Polycyclic Aromatic Hydrocarbons in Wooden Railway Beams Impregnated with Coal Tar: Extraction and Quantification by GC-MS

Maria Ochsenkühn-Petropoulou*1, Angeliki Lampropoulou1, Hansjürgen Becker2, and Wolfgang Spyra2

1 Laboratory of Inorganic and Analytical Chemistry, Department of Chemical Engineering, National Technical University of Athens, Iron Polytechniou 9, 15773 Athens, Greece
2 Faculty of Environmental Sciences and Process Engineering, Brandenburg Technical University of Cottbus, Karl-Marx Str. 17, D-03044, Cottbus, Germany

Abstract. An analytical technique for the simultaneous determination of PAHs (polycyclic aromatic hydrocarbons) in wooden railway beams, impregnated with coal tar for their protection, has been developed, based on the effective extraction of the PAHs and their determination by GC-MS. Two extraction techniques, the Soxhlet and the ultrasonic one, using two different solvents, hexane and toluene have been compared for their efficiency for PAHs which can be determined in ppb-ppt range after optimised clean up and enrichment. Several parameters, such as the degree of impregnation of the wooden beams, the effect of sun radiation on the degradation of the PAHs and their migration to the soil have been investigated by following the concentration of the PAHs and that of their methylated products found at various sampling positions. The results are useful for the decision about recycling procedure or their further disposal.

Key words: Wooden railway beams; impregnation with coal tar; PAHs; extraction of PAHs; GC-MS.

The need to protect wood against attack from microorganisms and weather phenomena led to the development of impregnation techniques. The impregnation of wooden railway beams with coal tar was the dominating technique for their conservation, as coal tar was proven to be effective for more than 40 years [1]. Due to the fact that a high concentration of toxic polycyclic aromatic hydrocarbons (PAHs) exists in coal tar, the investigation about the reuse of these beams, which are currently lying in large amounts in the open environment, by the wood industry, or their disposal is of great interest.

PAHs are organic compounds with two and more aromatic rings, deriving from incomplete combustion or pyrolytic processes (>700°C) of organic material containing carbon and hydrogen [2]. Since these processes take place almost everywhere in the ecological system, PAHs are found in exhaust, tar, fumes, carbon and petroleum industry, cigarette smoke, forest fires, burning of energy resources, smoked food, water, air and soil [3, 4]. Although the formation mechanisms of PAHs are various and complex, their formation generally takes place through highly reactive free radicals or by the addition of aromatic rings to an easily available PAH (precursor system) [5]. The addition takes place either by ring closing reactions or Diels-Alder reactions or cycloaddition. PAHs appear in the atmosphere adsorbed on small particles (d < 5 μm) consisting of other matter and by this way, they are transported over long distances [6, 7]. In the water they form bonds with aqueous colloids and they end up in the soil under the influence of gravity or rain. Photooxidation reactions, along with microbial transformations, are considered the most important ones for the degradation of PAHs and their removal from the environment. Due to their wide presence in the environment in combination with their carcinogenic effects on human nature, PAHs have received particular attention. 16 PAHs are usually investigated in analy-
tical works, which according to the US EPA (Environmental Protection Agency) are the most widespread and are included in their priority list [8].

A wide number of techniques have been developed for the determination of PAHs. Chromatographic techniques, such as GC, LC, or HPLC, coupled with FID, MS, UV/VIS detectors are the most frequently used. Furthermore, depending on the sample, extraction techniques are also required, with Soxhlet and ultrasonic extraction being the most common ones, using a variety of solvents, such as cyclohexane, hexane, toluene or acetonitrile [9–15].

In this work, PAHs were extracted from wooden railway beams, impregnated for their protection with coal tar, as well as from soil samples underneath the piles, using Soxhlet and ultrasonic extraction techniques, with hexane and toluene as solvents and they were determined by GC-MS. The aim was to identify and determine the level of concentration of the PAHs in the investigated samples, the effect of some environmental parameters, such as the effect of sun radiation to the degradation of PAHs, their migration to the soil, as well as the degree of impregnation of the beams with coal tar. The results are useful and necessary for the decision for recycling procedures or their further disposal [16]. For on-site remediation, various microorganisms and enzymes have been developed, which can successfully degrade PAHs in-situ [17–19].

