



Chapter 5

On-line analysis of aldehydes and amines using Open Tubular and Multichannel PDMS traps

The bulk of the work presented in this chapter is the result of a collaborative study between the University of Pretoria, South Africa, and the Institute for Ecological Chemistry, GSF Research Centre, Germany. The German partner was interested in extending the analysis range of its home-built REMPI-TOFMS instrument. Not only should aromatic compounds be detected by the REMPI-TOFMS but also non-aromatics such as aliphatic aldehydes and amines. This could be achieved through the use of PDMS MCT newly developed by the South African partner, which had been used to demonstrate the *in situ* derivatization of low molecular mass aldehydes, using O- (2, 3, 4, 5, 6)-Pentafluorobenzylhydroxylamine (PFBHA) [61], effectively attaching an aromatic tag to an aliphatic compound (see Chapter 3, section 3.2.2).

Problems were anticipated with low level formaldehyde measurements, since formaldehyde is a ubiquitous compound and is frequently present in the reagent blank. Hence, the initial work described below is a continuation of my MSc project, where an attempt was made to decrease the formaldehyde content in the PFBHA derivatizing reagent used. The detection limit for formaldehyde using *in situ* derivatization on the MCT was severely constrained by the lack of a good reagent blank (*see section 6.3 MSc Thesis* [61]).

5.1. Loading the derivatizing reagent into the PDMS MCT by preparative gas chromatography

The aim in this experiment was to find a simple, repeatable and efficient method for loading excess PFBHA vapour into the PDMS MCT. Initial methods for saturating the silicone rubber included: loading the dynamic headspace of PFBHA from an aqueous solution of PFBHA in an impinger-type device and loading the dynamic headspace of PFBHA from the pure reagent packed in a glass tube (*see section 6.3 MSc Thesis [61]*). In the process of saturating the PDMS with PFBHA, the presence of HCHO-oxime impurity in the reagent was observed. Therefore, in addition to the above techniques, a method to remove the HCHO-oxime impurity before loading the PFBHA had to be determined. Figure 5.1 illustrates a typical reagent blank for PFBHA.

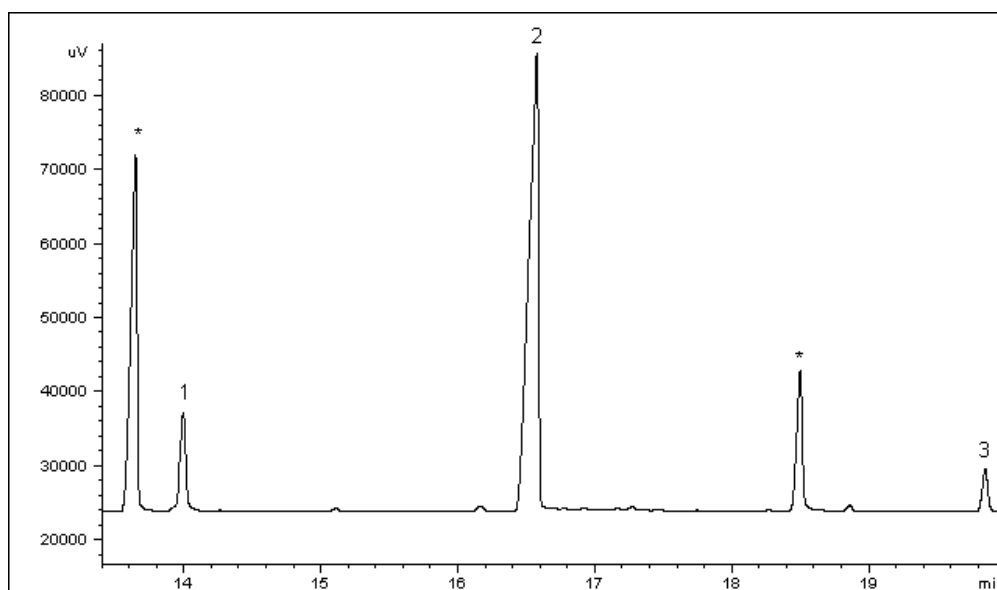


Figure 5.1 Enlarged GC-FID chromatogram obtained by loading PFBHA headspace from the solid reagent into the PDMS MCT. * PDMS thermal degradation peak, 1: Formaldehyde-Oxime, 2: PFBHA, 3: Dodecane (internal standard used to monitor the completeness of desorption of the analytes off the trap. It was added after derivatization using a glass syringe.)

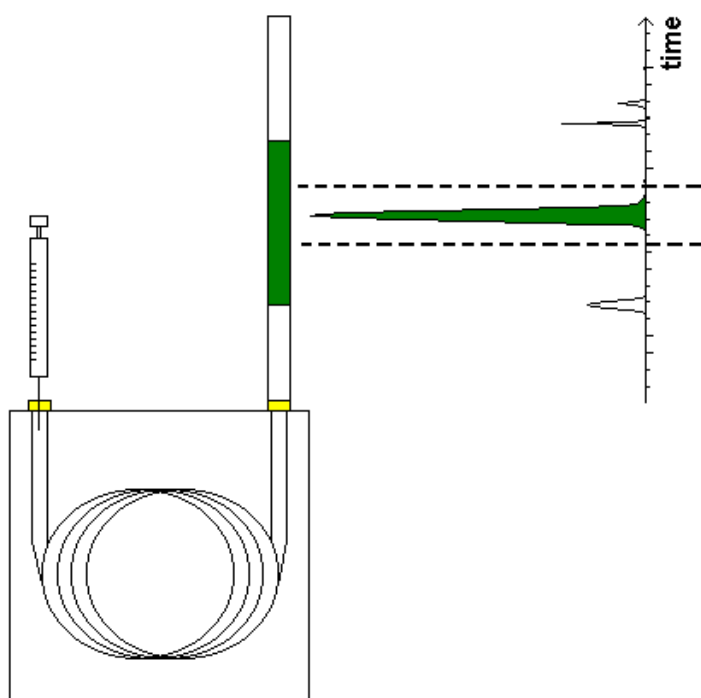


Figure 5.2 The experimental setup using preparative gas chromatography to selectively introduce the PFBHA reagent into the PDMS MCT.

Preparative chromatography using a polar packed column (OV-225) was used in the investigation. With this technique only the PFBHA peak was collected at its respective elution time by fitting the PDMS MCT with a Teflon® connection over the unlit FID detector. A Carlo Erba Fractovap 4200 GC was used for this procedure. The PFBHA was dissolved in hexane (17 g/L). One microlitre of the solution was injected into the GC and the chromatographic data collected. The retention time of the overloaded PFBHA peak was read from the chromatogram. The flame was then switched off and the separation repeated on the GC. The PDMS MCT was then pressed tightly on the unlit FID detector 30 seconds prior to the PFBHA peak retention time (time is monitored with a stop watch), for 1 minute. This collection procedure is sufficient to exclude the formaldehyde derivative peak eluting near the PFBHA peak. The setup is shown in figure 5.2.

For each loading technique, several measurements were made to determine the repeatability of the PFBHA and formaldehyde-oxime amounts loaded onto the trap. Loading the PFBHA headspace from an aqueous solution of PFBHA was performed for 5 min at a flow rate of 10 ml/min. Two sets of measurements were adopted for the collection of PFBHA headspace from the pure reagent, one for 5 min at a flow rate of 10 ml/min, and the other for 10 min at a flow rate of 5 ml/min.



Table 5.1 shows a comparison of the results obtained using the different loading techniques. As expected, the preparative chromatography method is the most promising as it introduces the lowest percentage of formaldehyde-oxime impurity relative to the amount of PFBHA loaded. The repeatability of the amount of HCHO impurity present is also much higher for this method. Unfortunately, even with chromatographic separation of the impurity and PFBHA, some impurity is still present after desorption.

Table 5.1 Comparison of the repeatability of different PFBHA loading techniques.

	PFBHA (aq) 1 min at 10 ml/min	PFBHA (s) 5 min at 10 ml/min	PFBHA (s) 10 min at 5 ml/min	PFBHA (g) Preparative chromatography
%RSD PFBHA peak area	27	96	23	43
%RSD HCHO-oxime peak area	101	62	26	11
% HCHO- oxime relative to PFBHA	12	8	14	2
n	10	4	5	4

We suspect that this HCHO amount recorded after separation must be present in the lab air or in the desorption unit. Similar contamination problems have also been experienced by other users of PFBHA [141, 140, 225, 226]. (Our lab air was not tested using a different analytical technique. Formaldehyde is found in buildings where particleboard (used in flooring and furniture) and hardwood plywood panelling has been treated with urea-formaldehyde based resins. Tobacco smoke, combustion gases from gas appliances, disinfectants and water based paints all release formaldehyde indoors. It is also possible that the air is contaminated in the laboratory by the formaldehyde gas standard, formed by the thermal depolymerisation of paraformaldehyde at 90°C Although the exhaust of the formaldehyde permeation gas standard was vented to the outside of the laboratory through an extraction duct, the removal procedure may not have been as effective.

The thermal desorption unit could have residual unreacted formaldehyde present in the system. It was shown in my MSc thesis that the trapping efficiency of a PFBHA coated PDMS MCT for formaldehyde is 75% for a concentration of 6 ppm and 95 % for a concentration of 0.1 ppm. It was assumed that unreacted formaldehyde flies through the trap and none remains underivatized inside the PDMS MCT prior to desorption.)

5.2. The approach for on-line concentration and derivatization

Potential derivatization reactions were first investigated for the conversion of aldehydes and amines into REMPI-TOFMS detectable compounds. The “on-line” reaction and concentration had to be simulated to determine the suitability of the reagent and PDMS for on-line analysis. Once these factors were determined the method could be tested on the on-line REMPI-TOFMS instrument.

As the Solid-Phase Microextraction (SPME) device has a comparable PDMS volume to the PDMS capillary trap that would be used for on-line sampling, the proof of principle (i.e. of efficient PDMS-mediated derivatization) was tested using SPME with GC/MS and GC-FID analysis. The low volume PDMS devices that would be used for the on-line analysis are depicted in figure 5.3.

