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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

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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 μl/min. The trap was dried and 5 μl 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: t*ert*-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

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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 ontwrig 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. Formaldehied 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 reaksiemedium 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 analiete as gevolg van die groot volume PDMS beskikbaar vir konsentrering. Die derivatiseringsreaksie kan binne-in die val uitgevoer word, wat 'n "eenpot konsentrerings- en reaksietoestel" tot gevolg het. Dit lei tot 'n verminderde risiko van kontaminasie en/of verliese 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 konsentrering en *in situ* derivatisering van vlugtige polêre analiete uit lug, gevolg deur REMPI-TOFMS (resonansversterkte multifotonionisasie - vlugtydmassaspektrometrie) deteksie, en 2) die konsentrering van fenoliese lipofiliese analiete uit water, met derivatisering voor analise met GC-MS (gaschromatografie – massaspektrometrie).

1) Analiet 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 katalisatore. Formaldehied het ondoeltreffend gereageer en gekonsentreer (41%) met fenielhidrasien in PDMS, terwyl asetaldehied, akroleïen en krotonal baie beter waardes gegee het, nl. 92%, 61% en 74% respektiewelik. Beide propielamien en butielamien het 'n doeltreffendheid van 28% gehad met bensaldehied in die PDMS-matrys. Deteksielimiete met hierdie tegniek was aansienlik laer as die toelaatbare blootstellingslimiete van die Beroepsveiligheids- en Gesondheidsadministrasie.

2) Waterige analiete is in die PDMS gekonsentreer met 'n swaartekragvloeitempo van ongeveer 50 µl/min. Die val is gedroog en 5 µl derivatiseringsreagens is bygevoeg. By kamertemperatuur en sonder katalis was die reaksie van alkielfenole met trifluoorasynsuuranhidried 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. Ekstraksie-doeltreffendhede 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 klompe 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 deteksielimiete by die dele-per-triljoenvlak. Regte veldmonsters is ook getoets.

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My babies, Matthew and Kiara for the smiles at the end of the day,

My Lord and Saviour, Jesus Christ,

Thank you
Maria

CONTENTS

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_o	-	initial analyte concentration in sample
C_{PDMS}	-	PDMS concentration
CW	-	carbowax
C_w	-	water concentration
D_c	-	analyte distribution ratio between 2 phases
D_M	-	diffusion constant $(m^2.s^{-1})$ of analyte in mobile phase
DNBS	-	dinitrobenzene sulphonic acid
DNFB	-	dinitrofluorobenzene
DNPH	-	dintirophenylhydrazine
DNSH	-	dansylhydrazine
d_p	-	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 chromatgraphy
GWRC	-	Global Water Research Coalition
H	-	plate height
HCHO	-	formaldehyde
HFB-	-	heptafluorobutyrl
HFBA	-	heptafluorobutyric acid anhydride
HFBCl	-	heptafluorobutanoyl chloride
HMP	-	hydroxymethylpiperidine
HPLC	-	high performance liquid chromatography
h_r	-	reduced plate height
HSSE	-	headspace sorptive extraction
ITD	-	ion trap detector
k	-	capacity factor

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	**-**	**L**ight **A**mplification by **S**timulated **E**mission of **R**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-(*tert*-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	-	pentaflurobenzoyl chloride
PFBHA	-	pentafluorobenzylhydroxylamine
PFBOH	-	pentaflurobenzoic acid
PFP-	-	pentafluoropropionyl
PFPAA	-	pentafluoropropionic acid anhydride
PFPH	-	pentafluorophenylhydrazine
PTV	-	programmed temperature vaporization
p_i	-	column inlet pressure
p_m	-	flow meter pressure

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
Tc	-	column temperature
T	-	absolute temperature
T	-	17β -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	-	*tert*-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
β	-	phase ratio
ν	-	reduced velocity in the trap (packed column)
ω	-	base width of analyte peak

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   1. B: High purity helium carrier gas flow during injection phase

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   3. Wide bore fused silica capillary cold trap

   4. Heated desorption oven

   5. Liquid nitrogen – cooled chamber

   6. Ambient desorption oven

   7. Ballistically heated cold trap

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