



*Concentration and derivatization in silicone rubber  
traps for mass spectrometric and gas chromatographic  
analysis of air and water pollutants*

BY

**MARIA JOSÉ FERNANDES-WHALEY**

Submitted in partial fulfilment of the requirements for the degree

*Doctor of Philosophy*

*Chemistry*

in the Faculty of Natural and Agricultural Science

University of Pretoria

Pretoria

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**SUMMARY**

Estrogens, alkylphenols and bisphenol-A, enter the environment through waste water systems and waste disposal of manufactured products e.g. detergents, paints, polycarbonates and flame-retardants. These analytes disrupt the endocrine function of living organisms affecting their reproductive health and those of future generations. Gas phase low molecular- mass aldehydes and amines are typically eye, nose, and throat irritants. Formaldehyde is classified as a probable human carcinogen. Given their negative impact on human health it is urgent to monitor pollutants at extremely low levels in both air and water. The aqueous pollutants are often concentrated using solid phase extraction cartridges or liquid-liquid extraction followed by derivatization. Methods that can most effectively and selectively pre-concentrate aldehydes and amines involve *in situ*

derivatization. Unfortunately, the derivatizing reagents as well as their associated solvents or adsorbents, are responsible for problems encountered with these methods.

Polydimethylsiloxane (PDMS) has emerged as the ideal concentration and reaction medium for trace analysis. However the expensive commercial devices such as SPME and SBSE both require the samples to be returned to the laboratory for concentration. Due to the open tubular nature of the PDMS multichannel trap (MCT), developed in our laboratory, it is ideally suited for on-site and on-line sampling. The MCTs have a high analyte capacity owing to the large volume of PDMS available for concentration. The derivatization reaction can be performed *in situ* providing a “one-pot concentration and reaction device”. This allows for reduced risk of contamination of / or losses of the sample and a sampling method that can cater for both air and water samples.

To demonstrate the versatility of the PDMS MCT, two approaches for concentration in PDMS were investigated in this study, namely, 1) the on-line concentration and *in situ* derivatization of volatile polar analytes from air followed by REMPI-TOFMS detection, and 2) the concentration of phenolic lipophilic analytes from water requiring derivatization prior to analysis by GC/MS.

1) Analyte and derivatizing reagent were simultaneously introduced into the PDMS trap using a y-press-fit connector. The reaction occurs *in situ* followed by thermal desorption using a thermal modulator array alone or in conjunction with a thermal desorption unit. The aldehydes and amine derivatives were successfully detected by the REMPI-TOFMS. Reaction efficiencies were determined at room temperature without catalysts. Formaldehyde yielded a low reaction/concentration efficiency of 41 % with phenylhydrazine in PDMS, while acetaldehyde, acrolein and crotonal displayed much improved values of 92, 61 and 74 % respectively. Both propylamine and butylamine yielded 28 % reaction/concentration efficiency with benzaldehyde in the PDMS matrix. Detection limits obtained with this technique were significantly lower than the permissible exposure limits set by the Occupational Safety and Health Administration. It should be noted that the detection limits were not determined by actual measurement but by extrapolation from a larger signal.

2) Aqueous analytes were concentrated in the PDMS MCT using a gravity flow rate of ~50  $\mu\text{l}/\text{min}$ . The trap was dried and 5  $\mu\text{l}$  derivatizing reagent added. At room temperature and without the presence of a catalyst, the reaction of alkylphenols with trifluoroacetic acid anhydride in the PDMS matrix was 100% complete after 5 minutes. Bisphenol-A reacted less than 50 % to completion



during this period, but the amount of derivative formed remained constant. This study revealed that extraction efficiencies of the alkylphenols and bisphenol-A off the PDMS trap have poor batch-to-batch repeatability indicating that the PDMS matrix was not homogenous. For two different PDMS batches: *tert*-octylphenol displayed an extraction efficiency of 70 and 79%, nonylphenol displayed 84 and 43% while Bisphenol-A displayed 10 and 26% respectively. The thermally desorbed derivatives were analysed by GC/MS. Despite background contamination in the desorption unit, detection limits were at the ppt level. Detection limits were not determined by actual measurement but by extrapolation from a larger signal.

Real samples were also tested.

