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APPENDIX 1: Table 1. A comparison of various adsorbents [48, 69, 70-72, 82, 115, 116]

	ADSORBENT	COMPOSITION	SURFACE AREA (m ² /g)	PORE DIAMETER (nm)	APPLICATIONS	ADVANTAGES	DISDAVANTAGES
CARBON – BASED	Activated carbon Anasorb 747	Coconut/ petroleum based charcoal	800-1000	2.0 / 1.8-2.2	Non-specific i.e. Most organic and inorganic compounds. Non-polar, polar, reactive and/or volatile. Mercury-vapour.	Cheap, efficient, permanent gases not adsorbed – H ₂ , N ₂ , O ₂ , CO, CH ₄ . Anasorb absorbs less H ₂ O and desorption efficiencies for polar compounds are improved.	Polar compounds irreversibly adsorbed. Incomplete desorption. H ₂ O reduces sorption of other compounds. Catalytic activity. Reacts with oxygen or sulphur derivatives.
	Graphitised carbon black Carbotraps	Pre-treated carbon black under vacuum and inert gas/ reductive atmosphere at 3000°C			Non-specific, as above.	No irreversible adsorption sites. No retention of H ₂ O and low molecular mass compounds (CO _x , CH ₄)	High desorption temperatures (400°C) required. Tiny particles of carbon can enter desorption unit.

APPENDIX 1: Table 1. A comparison of various adsorbents [48, 69, 70-72, 82, 115, 116]

	ADSORBENT	COMPOSITION	SURFACE AREA (m ² /g)	PORE DIAMETER (nm)	APPLICATIONS	ADVANTAGES	DISDAVANTAGES
CARBON – BASED	Carbon molecular sieves Carbosieves	Thermally decomposed polymer e.g. polyvinyl chloride			Adsorption of hydrocarbons and low-boiling C1-C4 hydrocarbons, methyl formate and alkyl mercury compounds.	High capacity for small volatile molecules. Suitable for thermal desorption.	Inefficient retention of polar compounds. Solvent with high heat of adsorption required for displacement of adsorbates. H ₂ O can block cryotrap.
INORGANIC	Silica gel	Si-OH groups on surface	100-800	2-4	Polar compounds from air. Amines, halogens, oxygen derivatives, organo-metallics, MeOH, HCHO and DMF. Silica gel is often used as a substrate for coating with derivatizing reagents.	Cooling the sorbent allows trapping of C1-C4 hydrocarbons	Hydrophilicity decreases sorption capacity. Thermal desorption difficult. Silica gel retains H ₂ O and CO ₂
	Aluminium oxide	Al ₂ O ₃					

APPENDIX 1: Table 1. A comparison of various adsorbents [48, 69, 70-72, 82, 115, 116]

	ADSORBENT	COMPOSITION	SURFACE AREA (m ² /g)	PORE DIAMETER (nm)	APPLICATIONS	ADVANTAGES	DISDAVANTAGES
INORGANIC	Molecular sieves	Zeolites	Varied	Varied	Toxic inorganic compounds. Small conc. of H ₂ S	Thermally desorbed at 240°C/extract with ice H ₂ O	Organic compounds are irreversibly adsorbed excl. HCHO, acrolein and certain S-compounds. H ₂ O block cryotrap
POROUS POLYMERS	Tenax	Poly-2,6-diphenyl-p-phenylene oxide	19	140	Organic bases, neutral and high boiling compounds. Chlorohydrocarbons. Support for derivatising reagents. Broad trapping range of compounds of varied molecular mass and polarity.	Tenax has a high thermal limit 350-400°C. Ideal for thermal desorption.	Not suited to solvent extraction due to low capacity for volatiles and is incompatible with many solvent systems.

APPENDIX 1: Table 1. A comparison of various adsorbents [48, 69, 70-72, 82, 115, 116]

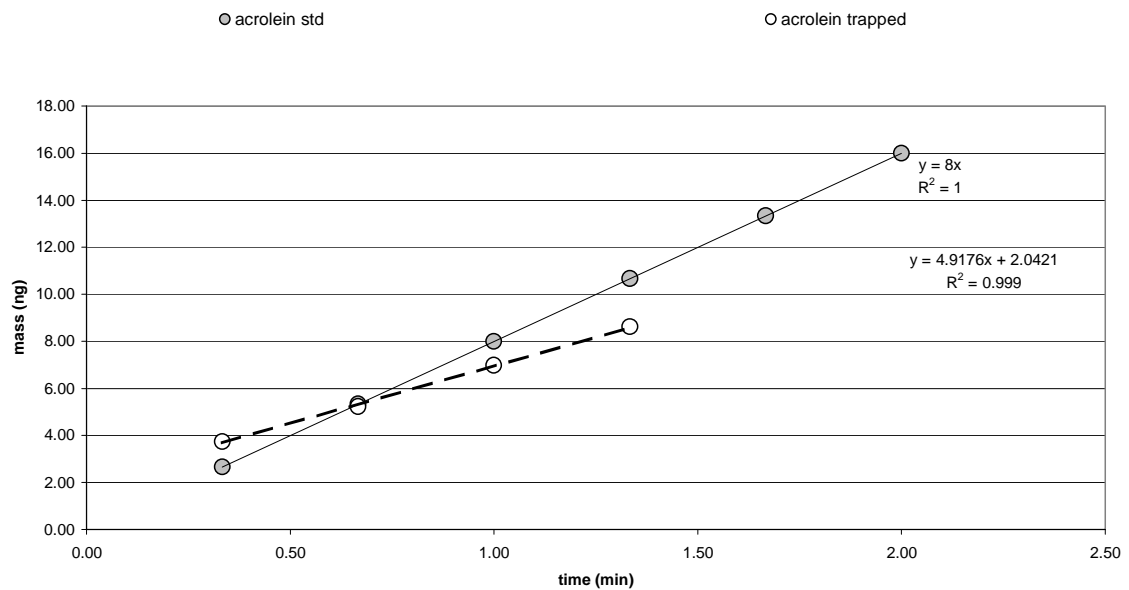
	ADSORBENT	COMPOSITION	SURFACE AREA (m ² /g)	PORE DIAMETER (nm)	APPLICATIONS	ADVANTAGES	DISDAVANTAGES
POROUS POLYMERS	XAD-2 (Amberlite, Chromosorb 102)	Copolymer in which one moiety is styrene or ethylvinylbenzene and the other monomer a polar vinyl compound.	300-400	8.5	Nitroso-compounds and polychlorinated biphenyls, aromatic, aliphatic nitro-compounds.	XAD's, Porapaks and Chromosorbs come in wide ranges of polarity. Chromosorb 106 greater capacity than Tenax, suited to thermal desorption.	
	Porapak		600-650	7.5	Depending on polarity. Non-polar to polar compounds can be adsorbed. Chromosorbs adsorb inorganic compounds		Polar Porapaks retain H ₂ O and require great amount of energy to remove sorbates. Can't withstand the high temperature.
	Chromosorb101, 103, 104, 106, 108.		50 varied	300-400 varied			

Appendix 2

Reaction efficiency data

Additional experimental data obtained for results discussed in section 5. 4.

Acrolein Reaction Efficiency



Crotonal Reaction Efficiency

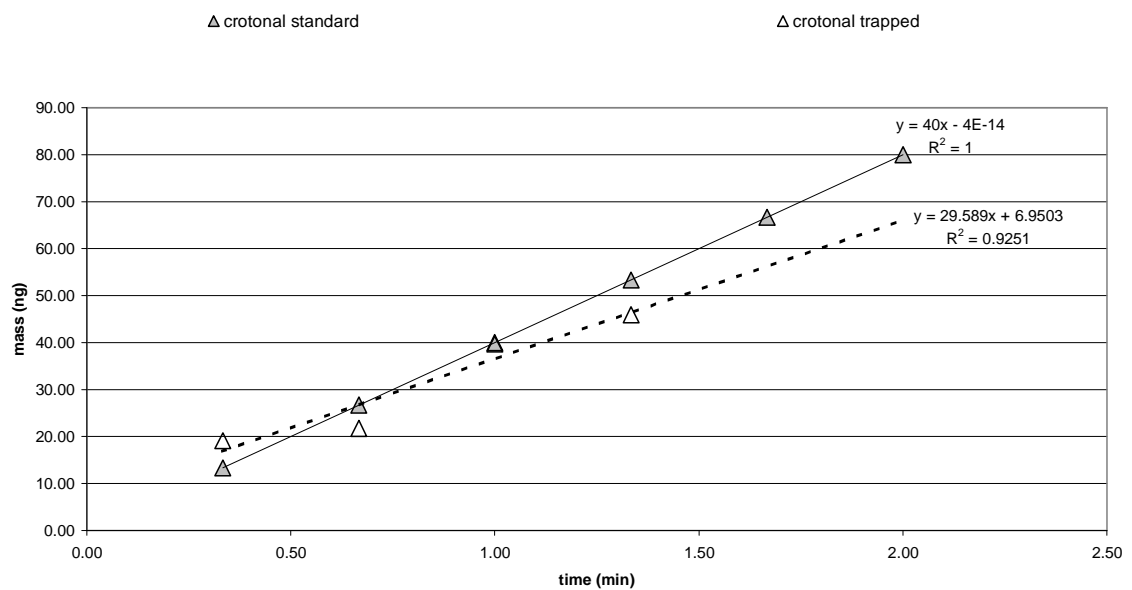


Figure A2.1 Reaction efficiency graphs for the on-line derivatization of acrolein and crotonal with phenylhydrazine. The graph displays i) the amount of gas standard released over that time interval as determined by their permeation rate and ii) the amount of analyte gas trapped using *in-situ* derivatization 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. 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.