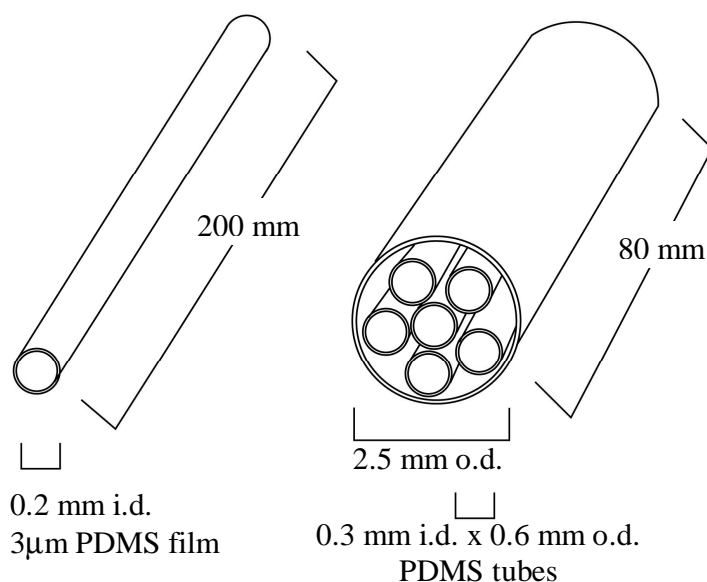


Figure 5.3 Two variations of silicone (PDMS) concentrators namely the thick film open tubular trap (OTT) and the multi-channel silicone rubber trap (MCT).

Chapter 5 – On-line analysis of aldehydes and amines

Reagents investigated were phenylhydrazine to form the phenylhydrazone derivative with the aldehydes and benzaldehyde for the derivatization of amines to form the respective benzaldehyde alkylimine derivatives. The derivatization reaction schemes for aldehydes and amines are depicted in figures 5.4 and 5.5 respectively.

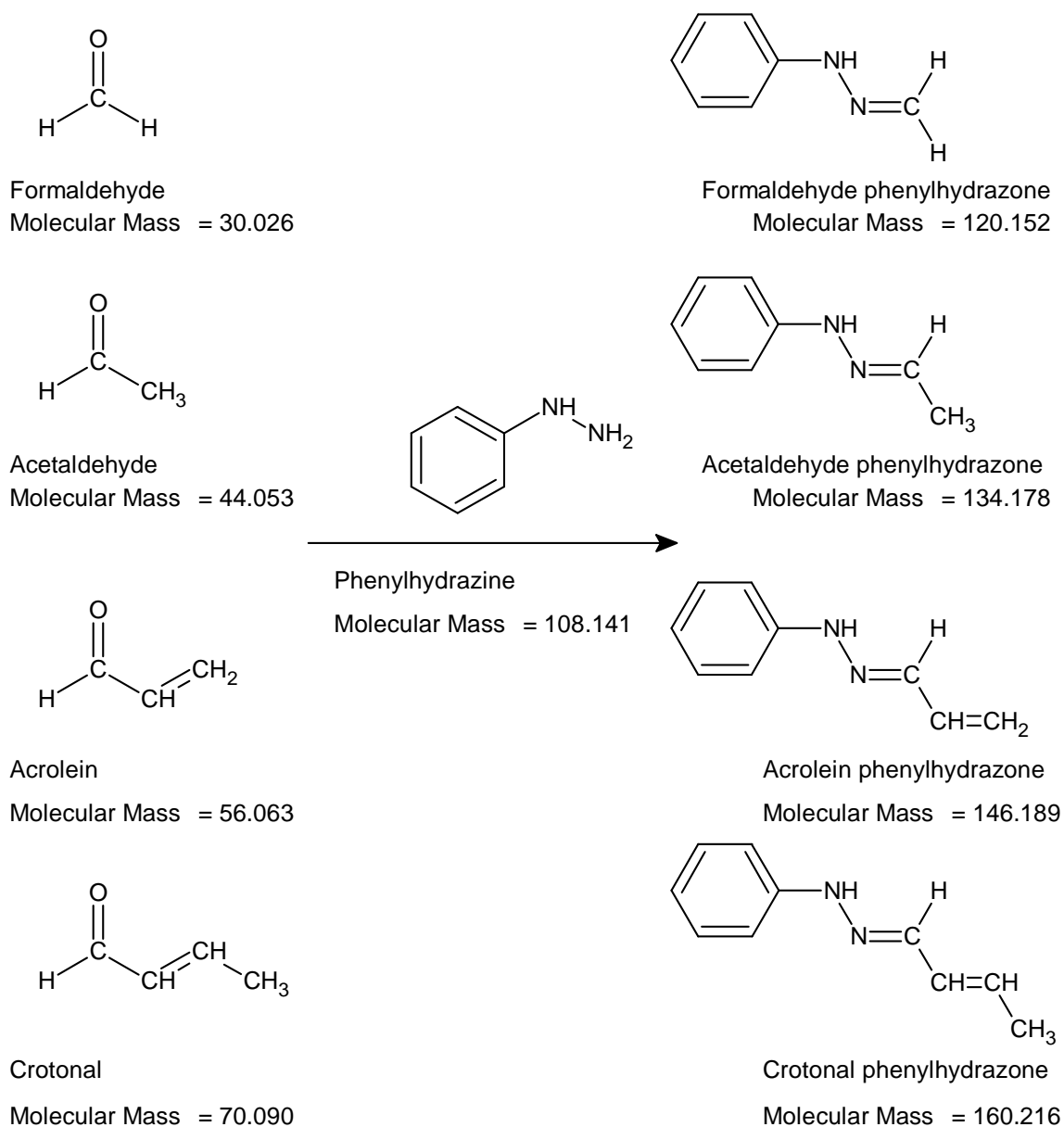


Figure 5.4 Reaction scheme for the derivatization of low molecular mass aldehydes with phenylhydrazine.

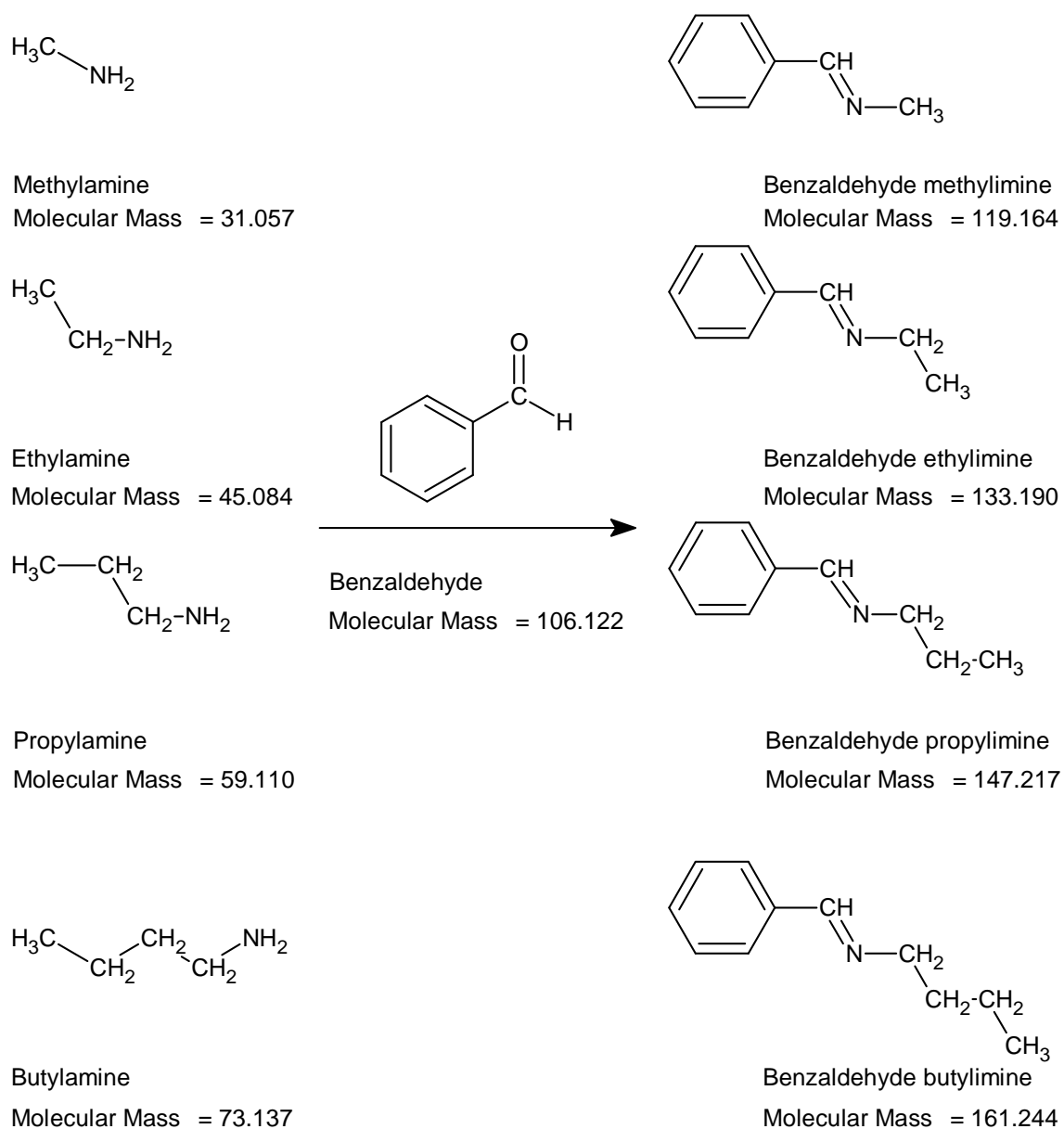


Figure 5.5 Reaction scheme for the derivatization of low molecular mass alkyl amines with benzaldehyde.



5.3. Derivatization Reaction for “Photo-ionization Labelling” of Amines and Aldehydes.

Schemes for the derivatization reagents, analytes, and products formed are shown in Figures 5.4 and 5.5. These reagents were selected to introduce a REMPI-active chromophore to the analyte structure. Substituted rings, such as pentafluorinated benzaldehyde, were discarded in this case as they pose the risk of reducing the REMPI efficiency. In addition, in order for the reaction to occur efficiently, both reagents had to possess a significant vapour pressure to ensure that the reagent would be present in excess in the gas phase.

5.3.1. Initial synthesis of the derivatives

Since commercial standards and library mass spectra of the derivatives were not available the derivatives had to be prepared. Three derivatives were prepared, namely the formaldehyde and acrolein phenylhydrazones and benzaldehyde propylimine. The derivatives were prepared using slightly altered methods to those described in Vogel’s Handbook of Practical Organic Chemistry [227]. Mass spectra obtained from these derivatives were compared with derivative mass spectra obtained by *in situ* derivatization on the SPME fibre and with those obtained by the REMPI-TOFMS.

