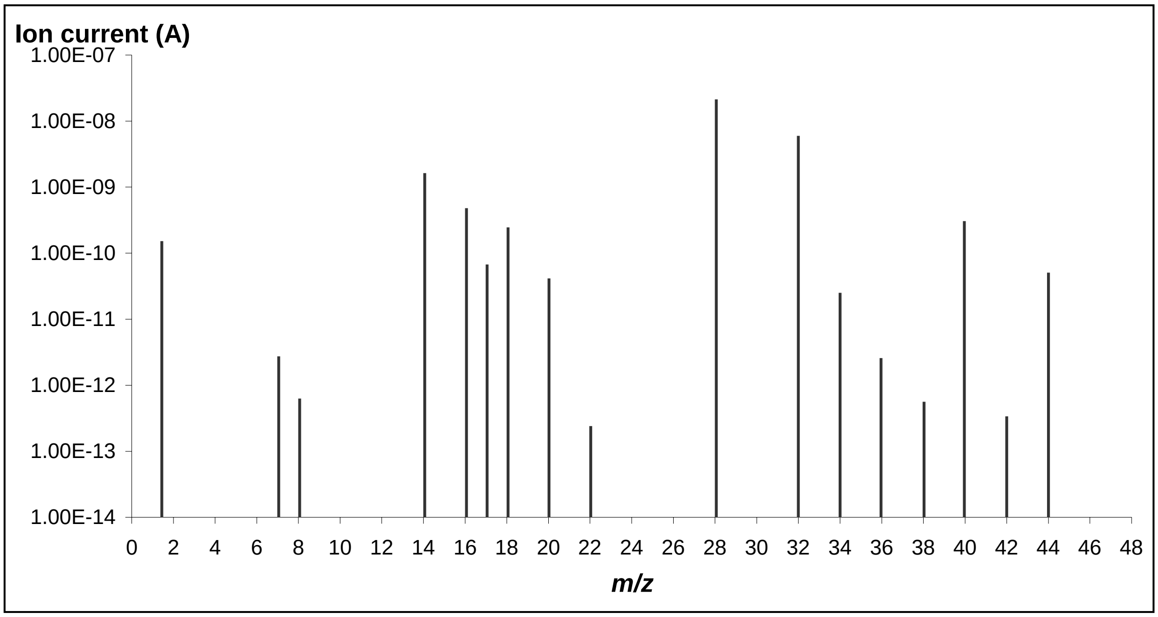


Figure 3.6: Air Scan Bargraph spectrum, intensity of the peaks represented as ion current

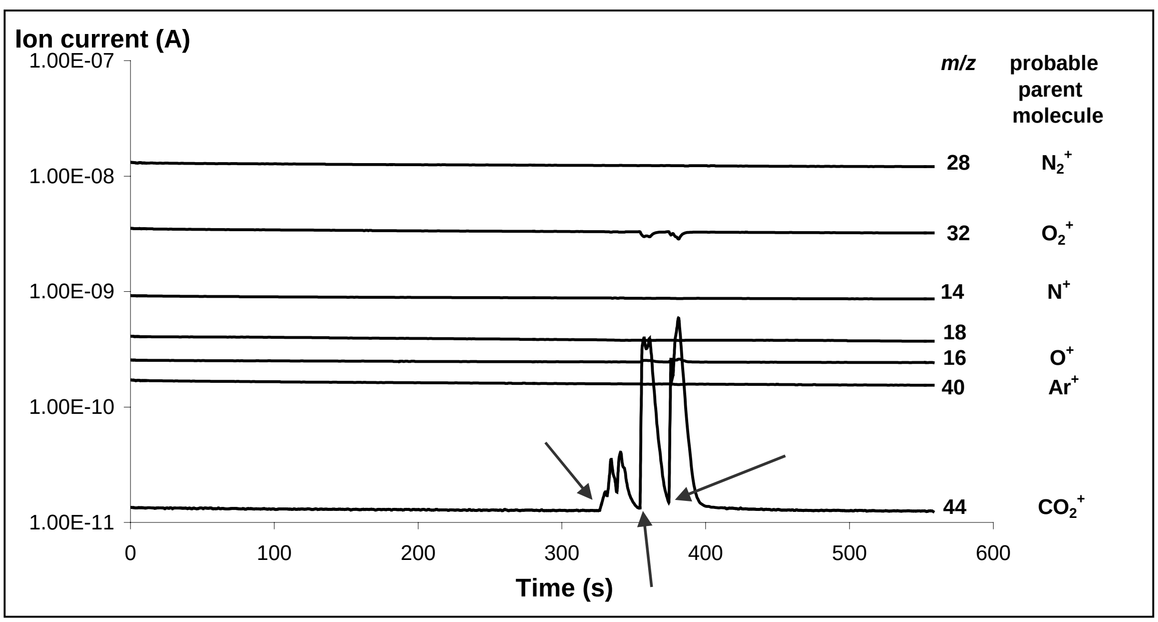


Figure 3.7: MS-MID profile for air. The arrows indicate times of exhaling over the MS capillary.

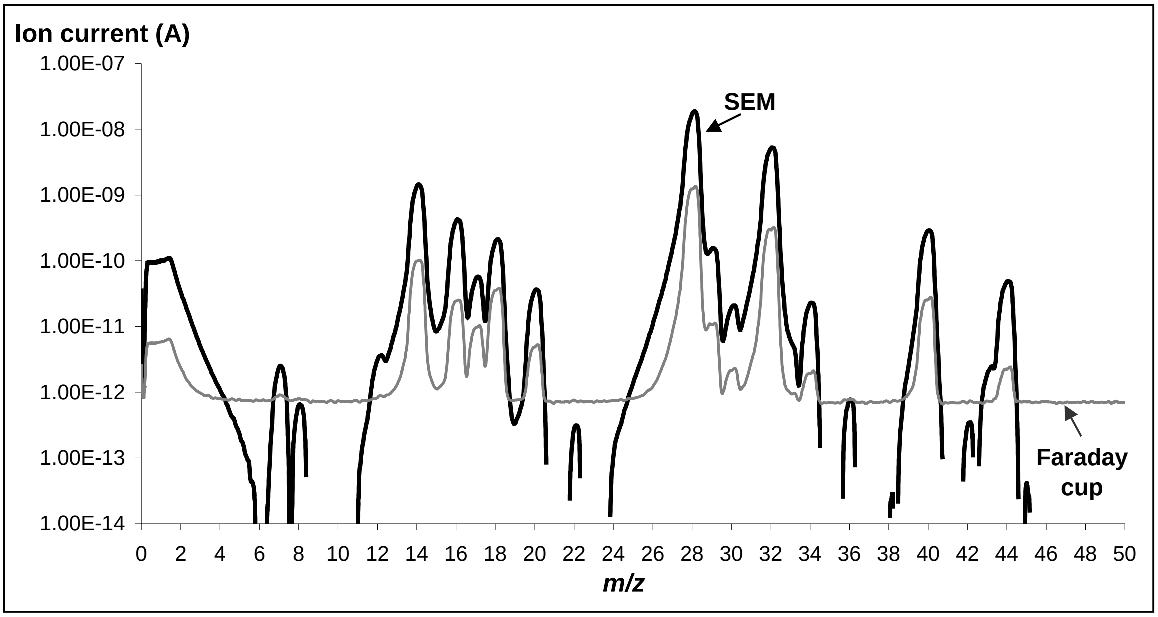


Figure 3.8: Faraday and SEM detectors test. Air Scan Analog spectra.

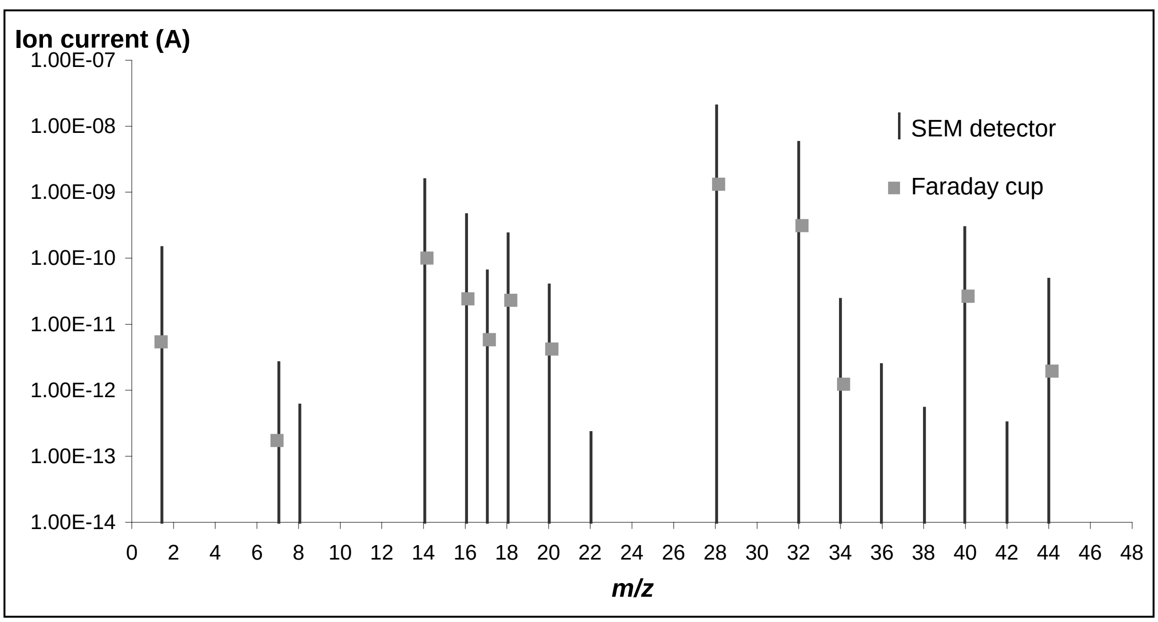


Figure 3.9: Faraday and SEM detectors test. Air Scan Bargraph spectra.

Neat benzene, chloroform and toluene spectra were acquired individually in order to ensure detection by the MS, Figures 3.10, 3.11 and 3.12. The spectra reported by the National Institute of Standards and Technology (NIST) are reproduced also in Figures 3.10, 3.11, and 3.12 for comparison. It is important to mention that the spectra of these organic compounds were obtained using electron ionization of 90 eV, since 70 eV, which is the typical ionization energy, did not ionize the samples efficiently. A range of voltages was tested, and 90 eV was the minimum energy to efficiently ionize the organic samples to produce a spectrum. Therefore, an electron ionization energy of 90 eV was used in this study. The conditions under which the organic spectra were acquired were not optimal due to the presence of air in the headspace of the glass septa bottles. This produced spectra consisting of both the organic compounds and air. The open-air spectrum was used as a background and was subtracted from the organic compounds spectrum to observe a "clean" spectrum.

Some ions are typical of given structures. Molecules with a phenyl ring, such as toluene and benzene often yield a phenylium ion at *m/z* 77, accompanied by a fragment corresponding to acetylene loss at *m/z* 51. (de Hoffmann and Stroobant 2001) Both *m/z* 51 and 77 peaks were observed in the MS spectra acquired. In the case of toluene, with a methyl bonded to the phenyl ring, *m/z* 91 corresponds to a mixture of benzylium and tropylium structures. Lost of an acetylene produced a fragment observed at *m/z* 65. (de Hoffmann and Stroobant 2001) The toluene spectrum revealed also the *m/z* 91 peak.

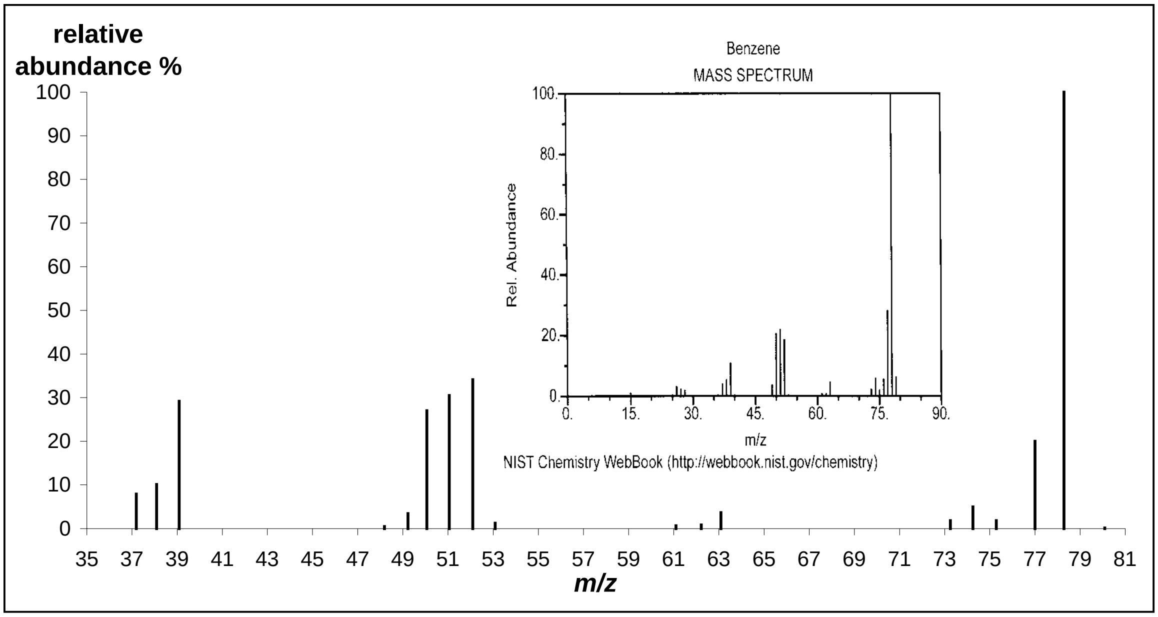


Figure 3.10: Benzene Scan Bargraph spectrum. Inset: Benzene mass spectrum reported by NIST.

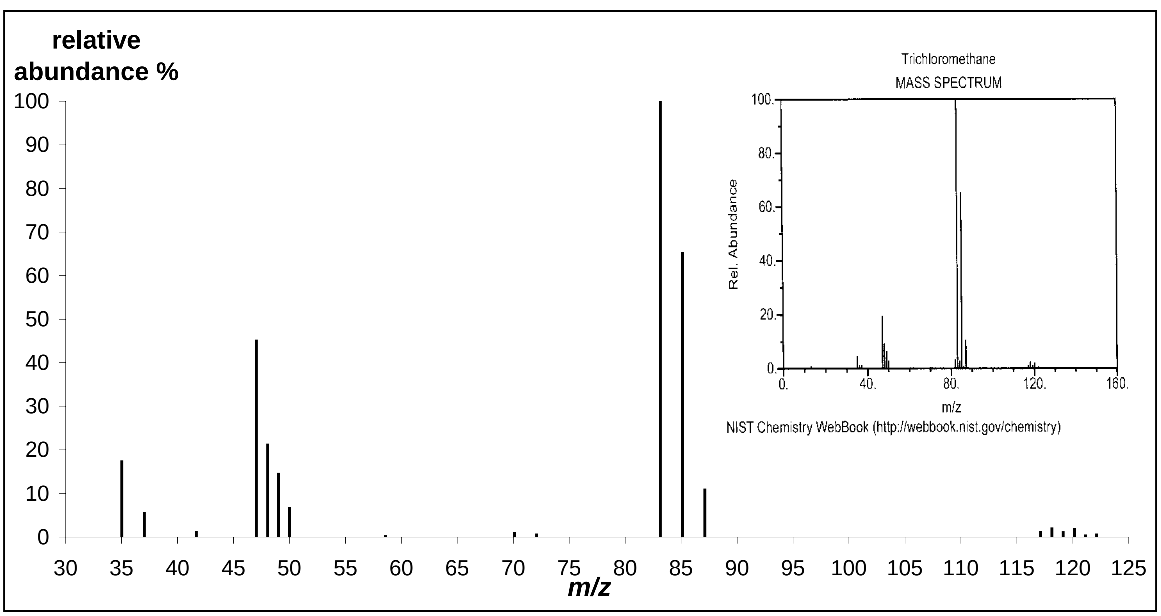


Figure 3.11: Chloroform Scan Bargraph spectrum. Inset: Chloroform mass spectrum reported by NIST.

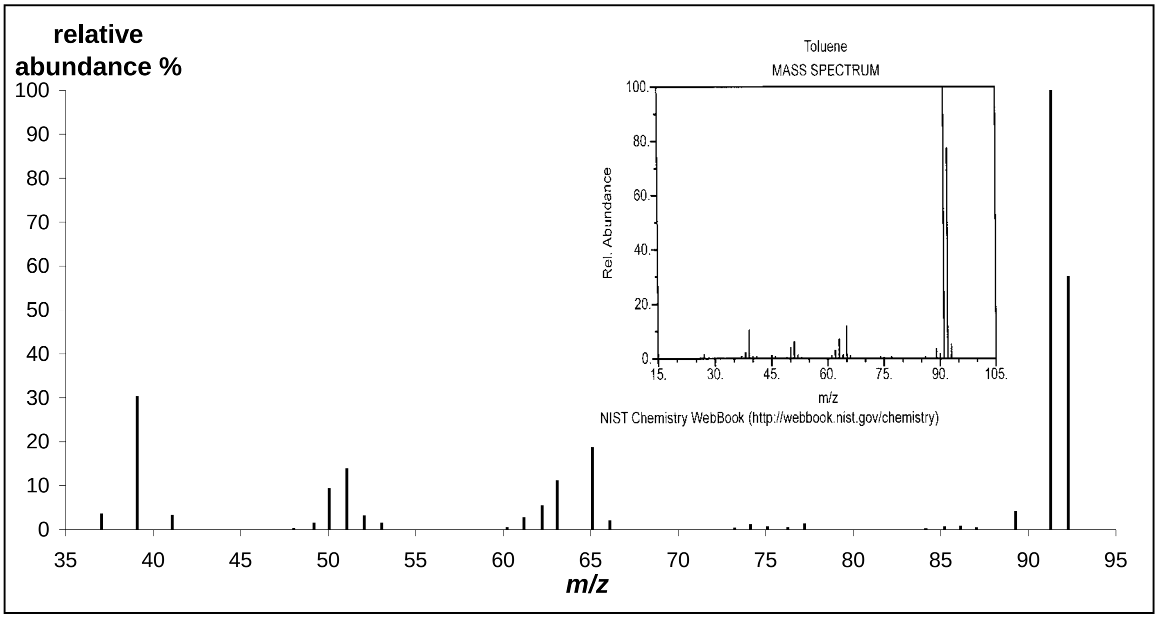


Figure 3.12: Toluene Scan Bargraph spectrum. Inset: Toluene mass spectrum reported by NIST.

Benzene and toluene peaks (*m/z*) and their relative abundances are found in Table 3.2 and 3.3 respectively. In general, both spectra show good agreement with the NIST spectra. Peaks at *m/z* 15, 25, 26, 27, 76 and 79 were not observed in the benzene spectrum, perhaps due to their low relative abundances. It is important to mention that the *m/z* 77 peak is observed in 25% of the cycles performed. As for the toluene spectrum, peaks at *m/z* 26, 27, 43, 46, 55, 57, 64, 83, 90, 93 and 94 are not observed. As for the benzene, their relative abundances are quite small.

NIST spectra are shown in Figures 3.10, 3.11, and 3.12 for comparison with the MS spectra obtained for neat organic compounds. The relative abundance of most peaks in this study is higher compared to those reported by NIST, Tables 3.2 and 3.3. This is likely due to the higher electron ionization energy used (90 eV). The most relative abundant peaks (*m/z* 78 for benzene and 91 for toluene) as well as those of the typical fragment ions are observed in both the benzene and toluene MID spectra. Therefore, *m/z* 78 for benzene and *m/z* 91 for toluene are used as the specific markers in the MIMS experiments.

Chloroform ions and their relative abundances are presented in Table 3.4. Compounds containing Cl exhibit peaks separated by 2 amu, corresponding to the isotopes ^{35}Cl and ^{37}Cl. (Lee 1998) This is observed with the highest peaks at *m/z* 83 ($CH^{35}Cl^{35}Cl^{+}$), 85 ($CH^{35}Cl^{37}Cl^{+}$) and 87 ($CH^{37}Cl^{37}Cl^{+}$) and those at *m/z* 118 ($CH^{35}Cl^{35}Cl\,^{35}Cl^{+}$), 120 ($CH^{35}Cl^{35}Cl\,^{37}Cl^{+}$) and 122 ($CH^{35}Cl^{37}Cl\,^{37}Cl^{+}$). The spectrum obtained is in good agreement with the NIST spectrum. The fragment ion at *m/z* 83, with a relative abundance of 100% was used to identify chloroform in the MIMS experiments.

m/z	**Relative abundance (NIST)**	**Relative abundance experimental**
15	1.2	N
25	0.7	N
26	3.4	N
27	2.6	N
28	2.1	O
36	0.6	O
37	4.2	7.9
38	5.6	10.1
39	11.1	29.2
40	0.7	O
48	0.4	0.4
49	3.9	3.4
50	20.8	27
51	22.1	30.5
52	18.8	34.1
53	0.7	1.2
61	1	0.7
62	1.1	0.8
63	4.9	3.7
73	2.4	1.8
74	6.2	5.0
75	2.2	1.8
76	5.8	N
77	28.3	20
78	100	100
79	6.5	N

Table 3.2: Benzene ion fragment by NIST and obtained in the lab (N: peak not observed, O: peak overlapping with air fragment ions).

m/z	**Relative abundance (NIST)**	**Relative abundance experimental**
26	0.5	N
27	1.7	N
28	0.2	O
37	1.0	3.3
38	2.4	O
39	10.7	30.0
40	1.1	O
41	1.1	3.0
43	0.1	N
44	0.1	O
45	1.4	O
46	0.9	N
49	0.6	1.3
50	4.1	9.2
51	6.4	13.6
52	1.5	2.9
53	0.7	1.3
55	0.1	N
57	0.1	N
60	0.1	0.3
61	1.4	2.5

m/z	**Relative abundance (NIST)**	**Relative abundance experimental**
62	3.2	5.2
63	7.4	10.9
64	1.5	N
65	12.1	18.4
66	1.4	1.8
73	0.1	0.1
74	0.9	0.9
75	0.6	0.4
76	0.3	0.2
77	0.9	1.0
83	0.1	N
85	0.4	0.4
86	0.8	0.6
87	0.4	0.2
89	3.9	3.9
90	2.1	N
91	100	100
92	77.6	57.4
93	5.4	N
94	0.1	N

Table 3.3: Toluene fragment ions (*m/z*) and their relative intensities by NIST (N: peak not observed, O: peak overlapping with air fragment ions)

m/z	**Relative abundance (NIST)**	**Relative abundance experimental**
12	0.3	O
13	0.9	N
35	4.6	17.2
36	1.4	O
37	1.4	5.4
38	0.4	O
41	0.3	1.1
42	0.2	O
45	0.1	O
47	19.6	45.0
48	9.3	21.1
49	6.6	14.5
50	3.0	6.5
58	0.1	0.8
70	0.5	0.8
72	0.3	0.5
82	3.3	N
83	100	100
84	0.3	N
85	65.3	65.0
86	0.9	N
87	10.6	10.8
88	0.2	N
117	1.2	1.1
118	2.5	1.9
119	1.2	1.0
120	2.1	1.7
121	0.4	0.3
122	0.7	0.5

Table 3.4: Chloroform fragment ions (m/z) and their relative intensities by NIST (N: peak not observed, O: peak overlapping with air fragment ions).

Figure 3.13 shows the response of a neat benzene-chloroform-toluene mixture as a function of time to the MS. Figure 3.13 reveals that the MS has the greatest sensitivity for benzene and the least for toluene. This MS-MID profile was acquired to compare with MIMS-MID profile of the aqueous mixture. The MS-MID profile will be discussed in Section 5.3.

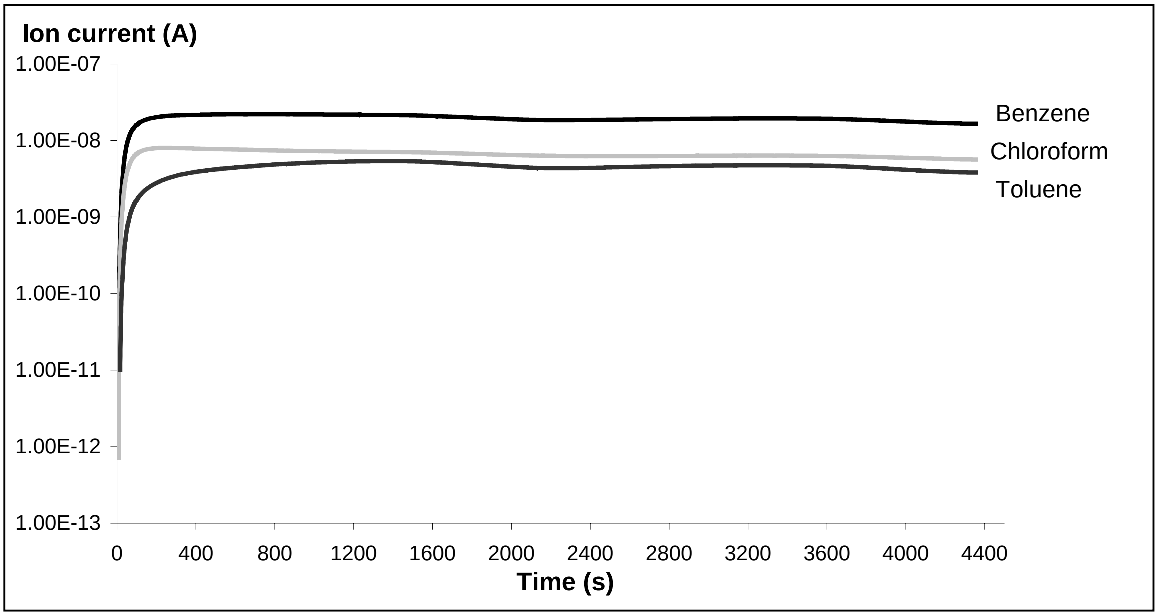


Figure 3.13: MS-MID profile for the headspace of a neat benzene-chloroform-toluene mixture as a function of time.

CHAPTER 4

MEMBRANE INTRODUCTION MASS SPECTROMETRY DEVELOPMENT

Before studying the parameters that affect membrane introduction mass spectrometry (MIMS), it was important to develop and establish the experimental conditions of the MIMS system. Therefore, mass spectra of benzene, toluene, and chloroform solutions were obtained under different conditions.

4.1 Apparatus System

Mass Spectrometer

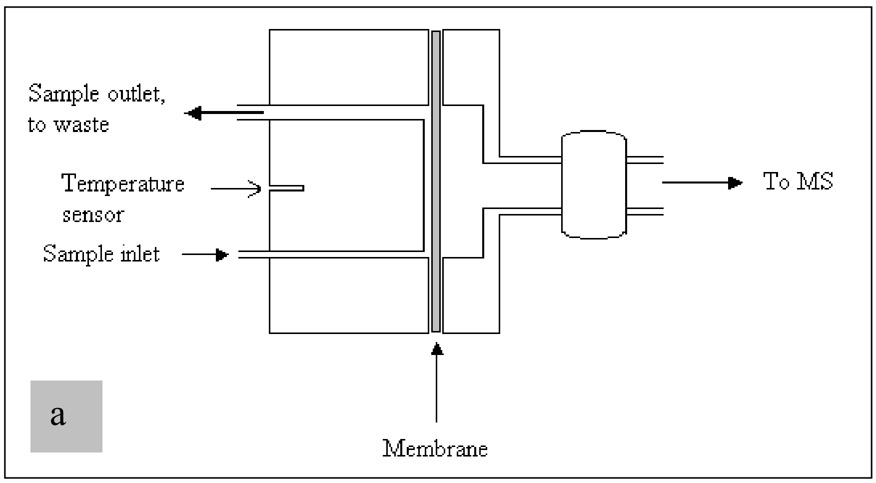
The mass spectrometer used in this study was an Omnistar GSD 300 described in Chapter 3 (section 3.2.1) using 90eV electron ionization (EI) and SEM detection at 1200 V, unless otherwise specified.

Membrane Apparatus

Schematics of the membrane apparatus are shown in Figure 4.1a and a picture of the actual membrane apparatus is shown in Figure 4.2. The membrane apparatus used for this thesis was based upon the design of A.R. Dongré and M.J. Hayward (Dongré and Hayward 1996) with some modifications. The membrane was positioned between two machined stainless steel blocks. A heat tape, controlled by a power controller

(Electrothermal), heated the entire apparatus. The temperature was maintained in the range of 90 °C- 98 °C, while the MS capillary was heated by the MS heating tube to 180 °C. The temperature was monitored by a multimeter (Fluke 16 multimeter). The heat tape surrounded the membrane apparatus, the Swagelock fittings, and the end of the MS capillary, which was not covered by the heating tube. Thus, the heat tape arrangement and the fact that the membrane apparatus was a 1 kg block of stainless steel ensured that the heating of the apparatus was uniform.

The portion of the apparatus that is exposed to the solution flow in the sample flow channel is shown in Figure 4.1b. The dimensions of the milled slot are intended to maximize the ratio of the membrane surface area exposed to the sample solution to the sample volume exposed to the membrane. In this way, the contact of the analyte to the membrane is maximized. Another significant feature of the experimental design is the cross-sectional area. As the solution flows into the region of the membrane, the cross-sectional area of the flow path increases so that the back pressure on the membrane is minimized. The outlet was located in the uppermost position to facilitate the passage of any gas bubbles through the interface. (Dongré and Hayward 1996) This design of membrane apparatus was selected because it permits the use of any sheet material as a membrane. Figures 4.2a and 4.2b show the actual membrane apparatus used for this thesis (4.2a) and its size (2.00 in. (5.08 cm) x 1.75 in. (4.44 cm) x 1.75 in., W x L x H) compared to a penny (4.2b) The membrane used for the experiments described in this chapter was a silicone sheeting (medical grade silicone rubber subdermal material for short term implantation, Advanced Bio-Technologies, Inc.). The thickness of this membrane was 0.010 in. (0.254 mm). The membranes were washed with nanopure deionized water (18.3 MΩ cm) and handled with powder-free nitrile gloves before placing them in the membrane apparatus. The washing was performed to remove any salts or particulates. (Dongré and Hayward 1996) The membrane apparatus was connected to the 1/16 in. (1.58 mm) stainless steel MS capillary via a 1/4 in. (6.35 mm) to 1/8 in. (3.18 mm) and a 1/8 in. to 1/16 in. reducing couplings, Figure 4.3.



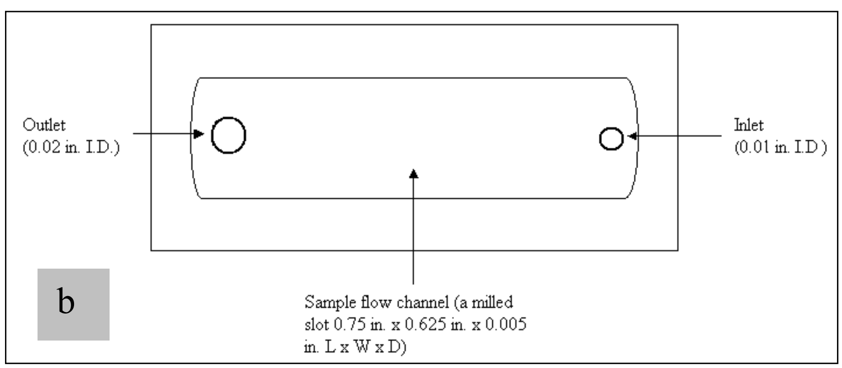


Figure 4.1: Schematic of the MIMS a: MIMS apparatus. b: Schematic of the sample flow channel. This region is exposed to the membrane (components not drawn to scale).

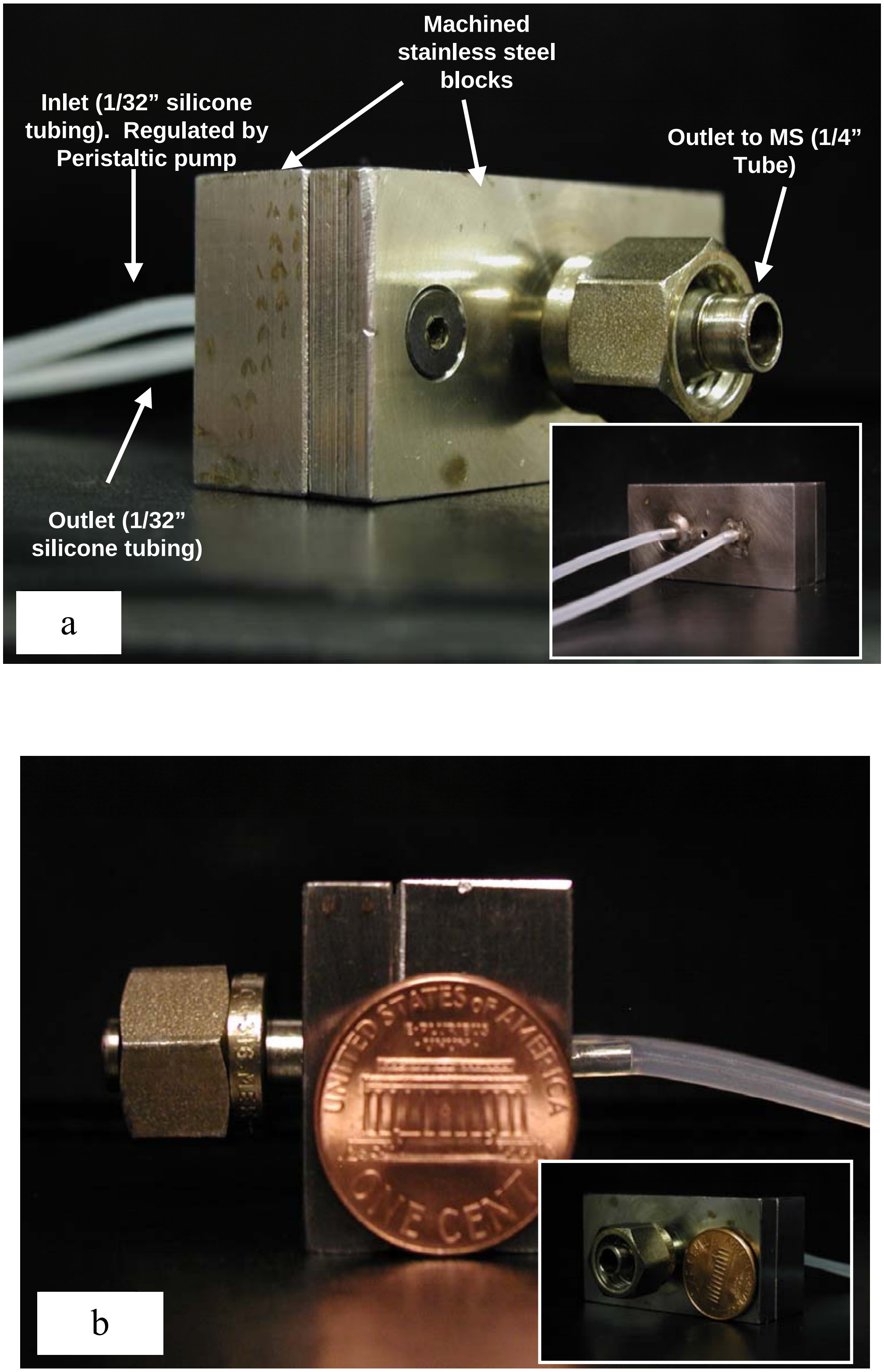


Figure 4.2: Photographs of the membrane apparatus. a: general view of the membrane apparatus. b: MIMS apparatus size compared to a penny.

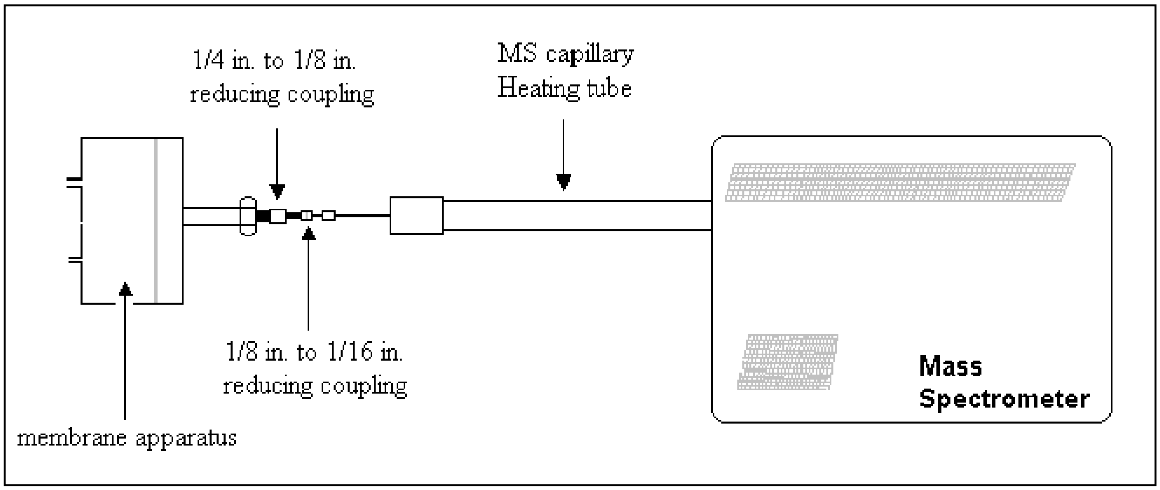


Figure 4.3: Detailed schematic of the membrane apparatus connected to the MS capillary (components not drawn to scale).

4.2 Sample Preparation

The chemicals used were 99.9+%, HPLC grade. Chloroform and toluene were obtained from Sigma-Aldrich Canada Ltd, while benzene was obtained from Sigma-Aldrich USA. Aqueous mixtures of the organic compounds were prepared with nanopure deionized water (18.3 MΩ cm). 67 µL of chloroform, 115 µL of toluene and 114 µL of benzene were diluted to 1 L using nanopure deionized water (18.3 MΩ cm) to produce a 100 ppm stock solution. The stock solution was kept at 4 °C. The following concentrations were used for the experiments described in this chapter: 50 ppb, 100 ppb, 200 ppb, 400 ppb, 500 ppb, 600 ppb, 700 ppb, 800 ppb, 900 ppb and 1 ppm to construct a calibration curve. Solutions were prepared in pyrex volumetric flasks previously cleaned using a 0.8 M solution of ammonium peroxydisulfate in concentrate sulfuric acid. The glassware was filled with this solution and left for twenty minutes, and rinsed eight times with nanopure deionized water (18.3 MΩ cm).

4.3 Experimental Procedures

Experimental solutions of different concentrations were prepared by further dilutions of the 100 ppm stock solution. All the aqueous mixtures were pumped continuously to the membrane apparatus at a rate of 0.5 mL/min using a variable-flow peristaltic pump (Pump II-low flow, Control Company) connected to the inlet of the membrane apparatus. The peristaltic pump was set up with 1/32 in. (0.79 mm) I.D. (Internal Diameter) silicone tubing for the inlet and outlet, while the tubing wrapping around the pump head was 1/16 in. (1.58 mm) I.D. The outlet 1/32 in. tubing went directly through the inlet of the membrane apparatus. The membrane apparatus outlet tubing was 1/32 in. silicone tubing going to a waste container; a schematic of this configuration appears in Figure 4.4. All the experiments were carried out at room temperature (22 ± 1 °C).

As a first test of the MIMS system, a benzene, chloroform and toluene mixture (1 ppm each) was analyzed. The first step before running each sample was to insure that the membrane was not contaminated with organic residuals. Therefore before pumping each sample through the membrane apparatus, a blank spectrum was acquired as follows: nanopure water (18.3 MΩ cm) was circulated continuously through the membrane apparatus while acquiring Scan Bargraph data. If there was no contamination, the sample could be analyzed. Otherwise nanopure water had to be circulated through the membrane apparatus until the Scan Bargraph spectrum showed no contamination (benzene, chloroform or toluene peaks). Ten minutes of water circulation usually was enough to obtain a clean spectrum after running mixture samples, however thirty minutes was used to insure that the membrane apparatus and the tubing were cleaned of contamination.