**Keywords:** air pollutants, water pollutants, concentration, *in situ* derivatization, polydimethylsiloxane, PDMS, multichannel traps, thermal desorption, gas chromatography, mass spectrometry, resonance enhanced time-of-flight mass spectrometry.

***Konsentrering en derivatisering in silikoonrubbervalle vir  
massaspektrometriese en gaschromatografiese analise van lug-  
en waterbesoedelstowwe***

DEUR

**MARIA JOSÉ FERNANDES-WHALEY**

Voorgelê ter vervulling van 'n gedeelte van die vereiste vir die graad PhD, Chemie  
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**SAMEVATTING**

Estrogene, soos alkielfenole en bisfenol-A, beland in die omgewing deur afvalwatersisteme en die wegdoening van vervaardigde produkte soos wasmiddels, verf, polikarbonate en vlamvertragers. Hierdie analiete ontwig die endokrienfunksie van lewende organismes, en affekteer hul eie voortplantingsgesondheid sowel as dié van hul toekomstige geslagte. Gasfase laemolekulêremassa aldehiede en amiene is tipies oog-, neus- en keel-irritanse. Formaldehyd is geklassifiseer as 'n waaarskynlike menslike karsinogeen. In die lig van hul negatiewe impak op menslike gesondheid is dit dringend noodsaaklik om hierdie besoedelstowwe te moniteer by uiters lae konsentrasies in beide lug en water. Besoedelstowwe in water word dikwels gekonsentreer met soliedefase-ekstraksiepatrone gevolg deur derivatisering. Metodes wat aldehiede en amiene doeltreffend vooraf konsentreer, behels *in situ* derivatisering. Ongelukkig is die derivatiseringsreagense sowel as hul oplosmiddels of adsorbente verantwoordelik vir probleme met hierdie metodes.

Polidimetielsiloksaan (PDMS, silikoon) het ontluik as die ideale konsentrerings- en reaksiedium vir spooranalise. Die duur kommersiële toestelle soos SPME (soliedefase-mikroekstraksie) en SBSE (magnetieseroerder-ekstraksie) vereis egter dat die monsters na die laboratorium gestuur moet word vir konsentrering. As gevolg van die oopbuis geaardheid van die PDMS multikanaalval

(MKV) wat in ons laboratorium ontwikkel is, is dit ideaal geskik vir ter plaatse- en aanlynmonstering. Die MKV's het 'n groot kapasiteit vir analiese as gevolg van die groot volume PDMS beskikbaar vir konsentring. Die derivatiseringsreaksie kan binne-in die val uitgevoer word, wat 'n “eenpot konsentring- en reaksietoestel” tot gevolg het. Dit lei tot 'n verminderde risiko van kontaminasie en/of verlies van die monster, en 'n monsteringsmetode wat geskik is vir beide water- sowel as lugmonsters.

Om die veelsydigheid van die PDMS multikanaalval te demonstreer is twee prosedures ondersoek om stowwe in PDMS te konsentreer, naamlik: 1) aanlyn konsentring en *in situ* derivatisering van vlugtige polêre analiese uit lug, gevolg deur REMPI-TOFMS (resonansversterkte multifotonionisasie - vlugtydmassaspektrometrie) deteksie, en 2) die konsentring van fenoliese lipofiliese analiese uit water, met derivatisering voor analiese met GC-MS (gaschromatografie – massaspektrometrie).