The phenylhydrazone derivatives were prepared by adding approximately 0.8 g sodium acetate to 400 µl phenylhydrazine in 5 ml water. 500 µl of the aldehyde in 500 µl of ethanol was added to this solution. *Caution: As phenylhydrazine is highly poisonous and formaldehyde is a potential carcinogen, it is essential always to wear gloves and avoid inhalation when working with these reagents.* The reaction mixture was shaken until it became clear adding where necessary extra ethanol. The reaction mixture was warmed in a water bath at ~40°C for 10 to 15 minutes and then allowed to cool. The crystalline derivative was then filtered and recrystallized from dilute ethanol in water. The crystals were dissolved in dichloromethane. 0.4 µl of this solution was injected splitless into the GC- (ITD) MS for analysis. Figures 5.6 and 5.7 present the ITD mass spectra obtained for the formaldehyde and acrolein phenylhydrazone derivatives.



The benzaldehyde propylimine derivative was prepared by dissolving 325 μl propylamine in 500 μl methanol. 400 μl of benzaldehyde was added to this solution. The reaction mixture was heated to 80°C for 35 minutes and allowed to crystallize overnight. The product was recrystallized in ethanol. The crystals were dissolved in dichloromethane. 0.4 μl of this solution was injected splitless into the GC-(ITD) MS for analysis. Figure 5.8 shows the ITD mass spectra obtained for the benzaldehyde propylimine derivative.

Each of the derivatives displays an abundant molecular ion (M^+). In addition, because ions are held in the ion trap and collide with mass neutrals before mass separation, a strong $M+1$ peak is sometimes observed as a result of self-chemical ionization protonation. Benzene (m/z 77) and the tropyllium (m/z 91) mass fragments were also present in the mass spectra obtained.

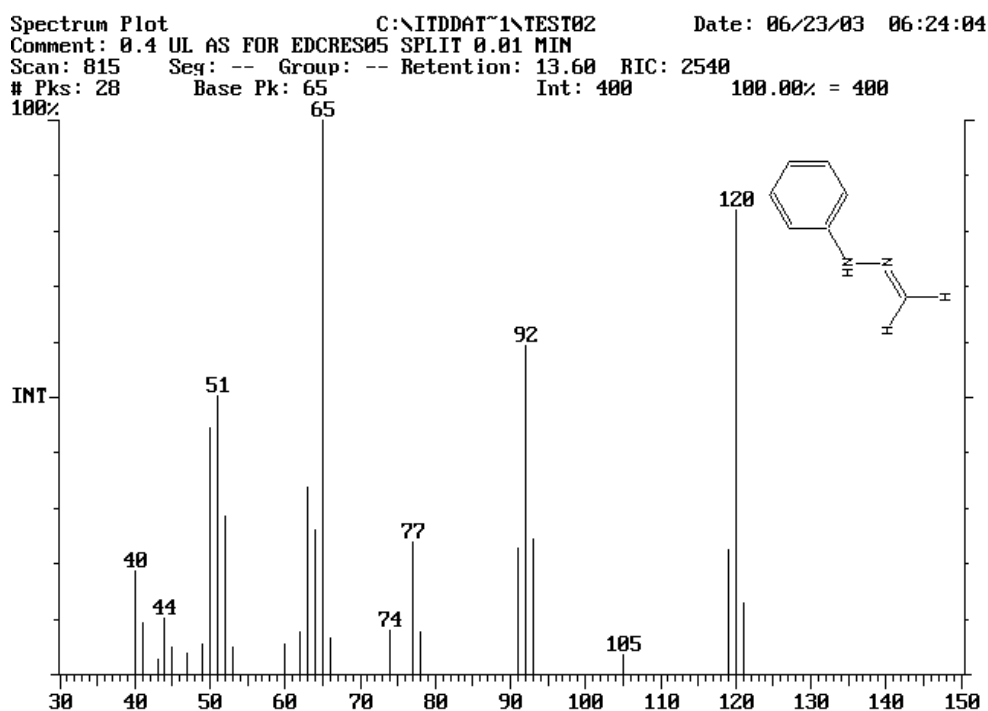


Figure 5.6 ITD Mass spectrum of the formaldehyde phenylhydrazone derivative (M^+120).

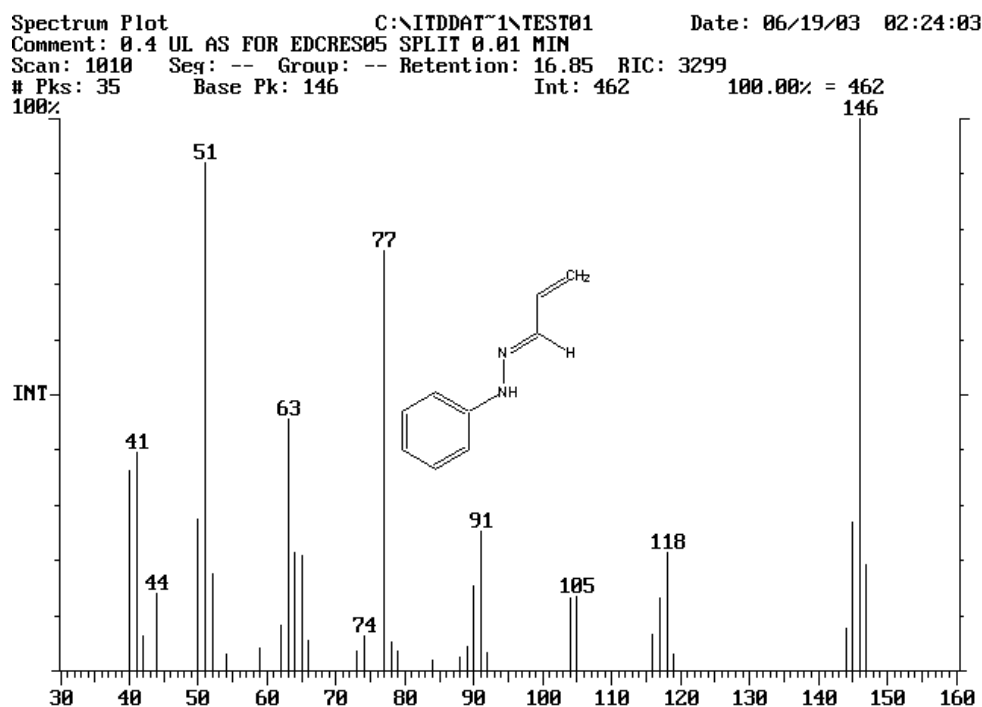


Figure 5.7 ITD Mass spectrum of the acrolein phenylhydrazone derivative (M^+ 146).

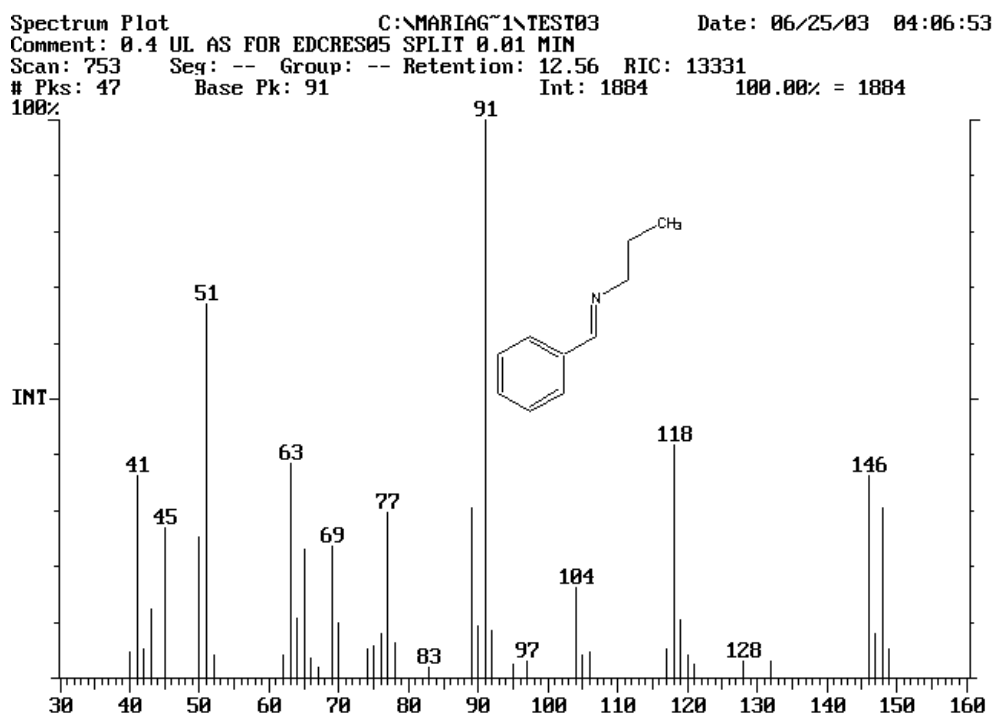


Figure 5.8 ITD Mass spectrum of the benzaldehyde propylimine derivative (M^+ 147). Notice the strong $M+1$ peak as m/z 148 that we ascribe to inadvertent chemical ionisation in the ITD.

5.4. Setup for SPME GC-FID-Based Testing of the PDMS mediated derivatization reactions

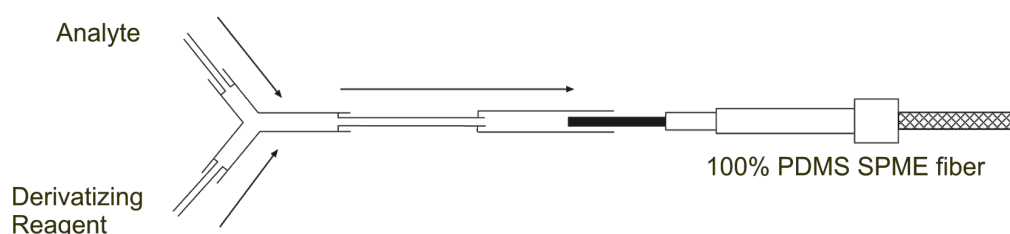


Figure 5.9 A simulation of the on-line REMPI-TOFMS set-up using SPME to determine approximate reaction efficiencies for the on-line derivatization reactions.

Simple reaction tests were performed to determine whether the selected derivatization reaction would take place in the PDMS and to estimate how efficiently the arrangement would trap the analyte. Figure 5.9 shows the on-line setup used to determine the approximate reaction efficiency for the various derivatization reactions.

Stable gaseous concentrations of the analytes were obtained by preparing permeation gas standards of the respective aldehydes and amines. Gas standard preparation and measurement has been described in my MSc thesis and in the literature [228, 229]. Two sets of gas standards were prepared: the first set was prepared in South Africa and used to determine the reaction efficiencies of the analytes; the second set was prepared in Germany to test the on-line REMPI-TOFMS technique. Concentrations provided by the gas standards are listed in Table 5.2. Figure 5.10 illustrates how the permeation rate is obtained. Plotting a graph of mass loss over time for each analyte should provide a straight line of which the gradient (mass-loss/ time) is the permeation rate. Unfortunately the formaldehyde gas standard, which is formed by the thermal depolymerization of paraformaldehyde at 80°C [61], was depleted before the REMPI-TOFMS experiments could be performed. The headspace from formaldehyde (stabilized with methanol in water) was then used as the formaldehyde gas source. This concentration was rather high and could not be determined in the framework of the experiments presented here.