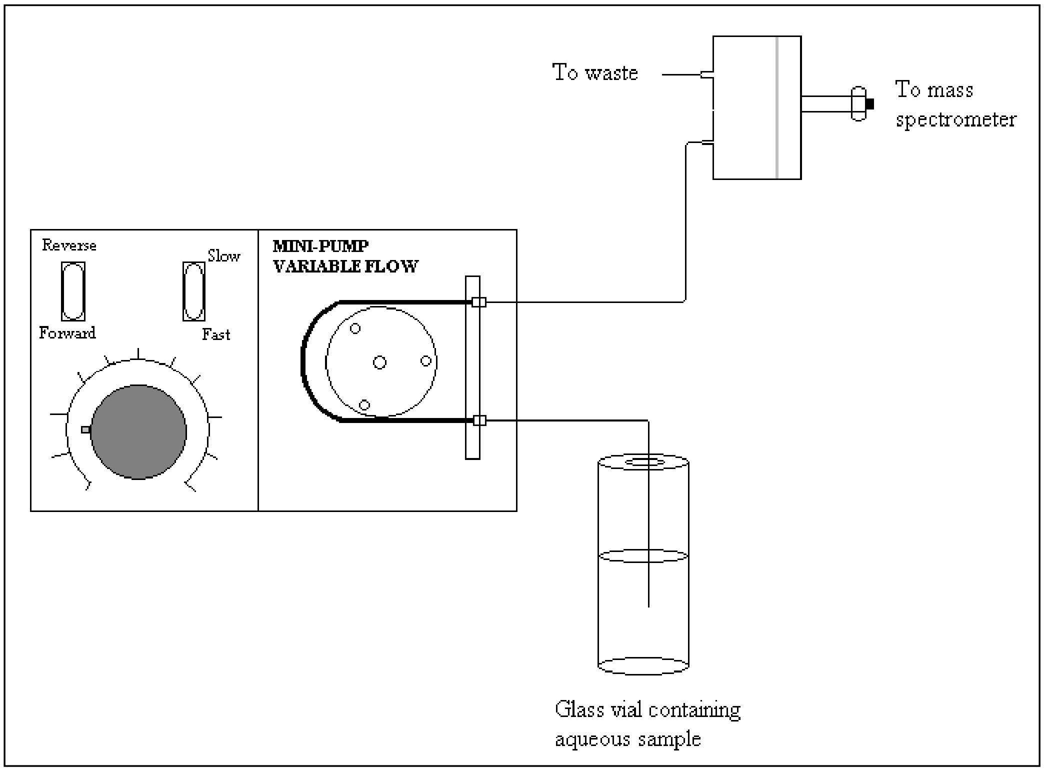


Figure 4.4: Schematic representation of the MIMS system (components not drawn to scale).

Qualitative identification of each compound was performed using Scan Bargraph mode. Mass spectra were acquired in the mass range 40-100 *m/z* at 1 scan/min. This experiment was performed with a 1 ppm aqueous mixture as follows: First, the blank spectrum was obtained. The aqueous flow was then interrupted, and air was pumped through the membrane apparatus to eliminate all water from the tubing and the membrane apparatus. A vial with the sample was then connected to the peristaltic pump. Since the tubing was transparent, it was easy to observe the sample flow. When the aqueous solution reached the membrane apparatus, data acquisition was started. This insured that the spectrum corresponded to the sample analyzed since the gas sample reaches the ion source in 0.5 s (see chapter 3, section 3.2.2).

As mentioned in the previous chapter the SEM detector was set at 1200 V, Figures 3.6 and 3.7 show that the intensity of the highest peak (N_2^+) is less than 1 X 10^{-7} A. To increase the ion current signal a test was performed using different SEM voltages. This was done to detect possible contamination problem (explained in the next section, Results). The SEM voltage test was carried out by analyzing air in the Scan Analog mode. The voltage was increased until the larger ion current signal (N_2^+) reached a maximum of 1 X 10^{-6} A. Exceeding this limit could accelerate the wearing of the detector. Thus, all the following experiments were conducted with a higher SEM voltage of 2400 V.

Since the SEM detector started being used with a new voltage (2400 V), the qualitative identification of the organic compounds in the mixture solution was conducted again. Mass spectra were acquired under the same conditions using Scan Analog mode. Eleven cycles (scans) were obtained. Each solution was circulated through the membrane apparatus continuously while its scans were obtained.

The detection limit, quantification limit, and linearity of the system were determined by creating a calibration curve with the following concentrations of each analyte in the mixture: 50 ppb, 100 ppb, 200 ppb, 400 ppb, 500 ppb, 600 ppb, 700 ppb, 800 ppb, 900 ppb, and 1 ppm. Lower concentrations were tested first, and then concentrations were stepped up to the higher concentrations. The calibration curve was determined using the MID mode to obtain quantitative data on the individual compounds. The mixtures were monitored on-line for 40 minutes resulting in MIMS-MID profiles.

The ions selected to follow were at *m/z* 78 (benzene), 83 (chloroform) and 91 (toluene). For these experiments, in order to obtain a well-defined initial state, the membrane apparatus was flushed with nanopure water for 30 min before each measurement. Three replicates were performed for each concentration.

Quantitative data were obtained by measuring the intensity of the ions characteristic of the single compounds. The definition of an intensity response for each measurement was very difficult since the response is not a simple exponent transient reaching a maximum at a specific time. Therefore, we arbitrarily define the intensity of each concentration as the mean value of all the intensities measured during the 40 min.

4.4 Results and discussion

Identification tests are intended to insure the identity of an analyte in a sample. Since the MS was previously demonstrated to be capable of identifying the neat analytes of interest, it was important to test the capabilities of the membrane apparatus to separate these analytes from the matrix used (nanopure water). This qualitative identification of each compound was achieved using Scan Bargraph mode and a SEM voltage of 1200 V, Figure 4.5. It is observed that the MS detected the three organic compounds; therefore the membrane apparatus was capable of separating them from the water. The spectrum presented is the result of 4 scans performed continuously. The spectrum shows all the fragment ions, without reference to frequency of ocurrence. The frequency in percentage (%) at which peaks are measured in the selected number of cycles is shown in Table 4.1, where 100 % means that the peak was found in every cycle, 50 % means that the peak was found only in half of the cycles.

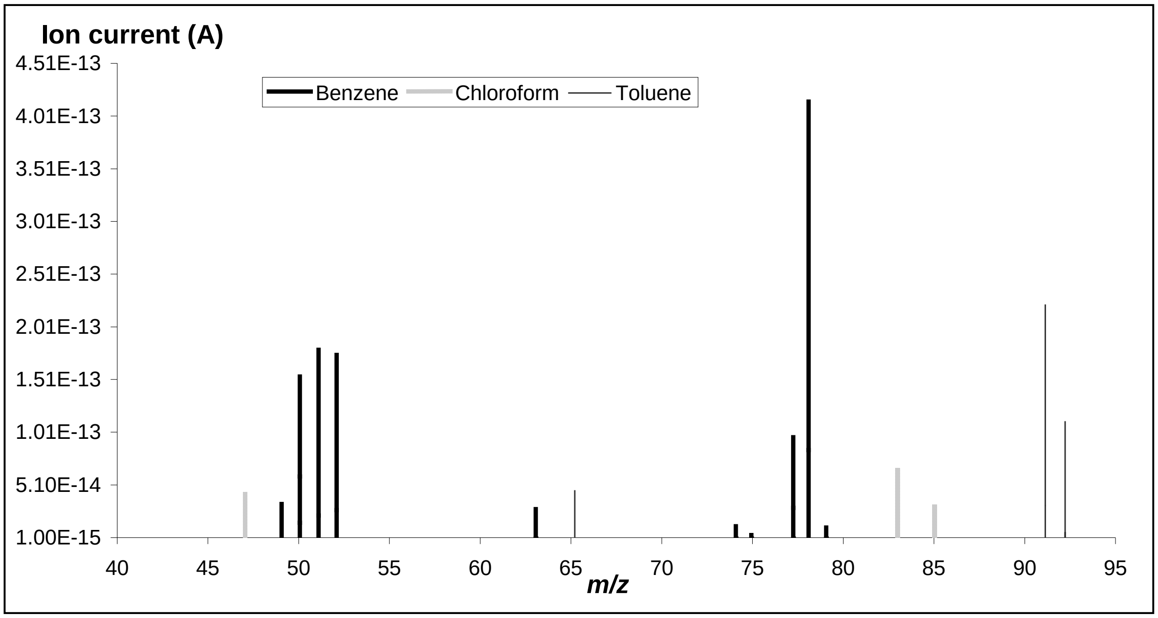


Figure 4.5: Mass spectrum of a 1 ppm aqueous mixture of each compound obtained using SEM detector 1200 V.

m/z	Frequency %	Organic compound
47	25	Chloroform
49	25	Benzene
50	75	Benzene
51	75	Benzene
52	75	Benzene
63	25	Benzene
65	25	Toluene
74	25	Benzene
75	25	Benzene
77	50	Benzene
78	100	Benzene
79	25	Benzene
83	50	Chloroform
85	25	Chloroform
91	100	Toluene
92	50	Toluene

Table 4.1: Frequency of occurrence at which peaks were measured in the 1 ppm aqueous mixture

Comparing the MIMS spectrum obtained (Figure 4.5) with the MS spectra in which each of the chemicals was individually analyzed using the headspace gas of the neat compounds (Figures 3.10 – 3.12), two differences were encountered: (1) fewer fragment ions were detected by MIMS for each analyte of the mixture, and (2) the frequency of some of the ions present in the MIMS spectrum is lower compared to the respective MS spectra. In the MIMS spectrum (Figure 4.5) ten ion fragments were identified for benzene out of the fourteen previously measured using the headspace gas of neat benzene (Figure 3.10) in the range of *m/z* 40-90. As for toluene, three peaks are observed in the MIMS spectrum (Figure 4.5), while in the MS spectrum (Figure 3.11), 23 peaks are observed (Table 3.3). As for chloroform, three ion fragments are shown in the

MIMS spectrum (Figure 4.5), whereas 17 peaks are observed in the MS spectrum (Figure 3.12, Table 3.4). Regarding the frequency at which each peak was measured, the peaks at *m/z* 78 (benzene ion) and 91 (toluene ion) were the only ones that were found in all the scans performed, while the peaks at *m/z* 50, 51, and 52, all of them benzene fragment ions, had a frequency of 75 %. Peaks at *m/z* 77 (benzene fragment ion), 83 (chloroform fragment ion), and 92 (toluene fragment ion) appeared in 50 % of the scans. Thus, the MIMS spectrum of the solution mixture showed in 100 % of the scans the most relative abundant fragment ions of benzene and toluene, while the most relative abundant ion of chloroform appeared just in 50 % of the scans. One more conclusion can be reached from this experiment; most of the peaks obtained in the aqueous mixture spectrum are benzene fragment ions, whereas just three peaks correspond to toluene and another three to chloroform. These differences may be due to the different ionization efficiency that each compound has in the MS.

Figure 4.6 shows an air spectrum obtained using different SEM detector voltages: 1200, 2100, and 2400 V. This voltage test was conducted to detect a possible contamination problem. After running benzene solutions, the instrument was baked out overnight (MS capillary at 180 °C) to eliminate any organic compounds. Upon baking the MS out, a blank (nanopure water) MIMS-MID profile was acquired measuring the following *m/z* 14, 16, 18, 78 and 85, Figure 4.7. The organic compound-signals decreased to $1X10^{12}$ A, but never decreased to zero, suggesting that organic compounds were trapped in the MS. When the Scan Analog mode was used to analyze nanopure water, this “contamination” was also observed, Figure 4.8. These spectra were sent to S. Foster (Pfeiifer vacuum, Technical support), who suggested increasing the voltage of the detector and perform an offset calibration everyday before conducting any experiment. These changes were carried out and the "new" SEM detector voltage was 2400 V. With this new voltage, the signals were increased by two orders of magnitude; for instance, the N_2^+ (*m/z* 28) intensity was 1 X 10^{-8} A at 1200 V and 1X10^{-6} A at 2400 V.

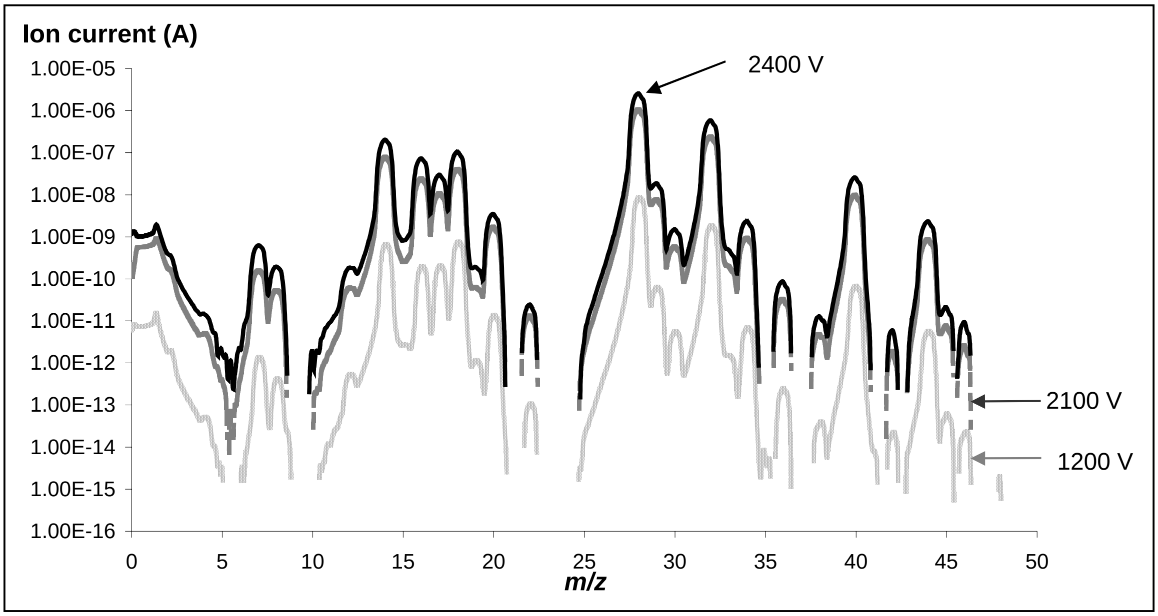


Figure 4.6: SEM voltage test for an air spectrum.

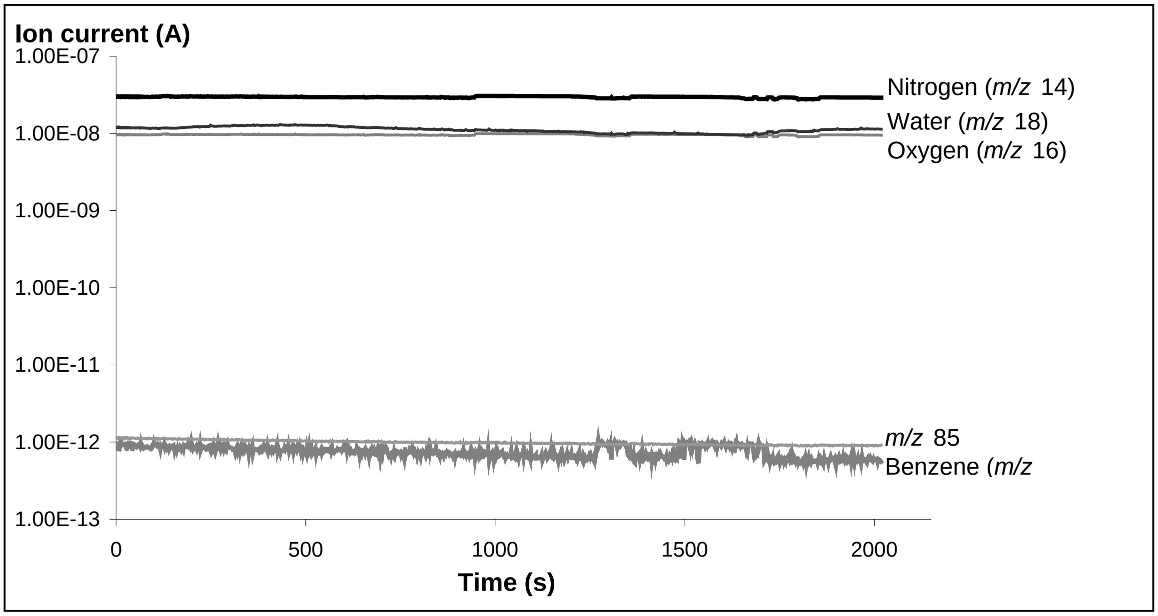


Figure 4.7: MS-MID profile during a baking scan.

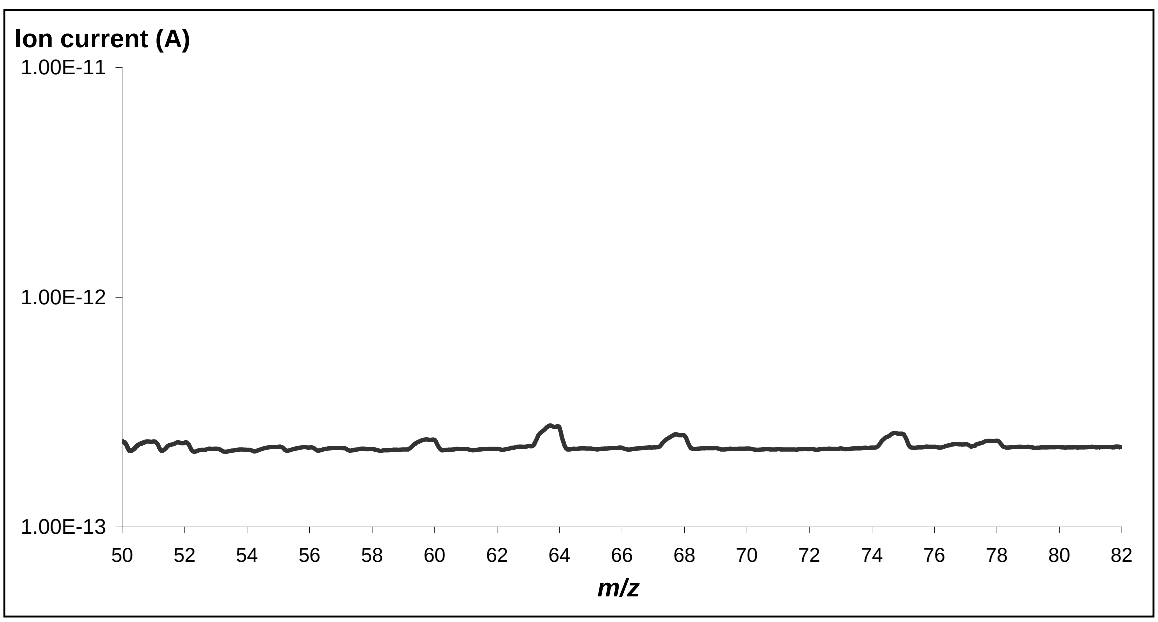


Figure 4.8: Nanopure water mass spectrum (Scan Analog) showing organic contamination.

Qualitative identification of the organic compounds in the solution was again performed using the SEM detector at 2400 V. Figure 4.9 shows the Scan Analog spectrum of a 1 ppm mixture solution. To obtain the spectrum in a shorter period of time, 3 channels (*m/z* ranges) were used: 75-79, 82-85, and 90-93. 11 scans were acquired from which scans 2, 3, 4, 5, and 9 appear in Figure 4.9. For this experiment, various scans were acquired to observe signal changes as a function of time. As time elapsed the peak intensity increased. At the SEM voltage of 2400 V benzene, chloroform and toluene peaks were identified. Therefore, MID mode was used to acquire data (signal intensity as a function of time), Figure 4.10.

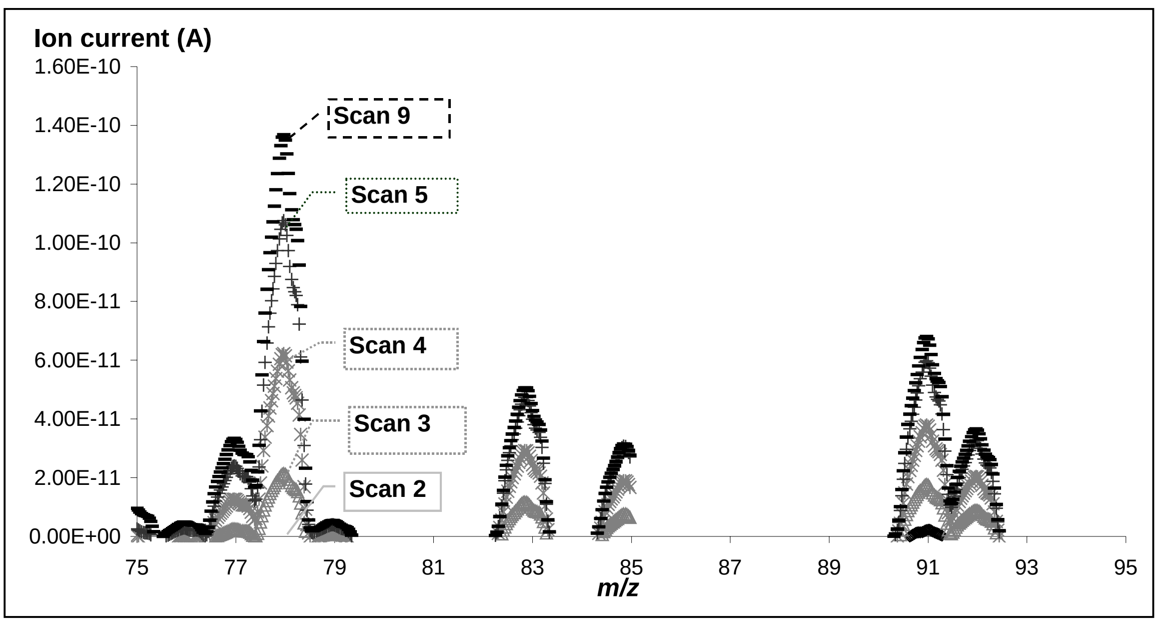


Figure 4.9: VOC mixture (1 ppm) spectrum showing scans 2, 3, 4, 5 and 9. The signal intensities increase as the number of scans increase (spectrum acquired with an SEM detector of 2400 V).

To determine the capabilities of the MIMS system, a calibration curve was constructed by analyzing the following concentrations: 50 ppb, 100 ppb, 200 ppb, 400 ppb, 500 ppb, 600 ppb, 700 ppb, 800 ppb, 900 ppb and 1 ppm. MID mode was used to acquire the signal intensities for each solution. As explained in the experimental section, all the aqueous mixtures were pumped continuously to the membrane apparatus for 40 minutes to acquire a MIMS-MID profile. Figure 4.10 shows the resulting MIMS-MID profile of a 500 ppb mixture. The signal intensity increased rapidly, however it did not level off as it appears in Figure 4.10. The measurements fluctuated in a small range of intensities making very difficult to define a single intensity for each solution at any time. Therefore, an average of all the intensity measurements taken during the 40 min was used as the signal intensity for each solution. This behavior of the response for each compound will be discussed in chapter 5.

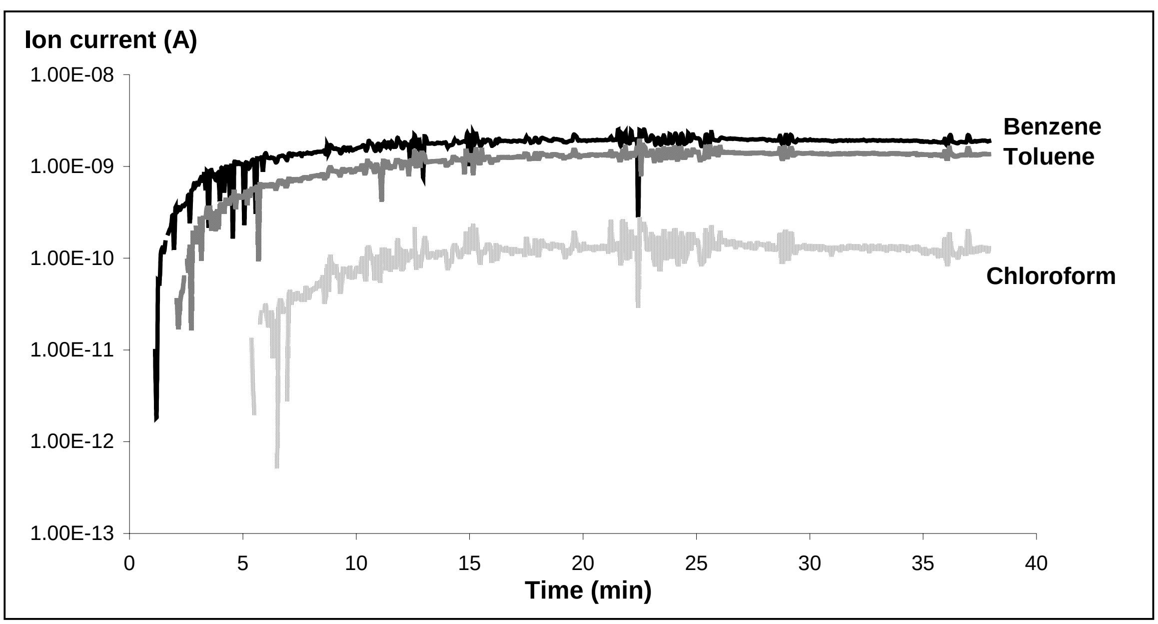


Figure 4.10: MIMS-MID profile for a 500 ppb mixture.

Table 4.2 shows the average signal intensity for each organic compound. Benzene, toluene and chloroform were not detected at 50 ppb (0.05 ppm) and 100 ppb (0.1 ppm). Chloroform was not detected at 200 ppb (0.2 ppm) and 400 ppb (0.4 ppm). For the 100 ppb (0.1 ppm) mixture, benzene was detected for 5 min 30 min after initializing measurement in only one of the three replicates, Figure 4.11. Figure 4.11 reveals the very poor detection of benzene in the 50 ppb mixture. It also shows that the signal intensities fluctuated over a wide range (from 1×10^{-12} A to 1×10^{-10} A). Poor detection was also observed for chloroform for mixtures concentrated at 500 ppb and 600 ppb, and therefore their signal intensities are not reported, nor were they used to construct the calibration curve.

Concentration (ppm)	**Benzene**	**Ion current (A)** **Chloroform**	**Toluene**
0.05	ND	ND	ND
0.1	ND	ND	ND
0.2	1.88×10^{-10}	ND	3.25×10^{-11}
0.4	2.38×10^{-10}	ND	6.33×10^{-11}
0.5	6.27×10^{-10}	D	3.53×10^{-10}
0.6	1.22×10^{-9}	D	7.72×10^{-10}
0.7	1.33×10^{-9}	6.14×10^{-11}	8.75×10^{-10}
0.8	1.38×10^{-9}	9.92×10^{-11}	8.98×10^{-10}
0.9	2.29×10^{-9}	2.64×10^{-10}	1.52×10^{-9}
1	2.83×10^{-9}	3.72×10^{-10}	1.92×10^{-9}

Table 4.2: Ion current obtained to construct a calibration curve of mixture solutions. The ion currents are the mean of three replicates performed. ND indicates not detected, D indicates (poorly) detected and therefore the intensity is not reported.

Benzene and toluene were detected at 200 and 400 ppb, however, the signal intensities of both compounds at those concentrations are slightly different. The calibration curves generated by these solutions appear in Figure 4.12. These curves show an acceptable linearity: R^2 93.94 % for benzene, R^2 94.369 % for toluene and R^2 95.36 % for chloroform

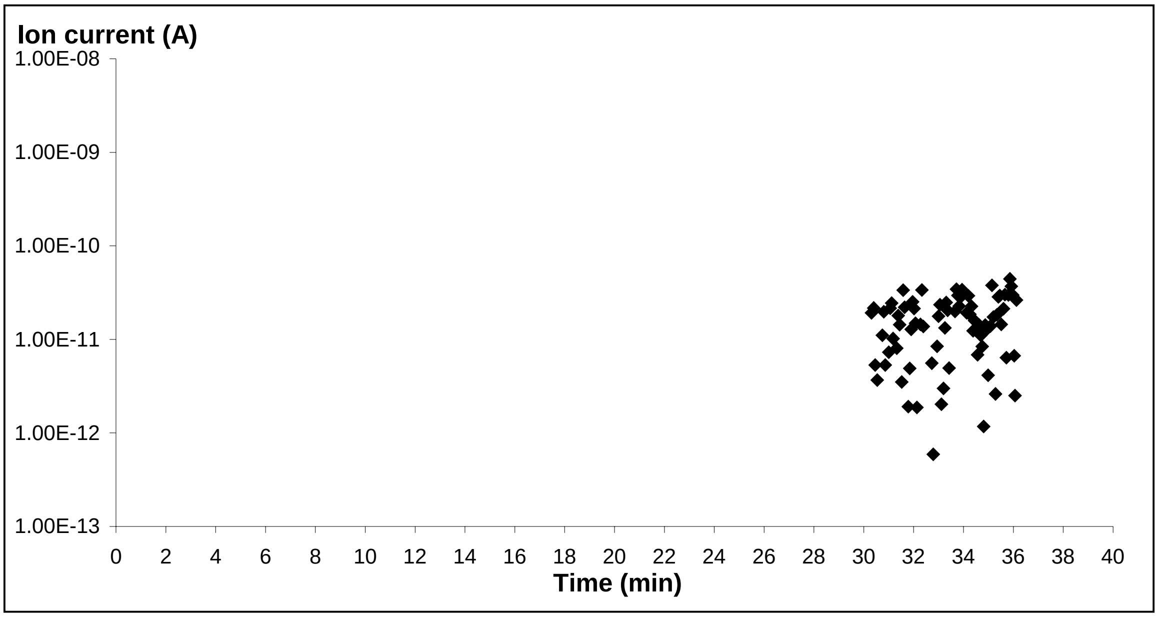


Figure 4.11: Benzene data points for a 50 ppb benzene-chloroform-toluene mixture. Benzene was the only compound detected for 5 min 30 min after initializing measurement in only one of the three replicates.

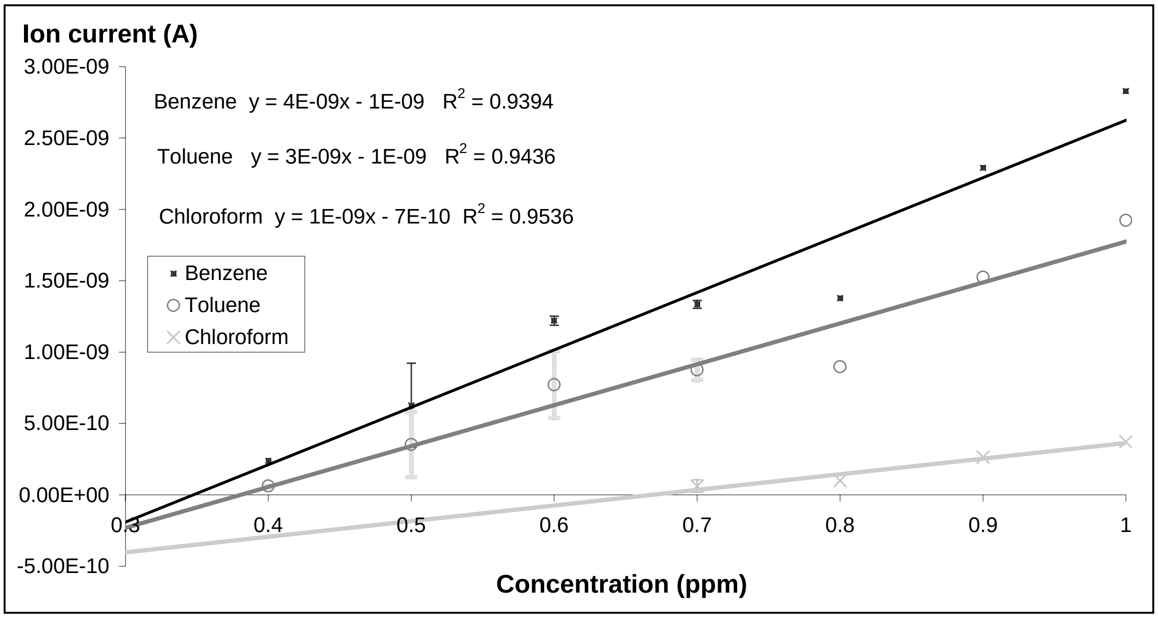


Figure 4.12: Calibration curves for benzene, toluene and chloroform obtained in the range of 0.2 ppm – 1 ppm.

Figure 4.12 shows that the linearity of the system is better above concentrations of 500 ppb for benzene and toluene, while the chloroform curve shows improved linearity above 700 ppb. The calibration curves reveal that benzene and toluene cannot be detected below concentrations of *ca.* 350 ppb and 370 ppb, respectively. As for chloroform, its trendline indicates that it can only be detected at concentrations higher than 650 ppb.

Sensitivity is defined as the ability of an instrument or a method to discriminate between small differences in analyte concentration. (Skoog *et al* 1998) Thus, under the conditions tested, MIMS showed a sensitivity of 0.1 ppm (in the 600 ppb to 1 ppm range, Figure 4.12). A generally accepted qualitative definition of detection limit is the minimum concentration of analyte that can be detected at a known confidence level. (Skoog *et al* 1998) Detection limit is measured at the limit of a reasonable signal-to-noise ratio of 3 (S/N =3), where the signal is defined as the mean of the measurements, and the noise is defined as the standards deviation of the measurements of the signal. A S/N 3 corresponds to the detection limit, while a S/N 10 defines the quantification limit. Since calibration curves showed reasonable linearity above 0.6 ppm, S/N was calculated using measurements over the 0.6 – 1.0 ppm range. Solutions concentrated at 0.6, 0.7, and 0.8 ppm showed a S/N between 3 and 10 for benzene, toluene and chloroform. Solutions concentrated at 0.9 ppm showed similar S/N ratios for toluene and chloroform, while the 1 ppm-solution had a S/N ratio of approximately 7 for chloroform. Thus, according to these results, chloroform could not be quantified in the range of 0.5-1 ppm, while the quantification limit for benzene would be 0.9 ppm, and 1 ppm for toluene.

Qualitative identification of benzene, chloroform, and toluene in aqueous mixtures was achieved with the constructed MIMS system. An SEM detector voltage of 2400 V resulted in higher signal intensities and therefore was used in subsequent experiments. MIMS-MID profiles were acquired to construct a calibration curve. The calibration curve shows that benzene, toluene, and chloroform can be detected at concentrations above 350 ppb (0.35 ppm), 400 ppb (0.4 ppm) and 700 ppb (0.7 ppm), respectively.

CHAPTER 5

ANALYSIS OF MEMBRANE, TEMPERATURE AND SAMPLE FLOW RATE EFFECTS

Many issues had to be dealt with before the MIMS experiments could be performed. Some related to technical problems with the MS (see Appendix B for detailed description of MS troubleshooting), and others related to the establishment of appropriate working conditions. The determined experiment conditions included setting the SEM detector voltage, working in data acquisition mode, signal measurement, and temperature control, among others. This chapter describes the effects of three parameters on the MIMS: membrane thickness, temperature, and flow rate.

The effects of temperature and flow rate on MIMS were studied using an SEM voltage of 3000 V, MID acquisition mode for 60 minutes, and determining the intensity signal as the average of the intensities. While the effect of membrane thickness was determined using Scan Analog mode, the other experiment conditions remained the same. To describe and compare the effects of these parameters, the signal intensities and the response times were measured. Each parameter was studied individually using a mixture containing 1 ppm each of benzene, chloroform and toluene. The effect of membrane thickness on response time was examined using 0.007 in. (0.178 mm), and 0.010 in. (0.254 mm) thick membranes. The effect of solution flow rate was investigated at

0.5 mL/min, and 5 mL/min. Response times were measured at five temperatures, 24 °C, 40, 55, 70, and 90 ± 1°C.

5.1 MIMS System

Mass Spectrometer

All experiments were conducted at 90 eV (EI) with the Quadrupole MS Omnistar GSD 300 described previously. The SEM detector was set at 3000 V.

Section 2.2.2 details how the MS capillary is connected to the MS via a valve block. When the valve is opened the gas drawn into the MS has to pass through a platinum orifice (I.D. 0.02 mm). Since the internal diameter of the orifice determines the rate of entrance of the gas to the ion source, the 0.02 mm orifice was replaced with a 0.1 mm orifice in order to improve the detection limits of the system. The 0.1 mm orifice was used to perform the temperature and flow rate experiments, whereas the membrane thickness effects were investigated with the 0.02 mm orifice. The gas inlet (valve block) and the orifice appear in Figure B.1.

Membrane Apparatus

Characteristics of the membrane apparatus are reported in section 4.1. For these experiments, the temperature of the membrane apparatus was set to the desired temperature (± 1 °C) by using a temperature controller (series 96, Watlow). This improvement ensured consistent results. The temperature was maintained at the set temperature ± 1 °C during the 60 minutes of each experiment and during the cleaning of the membrane. In addition, the MIMS system was reconfigured in order to improve the response times. In this configuration the membrane apparatus was connected directly to the valve block. For this, the MS capillary was removed from the valve block and the membrane apparatus was connected to the valve block using the reducing couples mentioned in Section 3.2.2 and a 1-in long capillary to ensure a connection similar to the MS capillary. With this improvement, response times were expected to be reduced by 0.5 s since this is the time required for the gas to reach the ion source via the original MS capillary.

Aside from the changes described above, the remainder of the system (peristaltic pump, membrane sheeting type and MS parameters) was left unchanged. The effects of the system-improvements will be discussed later.

5.2 Experimental Procedures

Benzene-chloroform-toluene aqueous mixtures of 1 ppm each were prepared to perform all the experiments described in this chapter. Sample preparation and introduction of aqueous mixtures to the membrane apparatus are explained in section 4.2 and 4.3, respectively.

Effects of membrane thickness

Experiments were conducted using 0.007 in. (0.178 mm) and 0.010 in. (0.254 mm) thick membranes (silicone sheeting with constant mesh size) at a flow rate of 0.5 mL/min and at temperatures of 90-98 °C. Mass spectra were acquired using Scan Analog Mode in the mass range 76-95 *m/z* and an acquisition rate of 1 scan/1.5 min. Eleven and twenty scans were acquired for the 0.010 in. and the 0.007 in. membranes, respectively and then graphed according to the *m/z* of interest (78, 83, and 91 *m/z*) as a function of time. 100 ppb and 10 ppb solutions were tested using the 0.007 in. (0.178 mm) membrane since 200 ppb was previously shown to be the detection limit using a 0.010 in. (0.254 mm) thick membrane.

Effects of temperature and flow rate

As in the membrane thickness experiments, 1-ppm benzene-chloroform-toluene mixtures were tested. Five temperatures were investigated: 24, 40, 55, 70, and 90 °C. Mixture samples were circulated continuously to the membrane apparatus for 60 minutes at the temperatures mentioned above at two different flow rates: 0.5 mL/min (Pump II-low flow, Control Company) and 5mL/min (Pump III-Medium Flow, Control Company). The long time was selected in order to observe an equilibrium response. Although 60 minutes is greater than the time required to achieve equilibrium, it allowed enough data points to be sampled to calculate a mean signal with a small standard deviation. Sample sizes of 30 mL and 300 mL were used for the 0.5 mL/min and 5.0 mL/min flow rates, respectively. Regardless of the flow rate, the 40 mL-septa vials used to hold the samples were refilled of sample during the experiment to avoid volatilization of the organic compounds. MIMS profiles were acquired using Multiple Ion Detector Mode (MIMS-MID). The selected ions were at m/z 78 (benzene), 83 (chloroform), and 91 (toluene). As in the previous MIMS experiments, blank spectra were acquired before analyzing each sample to insure the membrane and the system had no organic residuals from previous samples. Three replicates were performed for each variable.

Measurement of response

Analytical responses were obtained by averaging all the acquired data points, as explained in Section 4.3. The response time has been defined as the time required to reach 90 % of the steady state signal, t_{90}, following a step change in sample concentration at t_{10}. (Dawson 1976; Lauritsen 1990; LaPack *et al* 1996) For comparison of the investigated parameters that affect MIMS, two response times are defined in this thesis: (1) lag-time is the time interval between exposure of the sample to the membrane apparatus and the onset of the first positive data point measured, and (2) the time interval between 10 and 90 % of the analytical response, t_{90-10}. For this, 100 % response was defined as the mean value of all the intensities measured during the 60 minutes of each experiment.