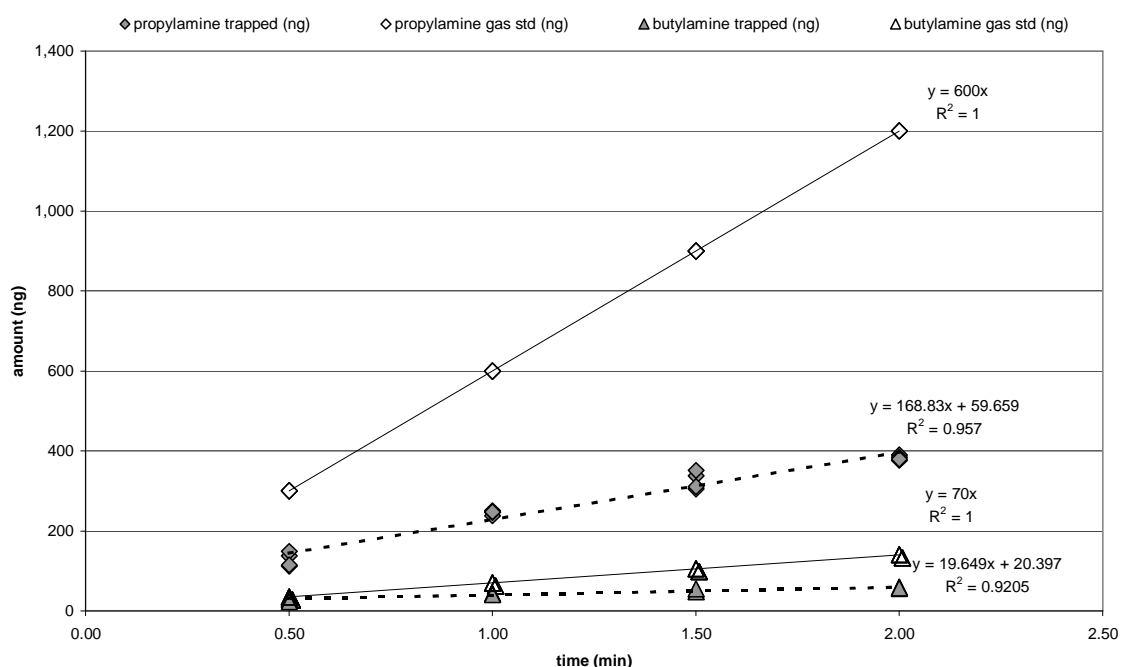


Figure A2.2 Reaction efficiency graphs for the on-line derivatization of propylamine and butylamine with benzaldehyde. The graph displays i) the amount of gas standard released over that time interval as determined by their permeation rate and ii) the amount of analyte gas trapped using *in-situ* derivatization 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. 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.

Appendix 3

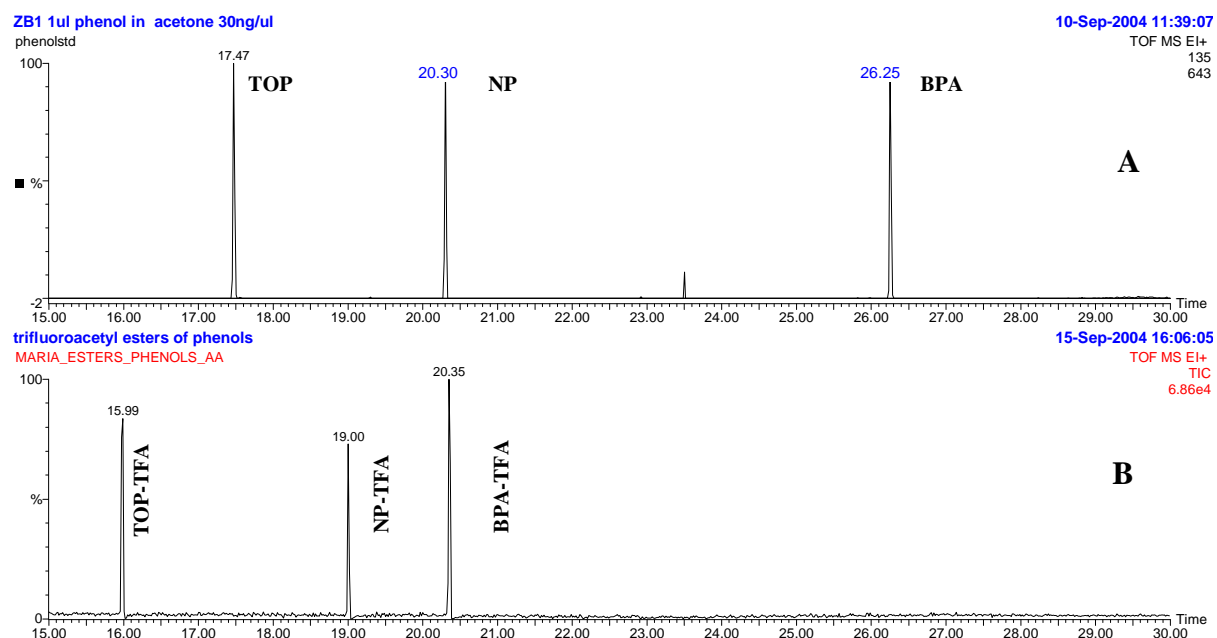
Confirmation of the alkylphenol-TFA derivatives

Figure A3.1

A) GC-TOFMS chromatogram obtained for the underivatized phenols, TOP $t_R = 17.47$ min, NP $t_R = 20.30$ min and BPA $t_R = 26.25$ min.

B) GC-TOFMS confirmation chromatogram for the trifluoroacetate derivatives prepared in a vial in acetone as described in section 6.2.6. TOP-TFA $t_R = 15.99$ min, NP-TFA $t_R = 19.00$ min and BPA-TFA $t_R = 20.35$ min. Notice the absence of underivatized phenols.

The TFA derivatives elute earlier than the underivatized phenols allowing for shorter chromatographic runs, while the mass spectra yields masses higher up in the mass range allowing for improved selectivity during analysis.

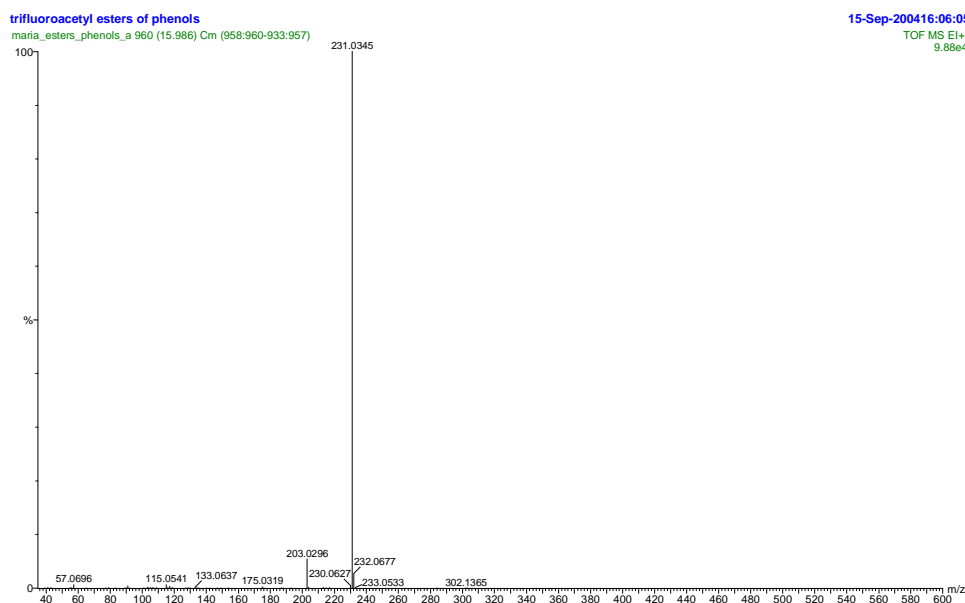


Figure A3.2 GC-TOFMS mass spectrum obtained for the TOP-TFA derivative $t_R = 15.99$ min. M^+ m/z 302, base peak m/z 231.