Table 5.2 Summary of the aldehyde and amine permeation gas standards prepared.

Compound:	Pretoria			Munich		
	Permeation Rate			Permeation Rate		
	(ng/ min):	R ²	n	(ng/ min):	R ²	n
Formaldehyde	40	0.9979		60	0.9962	3
Acetaldehyde	70	0.9355	6	20	0.9823	3
Propanal	~	~	~	10	0.9989	4
Acrolein	8	0.9909	4	90	0.9984	4
Crotonal	40	0.9804	6	80	0.999	4
Diethylamine	~	~	~	200	0.9999	4
n-Propylamine	600	0.9998		100	0.9997	4
n-Butylamine	70	0.9935		40	0.9999	4

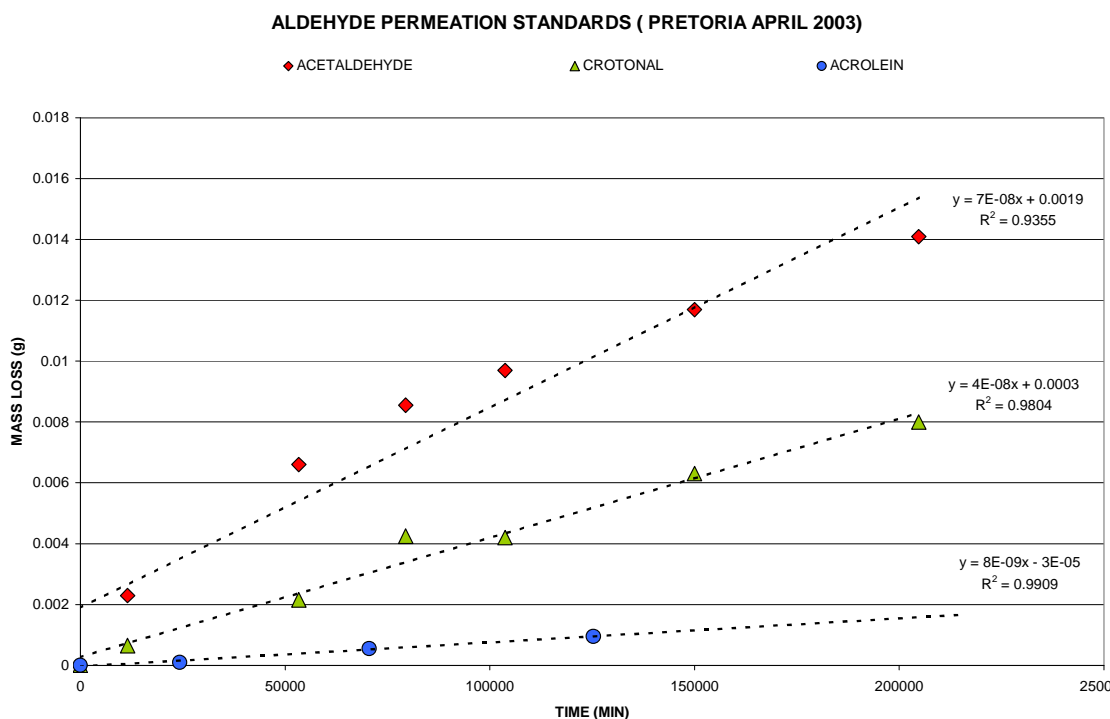


Figure 5.10 Graph of mass loss over time for acetaldehyde, acrolein and crotonal. The gradient of the straight line is the permeation rate (g/ min).



The gas standards were purged with nitrogen gas at a flow rate of 4 mL/ min. The gas standards provide a known concentration of analyte gas into the glass Y press-fit connector [230] (obtained from Chromatography Research Supplies, Inc., Louisville, KY) via an uncoated length of fused-silica capillary. Similarly, the derivatizing reagent, also being purged with nitrogen gas at 4 mL/min, was introduced at the other end of the Y press-fit connector. A 1-mL portion of the derivatizing reagent was placed in a 2 mL vial and sealed with a crimp cap. Two holes were pierced in the septum of the vial. A length of uncoated fused-silica capillary was pushed through each hole in the septum. One capillary was connected to the nitrogen gas, the other to the Y press-fit connector. Leading from the combined exit of the Y press-fit connector was another length of uncoated fused-silica capillary. The measured flow rate at this point was 8 mL/min, similar to the flows obtained from the REMPI-TOFMS vacuum. The exiting capillary was sealed into another glass press-fit connector, the opposite end of which was modified to house the exposed SPME fibre.

The SPME device consisted of a 100 μm PDMS-coated fibre [49] that was exposed over increasing time intervals to the on-line arrangement shown in figure 5.9. The SPME assembly and 100- μm PDMS fibres were obtained from Supelco (Bellefonte, PA). The fibre was desorbed in the heated inlet of a Varian 3300 GC at 150°C for 1 min. Quantitation was performed by flame ionization detection (FID) using undecane as internal standard and (calculated) effective carbon number responses of the derivatives, for which commercial standards are not available[61, 231, 232]. 1 μl of a 20ng/ μl undecane in CS_2 standard was injected, 2 minutes after desorption of the SPME fibre.

Thermal desorption of the SPME fibre is performed simply and quickly in the heated inlet of the GC oven; however, desorption of the silicone trap requires a desorption unit with some form of cooling in order to focus the desorbed contents onto the GC column. This is usually a longer process [61]. When the above procedure is carried out in GC-FID or GC/MS, the low initial temperature of the GC oven also acts to focus or concentrate the derivatized analyte in a short band. For real-time on-line applications, in the absence of such a focusing mechanism in the direct coupling of the trap to the TOFMS, another concentration device is required to enhance detectability. The reaction efficiency graphs shown in Figure 5.11 for the on-line derivatization of formaldehyde and acetaldehyde with phenylhydrazine display the increasing mass accumulation of derivative on the SPME fibre over time. Additional graphs for acrolein, crotonal, propylamine and butylamine can be found in the appendix.

Chapter 5 – On-line analysis of aldehydes and amines

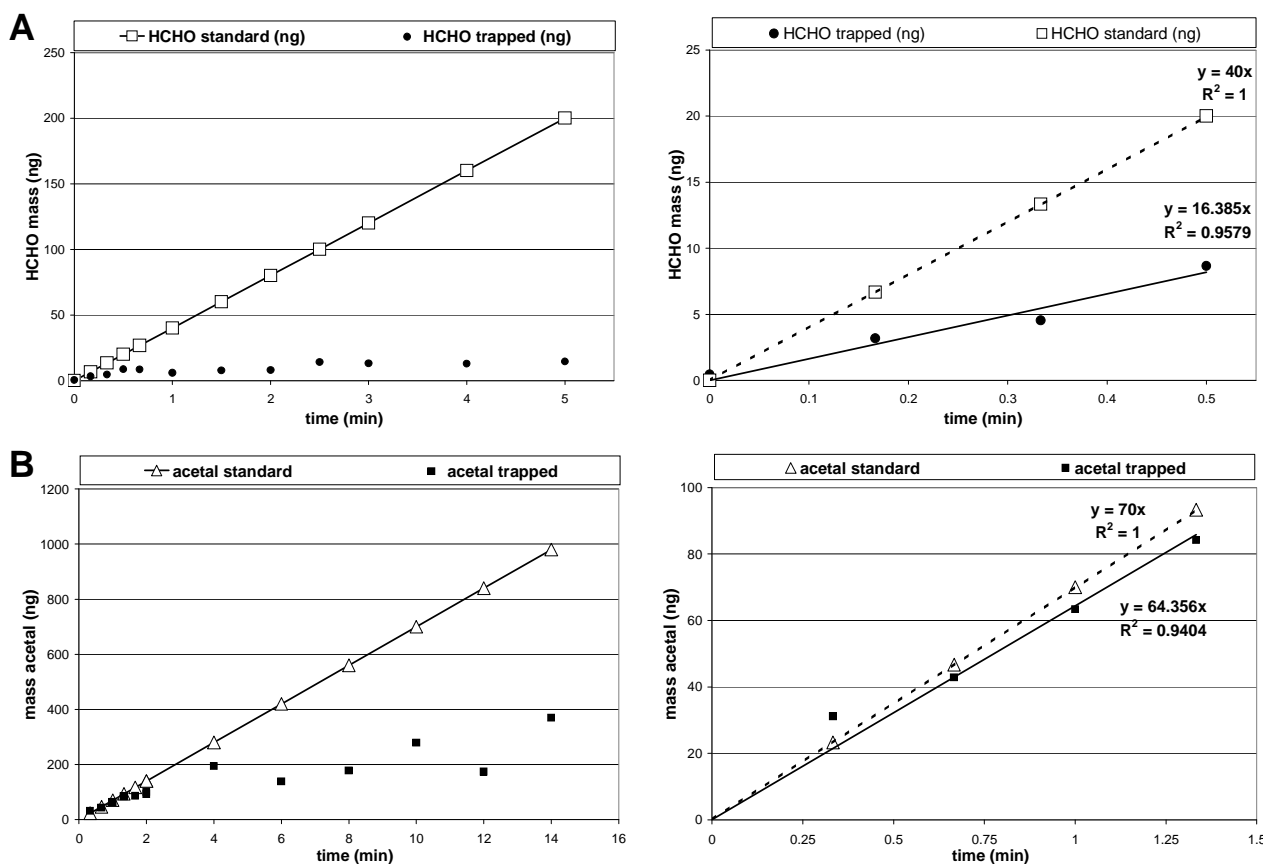


Figure 5.11 Reaction efficiency results for the on-line derivatization of A; formaldehyde and B; acetaldehyde with phenylhydrazine.

Both graphs display i) the calculated amount of gas standard released over the time interval using their gravimetrically determined permeation rate and ii) the amount of analyte gas trapped using *in situ* derivatization on the SPME fibre as calculated using the internal standard and effective carbon number response for the signal obtained from the GC-FID for the derivative. The graphs on the right hand side represent an enlargement of the left hand side graphs, where the initial accumulation on the SPME fibre appears linear. A comparison of the gradients obtained from the standard and the actual amount of analyte trapped gives an approximation of the reaction/trapping efficiency for this reaction before breakthrough starts to occur in the simple fibre/tube column.