5.3 Results and Discussion

The membrane thickness experiments were performed first. Mass scan ranges of 76-95 *m/z* were acquired for the benzene-chloroform-toluene mixture. Individual ion current intensities were extracted for *m/z* 78 (benzene), 83 (chloroform), and 91 (toluene) and plots of intensity as a function of time for each compound appear in Figures 5.1 (benzene), 5.2 (chloroform) and 5.3 (toluene).

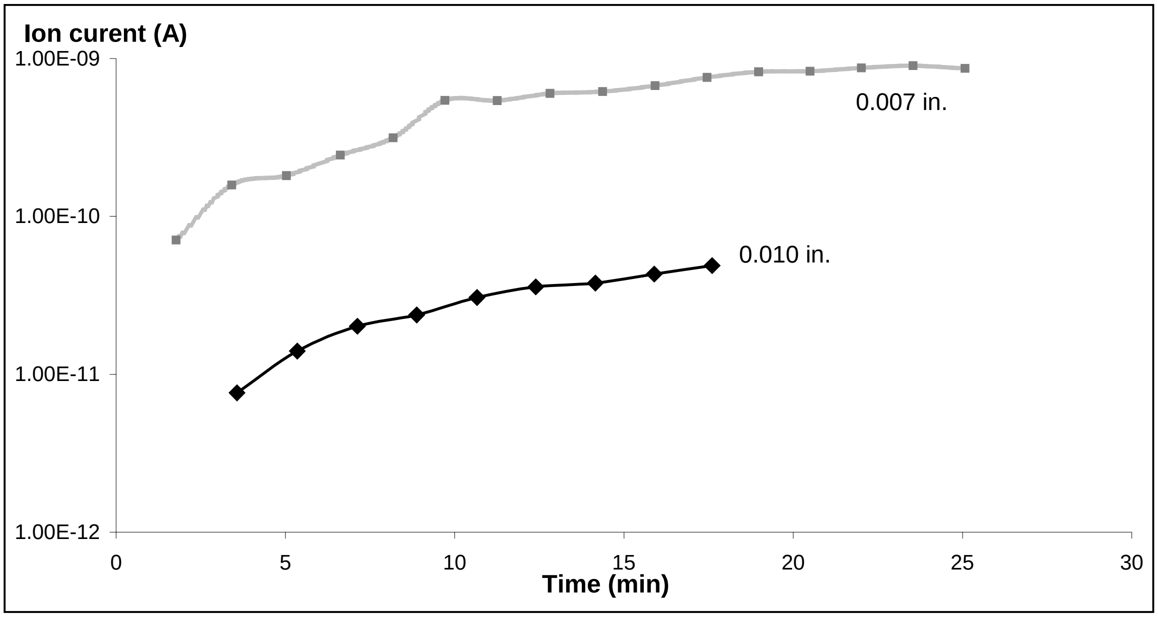


Figure 5.1: Response for benzene (based on Scan Bargraph) to membrane thicknesses of 0.007 in. (0.178 mm) and 0.010 in. (0.254 mm) as a function of time.

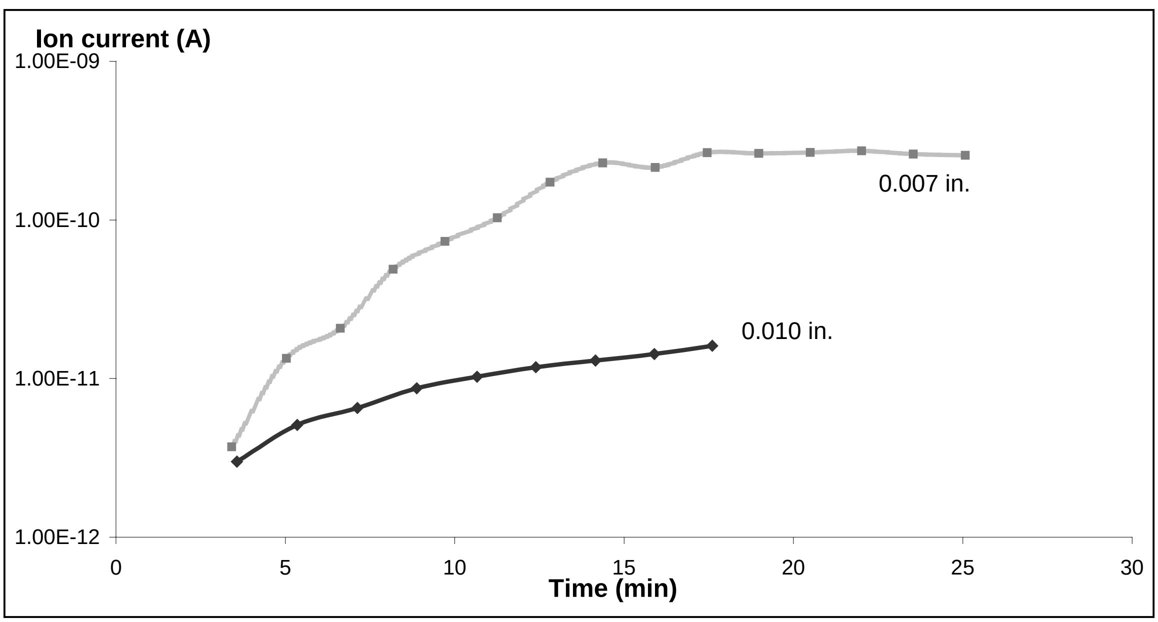


Figure 5.2: Response for chloroform (based on Scan Bargraph) to membrane thickness as a function of time.

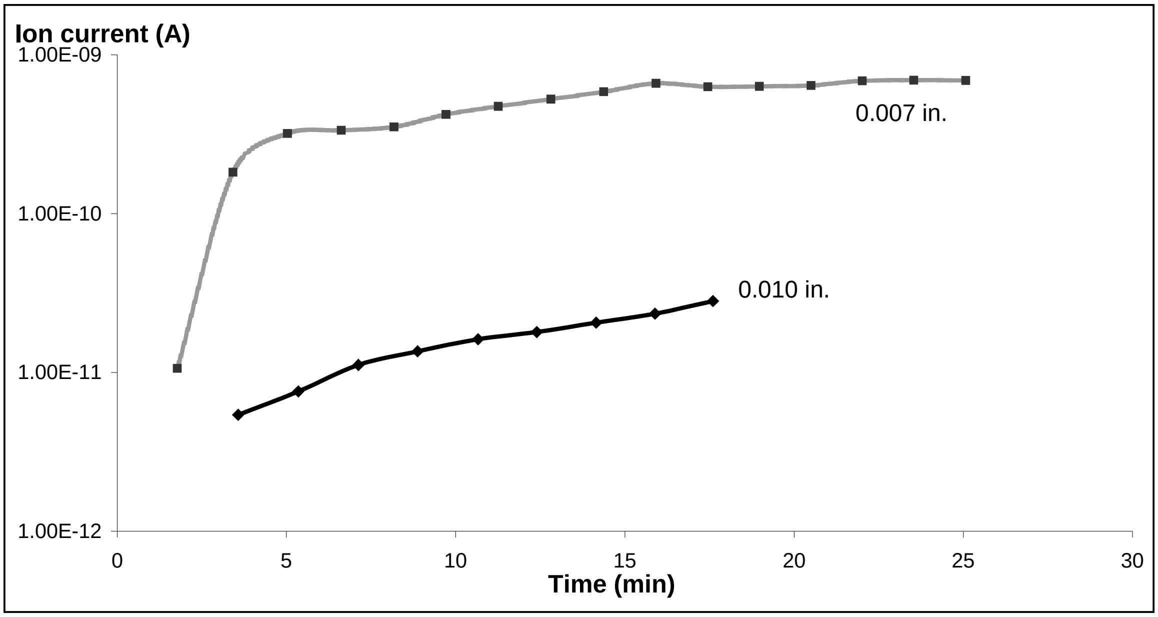


Figure 5.3: Response for toluene (based on Scan Bargraph) to membrane thickness as a function of time.

Clearly, the observed trend in Figures 5.1-5.3 is that signal intensity increases with decreasing membrane thickness. For benzene and toluene the signal intensities obtained with the thinner membrane were one order of magnitude higher than with the 0.010 in. membrane during the first 18 minutes of the run. The chloroform signal intensity obtained with the 0.007 in. (0.178 mm) membrane during the first seven minutes was only a half order of magnitude higher than with the 0.010 in. (0.254 mm) membrane. After the first seven minutes the signal intensity with the 0.007 in. membrane was ten times greater than that with the 0.010 in. membrane. Although, the measurement times were *ca*. 25 and 20 minutes for the 0.007 in. and 0.010 in. membranes, it was observed that the intensities of the three VOCs tended to level off by the end of the run when the 0.007 in. membrane was used as interface. The responses using the 0.010 in. membrane continued to rise during the 20 minutes of the experiment and did not reach a maximum. Since these spectra were acquired by scanning a 76–90 *m/z* mass range, response times were not determined. Nevertheless, the time at which the first data points appeared are used for comparison, Table 5.1.

Membrane thickness (in.)	**Lag-time (s)**		
	Benzene	**Toluene**	**Chloroform**
0.007	106.43	106.43	205.05
0.010	214.29	214.29	214.29

Table 5.1: Response time (lag-time, based on Scan Bargraph) as a function of membrane thickness.

The observed trend for the initial appearance is that a decrease in membrane thickness resulted in an earlier appearance time for benzene, toluene and chloroform. Table 5.1 shows that the lag-time for benzene and toluene is 106.43 seconds with the 0.007 in. (0.178 mm) thick membrane, while with the 0.010 in. (0.254 mm) thick membrane it was 214.29 seconds. In other words, the observed lag-times for benzene and toluene with the 0.007 in. thick membrane were half the lag-times with the 0.010 in. thick membrane. The observed lag-time for chloroform with the 0.010 in. thick membrane was 214.29 seconds, while with the 0.007 in. thick membrane the observed lag-time decreased only to 205.05 seconds. One notable difference is that the toluene response rose much more rapidly than that of benzene or chloroform with the 0.007 in. membrane. The toluene response tended to level off after 15 minutes while responses of chloroform and benzene did so after 20 minutes, Figure 5.4. This behavior was not observed in the 0.010

in. membrane experiments, Figure 5.5. In these the benzene response was greatest and chloroform again had the lowest signal intensity.

The permeation process is described by Fick's Equation of diffusion (see Equation 2.1 in Chapter 2). Equations 2.1 and 2.2 suggest that the membrane thickness and the nature of the membrane material play important roles in the performance of a MIMS system. Equation 2.1, also known as Fick's first law of diffusion, indicates that the analyte flow through the membrane is inversely proportional to the membrane thickness. Fick's second law of diffusion, Equation 2.2, shows that the change in concentration with time is proportional to the diffusion coefficient, and inversely proportional to the square of the membrane thickness. These equations suggest that response time should increase as the membrane thickness increases. The results shown in Table 5.1 are consistent with Fick's laws. Benzene and toluene had the lowest response times with the 0.007 in. membrane, suggesting that less polar analytes tend to have higher permeabilities through silicone membranes. In addition, vapor pressure plays a role in permeability. Regardless the highest vapor pressure of chloroform (Table 5.11), its lag-time was the longest. This indicates that permeability is determined by the solubility of an analyte in the membrane. (Dongré and Hayward 1996) These results were not observed with the 0.010 in. membrane. Nevertheless, it was observed that the intensity of the response, which reflects the concentration of the analyte, decreased as the thickness of the membrane increased. Fick's second law expresses that the change of concentration with time is inversely proportional to the square of the membrane thickness, and this was observed in these experiments. It is important to mention that the signal intensities of the analytes depend not only on their permeabilities through the silicone membrane but also on their ionization efficiency in the MS.

There are a few studies of the membrane thickness effects in MIMS in the literature. (LaPack *et al* 1990; Futo and Degn 1994; Dongré and Hayward 1996) However, a mixture containing volatile organic contaminants (for instance, benzene, xylene, carbon tetrachloride, and toluene) and disinfection byproducts (chloroform and bromate for example) has not been tested previously. The present thesis analyzed a three-component mixture of benzene, chloroform and toluene. This mixture was chosen because these molecules are common compounds in waste and environmental VOC testing. The results obtained are consistent with those found in previous investigations.

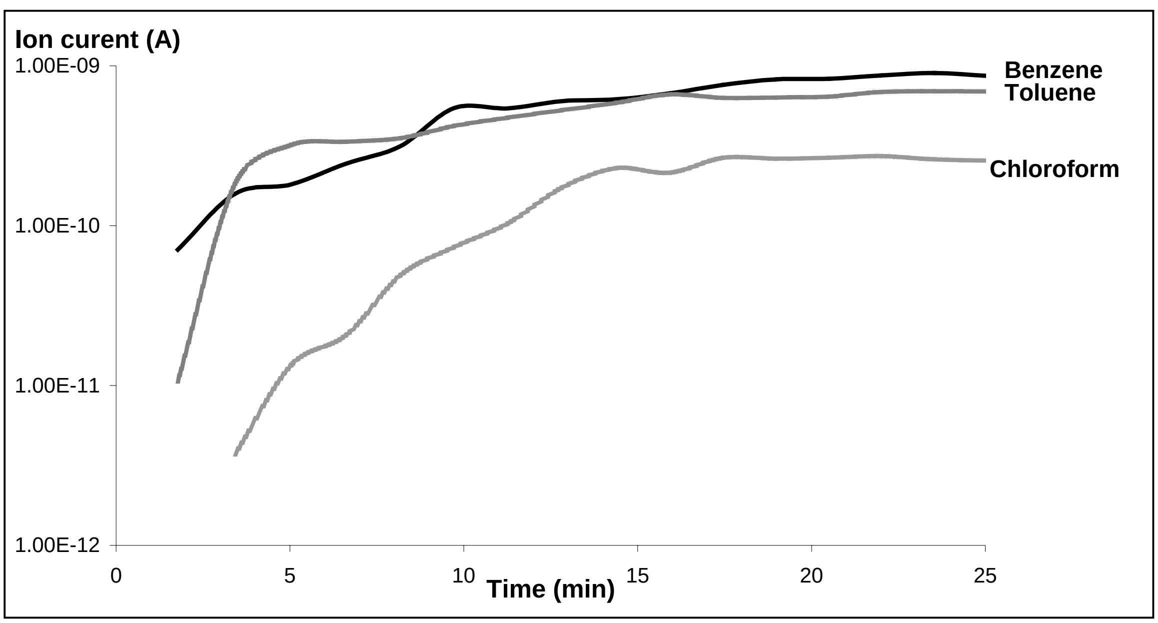


Figure 5.4: MIMS-MID profile for benzene-chloroform-toluene mixture with the 0.007 in. membrane.

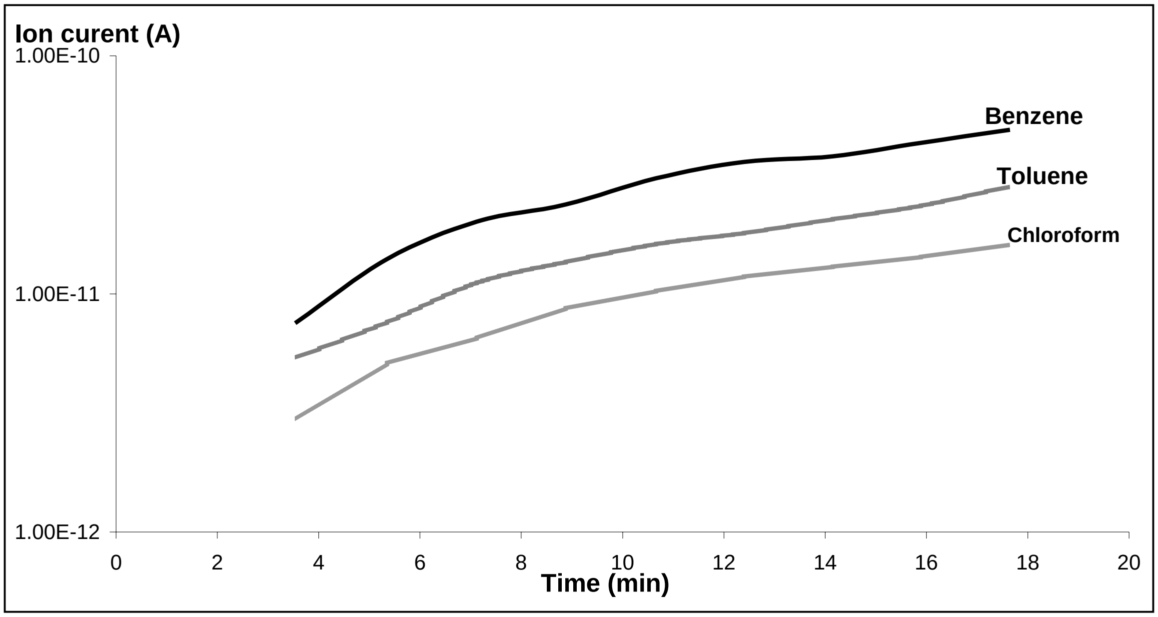


Figure 5.5. MIMS-MID profile for benzene-chloroform-toluene mixture with the 0.010 in. membrane.

The data acquisition modes described in Chapter 3 can be generalized into two major categories: continuous measurement of spectra (CMS) and selected ion monitoring (SIM). In CMS mode ions are detected by scanning a region of *m/z*, and the *m/z* values and abundances are stored by the data system as a complete mass spectrum. The total number of complete spectra acquired and stored during an analysis depends on the starting and ending times of the (mass spectral) data acquisition, the mass range scanned, the scan speed, and any delays between scans. In SIM mode ions are measured in real time at only selected *m/z* values as substances enter the MS. In SIM mode the selected ions are integrated over a longer time than is possible with CMS, increasing the signal to noise ratio of the selected ions. (Budde 2001) Since membrane thickness effects spectra were acquired in CMS mode, response times were not calculated because they would have been inaccurate. Nonetheless the first data point time was used for comparison as a reflection of the response time. On the other hand, SIM mode (MID mode in the Balzers software) was used to acquire temperature and flow rate effect spectra. Therefore, response times as a function of temperature and flow rate are measured to analyze these parameters effects on MIMS.

Membrane permeation rates are affected by temperature in two competing ways: the solubility of an analyte in the membrane decreases with increasing temperature, whereas the diffusivity through the membrane increases with increasing temperature. At high temperatures, the diffusivity effect dominates resulting in an increase in permeation rate. Therefore, water monitoring is most efficient at elevated temperatures. (Johnson *et al* 2000)

Contrary to membrane thickness effects, there are many studies in the literature that have investigated the effect of temperature of the membrane apparatus on detection responses. (LaPack *et al* 1990; Slivon *et al* 1991; Wong and Cooks 1995; Dongré and Hayward 1996; Maden and Hayward 1996; Ristoiu *et al* 1998) It is important to mention that only the temperature of the membrane apparatus was tested. Consistent with the general effects of temperature described above, those studies show an increase in response with increasing temperature for common VOCs. While these studies show the same trend, the response and the optimum temperature vary with the system employed and the analyte under investigation. For instance, in one study the benzene response times through a silicone membrane were found to improve from 30° to 60°C, (Maden and Hayward 1996) whereas in another study the benzene response time was optimal at 70°C. (Dongré and Hayward 1996) It was therefore necessary to observe the temperature effects on response time under the working conditions employed in this investigation for the benzene-chloroform-toluene mixture.

Response times were measured at five different temperatures: 24, 40, 55, 70, and 90 °C. At 24 °C only benzene was detected. Tables 5.2 and 5.3 show the lag-time and response times, $t_{90\text{-}10}$, respectively at 40, 55, 70, and 90 °C at a flow rate of 0.5 mL/min. Tables 5.4 and 5.5 show the same results but at a flow rate of 5 mL/min. The trend for all three components is the same. Lag-time appears to exponentially decrease with increasing temperature (and therefore improved), Figure 5.6. These results are consistent with those observed by others. (Dongré and Hayward 1996; Maden and Hayward 1996) This trend is also consistent with Arrhenius theory. (LaPack *et al* 1990) Equation 5.1:

$$P = P_0^{[-E_p(1/RT - 1/RT_0)]} \qquad (5.1)$$

where P_0 is the initial permeability at some initial temperature, T_0. E_p, the activation energy for permeation, is the sum of the activation energy for diffusion, E_d; and the difference in the heats of solution between the membrane and the sample matrix, Equations 5.2 and 5.3:

$$E_p = E_d + \Delta H_s \qquad (5.2)$$

$$\Delta H_s = H_s(membrane) - H_s(matrix) \quad (5.3)$$

Substituting Equation 5.2 into Equation 5.1:

$$P = P_0^{[-(E_d + \Delta H_s)(1/RT - 1/RT_0)]} \qquad (5.4)$$

The activation energy E_d is greater than zero (positive), while for most volatile organic compounds ΔH_s is less than zero (negative). Therefore the change in permeability as a function of temperature depends upon whether the change in the diffusivity or the distribution ratio dominates, Equations 5.5 and 5.6: (LaPack *et al* 1990)

$$P = DK \qquad (5.5)$$

where D is the diffusivity of the substance through the membrane and K is defined as the distribution ratio of the analyte concentration in the membrane to the concentration in the sample, Equation 5.6: (LaPack *et al* 1990)

$$K = C_{membrane} / C_{sample} \qquad (5.6)$$

Substituting Equation 5.5 into Equation 5.4:

$$DK = D_0 K_0^{[-(Ed + \Delta H_s)(1/RT - 1/RT_0)]} \qquad (5.7)$$

As for $t_{90\text{-}10}$, similar results were obtained. Response time, $t_{90\text{-}10}$, decreased exponentially with increasing temperature over the range of 24 °C to 70 °C, Table 5.3. At 90 °C the response time increased. For instance, at 90 °C the chloroform response time was almost twice that observed at 40 °C. The benzene response time at 90 °C was similar to that observed at 40 °C while the 90 °C toluene response was similar to that observed at 55 °C, Table 5.3. It is important to mention that at 90 °C water vapor was observed in the exit tubing. Water solubility is low in silicone membranes and therefore its flux across the membrane is low and generally does not interfere with the analysis. However, when operating at temperatures close to the boiling point of water, the permeability of water increases because increasing diffusivity dominates the water permeability-temperature relationship. (LaPack *et al* 1990; Wong and Cooks 1995) This increased water flux can decrease membrane sensitivity to the analyte. In a similar study, (Dongré and Hayward 1996) gas bubbles were observed over the 65 - 100 °C temperature range, but this wide range may have been due to the use of helium as a carrier gas. It was suggested that variations in response times could be due to the competition between the carrier gas and analyte gas molecules. The reduction in available membrane surface area for the analyte may have caused the observed variations.

An interesting feature noted is that the signal intensity increases for the three compounds with increasing temperature, Figures 5.7 (benzene), 5.8 (chloroform), and 5.9 (toluene), indicating that increasing temperature improves not only the response time but also sensitivity.

Temperature (°C)		**Lag-time (s)**	
	Benzene	**Toluene**	**Chloroform**
24	860	ND	ND
40	76.32	207.26	152.18
55	45.82	79.89	91.29
70	28.06	35.61	43.19
90	19.12	22.93	38.05

Table 5.2: Effect of temperature on lag-time (t_0) for a benzene-chloroform-toluene solution mixture (1 ppm each) at 0.5 mL/min. ND indicates not detected.

Temperature (°C)		**Response time t_{90-10} (s)**	
	Benzene	**Toluene**	**Chloroform**
24	980	ND	ND
40	313	479	232
55	178	219	175
70	95	121	90
90	324	219	454

Table 5.3: Effect of temperature on response time, t_{90-10}, for a benzene-chloroform-toluene (1 ppm each) solution mixture at 0.5 mL/min. ND indicates not detected

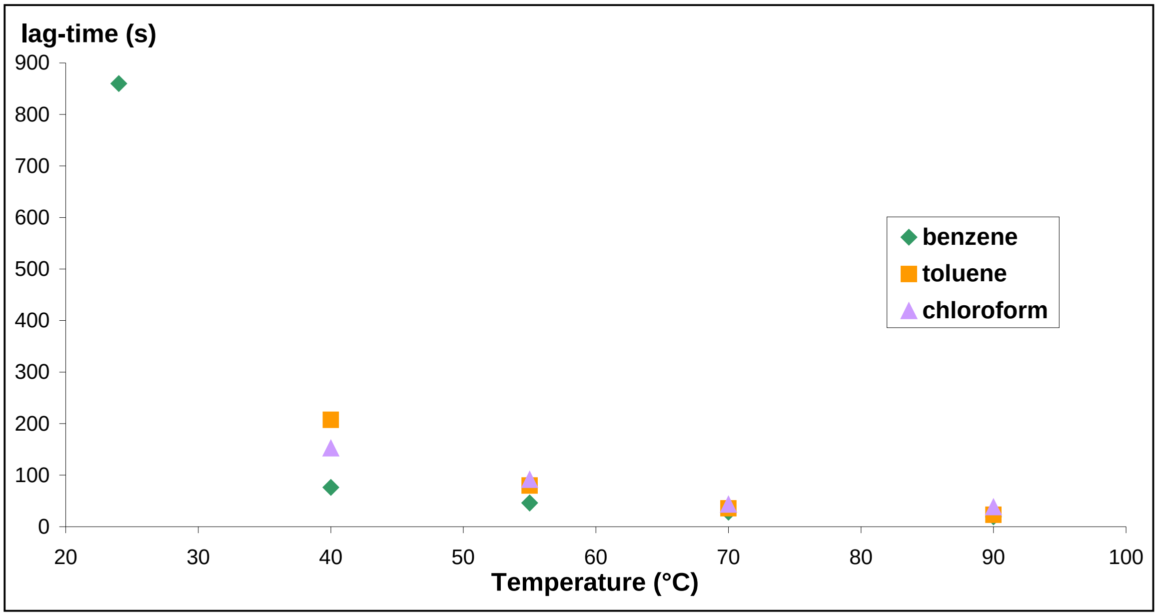


Figure 5.6: Lag-time response as a function of temperature for the benzene-chloroform-toluene mixture at a flow rate of 0.5mL/min.

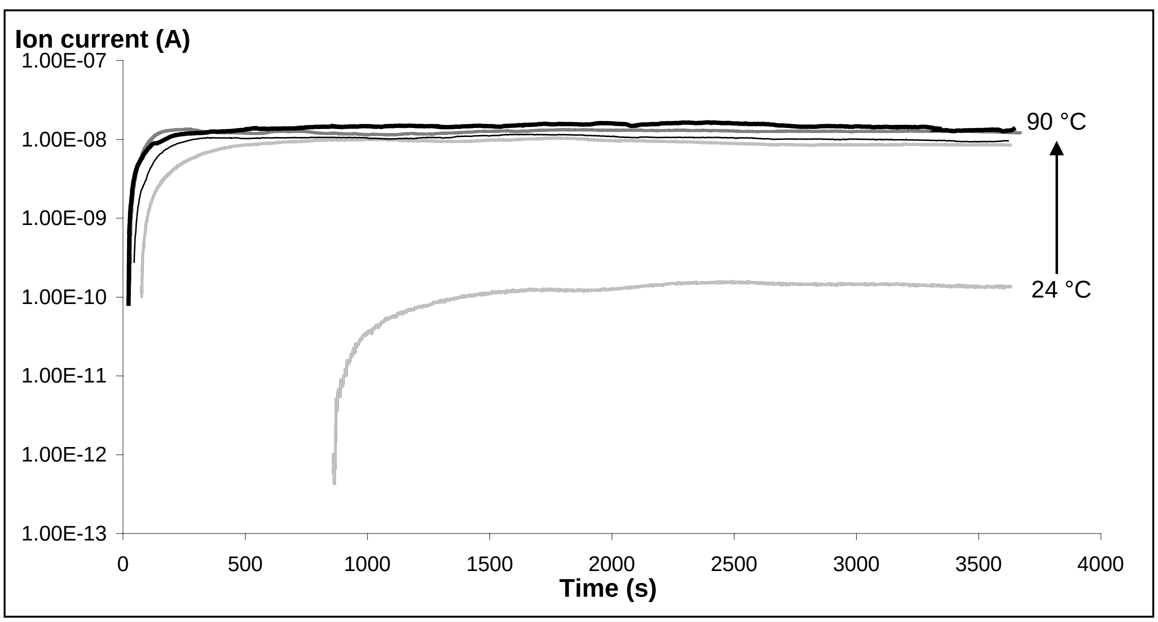


Figure 5.7: MIMS-MID benzene profile as a function of temperature at 0.5 mL/min. Temperatures: 24, 40, 55, 70, and 90 °C.

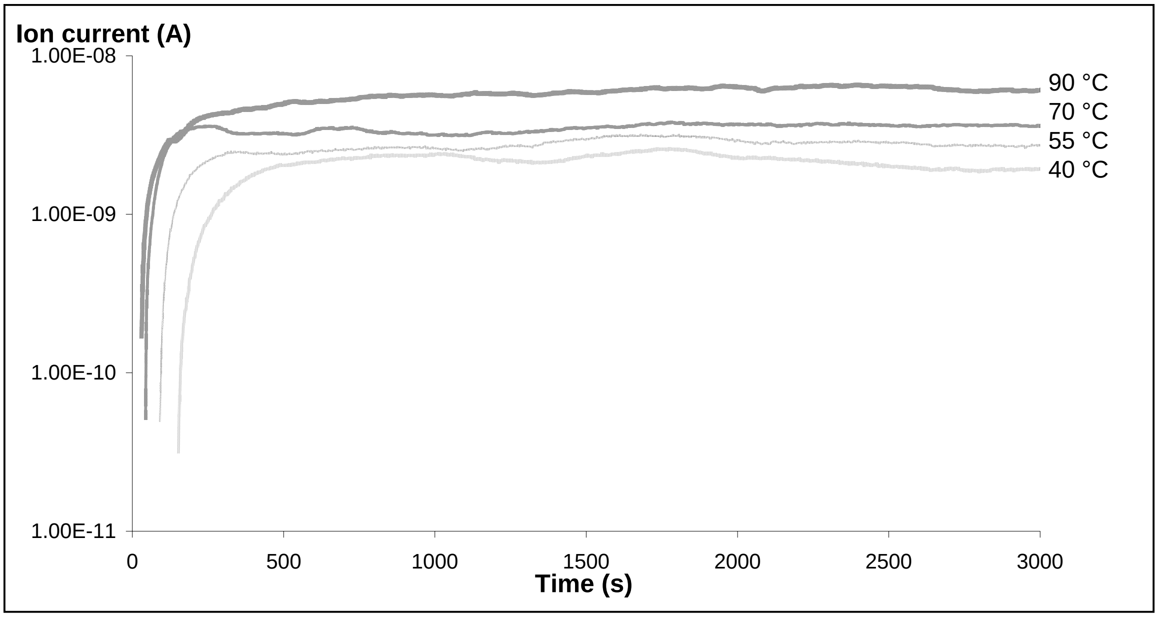


Figure 5.8: MIMS-MID chloroform profile as a function of temperature at 0.5 mL/min.

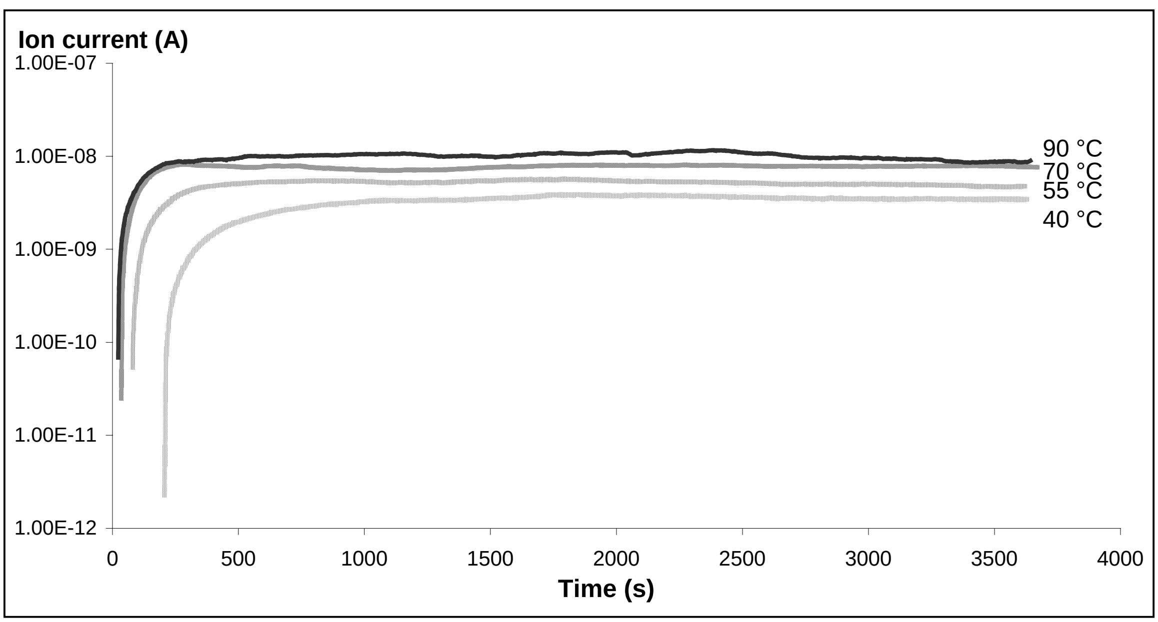


Figure 5.9: MIMS-MID toluene profile as a function of temperature at 0.5 mL/min.

The effect of the sample flow rate on lag-time, response time and signal intensity were also studied. Two flow rates were analyzed: 0.5 mL/min and 5 mL/min. The latter resulted in a 1 x 10^{-4} mbar pressure at 70 °C in the mass spectrometer. Preliminary studies of flow-rates higher than 5 mL/min led to pressures greater than 2 x 10^{-4} mbar in the mass spectrometer. Since increased pressures have adverse effects on the instrument and on the analysis, 5 mL/min was chosen as the maximum flow rate. Tables 5.4 and 5.5 show the lag-time and response times, t_{90-10}, respectively at 40, 55, 70, and 90°C at a flow rate of 5 mL/min. The base pressures for the instrument under the different MIMS conditions are shown in Table 5.6. It is important to mention that at 5 mL/min flow rate and 90 °C, the pressure was also greater than 2 x 10^{-4} mbar; therefore, data under these conditions were not acquired.

Temperature (°C)	**Lag-time (s)**		
	Benzene	**Toluene**	**Chloroform**
24	42.10	106.47	57.33
40	18.99	26.56	26.56
55	11.44	15.21	15.21
70	11.43	11.43	11.43

Table 5.4: Effect of temperature on lag-time for a benzene-chloroform-toluene (1 ppm each) solution mixture at 5 mL/min.

Temperature (°C)	Response time t_{90-10} (s)		
	Benzene	Toluene	Chloroform
24	403	701	254
40	163	396	114
55	118	254	101
70	243	367	173

Table 5.5: Effect of temperature on response time, t_{90-10}, for a benzene-chloroform-toluene (1 ppm each) solution mixture at 5 mL/min.

Temperature (°C)/flow rate (mL/min) conditions	Mass spectrometer pressure (mbar)
All temperatures/0.5	1×10^{-5}
< 70/5	5×10^{-5}
70/5	1×10^{-4}
90/5	2×10^{-4}

Table 5.6: Pressure of the mass spectrometer under the different MIMS conditions tested.

Previous studies (Harland *et al* 1987; Bier *et al* 1990; LaPack *et al* 1990; Dongré and Hayward 1996) have reported the effects of flow rate on MIMS. However, these flow rate experiments were performed at one temperature. Thus, one goal of this thesis was to investigate the effect of sample flow rate over a temperature range of 24 °C - 90 °C. The results reported here are in good agreement with those reported previously. (LaPack *et al* 1990; Slivon 1991; Wong 1995; Dongré and Hayward 1996; Maden and Hayward 1996; Ristoiu *et al* 1998) Lag-times as a function of flow rate for each compound are shown in Table 5.7. As for the response time, t_{90-10}, similar results were observed at 40 °C and at 55 °C for benzene and chloroform, while an increase in response was observed at 70 °C for the three VOCs when the sample flow rate was increased. Table 5.8 shows all the response times, $t_{90\text{-}10}$, at the different temperatures. Increasing the sample flow rate from 0.5 mL/min to 5 mL/min resulted in decreases of more than 50% in lag-time, Table 5.9. Table 5.10 reveals the changes in response time, $t_{90\text{-}10}$, as flow rate was increased from 0.5 mL/min to 5 mL/min. At 40 °C and 55 °C, the benzene and chloroform response times, $t_{90\text{-}10}$, were reduced by less than 50 %, while at 40 °C the toluene response time improved 17 %. At 70 °C the benzene and chloroform response times increased by more than *ca*. 50 % and 90 %, respectively. The toluene response time increased by 15 % at 55 °C and by 203 % at 70 °C.

Flow rate (mL/min) ± 0.2	**Lag-time (s)**		
	Benzene	**Toluene**	**Chloroform**
	40 °C		
0.5	76.32	207.26	152.18
5.0	18.99	26.56	26.56
	55 °C		
0.5	45.82	79.89	91.29
5.0	11.44	15.21	15.21
	70 °C		
0.5	28.06	35.61	43.19
5.0	11.43	11.43	11.43

Table 5.7: Effect of flow rate on lag-time for a benzene-chloroform-toluene (1 ppm each) solution at different temperatures.

Flow rate (mL/min) ± 0.2	Response time t_{90-10} (s)		
	Benzene	**Toluene**	**Chloroform**
		40 °C	
0.5	313	479	232
5.0	163	396	114
		55 °C	
0.5	178	219	175
5.0	118	254	101
		70 °C	
0.5	95	121	90
5.0	243	367	173

Table 5.8: Effect of flow rate on response time, t_{90-10}, for a benzene-chloroform-toluene (1 ppm each) solution at different temperatures.

Temperature (°C)	Change in lag-time (%)		
	Benzene	**Toluene**	**Chloroform**
40	- 75.61	- 87.18	- 82.54
55	- 75.03	- 80.96	- 82.38
70	- 59.26	- 67.90	- 73.53

Table 5.9: % of lag-time change at same temperatures when the sample flow rate was increased from 0.5 mL/min to 5 mL/min. The negative sign indicates a decrease in response time.

Temperature (°C)	Change of response time t_{90-10} (%)		
	Benzene	**Toluene**	**Chloroform**
40	- 47.92	- 17.32	- 50.86
55	- 33.70	+ 15.98	- 42.28
70	+ 55.28	+ 203.30	+ 92.22

Table 5.10: % of change at same temperatures when the sample flow rate was increased from 0.5 mL/min to 5 mL/min. The negative sign indicates a decrease in response time, while the positive indicates an increase in response time.

The volatility and polarity of the analytes likely contribute to the permeation process through the membrane. Boiling points, vapor pressures, and solubilities of the analyzed compounds are shown in Table 5.11. Chloroform has the highest vapor pressure but is the most soluble in water. On the other hand, toluene is the least soluble in water and therefore should cross the membrane quickly, however, its vapor pressure is the lowest. Benzene, at all flow rates and all temperatures, showed the shortest lag-times, Tables 5.2 and 5.4. Chloroform had the longest lag-time at 0.5 mL/min at temperatures higher than 55 °C. Thus, at low flow rates (0.5 mL/min) analyte polarity becomes more important than volatility for lag-time. At high flow rates (5 mL/min), the lag-time of benzene is the shortest, Table 5.4, but the lag-times of the other analytes are similar. The lag-times of toluene and chloroform are the same at temperatures above 40 °C. Clearly, sample flow rate plays a very important role in determining lag and response times.

Analyte	**Boiling point (°C)**	**Vapor pressure at 25 °C (mmHg)**	**Solubility (g/100 mL)**
Chloroform	61.7	194.24	0.795
Benzene	80.1	100.84	0.18
Toluene	110	28.47	0.05206

Table 5.11: Boiling points of the three organic compounds analyzed.

The effect of analyte volatility is more evident in the response time, $t_{90\text{-}10}$ (recall that response time, $t_{90\text{-}10}$, is defined as the time interval between 10 and 90 % of the analytical response). Toluene has the highest boiling point and showed the longest response time, $t_{90\text{-}10}$, at all flow rates and all temperatures, Tables 5.3 and 5.5. Whereas at

0.5 mL/min benzene and chloroform gave similar responses, Table 5.3. This is likely due to their relatively close boiling points. At high flow rates (5 mL/min), chloroform reached 90 % of its maximum signal in the shortest time, Table 5.5. Clearly at high flow rates the time required to reach the maximum response depends on the volatility of the analyte.

