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RESEARCH PAPER

Determination of 16 Kinds of Polycyclic Aromatic Hydrocarbons in Atmospheric Fine Particles by Accelerated Solvent Extraction Coupled with High Performance Liquid Chromatography

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Abstract: A method for determination of 16 kinds of polycyclic aromatic hydrocarbons (PAHs) in atmospheric fine particles (PM2.5) was developed based on accelerated solvent extraction-direct injection coupled with high performance liquid chromatography (HPLC). PM2.5 sample was collected by glass fiber membrane filter and pretreated with acetonitrile by accelerated solvent extraction. The extract was separated by ZORBAX Eclipse PAH column with acetonitrile and water as mobile phase, and then detected by ultraviolet and fluorescence detectors. The result showed that the 16 kinds of PAHs were well extracted, separated and detected with good linear relationships ($r \geq 0.9998$) in the concentration range of 0.025–5.00 μg mL^{-1}. The recoveries were from 78.3% to 113.2%. The relative standard deviations ranged from 0.5% to 9.5%. The detection limits were 0.007–0.062 ng m^{-3}. The method was simple, rapid, accurate and sensitive, and suitable for the simultaneous determination of 16 kinds of PAHS in PM2.5.

Key Words: Accelerated solvent extraction; Atmospheric fine particles; Polycyclic aromatic hydrocarbons; High performance liquid chromatography

1 Introduction

Recent years, smog weather in China occurs frequently, and has become a chronic problem in winter in some large and middle-sized cities. Smog is mainly composed of inhalable particulates, sulfides and nitrogen oxides, while, among inhalable particulates, PM2.5 accounts for a considerable proportion[1]. Polycyclic aromatic hydrocarbons (PAHs), a family of persistent organic pollutants adsorbed by PM2.5, are hydrocarbon compounds having two or more benzene rings in the molecule. PAHs can exist long in the atmosphere and enter with breathing into the human upper respiratory tract, bronchi and pulmonary alveoli. PAHs do not readily metabolize in the human body and have strongly toxicity and carcinogenicity, which has aroused extensive social concerns[2]. In 2012, the Ministry of China's Environmental Protection promulgated the updated ambient air quality standard, including a new analysis of PM2.5[3]. In 2013, the National Health and Family Planning Commission of China initiated surveillance of the impact of air pollution (smog) on human health simultaneously in multiple cities. Thus, it is of important practical significance to accurately determine the concentrations of PAHs in PM2.5 for evaluating the severity of atmospheric pollution and protecting people's health.

For now, the pretreatment methods for PAHs in PM2.5 sample mainly include Soxhlet extraction[4,5], ultrasound-assisted extraction[6,7], microwave-assisted extraction[8,9], solid-phase (micro) extraction[10–12], secondary thermal desorption[13], and supercritical fluid extraction[14], etc. Accelerated solvent extraction (ASE), a new PAHs extraction method, has been relatively less used[15–17]. ASE can accelerate the dissolution of analytes from solid or semi-solid samples into

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the solvent by using high temperatures and high pressures, and has such advantages as simple operation, low organic reagent consumption, rapid extraction speed, high efficiency and good reproducibility. The methods for determination of PAHs in PM2.5 sample reported in publications include fluorescence spectroscopy (FL)[18], room temperature phosphorescence spectroscopy (RTPS)[19], gas chromatography (GC)[20], high performance liquid chromatography (HPLC)[21,22], gas chromatography-mass spectrometry (GC-MS)[6,12,23], and gas chromatography-mass spectrometry/mass spectrometry (GC-MS/MS)[24,25], etc. FL is highly sensitive, however, its separation effect is poor for samples with complicated matrices and a pre-separation is needed. RTPS is convenient, rapid and resistant to interference but not sufficiently sensitive. With GC, PAHs with high boiling points and their isomers cannot be easily separated. GC-MS is highly sensitive and highly capable in identification of PAHs, but has the same defects as GC. GC-MS/MS is highly sensitive, but the instruments are expensive. HPLC is not limited by volatility and thermal stability of PAHs and has such advantages as simple and rapid operation, high sensitivity, low cost, etc. In this study, the 16 kind of PAHs under priority control proposed by the United States Environmental Protection Agency (US EPA) were extracted with acetonitrile, and the extract was directly injected for analysis without complicated procedures such as concentration, filtration, etc., effectively avoiding loss of PAHs. Thereby, a new method for determination of 16 PAHs in PM2.5 sample by accelerated solvent extraction-high performance liquid chromatography with direct injection has been established.

2 Experimental

2.1 Instruments and reagents

The sample separation of PAHs were performed on a 1260 high performance liquid chromatography equipped with an ultraviolet detector, a fluorescence detector (Agilent Technologies, USA) and a ZORBAX Eclipse PAH column (150 mm × 4.6 mm, 5 μm, Agilent Technologies, USA). Milli-Q ultrapure water system (Millipore, USA), N-EVAP-112 nitrogen evaporator (Organomation, USA), ASE350 accelerated solvent extractor (Dionex, USA), TH-150C PM2.5 sampler (Wuhan Tianhong Instruments Co., Ltd) and glass fiber filters (about 90 mm in diameter) (Pall, USA) were also used in this experiment.

A standard mixture (500 μg mL^{-1}) of 16 PAHs (naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), penanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBA) benzo[g,h,i]perylene (BghiP), indeno[1,2,3-cd]pyrene (IND), numbered from 1 to 16, was purchased from Accstandard (USA). HPLC grade acetonitrile, dichloromethane, *n*-hexane and acetone were purchased from Scientific (USA). Ultrapure water was self-made.

2.2 Sampling

By reference to the sampling method in HJ 646-2013 and HJ 647-2013 (Environmental protection industry standards, China), three sampling points were set in Chengdu and air sampling was performed on seven consecutive days each month from January to March 2016 (smog persisted in March, and sampling was performed on 12 consecutive days) at a flow rate of 100 L min^{-1} for 24 h. All of the sampling points were set with avoidance of pollution sources and obstacles.

2.3 Sample pretreatment

The samples were pretreated using an accelerated solvent extractor. Within a specified static extraction period, high temperature and high pressure were applied to accelerate dissolution of analytes in the extraction solvent. Each glass fiber filter sample was cut into four equal parts. One of the four parts was cut into pieces and mixed well with diatomaceous earth. The mixture was then filled into a 5-mL extraction cell, followed by addition of 2 mL acetonitrile. The extraction parameters were set as follows: temperature, 100 ºC; pressure of 1500 psi; static extraction time, 5 min; cycles, 1; N_2 purge time, 30 s. The extract was directly injected for analysis.

2.4 Instrumental conditions

Chromatographic separation was performed under the conditions as that in HJ 647-2013 with appropriate modifications, as follows: acetonitrile and ultrapure water were employed as mobile phase A and mobile phase B, respectively; the flow rate was 2.0 mL min^{-1}. The elution gradient started with 40% A (isocratic for 20 min) and increased linearly to 100% A within 5 min, then reverted to 40% A within 5 min. The column temperature was 25 ºC and the injection volume was 10 μL. The wavelength switching program of the fluorescence detector was set as described in Table 1. Due to the absence of fluorescence, AcPy was quantified using an ultraviolet detector at a wavelength of 220 nm.

2.5 Quality control

A blank filter determination was conducted for each batch of the glass fiber filter samples to ensure the contents of NaP and PA were < 50 ng and the contents of other PAHs were < 10 ng in blank filters[26]. Blank samples were collected each day for each sampling point. The samples were preserved in tightly closed containers and stored at low temperatures with light protection. Extraction and determination were completed