**Experimental**

**Reagents**

The following reagents were used: Standard of a mixture of 16 PAHs (compounds, with their abbreviations are given in Table 1), 2000 µg/mL each, in CH₂Cl₂/benzene (1:1, v/v) (J. T. Baker B. V.), internal standard of 5 deuterated PAHs (naphthalene d-8, acenaphthene d-10, phenanthrene d-10, chrysene d-12, perylene d-12), 2000 µg/mL each, in CH₂Cl₂ (J. T. Baker B. V.), toluene, (Merck, p.a. 99.8%), hexane (Merck, p.a. 95%), dry silica gel 60 (SiOH), 100–200 mesh.

**Sampling and Storage**

The sampling was performed using a saw for wood cutting. The samples obtained, had a size of 5×0.5 cm approximately and were about 1 mm thin. Afterwards, they were cut by hand in even smaller pieces of about 0.5×0.5 cm size. In this way, various samples were taken from the surface (0 cm), the middle (6 cm) and the centre (12 cm) of the wooden beams, having a length of 380 cm, a width of 25 cm and a height of 17 cm. Additionally, samples from the surface of beams lying on the top of the pile and from the surface of beams lying at the bottom of the pile were analysed, as well as soil samples underneath the piles of the beams, taken at 3 different sampling points (soil samples underneath piles of 1.75 m, 2.40 m and 2.80 m height) and the fourth sampling point was 100 m far from the piles of the beams.

All samples were dried according to DIN 52183. The water content of the beams in the different sampling positions was as following: At the surface 13%, in 6 cm depth 31% and in 12 cm depth 37%, respectively. The soil samples of about 0.5 kg and a moisture of 6%, were taken from the surface, ground and homogenised. The samples, the extracts and the standard solutions were stored in dark glass bottles in the refrigerator protected from sunlight.

**Apparatus and Instrumentation**

For the extraction of the PAHs, a Soxhlet apparatus (100 ml extractor) and an ultrasonic extraction unit (USE, Bandelin electronic, Model RK 1028) were used, for the clean-up a solid phase extraction (spe) column filled with dry silica gel and a Baker spe-12 G System and for the enrichment a rotating vacuum distiller.

The determination of the PAHs was performed with a gas chromatograph (Fisons, Model GC 8065) coupled with a quadrupole mass spectrometer (Fisons, Model MD 800) as detector, with electron impact and full scanning for the mass range of 100–555 amu with a rate of 0.7 min/scan. For the automatic injection of the samples an autosampler (Fisons, Model A200S) was used. The separation column was an M&N (Macherey-Nagel) Optima 5 column with 60 m length×0.25 mm ID×0.25 µm film thickness, with a stationary phase of 5% diphenyl-95% dimethylpolysiloxane and as pre-column a capillary column 4 m×0.53 mm ID fused silica was used.

**Analytical Procedure**

**Ultrasonic Extraction**. 3 g of the sample were put into a conic glass bottle along with 60 mL of solvent (hexane or toluene). The bottle was closed with a glass cap and the system was left in the ultrasonic bath for 24 h at room temperature. The extract was filtered and stored in brown glass bottles in the refrigerator.

**Soxhlet Extraction**. 7.5 g of the sample were put into the extraction vessel of the Soxhlet apparatus and 150 mL of toluene were added. The extraction took place for 24 h at a temperature of 120 °C. The extract was put into a volumetric cylinder and adjusted to 150 mL with toluene.

**Clean-up of the Soil Samples**. The separation column was conditioned with 10 mL of hexane/toluene (7/3, v/v). When the column was fully conditioned, the extract was percolated through the column. The column was eluted with 10 mL hexane/toluene (7/3, v/v) and the extract was collected in a volumetric cyclinder of 10 mL.

**Enrichment of the Soil Samples**. 10 mL of the extract after the cleanup were put into the round glass bottle of the rotating distiller and 0.5 mL of internal standard were added. The extract was enriched by evaporation under vacuum to 1 mL.

**Determination of PAHs by GC-MS**. To avoid the overloading of the column, all the extracts of the wooden beams were diluted up to 1000 times with toluene, before they are injected into the gas chromatograph, while the soil samples were cleaned up and enriched 20 times. 1 mL of the sample extract was mixed with 1 mL of the diluted internal standard of 1 µg/mL of each d-PAH and 2 µL of this mixture were injected into the gas chromatograph,