It has been suggested that slower flow rates yield a decreased time response due to the formation of boundary layers at the surface of the membrane, hindering the transfer of the organic compounds through the membrane. (Harland *et al* 1987; Bier *et al* 1990; LaPack *et al* 1990; Dongré and Hayward 1996) Laminar flow is characteristic of low flow rates. A laminar flow consists of a fluid that moves smoothly in streamlines in parallel layers or sheets. (Chang 2000) The parallel movement of all the particles of the liquid causes poor mixing at the sample-membrane interface. Therefore, high sample flow rates that cause turbulent flows are preferred in order to overcome the boundary layers at the membrane surfaces. (LaPack *et al* 1990) The Reynolds number, N_{Re}, is the ratio of inertial forces to viscous forces, Equation 5.8.

$$N_{\mathrm{Re}} = \frac{2Rv\rho}{\eta} \qquad (5.8)$$

where R is the radius of the tube through which the sample flows, v is the sample velocity through the tube, ρ is the density of the sample, and η is the sample viscosity. As mentioned in Section 4.3 the diameter of the tubing (2*R*) was 1/32 in. and velocities (v) were 9.14 x 10^{-2} m/s (5 mL/min) and 9.14 x 10^{-3} m/s (0.5 mL/min). A Reynolds number of less than 2000 indicates laminar flow, a number greater than 3500 indicates turbulent flow, while intermediate values can indicate either type of flow. The greatest Reynolds number calculated was 223 at a flow rate of 5 mL/min and at 90 °C. Thus, under all the experimental conditions, the movement of the sample was laminar flow. Looking at Equation 5.8, flow rates of *ca*. 50 mL/min and inner diameter tubing of 1/16 in. are required to achieve Reynolds numbers of 3500. However, higher sample flow rates and bigger inner diameter-tubing would have led to higher MS pressures. Although no turbulent flow was achieved, the increase in flow rate did reduce lag-times and response times, $t_{90\text{-}10}$, as explained above.

The effects of sample flow-rates are shown in Figures 5.10 (benzene), 5.11 (chloroform) and 5.12 (toluene). Greater intensities are observed as the sample flow rate and temperature are increased. The mass spectra of benzene, chloroform, and toluene, Figures 5.10, 5.11, and 5.12, show that the signal intensities increase by one order of magnitude when the sample flow rate increases from 0.5 mL/min to 5 mL/min at a constant temperature. Therefore, sensitivity is not only enhanced by the increase of temperature but also by greater sample flow rates. It is important to note that the 5 mL/min sample flow rate made possible the detection of the three organic compounds at 24 °C, whereas with a sample flow rate of 0.5 mL/min, only benzene was detected. Also, the benzene intensity was two orders of magnitude greater at a sample flow rate of 5 mL/min than at 0.5 mL/min at 24 °C, indicating that flow rate contributes significantly to the analyte detection.

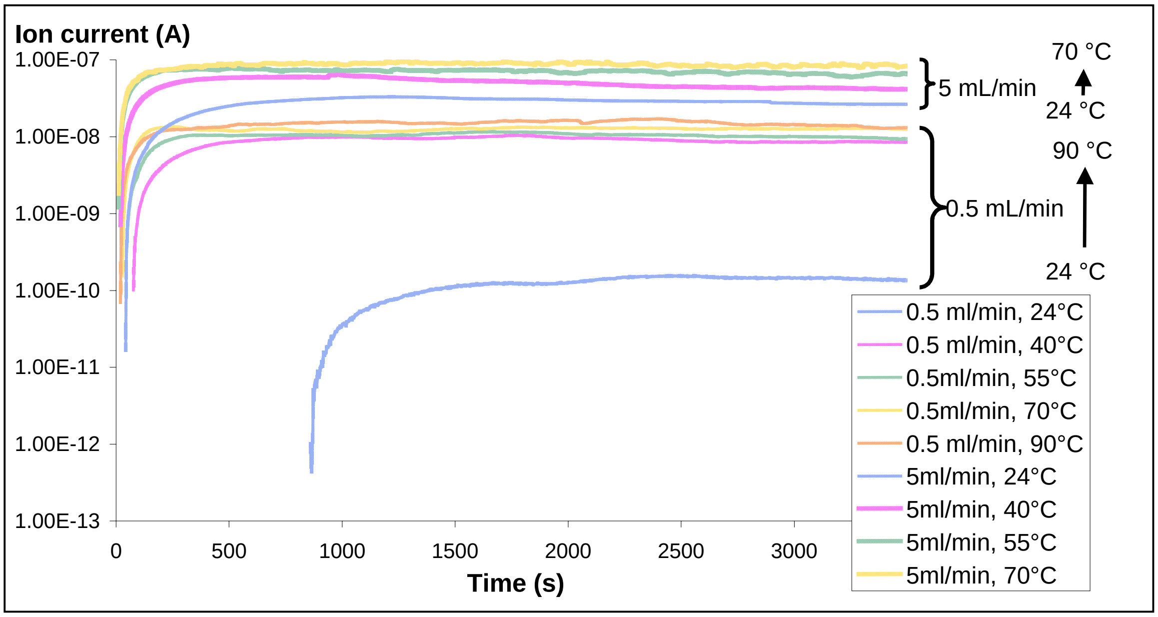


Figure 5.10: Effect of sample flow rate on MIMS-MID profile with increasing temperature for benzene

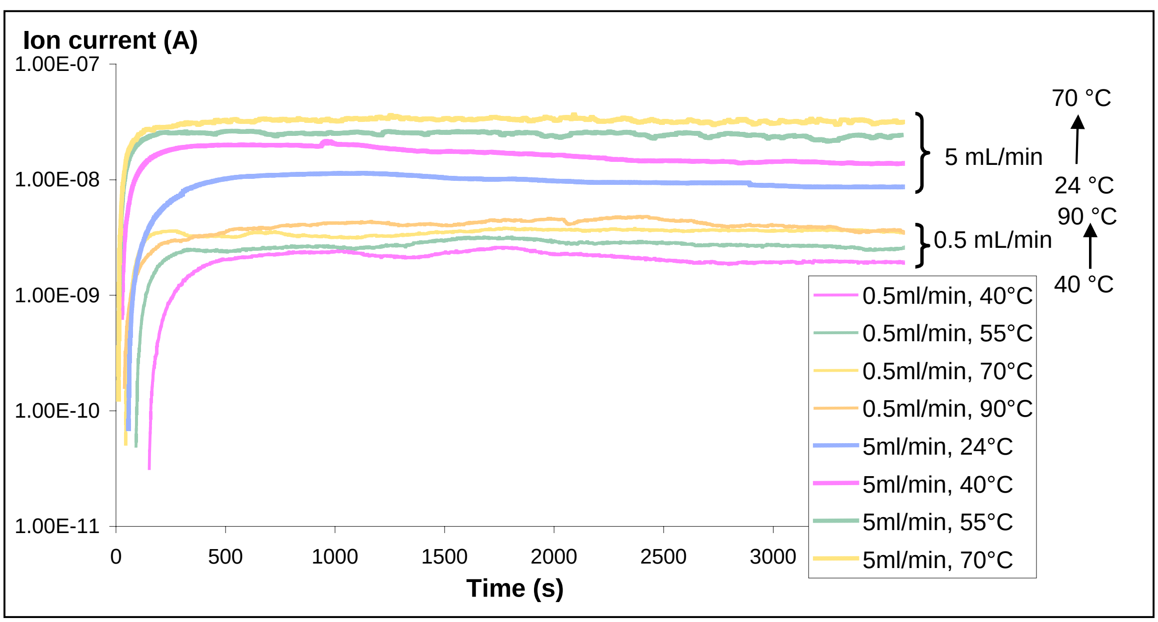


Figure 5.11: Effect of sample flow rate on MIMS-MID profile with increasing temperature for chloroform

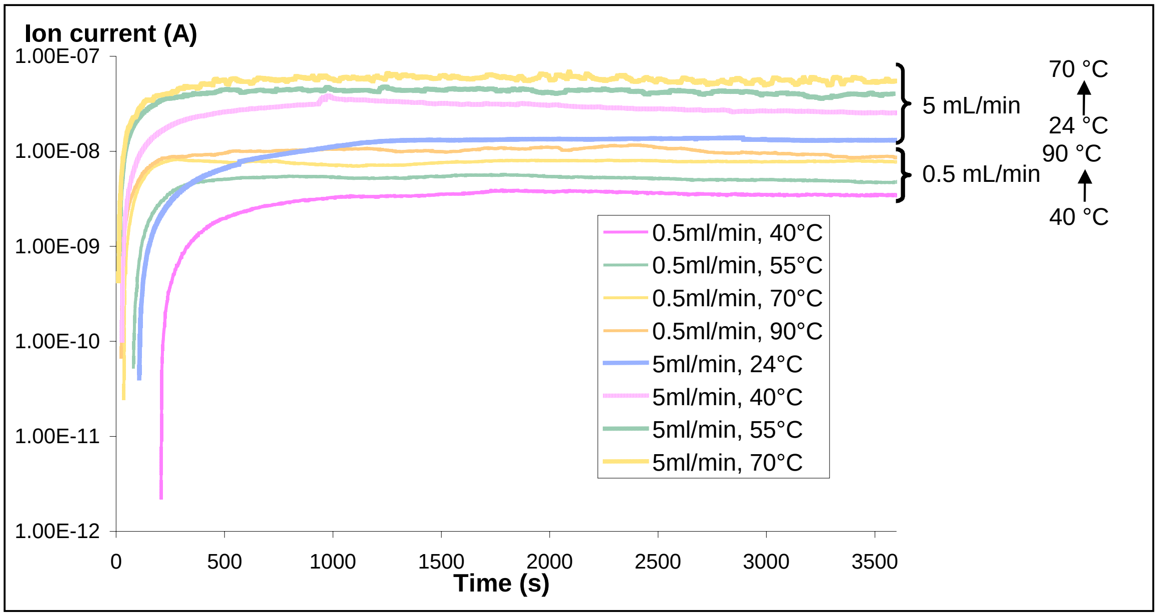


Figure 5.12: Effect of sample flow rate on MIMS-MID profile with increasing temperature for toluene.

Changes in lag-time and response time (%) with increasing temperature are shown in Tables 5.12 and 5.13, respectively. At 0.5 mL/min, an increase in temperature from 24 °C to 40 °C resulted in a significant reduction of the lag-time. The benzene lag-time was reduced by 91.12 %, while toluene and chloroform (not detected at 24 °C in one hour of monitoring) were detected at 40 °C in less than four minutes. At 5 mL/min, the reduction in lag-time was slightly more than 50 % for benzene and chloroform, while it was 75 % for toluene (which is the least volatile compound). Similar changes in lag-time were observed at 0.5 mL/min and 5 mL/min by increasing the temperature from 40 °C to 55 °C for benzene and chloroform. The change in lag-time with increasing temperature for toluene was greater at 0.5 mL/min than at 5 mL/min. The reduction in lag-time for the three VOCs was greater at 0.5 mL/min than 5 mL/min when increasing the temperature from 55 °C to 70 °C. These trends in lag-time change are comparable with those of response time, t_{90-10}, over the 24 °C – 55 °C range, Table 5.13. These observations indicate that increasing the temperature at low flow rates resulted in greater changes than at high flow rates over the 0.5 mL/min – 5 mL/min sample flow range.

Temperature (°C)	**Change in lag-time (%)**					
	Benzene		**Toluene**		**Chloroform**	
	0.5 mL/min	**5.0 mL/min**	**0.5 mL/min**	**5.0 mL/min**	**0.5 mL/min**	**5.0 mL/min**
24 → 40	- 91.12	- 54.89	NA	- 75.05	NA	- 53.67
40 → 55	- 39.96	- 39.75	- 61.45	- 42.73	- 40.01	- 42.73
55 → 70	- 38.76	- 0.08	- 55.42	- 24.85	- 52.68	- 24.85
70 → 90	- 32.10	NA	- 35.60	NA	- 11.90	NA

Table 5.12: Change in lag-time (%) for a benzene-chloroform-toluene solution mixture (1 ppm each) at 0.5 mL/min. NA indicates not applicable. The negative sign indicates a decrease in lag-time.

Temperature (°C)	**Change in response time t_{90-10} (%)**					
	Benzene		**Toluene**		**Chloroform**	
	0.5 mL/min	**5.0 mL/min**	**0.5 mL/min**	**5.0 mL/min**	**0.5 mL/min**	**5.0 mL/min**
24 → 40	- 68.06	- 59.55	NA	- 43.51	NA	- 55.12
40 → 55	- 43.13	- 27.60	- 54.27	- 35.85	- 24.56	- 11.40
55 → 70	- 46.63	+ 105.5	- 44.74	+ 44.49	- 48.57	+ 71.28
70 → 90	+ 241.0	NA	+ 80.99	NA	+ 400.44	NA

Table 5.13: Change in response time, t_{90-10}, (%) for a benzene-chloroform-toluene solution mixture (1 ppm each) at 0.5 mL/min. NA indicates not applicable. The negative sign indicates a decrease in time and the positive indicates an increase in response time.

SUMMARY

Mixtures of organic compounds were analyzed to investigate the permeability of one compound versus another through the membrane. Membrane selectivity is determined by the relative permeability of different compounds through the membrane. (LaPack *et al* 1990) However, matrix effects in MIMS-MID profile depend not only on analyte permeation through the membrane but also on the ionization efficiency in the MS. MS spectra of neat benzene-chloroform-toluene mixtures were obtained to determine the ionization efficiency by comparing the MS spectra with the MIMS spectra of aqueous solution mixtures. The headspace of the neat ternary mixture was analyzed by MID mode (see Section 3.2.2). It is assumed that the ternary neat mixture is an ideal solution, in which all intermolecular forces are equal. Since the composition of each compound in the solution is the same (33.33%), the composition of the vapor in equilibrium depends only on the vapor pressures of pure (neat) chloroform, benzene, and toluene. Chloroform, having the highest vapor pressure (194.24 mmHg, Table 5.11), is the major component of the vapor (headspace of the vial), while toluene with the lowest vapor pressure (28.47 mmHg, Table 5.11) is the minor component of the vapor. The MS-MID profile, Figure 3.13, reveals that the MS has the greatest sensitivity for benzene and the least for toluene. Thus, the MS response is determined by the ionization efficiency, with benzene being the most efficiently ionized molecule, and toluene is the least efficiently ionized molecule. On the other hand, the MIMS-MID profile, for instance Figures 4.10, 4.12, 4.13, shows a different behavior for the aqueous mixtures. The benzene signal is still the most intense indicating that benzene is the most permeable analyte through the membrane. The chloroform signal is the weakest, indicating that the membrane is least permeable to it.

Upon analysis of a neat organic mixture, the MS spectrum reveals that the shortest lag-times and response times, $t_{90\text{-}10}$, correspond to the most volatile analytes, and the longest times are for the least volatile analyte, toluene, Table 5.14. Since the MS spectrum of the neat organic mixture, Figure 3.13 shows very similar intensities for toluene and chloroform, the volatility does not greatly affect the MIMS signal intensity.

Analyte	Lag-time (s)	Response time $t_{90\text{-}10}$ (s)
Chloroform	8.21	22
Benzene	8.21	24.01
Toluene	16.293	44

Table 5.14: Lag-time and response time, $t_{90\text{-}10}$, for a neat organic mixture MS spectrum.

In general, response times (lag-time and $t_{90\text{-}10}$) depend on the volatility of the analyte, and on MIMS parameters including temperature, sample flow rate, and membrane permeability. Signal intensity depends on the above MIMS parameters and on the ionization efficiency of the MS.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Experiments were conducted to determine the optimal instrument conditions for the identification of benzene, toluene and chloroform using an Omnistar GSD 300 O MS. These included an electron ionization 90 eV, a SEM detection voltage of 3000 V, and an electron emission current of 1.0 mA.

Membrane apparatus temperature and sample flow rate are important factors affecting analyte lag-time, response time and signal intensity. Lag-time responses were enhanced by temperature and sample flow rate to improve analyte permeability through the membrane. Response time was primarily improved by increasing the temperature to increase analyte volatility. Signal intensity was greatly enhanced by increasing the sample flow rate from 0.5 to 5.0 mL/min. Signal intensity was also improved by increasing the temperature. The MIMS system showed the greatest sensitivity for benzene and the lowest for chloroform.

Five-minute analysis were achieved with the membrane apparatus constructed for this study at a temperature of 55 °C and a sample flow rate of 0.5 mL/min using a 0.010 in. thick membrane. EPA current methods for the analysis of VOCs are usually one hour long, whereas MIMS provided a complete analysis in five minutes. In addition, MIMS offers on-line analysis.

The above-mentioned conditions were determined using the 0.010 in. thick membrane. Future study with the 0.007 in. thick membrane at the optimum conditions (55 °C and 0.5 mL/min) is needed to compare the response times obtained in this investigation with those obtainable with a thinner membrane. For completeness of this study, it is also recommended to perform experiments at all temperatures and flow rates, with the 0.007 in. membrane to have a complete analysis of these parameters.

Finally, new calibration curves at the optimum conditions of membrane apparatus temperature, sample flow rate, and membrane thickness should be constructed to determine the detection and quantification limits for this method.

Membrane Introduction Mass Spectrometry was successfully used for the analysis of mixtures of volatile organic compounds in aqueous solution. MIMS shows promise for the fast on-line analysis of real water samples in real time.

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APPENDIX A

ELECTRON IONIZATION AND QUADRUPOLE ANALYZER NOTES

A Quadrupole mass spectrometer (Omnistar GSD 300 O) equipped with an electron ionization source was used in this thesis, therefore a few details are present here.

Electron Ionization Source

In a typical curve of the number of ions produced by a given electron current when the acceleration potential of the electrons (or their kinetic energy) is varied, the energy is lower than the molecule ionization energy at low potentials. At high potentials, the wavelength becomes too small and molecules become “transparent” to these electrons. In the case of organic molecules, a wide maximum appears at around 70eV. At this level, small changes in the electron energy do not significantly affect the pattern of the spectrum. (de Hoffmann and Stroobant 2001) Since 10 eV are enough to ionize most organic molecules, the excess energy leads to extensive fragmentation. This fragmentation can be useful because it provides structural information for structure elucidation of an unknown analyte. At a given acceleration potential and a constant temperature, the number of ions I produced per unit time in a volume V is linked to the pressure p and to the electron current i through Equation A.1:

$$I = NpiV \qquad \text{(A.1)}$$

where is a constant of proportionality. This equation shows that the sample pressure is correlated directly with the resulting ionic current. This allows the electron ionization source to be used in quantitative measurements. (de Hoffmann and Stroobant 2001)

Quadrupole Analyzer

The transmission Quadrupole mass spectrometer consists of four accurately ground stainless steel (or molybdenum) rods. The rods must be perfectly parallel (the accuracy on alignment is in the order of 1µm), held in place by ceramic spacers , Figure A-1. A constant voltage (dc) and a radiofrequency (RF) oscillating voltage is superimposed and added to opposite rods. The exact opposite voltages are added to the other rod pair. (de Hoffmann 2001; Harris 2002)

A positive ion entering the space between the rods will be drawn towards a negative rod. If the potential changes sign before it discharges itself on this rod, the ion will change direction. Ions traveling along the z-axis are subjected to the influence of a total electric field made up of a quadrupolar alternative field superposed on a constant field resulting from the application of the potentials upon the rods, Equation A.2:

$$\phi_0 = +(U - V\cos\omega t) \text{ and } -\phi_0 = -(U - V\cos\omega t) \qquad \text{(A.2)}$$

In Equation A.2, ϕ_0 represents the potential applied to the rods, ω is the angular frequency (in rads s^{-1}) = 2 πv, where v is the frequency of the radiofrequency, U is the direct potential and V is the "zero to peak" amplitude of the RF voltage. Typically, U will vary from 500 to 2000 V and V from 0 to 3000 V (from –3000 to + 3000 V peak to peak). (de Hoffmann and Stroobant 2001)

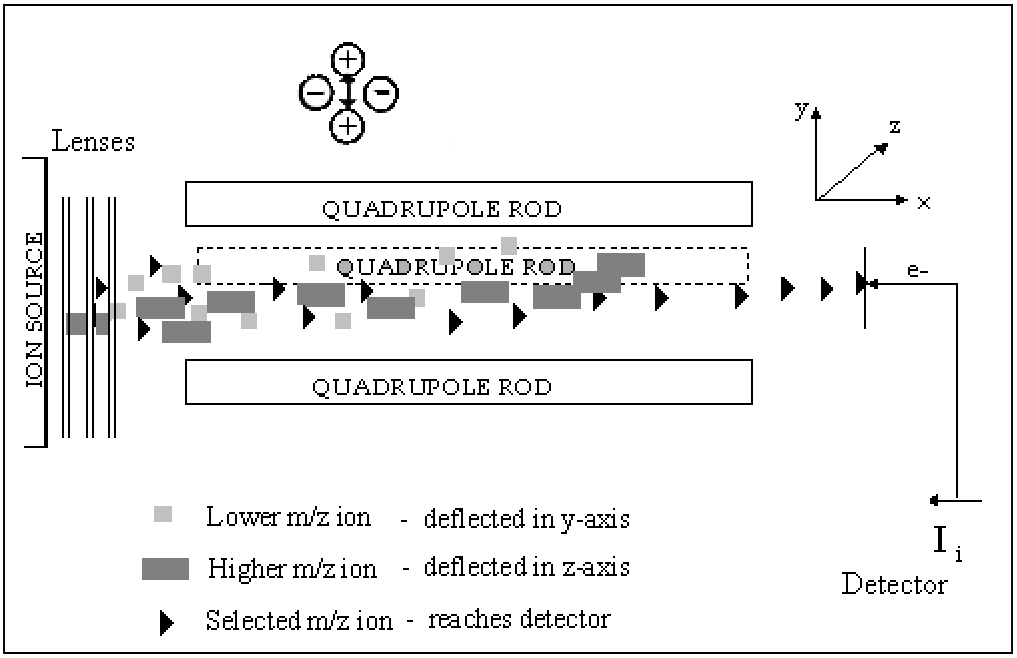

Figure A.1: Quadrupole instrument made up of the source, the focusing lenses, the quadrupole cylindrical rods and the detector. Adapted from (de Hoffmann and Stroobant 2001; Foster 2002)

The ions accelerated along the z-axis enter the space between the quadrupole rods and maintain their velocity along the axis. However, they are submitted to accelerations along x and y that result from the forces induced by the electric fields, Equations A.3 and A.4, Figure A.1:

$$F_x = m\frac{d^2x}{dt^2} = -ze\frac{\partial\phi}{\partial x} \qquad \text{(A-3)}$$

$$F_y = m\frac{d^2y}{dt^2} = -ze\frac{\partial\phi}{\partial y} \qquad \text{(A-4)}$$

where ϕ is a function of ϕ_0, Equation A.5:

$$\phi_{(x,y)} = \phi_0(x^2 - y^2)/r_0^2 = (x^2 - y^2)(U - V\cos\omega t)/r_0^2 \qquad \text{(A.5)}$$

Equations of motion (Equations A.6 and A.7) are obtained by taking the derivative of equation A.5 and by rearranging the terms:

$$\frac{d^2x}{dt^2}+\frac{2ze}{mr_0^{\ 2}}(U-V\cos\omega t)x=0 \qquad \text{(A.6)}$$

$$\frac{d^2y}{dt^2}+\frac{2ze}{mr_0^{\ 2}}(U-V\cos\omega t)y=0 \qquad \text{(A.7)}$$

The trajectory of an ion will be stable if the value of x and y never reach r_0, for instance if the ion never collides with the rods.

The following equation describes the propagation of waves in membranes, Equation A.8:

$$\frac{d^2u}{d\xi^2}+(a_u-2q_u\cos 2\xi)u=0 \qquad \text{(A.8)}$$

where u stands for either x or y. Comparing the preceding equations with equation A.8, and taking into account that the potential along y has an opposite sign to the one along x, the following change of variables allow the equations of motion to be depicted in the form of the Mathieu Equation, equations A.9 and A.10 (Skoog *et al* 1998; de Hoffmann and Stroobant 2001):

$$\xi=\frac{\omega t}{2}, \quad a_u=a_x=-a_y=\frac{8zeU}{m\omega^2r_0^{\ 2}} \qquad \text{(A.9)}$$

$$q_u=q_x=-q_y=\frac{4zeV}{m\omega^2r_0^{\ 2}} \qquad \text{(A.10)}$$

These equations establish a relationship between the coordinates of an ion and time. As long as x and y remain less than r_0, the ion will be able to pass the quadrupole without touching the rods.

The quadrupole is a true mass-to-charge ratio analyzer. It does not depend on the kinetic energy of the ions when they leave the source. The only requirements are that the time for crossing the analyzer be short compared with the time necessary to switch from one mass to the other, and that the ions remain long enough between the rods for a few oscillations of the alternative potential to occur. This means that the kinetic energy at the source exit must range from one to a few hundred electronvolts. (de Hoffmann and Stroobant 2001)

APPENDIX B

SYSTEM TROUBLESHOOTING

During the performance of both MS and MIMS experiments, a number of problems were encountered. This section describes the symptoms, procedures for localizing and diagnosing Quadrupole MS Omnistar GSD 300 malfunctions, as well as the actions taken to solve them.

Symptom: High pressure in the MS

While acquiring a spectrum, the MS suffered a shutdown due to a power outage. Upon restarting, the internal pressure reading was 1 x 10^{+01} mbar of total pressure. Two possible sources can cause high pressure (in addition to a leak in the chamber): (1) the rupture of one or both of the diaphragms of the diaphragm pump. This is a normal failure mode for this type of pump and can occur after a sudden power loss and restart. (2) A fault in the gauge reading. Diagnosing a faulty gauge can be done by checking whether the turbo pump is coming up to speed, which it cannot do if the pressure is really 1 x 10^{+01} mbar. Monitor of the turbo speed and current from the SERVICE program is as follows:

1. Shut the system down and wait 15 minutes
2. Turn the system on

3. Start the SERVICE program
4. Choose MANUAL AI/AO and set AO #3 to –5 V. Hit the TAB key
5. AI's are activated on the left and these will indicate the turbo speed and the current
6. The speed (AI 0) should go from 0-3 V, indicating speeds of 0 to 90 000 RPM
7. The current (AI 1) should go from ~2 to 0.6, indicating a current of 2 to 0.6 A.
8. The MS must reach 10^{-05} mbar or lower after 3 minutes. At this time the turbo pump must be at 90 000 rpm and drawing 0.6 AMPS of current.

After this test, the readings were:

AI 0: 4.873 V

AI 1: 0.025

Total pressure: $1.138 \times 10^{+01}$ mbar

The readings indicated that the turbo pump was unable to reach full speed. The turbo pump will turn on when the diaphragm pump pumps below 10 mbar. If this does not happen the turbo pump will shut down after a few minutes. Therefore, the most likely cause of the high pressure was that one or both diaphragms were fractured. This was not unusual since the MS at that time was 2 years old. The diaphragm pump was checked and one of the diaphragms was broken.

Solution: replacement of the broken diaphragm.

Symptom: High pressure after replacing the diaphragm

Upon replacement of the diaphragm, the MS was re-started but the total pressure was even higher (10^{+04} mbar) than with the initial problem. Also, a “strange” sound was perceived immediately after turning the unit on. There are two possible reasons for a strange sound in the MS: (1) some of the washers were not replaced. This would give too much clearance in the pump causing higher pressures. Washers may be stuck to the old diaphragm or may fall into the pump body when replacing the pump. (2) The diaphragm was not fully tightened, causing a lot of rattling which would eventually cause the threads to be stripped. If this is the case, the pump must be replaced because once the threads are stripped, the pump is NOT reparable (the diaphragm was sent to the Machine Shop of the Chemistry Department at The Ohio State University; however it was not repaired since the tolerances are critical and require special tools).

Solution: The pump was replaced.

It is important to mention that the MS had to be baked out overnight after replacing the pump. This was necessary since the MS had been off for long time causing relative high pressures (10^{-05} mbar). The total pressure after replacing the pump and baking out the MS was 10^{-07} mbar.

Filament 1 and 2 defective, error message

The next error message was displayed while trying to turn the filament on:

“ Filament 1 defect

Filament 2 defect”

According to the Balzers Quadstar™ 422 Software Manual, this message means "Filaments defective". In other words, both filaments are open or missing. The checking of the filament procedure is as follows:

1. Open TUNE menu
2. Select TUNE DATA
3. The small SEM/EMISS CONTROL box appears, DO NOT turn the filament on
4. Click OK
5. Reduce the window and move it to the top of the screen
6. Open PARAMETERS menu
7. Select ION SOURCE, reduce the window and move it to the bottom of the screen
8. In the ION SOURCE window it can been seen which filament is selected
9. Press Ctrl + s on the key board, the SEM/EMISS CONTROL box appears
10. Click ON emission and watch the Filament Current in the TUNE data window. It should increase to 3.5 A. An emission current should follow
11. If the filament current stays at zero, the filament is open
12. If a filament current is obtained but no emission current the filament may be contaminated. The diagnosing procedure is as follows:
    a. Reduce the emission current setting in the ION SOURCE window to 0.1 mA
    b. When the emission current stays on, increase it slowly to the full EMISS setting

The check test revealed a Filament current of zero. The filament had burnt out and needed to be replaced. To do this, follow the "Omnistar/Thermostar Filament Replacement Procedure" provided by Pfeiffer Vacuum.

Solution: Filament Replacement

Symptom: low total pressure with the inlet valves opened

The total pressure is to be checked with the inlet valves closed and opened. The pressure with the inlet valves open should be 10 times greater than that with the inlet valves closed. When this problem arose the pressures were:

Closed inlet valves: 1.6×10^{-07} mbar

Open inlet valves: 7.6×10^{-07} mbar

Air spectra were obtained with the inlet valves both opened and closed. The resulting intensity signals were very similar. With the valves closed the air signals should be 100 times smaller compared to those with the valves opened. Low pressure can be due to a blockage in the MS capillary or orifice. Since the capillary usually clogs at the entrance, a short piece (1 in.) from the MS capillary was cut off. However, the "open" total pressure was still low. The platinum orifice was replaced by a new one, Figure B.1. The replacement procedure is given in the Operating Manual. The open total pressure with the new platinum orifice was 10^{-06} mbar.

Solution: Platinum orifice replacement.

Optimizing Source Parameters

After a filament or platinum orifice replacement, an optimization of the ion source parameters has to be performed. For this, proceed as follows:

1. Check that the system is leak tight by doing an analog scan and verifying that there is not much air in the spectra
2. Bake out the MS overnight
3. Allow room air into the system by opening the inlet valve (turn off the filament just before doing this)
4. Go to TUNE
5. Choose ION SOURCE
6. Choose DISPLAY>MEASURE DATA and set up a scan from mass 26 to 32 to see the nitrogen peaks (28, 29, and 30)
7. Change the voltages on the CATHODE and EXTRACTION while watching the scan. Optimum tuning is where the signal is the highest without having the peak shape degrade (become non-rounded). The cathode voltage must stay above 50 V.

Send/receive time out detected, error message

This message was displayed a few times while acquiring data. The Balzers Quadstar^{TM} 422 Software Manual indicates this message means "QMS off or not available", which means that the connection was lost and it is necessary to shut the MS down and re-start it.

Solution: Restart the mass spectrometer

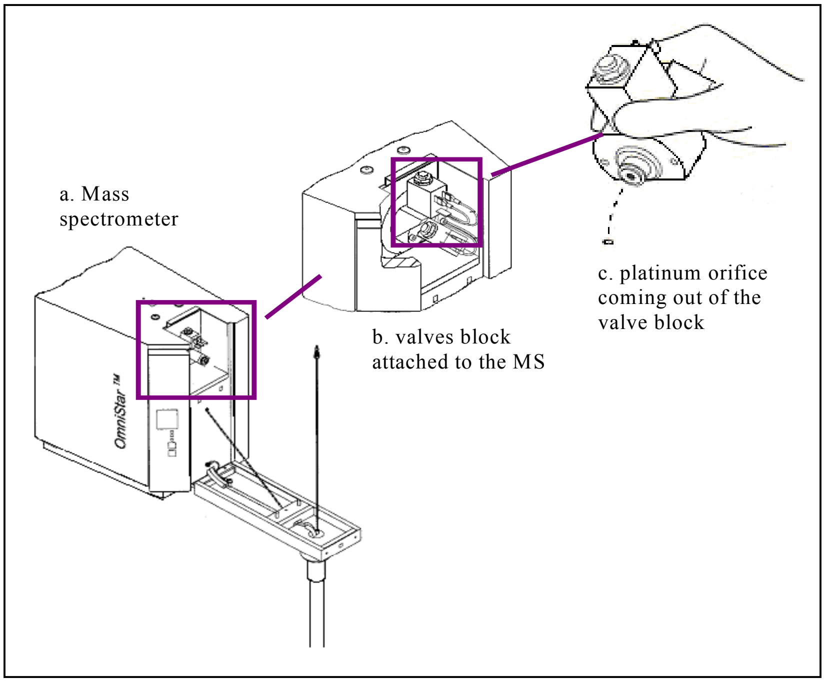

Figure B.1: Diagram of the inlet valves showing the orifice.
(Balzers 2001)

APPENDIX C

DATA TABLES

Concentration (ppm)	replicate 1	replicate 2	replicate 3	average	stdev	S/N
0.6		6.27E-10		6.27283E-10		
0.7	1.6E-09			1.60087E-09		
0.8	1.47E-09		1.89E-09	1.68298E-09	2.95073E-10	5.70359
0.9	2.64E-09	2.59E-09		2.61537E-09	3.2087E-11	81.5087
1	2.86E-09	2.82E-09	2.81E-09	2.83002E-09	2.75445E-11	102.7435

Table C.1: Calibration curve data for benzene.

Concentration (ppm)	replicate 1	replicate 2	replicate 3	average	stdev	S/N
0.6		3.53E-10		3.52729E-10		
0.7	1.03E-09			1.03228E-09		
0.8	9.72E-10		1.3E-09	1.13448E-09	2.29079E-10	4.952346
0.9	1.92E-09	1.59E-09		1.75463E-09	2.33912E-10	7.501237
1	2E-09	1.92E-09	1.86E-09	1.92393E-09	7.05148E-11	27.28408

Table C.2: Calibration curve data for toluene.

Concentration (ppm)	replicate 1	replicate 2	replicate 3	average	stdev	S/N
0.6		-3.3E-11		-3.30101E-11		
0.7	8.78E-11	1.58E-11		5.17922E-11	5.09656E-11	1.016219
0.8	4.94E-11		2.57E-10	1.53248E-10	1.46842E-10	1.043623
0.9	2.49E-10	3.54E-10		3.01307E-10	7.43885E-11	4.050458
1	3.21E-10	3.98E-10	3.97E-10	3.72094E-10	4.41666E-11	8.424769

Table C.3: Calibration curve data for chloroform.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-5.78422E-11	860.5645	1.00918E-12	1047.6225	4.46073E-11	1235.81	7.811E-11	1423.915	1.03795E-10
3.9985	-5.63492E-11	864.36275	4.3205E-13	1051.4275	4.36655E-11	1239.6075	7.656E-11	1427.74	1.02743E-10
7.952	-5.76031E-11	868.14375	8.82225E-13	1055.29	4.63368E-11	1243.3975	7.712E-11	1431.6575	1.05769E-10
11.898	-5.88524E-11	871.93175	4.9686E-12	1059.155	4.81638E-11	1247.2375	7.8E-11	1435.46	1.03331E-10
15.849	-6.05961E-11	875.71775	3.70303E-12	1062.9925	4.80038E-11	1251.07	7.896E-11	1439.28	1.06555E-10
19.8275	-5.64918E-11	879.526	6.0205E-12	1066.8475	4.97148E-11	1254.87	7.977E-11	1443.0975	1.06059E-10
23.796	-5.63689E-11	883.33175	6.7318E-12	1070.665	5.0453E-11	1258.665	8.082E-11	1446.9775	1.07174E-10
27.74975	-6.01723E-11	887.16525	5.58028E-12	1074.4925	5.17025E-11	1262.4725	8.127E-11	1450.8725	1.07503E-10
31.7035	-7.21211E-11	890.97325	8.77243E-12	1078.4075	5.38935E-11	1266.2775	8.266E-11	1454.73	1.07426E-10
35.6445	-9.53225E-11	894.78675	7.46733E-12	1082.2075	5.1884E-11	1270.18	8.412E-11	1458.5325	1.07857E-10
39.59575	-1.50383E-10	898.59775	7.40773E-12	1086.0325	5.37025E-11	1273.98	8.565E-11	1462.3825	1.10217E-10
43.55925	-1.9477E-10	902.4435	9.8682E-12	1089.8575	5.4005E-11	1277.785	8.614E-11	1466.175	1.07204E-10
47.52775	-2.1173E-10	906.25675	9.98058E-12	1093.655	5.43645E-11	1281.5875	8.569E-11	1470.0175	1.06065E-10
51.45375	-2.20023E-10	910.11025	1.18592E-11	1097.4975	5.54603E-11	1285.39	8.647E-11	1473.84	1.11103E-10
55.40975	-2.21578E-10	913.946	1.03891E-11	1101.3	5.61278E-11	1289.25	8.509E-11	1477.66	1.07199E-10
59.5035	-2.40618E-10	917.7345	1.54404E-11	1105.155	5.60218E-11	1293.0725	8.731E-11	1481.5225	1.08756E-10
63.452	-2.77756E-10	921.54525	1.42499E-11	1108.99	5.77528E-11	1296.8875	8.834E-11	1485.355	1.1145E-10
67.38525	-3.51383E-10	925.37125	1.52565E-11	1112.805	5.58098E-11	1300.68	8.969E-11	1489.1825	1.11943E-10
71.30625	-4.32897E-10	929.22725	1.58193E-11	1116.6625	5.7447E-11	1304.5225	8.676E-11	1493.0225	1.0989E-10
75.25475	-4.73623E-10	933.02775	1.84374E-11	1120.4975	5.8412E-11	1308.3125	9.069E-11	1496.8525	1.10254E-10
79.19825	-5.13993E-10	936.83375	1.81336E-11	1124.3325	6.18373E-11	1312.195	8.919E-11	1500.6775	1.13395E-10
83.09175	-5.53877E-10	940.64675	1.93289E-11	1128.175	6.1515E-11	1316.0425	8.745E-11	1504.4725	1.12849E-10
86.98525	-5.65501E-10	944.4955	2.21285E-11	1131.9775	6.29708E-11	1319.9075	9.164E-11	1508.31	1.11118E-10
90.86875	-5.88876E-10	948.27825	1.97896E-11	1135.8425	6.21453E-11	1323.7825	9.323E-11	1512.1525	1.17419E-10
94.76725	-5.78865E-10	952.07425	2.52259E-11	1139.655	6.44565E-11	1327.6625	9.161E-11	1516.015	1.14706E-10
98.67575	-5.80934E-10	955.87	2.33075E-11	1143.4975	6.12683E-11	1331.4775	9.237E-11	1519.8175	1.16075E-10
102.54925	-5.75402E-10	959.696	2.48103E-11	1147.4325	6.501E-11	1335.3075	9.106E-11	1523.6725	1.1476E-10
106.4425	-5.70805E-10	963.577	2.5573E-11	1151.2725	6.51735E-11	1339.1475	9.359E-11	1527.49	1.12539E-10
110.32575	-5.65337E-10	967.45525	2.80278E-11	1155.1325	6.38853E-11	1343.1525	9.398E-11	1531.3025	1.15329E-10
114.2145	-5.60654E-10	971.28375	2.92238E-11	1158.9825	6.491E-11	1347.0675	9.442E-11	1535.0975	1.14685E-10
118.03275	-5.54501E-10	975.17725	2.87545E-11	1162.7925	6.77995E-11	1350.8675	9.401E-11	1538.9075	1.1735E-10
121.93125	-5.50131E-10	978.99525	3.0922E-11	1166.5925	6.81045E-11	1354.6825	9.631E-11	1542.72	1.17644E-10
125.792	-5.45663E-10	982.82875	3.21864E-11	1170.4075	6.94955E-11	1358.565	9.507E-11	1546.54	1.14368E-10
129.6605	-5.40077E-10	986.6795	3.23388E-11	1174.2575	6.85043E-11	1362.4125	9.585E-11	1550.36	1.16492E-10
133.529	-5.35986E-10	990.463	3.44293E-11	1178.095	6.97853E-11	1366.2525	9.752E-11	3598.015	1.3511E-10
137.3695	-5.30655E-10	994.25925	3.32288E-11	1181.87	6.88923E-11	1370.1625	9.7E-11	3601.7925	1.30745E-10
141.213	-5.24625E-10	998.036	3.41348E-11	1185.6975	6.88435E-11	1373.9975	9.828E-11	3605.6	1.3631E-10
145.1115	-5.20267E-10	1001.82225	3.61568E-11	1189.485	7.06128E-11	1377.8575	9.941E-11	3609.5	1.34421E-10
148.95	-5.15575E-10	1005.6175	3.6542E-11	1193.285	7.088E-11	1381.79	1E-10	3613.2775	1.36071E-10
152.79075	-5.09831E-10	1009.4475	3.72963E-11	1197.0675	7.32355E-11	1385.585	9.969E-11	3617.0875	1.35135E-10
156.619	-5.04482E-10	1013.23	3.7427E-11	1200.885	7.26073E-11	1389.4175	1.03E-10	3620.8725	1.35727E-10
160.465	-4.98625E-10	1017.125	3.46045E-11	1204.71	7.4032E-11	1393.265	1.038E-10	3624.7175	1.34172E-10
164.2935	-4.93362E-10	1021.005	3.903E-11	1208.5325	7.48253E-11	1397.0875	1.008E-10	3628.5425	1.34909E-10
168.14675	-4.88058E-10	1024.7925	3.92968E-11	1212.3725	7.46863E-11	1400.9	1.03E-10	3632.395	1.36595E-10
171.99775	-4.83533E-10	1028.615	4.01053E-11	1216.215	7.5874E-11	1404.76	1.017E-10		