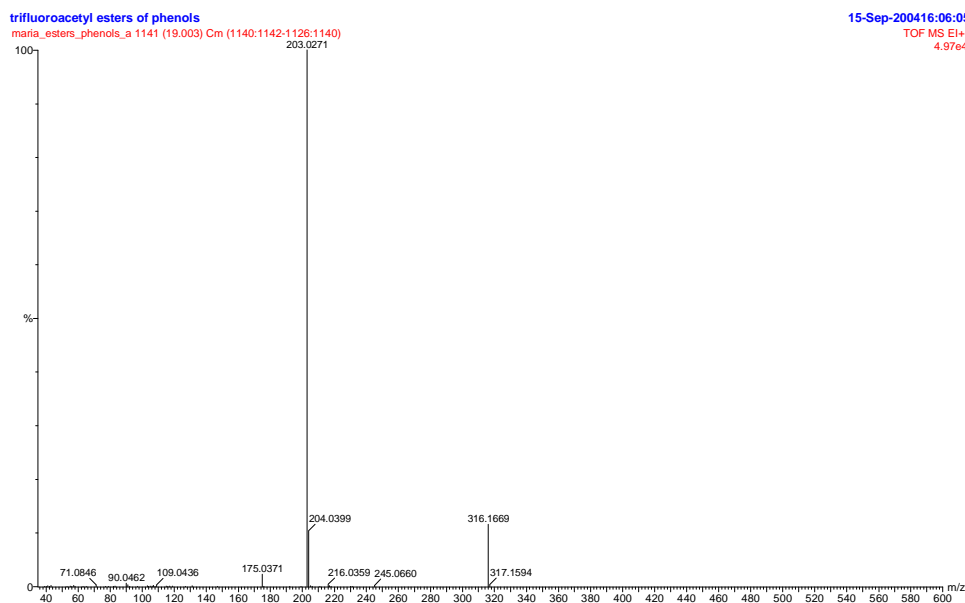


Figure A3.3 GC-TOFMS mass spectrum obtained for the NP-TFA derivative $t_R = 19.00$ min. M^+ m/z 316, base peak m/z 203.

trifluoroacetyl esters of phenols

maria_esters_phenols_a_1222 (20.352) Cm (1222:1223-1154:1213)

15-Sep-200416:06:05

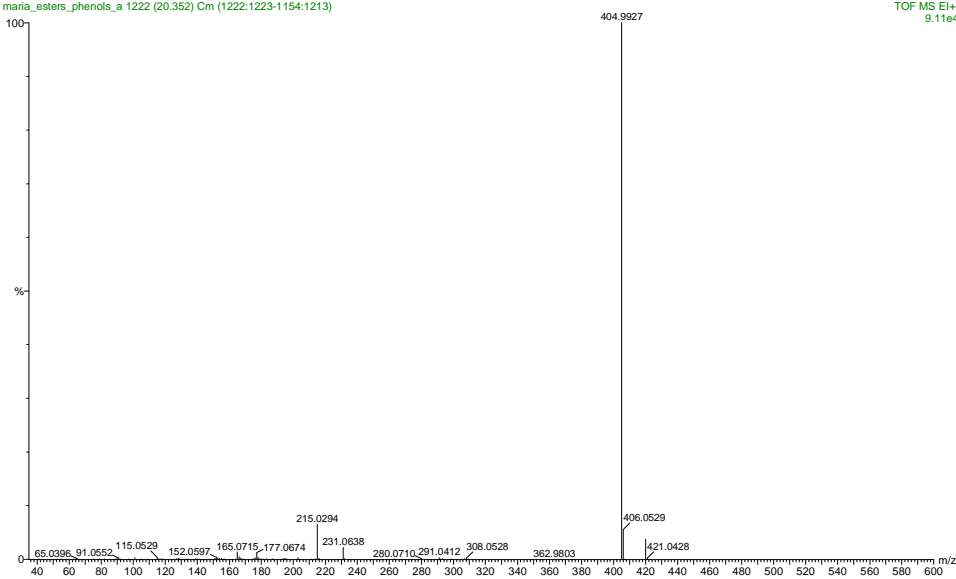
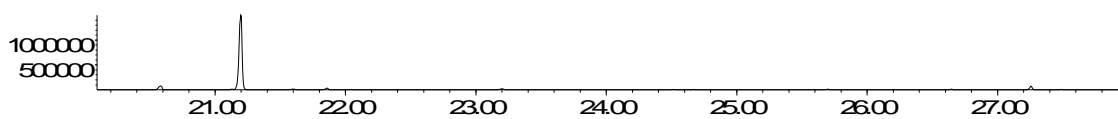
TOF MS EI+
9.11e4

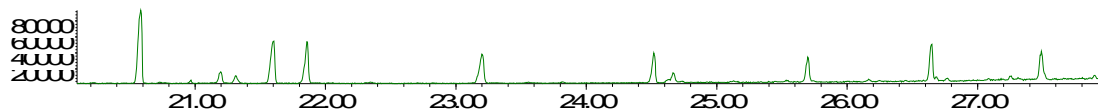
Figure A3.4 GC-TOFMS mass spectrum obtained for the BPA-TFA derivative $t_R = 20.35$ min. M^+ m/z 420, base peak m/z 405.

Abundance

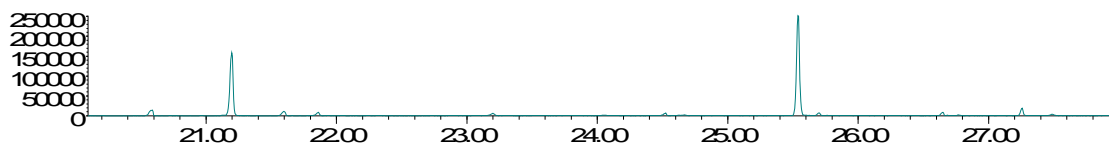
Ion 231.00 (230.70 to 231.70): 08050604.D

Time-->
Abundance

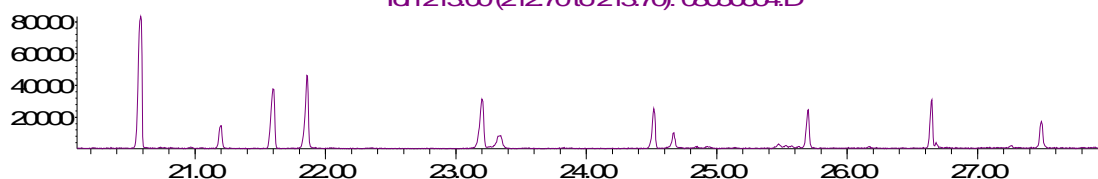
Ion 135.00 (134.70 to 135.70): 08050604.D

Time-->
Abundance

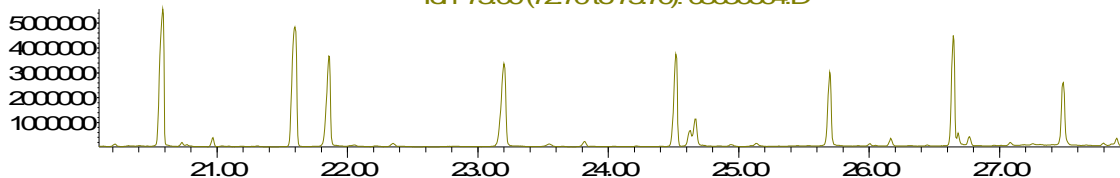
Ion 203.00 (202.70 to 203.70): 08050604.D

Time-->
Abundance

Ion 213.00 (212.70 to 213.70): 08050604.D

Time-->
Abundance

Ion 73.00 (72.70 to 73.70): 08050604.D



Time-->

Figure A3.5 Reconstructed ion chromatograms for m/z 231 and m/z 203 representing the TFA derivatives of TOP and NP respectively, along with m/z 135 and m/z 213 representing ions for the corresponding underivatized alkylphenols. The PDMS degradation peaks are indicated by the m/z 73 ion trace.

From figure A3.1, the unreacted phenols are expected to elute after the TFA derivatives. There is no clear evidence from the RICs that the underivatized phenols are present. Ions 213 and 135 that are present appear to originate from the PDMS thermal degradation peaks. See section 6.7.1.