- 1) Analiese en derivatiseringsreagens is tegelykertyd gevoer in 'n PDMS-val met 'n Y-koppelstuk. Die reaksie vind *in situ* plaas, gevolg deur termiese desorpsie met 'n termiese modulatoropstelling alleen, of saam met 'n termiese desorpsie-eenheid. Die aldehiede en amienderivate is suksesvol aangedui met 'n REMPI-TOFMS. Reaksiedoeltreffendhede is bepaal by kamertemperatuur sonder katalisator. Formaldehid het ondoeltreffend gereageer en gekonsentreer (41%) met fenielhidrasien in PDMS, terwyl asetaldehid, akroleien en krotonal baie beter waardes gegee het, nl. 92%, 61% en 74% respektiewelik. Beide propielamien en butielamien het 'n doeltreffendheid van 28% gehad met bensaldehid in die PDMS-matrys. Deteksielimiëte met hierdie tegniek was aansienlik laer as die toelaatbare blootstellingslimiëte van die Beroepsveiligheids- en Gesondheidsadministrasie.
- 2) Waterige analiese is in die PDMS gekonsentreer met 'n swaartekragvloeiempo van ongeveer 50  $\mu\text{l}/\text{min}$ . Die val is gedroog en 5  $\mu\text{l}$  derivatiseringsreagens is bygevoeg. By kamertemperatuur en sonder katalisator was die reaksie van alkielfenole met trifluorasynsuuranhidried in die PDMS-matriks 100% volledig na 5 minute. Bisfenol-A het minder as 50% volledig gereageer in hierdie tydperk, maar die hoeveelheid derivaat wat gevorm het, het konstant gebly. Ekstraksiedoeltreffendhede van alkielfenole en bisfenol-A het swak herhaalbaarheid getoon tussen besendings buise, wat aandui dat die PDMS-matriks nie homogeen was nie. Vir twee verskillende klompes PDMS het *ters*-oktielfenol 'n doeltreffendheid getoon van 70% en 79%, nonielfenol 84% en 43%, en bisfenol-A 10% en 26%. Die termiesgedesorbeerde derivate is geanaliseer met GC-MS. Ten spyte van agtergrondkontaminasie in die desorbeerder was deteksielimiëte by die dele-per-triljoenvlak. Regte veldmonsters is ook getoets.



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*Maria*





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## ABBREVIATIONS

AAA	-	acetic acid anhydride
ACGIH	-	American Conference of Governmental Industrial
BEA	-	benzylethanolamine
BPA	-	Bisphenol-A
BSA	-	n-o-bis(trimethylsilyl) acetamide
BSTFA	-	n-o-bis (trimethylsilyl) trifluoroacetamide
C	-	analyte concentration/ alkane carbon number
CIS	-	cooled injection system
CL	-	confidence level
C <sub>o</sub>	-	initial analyte concentration in sample
C <sub>PDMS</sub>	-	PDMS concentration
CW	-	carbowax
C <sub>w</sub>	-	water concentration
D <sub>c</sub>	-	analyte distribution ratio between 2 phases
D <sub>M</sub>	-	diffusion constant (m <sup>2</sup> .s <sup>-1</sup> ) of analyte in mobile phase
DNBS	-	dinitrobenzene sulphonic acid
DNFB	-	dinitrofluorobenzene
DNPH	-	dintirophenylhydrazine
DNSH	-	dansylhydrazine
d <sub>p</sub>	-	particle diameter
DVB	-	divinylbenzene
E1	-	estrone
E2	-	17β-estradiol
E3	-	estriol
ECD	-	electron capture detector
EDC	-	endocrine disrupting compound
EDU	-	Airsense® enrichment desorption unit
EE2	-	17α-ethinylestradiol
EI	-	electron impact ionization
ELISA	-	enzyme linked immunosorbent assay
EPA	-	U.S. Environmental Protection Agency
ESI	-	electrospray ionization
F	-	column flow rate
FIA	-	flow injection analysis
FID	-	flame ionization detector/ detection
GC	-	gas chromatography
GWRC	-	Global Water Research Coalition
H	-	plate height
HCHO	-	formaldehyde
HFB-	-	heptafluorobutyl
HFBA	-	heptafluorobutyric acid anhydride
HFBCl	-	heptafluorobutanoyl chloride
HMP	-	hydroxymethylpiperidine
HPLC	-	high performance liquid chromatography
h <sub>r</sub>	-	reduced plate height
HSSE	-	headspace sorptive extraction
ITD	-	ion trap detector
k	-	capacity factor