Table C.4: Benzene data at 24 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-5.5046E-10	192.0835	3.72537E-09	382.0413	7.3444E-09	572.36425	8.85308E-09	1847.185	1.02419E-08
3.90875	-5.5213E-10	195.86425	3.84404E-09	385.8295	7.399E-09	576.338	8.83829E-09	1850.9925	1.02548E-08
7.71925	-5.483E-10	199.6625	3.93144E-09	389.6478	7.457E-09	580.1515	8.87771E-09	1854.9375	1.02414E-08
11.53	-5.388E-10	203.45075	4.04211E-09	393.6665	7.5086E-09	583.9495	8.85384E-09	1858.6425	1.019E-08
15.3285	-5.1303E-10	207.26425	4.1702E-09	397.4823	7.5988E-09	587.918	8.89993E-09	1862.44	1.01076E-08
19.142	-4.7131E-10	211.06025	4.24523E-09	401.2705	7.5878E-09	591.7015	8.8699E-09	1866.24	1.01049E-08
22.925	-5.8166E-10	214.853	4.33545E-09	405.049	7.6528E-09	595.47975	8.91805E-09	1870.05	1.0178E-08
26.74575	-6.788E-10	218.6315	4.40771E-09	408.837	7.696E-09	599.47375	8.91906E-09	1873.9125	1.01104E-08
30.539	-8.8378E-10	222.41225	4.51643E-09	412.6155	7.7309E-09	603.27875	8.9423E-09	1877.72	1.01656E-08
34.365	-9.0967E-10	226.18825	4.62651E-09	416.391	7.8162E-09	607.2275	8.93315E-09	1881.545	1.01137E-08
38.156	-9.9639E-10	230.01375	4.69285E-09	420.177	7.8086E-09	611.2765	8.94797E-09	1885.3725	1.00358E-08
41.95175	-1.0762E-09	233.792	4.78558E-09	423.965	7.885E-09	615.05475	8.96524E-09	1889.1875	9.96734E-09
45.78	-9.6877E-10	237.5655	4.85618E-09	427.7785	7.9057E-09	618.84525	8.98579E-09	1893.015	1.00333E-08
49.553	-8.9112E-10	241.35625	4.92608E-09	431.567	7.9128E-09	622.7035	9.05377E-09	1896.855	1.00641E-08
53.3615	-7.4898E-10	245.13475	5.01983E-09	435.3425	7.9723E-09	626.61975	9.08573E-09	1900.6725	1.00374E-08
57.1525	-6.1191E-10	248.93775	5.12516E-09	439.1158	8.0453E-09	630.546	9.08438E-09	1904.475	9.98774E-09
60.933	-4.7423E-10	252.7335	5.16498E-09	442.894	8.0666E-09	634.33425	9.08507E-09	1908.275	9.85795E-09
64.93175	-2.9658E-10	256.547	5.24807E-09	446.675	8.0832E-09	638.1225	9.16025E-09	1912.08	9.92302E-09
68.72475	-1.8951E-10	260.368	5.33793E-09	450.4533	8.1701E-09	641.97325	9.13943E-09	1915.885	9.93602E-09
72.49825	-3.8763E-11	264.1435	5.37975E-09	454.2513	8.2114E-09	645.917	9.17195E-09	1919.6825	9.90522E-09
76.31675	1.0132E-10	267.924	5.46583E-09	458.0345	8.2032E-09	649.695	9.17633E-09	1923.545	9.89844E-09
80.12775	2.638E-10	271.705	5.56683E-09	461.8155	8.2334E-09	653.53575	9.21764E-09	1927.345	9.85446E-09
83.8955	4.2157E-10	275.5035	5.6367E-09	465.6065	8.267E-09	657.329	9.24181E-09	1931.1525	9.82749E-09
87.67625	5.3597E-10	279.2995	5.70517E-09	469.4098	8.2891E-09	661.13	9.25174E-09	1934.9575	9.84749E-09
91.48225	6.7693E-10	283.07475	5.74801E-09	473.213	8.3269E-09	664.9035	9.20929E-09	1938.76	9.82045E-09
95.26325	8.5116E-10	286.95825	5.81579E-09	476.996	8.3413E-09	668.694	9.24747E-09	1942.59	9.79252E-09
99.03625	9.7608E-10	290.75675	5.87517E-09	480.8245	8.3363E-09	672.9405	9.28434E-09	1946.3925	9.7322E-09
102.832	1.1529E-09	294.61025	5.94048E-09	484.6055	8.3838E-09	676.8715	9.25046E-09	1950.2	9.81014E-09
106.62275	1.2606E-09	298.39075	6.03516E-09	488.3885	8.4369E-09	680.66225	9.32885E-09	1954.005	9.80756E-09
110.43625	1.4054E-09	302.17925	6.09365E-09	492.1768	8.4137E-09	684.45325	9.36745E-09	1957.805	9.73988E-09
114.31475	1.5369E-09	305.95475	6.20047E-09	495.9928	8.4649E-09	688.26125	9.33952E-09	1961.6075	9.7565E-09
118.12025	1.6905E-09	309.75075	6.28542E-09	499.811	8.4597E-09	692.04725	9.35325E-09	1965.4	9.71869E-09
121.90625	1.8164E-09	313.54425	6.3145E-09	503.6068	8.4986E-09	696.64675	9.3966E-09	1969.2125	9.68107E-09
125.687	1.934E-09	317.33475	6.4121E-09	507.5978	8.4999E-09	700.43775	9.48001E-09	1973.0375	9.68277E-09
129.4855	2.0509E-09	321.138	6.45113E-09	511.3838	8.5151E-09	704.22575	9.29005E-09	1976.8775	9.66114E-09
133.261	2.1719E-09	324.90875	6.54339E-09	515.1798	8.5465E-09	708.0115	9.339E-09	1980.735	9.66891E-09
137.03675	2.2773E-09	328.71975	6.56438E-09	519.1255	8.5812E-09	719.94975	9.43678E-09	1984.5375	9.64418E-09
140.8175	2.4046E-09	332.513	6.6225E-09	522.919	8.5639E-09	723.896	9.35013E-09	1988.3325	9.59664E-09
144.591	2.5075E-09	336.32625	6.72613E-09	526.7098	8.5823E-09	727.66425	9.38774E-09	1992.125	9.65165E-09
148.37175	2.5971E-09	340.112	6.7662E-09	530.4903	8.6295E-09	731.44975	9.49579E-09	1995.93	9.66651E-09
152.18	2.7034E-09	343.9505	6.82748E-09	534.3263	8.6429E-09	735.24575	9.47028E-09	1999.73	9.60917E-09
155.953	2.8192E-09	347.72625	6.84775E-09	538.1495	8.6668E-09	739.029	9.46227E-09	2003.5325	9.59917E-09
161.6745	2.9939E-09	351.5145	6.89903E-09	541.938	8.67E-09	742.82225	9.52814E-09	2007.335	9.61252E-09
165.61075	3.0765E-09	355.30025	6.98333E-09	545.7235	8.6757E-09	746.6055	9.4581E-09	2011.135	9.57878E-09
169.38375	3.2019E-09	359.0885	7.03279E-09	549.512	8.7349E-09	750.38625	9.5864E-09	2015.1125	9.56935E-09
173.1695	3.2921E-09	362.877	7.08259E-09	553.2953	8.6769E-09	754.966	9.49714E-09	2018.925	9.58283E-09

Table C.5: Benzene data at 40 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-6.4931E-10	219.9256667	8.7878E-09	394.075	1.03895E-08	568.5986667	1.04324E-08	2774.163333	1.00998E-08
3.94933333	-6.76401E-10	223.705	8.8318E-09	397.8476667	1.04215E-08	572.3876667	1.04967E-08	2777.97	1.00913E-08
7.76533333	-6.98396E-10	227.4876667	8.948E-09	401.637	1.04086E-08	576.18	1.04245E-08	2781.763333	1.00752E-08
11.5943333	-7.05042E-10	231.263	8.9767E-09	405.4193333	1.03785E-08	579.989	1.04138E-08	2785.543333	1.00743E-08
15.3933333	-6.75473E-10	235.0386667	9.0653E-09	409.188	1.04092E-08	583.7683333	1.04587E-08	2789.343333	1.00972E-08
19.1956667	-6.66843E-10	238.8213333	9.1317E-09	412.9773333	1.04396E-08	587.561	1.04499E-08	2793.14	1.00441E-08
23.0016667	-5.71459E-10	242.6073333	9.2015E-09	416.75	1.03982E-08	591.3966667	1.04308E-08	2796.916667	1.00942E-08
26.811	-5.14682E-10	246.383	9.2818E-09	420.539	1.03747E-08	595.179	1.04806E-08	2800.713333	1.00692E-08
30.6133333	-7.49331E-10	250.1686667	9.3375E-09	424.3183333	1.04069E-08	598.9683333	1.0461E-08	2804.523333	1.00925E-08
34.4056667	-5.10147E-10	253.951	9.4381E-09	428.1036667	1.03792E-08	602.8443333	1.04248E-08	2808.33	1.00945E-08
38.1983333	-2.49708E-10	257.7303333	9.5252E-09	431.883	1.0388E-08	606.7203333	1.04205E-08	2812.123333	1.00841E-08
42.0006667	-2.14547E-11	261.5026667	9.541E-09	435.669	1.04818E-08	610.5023333	1.04116E-08	2815.913333	1.00449E-08
45.82	2.77131E-10	265.2786667	9.6207E-09	439.4513333	1.04182E-08	614.2916667	1.04269E-08	2819.703333	1.01298E-08
49.6586667	5.05004E-10	269.0673333	9.725E-09	443.247	1.04221E-08	618.0673333	1.05132E-08	2823.493333	1.00876E-08
53.4546667	7.79269E-10	272.8466667	9.7577E-09	447.026	1.04086E-08	621.8466667	1.04727E-08	2827.28	1.01112E-08
57.2273333	1.04328E-09	276.6356667	9.8025E-09	450.8053333	1.04079E-08	625.6356667	1.0538E-08	2831.086667	1.01168E-08
61.0033333	1.33121E-09	280.4283333	9.8743E-09	454.601	1.04288E-08	629.4146667	1.05391E-08	2834.9	1.01046E-08
64.7823333	1.55285E-09	284.2073333	9.9589E-09	458.397	1.04534E-08	633.2003333	1.04453E-08	2838.73	1.00909E-08
68.5576667	1.8168E-09	287.9796667	9.9635E-09	462.189	1.04451E-08	636.9796667	1.04878E-08	2842.606667	1.01168E-08
72.347	2.06189E-09	291.7923333	1.0005E-08	466.182	1.04356E-08	640.769	1.04562E-08	2846.42	1.01257E-08
76.1163333	2.27492E-09	295.5913333	1.0076E-08	469.9846667	1.04211E-08	644.548	1.04783E-08	2850.23	1.01096E-08
79.8853333	2.42718E-09	299.3873333	1.0093E-08	473.7636667	1.04026E-08	648.33	1.04754E-08	2854.023333	1.00529E-08
83.6706667	2.623E-09	303.1933333	1.0117E-08	477.553	1.03534E-08	652.1026667	1.04832E-08	2857.833333	1.01131E-08
87.4533333	2.74145E-09	306.989	1.0173E-08	481.3416667	1.03134E-08	655.8853333	1.0431E-08	2861.646667	1.00816E-08
91.2393333	2.94261E-09	310.7676667	1.0232E-08	485.121	1.02763E-08	659.6676667	1.04348E-08	2865.426667	1.00473E-08
95.0383333	3.08401E-09	314.5536667	1.0308E-08	488.91	1.02752E-08	663.4533333	1.04399E-08	2869.23	1.00756E-08
98.8176667	3.39928E-09	318.3396667	1.0327E-08	492.6893333	1.03416E-08	667.2556667	1.04225E-08	2873.03	1.00376E-08
102.616333	3.68241E-09	322.1153333	1.0278E-08	496.4686667	1.02656E-08	671.0283333	1.04848E-08	2876.83	1.0042E-08
106.392333	3.9329E-09	325.911	1.0358E-08	500.3943333	1.02731E-08	674.8176667	1.05133E-08	2880.633333	1.00269E-08
110.178333	4.19112E-09	329.7033333	1.0392E-08	504.18	1.02789E-08	678.65	1.05092E-08	2884.416667	1.00278E-08
113.977333	4.38962E-09	333.506	1.0392E-08	507.966	1.03099E-08	682.4286667	1.04808E-08	2888.273333	9.99939E-09
117.763	4.60553E-09	337.292	1.0367E-08	511.7583333	1.02632E-08	686.2113333	1.05206E-08	2892.056667	9.9702E-09
121.545667	4.81664E-09	341.0706667	1.0475E-08	515.554	1.02888E-08	690.0773333	1.04899E-08	2895.883333	1.00223E-08
125.318	5.10799E-09	344.8566667	1.0555E-08	519.3333333	1.03502E-08	693.8833333	1.05016E-08	2899.693333	1.00039E-08
129.103667	5.30275E-09	348.6256667	1.0449E-08	523.119	1.02986E-08	697.6726667	1.05183E-08	2903.483333	1.00189E-08
132.879667	5.55227E-09	352.4016667	1.0471E-08	526.9046667	1.02963E-08	701.448	1.05394E-08	2907.283333	9.98873E-09
136.658667	5.77436E-09	356.181	1.0519E-08	530.6873333	1.0344E-08	705.2503333	1.05344E-08	2911.086667	9.97998E-09
140.508	5.95119E-09	359.9763333	1.0368E-08	534.4763333	1.0338E-08	709.0863333	1.05307E-08	2914.93	9.9452E-09
144.307333	6.14095E-09	363.759	1.0453E-08	538.2553333	1.03629E-08	712.9023333	1.04599E-08	2919.356667	9.98189E-09
148.092667	6.30243E-09	367.5413333	1.0488E-08	542.0346667	1.0323E-08	716.848	1.04909E-08	2923.206667	9.97837E-09
151.868333	6.50193E-09	371.324	1.0481E-08	545.827	1.03938E-08	720.654	1.05237E-08	2926.993333	9.98312E-09
155.647667	6.65452E-09	375.1393333	1.0451E-08	549.6063333	1.0369E-08	724.6003333	1.04616E-08	2930.916667	9.94333E-09
159.433667	6.74937E-09	378.922	1.0433E-08	553.4116667	1.04284E-08	728.4263333	1.05062E-08	2934.693333	9.94176E-09
197.244667	8.15863E-09	382.698	1.0427E-08	557.2076667	1.03704E-08	732.215	1.04478E-08	2938.483333	9.9467E-09
201.02	8.23819E-09	386.4936667	1.0468E-08	560.987	1.03398E-08	736.0106667	1.04964E-08	2942.393333	1.00044E-08
204.799333	8.33856E-09	390.2996667	1.0466E-08	564.7826667	1.04078E-08	739.8266667	1.04396E-08	2946.183333	1.00364E-08

Table C.6: Benzene data at 55 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-5.1352E-10	190.223667	1.29819E-08	801.461	1.20086E-08	1000.22233	1.14928E-08	3421.46	1.26848E-08
5.23133333	-5.1063E-10	194.019667	1.30501E-08	805.27	1.19737E-08	1004.03433	1.14544E-08	3425.26	1.27182E-08
9.10733333	-5.0076E-10	197.862333	1.31185E-08	809.0693333	1.19468E-08	1007.83967	1.14511E-08	3429.05	1.27048E-08
12.8993333	-4.3947E-10	201.878	1.30655E-08	812.882	1.19344E-08	1011.68167	1.15159E-08	3432.856667	1.2665E-08
16.742	-7.3512E-10	205.727333	1.31585E-08	816.801	1.18942E-08	1015.49667	1.1523E-08	3436.653333	1.27429E-08
20.5146667	-7.0653E-10	209.53	1.32214E-08	820.607	1.18869E-08	1019.29	1.1623E-08	3440.446667	1.26902E-08
24.284	-3.2765E-10	213.366	1.3224E-08	824.456	1.18621E-08	1023.09333	1.16641E-08	3444.246667	1.26671E-08
28.0623333	1.53641E-10	217.165333	1.32481E-08	828.2486667	1.18904E-08	1026.91333	1.15672E-08	3448.043333	1.26639E-08
31.8383333	6.69755E-10	221.007333	1.33338E-08	832.051	1.18395E-08	1030.7	1.15709E-08	3451.856667	1.26852E-08
35.611	1.17998E-09	224.806667	1.3256E-08	835.9203333	1.18461E-08	1034.49333	1.15763E-08	3455.783333	1.2616E-08
39.4103333	1.69421E-09	228.599	1.33248E-08	839.7523333	1.1824E-08	1038.29333	1.15499E-08	3459.61	1.26394E-08
43.1926667	2.2729E-09	232.391667	1.3317E-08	843.5583333	1.1891E-08	1042.08333	1.15432E-08	3463.413333	1.26129E-08
46.9713333	2.73227E-09	236.187333	1.333E-08	847.3743333	1.19195E-08	1045.87667	1.14926E-08	3467.433333	1.26171E-08
50.7706667	3.25003E-09	239.983	1.33238E-08	851.187	1.19237E-08	1049.67667	1.14861E-08	3471.24	1.25738E-08
54.55	3.66893E-09	243.795667	1.33474E-08	855.113	1.19075E-08	1053.50333	1.1571E-08	3475.04	1.25558E-08
58.3323333	4.08148E-09	247.581333	1.3375E-08	858.9286667	1.18872E-08	1057.3	1.14845E-08	3478.856667	1.26164E-08
62.118	4.51698E-09	251.380667	1.33688E-08	862.7546667	1.20236E-08	1061.10333	1.14873E-08	3482.68	1.26359E-08
65.9273333	4.92071E-09	255.186333	1.34193E-08	866.5736667	1.19534E-08	1064.89667	1.1468E-08	3486.48	1.25329E-08
69.73	5.38106E-09	258.992	1.34327E-08	870.376	1.19117E-08	1068.69667	1.14804E-08	3490.323333	1.26076E-08
73.559	5.87595E-09	262.804667	1.33922E-08	874.3156667	1.18918E-08	1072.48333	1.14491E-08	3494.306667	1.25598E-08
77.7886667	6.46038E-09	266.600667	1.3374E-08	878.1913333	1.18638E-08	1076.29333	1.14476E-08	3498.103333	1.25432E-08
81.5876667	6.87159E-09	270.393333	1.34038E-08	882.047	1.17943E-08	1080.09	1.14284E-08	3502.04	1.25141E-08
85.4636667	7.30948E-09	274.195333	1.34222E-08	885.873	1.17349E-08	1083.89333	1.14181E-08	3505.866667	1.25623E-08
89.3	7.70716E-09	278.385	1.33625E-08	889.7456667	1.17684E-08	1087.68	1.14437E-08	3509.696667	1.25029E-08
93.1756667	8.10598E-09	282.171	1.33147E-08	893.5483333	1.17863E-08	1091.47667	1.14286E-08	3513.503333	1.25038E-08
96.978	8.46933E-09	285.963667	1.32663E-08	897.3773333	1.17411E-08	1095.29	1.14763E-08	3517.306667	1.24901E-08
100.780667	8.79299E-09	289.752667	1.32229E-08	901.1766667	1.17308E-08	1099.08667	1.14465E-08	3521.09	1.245E-08
104.576333	9.16769E-09	293.544667	1.31479E-08	904.979	1.16873E-08	1102.87667	1.14064E-08	3524.906667	1.25114E-08
108.458667	9.46684E-09	297.360667	1.30115E-08	908.8013333	1.17646E-08	1106.68333	1.14412E-08	3528.7	1.25234E-08
112.244667	9.76158E-09	301.156667	1.30093E-08	912.6073333	1.16923E-08	1110.49333	1.14602E-08	3532.49	1.2462E-08
116.027333	1.00838E-08	304.966	1.29427E-08	916.3996667	1.17091E-08	1114.3	1.14395E-08	3536.3	1.2501E-08
119.819667	1.03165E-08	308.825	1.28768E-08	920.356	1.17266E-08	1118.09333	1.14298E-08	3540.143333	1.24871E-08
123.598667	1.06185E-08	312.627333	1.28498E-08	924.1516667	1.16932E-08	1121.89	1.15317E-08	3543.923333	1.24794E-08
127.387667	1.09061E-08	316.433333	1.2787E-08	927.954	1.16649E-08	1125.71667	1.14784E-08	3547.906667	1.24395E-08
131.187	1.11046E-08	320.236	1.26647E-08	931.7633333	1.17076E-08	1129.52	1.15412E-08	3551.74	1.24361E-08
134.996333	1.1346E-08	324.058333	1.26325E-08	935.5656667	1.17065E-08	1133.57333	1.15521E-08	3555.556667	1.24321E-08
138.802	1.15437E-08	327.860667	1.25664E-08	939.365	1.16959E-08	1137.42	1.16255E-08	3559.363333	1.23914E-08
144.460333	1.18116E-08	331.686333	1.25074E-08	943.174	1.17534E-08	1141.21667	1.16151E-08	3563.16	1.24038E-08
148.243	1.19734E-08	335.482333	1.24829E-08	946.9733333	1.17743E-08	1145.01333	1.16623E-08	3566.953333	1.24004E-08
152.032	1.21551E-08	339.311667	1.2459E-08	950.7956667	1.17352E-08	1148.82	1.17429E-08	3570.76	1.23479E-08
155.844667	1.22803E-08	343.150667	1.24182E-08	954.6013333	1.17296E-08	1152.60333	1.17534E-08	3574.56	1.23412E-08
159.643667	1.24224E-08	346.953333	1.24266E-08	958.4006667	1.16867E-08	1156.39	1.17479E-08	3578.36	1.23186E-08
163.476	1.2501E-08	350.745667	1.23728E-08	962.2366667	1.167E-08	1160.2	1.17834E-08	3582.24	1.23586E-08
167.262	1.25553E-08	354.594667	1.22991E-08	966.0256667	1.1605E-08	1163.98333	1.17922E-08	3586.053333	1.23315E-08
171.054667	1.27008E-08	358.410667	1.22876E-08	969.8316667	1.16077E-08	1167.79333	1.17575E-08	3589.873333	1.2343E-08
174.860667	1.27848E-08	362.216667	1.23329E-08	973.6236667	1.16016E-08	1171.59333	1.18681E-08	3593.683333	1.2368E-08

Table C.7: Benzene data at 70 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-5.01693E-10	174.737	1.10243E-08	349.269	1.28164E-08	930.156	1.52711E-08	3330.53	1.32546E-08
3.936	-5.18252E-10	178.528	1.11286E-08	353.1145	1.29694E-08	933.942	1.53247E-08	3334.355	1.32295E-08
7.747	-4.97164E-10	182.329	1.1237E-08	356.905	1.30752E-08	937.7425	1.53374E-08	3338.16	1.32148E-08
11.548	-3.55789E-10	186.134	1.13889E-08	360.701	1.3055E-08	941.5335	1.53763E-08	3342.135	1.32163E-08
15.3535	-3.2747E-10	189.93	1.15309E-08	364.492	1.31038E-08	945.329	1.53531E-08	3345.945	1.31649E-08
19.1245	7.03633E-11	193.711	1.16102E-08	368.278	1.30856E-08	949.13	1.5327E-08	3349.725	1.30962E-08
22.93	6.08801E-10	197.512	1.17519E-08	372.159	1.3139E-08	952.916	1.53755E-08	3353.98	1.30366E-08
26.696	1.15078E-09	201.303	1.18354E-08	375.949	1.30265E-08	956.7065	1.54382E-08	3357.785	1.30539E-08
30.5065	1.69288E-09	205.098	1.19057E-08	379.74	1.30297E-08	960.5075	1.54462E-08	3361.605	1.30521E-08
34.2825	2.15357E-09	208.909	1.19753E-08	383.596	1.29711E-08	964.298	1.54691E-08	3365.41	1.31028E-08
38.0535	2.66319E-09	212.695	1.20281E-08	387.7475	1.30025E-08	968.124	1.54479E-08	3369.215	1.31034E-08
41.829	3.15195E-09	216.481	1.20795E-08	391.5935	1.29941E-08	971.925	1.54812E-08	3373.03	1.29967E-08
45.6145	3.56321E-09	220.277	1.20632E-08	395.399	1.30371E-08	975.7255	1.55081E-08	3376.85	1.29519E-08
49.3805	3.95744E-09	224.067	1.20887E-08	399.21	1.30737E-08	979.5065	1.54957E-08	3380.655	1.28441E-08
53.1615	4.37818E-09	227.863	1.21218E-08	403.066	1.31069E-08	983.307	1.5497E-08	3384.46	1.28326E-08
56.9375	4.67217E-09	231.669	1.21415E-08	406.8565	1.31903E-08	987.103	1.55242E-08	3388.265	1.28202E-08
60.7225	5.02838E-09	235.455	1.21712E-08	410.6775	1.311E-08	990.899	1.55426E-08	3392.12	1.27827E-08
64.5435	5.31064E-09	239.251	1.22669E-08	414.513	1.31208E-08	994.705	1.55018E-08	3395.96	1.27505E-08
68.3195	5.49625E-09	243.051	1.2239E-08	418.334	1.31749E-08	998.496	1.5519E-08	3399.885	1.27556E-08
72.0905	5.79916E-09	246.847	1.22844E-08	422.135	1.32017E-08	1002.29	1.55497E-08	3403.72	1.27653E-08
75.871	6.05051E-09	250.638	1.22872E-08	425.961	1.31517E-08	1006.085	1.55873E-08	3407.585	1.2897E-08
79.6565	6.27626E-09	254.434	1.23571E-08	429.827	1.32469E-08	1009.88	1.56406E-08	3411.39	1.29125E-08
83.4275	6.59329E-09	258.2195	1.23096E-08	433.6225	1.32263E-08	1013.675	1.55129E-08	3415.33	1.29179E-08
87.2285	6.9064E-09	262.005	1.23917E-08	437.443	1.32147E-08	1017.465	1.54675E-08	3419.265	1.29361E-08
91.0045	7.1386E-09	265.801	1.23933E-08	441.274	1.32749E-08	1021.255	1.5455E-08	3423.07	1.2884E-08
94.78	7.3565E-09	269.582	1.24392E-08	445.08	1.32049E-08	1025.07	1.5445E-08	3426.88	1.29052E-08
98.5605	7.59923E-09	273.378	1.23991E-08	448.906	1.32637E-08	1028.885	1.54499E-08	3430.7	1.28896E-08
102.3415	7.86641E-09	277.1685	1.23544E-08	452.712	1.3257E-08	1032.67	1.55707E-08	3434.51	1.29327E-08
106.1325	8.13266E-09	280.954	1.23395E-08	456.5125	1.31942E-08	1036.475	1.55417E-08	3438.365	1.29557E-08
109.933	8.32569E-09	284.76	1.23767E-08	460.5585	1.33488E-08	1040.27	1.55321E-08	3442.16	1.29604E-08
113.7135	8.66244E-09	288.546	1.2314E-08	464.3445	1.32974E-08	1044.065	1.5444E-08	3445.965	1.30131E-08
117.4895	8.90228E-09	292.342	1.2348E-08	468.1305	1.33955E-08	1047.87	1.54533E-08	3449.78	1.29777E-08
121.5105	9.18578E-09	296.1425	1.23537E-08	471.921	1.33787E-08	1051.655	1.54872E-08	3453.6	1.30059E-08
125.3165	9.22251E-09	299.928	1.24476E-08	475.7465	1.34928E-08	1055.44	1.5539E-08	3457.42	1.30624E-08
129.1175	9.42554E-09	303.719	1.25038E-08	479.618	1.35502E-08	1059.24	1.56111E-08	3461.26	1.30348E-08
132.918	9.57613E-09	307.525	1.24003E-08	483.3935	1.35684E-08	1063.075	1.55808E-08	3465.07	1.30792E-08
136.719	9.71318E-09	311.311	1.2388E-08	487.1745	1.34888E-08	1066.885	1.56118E-08	3469.015	1.2968E-08
140.515	9.84218E-09	315.1015	1.23953E-08	490.985	1.35591E-08	1070.705	1.56112E-08	3472.965	1.30081E-08
144.3105	1.00136E-08	318.897	1.24769E-08	494.781	1.36476E-08	1074.525	1.57053E-08	3476.78	1.30322E-08
148.1015	1.01334E-08	322.678	1.24759E-08	498.652	1.3735E-08	1078.44	1.56283E-08	3480.605	1.31346E-08
151.962	1.02459E-08	326.464	1.25442E-08	502.483	1.38905E-08	1082.27	1.56491E-08	3484.69	1.31093E-08
155.768	1.03963E-08	330.26	1.25293E-08	506.299	1.39449E-08	1086.055	1.56007E-08	3488.515	1.31105E-08
159.554	1.0536E-08	334.035	1.26492E-08	510.084	1.40765E-08	1089.86	1.55972E-08	3492.35	1.30718E-08
163.36	1.0645E-08	337.831	1.26521E-08	513.94	1.40349E-08	1093.655	1.56198E-08	3496.22	1.31804E-08
167.155	1.07479E-08	341.627	1.27078E-08	518.0215	1.40245E-08	1097.44	1.56518E-08	3500.045	1.31345E-08
170.936	1.09049E-08	345.468	1.27561E-08	521.8025	1.41582E-08	1101.235	1.57213E-08	3503.875	1.32002E-08

Table C.8: Benzene data at 90 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-8.83E-10	189.729	1.14E-08	379.259	2.11E-08	554.967	2.65E-08	2571.39	2.87E-08
3.795	-8.79E-10	193.515	1.16E-08	383.055	2.13E-08	558.753	2.65E-08	2575.16	2.87E-08
7.781	-8.68E-10	197.301	1.19E-08	386.83	2.14E-08	562.549	2.66E-08	2578.95	2.87E-08
11.617	-8.25E-10	201.087	1.21E-08	390.616	2.15E-08	566.495	2.67E-08	2582.75	2.87E-08
15.453	-7.22E-10	204.872	1.24E-08	394.402	2.17E-08	570.501	2.68E-08	2586.55	2.86E-08
19.229	-5.73E-10	208.688	1.26E-08	398.188	2.19E-08	574.307	2.69E-08	2590.34	2.86E-08
23.095	-3.74E-10	212.474	1.28E-08	402.094	2.20E-08	578.233	2.70E-08	2594.13	2.87E-08
26.861	-1.09E-09	216.26	1.30E-08	405.89	2.21E-08	582.019	2.70E-08	2597.93	2.86E-08
30.706	-8.58E-10	220.056	1.33E-08	409.665	2.23E-08	585.814	2.71E-08	2601.7	2.86E-08
34.492	-5.87E-10	223.841	1.35E-08	413.451	2.24E-08	589.6	2.72E-08	2605.5	2.86E-08
38.268	-2.96E-10	227.637	1.37E-08	417.247	2.25E-08	593.396	2.72E-08	2609.32	2.86E-08
42.104	1.66E-11	231.433	1.40E-08	421.023	2.26E-08	597.202	2.73E-08	2613.12	2.86E-08
45.89	3.10E-10	235.209	1.42E-08	424.879	2.27E-08	601.018	2.74E-08	2616.93	2.86E-08
49.715	6.24E-10	239.005	1.44E-08	428.674	2.28E-08	604.833	2.75E-08	2620.73	2.87E-08
53.481	9.30E-10	242.78	1.46E-08	432.48	2.29E-08	608.639	2.75E-08	2624.54	2.87E-08
57.327	1.23E-09	246.546	1.48E-08	436.326	2.31E-08	612.475	2.75E-08	2628.34	2.87E-08
61.083	1.53E-09	250.322	1.50E-08	440.242	2.32E-08	616.291	2.75E-08	2632.13	2.87E-08
64.869	1.85E-09	254.118	1.52E-08	444.038	2.33E-08	620.077	2.76E-08	2635.94	2.87E-08
68.654	2.16E-09	257.893	1.55E-08	448.074	2.35E-08	623.903	2.77E-08	2639.72	2.87E-08
72.42	2.46E-09	261.689	1.56E-08	451.92	2.36E-08	627.799	2.77E-08	2643.51	2.87E-08
76.206	2.77E-09	265.465	1.59E-08	456.186	2.38E-08	631.594	2.78E-08	2647.34	2.87E-08
79.992	3.07E-09	269.241	1.61E-08	459.982	2.39E-08	635.49	2.79E-08	2651.13	2.87E-08
83.767	3.39E-09	273.277	1.63E-08	463.798	2.40E-08	639.296	2.79E-08	2654.93	2.87E-08
87.563	3.67E-09	277.033	1.65E-08	467.594	2.42E-08	643.112	2.80E-08	2658.74	2.87E-08
91.339	3.98E-09	280.808	1.67E-08	471.37	2.42E-08	647.008	2.80E-08	2662.61	2.87E-08
95.135	4.28E-09	284.604	1.69E-08	475.155	2.43E-08	650.844	2.81E-08	2666.39	2.87E-08
98.921	4.58E-09	288.38	1.70E-08	479.021	2.44E-08	654.64	2.82E-08	2670.25	2.88E-08
102.696	4.87E-09	292.166	1.72E-08	482.807	2.45E-08	658.435	2.82E-08	2674.03	2.87E-08
106.472	5.13E-09	295.952	1.74E-08	486.693	2.46E-08	662.231	2.83E-08	2677.83	2.85E-08
110.248	5.42E-09	299.717	1.76E-08	490.489	2.48E-08	666.037	2.83E-08	2681.62	2.87E-08
114.024	5.68E-09	303.493	1.77E-08	494.295	2.49E-08	669.843	2.84E-08	2685.4	2.87E-08
117.799	5.98E-09	307.309	1.79E-08	498.07	2.50E-08	673.689	2.84E-08	2689.19	2.87E-08
121.585	6.26E-09	311.075	1.81E-08	501.856	2.51E-08	677.635	2.85E-08	2693.04	2.87E-08
125.361	6.53E-09	314.85	1.83E-08	505.662	2.52E-08	681.431	2.86E-08	2696.84	2.87E-08
129.137	6.81E-09	318.636	1.85E-08	509.478	2.53E-08	685.286	2.86E-08	2700.64	2.87E-08
132.913	7.08E-09	322.422	1.86E-08	513.264	2.54E-08	689.082	2.86E-08	2704.43	2.87E-08
136.678	7.34E-09	326.218	1.89E-08	517.049	2.55E-08	692.898	2.87E-08	2708.21	2.86E-08
140.464	7.95E-09	330.004	1.91E-08	520.835	2.56E-08	696.694	2.88E-08	2711.99	2.87E-08
144.25	8.23E-09	333.819	1.92E-08	524.611	2.58E-08	700.48	2.88E-08	2715.79	2.87E-08
148.036	8.54E-09	337.615	1.93E-08	528.397	2.58E-08	704.275	2.89E-08	2719.57	2.86E-08
151.841	8.79E-09	341.401	1.95E-08	532.172	2.60E-08	708.081	2.89E-08	2723.42	2.87E-08
155.617	9.08E-09	345.187	1.97E-08	535.948	2.60E-08	711.897	2.90E-08	2727.21	2.87E-08
159.403	9.34E-09	348.983	1.98E-08	539.764	2.61E-08	715.683	2.90E-08	2731	2.86E-08
163.219	9.60E-09	352.768	2.00E-08	543.58	2.62E-08	719.489	2.90E-08	3602.95	2.64E-08
166.995	9.95E-09	356.544	2.01E-08	547.356	2.63E-08	723.294	2.91E-08	3606.78	2.63E-08
170.78	1.02E-08	360.34	2.03E-08	551.182	2.64E-08	727.11	2.91E-08	3610.6	2.64E-08

