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CHARACTERISATION OF ENVIRONMENTAL POLLUTION BY GC-MS ANALYSIS OF POLYCYCLIC AROMATIC COMPOUNDS IN WATER AND SOIL

By

Willem Jacobus Havenga

Submitted in partial fulfilment of the requirements for the degree

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SUMMARY

Polycyclic aromatic hydrocarbons (PAHs) have long been known to pose health risks in humans and have become one of the major environmental issues. Coal tar products, refined petroleum products and lubricating oils are among the anthropogenic sources, which contain highly toxic substances of which benzo[a]pyrene and dibenz[a,h]anthracene are the most potent carcinogens. Sensitive and reliable chemical analyses of contaminated soil and water are imperative for health risk assessments and chemical fingerprinting. The development of techniques that can determine the pollution source is motivated in part by the cleanup costs, legal fees, and fines incurred by the polluter.

In this thesis, direct solid-phase microextraction (DISPME), followed by capillary gas chromatography (GC) and mass spectrometry (MS) in the selected ion storage (SIS) mode was investigated for the determination and characterisation of PAHs in aqueous samples. The SPME method of extraction is also compared to a traditional liquid-liquid extraction method that was based on USEPA method 8270. It was found that several factors affected the extraction efficiency with a single stage SPME extraction, such as the degree of alkylation, fiber condition, absorption time, sample pH, sample matrix, sample temperature, agitation method, etc. The technique of multiple extractions (MESPME) was investigated and found to compensate for variations in analytical conditions or sample matrix. The suitability of the method for health risk assessments was investigated. The results were acceptable for this purpose because the limits of detection were estimated at the pg/cm^3 levels that were considerably lower than the health risk based guideline concentrations (10^{-6} cancer risk) for drinking water specified by the United States Environmental Protection Agency (USEPA). The guideline concentration for dibenz[a,h]anthracene (the most potent carcinogen) is for example 0.0092 ng/cm^3 compared to a detection limit of 0.0045 ng/cm^3 achieved with the SPME-GC/MS method. Detection limits for the other carcinogenic PAHs were also found to be lower than the USEPA guideline concentrations. The method was also developed to include the quantification of alkyl-PAHs, which is important for interpretative methods such as chemical fingerprinting (source identification). For this purpose detection limits of at least 0.01 ng/cm^3 are required for individual PAHs. The SPME extraction method used in conjunction with GC/MS was found to be sensitive enough for this purpose with detection limits lower than 0.01 ng/cm^3 for all the PAHs. The method was in many respects superior to traditional extraction methods.

A headspace SPME (HSSPME) method, followed by GC/MS, was developed for the screening of soil samples. Vapor pressures of target analytes were determined using a capillary GC method to identify environmentally important components with a sufficiently high vapor pressure to be analyzed in the headspace mode. The method was optimized under non-equilibrium conditions with simplicity and automation in mind and does not require any extraction procedure or sample preparation, other than grinding, drying and homogenizing. The analytical performance and the significance of the results for the purpose of chemical characterisation, source discrimination, determination of individual isomer distributions and the calculation of source and weathering ratios, are discussed. The SPME method of extraction was also compared to the relatively new extraction technique known as Pressurised Liquid Extraction (PLE). HSSPME was found to be a very efficient and sensitive technique for the confirmation of PAHs of up to four-ring structures and suitable for a tiered and adaptive approach.

The selective extraction and analysis techniques that have been developed in this thesis were finally used to develop diagnostic ratios, which can be used to trace contamination in the environment to its source. The successful use of the analytical data to match the chemical patterns of target analytes with potential sources was shown.