Figure 5.12 depicts a GC-FID chromatogram of acetaldehyde, acrolein and crotonal (determined simultaneously). Formaldehyde gas was determined separately. As stated earlier, formaldehyde gas was prepared in an oven, while the remaining standards were in a glass tube at room temperature. Apart from formaldehyde, all the aldehydes form *E-Z* isomers (across the nitrogen-carbon double bond) and appear as two peaks in the chromatogram. Both peaks were integrated for quantitation purposes.

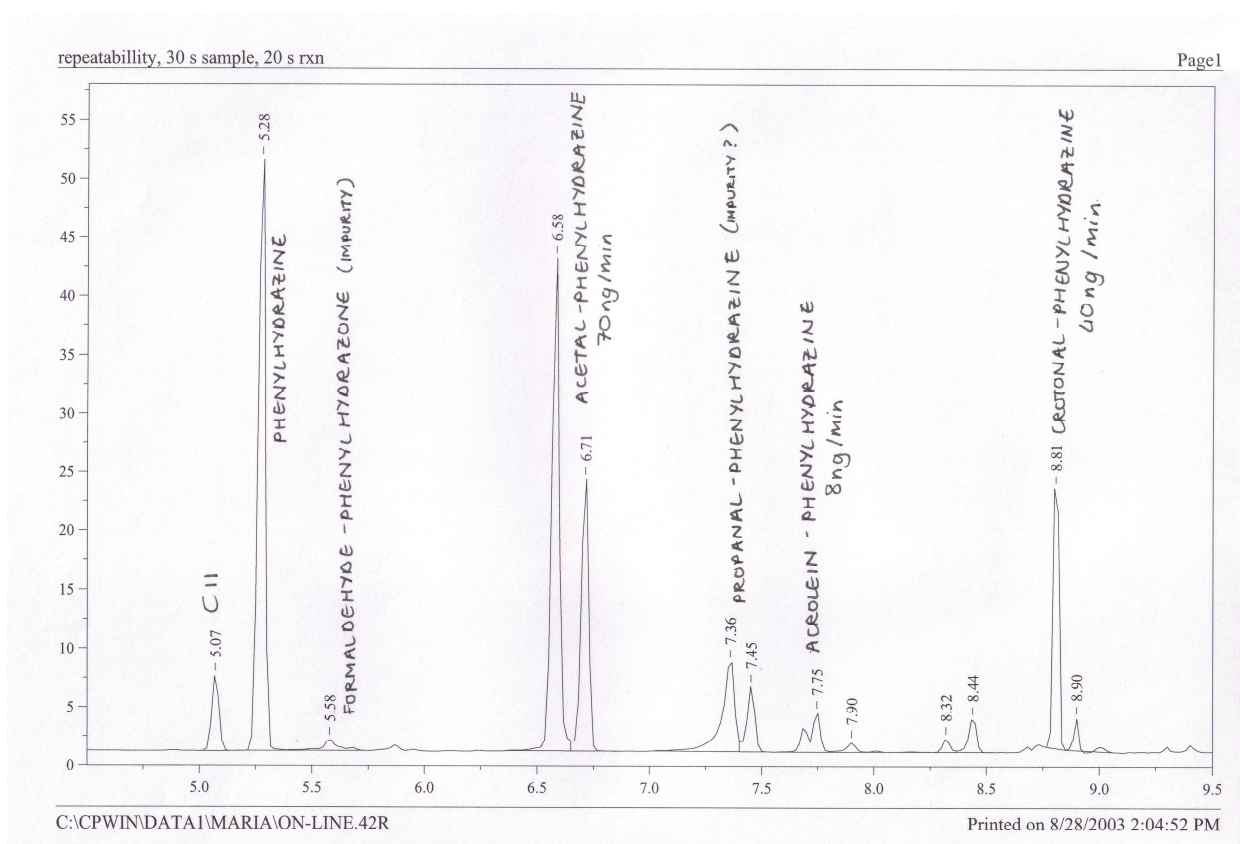


Figure 5.12 The GC-FID chromatogram obtained after desorption of a 100 μm PDMS SPME fibre exposed simultaneously for 30 seconds to the permeation gas standards of acetaldehyde, acrolein and crotonal and the phenylhydrazine derivatization reagent. Formaldehyde-phenylhydrazone impurity (5.58 min); Acetal-phenylhydrazone (6.58 & 6.71 min); Propanal-phenylhydrazone (7.36 & 7.45 min); Acrolein-phenylhydrazone (7.68 & 7.75 min) and Crotonal-phenylhydrazone (8.81 & 8.90 min). The double peaks for each derivative, excluding formaldehyde, represent *E-Z* isomers.



In figure 5.11, both graphs display (i) the amount of gas standard released over the time interval determined by their permeation rate, and (ii) the amount of analyte gas trapped using *in situ* derivatization on the SPME fibre, as calculated using an internal standard and the effective carbon number response for the signals obtained from the GC-FID for the desorbed derivatives [61, 232, 233]. The graphs on the right represent an enlargement of the graphs on the left, where the initial accumulation on the SPME fibre appears linear. A comparison of the initial gradients obtained from the analyte standard and the actual amount of analyte trapped gives an approximation of the reaction/trapping efficiency for this reaction [61]. The flattening off of the accumulation curves over time is the result of increased loss or “breakthrough” of the reaction product from the SPME fibre concentrator.

The reaction efficiency data, shown in Table 5.3 were obtained at room temperature using the arrangement, as shown in Figure 5.9. In Table 5.3, approximate reaction efficiencies of 28% for the reaction of propylamine and butylamine with benzaldehyde, 41% for the formaldehyde reaction with phenylhydrazine, and around 70% for the aldehydes with phenylhydrazine are indicated.

Table 5.3. Approximation of on-line reaction efficiencies, at room temperature without catalyst, as determined by the SPME set-up (figure 5.9).

Compound	Reagent	%Reaction efficiency	R ² (n)
Formaldehyde	Phenylhydrazine	41	0.9579 (4)
Acetaldehyde	Phenylhydrazine	92	0.9404 (4)
Acrolein	Phenylhydrazine	61	0.9990 (4)
Crotonal	Phenylhydrazine	74	0.9251 (4)
Propylamine	Benzaldehyde	28	0.9570 (4)
Butylamine	Benzaldehyde	28	0.9205 (4)

5.5. On-line derivatization setup

In Germany, an experimental on-line derivatization setup was built and coupled to the REMPI-TOFMS system. Two different variants were used for the derivatization procedure. In the first setup, a thermal modulator array (TMA) [216] with a fused-silica open tubular trap (OTT) (3- μm silicone film, DB-1 equivalent) was used to absorb, derivatize, desorb, and refocus the analytes. The second setup consisted of an enrichment desorption unit (EDU; Airsense Analytics, Schwerin, Germany) [234] with a PDMS MCT [61, 65, 66] as PDMS medium for derivatization followed by the above-mentioned arrangement with the TMA [216]. These experimental setups are shown in Figure 5.13 (A and B respectively). The TMA and EDU are described in chapter 4.

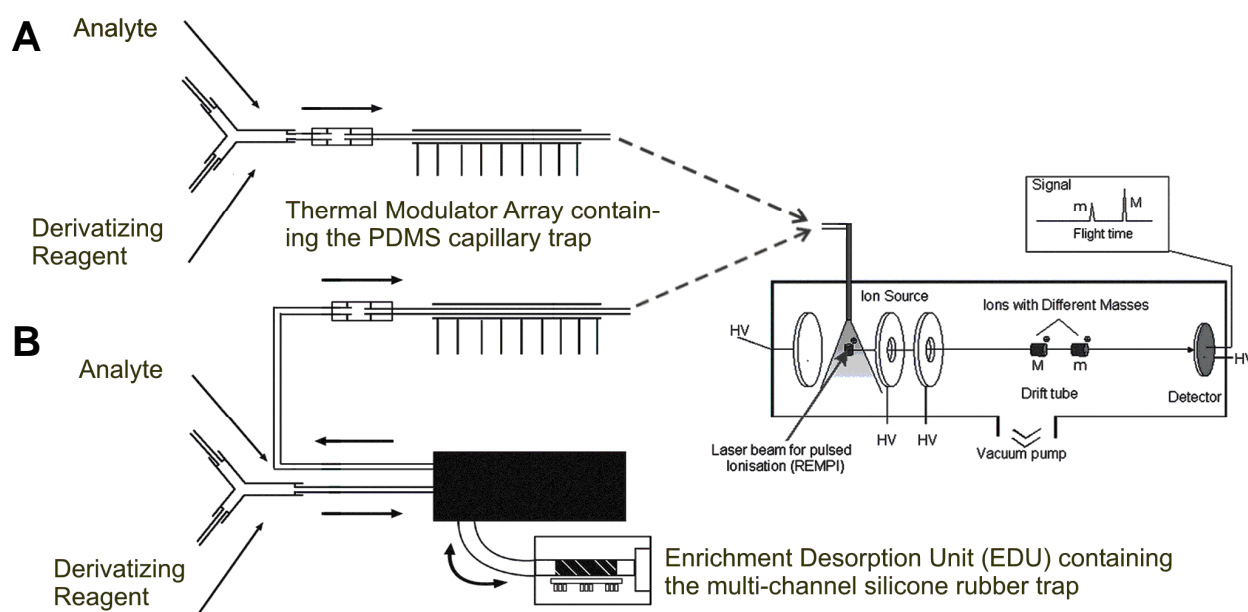


Figure 5.13 The experimental set-up used for:

A) On-line concentration and derivatization for REMPI-TOFMS using the thermal modulator array (TMA) with a thick film OTT as enrichment and reaction medium

B) On-line concentration and derivatization for REMPI-TOFMS using a multi-channel silicone rubber trap (MCT) in an enrichment and desorption unit (EDU) as enrichment and reaction medium and the thermal modulator array (TMA) with a thick film OTT for analyte modulation.