Table C.9: Benzene data at 24 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-4.96517E-10	174.267	4.12289E-08	348.773	5.5012E-08	524.221	5.8641E-08	3007.1	4.3224E-08
3.806	-5.00647E-10	178.062	4.16922E-08	352.539	5.51756E-08	528.057	5.85904E-08	3010.88	4.32911E-08
7.582	-5.29764E-10	181.838	4.2159E-08	356.365	5.53445E-08	531.843	5.85438E-08	3014.68	4.33154E-08
11.368	-1.08743E-09	185.604	4.26637E-08	360.231	5.54894E-08	535.619	5.84758E-08	3018.46	4.32993E-08
15.164	-3.52584E-10	189.39	4.3101E-08	363.997	5.56314E-08	539.404	5.86588E-08	3022.24	4.32768E-08
18.989	7.11713E-10	193.176	4.35374E-08	367.772	5.56632E-08	543.18	5.86981E-08	3026.15	4.32485E-08
22.775	1.93528E-09	196.961	4.39588E-08	371.558	5.57025E-08	546.996	5.86316E-08	3029.94	4.32487E-08
26.561	3.25587E-09	200.747	4.44236E-08	375.404	5.58529E-08	550.802	5.8696E-08	3033.73	4.32922E-08
30.337	4.6452E-09	204.513	4.47871E-08	379.19	5.60012E-08	554.578	5.87783E-08	3037.61	4.32646E-08
34.113	6.05242E-09	208.289	4.51796E-08	382.966	5.61789E-08	558.454	5.89479E-08	3041.62	4.33271E-08
37.898	7.694E-09	212.084	4.5577E-08	386.751	5.62504E-08	562.139	5.91407E-08	3045.61	4.33501E-08
41.674	9.27818E-09	215.87	4.59287E-08	390.617	5.63746E-08	566.005	5.92095E-08	3049.37	4.34589E-08
45.48	1.06798E-08	219.656	4.63259E-08	394.393	5.64013E-08	569.791	5.92787E-08	3053.15	4.35378E-08
49.266	1.20817E-08	223.452	4.66762E-08	398.179	5.63516E-08	573.567	5.92873E-08	3056.95	4.3547E-08
53.072	1.34684E-08	227.218	4.70552E-08	401.955	5.63529E-08	577.433	5.92536E-08	3060.76	4.35317E-08
56.837	1.47782E-08	231.083	4.73642E-08	405.72	5.64115E-08	581.489	5.92554E-08	3064.56	4.34528E-08
60.623	1.60746E-08	234.869	4.78041E-08	409.496	5.65336E-08	585.275	5.9063E-08	3068.34	4.34728E-08
64.389	1.73604E-08	238.645	4.81937E-08	413.262	5.66388E-08	589.11	5.91005E-08	3072.12	4.34328E-08
68.165	1.8567E-08	242.431	4.85767E-08	417.038	5.68281E-08	992.366	6.41311E-08	3075.91	4.34579E-08
71.96	1.97684E-08	246.207	4.89022E-08	420.833	5.69261E-08	996.212	6.36574E-08	3079.72	4.34598E-08
75.736	2.09113E-08	250.042	4.91991E-08	424.679	5.70283E-08	1000.05	6.32963E-08	3083.49	4.35368E-08
79.512	2.2026E-08	253.838	4.94419E-08	428.465	5.72058E-08	1003.83	6.30743E-08	3087.27	4.34473E-08
83.308	2.31207E-08	257.644	4.97238E-08	432.321	5.72568E-08	1007.71	6.27747E-08	3091.06	4.34644E-08
87.094	2.41327E-08	261.42	5.01103E-08	436.107	5.71996E-08	1011.5	6.25035E-08	3094.84	4.34764E-08
90.899	2.51487E-08	265.216	5.03775E-08	439.902	5.73057E-08	1015.4	6.24124E-08	3098.6	4.34754E-08
94.695	2.61177E-08	269.011	5.05836E-08	443.678	5.7335E-08	1019.3	6.22669E-08	3102.4	4.34436E-08
98.491	2.7078E-08	272.847	5.09007E-08	447.524	5.7443E-08	1023.13	6.22455E-08	3106.18	4.33266E-08
102.287	2.79524E-08	276.633	5.11782E-08	451.811	5.76763E-08	1027.1	6.21362E-08	3109.95	4.32939E-08
106.083	2.88381E-08	280.399	5.14877E-08	455.546	5.78343E-08	1030.94	6.20551E-08	3113.82	4.32294E-08
109.878	2.97299E-08	284.495	5.17334E-08	459.372	5.80124E-08	1034.75	6.20201E-08	3117.6	4.31964E-08
113.674	3.05396E-08	288.281	5.20459E-08	463.178	5.80366E-08	1038.61	6.20134E-08	3121.37	4.31809E-08
117.47	3.13664E-08	292.077	5.22489E-08	466.994	5.80515E-08	1042.43	6.19904E-08	3125.18	4.31147E-08
121.276	3.21891E-08	295.842	5.25111E-08	470.78	5.78864E-08	1046.32	6.18877E-08	3128.97	4.30454E-08
125.072	3.29317E-08	299.638	5.27385E-08	474.565	5.79754E-08	1050.15	6.20409E-08	3132.75	4.29972E-08
128.867	3.36699E-08	303.404	5.28385E-08	478.772	5.82101E-08	1053.99	6.19387E-08	3136.53	4.29346E-08
132.663	3.4418E-08	307.19	5.30274E-08	482.618	5.82871E-08	1057.89	6.16911E-08	3140.31	4.29085E-08
136.459	3.51553E-08	310.976	5.32027E-08	486.434	5.81961E-08	1061.72	6.14111E-08	3144.2	4.29291E-08
140.235	3.58364E-08	314.751	5.33267E-08	490.219	5.83154E-08	1065.6	6.1421E-08	3148.11	4.30499E-08
144.02	3.65607E-08	318.527	5.36294E-08	493.985	5.83098E-08	1069.39	6.14728E-08	3151.98	4.31177E-08
147.796	3.71793E-08	322.303	5.38791E-08	497.781	5.84194E-08	1073.26	6.15989E-08	3155.76	4.31066E-08
151.582	3.78539E-08	326.079	5.40882E-08	501.567	5.84632E-08	1077.14	6.17489E-08	3159.56	4.30532E-08
155.368	3.84112E-08	329.864	5.42795E-08	505.342	5.85422E-08	1081.02	6.17038E-08	3634.89	4.16536E-08
159.154	3.90479E-08	333.65	5.44282E-08	509.108	5.84544E-08	1084.93	6.16243E-08	3638.68	4.1696E-08
162.939	3.9638E-08	337.416	5.45364E-08	512.904	5.85584E-08	1088.78	6.15226E-08	3642.49	4.16577E-08
166.715	4.01746E-08	341.222	5.46783E-08	516.67	5.86717E-08	1092.62	6.14341E-08	3646.28	4.16437E-08
170.491	4.07218E-08	345.008	5.4832E-08	520.446	5.86951E-08	1096.42	6.13228E-08	3650.11	4.15806E-08

Table C.10: Benzene data at 40 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-8.27E-10	173.889	6.80E-08	347.14	7.53E-08	520.495	7.76E-08	2948.02	6.74E-08
3.836	-7.02E-10	177.655	6.84E-08	350.906	7.54E-08	524.261	7.73E-08	2951.8	6.74E-08
7.602	-7.75E-10	181.451	6.88E-08	354.692	7.52E-08	528.027	7.72E-08	2955.57	6.72E-08
11.438	1.20E-09	185.217	6.93E-08	358.468	7.58E-08	531.802	7.70E-08	2959.35	6.65E-08
15.214	3.90E-09	188.983	7.02E-08	362.243	7.59E-08	535.568	7.73E-08	2963.12	6.61E-08
18.98	6.99E-09	192.749	7.08E-08	366.009	7.56E-08	539.334	7.73E-08	2966.88	6.58E-08
22.755	1.07E-08	196.524	7.15E-08	369.775	7.55E-08	980.838	7.45E-08	2970.67	6.55E-08
26.531	1.40E-08	200.29	7.18E-08	373.541	7.58E-08	984.604	7.41E-08	2974.44	6.44E-08
30.317	1.73E-08	204.076	7.23E-08	377.316	7.58E-08	988.38	7.36E-08	2978.22	6.38E-08
34.093	2.05E-08	207.842	7.29E-08	381.082	7.53E-08	992.156	7.28E-08	2982.01	6.42E-08
37.869	2.35E-08	211.618	7.30E-08	384.848	7.50E-08	995.932	7.25E-08	2985.77	6.51E-08
41.665	2.64E-08	215.394	7.31E-08	388.624	7.51E-08	999.697	7.24E-08	2989.54	6.52E-08
45.441	2.91E-08	219.159	7.33E-08	392.39	7.54E-08	1003.47	7.22E-08	2993.32	6.55E-08
49.226	3.16E-08	222.935	7.36E-08	396.155	7.57E-08	1007.25	7.23E-08	2997.09	6.56E-08
53.012	3.40E-08	226.721	7.38E-08	399.941	7.57E-08	1011.03	7.23E-08	3000.86	6.57E-08
56.788	3.61E-08	230.517	7.40E-08	403.697	7.55E-08	1014.8	7.20E-08	3004.65	6.56E-08
60.574	3.83E-08	234.293	7.40E-08	407.463	7.52E-08	1018.57	7.19E-08	3008.42	6.55E-08
64.35	4.02E-08	238.069	7.40E-08	411.238	7.51E-08	1022.35	7.20E-08	3012.2	6.53E-08
68.116	4.21E-08	241.279	7.37E-08	415.004	7.48E-08	1026.16	7.24E-08	3015.97	6.54E-08
71.882	4.38E-08	245.064	7.36E-08	418.76	7.44E-08	1029.92	7.25E-08	3019.73	6.53E-08
75.657	4.53E-08	248.85	7.33E-08	422.546	7.47E-08	1033.7	7.24E-08	3023.51	6.53E-08
79.433	4.68E-08	252.636	7.36E-08	426.301	7.51E-08	1037.47	7.26E-08	3027.27	6.53E-08
83.219	4.83E-08	256.412	7.35E-08	430.067	7.49E-08	1041.25	7.25E-08	3031.04	6.50E-08
87.005	4.97E-08	260.188	7.36E-08	433.823	7.45E-08	1045.03	7.26E-08	3034.82	6.49E-08
90.771	5.11E-08	263.983	7.35E-08	437.579	7.44E-08	1048.81	7.28E-08	3038.58	6.46E-08
94.567	5.25E-08	267.769	7.37E-08	441.354	7.41E-08	1052.58	7.26E-08	3042.35	6.41E-08
98.342	5.35E-08	271.555	7.38E-08	445.13	7.42E-08	1056.36	7.23E-08	3046.12	6.40E-08
102.118	5.47E-08	275.331	7.38E-08	448.886	7.41E-08	1060.14	7.23E-08	3049.89	6.50E-08
105.904	5.57E-08	279.106	7.42E-08	452.662	7.37E-08	1063.91	7.23E-08	3053.66	6.55E-08
109.67	5.66E-08	282.882	7.47E-08	456.437	7.42E-08	1067.69	7.24E-08	3057.44	6.58E-08
113.436	5.76E-08	286.658	7.48E-08	460.193	7.49E-08	1071.47	7.29E-08	3061.22	6.58E-08
117.222	5.85E-08	290.454	7.50E-08	463.969	7.52E-08	1075.25	7.31E-08	3065.01	6.60E-08
120.998	5.94E-08	294.22	7.51E-08	467.735	7.56E-08	1079.04	7.34E-08	3068.78	6.63E-08
124.783	6.03E-08	298.005	7.47E-08	471.49	7.60E-08	1082.83	7.30E-08	3072.54	6.64E-08
128.569	6.09E-08	301.791	7.44E-08	475.266	7.61E-08	1086.63	7.30E-08	3076.31	6.64E-08
132.345	6.16E-08	305.577	7.41E-08	479.032	7.61E-08	1090.42	7.35E-08	3080.08	6.65E-08
136.111	6.22E-08	309.343	7.45E-08	482.798	7.68E-08	1094.19	7.34E-08	3083.85	6.64E-08
139.887	6.28E-08	313.118	7.56E-08	486.583	7.70E-08	1097.97	7.37E-08	3087.63	6.65E-08
143.653	6.35E-08	316.894	7.62E-08	490.339	7.73E-08	1101.75	7.38E-08	3091.4	6.67E-08
147.418	6.42E-08	320.67	7.63E-08	494.115	7.75E-08	1105.54	7.33E-08	3552.09	6.62E-08
151.204	6.50E-08	324.456	7.51E-08	497.891	7.74E-08	1109.32	7.35E-08	3555.85	6.61E-08
154.97	6.56E-08	328.221	7.43E-08	501.646	7.73E-08	1113.09	7.36E-08	3559.62	6.61E-08
158.736	6.61E-08	331.987	7.48E-08	505.422	7.74E-08	1116.87	7.34E-08	3563.39	6.61E-08
162.522	6.67E-08	335.773	7.54E-08	509.188	7.76E-08	1120.65	7.32E-08	3578.48	6.68E-08
166.308	6.70E-08	339.569	7.56E-08	512.964	7.76E-08	1124.42	7.32E-08	3582.25	6.68E-08
170.094	6.75E-08	343.355	7.56E-08	516.729	7.78E-08	1128.21	7.30E-08	3586.04	6.70E-08

Table C.11: Benzene data at 55 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-5.75E-10	173.925	7.08E-08	347.941	8.18E-08	523.059	8.44E-08	2854.52	8.74E-08
3.785	-4.88E-10	177.701	7.24E-08	351.727	8.18E-08	526.844	8.77E-08	2858.29	8.66E-08
7.681	-4.23E-10	181.477	7.28E-08	355.503	8.17E-08	530.63	8.90E-08	2862.05	8.73E-08
11.427	1.82E-09	185.263	7.31E-08	359.288	8.18E-08	534.406	8.96E-08	2865.84	8.85E-08
15.193	4.80E-09	189.028	7.34E-08	363.064	8.22E-08	538.192	8.98E-08	2869.61	8.84E-08
18.958	8.61E-09	192.804	7.41E-08	366.83	8.20E-08	541.957	8.97E-08	2873.4	8.79E-08
22.744	1.23E-08	196.62	7.37E-08	370.616	8.12E-08	545.733	9.00E-08	3446.7	8.36E-08
26.53	1.63E-08	200.396	7.34E-08	374.391	8.04E-08	549.519	8.97E-08	3450.47	8.32E-08
30.306	2.04E-08	204.191	7.36E-08	378.187	7.99E-08	553.285	8.89E-08	3454.25	8.17E-08
34.102	2.37E-08	207.987	7.36E-08	381.973	8.09E-08	557.061	8.76E-08	3458.04	8.08E-08
37.887	2.67E-08	211.763	7.38E-08	385.749	8.15E-08	560.826	8.69E-08	3461.81	8.04E-08
41.673	3.00E-08	215.549	7.39E-08	389.525	8.16E-08	564.592	8.64E-08	3465.58	8.08E-08
45.469	3.37E-08	219.315	7.42E-08	393.31	8.33E-08	568.388	8.59E-08	3469.39	8.09E-08
49.235	3.72E-08	223.1	7.45E-08	397.086	8.45E-08	572.164	8.61E-08	3473.16	8.11E-08
53	3.98E-08	226.886	7.46E-08	400.852	8.50E-08	575.939	8.56E-08	3476.92	8.16E-08
56.846	4.19E-08	230.652	7.44E-08	404.628	8.49E-08	579.725	8.55E-08	3480.71	8.19E-08
60.622	4.38E-08	234.428	7.48E-08	408.614	8.44E-08	583.491	8.53E-08	3484.51	8.19E-08
64.398	4.51E-08	238.203	7.49E-08	412.4	8.41E-08	587.287	8.52E-08	3488.3	8.20E-08
68.174	4.68E-08	242.019	7.48E-08	416.195	8.36E-08	591.072	8.54E-08	3492.08	8.29E-08
71.949	4.90E-08	245.795	7.51E-08	419.981	8.39E-08	594.838	8.55E-08	3495.86	8.29E-08
75.735	5.07E-08	249.591	7.52E-08	423.877	8.41E-08	598.624	8.55E-08	3499.64	8.31E-08
79.491	5.20E-08	253.387	7.51E-08	428.033	8.45E-08	602.41	8.55E-08	3503.44	8.31E-08
83.257	5.31E-08	257.172	7.54E-08	431.799	8.42E-08	606.196	8.57E-08	3507.22	8.27E-08
87.032	5.36E-08	260.948	7.61E-08	435.585	8.45E-08	609.971	8.57E-08	3511.03	8.19E-08
90.808	5.43E-08	264.714	7.71E-08	439.351	8.45E-08	613.747	8.55E-08	3514.82	8.24E-08
94.584	5.51E-08	268.48	7.74E-08	443.126	8.39E-08	617.513	8.54E-08	3518.71	8.27E-08
98.36	5.77E-08	272.255	7.68E-08	446.902	8.40E-08	621.289	8.50E-08	3522.51	8.30E-08
102.126	5.98E-08	276.021	7.73E-08	450.668	8.53E-08	625.064	8.39E-08	3526.29	8.32E-08
105.891	6.09E-08	279.807	7.77E-08	454.624	8.83E-08	628.83	8.43E-08	3530.07	8.30E-08
109.667	6.16E-08	283.613	7.81E-08	458.44	8.90E-08	632.636	8.51E-08	3533.86	8.33E-08
113.443	6.24E-08	287.399	7.92E-08	462.206	8.90E-08	636.412	8.64E-08	3537.62	8.36E-08
117.219	6.33E-08	291.184	8.00E-08	465.981	8.83E-08	640.188	8.73E-08	3541.4	8.38E-08
121.004	6.41E-08	294.98	7.99E-08	469.777	8.65E-08	643.973	8.85E-08	3545.21	8.32E-08
124.79	6.48E-08	298.756	8.08E-08	473.583	8.57E-08	647.739	8.80E-08	3548.98	8.39E-08
128.556	6.67E-08	302.532	8.07E-08	477.499	8.69E-08	651.505	8.81E-08	3552.75	8.50E-08
132.342	6.78E-08	306.327	8.08E-08	481.285	8.75E-08	655.291	8.96E-08	3556.53	8.59E-08
136.117	6.84E-08	310.113	7.98E-08	485.061	8.76E-08	659.066	9.07E-08	3560.31	8.58E-08
139.903	6.87E-08	313.919	8.02E-08	488.826	8.71E-08	662.842	9.04E-08	3564.08	8.47E-08
143.689	6.96E-08	317.715	8.20E-08	492.632	8.74E-08	666.658	8.98E-08	3567.87	8.34E-08
147.465	6.98E-08	321.481	8.26E-08	496.468	8.77E-08	670.424	9.03E-08	3571.65	8.26E-08
151.251	6.93E-08	325.256	8.27E-08	500.404	8.84E-08	674.209	8.99E-08	3575.41	8.27E-08
155.016	6.94E-08	329.022	8.15E-08	504.19	8.81E-08	677.995	9.03E-08	3579.19	8.29E-08
158.802	6.96E-08	332.798	8.07E-08	507.966	8.60E-08	681.761	9.05E-08	3582.96	8.26E-08
162.598	6.93E-08	336.594	8.11E-08	511.741	8.47E-08	685.557	8.97E-08	3586.76	8.27E-08
166.374	6.87E-08	340.38	8.21E-08	515.517	8.45E-08	689.343	8.93E-08	3590.53	8.30E-08
170.139	6.93E-08	344.165	8.22E-08	519.293	8.43E-08	693.118	8.96E-08	3594.31	8.33E-08

Table C.12: Benzene data at 70 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-6.75E-10	180.7363	2.95E-10	359.0885	1.60E-09	538.1495	2.07E-09	3139.95	1.97E-09
3.90875	-6.59E-10	184.5195	3.11E-10	362.877	1.62E-09	541.938	2.07E-09	3143.748	1.94E-09
7.71925	-6.58E-10	188.3053	3.81E-10	366.7103	1.62E-09	545.7235	2.10E-09	3147.535	1.93E-09
11.53	-6.52E-10	192.0835	4.03E-10	370.5035	1.64E-09	549.512	2.09E-09	3151.343	1.94E-09
15.3285	-6.42E-10	195.8643	4.36E-10	374.4495	1.66E-09	553.2953	2.09E-09	3155.125	1.93E-09
19.142	-6.03E-10	199.6625	4.83E-10	378.2453	1.70E-09	557.1235	2.09E-09	3472.123	1.93E-09
22.925	-5.82E-10	203.4508	5.22E-10	382.0413	1.69E-09	560.902	2.12E-09	3475.93	1.92E-09
26.74575	-5.47E-10	207.2643	5.44E-10	385.8295	1.72E-09	564.6978	2.13E-09	3479.758	1.94E-09
30.539	-5.01E-10	211.0603	6.00E-10	389.6478	1.74E-09	568.526	2.11E-09	3483.74	1.92E-09
34.365	-4.68E-10	214.853	6.28E-10	393.6665	1.75E-09	572.3643	2.13E-09	3487.553	1.92E-09
38.156	-4.36E-10	218.6315	6.67E-10	397.4823	1.78E-09	576.338	2.13E-09	3491.365	1.93E-09
41.95175	-4.14E-10	222.4123	6.89E-10	401.2705	1.77E-09	580.1515	2.14E-09	3495.42	1.93E-09
45.78	-4.35E-10	226.1883	7.28E-10	405.049	1.81E-09	583.9495	2.11E-09	3499.303	1.92E-09
49.553	-7.13E-10	230.0138	7.62E-10	408.837	1.81E-09	587.918	2.14E-09	3503.115	1.93E-09
53.3615	-1.08E-09	233.792	7.99E-10	412.6155	1.82E-09	591.7015	2.14E-09	3506.928	1.95E-09
57.1525	-1.17E-09	237.5655	8.44E-10	416.391	1.85E-09	595.4798	2.13E-09	3511.078	1.92E-09
60.933	-1.19E-09	241.3563	8.54E-10	420.177	1.84E-09	599.4738	2.12E-09	3514.89	1.95E-09
64.93175	-1.13E-09	245.1348	8.80E-10	423.965	1.86E-09	603.2788	2.12E-09	3518.723	1.93E-09
68.72475	-1.07E-09	248.9378	9.06E-10	427.7785	1.86E-09	1199.57	2.19E-09	3522.545	1.94E-09
72.49825	-1.02E-09	252.7335	9.42E-10	431.567	1.90E-09	1203.365	2.19E-09	3526.338	1.93E-09
76.31675	-9.70E-10	256.547	9.48E-10	435.3425	1.90E-09	1207.16	2.17E-09	3530.148	1.93E-09
80.12775	-9.21E-10	260.368	9.89E-10	439.1158	1.92E-09	1210.94	2.13E-09	3533.928	1.95E-09
83.8955	-8.65E-10	264.1435	1.02E-09	442.894	1.93E-09	1214.745	2.17E-09	3537.738	1.92E-09
87.67625	-8.04E-10	267.924	1.06E-09	446.675	1.94E-09	1218.538	2.17E-09	3541.525	1.93E-09
91.48225	-7.59E-10	271.705	1.08E-09	450.4533	1.93E-09	1222.33	2.19E-09	3545.33	1.92E-09
95.26325	-6.94E-10	275.5035	1.10E-09	454.2513	1.95E-09	1226.113	2.21E-09	3549.153	1.93E-09
99.03625	-6.41E-10	279.2995	1.14E-09	458.0345	1.97E-09	1229.898	2.19E-09	3552.955	1.93E-09
102.832	-6.13E-10	283.0748	1.15E-09	461.8155	1.96E-09	1233.698	2.19E-09	3556.775	1.93E-09
106.6228	-5.33E-10	286.9583	1.21E-09	465.6065	1.97E-09	1237.473	2.19E-09	3560.6	1.93E-09
110.4363	-4.92E-10	290.7568	1.22E-09	469.4098	1.97E-09	1241.27	2.18E-09	3565.308	1.94E-09
114.3148	-4.30E-10	294.6103	1.22E-09	473.213	2.01E-09	1245.053	2.19E-09	3569.293	1.91E-09
118.1203	-3.79E-10	298.3908	1.24E-09	476.996	2.00E-09	1248.843	2.17E-09	3573.125	1.92E-09
121.9063	-3.25E-10	302.1793	1.25E-09	480.8245	2.03E-09	1252.695	2.20E-09	3576.933	1.95E-09
125.687	-2.90E-10	305.9548	1.32E-09	484.6055	2.02E-09	1256.49	2.16E-09	3580.725	1.92E-09
129.4855	-2.12E-10	309.7508	1.35E-09	488.3885	2.05E-09	1260.273	2.17E-09	3584.518	1.93E-09
133.261	-1.86E-10	313.5443	1.33E-09	492.1768	2.04E-09	1264.053	2.18E-09	3588.32	1.94E-09
137.0368	-1.39E-10	317.3348	1.37E-09	495.9928	2.03E-09	1267.85	2.17E-09	3592.11	1.92E-09
140.8175	-1.02E-10	321.138	1.39E-09	499.811	2.03E-09	1271.635	2.12E-09	3595.928	1.90E-09
144.591	-7.18E-11	324.9088	1.41E-09	503.6068	2.03E-09	1275.415	2.15E-09	3599.713	1.93E-09
148.3718	-1.14E-11	328.7198	1.46E-09	507.5978	2.03E-09	1279.25	2.17E-09	3603.515	1.92E-09
152.18	3.16E-11	332.513	1.46E-09	511.3838	2.05E-09	1283.045	2.16E-09	3607.313	1.93E-09
155.953	6.44E-11	336.3263	1.48E-09	515.1798	2.04E-09	1286.845	2.16E-09	3611.1	1.91E-09
161.6745	1.34E-10	340.112	1.50E-09	519.1255	2.06E-09	1290.845	2.14E-09	3614.9	1.91E-09
165.6108	1.64E-10	343.9505	1.51E-09	522.919	2.04E-09	1294.633	2.14E-09	3618.685	1.92E-09
169.3838	2.02E-10	347.7263	1.53E-09	526.7098	2.06E-09	1298.435	2.15E-09	3622.498	1.92E-09
173.1695	2.37E-10	351.5145	1.54E-09	530.4903	2.07E-09	1302.225	2.14E-09	3626.295	1.90E-09
176.9503	2.55E-10	355.3003	1.59E-09	534.3263	2.05E-09	1306.038	2.15E-09	3630.125	1.90E-09

Table C.13: Chloroform data at 40 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-6.38E-10	189.6797	1.76E-09	359.97633	2.45E-09	530.6873	2.39E-09	3372.29	2.56E-09
3.9493333	-6.24E-10	193.4757	1.78E-09	363.759	2.45E-09	534.4763	2.42E-09	3376.073	2.57E-09
7.7653333	-6.22E-10	197.2447	1.81E-09	367.54133	2.46E-09	538.2553	2.42E-09	3379.873	2.57E-09
11.594333	-6.16E-10	201.02	1.85E-09	371.324	2.43E-09	542.0347	2.43E-09	3383.717	2.56E-09
15.393333	-5.84E-10	204.7993	1.87E-09	375.13933	2.47E-09	545.827	2.41E-09	3387.567	2.57E-09
19.195667	-5.19E-10	208.5753	1.90E-09	378.922	2.47E-09	549.6063	2.41E-09	3391.487	2.54E-09
23.001667	-4.58E-10	212.3443	1.93E-09	382.698	2.45E-09	553.4117	2.45E-09	3395.293	2.56E-09
26.811	-4.13E-10	216.1467	1.97E-09	386.49367	2.42E-09	557.2077	2.45E-09	3399.307	2.55E-09
30.613333	-4.15E-10	219.9257	2.00E-09	390.29967	2.43E-09	560.987	2.46E-09	3403.147	2.54E-09
34.405667	-6.22E-10	223.705	2.03E-09	394.075	2.42E-09	564.7827	2.42E-09	3406.93	2.51E-09
38.198333	-8.69E-10	227.4877	2.04E-09	397.84767	2.42E-09	568.5987	2.46E-09	3410.75	2.50E-09
42.000667	-8.38E-10	231.263	2.07E-09	401.637	2.40E-09	572.3877	2.47E-09	3414.55	2.48E-09
45.82	-7.37E-10	235.0387	2.10E-09	405.41933	2.43E-09	576.18	2.48E-09	3498.573	2.48E-09
49.658667	-6.60E-10	238.8213	2.10E-09	409.188	2.39E-09	579.989	2.50E-09	3502.36	2.48E-09
53.454667	-6.18E-10	242.6073	2.15E-09	412.97733	2.45E-09	583.7683	2.50E-09	3506.24	2.49E-09
57.227333	-5.35E-10	246.383	2.16E-09	416.75	2.42E-09	587.561	2.48E-09	3510.243	2.51E-09
61.003333	-4.87E-10	250.1687	2.16E-09	420.539	2.41E-09	591.3967	2.50E-09	3514.053	2.50E-09
64.782333	-3.94E-10	253.951	2.21E-09	424.31833	2.42E-09	595.179	2.44E-09	3517.86	2.50E-09
68.557667	-3.36E-10	257.7303	2.22E-09	428.10367	2.42E-09	598.9683	2.50E-09	3521.687	2.50E-09
72.347	-2.48E-10	261.5027	2.22E-09	431.883	2.41E-09	602.8443	2.50E-09	3525.517	2.49E-09
76.116333	-1.91E-10	265.2787	2.27E-09	435.669	2.42E-09	606.7203	2.51E-09	3529.38	2.51E-09
79.885333	-1.36E-10	269.0673	2.25E-09	439.45133	2.43E-09	610.5023	2.50E-09	3533.167	2.49E-09
83.670667	-8.24E-11	272.8467	2.28E-09	443.247	2.43E-09	614.2917	2.48E-09	3536.973	2.52E-09
87.453333	-2.58E-11	276.6357	2.32E-09	447.026	2.42E-09	618.0673	2.52E-09	3540.767	2.51E-09
91.239333	4.95E-11	280.4283	2.32E-09	450.80533	2.44E-09	621.8467	2.51E-09	3544.55	2.51E-09
95.038333	1.14E-10	284.2073	2.32E-09	454.601	2.42E-09	625.6357	2.54E-09	3548.43	2.51E-09
98.817667	1.86E-10	287.9797	2.34E-09	458.397	2.47E-09	629.4147	2.51E-09	3552.227	2.48E-09
102.61633	2.87E-10	291.7923	2.34E-09	462.189	2.44E-09	633.2003	2.51E-09	3556.057	2.53E-09
106.39233	3.46E-10	295.5913	2.34E-09	466.182	2.43E-09	636.9797	2.51E-09	3559.94	2.50E-09
110.17833	4.34E-10	299.3873	2.37E-09	469.98467	2.41E-09	640.769	2.50E-09	3563.74	2.55E-09
113.97733	5.23E-10	303.1933	2.37E-09	473.76367	2.39E-09	1493.22	2.96E-09	3567.677	2.50E-09
117.763	6.14E-10	306.989	2.44E-09	477.553	2.40E-09	1497.02	2.94E-09	3571.523	2.52E-09
121.54567	6.93E-10	310.7677	2.42E-09	481.34167	2.43E-09	1500.823	2.99E-09	3575.42	2.53E-09
125.318	7.86E-10	314.5537	2.47E-09	485.121	2.40E-09	1504.633	3.00E-09	3579.203	2.53E-09
129.10367	8.28E-10	318.3397	2.43E-09	488.91	2.39E-09	1508.433	2.97E-09	3583.037	2.53E-09
132.87967	9.03E-10	322.1153	2.44E-09	492.68933	2.41E-09	1512.257	3.00E-09	3586.863	2.54E-09
136.65867	1.01E-09	325.911	2.49E-09	496.46867	2.38E-09	1516.073	3.02E-09	3590.823	2.56E-09
140.508	1.05E-09	329.7033	2.43E-09	500.39433	2.38E-09	1519.893	3.03E-09	3594.613	2.56E-09
144.30733	1.11E-09	333.506	2.45E-09	504.18	2.42E-09	1523.73	3.01E-09	3598.393	2.59E-09
148.09267	1.20E-09	337.292	2.48E-09	507.966	2.37E-09	1527.537	3.00E-09	3602.193	2.60E-09
151.86833	1.25E-09	341.0707	2.46E-09	511.75833	2.38E-09	1531.333	3.03E-09	3605.977	2.56E-09
155.64767	1.30E-09	344.8567	2.46E-09	515.554	2.40E-09	1535.13	3.07E-09	3609.777	2.58E-09
159.43367	1.35E-09	348.6257	2.47E-09	519.33333	2.41E-09	1538.92	3.05E-09	3613.61	2.56E-09
163.21933	1.41E-09	352.4017	2.48E-09	523.119	2.39E-09	1542.747	3.02E-09	3617.393	2.55E-09
166.99133	1.44E-09	356.181	2.48E-09	526.90467	2.40E-09	1546.61	3.05E-09	3621.187	2.56E-09

Table C.14: Chloroform data at 55 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-9.725E-10	174.8607	3.4193E-09	346.95333	3.22371E-09	522.85867	3.21136E-09	2821.82	3.61996E-09
5.231333	-9.208E-10	178.6593	3.4402E-09	350.74567	3.22026E-09	526.64767	3.18526E-09	2825.67	3.64926E-09
9.107333	-9.545E-10	182.4683	3.4399E-09	354.59467	3.21973E-09	530.49367	3.1711E-09	2829.47	3.62368E-09
12.89933	-9.557E-10	186.3377	3.4688E-09	358.41067	3.20219E-09	534.34633	3.18058E-09	2833.62	3.624E-09
16.742	-9.131E-10	190.2237	3.4486E-09	362.21667	3.21926E-09	538.15867	3.19743E-09	2837.43	3.62609E-09
20.51467	-7.954E-10	194.0197	3.4796E-09	366.01933	3.22891E-09	541.968	3.17179E-09	2841.34	3.61866E-09
24.284	-6.816E-10	197.8623	3.4903E-09	369.80467	3.20742E-09	545.80367	3.21473E-09	2845.15	3.62436E-09
28.06233	-6.15E-10	201.878	3.4782E-09	373.694	3.21099E-09	549.61967	3.19009E-09	2848.94	3.64206E-09
31.83833	-5.146E-10	205.7273	3.4994E-09	377.5	3.20708E-09	553.422	3.19385E-09	2852.77	3.62962E-09
35.611	-3.427E-10	209.53	3.539E-09	381.339	3.20571E-09	557.268	3.20362E-09	2856.56	3.63726E-09
39.41033	-1.464E-10	213.366	3.5437E-09	385.16167	3.22202E-09	561.11733	3.21627E-09	2860.38	3.65462E-09
43.19267	5.1751E-11	217.1653	3.5579E-09	388.97733	3.2401E-09	564.99967	3.23426E-09	2864.18	3.63084E-09
46.97133	2.3606E-10	221.0073	3.5558E-09	392.84333	3.23927E-09	568.78567	3.22133E-09	2867.98	3.64519E-09
50.77067	4.0393E-10	224.8067	3.5493E-09	397.033	3.23964E-09	572.58767	3.25293E-09	3421.46	3.59407E-09
54.55	5.4988E-10	228.599	3.5473E-09	401.68333	3.23813E-09	576.38033	3.27522E-09	3425.26	3.60799E-09
58.33233	6.7964E-10	232.3917	3.562E-09	405.47267	3.20449E-09	580.253	3.28131E-09	3429.05	3.62114E-09
62.118	8.1055E-10	236.1873	3.5585E-09	409.28167	3.21564E-09	584.052	3.31667E-09	3432.86	3.61915E-09
65.92733	9.5273E-10	239.983	3.5912E-09	413.091	3.22879E-09	587.85133	3.32165E-09	3566.95	3.50582E-09
69.73	1.0958E-09	243.7957	3.5721E-09	416.91367	3.2046E-09	591.63733	3.35766E-09	3570.76	3.51603E-09
73.559	1.257E-09	247.5813	3.5915E-09	420.71267	3.20334E-09	595.45633	3.36184E-09	3574.56	3.49606E-09
77.78867	1.4279E-09	251.3807	3.5858E-09	425.46667	3.23164E-09	599.255	3.37823E-09	3578.36	3.52705E-09
81.58767	1.5535E-09	255.1863	3.5835E-09	429.68267	3.23648E-09	603.10767	3.40932E-09	3582.24	3.47122E-09
85.46367	1.7092E-09	258.992	3.5895E-09	433.47533	3.24722E-09	606.90367	3.42509E-09	3586.05	3.50937E-09
89.3	1.8252E-09	262.8047	3.5692E-09	437.662	3.24451E-09	610.703	3.47868E-09	3589.87	3.47728E-09
93.17567	1.9712E-09	266.6007	3.5863E-09	441.45767	3.25079E-09	614.499	3.43717E-09	3593.68	3.52205E-09
96.978	2.0795E-09	270.3933	3.5788E-09	445.26	3.23515E-09	618.311	3.43338E-09	3597.49	3.48099E-09
100.7807	2.2253E-09	274.1953	3.5883E-09	449.109	3.22046E-09	622.1	3.47004E-09	3601.29	3.52473E-09
104.5763	2.3338E-09	278.385	3.569E-09	452.925	3.25017E-09	625.896	3.4892E-09	3605.1	3.51433E-09
108.4587	2.4245E-09	282.171	3.5141E-09	456.82767	3.21867E-09	629.702	3.47649E-09	3608.92	3.48965E-09
112.2447	2.535E-09	285.9637	3.5382E-09	460.64033	3.22619E-09	633.49467	3.48896E-09	3612.72	3.47569E-09
116.0273	2.6416E-09	289.7527	3.4759E-09	465.42767	3.2594E-09	637.28967	3.47932E-09	3616.52	3.45746E-09
119.8197	2.7029E-09	293.5447	3.4816E-09	469.22333	3.23947E-09	641.08233	3.47889E-09	3620.31	3.49457E-09
123.5987	2.7813E-09	297.3607	3.4516E-09	473.019	3.24027E-09	644.87833	3.47808E-09	3624.18	3.45633E-09
127.3877	2.8487E-09	301.1567	3.4335E-09	476.99533	3.24585E-09	648.671	3.47679E-09	3628	3.49364E-09
131.187	2.941E-09	304.966	3.411E-09	480.81433	3.2674E-09	652.47033	3.51452E-09	3631.78	3.46734E-09
134.9963	3.0254E-09	308.825	3.4195E-09	484.61367	3.21054E-09	656.279	3.48581E-09	3635.59	3.4561E-09
138.802	3.0621E-09	312.6273	3.3519E-09	488.51267	3.22517E-09	660.138	3.52122E-09	3639.39	3.48137E-09
144.4603	3.146E-09	316.4333	3.329E-09	492.33533	3.21522E-09	663.93733	3.49938E-09	3643.19	3.46949E-09
148.243	3.2037E-09	320.236	3.3094E-09	496.121	3.23809E-09	667.74667	3.45866E-09	3646.99	3.44614E-09
152.032	3.2356E-09	324.0583	3.3103E-09	499.94367	3.21414E-09	671.596	3.45937E-09	3650.9	3.436E-09
155.8447	3.2665E-09	327.8607	3.2702E-09	503.823	3.20754E-09	675.40167	3.45485E-09	3654.74	3.45381E-09
159.6437	3.3312E-09	331.6863	3.257E-09	507.59867	3.21946E-09	679.22067	3.43077E-09	3658.54	3.43778E-09
163.476	3.3296E-09	335.4823	3.2395E-09	511.398	3.21878E-09	683.02667	3.42973E-09	3662.47	3.41623E-09
167.262	3.3588E-09	339.3117	3.2492E-09	515.19667	3.20367E-09	686.82567	3.48801E-09	3666.29	3.41544E-09
171.0547	3.3686E-09	343.1507	3.2518E-09	519.026	3.19778E-09	690.70533	3.45474E-09	3670.08	3.41434E-09

Table C.15: Chloroform data at 70 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-5.6042E-10	170.936	2.46745E-09	341.627	3.14635E-09	513.94	3.62397E-09	3465.07	3.56834E-09
3.936	-5.5531E-10	174.737	2.49427E-09	345.468	3.1324E-09	518.0215	3.66666E-09	3469.015	3.57172E-09
7.747	-5.4687E-10	178.528	2.49687E-09	349.269	3.1609E-09	521.8025	3.68562E-09	3472.965	3.59324E-09
11.548	-4.781E-10	182.329	2.54769E-09	353.1145	3.20054E-09	525.6635	3.67599E-09	3476.78	3.58248E-09
15.3535	-3.7846E-10	186.134	2.60698E-09	356.905	3.25156E-09	529.509	3.68623E-09	3480.605	3.5801E-09
19.1245	-3.1782E-10	189.93	2.60706E-09	360.701	3.25449E-09	533.2895	3.697E-09	3484.69	3.64138E-09
22.93	-3.5773E-10	193.711	2.6468E-09	364.492	3.25956E-09	990.899	4.20251E-09	3488.515	3.61439E-09
26.696	-3.2087E-10	197.512	2.7157E-09	368.278	3.22648E-09	994.705	4.19703E-09	3492.35	3.62509E-09
30.5065	-1.4183E-10	201.303	2.73407E-09	372.159	3.25183E-09	998.496	4.21314E-09	3496.22	3.63615E-09
34.2825	-3.9828E-12	205.098	2.77232E-09	375.949	3.19436E-09	1002.29	4.19523E-09	3500.045	3.6778E-09
38.0535	1.58694E-10	208.909	2.77715E-09	379.74	3.2734E-09	1006.085	4.20955E-09	3503.875	3.63637E-09
41.829	2.86199E-10	212.695	2.81191E-09	383.596	3.26452E-09	1009.88	4.21872E-09	3507.73	3.66859E-09
45.6145	4.08608E-10	216.481	2.82597E-09	387.7475	3.21984E-09	1013.675	4.2139E-09	3511.57	3.61227E-09
49.3805	5.44558E-10	220.277	2.81883E-09	391.5935	3.24324E-09	1017.465	4.19478E-09	3515.42	3.59137E-09
53.1615	6.23933E-10	224.067	2.86511E-09	395.399	3.22396E-09	1021.255	4.18837E-09	3519.99	3.59047E-09
56.9375	7.27239E-10	227.863	2.87334E-09	399.21	3.25703E-09	1025.07	4.20621E-09	3523.815	3.64945E-09
60.7225	8.16427E-10	231.669	2.84996E-09	403.066	3.26867E-09	1028.885	4.20299E-09	3527.635	3.64696E-09
64.5435	9.25036E-10	235.455	2.83118E-09	406.8565	3.30436E-09	1032.67	4.22519E-09	3531.475	3.6484E-09
68.3195	1.00763E-09	239.251	2.90705E-09	410.6775	3.29876E-09	1036.475	4.22104E-09	3535.295	3.66826E-09
72.0905	1.06588E-09	243.051	2.90147E-09	414.513	3.28208E-09	1040.27	4.19663E-09	3539.105	3.66932E-09
75.871	1.1505E-09	246.847	2.90502E-09	418.334	3.29109E-09	1044.065	4.201E-09	3542.925	3.65186E-09
79.6565	1.20936E-09	250.638	2.93252E-09	422.135	3.29412E-09	1047.87	4.17497E-09	3546.735	3.65477E-09
83.4275	1.28298E-09	254.434	2.97186E-09	425.961	3.31568E-09	1051.655	4.19829E-09	3550.675	3.68944E-09
87.2285	1.35738E-09	258.2195	2.95082E-09	429.827	3.29595E-09	1055.44	4.25342E-09	3554.515	3.65118E-09
91.0045	1.40142E-09	262.005	2.95246E-09	433.6225	3.32541E-09	1059.24	4.25847E-09	3558.36	3.62714E-09
94.78	1.51107E-09	265.801	2.98416E-09	437.443	3.27009E-09	1063.075	4.21944E-09	3562.155	3.62131E-09
98.5605	1.55493E-09	269.582	2.999E-09	441.274	3.30925E-09	1066.885	4.25828E-09	3566.065	3.65251E-09
102.3415	1.62031E-09	273.378	2.9562E-09	445.08	3.33161E-09	1070.705	4.25466E-09	3569.89	3.65967E-09
106.1325	1.68683E-09	277.1685	2.9517E-09	448.906	3.3225E-09	1074.525	4.23033E-09	3573.715	3.68223E-09
109.933	1.75075E-09	280.954	2.96544E-09	452.712	3.32593E-09	1078.44	4.27032E-09	3577.5	3.63129E-09
113.7135	1.81209E-09	284.76	2.95922E-09	456.5125	3.34157E-09	1082.27	4.24515E-09	3581.32	3.63801E-09
117.4895	1.86144E-09	288.546	2.9774E-09	460.5585	3.35025E-09	1086.055	4.24389E-09	3585.2	3.59094E-09
121.5105	1.92762E-09	292.342	2.95222E-09	464.3445	3.34219E-09	1089.86	4.22551E-09	3589.27	3.56425E-09
125.3165	1.97119E-09	296.1425	2.92477E-09	468.1305	3.40413E-09	1093.655	4.25735E-09	3593.105	3.49536E-09
129.1175	2.00168E-09	299.928	2.96526E-09	471.921	3.42834E-09	1097.44	4.27713E-09	3596.915	3.45439E-09
132.918	2.06178E-09	303.719	2.98545E-09	475.7465	3.45192E-09	1101.235	4.26593E-09	3600.705	3.46029E-09
136.719	2.1069E-09	307.525	3.00899E-09	479.618	3.45027E-09	1105.025	4.25305E-09	3604.71	3.46071E-09
140.515	2.14454E-09	311.311	2.99994E-09	483.3935	3.47513E-09	1108.82	4.23777E-09	3608.51	3.47886E-09
144.3105	2.1859E-09	315.1015	2.97447E-09	487.1745	3.47796E-09	1112.62	4.25758E-09	3612.4	3.51601E-09
148.1015	2.23406E-09	318.897	3.00257E-09	490.985	3.44237E-09	1116.42	4.21491E-09	3616.2	3.54919E-09
151.962	2.26588E-09	322.678	2.99904E-09	494.781	3.48994E-09	1587.525	4.08566E-09	3620.09	3.56049E-09
155.768	2.28087E-09	326.464	3.00555E-09	498.652	3.50524E-09	1591.345	4.13631E-09	3623.915	3.58752E-09
159.554	2.3138E-09	330.26	3.04621E-09	502.483	3.54498E-09	1595.24	4.16994E-09	3627.72	3.54534E-09
163.36	2.39757E-09	334.035	3.08438E-09	506.299	3.60349E-09	1599.33	4.16391E-09	3639.425	3.71833E-09
167.155	2.40004E-09	337.831	3.11641E-09	510.084	3.58853E-09	1603.13	4.20638E-09	3643.235	3.7407E-09