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KARAKTERISERING VAN OMGEWINGSBESOEDELING IN GROND EN WATERMONSTERS DEUR GC/MS EN DIE ANALISE VAN POLISIKLIESE AROMATIESE VERBINDINGS

DEUR

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SAMEVATTING

Die gesondheidsrisiko wat polisikliese aromatiese koolwaterstowwe (PAHs) vir mense inhou is lankal reeds bekend en het in een van die mees belangrikste omgewingskwessies ontwikkel. Besoedelstowwe soos koolteer, petroleum produkte en smeermiddels bevat heelwat giftige en karsinogene verbindings waarvan benso[a]pireen en dibenso[a,h]antraseen die giftigste is. 'n Sensitiewe en betroubare chemiese analise van grond- en watermonsters word vir die ondersoek na PAH en ge-alkileerde PAH besoedeling, gesondheids gebaseerde risikobepalings en chemiese karakterisering benodig. Kostes verbonde aan opruiming, regskoste en boetes is deels die motivering vir die ontwikkeling van metodes wat besoedelingsbronne kan identifiseer.

Die toepassing van direkte vastestof mikroekstraksie (solid-phase microextraction - DISPME), gevolg deur kapillêre gaschromatografie (GC) en massaspekrtometrie (MS) in die geselekteerde ioon (selected ion storage - SIS) mode is vir die bepaling en karakterisering van PAHs in watermonsters ondersoek. Die SPME ekstraksiemetode is ook met die tradisonele vloeistof-vloeistof ekstraksiemetode, gebasseer op die USEPA metode 8270, vergelyk. Daar is gevind dat die effektiwiteit van 'n enkelstap SPME-ekstraksie deur verskeie faktore beinvloed word, soos byvoorbeeld die graad van alkilering, die SPME vesel se toestand, absorpsietyd, monster pH, monstermatrys, monster temperatuur, ens. Die tegniek van veelvuldige ekstrasies (MESPME) is suksesvol ondersoek om vir die variasies in analitiese kondisies en monstermatrys te kompenseer. Deteksielimiete vir individuele PAHs was in die pg/cm^3 gebied wat aansienlik laer is as die riglynkonsentrasie (10^{-6} kanker risiko), soos deur die USEPA (United States Environmental Protection Agency) voorgekryf. Die riglynkonsentrasie vir benso[a]pireen is voorbeeld 0.0092 ng/cm^3 in vergelyking met 'n deteksielimiet van 0.0045 ng/cm^3 wat met die SPME-GC/MS metode verkry is. Deteksie limiete vir die ander karsinogene PAHs was ook almal laer as die USEPA riglynkonsentrasies. Die metode is ook vir die kwantitatiewe bepaling alkiel-PAHs aangepas. Hierdie analietkomponente is belangrik vir interpreteringsmetodes, soos gevorderde chemiese karakterisering (bronallokering). Vir hierdie doel word 'n deteksielimiet van 0.01 ng/cm^3 vir al die PAHs vereis. Die SPME ekstraksiemetode, gevolg deur GC/MS, het aan hierdie vereistes voldoen en deteksiemiete van laer as 0.01 ng/cm^3 is vir al die PAHs verkry. Die metode was in baie opsigte beter as die tradisionele metodes is.

'n Dampruim SPME (HSSPME) metode, gevolg deur GC/MS, is vir die siftingsprosedure van PAHs in grondmonsters ontwikkel. Die dampdrukke van analietkomponente is met 'n kapillêre GC metode bepaal om vas te stel watter komponente in die dampruim geanaliseer kan word. Die metode is onder nie-ewewigskondisies geoptimiseer met eenvoud en outomatisasie in gedagte, terwyl geen spesiale monstervoorbereiding anders as droog, maal en homogenisering vereis word nie. Die betroubaarheid van die metode en die geskiktheid van die resultate vir chemiese karakterisering, bronallokering, bepaling van isomeer verspreidingspatrone en die bepaling van bron- en verouderingsverhoudings is ondersoek. Die metode is ook met die relatief nuwe ekstraksie metode, naamlik "Pressurised Liquid Extraction (PLE)" vergelyk. Daar is gevind dat HSSPME 'n baie effektiewe en sensitiewe metode vir die bepaling van PAHs tot en met vier-ring-strukture is.

Die selektiewe ekstraksie- en analisemetodes wat in hierdie studie onwikkel is, is uiteindelik vir die ontwikkeling van diagnostiese verhoudings tussen twee analiete gebruik. Hierdie verhoudings kan gebruik word om plaaslike besoedeling aan 'n besoedelingsbron te koppel. Daar is ook aangetoon dat die analitiese data suksesvol gebruik kan word om die chemiese patrone van analietkomponente in omgewingsmonsters aan potensiële bronne te koppel.