5.6. Resonance Enhanced Time of Flight Mass Spectrometry (REMPI-TOFMS)

5.6.1. Theory of Resonance-Enhanced Multi Photon Ionization (REMPI)

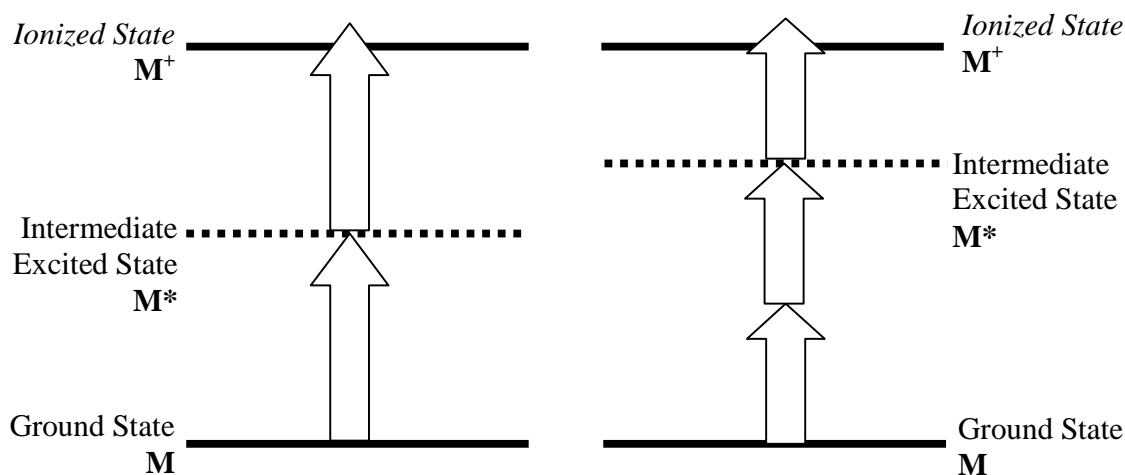


Figure 5.14 (1+1) and (2+1) Multi Photon Ionization processes [235]

The most familiar gas phase ionization technique is Electron Impact (EI) Ionization. High-energy electrons, usually 70 eV, bombard molecules as they enter the ionization chamber. Most molecules are ionized at this energy as they have ionization energies well below 70 eV. EI is also known as a hard ionization technique because it causes massive fragmentation of the ionized molecules. Less familiar (but well accepted) ionization techniques, particularly for on-line processes, are those using laser ionization, such as Single Photon Ionization (SPI) and Resonance Enhanced Multiphoton Ionization (REMPI). These are known as soft ionization techniques as lower energy photons are used to selectively ionize molecules resulting in very little to no fragmentation of the molecules [32, 235].

In laser ionization, a neutral molecule (M) is excited to a higher energy level through absorption of a UV photon, forming a high-energy neutral molecule (M*). Through the absorption of a second photon the molecule's ionization threshold is reached. The neutral molecule loses an electron to form the ionized molecule (M⁺). This is more commonly known as a (1+1) multiphoton ionization (MPI) process [235]. However, due to the critical energies required to reach the intermediate and ionization thresholds of small molecules, a higher order MPI process is frequently used, such as the (2+1) MPI process [235],



figure 5.14. Since each molecule has its own characteristic UV absorption spectrum, selective ionization of a molecule can be achieved through careful selection of a laser wavelength, at which the molecule undergoes selective absorption and (by resonant MPI) selective ionization [234]. 5

The REMPI process is based on a two-UV-photon absorption/ionization utilizing excited intermediate states (i.e. UV absorption bands), for resonance enhancement. Most aromatic compounds exhibit strong absorption bands in the 220-300-nm region. This wavelength region is easily accessible by commercial laser systems. REMPI is therefore a soft ionization source for selectively ionizing molecules with conjugated systems such as aromatic compounds and alkenes. However, increasing the laser intensity to obtain higher ionization yields will cause fragmentation of the molecule to occur [235]. After ionization, the charged molecules move into the TOFMS where separation is based on the differing masses of the ionized molecules that travel down the flight tube at differing speeds.

By comparison, with regards to ionization selectivity, the SPI technique lies between EI and REMPI [32]. In SPI, vacuum ultraviolet (VUV) photons are used. They have a much lower energy of 10.5 eV compared to EI electrons. This energy per photon is, however, high enough to cause ionization of selected molecules. In this case the VUV photons provide a single photon absorption/ ionization process where only molecules having a lower ionization potential than 10.5 eV, will be ionized [32].

5.6.2. Applications of REMPI-TOFMS

The home-built REMPI-TOFMS at the GSF, has been used for the on-line monitoring of dioxin surrogates and other aromatic trace species in waste incinerator emissions [32, 33], characterization of the formation of phenolic compounds during coffee roasting [34, 35], and puff-resolved analysis of toxic aromatic compound release during the cigarette smoking process [36] as well as the characterization of wood combustion [37]. In addition to the analysis of gaseous matrices, solid matrices can also be handled in a two-step process, using laser desorption followed by REMPI of the volatilized compounds [236-240].



5.6.3. The REMPI-TOFMS instrumentation

The resonance-enhanced multiphoton ionization time-of-flight mass spectrometer used for this application is a home-built system housed at the GSF, Oberschlesheim, Germany. The REMPI-TOFMS contains a pulsed Nd:YAG laser (Quanta-Ray INDI 50; Spectra Physics, Stratford, CT). The initial 1064-nm laser beam (repetition rate 10 Hz, pulse duration 10 ns) is frequency tripled, and the resulting wavelength of 355 nm is used to pump a β -BBO crystal of a thermally stabilized type II OPO laser system (GWU-Lasertechnik, Germany) to generate wavelength-tuneable laser pulses in the range of 220 nm to 2.5 μ m. The generated laser pulses ($\sim 106 \text{ W cm}^{-2}$) are directed into the ionization chamber of the TOF (Kaessdorf Instruments, Germany) underneath the jet capillary inlet by optical elements. Molecular ions formed are accelerated and extracted into the flight tube of the reflectron TOFMS.

Mass spectra were recorded via a transient recorder PC card (Aquiris, Switzerland, 250 MHz, 1 GS/s, 128 k) whereby data processing is done by LabView (National Instruments, Austin, TX)-based home-written software. Wavelengths of 244 and 246 nm were selected for REMPI-TOFMS analysis of the formaldehyde- and acrolein-phenylhydrazone derivatives, respectively, and 240 nm for the benzaldehyde alkylimine derivatives. Spectroscopic investigations showed that for the REMPI-TOFMS setup used, these wavelengths are very efficient.

5.7. Experimental

5.7.1. On-Line Derivatization Setup for REMPI-TOFMS

Figure 5.13 (A) and (B) show the on-line derivatization REMPI-TOFMS setups. Unlike the arrangement for initial testing using SPME (see figure 5.9), the gas standards and reagents were not purged with nitrogen gas. In this case, the mass spectrometer vacuum provides the flow into the REMPI-TOFMS. On-line *in situ* derivatization was investigated using two different PDMS enrichment desorption devices, namely:



- (i) a thermal modulator array (TMA) with a PDMS thick-film capillary OTT and
- (ii) an enrichment desorption unit with a PDMS MCT .

Two setup variants were tested. In the first setup, only the TMA (i) with a PDMS thick-film OTT was used, whereas in the second setup, the EDU with a PDMS MCT (ii) was applied in combination with the TMA with a PDMS thick-film OTT (i). The two experimental setups are described in more detail below.

5.7.2. First Setup: Direct Supply of Analytes and Reagents through the Thermal Modulator Array (TMA-REMPI-TOFMS)

The centrepiece of the derivatization setup is the segmented thermal modulator array (TMA) [216]. The modulator houses a narrow-bore capillary coated on the inside with a thick film of PDMS (capillary trap). This capillary represents the concentrating / derivatizing device. The amount of PDMS within the capillary is comparable to the amount of PDMS forming the SPME fibre.

The modulator capillary consisted of a fused-silica capillary column (0.2 mm i.d.) coated with non-polar phase PS-255 (3 μm film, DB-1 equivalent). A capillary of 20 cm length was used with 5 cm of the stationary phase stripped off on either end, as described in reference [216]. A stainless steel capillary (105 mm x 0.6 mm o.d. x 0.35 mm i.d.) was converted to a modulator [216]. An electronic sequencer was used to provide current to the modulator in steps from 1 to 10 A at 5 V with a time duration of 10-2500 ms. To maintain reasonable flow rates and operate at atmospheric pressure, jet restrictors yielding a flow rate of between 0.6 and 1.0 mL/min were prepared according to the method described in reference 676 from an uncoated capillary (30 cm x 0.32 mm i.d.). The restrictor was coupled to the modulator capillary with a suitable press-fit. All transfer capillaries and connection points were either directly heated to 150 °C by a heating mantle or surrounded by a copper tube, which was then heated by a heating mantle.

The outlet of the TMA device was directly coupled to the TOFMS. This setup was used for detecting amines using benzaldehyde as photo-ionization labelling compound. Reagent and analytes (amine gas standard) were introduced simultaneously for 10 min into the cooled, PDMS, narrow-bore, thick-film capillary trap (inside the modulator steel tube) where the reaction occurred. In this case, the MS vacuum



Chapter 5 – On-line analysis of aldehydes and amines

provided a sampling flow rate of 0.7 mL/min. During modulation, the derivatives were desorbed into the REMPI-TOFMS. Similarly, the derivatization of the aldehydes with phenylhydrazine was demonstrated using only the modulator trap, followed by REMPI-TOFMS detection. The results obtained with the TMA-REMPI-TOFMS setup are given in Table 5.4 and Figures 5.15 and 5.16.

Table 5.4 Gas standard concentrations and calculated detection limits for the aldehydes and amines studied. Permissible Exposure Limits (PEL) as set by the Occupational Safety and Health Administration (OSHA) are also listed [15]. Detection limit values were not directly measured but determined by extrapolation of the larger measured values to a S/N ratio of 2.

Analytes (m/z)	Gas standard	Detection limit	Gas standard	Detection limit	PEL OSHA (ppm)
	Concentration	(s/n = 2 AVG 10)	Concentration	(s/n = 2 AVG 10)	
	EDU - TMA (ppm v/v)	EDU - TMA (ppm v/v)	TMA (ppm v/v)	TMA (ppm v/v)	
Formaldehyde -120	-	-	-	-	0.75
Acetaldehyde -134	-	-	79.4	2.04	200
Acrolein -146	-	-	37.4	0.101	0.1
Crotonal -160	-	-	199	1.52	2
Methylamine -119	34.3	0.257	-	-	10
Ethylamine -133	1.4	0.01	21.7	0.324	10
Propylamine -147	1.8	0.024	27.6	0.138	-
Butylamine -161	2.9	0.1	44.7	0.501	5