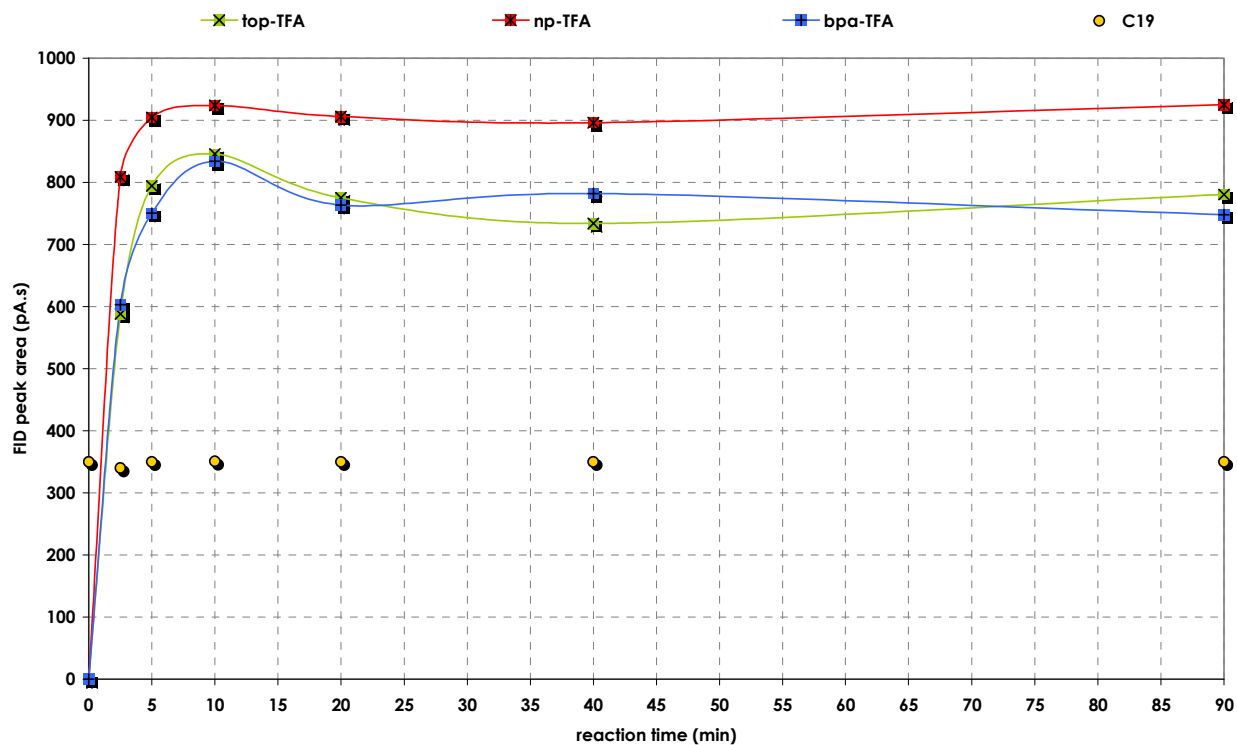


Figure A3.6 Reaction efficiencies, determined by placing 1 μ l 42 ng/ μ l TOP, 44 ng/ μ l NP and 54 ng/ μ l BPA in acetone on the PDMS trap, 5 μ l TFAA is added after the solvent has evaporated. The trap is then sealed with glass caps for the duration of the reaction. The reaction appears to be complete after 5 minutes. See section 6.7.2.

Appendix 4

Significance test for comparing extraction efficiency from two different PDMS batches

1. An F-test is used to compare the population standard deviations between the two batches of PDMS. These need to be the same in order to perform a t-test to compare the two mean results between the batches. The equation used to determine F is shown below [276]:

$$F = \frac{s_1^2}{s_2^2} \quad \text{A.4.1}$$

Where s_1 and s_2 are the standard deviations for the measurement series and are arranged so that $F > 1$.

Critical values of F for a two-tailed test ($P=0.05$) are obtained from table A.4, page 256 [276]. Where v_1 and v_2 are the degrees of freedom ($n-1$) for the number of measurements made (n) in the respective measurement series.

2. A t-test can now be used to compare the two mean results between the batches. The variance (s^2) needs to be calculated as shown in equation A.4.2, in order to determine t from equation A.4.3 [276].

$$s^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} \quad \text{A.4.2}$$

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{s \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \quad \text{A.4.3}$$

Where n is the number of measurements performed in each measurement series and x the average measurement result obtained.

Critical values of t for a two-tailed test ($P=0.05$) obtained from table A.2, page 254 [276], where t has $(n_1 + n_2 - 2)$ degrees of freedom (v).

Summary of results obtained using the equations as described above:

Table A.4 Summary of significance test results

	TOP batch 1	TOP batch 2	NP batch 1	NP batch 2	BPA batch 1	BPA batch 2
x	70	79	84	43	10	26
s	2.8	2.37	21.8	9.5	1.5	2.08
n	7	5	8	5	8	5
F_{crit}	9.197		9.074		9.074	
F	1.396		5.330		1.923	
$F < F_{crit}$	Population standard deviation of the two batches are equal		Population standard deviation of the two batches are equal		Population standard deviation of the two batches are equal	
t_{crit}	2.23		2.20		2.20	
t	5.83		3.92		16.19	
$t > t_{crit}$	Means of the two batches differ significantly		Means of the two batches differ significantly		Means of the two batches differ significantly	

Appendix 5

PDMS MCT trap drying investigation

A few drops of bromothymol blue indicator was added to a 5 ml Milli-Q water sample. The water was sampled at a flow rate of $\sim 50 \mu\text{l}/\text{min}$ through the PDMS MCT. The presence of the bromothymol blue gave a visual indication of water still trapped inside the PDMS channels. These drops of water were best removed by mechanical dropping of the trap, as opposed to purging with gas. Dropping the trap down a 1.5 m length of tube provided enough force to break the capillary action occurring between the water and PDMS walls.

After sampling the PDMS MCT was weighed on a 4 decimal place balance. The trap was weighed after each drying step. A summary of the results obtained for the drying steps performed in series are shown in the graph below. The trap appears to reach a constant mass after purging with hydrogen gas for 2 minutes at a flow rate of 500 ml/min. An equivalent result is obtained by purging for 1 min at 1L/min. The mass difference between the last drying step and thermal desorption of the trap is 0.2 mg. The mass balance performance was not monitored and this mass difference could easily fall within the uncertainty of the balance. However, this mass difference was later assumed to be residual water vapour, even though no water could be visually observed after the last drying step, degradation on the PDMS trap was still observed.

Weighing the trap after plugging with the silica gel caps was not performed as such a small mass cannot be determined accurately on the available mass balance.

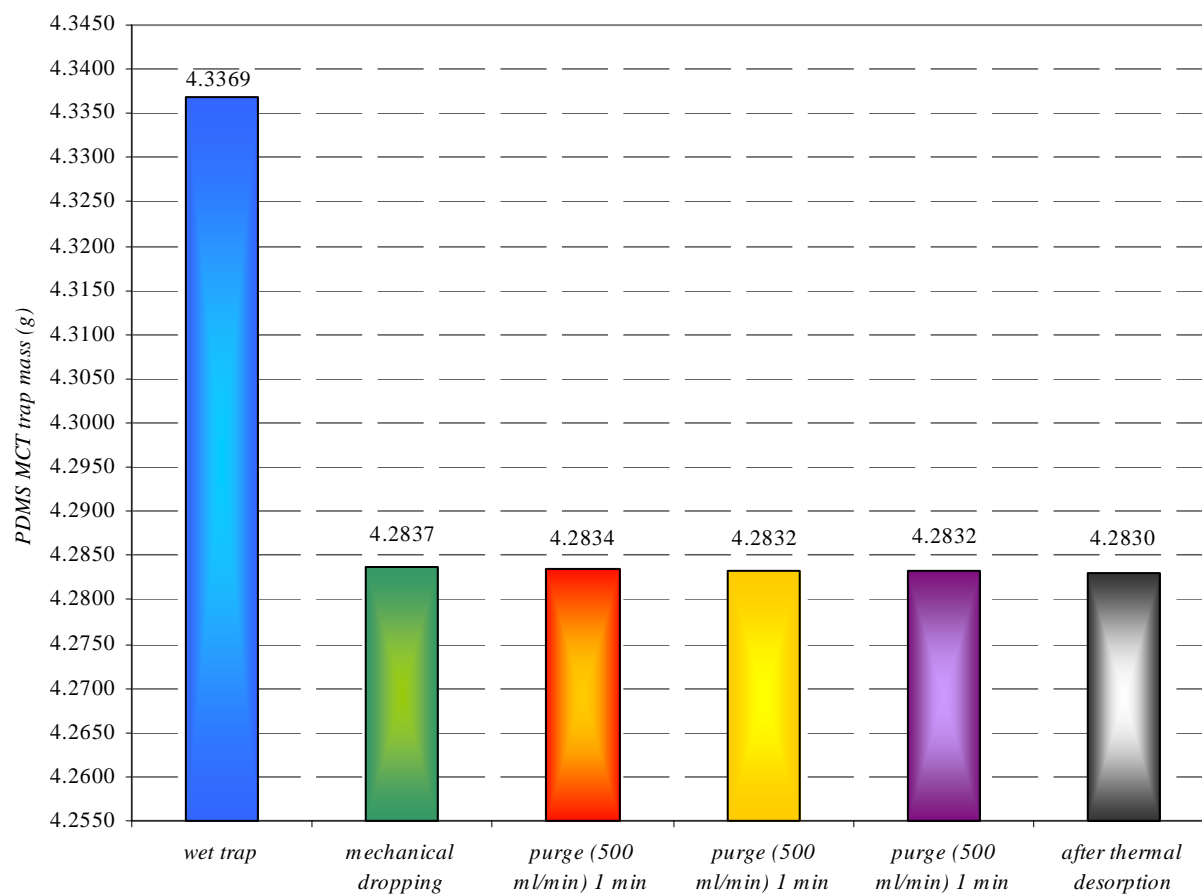


Figure A.5 Summary of the drying steps performed in series with the resulting PDMS MCT mass loss achieved from each drying step.