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Thank You
Willie

GLOSSARY AND ABBREVIATIONS

ACF	- Advanced chemical fingerprinting
Alkyl-PAHs	- Alkyl substituted polycyclic aromatic hydrocarbons
Anthropogenic	- Pollution caused by humans
ASE	- Accelerated solvent extraction
ATSDR	- Agency for Toxic Substances and Disease Registry
Carcinogenicity	- Ability of a substance to cause cancer.
Coal tar	- Heterogeneous mixture of various classes of compounds
CRM	- Certified reference material
DCM	- Dichloromethane
DISPME	- Direct solid phase microextraction
DL	- Detection limit
DNAPL	- Dense non-aqueous phase liquid
DQO	- Data quality objectives
Fugacity	- Relative escaping tendency
GC	- gas chromatography
HSSPME	- Headspace Solid Phase Microextraction
HPLC	- High performance liquid chromatography
K_{oc}	- Sorption coefficient on soil/sediment
K_{ow}	- Octanol-water partition coefficient
LNAPLS	- Light Non Aqueous Phase Liquids
m/z	- Mass over charge
MCL	- Maximum contaminant level
MDL	- Method detection limit
MESPME	- Multiple extraction solid phase microextraction
MQL	- Method quantification limit
MS	- mass spectrometry
NAPL	- Non-aqueous phase liquid
ng	- Nanogram
PAH	- Polycyclic aromatic hydrocarbons
PDMS	- Poly dimethylsiloxane
pg	- Picogram
PLE	- Pressurised liquid extraction
P^{o}_{L}	- Vapor pressure
psi	- Pounds per square inch
QA	- Quality assurance
QC	- Quality control
QL	- Quantification limit
R^2	- Regression coefficient
RI	- Temperature programmed retention index
RRF	- Relative response factor
RSD	- Relative standard deviation
S/N	- Signal to noise ratio

Sediment - Mud and debris
SIM - Single ion monitoring
SIS - Selected ion storage
SPME - Solid Phase Microextraction
SRS - Standard reference soil
STD - Standard
S_w - Water solubility
t_R - Retention time
USEPA - Unites States Environmental Protection Agency
Weathering - Dissolvation, evaporation, bio-degradation, photo oxidation

CHEMICAL COMPOUNDS

A - Anthracene
AC - Acenaphthene
AE - Acenaphthylene
BA - Benzo[a]anthracene
BB - Benzo[b]fluoranthane
BI - Biphenyl
BP - Benzo[ghi]perylene
BAP - Benzo[a]pyrene
BTEX - Benzene, toluene, ethyl benzene and xylenes
C1- Methyl group
C2- Methyl-methyl or ethyl group
C3- Trimethyl, methylethyl or propyl group
C4- Tetramethyl, ethylethyl, methylpropyl or butyl group
C - Chrysene
C1-C - C_1-Chrysene
C1-D - C_1-Dibenzothiophene
C1-F - C_1-Fluorenes
C1-N - C_1- Naphthalenes
C1-P - C1-Phenanthrene/anthracenes
C2-C - C_2-Chrysene
C2-D - C_2-Dibenzothiophene
C2-F - C_2-Fluorenes
C2-N - C_2- Naphthalenes
C2-P - C_2-Phenanthrene/anthracenes
C3-C - C_3-Chrysene
C3-D - C_3-Dibenzothiophene
C3-F - C_3-Fluorenes
C3-N - C_3- Naphthalenes
C3-P - C_3-Phenanthrene/anthracenes
C4-N - C_4- naphthalenes
C4-P - C_4-Phenanthrene/anthracenes
D - Dibenzothiophene
DA - Dibenz[ah]anthracene
DI - Dibenzofuran

F - Fluorene
FL - Fluoranthene
IP - Indeno[123-cd]pyrene
N - Naphthalene
P - Phenanthrene
PY - Pyrene

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