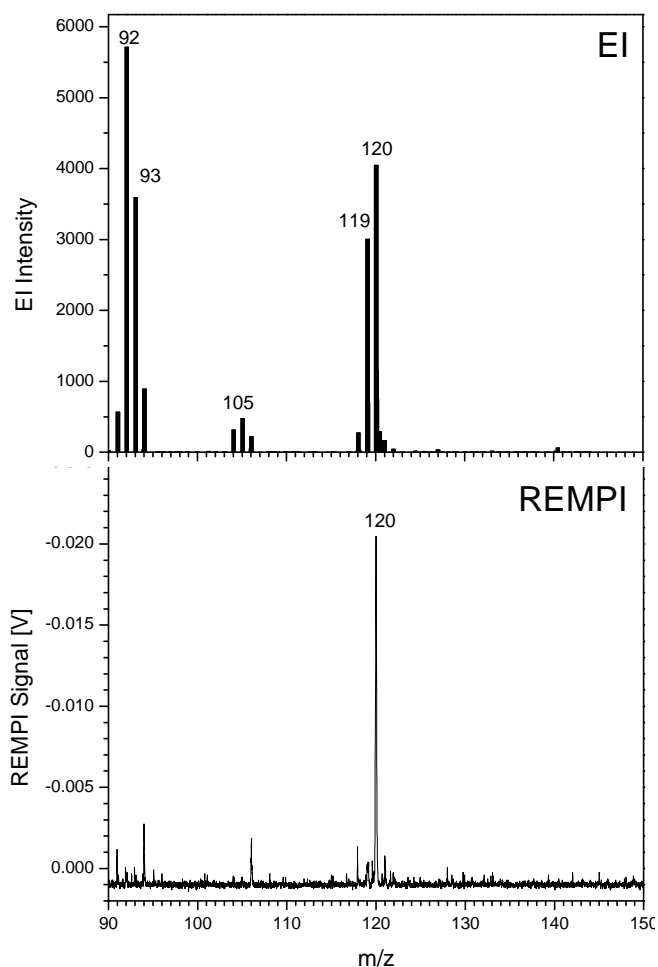


Figure 5.15 Mass spectra obtained for the formaldehyde phenylhydrazone derivative using two different ionization techniques. The Electron Impact (EI) mass spectrum was obtained from a prepared derivative on an accurate mass GC-TOFMS. The Resonance Enhanced Multiphoton Ionization (REMPI) mass spectrum was obtained from the on-line concentration and derivatization experiment.

5.7.3. Second Setup: Supply of Analytes and Reagents to an Enrichment Desorption Unit prior to the TMA (EDU-TMA-REMPI-TOFMS)

The second setup used is as shown in Figure 5.13 (B). Here, the MCT in the enrichment desorption unit (EDU) is used as the concentration-reaction medium, and the TMA is used for subsequent temporal focusing. The MCT is placed within the EDU, which is connected via the TMA to the REMPI-TOFMS



Chapter 5 – On-line analysis of aldehydes and amines

(EDU-TMA REMPI-TOFMS). The principal difference between SPME (or the application of TMA solely) and the MCT is the amount of PDMS available for concentration of analytes, with the MCT having a considerably larger amount of PDMS (approximate PDMS volumes are TMA trap 0.2 mm^3 and the EDU MCT 135 mm^3). As the MCT can concentrate and derivatize more analyte it has the potential to provide lower detection limits. The EDU system is described in chapter 4.

For *in situ* derivatization, the aromatic derivatizing reagent dissolves into the PDMS from the gas phase. Carbonyl compounds (aldehydes and ketones etc.) passing through the trap react selectively with the reagent and remain in the trap until they are thermally desorbed for analysis [60, 61]. In the case of the above-mentioned SPME-GC-FID approach, desorption is performed for some time in the heated GC injector, [49, 60, 61]. The derivatized analytes are refocused in a short band due to the low initial temperature of the GC oven.

For on-line real-time analytical applications, however, analyte focusing can also be important, for time resolution and sensitivity rather than for the enhancement of the chromatographic resolution. As described in the first set-up, analyte focusing can be achieved by repetitive thermal modulation. In this setup, the EDU is used in combination with a segmented TMA, as described above.

Conditions for the EDU used in these experiments were as follows: sampling for 130 s at 6°C with a sampling flow rate of 230 mL/min and thermal desorption for 60 s at 180°C . Injection occurs under reversed flow conditions. During injection, the desorbed compounds are drawn into the REMPI-TOFMS at a flow rate of 15 mL/min , as they are restricted by the capillary jet leading into the ion source. Both the sampling line and the transfer line into the MS are heated at 150°C . Benzaldehyde was sampled for 60 s through the heated sampling line. After 10 s, the amine gas mixture was sampled through the sampling line for 60 s. The sampling flow rate was 230 mL/min . Benzaldehyde accumulates in the PDMS multichannel trap, cooled to 6°C . The introduced amine gas subsequently reacts with the benzaldehyde in the trap. The reaction is further encouraged during desorption at 150°C for 1 min. During the injection phase, the derivatives are transferred to the TMA, which submits timely-focused concentrated pulses to the REMPI-TOFMS system. The results obtained with the EDU-TMA-REMPI-TOFMS setup are given in Table 5.4 and Figure 5.16.

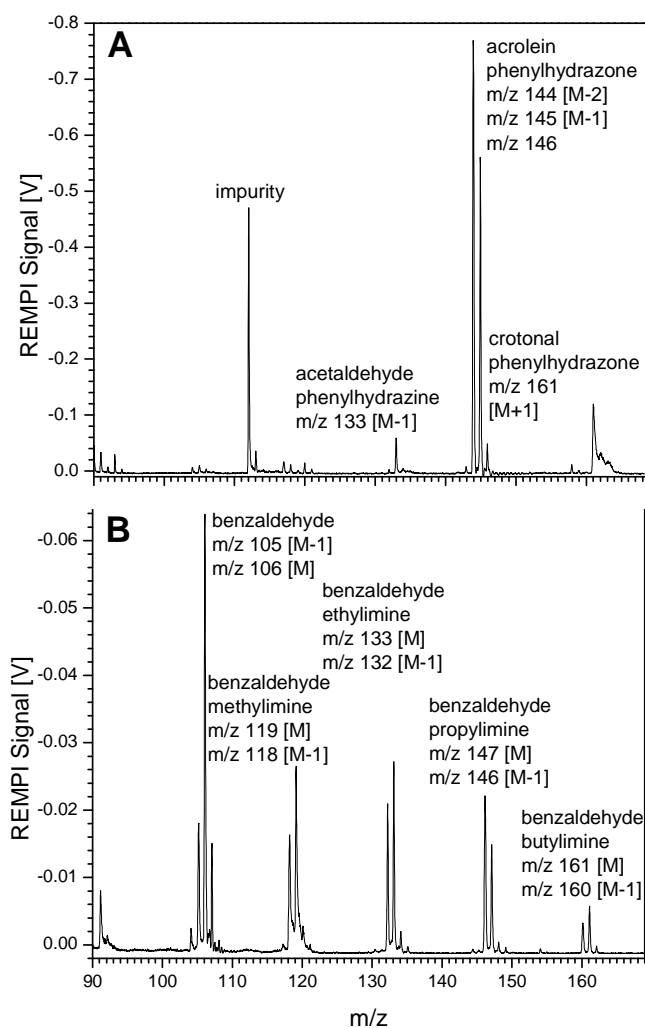


Figure 5.16 REMPI-TOF mass spectra obtained for the on-line concentration and derivatization of **A.** acetaldehyde, acrolein and crotonal with phenylhydrazine at 246 nm, and **B.** methylamine, ethylamine, propylamine and butylamine with benzaldehyde at 240 nm.

5.8. Results and Discussion

Incomplete reaction was confirmed by single photon ionization time-of-flight mass spectrometry (SPI-TOFMS) [32, 232] of the on-line, *in situ* derivatization of propylamine (59 m/z) and butylamine (m/z 73) with benzaldehyde (m/z 106). The presence of both derivatized (161 and 147 m/z) and underivatized analyte (59 and 73 m/z) was observed, as shown in figure 5.17. Although these derivatization reactions are not 100% efficient at room temperature, they still occur readily without the aid of any catalysts. Thus, for quantitation, the use of internal or external standards is required.

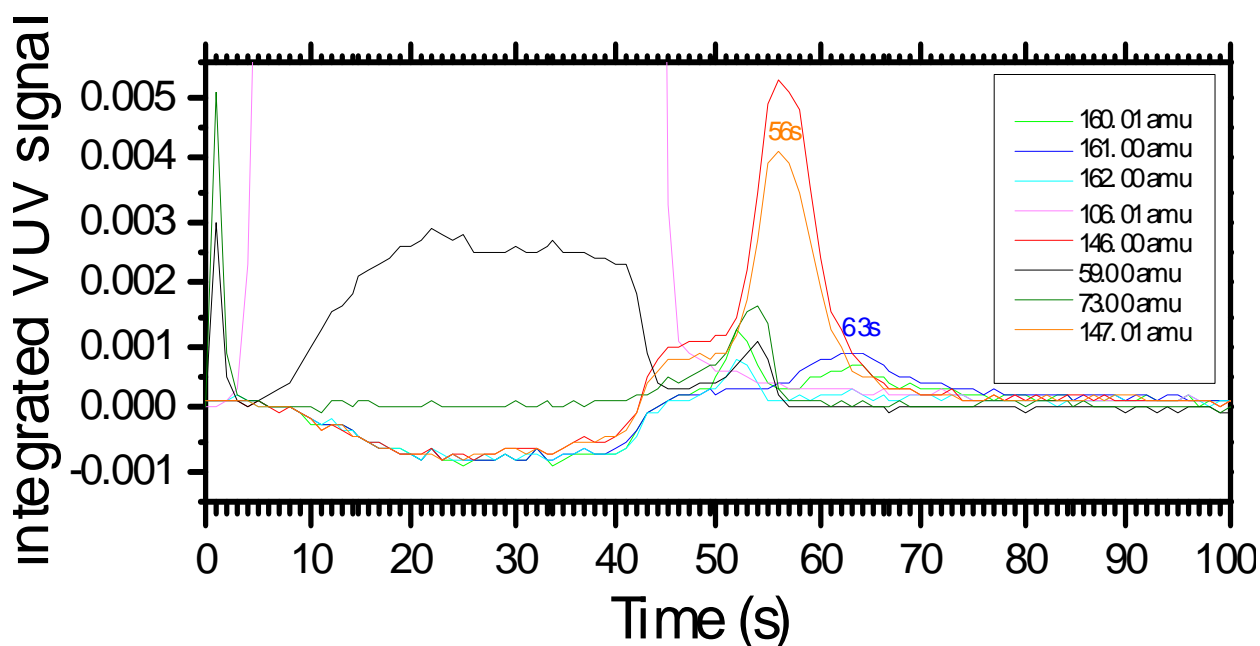


Figure 5.17 Single Photon Ionization (SPI) mass spectrum of the on-line, *in situ* derivatization of Propylamine (m/z 59) and butylamine (m/z 73) with benzaldehyde (m/z 106). The presence of both derivatized (m/z 161 and m/z 147) and underivatized analyte was observed.