## Abbreviations

K	-	equilibrium distribution coefficient
$K_a$	-	acid in water dissociation constant
$K_{fg}$	-	SPME fibre/ gas distribution constant
$K_{fh}$	-	SPME fibre/ headspace distribution constant
$K_{fs}$	-	distribution coefficient between the SPME fibre and sample
$K_{o/w}$	-	octanol-water partitioning coefficient
L	-	column/ trap length
LASER	-	<b>L</b> ight <b>A</b> mplification by <b>S</b> timulated <b>E</b> mission of <b>R</b> adiation
LC	-	liquid chromatography
LLE	-	liquid-liquid extraction
LOD	-	limit of detection
LOQ	-	limit of quantitation
LPME	-	liquid phase microextraction
LTPRI	-	linear temperature programmed retention index
M	-	neutral molecule
$M^*$	-	high-energy molecule
$m_0$	-	total mass of analyte in the sample
MCT	-	multichannel trap
$m_{PDMS}$	-	analyte mass in PDMS
MPI	-	multiphoton ionization
MS	-	mass spectrometry
MSD	-	mass selective detector
MSTFA	-	n-methyl-n-(trimethylsilyl)-trifluoroacetamide
MTBSTFA	-	n-( <i>tert</i> -butyldimethylsilyl)-n-methyltrifluoroacetamide
N	-	theoretical number of plates
n	-	amount extracted
NCI	-	negative chemical ionization
Nd:YAG	-	neodymium-doped yttrium aluminium garnet
NIOSH	-	National Institute for Occupational Safety and Health
NP	-	4-nonylphenol
NPD	-	nitrogen phosphorous detector
NSD	-	nitrogen specific detector
OSHA	-	Occupational Safety and Health Administration
OTT	-	open tubular trap
$p_0$	-	column outlet pressure
PA	-	polyacrylate
PAH	-	polyaromatic hydrocarbon
PCB	-	polychlorinated biphenyl
PDMS	-	polydimethylsiloxane
PEL	-	permissible exposure limits
PFBA	-	pentafluorobenzaldehyde
PFBBr	-	pentafluorobenzylbromide
PFBCl	-	pentafluorobenzoyl chloride
PFBHA	-	pentafluorobenzylhydroxylamine
PFBOH	-	pentafluorobenzoic acid
PFP-	-	pentafluoropropionyl
PFPA	-	pentafluoropropionic acid anhydride
PFPH	-	pentafluorophenylhydrazine
PTV	-	programmed temperature vaporization
$p_i$	-	column inlet pressure
$p_m$	-	flow meter pressure





## Abbreviations

ppb	-	part-per-billion
PPBT	-	packed particle bed trap
ppm	-	part-per-million
ppt	-	part-per-trillion
$p_w$	-	saturated water vapour pressure
REMPI	-	resonance enhanced multiphoton ionization
RI	-	retention index
RIC	-	reconstructed ion chromatogram
SBSE	-	stir bar sorptive extraction
SEP	-	sample enrichment probe
SIBA	-	n-succinimidyl benzoate
SIM	-	selected ion monitoring
SPE	-	solid phase extraction
SPI	-	single photon ionization
SPME	-	solid phase microextraction
$T_c$	-	column temperature
$T$	-	absolute temperature
T	-	17 $\beta$ -testosterone
TCPH	-	trichlorophenylhydrazine
TCT - CP 4020	-	Chrompack® thermal desorption cryotrap unit
TDS	-	thermal desorption system
TDU-CIS	-	Gerstel® thermal desorption unit cooled injection system
TFA	-	trifluoroacetic/acetate
TFAA	-	trifluoroacetic acid anhydride
TIC	-	total ion chromatogram
$t_m$	-	unretained compound retention time
$T_m$	-	flow meter temperature
TMA	-	thermal modulator array
TMCS	-	trimethylchlorosilane
TMS	-	trimethylsilyl
TMSI	-	n-trimethylsilylimidazole
TOFMS	-	time-of-flight mass spectrometry
TOP	-	<i>tert</i> -octylphenol
$t_r$	-	analyte retention time
u	-	linear velocity ( $m.s^{-1}$ )
UV	-	ultraviolet
$V_0$	-	void volume
$V_b$	-	breakthrough volume
$V_f$	-	volume of the fibre
$V_L$	-	column stationary phase volume
VOC	-	volatile organic compound
$V_{PDMS}$	-	PDMS volume
$V_r$	-	retention volume
$V_s$	-	sample volume
VUV	-	vacuum ultraviolet
$V_w$	-	water volume
WHO	-	World health organization
$\beta$	-	phase ratio
v	-	reduced velocity in the trap (packed column)
$\omega$	-	base width of analyte peak

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- 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. 199
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- 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.* 200
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