Appendix 6

Published article

Anal. Chem. **2005**, *77*, 1–10

Accelerated Articles

On-Line Derivatization for Resonance-Enhanced Multiphoton Ionization Time-of-Flight Mass Spectrometry: Detection of Aliphatic Aldehydes and Amines via Reactive Coupling of Aromatic Photo Ionization Labels

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Resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (REMPI-TOFMS) is a powerful technique for the on-line analysis of aromatic compounds with unique features regarding selectivity and sensitivity. Aliphatic compounds, however, are difficult to address by REMPI due to their unfavorable photo ionization properties. This paper describes the proof of concept for an on-line derivatization approach for converting nonaromatic target analytes into specific, photoionizable aromatic derivatives that are readily detectable by REMPI-TOFMS. A multichannel silicone trap or poly(dimethylsiloxane) (PDMS) open tubular capillary was used as a reaction medium for the derivatization of volatile alkyl aldehydes and alkylamines with aromatic “photoionization labels” and to concentrate the resulting aromatic derivatives. The aldehydes formaldehyde, acetaldehyde, acrolein, and crotonal, which when underivatized are poorly detectable by REMPI, were converted into their easily photoionizable phenylhydrazone derivatives by the on-line reaction with phenylhydrazine as reagent. Similarly, the methyl-, ethyl-, propyl-, and butylamines were converted into their REMPI-ionizable benzaldehyde alkylimine derivatives by the on-line reaction with benzaldehyde as reagent. The derivatives were thermally desorbed from the PDMS matrix and transferred into the REMPI-TOFMS for detection. The REMPI-TOFMS detection limits obtained for acetalde-

hyde; acrolein; crotonal; and methyl-, ethyl-, propyl-, and butylamine using this photo ionization labeling method were in the sub-parts-per-million range and, thus, readily below the permissible exposure limits set by OSHA.

There is an increasing awareness of the harmful effects that volatile aldehydes and amines, particularly formaldehyde, can have on human health. Formaldehyde is classified as a probable human carcinogen by the EPA, OSHA, NIOSH, and the ACGIH.^{1–3} Low-molecular-mass aldehydes and amines are typically eye, nose, and throat irritants.^{3–5} As volatile polar compounds, they are notoriously difficult to analyze. Real time monitoring of these trace

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^{||} Airsense Analytics.

- (1) *Chemical, Toxicity, Safety and Environmental Analysis Information for Formaldehyde*. <http://www.instantref.com/formald.htm>; Accessed Feb. 2, 2004.
- (2) Occupational Safety and Health Administration, U.S. Department of Labor. *OSHA Permissible Exposure Limits*; <http://www.osha-slc.gov/pls/oshaweb/>; Accessed Feb. 2, 2004.
- (3) Brabec, M. J. Aldehydes and Acetals. In *Patty's Industrial Hygiene and Toxicology*, 3rd rev. ed.; Clayton, G. D., Clayton, F. E., Eds.; John Wiley & Sons: New York, 1981; Vol 2A, pp 2692–2669.



organic compounds in air or process gases is not easily achieved. Measurement usually requires extended sample preconcentration, cleanup, and instrumental analysis, for example, by gas chromatography/mass spectrometry (GC/MS) in a well-equipped analytical laboratory.^{6–8} It involves a time-consuming and labor-intensive process that prevents the timely data generation required, for example, for effective pollution control measures.

Recently, several on-line monitoring methods based on direct inlet mass spectrometry (MS) with soft and selective ionization methods were established. This includes chemical ionization MS⁹ as well as photoionization MS techniques.^{10–19} One particularly powerful approach for real time monitoring of aromatic compounds is resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (REMPI-TOFMS). The REMPI-TOFMS method, for example, has been used for the on-line monitoring of dioxin surrogates and other aromatic trace species in waste incinerator emissions,^{15,16} characterization of the formation of phenolic compounds during coffee roasting,^{17,18} and puff-resolved analysis of toxic aromatic compound release during the cigarette smoking process¹⁹ as well as the characterization of wood combustion.²⁰ In addition to the analysis of gaseous matrixes, solid matrixes can be handled as well in a two-step process using laser desorption followed by REMPI of the volatilized compounds.^{21–25} 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 region is easily accessible by commercial laser systems. The combination of selectivity and immediate availability of mass spectral information eliminates the time-consuming separation step of gas chromatography. Unfortunately, many compounds not possessing an aromatic chromophore, such as aliphatic aldehydes and amines, cannot be easily detected by the rather simple one-color two-photon REMPI process. For example, many aldehydes require complicated REMPI schemes, which are based either on multilaser wavelength excitation or the inclusion of nonresonant multiphoton absorption steps. In other cases, as for many amines, the suitable REMPI wavelengths for the various compound homologues are different, preventing a simultaneous detection of the homologue profile.

A fast method for the on-line detection of aldehydes and amines, however, would have several potential applications in the field of process gas analysis, ambient air monitoring, or emission analysis. Furthermore, it would be desirable to also make use of the advantages of the REMPI-TOFMS method (i.e., selectivity, sensitivity, and measurement speed) for the detection of these aliphatic compounds. To make aldehydes and amines accessible to REMPI-TOFMS detection, a concept to convert the nonaromatic analytes into specific aromatic derivatives, which would then be detectable by the REMPI-TOFMS, was developed (“photoionization labeling”). Derivatization reactions which in principle can be used for “photoionization labeling” usually are performed in liquid solutions or, as recently demonstrated, in a poly(dimethylsiloxane) (PDMS) matrix as reaction medium. PDMS, for example, has been used for in situ derivatization of low-molecular-mass aldehydes for GC/MS analysis.^{26,27} The work presented here describes the development of a PDMS-based on-line “photoionization labeling” derivatization technique which can be directly hyphenated to the REMPI-TOFMS system. The PDMS devices are shown in Figure 1A. The principle of the “photoionization labeling” derivatization is as follows (depicted in Figure 1B).

The analytes from the sample gas current (i.e., containing traces of amines or aldehydes to be analyzed) as well as the derivatization reagent are coabsorbed in a PDMS trap. After a short enrichment phase, the trap is heated. The heating induces both the derivatization reaction itself and the thermal desorption of the formed derivatives. The desorbed derivatives are subsequently transferred to the REMPI-TOFMS spectrometer for analysis. This procedure can be repeated rapidly for a (quasi) on-line analysis.

At first, potential derivatization reactions were selected (derivatization of aldehydes with phenylhydrazine to form the respective phenylhydrazone derivatives and derivatization of amines with benzaldehyde to form the respective benzaldehyde alkylimine derivatives). The proof of principle (i.e., of efficient PDMS-mediated derivatization) was tested in a solid-phase microextraction (SPME) approach with GC/MS and GC-FID detection. Subsequently, an experimental on-line derivatization setup was built and coupled to the REMPI-TOFMS system. Two different setup variants were used for the derivatization procedure. In the first setup, a thermal modulator array²⁸ with a fused-silica capillary

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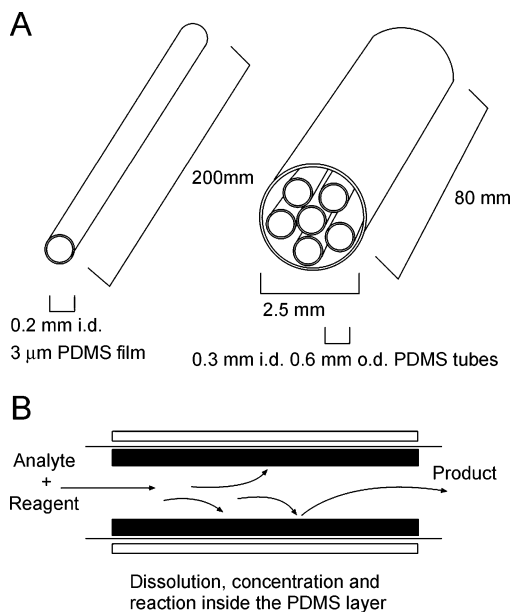


Figure 1. Two variations of silicone (PDMS) concentrators are shown in A, namely, the thick film capillary trap, used in the thermal modulator array (TMA), and the multichannel silicone rubber trap (MCSRT) used in the EDU. B Cross section of a capillary trap, which demonstrates the concentration and reaction within these concentrating devices.

column (3- μ m silicone film, DB-1 equivalent) is used to absorb, derivatize, desorb, and refocus the analytes. The second setup consists of an enrichment desorption unit (EDU; Airsense Analytics, Schwerin, Germany)²⁹ with a multichannel silicone rubber trap^{27,30,31} as PDMS medium for derivatization followed by the above-mentioned arrangement with the thermal modulator array.²⁸ These experimental setups are shown in Figure 2A, B, and C, respectively.

EXPERIMENTAL SECTION

(A) Derivatization Reaction for “Photoionization Labeling” of Amines and Aldehydes. Phenylhydrazine^{32,33} and benzaldehyde³³ were selected as “photoionization labeling compounds” and were used to derivatize the aldehydes (formaldehyde, acetaldehyde, acrolein, and crotonal) and amines (methylamine, ethylamine, propylamine, butylamine), respectively. Methylamine, ethylamine, propylamine, benzaldehyde, formaldehyde (36.5% in water), and phenylhydrazine were purchased from Aldrich (Taufkirchen, Germany). Acetaldehyde, acrolein, and crotonal were obtained from Merck (Darmstadt, Germany). Butylamine was obtained from ChemService (Johannesburg, S. A.). *Caution: Because 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.*

Schemes for the deriva formed are shown in Figure 3A and B. These reagents were selected to introduce a REMPI-active chromophore to the analyte structure. Substituted rings, such as pentafluorinated benzaldehyde, were discarded because 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 vapor pressure to ensure that the reagent would be present in excess in the gas phase. Stable gaseous concentrations of the analytes were obtained by preparing permeation and diffusion gas standards of the respective aldehydes and amines. Gas standard preparation and measurement has been described in the literature.^{34,35} Concentrations provided by the gas standards are listed in Table 1. Headspace from formaldehyde (stabilized with methanol in water) was used as the formaldehyde gas source. This concentration is rather high and could not be determined in the framework of the experiments presented here.

