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Development of a laser induced fluorescence technique for the analysis of organic air pollutants

by

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I declare that the thesis that I hereby submit for the degree PhD Chemistry at the University of Pretoria is my own work and has not previously been submitted by me for degree purposes at any other university or institution.

Date

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants which are of concern due to their potential human toxicity. They are formed during numerous combustion processes, including biomass burning and diesel vehicular emissions, which are of relevance in developing countries.

A novel analytical screening method for atmospheric polycyclic aromatic hydrocarbons (PAHs) was developed in this study based on laser induced fluorescence (LIF) of samples on quartz multi-channel polydimethylsiloxane (PDMS) traps. A tunable dye laser with a frequency doubling crystal provided the excitation radiation, and a double monochromator with a photomultiplier tube detected emitted fluorescence. The method allowed for the rapid (<5 min), cost effective analysis of samples. Those yielding interesting results could be further analysed by direct thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS, with limits of detection of $\sim 0.3 \text{ ng.m}^{-3}$), as photodegradation was minimal (<10 % over 5 min irradiation). Without any signal optimization, a LIF detection limit of $\sim 1 \text{ }\mu\text{g.m}^{-3}$ was established for naphthalene using a diffusion tube (diffusion rate of 2 ng.s^{-1}) and 292 nm excitation. Gas standards which facilitated the uniform distribution of analyte across each of the 22 PDMS tubes were provided by easily constructed diffusion tubes for naphthalene and by a gas chromatographic fraction collection method for the less volatile target PAHs.

The methods developed were successfully tested in a number of applications which are of relevance to southern Africa, as emissions from sugar cane burning, household fires, diesel vehicles and industries were monitored. The LIF method allowed for the differentiation between impacted and non-impacted industrial sites, and the importance of naphthalene as an indicator for atmospheric PAHs was verified in that this PAH was the most abundant in the various applications which were investigated. The multi-channel silicone rubber traps were also evaluated theoretically and practically in the denuder configuration, in order to monitor PAHs in both the gas and particle phases, which is important in terms of human health effects.

The novel LIF method developed in this study has the potential to serve as a screening tool to avoid the comprehensive and costly analysis of samples which do not contain appreciable levels of PAHs. The experimental procedure is simple and rapid, with acceptably low limits of detection, even with the initial, unoptimized optical arrangement and without extensive time-averaging. LIF also provides selectivity without the need for sample clean-up and separation processes.

The LIF method could be further optimized by improving the laser energy stability, as well as by the investigation of possible time resolution techniques. As equipment cost considerations were important, it is possible that the LIF screening method could find application in a centralized environmental laboratory for the southern African region. This would facilitate the widespread monitoring of atmospheric PAHs in a cost effective manner.

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Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
APINA	Air Pollution Information Network for Africa
AQA	Air Quality Act
ATSDR	Agency for Toxic Substances and Disease Registry
BBO	Beta Barium Borate
BVOC	Biogenic Volatile Organic Compound
CI	Chemical Ionization
CIS	Cooled Injection System
DCM	Dichloromethane
EI	Electron Ionization
EIA	Environmental Impact Assessment
EPA	Environmental Protection Agency
FAGE	Fluorescent Assay by Gas Expansion
FIA	Fluoranthene
FID	Flame Ionization Detector
GAW	Global Atmospheric Watch
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
IDLH	Immediately Dangerous to Life and Health
INEC	Infrastructure and Economic Cooperation
LIF	Laser Induced Fluorescence
LOD	Limit of Detection
LOQ	Limit of Quantitation
MS	Mass Spectrometry
MSD	Mass Selective Detector
Naph	Naphthalene
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
OECD	Organization for Economic Cooperation and Development
OPPO	Optically Pumped Parametric Oscillator
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyls
PCN	Polychlorinated aromatic hydrocarbons
PDMS	Polydimethylsiloxane
PhA	Phenanthrene
PM ₁₀	Particulate Matter of size ≤ 10 micron
PM _{2.5}	Particulate Matter of size ≤ 2.5 micron
PMT	Photomultiplier Tube

Py	Pyrene
POP	Persistent Organic Pollutant
PTFE	Polytetrafluoroethylene
PUF	Polyurethane Foam
RAPIDC	Regional Air Pollution in Developing Countries
RMS	Root Mean Square
SAFARI-92	Southern Africa Fire-Atmosphere Research Initiative of 1992
SAFARI 2000	Southern African Regional Science Initiative of 2000
SEANAC	Southern and Eastern Africa Network of Analytical Chemists
SEP	Sample Enrichment Probe
SIC	Single Ion Current
SIDA	Swedish International Development Cooperation Agency
SPME	Solid Phase Microextraction
STP	Standard Temperature and Pressure
SVOC	Semi-volatile Organic Compound
TD	Thermal Desorption
TDS	Thermal Desorption System
TIC	Total Ion Current
TSP	Total Suspended Particulates
UK	United Kingdom
USA	United States of America
UV	Ultraviolet
VOC	Volatile Organic Compound
WMO	World Meteorological Organization

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