Concentration and derivatisation in silicone rubber traps for gas chromatographic trace analysis of aldehydes

BY

MARIA JOSÉ FERNANDES

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South Africa

SUMMARY

Low molecular mass aldehydes, such as formaldehyde (HCHO) and acrolein, are introduced into the environment through incomplete fuel combustion and tobacco smoke. Indoors, formaldehyde is emitted mainly by Urea Formaldehyde (UF)-resin treated furniture. These aldehydes have long been suspected carcinogens and for this reason several methods exist to monitor them. The methods that can most effectively and selectively pre-concentrate aldehydes involve in-situ derivatisation. Unfortunately, the derivatising agents as well as their associated solvents or adsorbents, are responsible for problems encountered with these methods. A

recently developed method using Solid Phase MicroExtraction (SPME), introduced polydimethylsiloxane as the absorbent for the derivatising agent, with promising results. However, this method is not ideal for field sampling.

In our study, the use of the silicone rubber trap, developed in our laboratory, as a pre-concentrating device for volatile aldehydes in the air, was investigated. The silicone rubber is saturated with the dynamic headspace of O-(2,3,4,5,6-PentaFluoroBenzyl) Hydroxyl Amine (PFBHA). Carbonyl compounds are pre-concentrated, by reaction with the sorbed PFBHA, to form the stable oxime-derivative. The oxime-derivatives are then thermally desorbed, cryogenically focussed and analysed using Gas Chromatography-Mass Spectrometry and Gas Chromatography-Flame Ionisation Detection.

The reaction efficiency of HCHO with PFBHA was experimentally determined to be between 75% to 95%. Breakthrough of the HCHO-Oxime did not occur even after a collection volume of 3 litres. Our detection limit for HCHO is restricted by the HCHO-oxime impurity in the PFBHA blank. The minimum detected HCHO concentration was 0.1ppm. Lower detection limits for acetaldehyde, acrolein and crotonal were obtained as they are absent in the PFBHA blank. They were 0.035ppm, 0.057ppm and 0.064ppm respectively for a collection volume of 10ml, and s/n of 3. The trap was also tested on real gaseous indoor and outdoor air samples and headspace analysis of beer.

Derivatisation on a silicone rubber trap is a promising technique. The simpler method for coating the trap with PFBHA reduces sample preparation time. The silicone rubber is inert, and after thermal desorption is immediately reusable. Analysis of the traps can easily be automated, and the sampling set-up is inexpensive, convenient and portable for fieldwork.

Konsentrering en derivatisering in silikoonrubber-opvangers vir gaschromatografiese spooranalise van aldehiede

DEUR

MARIA JOSÉ FERNANDES

Promotor

Prof Dr E R Rohwer

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in die Fakulteit Natuur- & Landbouwetenskappe

Universiteit van Pretoria

Pretoria

Suid-Afrika

SAMEVATTING

Lae-molekulêremassa aldehiede, soos formaldehied (HCHO) en akroleïen, word vrygestel in die omgewing deur onvolledige verbrandingsprosesse en deur tabak-rook. Binnemuurs, word formaldehied hoofsaaklik vrygestel deur Ureum-Formaldehied (UF) - hars behandelde meubels. Hierdie aldehiede is lankal verdagte karsinogene, daarom bestaan daar 'n verskeidenheid metodes om hulle te moniteer. Die beste metodes wat aldehiede effektief en selektief prekonsentreer maak gebruik van *in-situ* derivatisering. Probleme word egter ondervind met die derivatiseringsmiddels asook hul geassosieerde oplosmiddels en adsorbeerders. 'n

Nuwe, baie belowende metode wat SoliedeFaseMikroEkstraksie (SFME) gebruik, stel polidimetielsiloksaan bekend as die absorbeerder vir die derivatiseringsreagens. Ongelukkig is hierdie metode minder geskik vir monsterneming buite die laboratorium.

In ons studie word die gebruik van silikoonrubber-opvangers, wat in ons laboratorium ontwikkel is, vir die prekonsentrasie van vlugtige aldehiede in lug ondersoek. Die silikoonrubber word versadig met die dinamiese dampruim van O-(2,3,4,5,6-PentaFluoroBenziel)HydroksielAmien (PFBHA). Karbonielverbindings word gekonsentreer, deur reaksie met die geabsorbeerde PFBHA, om stabiele oksiem-derivate te vorm. Die oksiem-derivate word daarna termies gedesorbeer, gefokus deur afkoeling en geanaliseer deur middel van gaschromatografie en gaschromatografie-massaspektrometrie.