Table C.16: Chloroform data at 90 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-8.63E-10	170.78	4.52E-09	341.401	8.45E-09	513.264	1.02E-08	3411.77	8.63E-09
3.795	-8.59E-10	174.576	4.64E-09	345.187	8.52E-09	517.049	1.03E-08	3415.62	8.63E-09
7.781	-8.44E-10	178.362	4.73E-09	348.983	8.57E-09	520.835	1.03E-08	3419.4	8.65E-09
11.617	-8.06E-10	182.148	4.87E-09	352.768	8.61E-09	524.611	1.04E-08	3423.2	8.63E-09
15.453	-7.32E-10	185.944	4.94E-09	356.544	8.68E-09	528.397	1.04E-08	3426.99	8.64E-09
19.229	-6.30E-10	189.729	5.03E-09	360.34	8.75E-09	532.172	1.04E-08	3430.77	8.62E-09
23.095	-4.97E-10	193.515	5.14E-09	364.126	8.79E-09	535.948	1.04E-08	3434.62	8.62E-09
26.861	-3.47E-10	197.301	5.23E-09	367.902	8.86E-09	539.764	1.04E-08	3438.43	8.61E-09
30.706	-1.88E-10	201.087	5.34E-09	371.697	8.92E-09	543.58	1.04E-08	3442.24	8.62E-09
34.492	-1.00E-09	204.872	5.43E-09	375.473	8.98E-09	547.356	1.05E-08	3446.21	8.63E-09
38.268	-8.23E-10	208.688	5.53E-09	379.259	9.00E-09	551.182	1.05E-08	3450.04	8.62E-09
42.104	-6.49E-10	212.474	5.64E-09	383.055	9.05E-09	845.03	1.11E-08	3453.84	8.62E-09
45.89	-4.67E-10	216.26	5.72E-09	386.83	9.12E-09	848.836	1.11E-08	3457.64	8.62E-09
49.715	-2.91E-10	220.056	5.82E-09	390.616	9.16E-09	852.722	1.11E-08	3461.46	8.65E-09
53.481	-1.17E-10	223.841	5.90E-09	394.402	9.20E-09	856.668	1.11E-08	3465.24	8.62E-09
57.327	6.96E-11	227.637	5.99E-09	398.188	9.23E-09	860.484	1.11E-08	3469.03	8.63E-09
61.083	2.46E-10	231.433	6.08E-09	402.094	9.30E-09	864.28	1.11E-08	3472.81	8.62E-09
64.869	4.25E-10	235.209	6.17E-09	405.89	9.34E-09	868.066	1.12E-08	3476.61	8.62E-09
68.654	6.03E-10	239.005	6.26E-09	409.665	9.37E-09	871.871	1.11E-08	3480.41	8.65E-09
72.42	7.72E-10	242.78	6.33E-09	413.451	9.43E-09	875.667	1.12E-08	3484.21	8.60E-09
76.206	9.38E-10	246.546	6.42E-09	417.247	9.45E-09	879.463	1.12E-08	3488.01	8.64E-09
79.992	1.12E-09	250.322	6.51E-09	421.023	9.45E-09	883.259	1.12E-08	3491.8	8.62E-09
83.767	1.28E-09	254.118	6.59E-09	424.879	9.52E-09	887.045	1.12E-08	3495.59	8.64E-09
87.563	1.43E-09	257.893	6.69E-09	428.674	9.52E-09	890.84	1.12E-08	3499.39	8.62E-09
91.339	1.62E-09	261.689	6.76E-09	432.48	9.56E-09	894.676	1.12E-08	3503.17	8.64E-09
95.135	1.77E-09	265.465	6.81E-09	436.326	9.61E-09	898.482	1.12E-08	3507.13	8.63E-09
98.921	1.93E-09	269.241	6.91E-09	440.242	9.63E-09	902.298	1.12E-08	3510.93	8.62E-09
102.696	2.07E-09	273.277	6.97E-09	444.038	9.70E-09	906.154	1.12E-08	3514.73	8.61E-09
106.472	2.21E-09	277.033	7.06E-09	448.074	9.71E-09	909.95	1.12E-08	3518.52	8.62E-09
110.248	2.36E-09	280.808	7.09E-09	451.92	9.77E-09	913.866	1.12E-08	3522.45	8.63E-09
114.024	2.51E-09	284.604	7.19E-09	456.186	9.81E-09	917.691	1.12E-08	3526.42	8.62E-09
117.799	2.67E-09	288.38	7.21E-09	459.982	9.86E-09	921.477	1.12E-08	3530.36	8.61E-09
121.585	2.79E-09	292.166	7.27E-09	463.798	9.90E-09	925.263	1.12E-08	3534.17	8.62E-09
125.361	2.93E-09	295.952	7.35E-09	467.594	9.91E-09	929.069	1.12E-08	3538.08	8.61E-09
129.137	3.07E-09	299.717	7.56E-09	471.37	9.95E-09	932.855	1.12E-08	3541.88	8.60E-09
132.913	3.22E-09	303.493	7.48E-09	475.155	9.98E-09	936.65	1.12E-08	3545.78	8.65E-09
136.678	3.36E-09	307.309	7.92E-09	479.021	1.00E-08	940.636	1.12E-08	3549.55	8.62E-09
140.464	3.47E-09	311.075	7.97E-09	482.807	1.00E-08	944.382	1.12E-08	3583.8	8.64E-09
144.25	3.60E-09	314.85	8.04E-09	486.693	1.01E-08	948.168	1.13E-08	3587.61	8.63E-09
148.036	3.74E-09	318.636	8.14E-09	490.489	1.01E-08	952.054	1.12E-08	3591.4	8.62E-09
151.841	3.88E-09	322.422	8.16E-09	494.295	1.01E-08	955.84	1.13E-08	3595.19	8.64E-09
155.617	3.98E-09	326.218	8.30E-09	498.07	1.01E-08	959.615	1.12E-08	3598.99	8.62E-09
159.403	4.12E-09	330.004	8.34E-09	501.856	1.01E-08	963.411	1.12E-08	3602.95	8.61E-09
163.219	4.23E-09	333.819	8.38E-09	505.662	1.02E-08	967.237	1.12E-08	3606.78	8.64E-09
166.995	4.37E-09	337.615	8.41E-09	509.478	1.02E-08	971.043	1.12E-08	3610.6	8.63E-09

Table C.17: Chloroform data at 24 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-7.46E-10	170.491	1.59E-08	341.222	1.93E-08	512.904	1.99E-08	3026.15	1.43E-08
3.806	-7.39E-10	174.267	1.60E-08	345.008	1.94E-08	516.67	1.99E-08	3485.68	1.38E-08
7.582	-6.41E-10	178.062	1.61E-08	348.773	1.94E-08	520.446	1.99E-08	3489.45	1.38E-08
11.368	-3.80E-10	181.838	1.63E-08	352.539	1.94E-08	524.221	1.99E-08	3493.23	1.38E-08
15.164	-1.17E-09	185.604	1.64E-08	356.365	1.95E-08	528.057	1.98E-08	3497.04	1.38E-08
18.989	-6.33E-10	189.39	1.65E-08	360.231	1.95E-08	531.843	1.98E-08	3500.83	1.38E-08
22.775	-2.02E-11	193.176	1.67E-08	363.997	1.95E-08	535.619	1.98E-08	3504.65	1.38E-08
26.561	6.40E-10	196.961	1.68E-08	367.772	1.95E-08	539.404	1.98E-08	3508.42	1.38E-08
30.337	1.31E-09	200.747	1.69E-08	371.558	1.95E-08	543.18	1.99E-08	3512.2	1.38E-08
34.113	1.98E-09	204.513	1.70E-08	375.404	1.95E-08	546.996	1.98E-08	3516.04	1.38E-08
37.898	2.66E-09	208.289	1.71E-08	379.19	1.96E-08	550.802	1.99E-08	3519.87	1.38E-08
41.674	3.32E-09	212.084	1.72E-08	382.966	1.96E-08	554.578	1.99E-08	3523.67	1.38E-08
45.48	3.96E-09	215.87	1.73E-08	386.751	1.96E-08	558.454	1.99E-08	3527.45	1.38E-08
49.266	4.59E-09	219.656	1.74E-08	390.617	1.96E-08	562.139	2.00E-08	3531.24	1.38E-08
53.072	5.19E-09	223.452	1.75E-08	394.393	1.96E-08	566.005	2.00E-08	3535.07	1.38E-08
56.837	5.77E-09	227.218	1.76E-08	398.179	1.96E-08	569.791	2.00E-08	3538.86	1.38E-08
60.623	6.32E-09	231.083	1.77E-08	401.955	1.96E-08	573.567	2.00E-08	3542.72	1.38E-08
64.389	6.94E-09	234.869	1.78E-08	405.72	1.96E-08	577.433	2.00E-08	3546.54	1.37E-08
68.165	7.61E-09	238.645	1.79E-08	409.496	1.96E-08	581.489	1.99E-08	3550.45	1.37E-08
71.96	8.22E-09	242.431	1.80E-08	413.262	1.96E-08	585.275	1.99E-08	3554.46	1.37E-08
75.736	8.72E-09	246.207	1.81E-08	417.038	1.97E-08	589.11	1.99E-08	3558.21	1.38E-08
79.512	9.15E-09	250.042	1.82E-08	420.833	1.97E-08	592.866	1.99E-08	3562.07	1.37E-08
83.308	9.59E-09	253.838	1.82E-08	424.679	1.97E-08	596.632	1.99E-08	3565.92	1.37E-08
87.094	1.00E-08	257.644	1.83E-08	428.465	1.98E-08	600.498	1.99E-08	3569.73	1.37E-08
90.899	1.04E-08	261.42	1.84E-08	432.321	1.97E-08	604.594	1.99E-08	3573.57	1.37E-08
94.695	1.08E-08	265.216	1.84E-08	436.107	1.97E-08	608.46	1.99E-08	3577.42	1.37E-08
98.491	1.12E-08	269.011	1.85E-08	439.902	1.97E-08	612.236	1.99E-08	3581.2	1.38E-08
102.287	1.15E-08	272.847	1.86E-08	443.678	1.98E-08	616.022	1.99E-08	3585.02	1.38E-08
106.083	1.18E-08	276.633	1.86E-08	447.524	1.98E-08	619.797	1.99E-08	3588.84	1.38E-08
109.878	1.22E-08	280.399	1.87E-08	451.811	1.98E-08	623.573	2.00E-08	3592.66	1.38E-08
113.674	1.25E-08	284.495	1.87E-08	455.546	1.99E-08	627.389	2.00E-08	3596.49	1.38E-08
117.47	1.28E-08	288.281	1.88E-08	459.372	1.99E-08	631.255	1.99E-08	3600.3	1.38E-08
121.276	1.31E-08	292.077	1.89E-08	463.178	1.99E-08	635.031	1.99E-08	3604.15	1.38E-08
125.072	1.33E-08	295.842	1.89E-08	466.994	1.99E-08	638.786	1.98E-08	3607.95	1.38E-08
128.867	1.36E-08	299.638	1.90E-08	470.78	1.98E-08	642.562	1.98E-08	3611.74	1.38E-08
132.663	1.38E-08	303.404	1.90E-08	474.565	1.99E-08	646.338	1.99E-08	3615.52	1.38E-08
136.459	1.41E-08	307.19	1.90E-08	478.772	1.99E-08	650.104	1.99E-08	3619.3	1.39E-08
140.235	1.43E-08	310.976	1.90E-08	482.618	1.99E-08	653.869	1.99E-08	3623.1	1.38E-08
144.02	1.45E-08	314.751	1.91E-08	486.434	1.99E-08	657.645	1.99E-08	3626.91	1.38E-08
147.796	1.47E-08	318.527	1.91E-08	490.219	1.99E-08	661.411	1.99E-08	3630.81	1.38E-08
151.582	1.50E-08	322.303	1.92E-08	493.985	1.99E-08	665.197	1.99E-08	3634.89	1.38E-08
155.368	1.52E-08	326.079	1.92E-08	497.781	1.99E-08	668.952	1.99E-08	3638.68	1.39E-08
159.154	1.53E-08	329.864	1.93E-08	501.567	1.99E-08	672.728	1.98E-08	3642.49	1.38E-08
162.939	1.55E-08	333.65	1.93E-08	505.342	1.99E-08	676.584	1.98E-08	3646.28	1.38E-08
166.715	1.57E-08	337.416	1.93E-08	509.108	1.99E-08	680.931	1.98E-08	3650.11	1.38E-08

Table C.18: Chloroform data at 40 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-8.10E-10	170.094	2.42E-08	339.569	2.56E-08	509.188	2.62E-08	3151.79	2.36E-08
3.836	-6.98E-10	173.889	2.43E-08	343.355	2.55E-08	512.964	2.63E-08	3155.56	2.34E-08
7.602	-6.92E-10	177.655	2.44E-08	347.14	2.54E-08	516.729	2.63E-08	3427.58	2.37E-08
11.438	-2.37E-10	181.451	2.45E-08	350.906	2.55E-08	520.495	2.63E-08	3431.34	2.36E-08
15.214	1.02E-09	185.217	2.47E-08	354.692	2.53E-08	524.261	2.63E-08	3435.13	2.36E-08
18.98	2.41E-09	188.983	2.49E-08	358.468	2.55E-08	528.027	2.63E-08	3438.89	2.36E-08
22.755	3.84E-09	192.749	2.51E-08	362.243	2.55E-08	531.802	2.62E-08	3442.66	2.34E-08
26.531	5.26E-09	196.524	2.52E-08	366.009	2.54E-08	535.568	2.63E-08	3446.44	2.31E-08
30.317	6.64E-09	200.29	2.53E-08	369.775	2.55E-08	539.334	2.63E-08	3450.2	2.29E-08
34.093	8.20E-09	204.076	2.54E-08	373.541	2.56E-08	543.1	2.63E-08	3453.99	2.29E-08
37.869	9.47E-09	207.842	2.55E-08	377.316	2.55E-08	546.866	2.63E-08	3457.76	2.29E-08
41.665	1.06E-08	211.618	2.55E-08	381.082	2.54E-08	550.641	2.62E-08	3461.53	2.31E-08
45.441	1.17E-08	215.394	2.55E-08	384.848	2.52E-08	554.397	2.62E-08	3465.29	2.33E-08
49.226	1.27E-08	219.159	2.56E-08	388.624	2.54E-08	558.163	2.62E-08	3469.06	2.34E-08
53.012	1.36E-08	222.935	2.56E-08	392.39	2.54E-08	561.949	2.61E-08	3472.82	2.36E-08
56.788	1.44E-08	226.721	2.56E-08	396.155	2.55E-08	565.724	2.60E-08	3476.6	2.40E-08
60.574	1.52E-08	230.517	2.56E-08	399.941	2.55E-08	569.5	2.60E-08	3480.38	2.41E-08
64.35	1.59E-08	234.293	2.56E-08	403.697	2.54E-08	573.266	2.61E-08	3484.17	2.42E-08
68.116	1.65E-08	238.069	2.55E-08	407.463	2.53E-08	577.022	2.60E-08	3487.95	2.42E-08
71.882	1.71E-08	241.279	2.54E-08	411.238	2.53E-08	580.787	2.59E-08	3491.71	2.41E-08
75.657	1.76E-08	245.064	2.53E-08	415.004	2.51E-08	584.553	2.60E-08	3495.49	2.38E-08
79.433	1.82E-08	248.85	2.52E-08	418.76	2.50E-08	588.319	2.60E-08	3499.27	2.38E-08
83.219	1.87E-08	252.636	2.53E-08	422.546	2.51E-08	592.095	2.60E-08	3503.03	2.37E-08
87.005	1.91E-08	256.412	2.52E-08	426.301	2.52E-08	595.86	2.60E-08	3506.81	2.36E-08
90.771	1.95E-08	260.188	2.53E-08	430.067	2.51E-08	599.626	2.62E-08	3510.58	2.35E-08
94.567	1.99E-08	263.983	2.53E-08	433.823	2.50E-08	603.402	2.62E-08	3514.35	2.34E-08
98.342	2.03E-08	267.769	2.53E-08	437.579	2.50E-08	607.188	2.62E-08	3518.11	2.33E-08
102.118	2.06E-08	271.555	2.53E-08	441.354	2.49E-08	610.963	2.62E-08	3521.89	2.32E-08
105.904	2.09E-08	275.331	2.53E-08	445.13	2.48E-08	614.739	2.62E-08	3525.66	2.31E-08
109.67	2.12E-08	279.106	2.55E-08	448.886	2.48E-08	618.545	2.63E-08	3529.42	2.30E-08
113.436	2.14E-08	282.882	2.56E-08	452.662	2.47E-08	622.311	2.62E-08	3533.21	2.32E-08
117.222	2.18E-08	286.658	2.56E-08	456.437	2.50E-08	626.097	2.62E-08	3536.97	2.36E-08
120.998	2.20E-08	290.454	2.57E-08	460.193	2.52E-08	629.852	2.61E-08	3540.75	2.37E-08
124.783	2.23E-08	294.22	2.57E-08	463.969	2.53E-08	633.618	2.60E-08	3544.54	2.39E-08
128.569	2.24E-08	298.005	2.55E-08	467.735	2.55E-08	637.394	2.59E-08	3548.31	2.40E-08
132.345	2.26E-08	301.791	2.54E-08	471.49	2.56E-08	641.16	2.59E-08	3552.09	2.40E-08
136.111	2.27E-08	305.577	2.52E-08	475.266	2.57E-08	644.925	2.59E-08	3555.85	2.40E-08
139.887	2.29E-08	309.343	2.55E-08	479.032	2.56E-08	648.691	2.59E-08	3559.62	2.40E-08
143.653	2.31E-08	313.118	2.58E-08	482.798	2.59E-08	652.447	2.59E-08	3563.39	2.40E-08
147.418	2.34E-08	316.894	2.59E-08	486.583	2.59E-08	656.223	2.58E-08	3567.16	2.40E-08
151.204	2.35E-08	320.67	2.58E-08	490.339	2.61E-08	659.988	2.57E-08	3570.93	2.40E-08
154.97	2.37E-08	324.456	2.53E-08	494.115	2.61E-08	663.744	2.56E-08	3574.71	2.42E-08
158.736	2.39E-08	328.221	2.52E-08	497.891	2.61E-08	667.54	2.54E-08	3578.48	2.42E-08
162.522	2.40E-08	331.987	2.54E-08	501.646	2.62E-08	671.306	2.54E-08	3582.25	2.42E-08
166.308	2.41E-08	335.773	2.56E-08	505.422	2.61E-08	675.081	2.53E-08	3586.04	2.43E-08

Table C.19: Chloroform data at 55 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-7.07E-10	170.139	2.69E-08	340.38	3.10E-08	511.741	3.16E-08	3427.79	3.24E-08
3.785	-6.01E-10	173.925	2.76E-08	344.165	3.10E-08	515.517	3.15E-08	3431.56	3.23E-08
7.681	-9.98E-10	177.701	2.80E-08	347.941	3.08E-08	519.293	3.15E-08	3435.35	3.22E-08
11.427	1.26E-10	181.477	2.81E-08	351.727	3.08E-08	523.059	3.17E-08	3439.13	3.19E-08
15.193	1.58E-09	185.263	2.82E-08	355.503	3.07E-08	526.844	3.26E-08	3442.91	3.17E-08
18.958	3.19E-09	189.028	2.84E-08	359.288	3.08E-08	530.63	3.29E-08	3446.7	3.14E-08
22.744	4.87E-09	192.804	2.85E-08	363.064	3.09E-08	534.406	3.31E-08	3450.47	3.11E-08
26.53	6.68E-09	196.62	2.82E-08	366.83	3.07E-08	538.192	3.32E-08	3454.25	3.05E-08
30.306	8.70E-09	200.396	2.82E-08	370.616	3.04E-08	541.957	3.32E-08	3458.04	3.02E-08
34.102	1.01E-08	204.191	2.82E-08	374.391	3.01E-08	545.733	3.32E-08	3461.81	3.03E-08
37.887	1.15E-08	207.987	2.83E-08	378.187	3.00E-08	549.519	3.31E-08	3465.58	3.04E-08
41.673	1.29E-08	211.763	2.83E-08	381.973	3.03E-08	553.285	3.28E-08	3469.39	3.05E-08
45.469	1.45E-08	215.549	2.83E-08	385.749	3.03E-08	557.061	3.23E-08	3473.16	3.06E-08
49.235	1.59E-08	219.315	2.84E-08	389.525	3.06E-08	560.826	3.22E-08	3476.92	3.09E-08
53	1.68E-08	223.1	2.85E-08	393.31	3.11E-08	564.592	3.19E-08	3480.71	3.10E-08
56.846	1.77E-08	226.886	2.85E-08	397.086	3.14E-08	568.388	3.19E-08	3484.51	3.11E-08
60.622	1.84E-08	230.652	2.84E-08	400.852	3.15E-08	572.164	3.19E-08	3488.3	3.12E-08
64.398	1.89E-08	234.428	2.85E-08	404.628	3.14E-08	575.939	3.17E-08	3492.08	3.15E-08
68.174	1.96E-08	238.203	2.86E-08	408.614	3.14E-08	579.725	3.17E-08	3495.86	3.14E-08
71.949	2.05E-08	242.019	2.85E-08	412.4	3.13E-08	583.491	3.17E-08	3499.64	3.15E-08
75.735	2.11E-08	245.795	2.86E-08	416.195	3.11E-08	587.287	3.18E-08	3503.44	3.15E-08
79.491	2.15E-08	249.591	2.86E-08	419.981	3.13E-08	591.072	3.18E-08	3507.22	3.13E-08
83.257	2.18E-08	253.387	2.86E-08	423.877	3.14E-08	594.838	3.18E-08	3511.03	3.12E-08
87.032	2.21E-08	257.172	2.88E-08	428.033	3.15E-08	598.624	3.18E-08	3514.82	3.13E-08
90.808	2.23E-08	260.948	2.90E-08	431.799	3.13E-08	602.41	3.18E-08	3518.71	3.14E-08
94.584	2.27E-08	264.714	2.93E-08	435.585	3.14E-08	606.196	3.20E-08	3522.51	3.15E-08
98.36	2.36E-08	268.48	2.93E-08	439.351	3.12E-08	609.971	3.18E-08	3526.29	3.15E-08
102.126	2.42E-08	272.255	2.91E-08	443.126	3.12E-08	613.747	3.19E-08	3530.07	3.16E-08
105.891	2.46E-08	276.021	2.94E-08	446.902	3.11E-08	617.513	3.19E-08	3533.86	3.16E-08
109.667	2.47E-08	279.807	2.95E-08	450.668	3.19E-08	621.289	3.15E-08	3537.62	3.18E-08
113.443	2.50E-08	283.613	2.97E-08	454.624	3.26E-08	625.064	3.14E-08	3541.4	3.16E-08
117.219	2.54E-08	287.399	3.01E-08	458.44	3.27E-08	628.83	3.15E-08	3545.21	3.15E-08
121.004	2.55E-08	291.184	3.02E-08	462.206	3.27E-08	632.636	3.18E-08	3548.98	3.18E-08
124.79	2.59E-08	294.98	3.03E-08	465.981	3.23E-08	636.412	3.21E-08	3552.75	3.22E-08
128.556	2.65E-08	298.756	3.06E-08	469.777	3.17E-08	640.188	3.25E-08	3556.53	3.24E-08
132.342	2.68E-08	302.532	3.04E-08	473.583	3.17E-08	643.973	3.27E-08	3560.31	3.23E-08
136.117	2.70E-08	306.327	3.04E-08	477.499	3.22E-08	647.739	3.25E-08	3564.08	3.19E-08
139.903	2.71E-08	310.113	3.00E-08	481.285	3.24E-08	651.505	3.27E-08	3567.87	3.14E-08
143.689	2.74E-08	313.919	3.04E-08	485.061	3.24E-08	655.291	3.32E-08	3571.65	3.12E-08
147.465	2.74E-08	317.715	3.11E-08	488.826	3.22E-08	659.066	3.35E-08	3575.41	3.13E-08
151.251	2.71E-08	321.481	3.12E-08	492.632	3.25E-08	662.842	3.34E-08	3579.19	3.14E-08
155.016	2.71E-08	325.256	3.11E-08	496.468	3.26E-08	666.658	3.33E-08	3582.96	3.13E-08
158.802	2.72E-08	329.022	3.05E-08	500.404	3.28E-08	670.424	3.35E-08	3586.76	3.14E-08
162.598	2.69E-08	332.798	3.03E-08	504.19	3.25E-08	674.209	3.34E-08	3590.53	3.15E-08
166.374	2.67E-08	336.594	3.07E-08	507.966	3.19E-08	677.995	3.36E-08	3594.31	3.16E-08

Table C.20: Chloroform data at 70 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-6.11497E-10	176.9503	-2.5618E-10	351.5145	1.15178E-09	526.7098	2.08433E-09	3224.23	3.53916E-09
3.90875	-6.09288E-10	180.7363	-2.0288E-10	355.3003	1.16639E-09	530.4903	2.08232E-09	3228.02	3.5184E-09
7.71925	-6.04219E-10	184.5195	-1.8746E-10	359.0885	1.20189E-09	534.3263	2.11826E-09	3464.538	3.4482E-09
11.53	-6.0301E-10	188.3053	-1.5855E-10	362.877	1.22403E-09	538.1495	2.1345E-09	3468.335	3.40455E-09
15.3285	-5.91558E-10	192.0835	-1.3722E-10	366.7103	1.25191E-09	541.938	2.13235E-09	3472.123	3.41028E-09
19.142	-5.76718E-10	195.8643	-9.5277E-11	370.5035	1.26462E-09	545.7235	2.17545E-09	3475.93	3.47496E-09
22.925	-5.54647E-10	199.6625	-5.1545E-11	374.4495	1.31622E-09	549.512	2.1503E-09	3479.758	3.39655E-09
26.74575	-5.42618E-10	203.4508	-2.2143E-11	378.2453	1.29884E-09	553.2953	2.1772E-09	3483.74	3.48699E-09
30.539	-5.22069E-10	207.2643	2.261E-12	382.0413	1.37537E-09	557.1235	2.20658E-09	3487.553	3.41051E-09
34.365	-5.06005E-10	211.0603	4.2368E-11	385.8295	1.37732E-09	560.902	2.20905E-09	3491.365	3.41096E-09
38.156	-4.72286E-10	214.853	8.54843E-11	389.6478	1.3918E-09	564.6978	2.24469E-09	3495.42	3.40236E-09
41.95175	-4.50509E-10	218.6315	1.10767E-10	393.6665	1.40394E-09	568.526	2.24706E-09	3499.303	3.51897E-09
45.78	-4.17219E-10	222.4123	1.41735E-10	397.4823	1.43634E-09	572.3643	2.25593E-09	3503.115	3.47675E-09
49.553	-3.75661E-10	226.1883	1.92534E-10	401.2705	1.45726E-09	576.338	2.28966E-09	3506.928	3.50359E-09
53.3615	-3.39306E-10	230.0138	2.15719E-10	405.049	1.4902E-09	580.1515	2.30117E-09	3511.078	3.41868E-09
57.1525	-3.15979E-10	233.792	2.52692E-10	408.837	1.51631E-09	583.9495	2.28659E-09	3514.89	3.48183E-09
60.933	-3.20393E-10	237.5655	2.76706E-10	412.6155	1.53402E-09	587.918	2.30616E-09	3518.723	3.4905E-09
64.93175	-4.64579E-10	241.3563	3.29655E-10	416.391	1.54384E-09	591.7015	2.34353E-09	3522.545	3.49644E-09
68.72475	-7.85777E-10	245.1348	3.41227E-10	420.177	1.60596E-09	595.4798	2.35731E-09	3526.338	3.47156E-09
72.49825	-1.01624E-09	248.9378	3.76522E-10	423.965	1.59039E-09	599.4738	2.32971E-09	3530.148	3.45024E-09
76.31675	-1.06095E-09	252.7335	4.10823E-10	427.7785	1.63771E-09	603.2788	2.37132E-09	3533.928	3.50604E-09
80.12775	-1.08132E-09	256.547	4.19823E-10	431.567	1.6401E-09	607.2275	2.3826E-09	3537.738	3.43697E-09
83.8955	-1.04917E-09	260.368	4.64884E-10	435.3425	1.68837E-09	611.2765	2.40311E-09	3541.525	3.44936E-09
87.67625	-1.04608E-09	264.1435	5.02577E-10	439.1158	1.69688E-09	615.0548	2.37874E-09	3545.33	3.47187E-09
91.48225	-1.01998E-09	267.924	5.08451E-10	442.894	1.71469E-09	618.8453	2.40937E-09	3549.153	3.44075E-09
99.03625	-9.43088E-10	275.5035	5.76976E-10	450.4533	1.74669E-09	626.6198	2.44291E-09	3556.775	3.41907E-09
102.832	-8.92323E-10	279.2995	6.29939E-10	454.2513	1.78336E-09	630.546	2.49478E-09	3560.6	3.49331E-09
106.6228	-8.51928E-10	283.0748	6.26064E-10	458.0345	1.79967E-09	634.3343	2.48896E-09	3565.308	3.44073E-09
110.4363	-8.12445E-10	286.9583	6.56282E-10	461.8155	1.8002E-09	638.1225	2.50433E-09	3569.293	3.47464E-09
114.3148	-7.85648E-10	290.7568	6.79516E-10	465.6065	1.83536E-09	641.9733	2.51251E-09	3573.125	3.44788E-09
118.1203	-7.58675E-10	294.6103	7.23758E-10	469.4098	1.83931E-09	645.917	2.53899E-09	3576.933	3.48881E-09
121.9063	-7.1083E-10	298.3908	7.63407E-10	473.213	1.86996E-09	649.695	2.52563E-09	3580.725	3.43619E-09
125.687	-6.8435E-10	302.1793	7.66591E-10	476.996	1.87632E-09	653.5358	2.54635E-09	3584.518	3.40946E-09
129.4855	-6.42785E-10	305.9548	8.35069E-10	480.8245	1.92481E-09	657.329	2.54268E-09	3588.32	3.48745E-09
133.261	-6.12141E-10	309.7508	8.39281E-10	484.6055	1.92087E-09	661.13	2.57212E-09	3592.11	3.45461E-09
137.0368	-5.69783E-10	313.5443	8.59826E-10	488.3885	1.93945E-09	664.9035	2.58862E-09	3595.928	3.49411E-09
140.8175	-5.36472E-10	317.3348	8.9286E-10	492.1768	1.95444E-09	668.694	2.58938E-09	3599.713	3.39376E-09
144.591	-5.03039E-10	321.138	9.42086E-10	495.9928	1.96881E-09	672.9405	2.6079E-09	3603.515	3.45702E-09
148.3718	-4.66997E-10	324.9088	9.81374E-10	499.811	1.96068E-09	676.8715	2.64179E-09	3607.313	3.4684E-09
152.18	-4.67448E-10	328.7198	9.8391E-10	503.6068	1.96246E-09	680.6623	2.62974E-09	3611.1	3.44139E-09
155.953	-4.27217E-10	332.513	1.00925E-09	507.5978	1.99175E-09	684.4533	2.63632E-09	3614.9	3.3942E-09
161.6745	-3.60203E-10	336.3263	1.03791E-09	511.3838	2.0286E-09	688.2613	2.67664E-09	3618.685	3.41612E-09
165.6108	-3.40074E-10	340.112	1.06511E-09	515.1798	2.03037E-09	692.0473	2.65367E-09	3622.498	3.43188E-09
169.3838	-3.09209E-10	343.9505	1.0924E-09	519.1255	2.0701E-09	696.6468	2.65619E-09	3626.295	3.44373E-09
173.1695	-2.71504E-10	347.7263	1.12986E-09	522.919	2.06103E-09	700.4378	2.68427E-09	3630.125	3.42271E-09

Table C.21: Toluene data at 40 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-6.59E-10	174.557	2.31109E-09	348.6257	4.62558E-09	523.119	5.1276E-09	3444.943	4.70113E-09
3.949333	-6.347E-10	178.339	2.39759E-09	352.4017	4.62096E-09	526.9047	5.12969E-09	3448.743	4.71076E-09
7.765333	-6.463E-10	182.121	2.47637E-09	356.181	4.59784E-09	530.6873	5.11391E-09	3452.583	4.69689E-09
11.59433	-6.596E-10	185.897	2.53041E-09	359.9763	4.64881E-09	534.4763	5.15758E-09	3456.443	4.71329E-09
15.39333	-6.474E-10	189.68	2.6747E-09	363.759	4.69469E-09	538.2553	5.16803E-09	3460.363	4.74304E-09
19.19567	-5.97E-10	193.476	2.67499E-09	367.5413	4.69566E-09	542.0347	5.15288E-09	3464.347	4.74409E-09
23.00167	-5.715E-10	197.245	2.72886E-09	371.324	4.6938E-09	545.827	5.15985E-09	3468.097	4.73128E-09
26.811	-5.679E-10	201.02	2.82201E-09	375.1393	4.69789E-09	549.6063	5.16498E-09	3471.9	4.73807E-09
30.61333	-5.2E-10	204.799	2.90382E-09	378.922	4.71839E-09	553.4117	5.21511E-09	3475.71	4.72054E-09
34.40567	-4.712E-10	208.575	2.9542E-09	382.698	4.76559E-09	557.2077	5.19638E-09	3479.553	4.74787E-09
38.19833	-6.215E-10	212.344	3.0262E-09	386.4937	4.7863E-09	560.987	5.22071E-09	3483.357	4.75699E-09
42.00067	-7.946E-10	216.147	3.03938E-09	390.2997	4.77262E-09	564.7827	5.21695E-09	3487.147	4.71233E-09
45.82	-7.804E-10	219.926	3.10118E-09	394.075	4.77448E-09	568.5987	5.21671E-09	3490.957	4.68807E-09
49.65867	-6.802E-10	223.705	3.22389E-09	397.8477	4.78496E-09	572.3877	5.21253E-09	3494.773	4.71061E-09
53.45467	-5.883E-10	227.488	3.23058E-09	401.637	4.77257E-09	576.18	5.26539E-09	3498.573	4.72565E-09
57.22733	-4.992E-10	231.263	3.27226E-09	405.4193	4.8246E-09	579.989	5.26328E-09	3502.36	4.7396E-09
61.00333	-4.048E-10	235.039	3.3906E-09	409.188	4.81653E-09	583.7683	5.28104E-09	3506.24	4.67577E-09
64.78233	-3.179E-10	238.821	3.5099E-09	412.9773	4.84317E-09	587.561	5.2647E-09	3510.243	4.73653E-09
68.55767	-2.072E-10	242.607	3.53239E-09	416.75	4.87207E-09	591.3967	5.28345E-09	3514.053	4.70941E-09
72.347	-1.097E-10	246.383	3.53948E-09	420.539	4.89738E-09	595.179	5.26506E-09	3517.86	4.70356E-09
76.11633	-2.356E-11	250.169	3.65915E-09	424.3183	4.89527E-09	598.9683	5.26724E-09	3521.687	4.70463E-09
83.67067	1.2956E-10	257.73	3.72575E-09	431.883	4.91361E-09	606.7203	5.28121E-09	3529.38	4.6983E-09
87.45333	2.0914E-10	261.503	3.80964E-09	435.669	4.93944E-09	610.5023	5.24719E-09	3533.167	4.68213E-09
91.23933	2.9851E-10	265.279	3.88137E-09	439.4513	4.91985E-09	614.2917	5.27501E-09	3536.973	4.67917E-09
95.03833	3.5893E-10	269.067	3.87854E-09	443.247	4.96359E-09	618.0673	5.2976E-09	3540.767	4.71838E-09
98.81767	4.7414E-10	272.847	3.92903E-09	447.026	4.91487E-09	621.8467	5.28513E-09	3544.55	4.68503E-09
102.6163	5.9048E-10	276.636	3.95743E-09	450.8053	4.99332E-09	625.6357	5.32404E-09	3548.43	4.69341E-09
106.3923	6.9397E-10	280.428	4.02611E-09	454.601	5.00692E-09	629.4147	5.30789E-09	3552.227	4.69585E-09
110.1783	7.7364E-10	284.207	4.05219E-09	458.397	4.98847E-09	633.2003	5.31323E-09	3556.057	4.72229E-09
113.9773	9.0901E-10	287.98	4.13112E-09	462.189	4.97542E-09	636.9797	5.27741E-09	3559.94	4.68484E-09
117.763	1.0165E-09	291.792	4.11581E-09	466.182	5.01812E-09	640.769	5.30319E-09	3563.74	4.71993E-09
121.5457	1.1295E-09	295.591	4.16044E-09	469.9847	5.04526E-09	644.548	5.3138E-09	3567.677	4.69839E-09
125.318	1.2209E-09	299.387	4.22831E-09	473.7637	5.02365E-09	648.33	5.29473E-09	3571.523	4.69492E-09
129.1037	1.2838E-09	303.193	4.23414E-09	477.553	5.03472E-09	652.1027	5.28473E-09	3575.42	4.68761E-09
132.8797	1.4249E-09	306.989	4.29384E-09	481.3417	5.0799E-09	655.8853	5.29277E-09	3579.203	4.70692E-09
136.6587	1.4946E-09	310.768	4.30141E-09	485.121	5.03338E-09	659.6677	5.26757E-09	3583.037	4.6904E-09
140.508	1.5969E-09	314.554	4.3258E-09	488.91	5.01967E-09	663.4533	5.31886E-09	3586.863	4.69887E-09
144.3073	1.6581E-09	318.34	4.40368E-09	492.6893	5.07915E-09	667.2557	5.30414E-09	3590.823	4.75615E-09
148.0927	1.7864E-09	322.115	4.38812E-09	496.4687	5.06532E-09	671.0283	5.31891E-09	3594.613	4.75884E-09
151.8683	1.8687E-09	325.911	4.4166E-09	500.3943	5.10061E-09	674.8177	5.32867E-09	3598.393	4.77751E-09
155.6477	1.9269E-09	329.703	4.48093E-09	504.18	5.07318E-09	678.65	5.34977E-09	3602.193	4.72649E-09
159.4337	1.9849E-09	333.506	4.49063E-09	507.966	5.04205E-09	682.4287	5.27678E-09	3605.977	4.78283E-09
163.2193	2.0863E-09	337.292	4.53739E-09	511.7583	5.08443E-09	686.2113	5.3147E-09	3609.777	4.77594E-09
166.9913	2.2029E-09	341.071	4.53831E-09	515.554	5.11542E-09	690.0773	5.33435E-09	3613.61	4.73479E-09
170.7673	2.2513E-09	344.857	4.58198E-09	519.3333	5.09777E-09	693.8833	5.34114E-09	3617.393	4.7589E-09

