Determination of 19 PAHs in air samples using gas chromatography - mass spectrometry

D.A. Sarigiannis[1,2], S. Nikolaki[1], D. Zikopoulos[1], M. Kermenidou[1]

[1]*Aristotle University of Thesaloniki, Department of Chemical Engineering, Environmental Engineering Laboratory, University Campus, Thessaloniki 54124, Greece*

[2]*Centre for Research and Technology Hellas (CE.R.T.H.), Thessaloniki, 57001, Greece*

Polycyclic Aromatic Hydrocarbons (PAHs) include a variety of semi-volatile organic compounds of low vapor pressure that can be transferred in long distances as they are mostly absorbed in fine and ultrafine particles. Such compounds may be long retained by human tissues due to their high lipophilicity. While about 90% of PAHs are emitted by vehicles, other sources include industry, biomass combustion, coke and tar production, as well as tobacco smoke. The most hazardous PAHs are mainly distributed in the particulate phase, including the benzo[a]pyrene (B[a]P) which is the only PAH classified as known carcinogen to humans by IARC.

The aim of our study was to develop an efficient and selective method for the determination and quantification of 19 PAH compounds in the atmospheric PM. This method was applied to PM collected in the area of Thessaloniki between January and April of 2013. Two sampling sites were used in the urban area of Thessaloniki: an urban background site and a traffic site. For the collection of aerosols, low volume samplers were used (TCR-Tecora). $PM_{1.0}$, $PM_{2.5}$ and PM_{10} samples were collected on PTFE filters (Pall Corporation, 47 mm diameter) for 24h.

All the collected filters were treated in accordance to the following method: each filter was cut in-half and spiked with known amount of surrogate standards (fluorene-d10 and pyrene-d10). This spiked filter part was extracted with dichloromethane in an ultrasonic bath for 20 min. The extract was filtered through a PTFE filter and purified using a chromatography column, containing florisil, alumina and Na_2SO_4. Hexane and a known amount of deuterated internal standard compounds (acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12) were added before the sample was concentrated to 0.5 ml. Analysis of the concentrated sample was performed by an Agilent gas chromatographer coupled with an inert MSD mass spectrometer. PAHs identification was accomplished using PAHs standards solutions. The calibration curves were estimated using the internal standard calibration method. For the quality assurance and control, laboratory blanks and field blanks were extracted and analyzed in the same way as the samples.

The analysed PAHs included naphthalene, 2-methylnaphthylene, acenaphthylene, acenaphthene, fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Per), indeno[1,2,3-cd]pyrene (Ind), dibenzo[a,h]anthracene (DbA) and benzo[g,h,i]perylene (BgP). It is noted that all calibration curves showed good linearity (over 0.995). The method detection limit (for a volume of air of 55 m^3) ranged from 0.008 to 0.27 ng/m^3, depending on the specific PAH compound considered. Validation of the analytical procedure was carried out by analyzing a standard reference material of urban particulate matter (NIST, SRM 1649b). This analysis was in good agreement to the certified values (i.e. PAH recoveries above 80%).

Concentrations in samples from the two monitoring stations showed variations both in PM fractions and PAH compounds. In the urban background monitoring station area, benzo[a]pyrene (B[a]P) concentration for PM_1, $PM_{2.5}$ and PM_{10} varied from 0.031 to 14.98 ng/m^3, 0.068 to 18.24 ng/m^3 and 0.075 to 19.68 ng/m^3, respectively. In the traffic monitoring station area B[a]P concentration for PM_1, $PM_{2.5}$ and PM_{10} varied from 0.046 to 4.45 ng/m^3, 0.055 to 6.29 ng/m^3 and 0.057 to 7.918 ng/m^3, respectively. The concentration of PMs and PAHs and TEQ increases during the winter time, and it progressively decreases as we move from the cold period to the warmer one. This, combined to the fact that higher levels of B[a]P were identified in the urban background station, indicate the presence of another strong combustion source beyond traffic, which was found to be the use of biomass burning for space heating. This was further confirmed by additional chemical analysis of levoglucosan (which is the main biomass burning tracer) presence of the different PM size fractions.