

Development and application of a direct thermal desorption gas chromatography-TOFMS method for analysis on PAH in urban particulate matter PM_{2.5}: Results from 2 years daily measurements

Jürgen Schnelle-Kreis, Martin Sklorz, Yongbo Liu, Jürgen Orasche, Ralf Zimmermann¹

¹Institute For Ecological Chemistry

INTRODUCTION:

Epidemiological studies have investigated the influence of the particles (mass or number) on health effects. Aim of this study is to investigate the association of particle associated polycyclic aromatic hydrocarbons (PAH) and oxidised PAH (PAH ketones and quinones, O-PAH) with health effects. Therefore an analytical procedure was developed and validated that allows sampling and analysis of particle associated PAH and O-PAH in PM_{2.5} on a daily basis ([1, 2]).

METHODS:

A simple but reliable DTD-GC-TOFMS method for daily monitoring of a large number of PAH and oxygenated PAH in ambient particulate matter (PM_{2.5}) was developed. Particulate matter was sampled with a PM_{2.5} sequential sampler on quartz fibre filters at a flow of 1 m³h⁻¹. The sampling period for each sample is 24 h. The sampling period started in summer 2002. Data of the first two years are reported here. Besides other SVOC the samples are analyzed for PAH and O-PAH by DTD-GC-TOFMS. For analysis filters are cut into pieces, each representing 1 m³ of sampled air. Filter aliquots are placed into the GC-liners, isotope labelled reference compounds are added for quantification and liners are closed with crimp caps. The liners are put into the cold injector by an autosampler. For desorption the temperature is raised to 320°C and kept for 10 Minutes. During desorption the analytes are focused on a retention gap at 50°C oven temperature. In most cases a filter aliquot representing 1 m³ of sampled air is sufficient for a single analysis run. Repeated analysis of 60 µg NIST SRM1649a (urban dust) showed good repeatability (relative standard deviation < 20%). The compound dependent LOQ are in the range of 10 to 100 pg m⁻³.

RESULTS:

12 PAH and 8 O-PAH are analyzed in the PM_{2.5} samples on a daily base resulting in a total number of 694 samples. Comparative analysis of DTD-GC-TOFMS and conventional liquid extraction, silica clean up followed by GC-HRMS analysis showed good reproducibility of the DTD Method. The average (and maximum) concentration of the particle associated PAH and O-PAH were in n gm⁻³: phenanthrene 0.47 (10.8), anthracene 0.08 (1.2), pyrene 0.98 (12.8), fluoranthene 0.95 (13.4), benz[a]anthracene 0.54 (8.52), crysene (and triphenylene) 1.43 (16.9), sum of benzofluoranthenes 1.99 (15.0), benzo[e]pyrene 0.55 (4.1), benzo[a]pyrene 0.69 (7.31), perylene 0.08 (0.82), indeno[1,2,3-cd]pyrene 0.28 (3.39), benzo[ghi]perylene 0.41 (5.5), 9H-fluoren-9-on 1.0 (26.0), 1H-phenalen-1-one 0.9 (18.5), anthracene-9,10-dione 0.8 (6.1), cyclopenta(def)phenanthrenone 0.5 (9.5), 11H-benzo[a]fluoren-11-one 0.4 (4.4), 11H-benzo[b]fluoren-11-one 0.4 (5.4), 7H-benz[de]anthracen-7-one 0.9 (14.9) and benz[a]anthracene-7,12-dione 0.1 (0.8). A high seasonality of the concentrations with maxima in the heating period was observed. The sources of PAH and O-PAH on airborne PM are discussed. Furthermore atmospheric influences are considered (ozone).

ACKNOWLEDGEMENTS:

This work was supported by the Bavarian State Ministry for Environment, Health and Customer Protection. The work was carried out in cooperation with the GSF-Focus-Network "Aerosols and Health" which coordinates aerosol-related research within the GSF Research Centre.

REFERENCES:

- 1.W. Welthagen, J. Schnelle-Kreis, and R. Zimmermann, *Journal of Chromatography A*, **2003**, 1019, 233-249.
- 2.J. Schnelle-Kreis, M. Sklorz, A. Peters, J. Cyrus, and R. Zimmermann, *Atmos. Environ.*, **2005**, in press.