(B) Setup for SPME GC-FID-Based Testing of the PDMS-Mediated 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 2A shows the on-line setup used to determine the approximate reaction efficiency for the various derivatization reactions. 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 connector³⁶ (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 into 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 fiber.

Current concentration methods are mainly off-line.^{37–39} Solid-phase microextraction (SPME)^{26,40} and the multichannel silicone rubber trap (MCSRT)²⁷ are two examples of a novel technique that uses poly(dimethylsiloxane) as the concentration and reaction medium, eliminating problems experienced with earlier concentration methods.^{27,37–39} In situ derivatization in PDMS has been used to trap low-molecular-mass aldehydes for GC-FID and GC/MS analysis.^{26,27} The PDMS concentrators used in this study are

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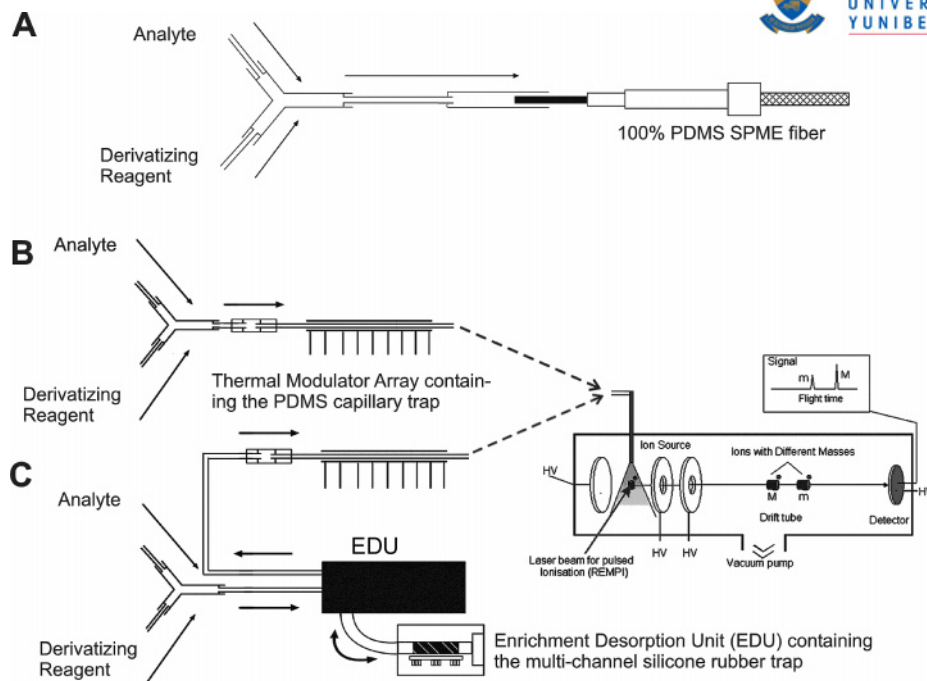


Figure 2. Experimental setup used for (A) determining the reaction efficiencies for the on-line derivatization reactions, (B) on-line concentration and derivatization for REMPI-TOFMS using the thermal modulator array (TMA) with a thick-film capillary as enrichment and reaction medium, and (C) on-line concentration and derivatization for REMPI-TOFMS using a MCSRT in an EDU as enrichment and reaction medium and the TMA with a thick film capillary for analyte modulation.

Table 1. Gas Standard Concentrations and Calculated Detection Limits for the Aldehydes and Amines Studied^a

analytes (<i>m/z</i>)	gas std concn EDU-TMA (ppm v/v)	detection limit (S/N = 2 av 10) EDU-TMA (ppm v/v)	gas std concn TMA (ppm v/v)	detection limit (S/N = 2 av 10) TMA (ppm v/v)	PEL OSHA (ppm)
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	0.010	21.7	0.324	10
propylamine (147)	1.8	0.024	27.6	0.138	
butylamine (161)	2.9	0.100	44.7	0.501	5

^a Permissible exposure limits (PEL) as set by OSHA are also listed (see ref 2).

depicted in Figure 1A. The SPME device consists of a 100- μ m PDMS-coated fiber mounted on the tip of a syringe needle, which is housed within the syringe barrel when not exposed during sampling.⁴⁰ A 100- μ m PDMS SPME fiber was exposed over increasing time intervals to a similar on-line arrangement used for the REMPI-TOFMS shown in Figure 2B. The SPME assembly and 100- μ m PDMS fibers were obtained from Supelco (Bellefonte, PA). The fiber 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 relative effective carbon number responses of the derivatives.^{27,41,42} Thermal desorption of the SPME fiber 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.²⁷ 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 results for this experiment are shown in Figure 4.

(C) REMPI-TOFMS. The resonance-enhanced multiphoton ionization time-of-flight mass spectrometer used for this application is a home-built system containing 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 ($\sim 10^6$ W cm⁻²) are directed into the ionization chamber of the TOF (Kaessdorf Instruments, Germany)

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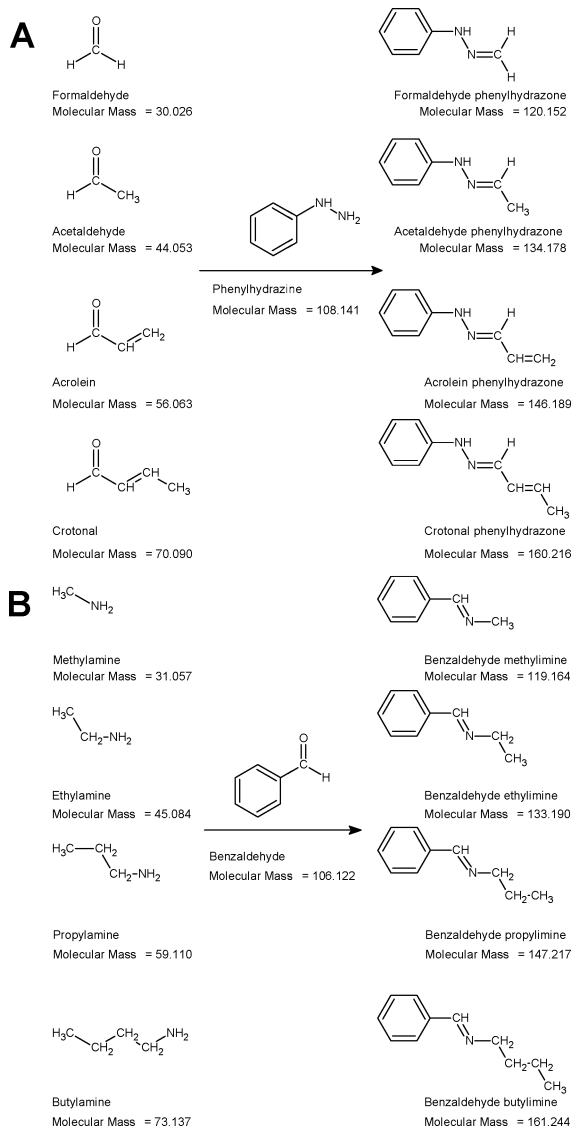


Figure 3. Reaction schemes for the derivatization of (A) the aldehydes with phenylhydrazine and (B) the alkylamines with benzaldehyde.

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 are 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.

(D) On-Line Derivatization Setup for REMPI-TOFMS.

Figure 2B and C shows the on-line derivatization REMPI-TOFMS setups. Unlike the arrangement for principal testing (SPME), 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 enrichment desorption devices:

(i) a thermal modulator ϵ trap (TMA) and (ii) an enrichment desorption unit with a multichannel PDMS rubber trap. Two setup variants were tested. In the first setup, only the thermal modulator array (i) with a PDMS thick-film capillary trap was used, whereas in the second setup, the enrichment desorption unit with a multichannel PDMS rubber trap (ii) was applied in combination with the thermal modulator array with a PDMS thick-film capillary trap (i).

In the following, the two experimental setups are described in more detail.

First Setup: Direct Supply of Analytes and Reagents through the Thermal Modulator Array (TMA-REMPI-TOFMS). The centerpiece of the derivatization setup is the segmented thermal modulator array.²⁸ 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 fiber. In detail, the modulator capillary consisted of a fused-silica capillary column (0.2-mm i.d.) coated with nonpolar phase PS-255 (3- μ m 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 28.

A stainless steel capillary (105 mm \times 0.6 mm o.d. \times 0.35 mm i.d.) was converted to a modulator.²⁸ 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 43 from an uncoated capillary (30 cm \times 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.

Modulators have predominantly been developed for use as an interface between two columns in comprehensive two-dimensional gas chromatography.⁴⁴ Its function is to rapidly focus fractions of effluent from the first column onto the head of the second column. In this work, a modulator is used to transfer and focus the effluent from the capillary trap into the REMPI-TOFMS.