Eksperimenteel is vasgestel dat die reaksie van HCHO met PFBHA tussen 75% en 95% volledig verloop. Geen deurbraak van die HCHO-oksiem het na 'n versamelvolume van 3 liter plaasgevind nie. Die deteksielimiet vir HCHO was beperk deur die HCHO-oksiem onsuiwerheid in die PFBHA. Die minimum waarneembare HCHO-konsentrasie was 0.1dpm. Laer deteksielimiete is moontlik vir asetaldehied, akroleïen en krotonaldehied omdat hul reaksieprodukte nie teenwoordig was in die PFBHA reagens nie. Hul deteksielimiete was 0.035dpm, 0.057dpm en 0.064dpm onderskeidelik vir 'n versamelvolume van 10ml (s/n 3). Die opvanger is ook getoets met werklike binne- en buitemuur lugmonsters en bier-dampruim.

Derivatisering in silikoonrubber-opvangers is 'n belowende tegniek. 'n Makliker metode om die opvanger met PFBHA te bedek verminder die hoeveelheid monstervoorbereidingstyd. Die silikoonrubber is inert en na termiese desorpsie is dit dadelik herbruikbaar. Analiese van die opvangers kan maklik geoutomatiseer word

en die monsternemingstelsel is goedkoop, gerieflik en draagbaar vir monsterneming buite die laboratorium.

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CONTENTS

ABBREVIATIONS

ACGIH	=	American Conference of Governmental Industrial Hygenists
%RSD	=	Percentage Relative Standard Deviation
amu	=	atomic mass units
BEA	=	N-(BenzylEthanol) Amine
CH_3CHO	=	Acetaldehyde
DNPH	=	2,4-DiNitroPhenylHydrazine
DNSH	=	Dansylhydrazine
DVB	=	DiVinylBenzene
ECD	=	Electron Capture Detector
EI	=	Electron Impact
EPA	=	Environmental Protection Agency
FID	=	Flame Ionisation Detector
GC	=	Gas Chromatography
HCHO	=	Formaldehyde
HID	=	Helium Ionisation Detector
HMP	=	2-HydroxyMethylPiperidine
HPLC	=	High Performance Liquid Chromatography
HSSE	=	Headspace Sorptive Extraction
ITD	=	Ion Trap Detector
k	=	capacity factor
K	=	distribution coefficient
LC-MS	=	Liquid Chromatography - Mass Spectrometry
LLE	=	Liquid-Liquid Extraction
MCT	=	MultiChannel Trap
MS	=	Mass Spectrometry

N	=	number of plates
NIOSH	=	National Institute for Occupational Safety and Health
NIST	=	National Institute for Standards and Technology
NPD	=	Nitrogen-Phosphorus Detector
OSHA	=	Occupational Safety and Health Administration
OTT	=	Open Tubular Traps
PDMS	=	PolyDiMethylSiloxane
PEL	=	Permissible Exposure Limit
PFBHA	=	O-(2,3,4,5,6-PentaFluoroBenzyl) Hydroxyl Amine
PFPH	=	O-(2,3,4,5,6-PentaFluoroPhenyl) Hydrazine
PLOT	=	Packed Layer Open Tubular
ppb	=	part-per-billion
ppm	=	part-per-million
PTFE	=	PolyTetraFluoroEthylene
SIM	=	Selected Ion Monitoring
SPE	=	Solid Phase Extraction
SPME	=	Solid Phase MicroExtraction
STEL	=	Short Term Exposure Limit
s / n	=	Signal - to - noise ratio
TCD	=	Thermal Conductivity Detector
TCPH	=	2,4,6-TriChloroPhenylHydrazine
TCT	=	Thermal Desorbtion - Cryogenic Trapping unit
TIC	=	Total Ion Chromatogram
TSD	=	Thermionic Specific Detection
TWA	=	Time Weighted Average
UF	=	Urea - formaldehyde
UV	=	Ultra-Violet

VOC	=	Volatile Organic Compound
V_b	=	breakthrough volume
WCOT	=	Wall-Coated Open Tubular
WHO	=	World Health Organisation

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