Measurements of Hydroxylated Polycyclic Aromatic Hydrocarbons in Atmospheric Aerosols from an Urban Site of Madrid (Spain)

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Abstract This paper describes an analytical methodology for the separation and quantitative determination by HPLC with fluorescence detection of hydroxylated polycyclic aromatic hydrocarbons (OH-PAHs) and their parents PAHs in atmospheric urban aerosol. The sampling site is located in the outskirts of Madrid and can be considered an open urban area. The aim of this work was the optimization of analytical methods, applied in several samples and characterize the concentration levels of selected PAHs-OH and PAHs. The preliminary results show concentrations between 2.5–53.2 pg/m^3 for 2-OHPhenathrene (2-OHPH) and 27.8–34.5 pg/m^3 for 1-OHPyrene (1-OHPYR).

Keywords Atmospheric urban aerosol, PAHs, OH-PAHs, HPLC/Fluorescence

Introduction

Hydroxylated polycyclic aromatic hydrocarbons (OH-PAHs) are known as the metabolites of the PAHs and commonly used to assess human exposure to PAHs from atmospheric air. These compounds are more toxic than the corresponding PAHs due to their direct carcinogenicity, thus OH-PAHs have showed a very big cito-toxicity because can form adducts with the DNA. For this reason, there are many paper related with the determination of the OH-PAHs in the urine. Regarding OH-PAHs, few literatures exist to measure these compounds in air samples, and in particular, HPLC measurements with fluorescence detection are rarely applied. Therefore, a sensitive and reliable method is necessary for monitoring of their concentrations in atmospheric as well as in biological fluid. OH-PAHs in atmosphere can be the result of direct emission from combustion sources, such as diesel engines, and/or formation in the atmosphere by the hydroxyl radical oxidation of PAHs.

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The present work shows the preliminary results of measurements of select OH-PAHs and their parent PAHs in order to characterize their concentrations levels and study their potential relationship.

Objective

The aim of this work was the optimization of analytical methods to determine the trace levels of 1-Hydroxypyrene (1-OHPYR) and 2-Hydroxyphenanthrene (2-OHPH) in airborne particulates. The analytical methods were applied to several ambient air samples.

Experimental Part

Air Sampling

Sampling site was located at CIEMAT, situated 2 km from the urban center of Madrid in the northwest of the city. The location is characterized by open areas, and can be considerate representative of urban background.

High volume MCV sampler equipped with a Whatman glass fibre filter, previously heated, was used to collect 16 ambient air samples from 15 March 2006 to 02 August 2006. The volume of ambient air draw through filter during 24 h sampling was about 720 m^3.

Chromatographic Analysis

After collection, filters were stored in a refrigerator until analysis. Samples were cut into a four pieces; two pieces extracted ultrasonically during 30 min with methanol to determine 1-OHPYR and 2-OHPH, and the others were ultrasonic extracted with dichloromethane, to determine their corresponding PAHs. Extracts were filtrated and evaporated under nitrogen flow, finally were refilled to 1.0 ml of methanol and dichloromethane respectively. Due to the good resolution of chromatographic peaks of selected OH-PAHs obtained a clean-up step was not necessary.

An Aliquot of 25 µl of these solutions were analyzed using a Hewlett-Packard series 1050 liquid chromatograph with a C18 Supelcosil thermostated column and an Agilent 1100 series fluorescence detector.

The mobile phase was a mixture of HPLC grade of acetonitrile/water (45:55) programed up to 100% of acetonitrile in 23 min and keeping it there for 10 min; the mobile phase flow rate was 1.5 mL min^{-1}. An equilibration delay of 6 min was applied to the next injection and the experimental conditions of fluorescence detector were obtained from literature.