In principle, the sorption and desorption of effluent from the stationary phase in the modulator capillary can be controlled by careful manipulation of the capillary temperature. This was originally achieved by painting a segment of the modulator capillary with an electrically conductive paint, thus allowing the capillary to be resistively heated.^{45,46} This modulator was tedious to prepare and did not prove robust. Alternatively, a copper wire could be coiled around the modulator capillary.⁴⁷ A mechanically driven thermal sweeper was developed to eliminate the high thermal inertia experienced by the metal painted modulator.⁴⁸ A moveable slotted heating element was used to “sweep” periodically over the modulator capillary. This design demonstrates good

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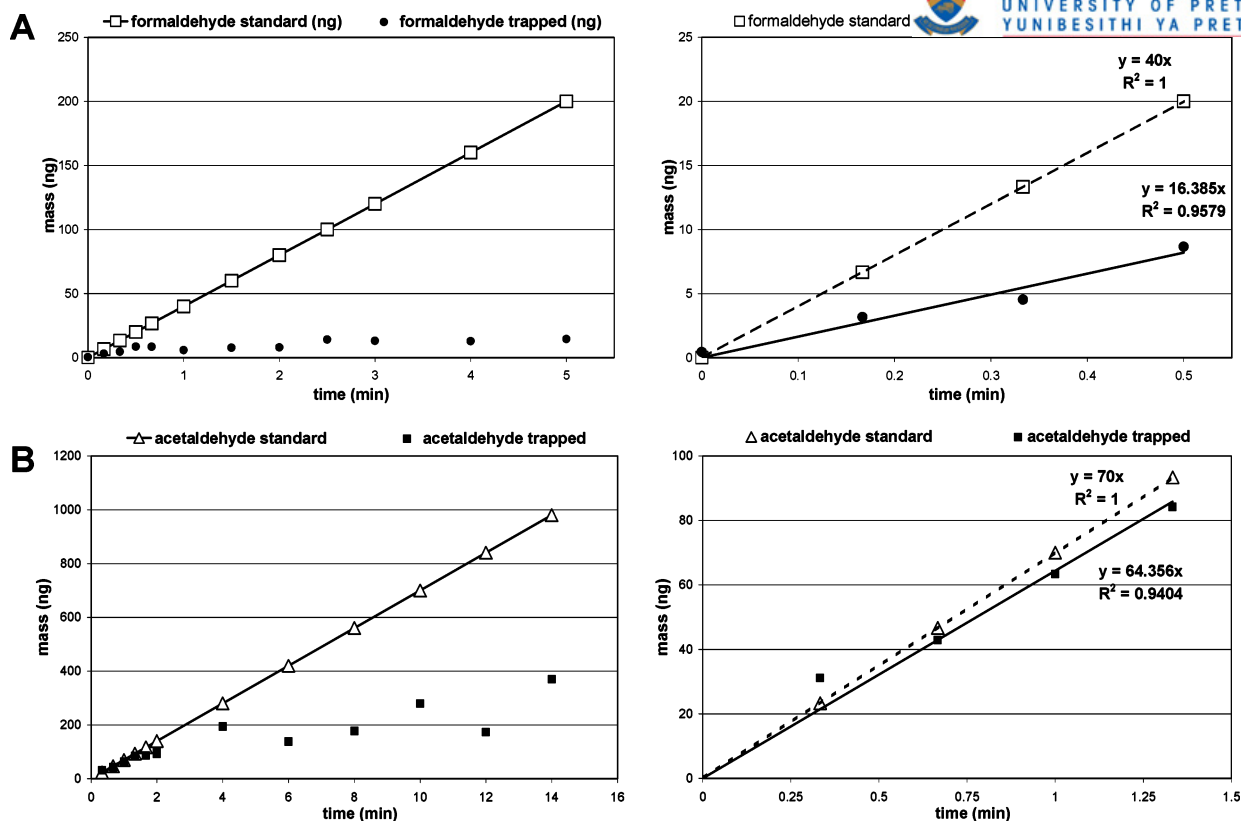


Figure 4. Reaction efficiency results for the on-line derivatization of (A) formaldehyde and (B) acetaldehyde with phenylhydrazine. Both graphs display (i) the amount of gas standard released over that time interval, as determined by their permeation rate, and (ii) the amount of analyte gas trapped using in situ derivatization on the SPME fiber 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 fiber 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.

temperature control and focusing, but is too bulky and complex, requiring the heating element to be at least 100°C higher in temperature than the capillary to effectively focus the effluent.⁴⁵ Thus, much attention has been given to cryogenic modulators. A longitudinal modulating cryogenic system^{49,50} consists of a moveable steel sleeve, which surrounds the capillary. Liquid CO₂ is supplied at timed intervals into the sleeve to cool the capillary. The GC oven provides heating to the capillary segments not being cooled by the moving sleeve. A similar approach in which the CO₂ is sprayed directly onto the capillary⁵¹ was also used; however, contact of the moving modulator with the second column often causes column breakage. Therefore, a nonmoving dual jet cooling modulator was developed. Two different types exist: the first uses two nonmoveable CO₂ jets to cool the capillary trap while the GC oven is used for heating.⁵² The second, from the ZOEX Corporation, uses two cold and two warm nonmoveable nitrogen jets to cool and reinject the effluent from the capillary into the second column.⁵³ Although the cryomodulators provide excellent refocus-

ing of effluent, they require expensive cryogenics that require attention when in use.

The thermal modulator array²⁸ is an improved combination of the metal-painted and “sweep” modulators described above. Rapid resistive heating of consecutive segments of a stainless steel tube surrounding the capillary focuses the effluent inside the modulator capillary. This provides the “sweeping” heat motion without the disadvantageous cold spots or moveable parts. The segmented heating of the effluent in the capillary speeds up the chromatographic process in the capillary column, “compressing” zones from the rear and providing a focused chromatographic band that enters the REMPI-TOFMS. Although not providing the shortest injection pulse widths, the TMA is simple and compact; it does not require cryogenic cooling and can operate unattended, making it suitable for on-line analysis with the REMPI-TOFMS.

The outlet of the TMA device was directly coupled to the TOFMS. This setup was tested for detecting amines using benzaldehyde as photoionization labeling 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 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

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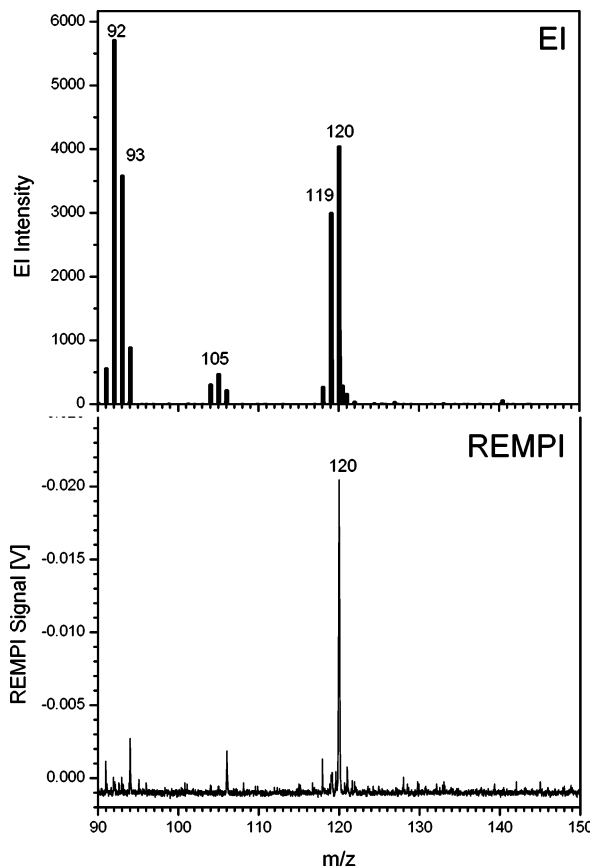


Figure 5. Mass spectra obtained for the formaldehyde–phenylhydrazone derivative using two different ionization techniques. The EI mass spectrum was obtained from a prepared derivative on an accurate mass GC/TOFMS. The REMPI mass spectrum at 244 nm was obtained from the on-line concentration and derivatization experiment (using the TMA setup).

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 1 and Figures 5 and 6.

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 2 C. Here, the multichannel silicone rubber trap in the enrichment desorption unit is used as concentration–reaction medium, and the TMA is used for subsequent temporal focusing. The multichannel silicone rubber trap consists of a glass tube containing several smaller silicone rubber tubes, each 10 cm long, arranged in parallel,^{27,30,31} as shown in Figure 1A. SIL-TEC medical grade silicone tubing for the silicone rubber trap was obtained from Technical Products Inc. (Georgia, U.S.A). It has been shown that the MCSRT can be used as an *inert* absorptive (off-line) concentrator^{27,30,31} having a very low pressure drop (or flow resistance) with properties similar to the packed PDMS trap,^{54–56} which has demonstrated better properties than other current off-line concentration methods.