Table C.22: Toluene data at 55 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-4.7106E-10	178.6593	6.99368E-09	354.595	7.97605E-09	534.3463	7.58379E-09	3490.323	7.85804E-09
5.231333	-4.8302E-10	182.4683	7.06356E-09	358.411	7.91784E-09	538.1587	7.57888E-09	3494.307	7.84216E-09
9.107333	-4.715E-10	186.3377	7.16666E-09	362.217	7.92698E-09	541.968	7.59132E-09	3498.103	7.81646E-09
12.89933	-4.3687E-10	190.2237	7.21841E-09	366.019	7.92168E-09	545.8037	7.57387E-09	3502.04	7.84996E-09
16.742	-7.7362E-10	194.0197	7.28357E-09	369.805	7.9362E-09	549.6197	7.59809E-09	3505.867	7.81947E-09
20.51467	-7.8432E-10	197.8623	7.33316E-09	373.694	7.95637E-09	553.422	7.56491E-09	3509.697	7.82792E-09
24.284	-6.9618E-10	201.878	7.43913E-09	377.5	7.9268E-09	557.268	7.55478E-09	3513.503	7.85954E-09
28.06233	-4.7648E-10	205.7273	7.48305E-09	381.339	7.91366E-09	561.1173	7.58617E-09	3517.307	7.89199E-09
31.83833	-2.3269E-10	209.53	7.55132E-09	385.162	7.97073E-09	564.9997	7.54456E-09	3521.09	7.83447E-09
35.611	2.48937E-11	213.366	7.63321E-09	388.977	7.91912E-09	568.7857	7.57331E-09	3524.907	7.83774E-09
39.41033	2.95954E-10	217.1653	7.65101E-09	392.843	7.91433E-09	572.5877	7.5924E-09	3528.7	7.82835E-09
43.19267	5.52172E-10	221.0073	7.72024E-09	397.033	7.9055E-09	576.3803	7.60633E-09	3532.49	7.85955E-09
46.97133	8.03756E-10	224.8067	7.74154E-09	401.683	7.8719E-09	580.253	7.60888E-09	3536.3	7.82276E-09
50.77067	1.05324E-09	228.599	7.75607E-09	405.473	7.88202E-09	584.052	7.66602E-09	3540.143	7.83889E-09
54.55	1.24427E-09	232.3917	7.84584E-09	409.282	7.85787E-09	587.8513	7.67489E-09	3543.923	7.81932E-09
58.33233	1.47303E-09	236.1873	7.8492E-09	413.091	7.82843E-09	591.6373	7.6771E-09	3547.907	7.78271E-09
62.118	1.69116E-09	239.983	7.90539E-09	416.914	7.85679E-09	595.4563	7.70636E-09	3551.74	7.80103E-09
65.92733	1.8834E-09	243.7957	7.98513E-09	420.713	7.87794E-09	599.255	7.74268E-09	3555.557	7.80364E-09
69.73	2.13184E-09	247.5813	8.00643E-09	425.467	7.84365E-09	603.1077	7.76409E-09	3559.363	7.79801E-09
73.559	2.38316E-09	251.3807	8.01539E-09	429.683	7.87274E-09	606.9037	7.82411E-09	3563.16	7.80669E-09
77.78867	2.65367E-09	255.1863	8.05584E-09	433.475	7.81054E-09	610.703	7.81734E-09	3566.953	7.77322E-09
81.58767	2.86849E-09	258.992	8.10089E-09	437.662	7.83468E-09	614.499	7.82765E-09	3570.76	7.79143E-09
85.46367	3.11293E-09	262.8047	8.14191E-09	441.458	7.79076E-09	618.311	7.80574E-09	3574.56	7.76541E-09
89.3	3.33809E-09	266.6007	8.13663E-09	445.26	7.80125E-09	622.1	7.84486E-09	3578.36	7.7969E-09
93.17567	3.56289E-09	270.3933	8.17007E-09	449.109	7.82276E-09	625.896	7.84141E-09	3582.24	7.76457E-09
100.7807	3.95316E-09	278.385	8.21683E-09	456.828	7.78471E-09	633.4947	7.83063E-09	3589.873	7.77099E-09
104.5763	4.20449E-09	282.171	8.17761E-09	460.64	7.79691E-09	637.2897	7.822E-09	3593.683	7.72127E-09
108.4587	4.42007E-09	285.9637	8.21739E-09	465.428	7.74016E-09	641.0823	7.85633E-09	3597.49	7.71178E-09
112.2447	4.56791E-09	289.7527	8.20517E-09	469.223	7.76121E-09	644.8783	7.85233E-09	3601.29	7.72327E-09
116.0273	4.7455E-09	293.5447	8.13467E-09	473.019	7.73344E-09	648.671	7.92346E-09	3605.1	7.75928E-09
119.8197	4.90103E-09	297.3607	8.16767E-09	476.995	7.77735E-09	652.4703	7.88684E-09	3608.923	7.73172E-09
123.5987	5.07073E-09	301.1567	8.19488E-09	480.814	7.77674E-09	656.279	7.86578E-09	3612.723	7.70394E-09
127.3877	5.21029E-09	304.966	8.12421E-09	484.614	7.7452E-09	660.138	7.89893E-09	3616.52	7.71278E-09
131.187	5.36729E-09	308.825	8.16409E-09	488.513	7.7243E-09	663.9373	7.83796E-09	3620.313	7.69773E-09
134.9963	5.59614E-09	312.6273	8.10862E-09	492.335	7.69473E-09	667.7467	7.88715E-09	3624.177	7.65852E-09
138.802	5.75453E-09	316.4333	8.06858E-09	496.121	7.70903E-09	671.596	7.83015E-09	3628	7.67914E-09
144.4603	5.9878E-09	320.236	8.06447E-09	499.944	7.68466E-09	675.4017	7.7814E-09	3631.783	7.69261E-09
148.243	6.07256E-09	324.0583	8.03789E-09	503.823	7.66688E-09	679.2207	7.7924E-09	3635.587	7.68682E-09
152.032	6.317E-09	327.8607	8.02203E-09	507.599	7.65522E-09	683.0267	7.8529E-09	3639.387	7.65852E-09
155.8447	6.3971E-09	331.6863	7.99406E-09	511.398	7.66716E-09	686.8257	7.78544E-09	3643.19	7.70338E-09
159.6437	6.53167E-09	335.4823	7.96835E-09	515.197	7.60511E-09	690.7053	7.80896E-09	3646.987	7.6421E-09
163.476	6.61189E-09	339.3117	7.98996E-09	519.026	7.60212E-09	694.5243	7.82841E-09	3650.897	7.62169E-09
167.262	6.7447E-09	343.1507	7.96726E-09	522.859	7.58831E-09	698.367	7.83835E-09	3654.743	7.63095E-09
171.0547	6.84615E-09	346.9533	7.97486E-09	526.648	7.56799E-09	702.266	7.86255E-09	3658.537	7.62114E-09
174.8607	6.90132E-09	350.7457	7.96176E-09	530.494	7.59283E-09	706.0553	7.83444E-09	3662.467	7.61352E-09

Table C.23: Toluene data at 70 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-5.351E-10	174.737	7.495E-09	349.269	8.99382E-09	525.664	1.00025E-08	3465.07	8.72802E-09
3.936	-5.388E-10	178.528	7.5203E-09	353.115	9.10696E-09	529.509	9.94148E-09	3469.015	8.67884E-09
7.747	-5.1898E-10	182.329	7.6598E-09	356.905	9.11013E-09	533.29	9.97753E-09	3472.965	8.63796E-09
11.548	-3.7575E-10	186.134	7.7916E-09	360.701	9.16822E-09	537.131	1.005E-08	3476.78	8.67716E-09
15.3535	-3.4279E-10	189.93	7.8099E-09	364.492	9.11533E-09	540.947	1.00602E-08	3480.605	8.77512E-09
19.1245	-2.6073E-10	193.711	7.9932E-09	368.278	9.20798E-09	544.798	1.00429E-08	3484.69	8.74777E-09
22.93	6.82871E-11	197.512	8.0842E-09	372.159	9.13986E-09	548.623	1.00879E-08	3488.515	8.75309E-09
26.696	3.81543E-10	201.303	8.1757E-09	375.949	9.09864E-09	552.469	1.00417E-08	3492.35	8.74831E-09
30.5065	7.09158E-10	205.098	8.1898E-09	379.74	9.15278E-09	556.335	1.00465E-08	3496.22	8.73688E-09
34.2825	1.009E-09	208.909	8.2588E-09	383.596	9.12469E-09	560.211	1.00711E-08	3500.045	8.7845E-09
38.0535	1.29073E-09	212.695	8.4393E-09	387.748	9.12277E-09	564.032	1.00652E-08	3503.875	8.76827E-09
41.829	1.57899E-09	216.481	8.4429E-09	391.594	9.14079E-09	568.048	1.00884E-08	3507.73	8.68803E-09
45.6145	1.83212E-09	220.277	8.4359E-09	395.399	9.08312E-09	571.979	1.00319E-08	3511.57	8.73705E-09
49.3805	2.06397E-09	224.067	8.4584E-09	399.21	9.15196E-09	575.765	9.96691E-09	3515.42	8.76926E-09
53.1615	2.33187E-09	227.863	8.4831E-09	403.066	9.20443E-09	579.561	9.99021E-09	3519.99	8.78775E-09
56.9375	2.52949E-09	231.669	8.4851E-09	406.857	9.18658E-09	583.372	9.96439E-09	3523.815	8.74915E-09
60.7225	2.77497E-09	235.455	8.5531E-09	410.678	9.21901E-09	587.167	9.93622E-09	3527.635	8.76789E-09
64.5435	2.95844E-09	239.251	8.5395E-09	414.513	9.20812E-09	590.948	9.96161E-09	3531.475	8.77242E-09
68.3195	3.15816E-09	243.051	8.6112E-09	418.334	9.27817E-09	594.734	9.99925E-09	3535.295	8.82003E-09
72.0905	3.35886E-09	246.847	8.6126E-09	422.135	9.22009E-09	598.51	9.94897E-09	3539.105	8.77161E-09
75.871	3.50406E-09	250.638	8.732E-09	425.961	9.27366E-09	602.366	9.97954E-09	3542.925	8.82278E-09
79.6565	3.73603E-09	254.434	8.7481E-09	429.827	9.2675E-09	606.252	9.97603E-09	3546.735	8.80672E-09
83.4275	3.96139E-09	258.2195	8.7591E-09	433.623	9.27464E-09	610.027	1.00081E-08	3550.675	8.85347E-09
87.2285	4.13098E-09	262.005	8.8239E-09	437.443	9.26808E-09	613.818	1.00533E-08	3554.515	8.8501E-09
91.0045	4.24062E-09	265.801	8.7989E-09	441.274	9.13831E-09	617.624	1.0026E-08	3558.36	8.83156E-09
94.78	4.45957E-09	269.582	8.7942E-09	445.08	9.14573E-09	621.405	1.00462E-08	3562.155	8.81371E-09
98.5605	4.67397E-09	273.378	8.762E-09	448.906	9.20416E-09	625.206	9.96723E-09	3566.065	8.79521E-09
102.3415	4.87905E-09	277.1685	8.7309E-09	452.712	9.09381E-09	629.006	9.99236E-09	3569.89	8.79192E-09
106.1325	5.03675E-09	280.954	8.6399E-09	456.513	9.18704E-09	632.807	1.00175E-08	3573.715	8.76006E-09
109.933	5.19956E-09	284.76	8.6657E-09	460.559	9.34082E-09	636.613	1.00073E-08	3577.5	8.81847E-09
113.7135	5.39488E-09	288.546	8.7974E-09	464.345	9.25895E-09	640.404	9.96844E-09	3581.32	8.81334E-09
117.4895	5.56823E-09	292.342	8.6987E-09	468.131	9.29743E-09	644.184	9.99995E-09	3585.2	8.74237E-09
121.5105	5.79186E-09	296.1425	8.7717E-09	471.921	9.42335E-09	647.985	9.97516E-09	3589.27	8.69007E-09
125.3165	5.89808E-09	299.928	8.8055E-09	475.747	9.38447E-09	651.781	1.00372E-08	3593.105	8.59804E-09
129.1175	6.0926E-09	303.719	8.8376E-09	479.618	9.44008E-09	655.562	1.00325E-08	3596.915	8.64761E-09
132.918	6.12073E-09	307.525	8.7343E-09	483.394	9.34804E-09	659.358	1.00376E-08	3600.705	8.58798E-09
136.719	6.28027E-09	311.311	8.7783E-09	487.175	9.45012E-09	663.153	1.00928E-08	3604.71	8.60661E-09
144.3105	6.60022E-09	318.897	8.7813E-09	494.781	9.51213E-09	670.73	9.96178E-09	3612.4	8.64244E-09
148.1015	6.74098E-09	322.678	8.732E-09	498.652	9.53096E-09	674.566	9.99618E-09	3616.2	8.64475E-09
151.962	6.78396E-09	326.464	8.8226E-09	502.483	9.58868E-09	678.357	9.98206E-09	3620.09	8.69824E-09
155.768	6.94876E-09	330.26	8.9067E-09	506.299	9.68313E-09	682.638	9.93266E-09	3623.915	8.71964E-09
159.554	7.07676E-09	334.035	8.9118E-09	510.084	9.70541E-09	686.419	9.97949E-09	3627.72	8.64691E-09
163.36	7.13495E-09	337.831	8.934E-09	513.94	9.67171E-09	690.21	9.95757E-09	3631.53	8.66971E-09
167.155	7.25699E-09	341.627	9.0617E-09	518.022	9.83168E-09	694.015	9.9457E-09	3635.41	8.76736E-09
170.936	7.39341E-09	345.468	9.0179E-09	521.803	9.83441E-09	697.816	9.93763E-09	3639.425	8.83474E-09

Table C.24: Toluene data at 90 °C and 0.5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-8.81E-10	170.78	1.41E-09	341.401	4.51E-09	513.264	6.74E-09	3419.4	1.31E-08
3.795	-8.85E-10	174.576	1.49E-09	345.187	4.57E-09	517.049	6.81E-09	3423.2	1.31E-08
7.781	-8.78E-10	178.362	1.57E-09	348.983	4.62E-09	520.835	6.84E-09	3426.99	1.31E-08
11.617	-8.67E-10	182.148	1.64E-09	352.768	4.68E-09	524.611	6.92E-09	3430.77	1.31E-08
15.453	-8.40E-10	185.944	1.71E-09	356.544	4.76E-09	528.397	6.93E-09	3434.62	1.31E-08
19.229	-7.95E-10	189.729	1.79E-09	360.34	4.80E-09	532.172	6.99E-09	3438.43	1.31E-08
23.095	-7.43E-10	193.515	1.86E-09	364.126	4.88E-09	535.948	7.03E-09	3442.24	1.31E-08
26.861	-6.93E-10	197.301	1.93E-09	367.902	4.91E-09	539.764	7.08E-09	3446.21	1.30E-08
30.706	-6.19E-10	201.087	2.01E-09	371.697	4.97E-09	543.58	7.08E-09	3450.04	1.31E-08
34.492	-5.49E-10	204.872	2.09E-09	375.473	5.05E-09	547.356	7.15E-09	3453.84	1.31E-08
38.268	-4.69E-10	208.688	2.14E-09	379.259	5.11E-09	551.182	7.19E-09	3457.64	1.30E-08
42.104	-3.91E-10	212.474	2.23E-09	383.055	5.13E-09	554.967	7.23E-09	3461.46	1.31E-08
45.89	-3.12E-10	216.26	2.30E-09	386.83	5.21E-09	558.753	7.24E-09	3465.24	1.31E-08
49.715	-2.32E-10	220.056	2.37E-09	390.616	5.25E-09	562.549	7.29E-09	3469.03	1.31E-08
53.481	-9.70E-10	223.841	2.43E-09	394.402	5.33E-09	566.495	7.33E-09	3472.81	1.31E-08
57.327	-1.06E-09	227.637	2.52E-09	398.188	5.39E-09	570.501	7.72E-09	3476.61	1.30E-08
61.083	-9.72E-10	231.433	2.59E-09	402.094	5.44E-09	574.307	7.79E-09	3480.41	1.31E-08
64.869	-8.83E-10	235.209	2.66E-09	405.89	5.52E-09	578.233	7.82E-09	3484.21	1.31E-08
68.654	-8.04E-10	239.005	2.73E-09	409.665	5.54E-09	582.019	7.82E-09	3488.01	1.31E-08
72.42	-7.15E-10	242.78	2.82E-09	413.451	5.59E-09	585.814	7.90E-09	3491.8	1.30E-08
76.206	-6.30E-10	246.546	2.86E-09	417.247	5.64E-09	589.6	7.93E-09	3495.59	1.31E-08
79.992	-5.43E-10	250.322	2.94E-09	421.023	5.67E-09	593.396	7.97E-09	3499.39	1.31E-08
83.767	-4.65E-10	254.118	3.03E-09	424.879	5.69E-09	597.202	8.01E-09	3503.17	1.30E-08
87.563	-3.71E-10	257.893	3.11E-09	428.674	5.76E-09	601.018	8.01E-09	3507.13	1.30E-08
91.339	-2.98E-10	261.689	3.15E-09	432.48	5.81E-09	604.833	8.07E-09	3510.93	1.30E-08
95.135	-2.10E-10	265.465	3.24E-09	436.326	5.87E-09	608.639	8.10E-09	3514.73	1.30E-08
98.921	-1.22E-10	269.241	3.31E-09	440.242	5.91E-09	612.475	8.11E-09	3518.52	1.30E-08
102.696	-5.24E-11	273.277	3.38E-09	444.038	5.94E-09	616.291	8.15E-09	3522.45	1.30E-08
106.472	4.08E-11	277.033	3.43E-09	448.074	5.99E-09	620.077	8.18E-09	3526.42	1.31E-08
110.248	1.14E-10	280.808	3.51E-09	451.92	6.06E-09	623.903	8.20E-09	3530.36	1.31E-08
114.024	1.96E-10	284.604	3.57E-09	456.186	6.11E-09	627.799	8.25E-09	3534.17	1.30E-08
117.799	2.68E-10	288.38	3.63E-09	459.982	6.15E-09	631.594	8.28E-09	3538.08	1.31E-08
121.585	3.57E-10	292.166	3.69E-09	463.798	6.22E-09	635.49	8.33E-09	3541.88	1.30E-08
125.361	4.46E-10	295.952	3.75E-09	467.594	6.23E-09	639.296	8.35E-09	3545.78	1.31E-08
129.137	5.15E-10	299.717	3.82E-09	471.37	6.27E-09	643.112	8.38E-09	3549.55	1.31E-08
132.913	6.01E-10	303.493	3.88E-09	475.155	6.33E-09	647.008	8.42E-09	3553.36	1.30E-08
136.678	6.75E-10	307.309	3.96E-09	479.021	6.38E-09	650.844	8.46E-09	3557.15	1.31E-08
140.464	7.69E-10	311.075	4.02E-09	482.807	6.41E-09	654.64	8.49E-09	3560.95	1.31E-08
144.25	8.56E-10	314.85	4.08E-09	486.693	6.45E-09	658.435	8.52E-09	3564.74	1.31E-08
148.036	9.20E-10	318.636	4.15E-09	490.489	6.50E-09	662.231	8.55E-09	3591.4	1.31E-08
151.841	1.00E-09	322.422	4.22E-09	494.295	6.55E-09	666.037	8.56E-09	3595.19	1.31E-08
155.617	1.08E-09	326.218	4.28E-09	498.07	6.55E-09	669.843	8.59E-09	3598.99	1.31E-08
159.403	1.16E-09	330.004	4.35E-09	501.856	6.64E-09	673.689	8.65E-09	3602.95	1.31E-08
163.219	1.24E-09	333.819	4.41E-09	505.662	6.66E-09	677.635	8.67E-09	3606.78	1.31E-08
166.995	1.33E-09	337.615	4.47E-09	509.478	6.72E-09	681.431	8.69E-09	3610.6	1.31E-08

Table C.25: Toluene data at 24 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-3.97099E-10	170.491	1.40091E-08	341.222	2.22075E-08	512.904	2.62198E-08	3454.94	2.53609E-08
3.806	-4.03067E-10	174.267	1.42155E-08	345.008	2.23178E-08	516.67	2.63091E-08	3458.72	2.52983E-08
7.582	-7.03781E-10	178.062	1.44784E-08	348.773	2.24571E-08	520.446	2.63097E-08	3462.85	2.53002E-08
11.368	-7.55157E-10	181.838	1.47102E-08	352.539	2.25597E-08	524.221	2.63515E-08	3466.67	2.54764E-08
15.164	-1.06768E-09	185.604	1.49469E-08	356.365	2.26911E-08	528.057	2.62912E-08	3470.51	2.56151E-08
18.989	-7.20843E-10	189.39	1.51901E-08	360.231	2.27713E-08	531.843	2.63353E-08	3474.29	2.55468E-08
22.775	-3.23622E-10	193.176	1.53831E-08	363.997	2.2907E-08	535.619	2.63952E-08	3478.07	2.54787E-08
26.561	1.03204E-10	196.961	1.56399E-08	367.772	2.29229E-08	539.404	2.6562E-08	3481.86	2.54291E-08
30.337	5.33557E-10	200.747	1.58475E-08	371.558	2.30152E-08	543.18	2.65728E-08	3485.68	2.53966E-08
34.113	9.82591E-10	204.513	1.60418E-08	375.404	2.30851E-08	546.996	2.65639E-08	3489.45	2.5373E-08
37.898	1.43603E-09	208.289	1.6283E-08	379.19	2.32514E-08	550.802	2.66563E-08	3493.23	2.54137E-08
41.674	1.87057E-09	212.084	1.65049E-08	382.966	2.33487E-08	554.578	2.68699E-08	3497.04	2.545E-08
45.48	2.31827E-09	215.87	1.66996E-08	386.751	2.34287E-08	558.454	2.69987E-08	3500.83	2.54111E-08
49.266	2.76789E-09	219.656	1.69276E-08	390.617	2.35107E-08	562.139	2.71088E-08	3504.65	2.54027E-08
53.072	3.20617E-09	223.452	1.7116E-08	394.393	2.35674E-08	566.005	2.72255E-08	3508.42	2.54191E-08
56.837	3.62846E-09	227.218	1.72916E-08	398.179	2.35118E-08	569.791	2.72519E-08	3512.2	2.54177E-08
60.623	4.04912E-09	231.083	1.75052E-08	401.955	2.35803E-08	573.567	2.7301E-08	3516.04	2.546E-08
64.389	4.44699E-09	234.869	1.77351E-08	405.72	2.36713E-08	577.433	2.73922E-08	3519.87	2.54942E-08
68.165	4.86133E-09	238.645	1.79395E-08	409.496	2.37739E-08	581.489	2.73035E-08	3523.67	2.55237E-08
71.96	5.28468E-09	242.431	1.8192E-08	413.262	2.38691E-08	585.275	2.72771E-08	3527.45	2.55004E-08
75.736	5.66578E-09	246.207	1.83633E-08	417.038	2.40069E-08	589.11	2.73085E-08	3531.24	2.55433E-08
79.512	6.05491E-09	250.042	1.85401E-08	420.833	2.41248E-08	592.866	2.73614E-08	3535.07	2.55829E-08
83.308	6.42918E-09	253.838	1.86839E-08	424.679	2.42579E-08	596.632	2.7381E-08	3538.86	2.54804E-08
87.094	6.89991E-09	257.644	1.88901E-08	428.465	2.43674E-08	600.498	2.74589E-08	3542.72	2.54546E-08
90.899	7.27268E-09	261.42	1.91023E-08	432.321	2.43901E-08	604.594	2.75566E-08	3546.54	2.54059E-08
94.695	7.7377E-09	265.216	1.92536E-08	436.107	2.44309E-08	608.46	2.76301E-08	3550.45	2.5363E-08
98.491	8.0868E-09	269.011	1.94254E-08	439.902	2.45184E-08	612.236	2.77693E-08	3554.46	2.5388E-08
102.287	8.51294E-09	272.847	1.95988E-08	443.678	2.46217E-08	616.022	2.79165E-08	3558.21	2.53816E-08
106.083	8.89728E-09	276.633	1.98024E-08	447.524	2.47524E-08	619.797	2.81146E-08	3562.07	2.52526E-08
109.878	9.21624E-09	280.399	1.99856E-08	451.811	2.49314E-08	623.573	2.8271E-08	3565.92	2.5206E-08
113.674	9.56062E-09	284.495	2.01634E-08	455.546	2.50914E-08	627.389	2.8128E-08	3569.73	2.52249E-08
117.47	9.89628E-09	288.281	2.0314E-08	459.372	2.522E-08	631.255	2.79991E-08	3573.57	2.52768E-08
121.276	1.02318E-08	292.077	2.04712E-08	463.178	2.53054E-08	635.031	2.7918E-08	3577.42	2.53804E-08
125.072	1.05502E-08	295.842	2.06574E-08	466.994	2.5192E-08	638.786	2.79838E-08	3581.2	2.53505E-08
128.867	1.08745E-08	299.638	2.07664E-08	470.78	2.52461E-08	642.562	2.80235E-08	3585.02	2.53715E-08
132.663	1.11755E-08	303.404	2.08261E-08	474.565	2.54362E-08	646.338	2.81761E-08	3588.84	2.5441E-08
136.459	1.14811E-08	307.19	2.09576E-08	478.772	2.55869E-08	650.104	2.8332E-08	3592.66	2.54558E-08
140.235	1.17995E-08	310.976	2.10978E-08	482.618	2.56118E-08	653.869	2.84261E-08	3596.49	2.54581E-08
144.02	1.20998E-08	314.751	2.1257E-08	486.434	2.56576E-08	657.645	2.84048E-08	3626.91	2.53534E-08
147.796	1.23922E-08	318.527	2.14538E-08	490.219	2.57146E-08	661.411	2.84839E-08	3630.81	2.53983E-08
151.582	1.26567E-08	322.303	2.16335E-08	493.985	2.57957E-08	665.197	2.8516E-08	3634.89	2.53853E-08
155.368	1.29364E-08	326.079	2.17703E-08	497.781	2.59152E-08	668.952	2.84816E-08	3638.68	2.54108E-08
159.154	1.32197E-08	329.864	2.18904E-08	501.567	2.60064E-08	672.728	2.84143E-08	3642.49	2.53539E-08
162.939	1.34853E-08	333.65	2.19742E-08	505.342	2.59901E-08	676.584	2.8387E-08	3646.28	2.53367E-08
166.715	1.3734E-08	337.416	2.20657E-08	509.108	2.61158E-08	680.931	2.84058E-08	3650.11	2.52804E-08

Table C.26: Toluene data at 40 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-8.15E-10	170.094	3.03E-08	339.569	3.92E-08	509.188	4.48E-08	3404.93	4.01E-08
3.836	-6.50E-10	173.889	3.07E-08	343.355	3.91E-08	512.964	4.49E-08	3408.7	4.03E-08
7.602	-1.00E-09	177.655	3.09E-08	347.14	3.92E-08	516.729	4.49E-08	3412.47	4.03E-08
11.438	-2.31E-10	181.451	3.13E-08	350.906	3.93E-08	520.495	4.45E-08	3416.24	4.01E-08
15.214	8.30E-10	185.217	3.18E-08	354.692	3.99E-08	524.261	4.45E-08	3420.01	4.00E-08
18.98	2.01E-09	188.983	3.23E-08	358.468	4.07E-08	528.027	4.42E-08	3423.81	3.98E-08
22.755	3.24E-09	192.749	3.28E-08	362.243	4.03E-08	531.802	4.42E-08	3427.58	3.95E-08
26.531	4.50E-09	196.524	3.32E-08	366.009	4.00E-08	535.568	4.46E-08	3431.34	3.96E-08
30.317	5.68E-09	200.29	3.36E-08	369.775	4.01E-08	539.334	4.46E-08	3435.13	3.98E-08
34.093	6.85E-09	204.076	3.41E-08	373.541	4.03E-08	543.1	4.45E-08	3438.89	3.99E-08
37.869	8.35E-09	207.842	3.43E-08	377.316	4.01E-08	546.866	4.45E-08	3442.66	3.97E-08
41.665	9.49E-09	211.618	3.46E-08	381.082	4.00E-08	550.641	4.43E-08	3446.44	3.92E-08
45.441	1.05E-08	215.394	3.48E-08	384.848	3.99E-08	554.397	4.43E-08	3450.2	3.93E-08
49.226	1.16E-08	219.159	3.51E-08	388.624	4.03E-08	558.163	4.43E-08	3453.99	3.97E-08
53.012	1.26E-08	222.935	3.54E-08	392.39	4.04E-08	561.949	4.37E-08	3457.76	3.92E-08
56.788	1.35E-08	226.721	3.56E-08	396.155	4.07E-08	565.724	4.35E-08	3461.53	3.95E-08
60.574	1.44E-08	230.517	3.58E-08	399.941	4.07E-08	569.5	4.34E-08	3465.29	3.99E-08
64.35	1.53E-08	234.293	3.60E-08	403.697	4.07E-08	573.266	4.25E-08	3469.06	3.99E-08
68.116	1.61E-08	238.069	3.60E-08	407.463	4.04E-08	577.022	4.18E-08	3472.82	4.06E-08
71.882	1.68E-08	241.279	3.59E-08	411.238	4.05E-08	580.787	4.15E-08	3476.6	4.09E-08
75.657	1.76E-08	245.064	3.59E-08	415.004	4.03E-08	584.553	4.16E-08	3480.38	4.11E-08
79.433	1.83E-08	248.85	3.60E-08	418.76	4.06E-08	588.319	4.16E-08	3484.17	4.12E-08
83.219	1.91E-08	252.636	3.61E-08	422.546	4.10E-08	592.095	4.17E-08	3487.95	4.09E-08
87.005	1.97E-08	256.412	3.60E-08	426.301	4.16E-08	595.86	4.19E-08	3491.71	4.03E-08
90.771	2.05E-08	260.188	3.61E-08	430.067	4.12E-08	599.626	4.22E-08	3495.49	3.97E-08
94.567	2.11E-08	263.983	3.63E-08	433.823	4.12E-08	603.402	4.24E-08	3499.27	3.98E-08
98.342	2.17E-08	267.769	3.65E-08	437.579	4.10E-08	607.188	4.25E-08	3503.03	3.98E-08
102.118	2.23E-08	271.555	3.65E-08	441.354	4.12E-08	610.963	4.29E-08	3506.81	3.97E-08
105.904	2.28E-08	275.331	3.67E-08	445.13	4.13E-08	614.739	4.30E-08	3510.58	3.97E-08
109.67	2.33E-08	279.106	3.71E-08	448.886	4.12E-08	618.545	4.29E-08	3514.35	3.94E-08
113.436	2.39E-08	282.882	3.74E-08	452.662	4.11E-08	622.311	4.29E-08	3518.11	3.94E-08
117.222	2.44E-08	286.658	3.75E-08	456.437	4.17E-08	626.097	4.29E-08	3521.89	3.91E-08
120.998	2.49E-08	290.454	3.76E-08	460.193	4.20E-08	629.852	4.31E-08	3525.66	3.89E-08
124.783	2.54E-08	294.22	3.76E-08	463.969	4.22E-08	633.618	4.31E-08	3529.42	3.85E-08
128.569	2.58E-08	298.005	3.74E-08	467.735	4.27E-08	637.394	4.31E-08	3533.21	3.91E-08
132.345	2.62E-08	301.791	3.74E-08	471.49	4.29E-08	641.16	4.32E-08	3536.97	3.97E-08
136.111	2.66E-08	305.577	3.75E-08	475.266	4.31E-08	644.925	4.34E-08	3540.75	3.98E-08
139.887	2.70E-08	309.343	3.81E-08	479.032	4.32E-08	648.691	4.38E-08	3544.54	4.00E-08
143.653	2.75E-08	313.118	3.88E-08	482.798	4.40E-08	652.447	4.40E-08	3548.31	4.01E-08
147.418	2.80E-08	316.894	3.92E-08	486.583	4.43E-08	656.223	4.39E-08	3552.09	3.99E-08
151.204	2.85E-08	320.67	3.91E-08	490.339	4.45E-08	659.988	4.41E-08	3555.85	3.99E-08
154.97	2.89E-08	324.456	3.82E-08	494.115	4.45E-08	663.744	4.39E-08	3559.62	3.98E-08
158.736	2.93E-08	328.221	3.83E-08	497.891	4.44E-08	667.54	4.39E-08	3563.39	3.97E-08
162.522	2.96E-08	331.987	3.89E-08	501.646	4.48E-08	671.306	4.40E-08	3567.16	3.97E-08
166.308	2.99E-08	335.773	3.91E-08	505.422	4.47E-08	675.081	4.40E-08	3570.93	3.99E-08

Table C.27: Toluene data at 55 °C and 5 mL/min.

time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)	time (s)	Intensity (A)
0	-4.93E-10	170.139	3.52E-08	340.38	4.79E-08	511.741	5.16E-08	3416.44	5.92E-08
3.785	-2.99E-10	173.925	3.66E-08	344.165	4.78E-08	515.517	5.13E-08	3420.21	5.89E-08
7.681	-6.30E-10	177.701	3.75E-08	347.941	4.77E-08	519.293	5.10E-08	3424.01	5.83E-08
11.427	4.31E-10	181.477	3.77E-08	351.727	4.75E-08	523.059	5.33E-08	3427.79	5.89E-08
15.193	1.69E-09	185.263	3.80E-08	355.503	4.73E-08	526.844	5.62E-08	3431.56	5.90E-08
18.958	3.03E-09	189.028	3.87E-08	359.288	4.77E-08	530.63	5.74E-08	3435.35	5.84E-08
22.744	4.50E-09	192.804	3.88E-08	363.064	4.79E-08	534.406	5.77E-08	3439.13	5.77E-08
26.53	6.18E-09	196.62	3.86E-08	366.83	4.72E-08	538.192	5.79E-08	3442.91	5.73E-08
30.306	7.95E-09	200.396	3.87E-08	370.616	4.67E-08	541.957	5.83E-08	3446.7	5.66E-08
34.102	9.09E-09	204.191	3.88E-08	374.391	4.58E-08	545.733	5.85E-08	3450.47	5.55E-08
37.887	1.03E-08	207.987	3.90E-08	378.187	4.60E-08	549.519	5.84E-08	3454.25	5.42E-08
41.673	1.19E-08	211.763	3.91E-08	381.973	4.77E-08	553.285	5.76E-08	3458.04	5.34E-08
45.469	1.37E-08	215.549	3.93E-08	385.749	4.75E-08	557.061	5.63E-08	3461.81	5.34E-08
49.235	1.53E-08	219.315	3.97E-08	389.525	4.89E-08	560.826	5.62E-08	3465.58	5.33E-08
53	1.64E-08	223.1	3.99E-08	393.31	5.06E-08	564.592	5.50E-08	3469.39	5.31E-08
56.846	1.75E-08	226.886	3.99E-08	397.086	5.13E-08	568.388	5.55E-08	3473.16	5.32E-08
60.622	1.81E-08	230.652	3.99E-08	400.852	5.19E-08	572.164	5.51E-08	3476.92	5.34E-08
64.398	1.88E-08	234.428	4.02E-08	404.628	5.11E-08	575.939	5.44E-08	3480.71	5.32E-08
68.174	1.99E-08	238.203	4.06E-08	408.614	5.14E-08	579.725	5.43E-08	3484.51	5.32E-08
71.949	2.09E-08	242.019	4.04E-08	412.4	5.06E-08	583.491	5.39E-08	3488.3	5.34E-08
75.735	2.17E-08	245.795	4.07E-08	416.195	5.03E-08	587.287	5.38E-08	3492.08	5.44E-08
79.491	2.26E-08	249.591	4.06E-08	419.981	5.05E-08	591.072	5.39E-08	3495.86	5.44E-08
83.257	2.27E-08	253.387	4.05E-08	423.877	5.07E-08	594.838	5.39E-08	3499.64	5.45E-08
87.032	2.28E-08	257.172	4.15E-08	428.033	5.11E-08	598.624	5.40E-08	3503.44	5.43E-08
90.808	2.31E-08	260.948	4.18E-08	431.799	5.07E-08	602.41	5.39E-08	3507.22	5.33E-08
94.584	2.41E-08	264.714	4.27E-08	435.585	5.16E-08	606.196	5.41E-08	3511.03	5.31E-08
98.36	2.59E-08	268.48	4.27E-08	439.351	5.03E-08	609.971	5.39E-08	3514.82	5.34E-08
102.126	2.70E-08	272.255	4.20E-08	443.126	5.05E-08	613.747	5.35E-08	3518.71	5.37E-08
105.891	2.79E-08	276.021	4.27E-08	446.902	5.02E-08	617.513	5.33E-08	3522.51	5.41E-08
109.667	2.86E-08	279.807	4.28E-08	450.668	5.47E-08	621.289	5.19E-08	3526.29	5.41E-08
113.443	2.92E-08	283.613	4.41E-08	454.624	5.65E-08	625.064	5.19E-08	3530.07	5.41E-08
117.219	2.99E-08	287.399	4.52E-08	458.44	5.73E-08	628.83	5.21E-08	3533.86	5.41E-08
121.004	3.02E-08	291.184	4.54E-08	462.206	5.75E-08	632.636	5.35E-08	3537.62	5.48E-08
124.79	3.14E-08	294.98	4.59E-08	465.981	5.61E-08	636.412	5.48E-08	3541.4	5.42E-08
128.556	3.27E-08	298.756	4.65E-08	469.777	5.48E-08	640.188	5.64E-08	3545.21	5.45E-08
132.342	3.33E-08	302.532	4.64E-08	473.583	5.45E-08	643.973	5.66E-08	3548.98	5.54E-08
136.117	3.38E-08	306.327	4.61E-08	477.499	5.58E-08	647.739	5.63E-08	3552.75	5.71E-08
139.903	3.42E-08	310.113	4.55E-08	481.285	5.62E-08	651.505	5.75E-08	3556.53	5.77E-08
143.689	3.49E-08	313.919	4.70E-08	485.061	5.58E-08	655.291	5.90E-08	3560.31	5.72E-08
147.465	3.48E-08	317.715	4.82E-08	488.826	5.54E-08	659.066	5.94E-08	3564.08	5.60E-08
151.251	3.45E-08	321.481	4.83E-08	492.632	5.60E-08	662.842	5.89E-08	3567.87	5.45E-08
155.016	3.48E-08	325.256	4.81E-08	496.468	5.63E-08	666.658	5.92E-08	3571.65	5.44E-08
158.802	3.49E-08	329.022	4.68E-08	500.404	5.66E-08	670.424	5.88E-08	3575.41	5.45E-08
162.598	3.43E-08	332.798	4.67E-08	504.19	5.51E-08	674.209	5.86E-08	3579.19	5.43E-08
166.374	3.44E-08	336.594	4.75E-08	507.966	5.24E-08	677.995	5.91E-08	3582.96	5.41E-08

Table C.28: Toluene data at 70 °C and 5 mL/min.