The results of the on-line tests with REMPI-TOFMS detection are discussed below. The experiments demonstrated that all investigated amines and aldehydes could be successfully derivatized, desorbed, and identified by REMPI-TOFMS using the on-line setups described above. Figure 5.15 displays the results obtained for formaldehyde. In the upper part (A), a conventional 70-eV EI mass spectrum for the formaldehyde phenylhydrazone derivative is shown. This mass spectrum was obtained from a formaldehyde phenylhydrazone derivative, prepared using the method described by Vogel *et al.* [241] on an accurate mass TOFMS (Micromass, GCT, U.K.). The formaldehyde phenylhydrazone derivative was detected at 120 m/z , together with a H loss of similar intensity (119 m/z). The base peak of the spectrum, however, is due to the $C_6H_5NH^+$ fragment at 92 m/z . The peak at 93 m/z is probably due to $C_6H_5NH_2^+$ formed in a rearrangement.

Figure 5.15 also displays the REMPI mass spectrum (244 nm, averaged over 10 transients) obtained from the equivalent on-line derivatization reaction of formaldehyde using the TMA REMPI-TOFMS setup described above. The soft ionization capability of REMPI provides simple mass spectra with

nearly no fragmentation. The mass peak 94 m/z in the REMPI spectrum is suspected to be due to an impurity in the phenylhydrazine reagent (most likely phenol). Although the emphasis of this study was not on using SPI-TOFMS (since most of the small molecules tested here, excluding formaldehyde, can be detected by SPI), the TMA set-up was also tested using SPI-TOFMS [32], for the detection of formaldehyde only. Figure 5.18 shows the SPI signal over time, obtained from the TMA set-up for m/z 120, the mass of the formaldehyde derivative. Figure 5.18 also displays the mass spectrum for a single transient taken from the SPI-TOFMS signal over time. A clean mass spectrum displaying only the molecular ion m/z 120 for the formaldehyde-phenylhydrazone derivative was observed using SPI. This result is significant as it is demonstrated that formaldehyde can be made visible not only to REMPI-TOFMS but also to SPI-TOFMS.

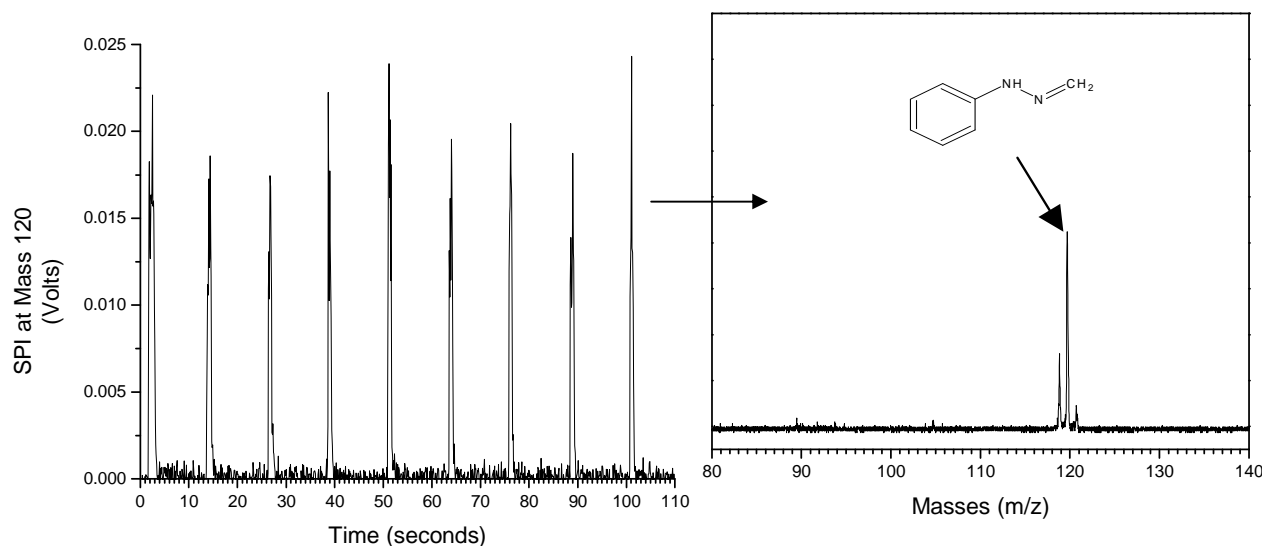


Figure 5.18 SPI signal over time, obtained by applying the on-line *in situ* derivatization TMA setup to the SPI-TOFMS [32] for the analysis of formaldehyde. The insert shows the mass spectrum obtained as a single shot from the time profile, depicting the formaldehyde-phenylhydrazone derivative.

Figure 5.16 shows the REMPI-TOF mass spectra obtained for the TMA and EDU-TMA on-line derivatization of the aldehydes (A) and the amines (B), respectively. The REMPI mass spectrum of the aldehyde derivatives at 246 nm (figure 5.16A) displays the $[M - 1]$ and $[M - 2]$ mass peak for the acrolein-phenylhydrazone derivative (145 and 144 m/z). $[M - 1]$ corresponds to the loss of a hydrogen atom and $[M - 2]$ to the loss of two hydrogen atoms.



The [M - 2] signal is off-scale. These peaks were also observed on the electron impact (EI) mass spectrum of the derivative (not shown here). Only the [M - 1] peak was observed for the acetaldehyde-phenylhydrazone derivative (133 m/z). The crotonal phenylhydrazone was detected as a [M + 1] peak (161 m/z). Additionally, only a very weak [M - 2] peak is visible (158 m/z). [M + 1] adduct peaks are commonly visible in chemical ionization mass spectra, and to a lesser extent in EI mass spectra obtained from ion trap mass spectrometers, when some unintentional chemical ionization can occur. However, [M + 1] peaks do not occur in photo-ionization TOF mass spectra under the chosen conditions (i.e., a pressure of 10^{-4} mbar in the ion source, avoiding protonation *via* ion-molecular reaction). The strong [M + 1] peak for crotonal phenylhydrazone is thus unexpected. It probably indicates that a side reaction has occurred during the derivatization. Because phenylhydrazine, like hydrazine, is a reducing agent, one possible explanation is the hydrogenation of the double bond of crotonal (either before or after the derivatization). The resulting derivative would be butanal phenylhydrazone (162 m/z), which may be detected as an [M - 1] peak (161 m/z), as found for the acetaldehyde and acrolein derivatives. However, it remains unexplained at the current level of research why the same hydrogenation does not take place for acrolein. If we summarize the result for the aldehydes, it can be stated that only formaldehyde can be detected at the unfragmented derivative mass [M] of 120 m/z .

The other aldehyde derivatives, however, were identifiable at either the respective [M - 1] or [M - 2] peak ([M + 1] for crotonal). The molecular ion [M] for acetaldehyde, acrolein, and the crotonal phenylhydrazone were not observed at the applied REMPI wavelength of 246 nm. An EI mass spectrum of the acrolein phenylhydrazone product, however, clearly shows the molecular ion mass peak at m/z 146. (Note that the peak at m/z 146 in Figure 5.16A is due to the ^{13}C isotope peak for the [M - 1] ion, not the molecular ion). This indicates that for higher aldehyde-phenylhydrazone derivatives, a photo-induced fragmentation is observable. This is not, however, a problem for the analytical application because the mass spectra are still very soft; i.e. only one (or two) peak(s) dominate the spectra. Phenylhydrazine itself was not observed at the selected REMPI wavelength. It should be noted that with other REMPI wavelengths or power densities, different relative sensitivities or photo-induced fragmentation activities for the different aldehydes may be observed.



The REMPI mass spectrum (240 nm) of the amine derivatives is shown in Figure 5.16B. Benzaldehyde-methylimine, -ethylimine, -propylimine, and -butylimine display two mass peaks of similar intensities, [M] and [M - 1], corresponding to the molecular ion and the hydrogen atom loss. This trend was also observed on the EI mass spectra. In addition, the derivatizing reagent, benzaldehyde, is also observed in the mass spectrum (Figure 5.16B).

The signal [M] m/z 106 is off-scale. The [M + 1] m/z 107 peak is, therefore, the ^{13}C isotope peak. The presence of m/z 106 confirms that the reagent is present in excess during the on-line reaction. A mass gate is required during on-line derivatization to deflect these ions from the detector when an excessive quantity of reagent, such as benzaldehyde, is present. The mass gate will prevent “blinding” of the detector to masses occurring after 106 mass units (the mass of benzaldehyde).

To summarize, the REMPI detectability of the amine derivatives is as successful as for the aldehydes: all analytes were detected as [M] and [M - 1] with no further fragments.

Detection limits were determined and are summarized in Table 5.4. They were calculated using the combined method of Heger *et al* [33] and Williams *et al* [242] using a S/N of 2 and an average of 10 mass spectra. The results obtained demonstrate the potential of this technique for future applications. The calculated detection limits for the analytes are markedly below permissible exposure limits set by the Occupational Safety and Health Administration (OSHA) [15]. The EDU, constructed specifically for use with the on-line REMPI-TOFMS, allows for the use of a MCT for pre-concentration. Lower detection limits were achieved with this setup, since more PDMS is available for pre-concentration. This is confirmed by the results obtained for the benzaldehyde-methylimine, -ethylimine, -propylimine, and -butylimine derivatives using the EDU-TMA and the TMA, respectively (see Table 5.4). In addition, off-line sampling together with a portable pump is also made possible, since the MCT trap is easily removed from the EDU.



5.9. Conclusions

This work demonstrates that on-line derivatization concepts can be used to expand the unique online analytical properties of the REMPI-TOFMS to aliphatic compound classes. Methods for on-line *in situ* derivatization of alkylamines with benzaldehyde and alkyl aldehydes with phenylhydrazine followed by thermal desorption and detection by the REMPI-TOFMS were successfully tested. The detection limits obtained for all analytes, for which concentration standards were made, are below the permissible exposure limits set by OSHA. Formaldehyde, which is not easily detected by mass spectrometry, can be detected as the phenylhydrazone derivative. In the future, formaldehyde gas standards of known concentration will be needed to determine formaldehyde's detection limit for the on-line reaction.

The potential analytical impact of the concept presented here should not be underestimated. Through the coupling of suitable photo labels to non aromatic compounds, a larger variety of compound classes can now be considered for REMPI-TOFMS detection, including compounds such as sugars, sulphur compounds, organic acids, or alcohols. Fast screening methods, for example for environmental samples, biological samples, or medical applications, may be developed on this basis.

As indicated in the introduction (chapter 1), that it is not possible to concentrate volatile underivatized compounds directly by PDMS. The study presented in this chapter provides an example of the use of derivatization reactions to enable both the collection and the concentration of polar volatile analytes as well as their detection with a selective detector.

The combined use of REMPI (and SPI) and the derivatization strategy provides sufficient selectivity to perform trace analysis of real samples without a lengthy chromatographic separation, allowing for on-line monitoring.