The MCSRT is placed within the enrichment desorption unit that is connected via the TMA to the REMPI-TOFMS (EDU-TMA-REMPI-TOFMS). The EDU is an automated stand-alone sampling

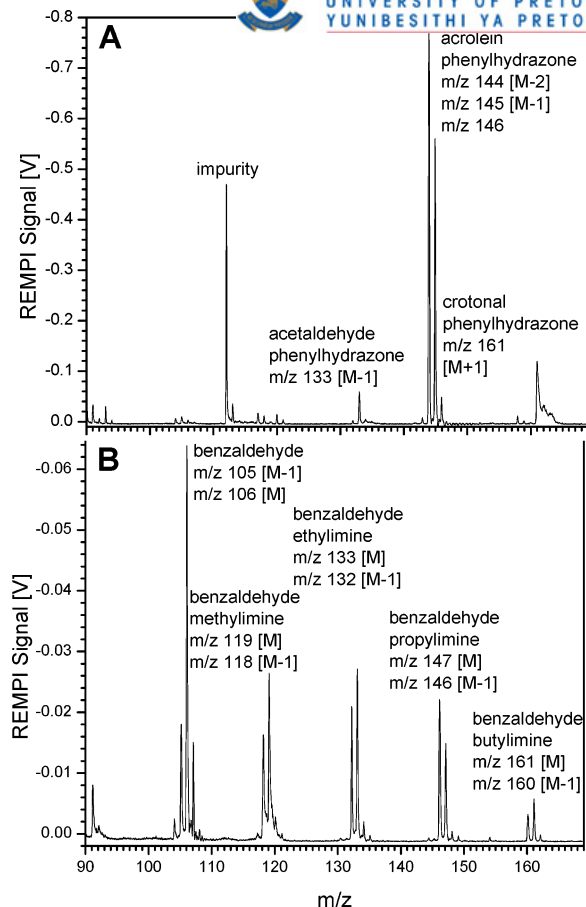


Figure 6. REMPI-TOF mass spectra obtained for the on-line concentration and derivatization of (A) acetaldehyde, acrolein, and crotonal with phenylhydrazine at 246 nm (using the TMA setup) and (B) methylamine, ethylamine, propylamine, and butylamine with benzaldehyde at 240 nm (using the EDU-TMA setup).

and desorption device (Airsense Analytics, Schwerin, Germany). The principal difference between SPME (or the application of TMA solely) and MCSRT is the amount of PDMS available for concentration of analytes, with the MCSRT having a considerably larger amount of PDMS (approximate PDMS volumes are TMA trap 0.2 mm³ and the MCSRT 135 mm³). Thus, the MCSRT can concentrate and derivatize more analyte and, therefore, has the potential to provide lower detection limits.

The EDU system used in this work is a unique trap and thermal desorption system developed by Airsense Analytics for the Institute of Ecological Chemistry, GSF. Gaseous substances are trapped at sampling temperatures (ambient or less) on, for example, Tenax adsorption tubes and analyzed after thermal desorption. The enrichment factor is related to many different physical and sampling parameters. It can be calculated on the basis of breakthrough volumes known from common tables. Typically, the detection limit can be reduced by a factor of 20 with volatile compounds and up to 1000 with low volatiles. Temperatures of the adsorbent during sampling and desorption phases can be adjusted via settings within the related software EDU.

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For increasing the speed of analysis, very small tubes with inner diameters of 1.5 mm filled with Tenax-TA can be used. With applications in very damp environments, this hydrophobic polymer is advantageous because it eliminates the negative influence of humidity on the analysis.

Peltier cooling is used in order to achieve sampling temperatures of 4 °C. After sampling, the tubes are desorbed by resistive heating. With this flash desorption, temperature increments of 200 °C are possible in just 4 s. The complete system is controlled by a microprocessor unit, which is programmed through a serial port.

By sucking air through a cold adsorption tube, the analytes are trapped. In the case of sampling hot gases, it is also possible to dilute the sampling gas to reduce the temperature of the gas. After sampling, a postsampling step is possible to sweep away noninteresting gases and vapors (e.g., humidity).

To extract analytes off the trap, thermal desorption is performed. For injection, the gas flow is reversed and leads into the detection system. Afterward, the tube is cleaned by heating it to a higher temperature than the desorption temperature and flushing the tube with cleaned air. After cooling to near ambient temperatures, the trap is ready for the next measurement. All analytical steps, sampling, postsampling, desorbing, injecting, cleaning, and cooling are performed automatically.

For in situ derivatization, illustrated in Figure 1B, the aromatic derivatizing reagent, in the gas phase, dissolves into the PDMS. Carbonyl compounds (aldehydes and ketones etc.), which pass through the trap, react selectively with the reagent and remain in the trap until they are thermally desorbed for analysis.^{26,27} In the case of the above-mentioned SPME-GC-FID approach, the desorption is performed for some time in the heated GC injector,^{26,27,40} and the derivatized analytes are refocused in a short band due to low initial temperature of the GC oven. For on-line real-time analytical applications, however, analyte focusing can also be important, although not for the enhancement of the chromatographic resolution, but for time resolution and sensitivity. Analyte focusing can be achieved, as described in the first setup, by repetitive thermal modulation. Therefore, in this setup, the EDU is used in combination with a segmented thermal modulator array, 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 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 1 and Figure 6.

Table 2. Approximation of Reaction Efficiency of On-Line Derivatization Reaction Efficiencies at Room Temperature without Catalyst, as Determined by SPME Setup (see Figure 2A)

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)

RESULTS AND DISCUSSION

In the first experiments, the reaction efficiency of the selected derivatization reagents with the selected analytes was tested with the SPME GC-FID approach. The reaction efficiency graphs shown in Figure 4 for the on-line derivatization of formaldehyde and acetaldehyde with phenylhydrazine display the increasing mass accumulation of derivative on the SPME fiber over time. Both graphs display (i) the amount of gas standard released over that time interval, as determined by their permeation rate, and (ii) the amount of analyte gas trapped using in situ derivatization on the SPME fiber, as calculated using an internal standard and the effective carbon number response for the signals obtained from the GC-FID for the desorbed derivatives.^{27,41,42} The graphs on the right represent an enlargement of the graphs on the left, where the initial accumulation on the SPME fiber 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.²⁷ The flattening off of the accumulation curves over time is the result of increased loss or “breakthrough” of the reaction product from the SPME fiber concentrator. The reaction efficiency data, shown in Table 2, were obtained at room temperature using the arrangement in Figure 2A. In Table 2, approximate reaction efficiencies of 28% for the reaction of propylamine and butylamine with benzaldehyde, 30% for the formaldehyde reaction with phenylhydrazine, and around 70% for the aldehydes with phenylhydrazine are indicated.

Incomplete reaction was confirmed by single photon ionization time-of-flight mass spectrometry (SPI-TOFMS)^{15,42} 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. 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. The results of the on-line tests with REMPI-TOFMS detection are given 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 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, pre-



pared using the method described by Vogel et al.,⁵⁸ on an accurate mass TOFMS (Micromass, GCT, U.K.). The formaldehyde–phenylhydrazone derivative is detected at 120 m/z , together with its 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 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).

Figure 6 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 6A, 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 commonly are visible in chemical ionization mass spectra, also 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 photoionization 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, thus, is unexpected and indicates that most likely 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 146 in Figure 6A 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 photoinduced fragmentation is observable, which is, however, not 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 used REMPI wavelength. Note, with other REMPI wavelengths or power densities, different relative sensitivities or photoinduced fragmentation activities for the different aldehydes may be observed.

The REMPI mass spectrum (240 nm) of the amine derivatives is shown in Figure 6B. 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 6B). 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 when an excessive quantity of reagent, such as benzaldehyde, is present to deflect these ions from the detector. 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 1. They were calculated using the combined method of Heger et al.¹⁶ and Williams et al.,⁵⁹ using a S/N of 2 and an average of 10 mass spectra. These results demonstrate the potential of this technique in future applications. The calculated detection limits for the analytes are markedly below permissible exposure limits set by the Occupational Safety and Health Administration (OSHA).²

The EDU, constructed specifically for use with the on-line REMPI-TOFMS, allows for the use of a multichannel silicone rubber trap for preconcentration. Lower detection limits were achieved with this setup, since more PDMS is available for preconcentration. 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 1). In addition, off-line sampling together with a portable pump is also made possible, since the MCSRT trap is easily removed from the EDU.

CONCLUSIONS

The work presented here, on one hand, demonstrates that on-line derivatization concepts can be used to expand the unique on-line analytical properties of the resonance-enhanced multiphoton ionization time-of-flight mass spectrometer to aliphatic compound classes. In detail, a method 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 was 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,

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can be detected as the phenylhydrazone derivative. In the future, formaldehyde gas standards of known concentration must be prepared 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 coupling of suitable photolabels to nonaromatic compounds, a larger variety of compound classes can now be considered for REMPI-TOFMS detection, including compounds such as sugars, sulfur compounds, organic acids, or alcohols. Fast screening methods, for example, for environmental samples, biological samples, or medical applications, may be developed on this basis.



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ACKNOWLEDGMENT

We thank Professor Ben Burger for the supply of one of his thermal modulator systems and the useful discussions regarding its application. Financial support from the National Research Foundations in South Africa (NRF), the GSF Research Center, the Federal German Ministry of Education and Scientific Research (BMBF, WIZ program), and the German Environmental Foundation (DBU-Deutsche Bundesstiftung Umwelt) is acknowledged.

Received for review August 11, 2004. Accepted October 21, 2004.

AC040151A