



A simple, comprehensive, and miniaturized solvent extraction method for determination of particulate-phase polycyclic aromatic compounds in air



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ABSTRACT

The method allowed simultaneous characterization of PAHs, nitro-PAHs and quinones in atmospheric particulate matter. This method employs a miniaturized micro-extraction step that uses 500 μL of an acetonitrile–dichloromethane mix and instrumental analysis by means of a high-resolution GC–MS. The method was validated using the SRM1649b NIST standard reference material as well as deuterated internal standards. The results are in good agreement with the certified values and show recoveries between 75% and 145%. Limit of detection (LOD) values for PAHs were found to be between 0.5 pg (benzo[a]pyrene) to 2.1 pg (dibenzo[a,h]anthracene), for nitro-PAHs ranged between 3.2 pg (1-nitrobenzo[e]pyrene) and 22.2 pg (3-nitrophenanthrene), and for quinones ranged between 11.5 pg (1,4-naphthoquinone) and 458 pg (9,10-phenanthraquinone). The validated method was applied to real PM_{10} samples collected on quartz fiber filters. Concentrations in the PM_{10} samples ranged from 0.06 to 15 ng m^{-3} for PAHs, from <LOD to 69.4 ng m^{-3} for nitro-PAHs, and from 0.27 to 115 ng m^{-3} for quinones. This procedure was found to be precise, accurate and suitable to be employed for determination of polycyclic aromatic compounds in airborne particles from both polluted and non-polluted atmospheres.

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1. Introduction

Atmospheric particulate matter has been extensively studied to better understand its impact on human health, due to evidences of harmful effects in the respiratory and cardiovascular systems [1–3]. Chronic respiratory effects related to particulate matter may include reduced lung function and increased symptoms of bronchitis in children and adults [4,5]. Among the substances that may either induce or increase particulate matter (PM) toxicity, can be cited are aldehydes, ketones, benzene, dioxins, polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs (alkyl-PAHs) and their nitrated (nitro-PAHs) and oxygenated (quinones) derivatives [6–8]. In this context, these compounds are key components to investigate biological effects that airborne aerosol may trigger in individuals.

Polycyclic aromatic compounds (namely as PAHs and their derivatives) associated to airborne particles are mainly generated

through man-made processes. PAHs are ubiquitous environmental contaminants, mainly formed during incomplete combustion or pyrolysis (such as biomass burning, forest fires, industrial fumes, fossil fuel burning, and hydrothermal processes) [9–16].

The PAH chemical structures contain two or more fused benzene rings arranged in linear, angular or in cluster dispositions then forming a varied group of more than 100 molecules [9,16,17]. In turn, PAH derivatives generally possess at least one heteroatom-containing substituted group attached to the parent fused-ring structures such as the ones found in nitro- (nitro-PAHs), carbonyl- and/or hydroxyl- (oxy-PAHs) groups, among others [18–21]. In regard to toxicity, the parent PAHs may undergo photochemical reactions with NO_2 , OH, and/or O_3 yielding even more toxic PAH derivatives, such as nitro-PAHs and oxy-PAHs (quinones and hydroxy-PAHs) [8,10,11,17,22,23]. PAHs, quinones and nitro-PAHs are suspect to cause overproduction of reactive oxygen species (ROS), contributing to oxidative stress and some inflammatory processes, supposedly responsible for triggering many diseases [8,11,24–29].

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Due to their toxicological properties and environmental importance, PAHs and their derivatives need to be closely monitored in the atmosphere. In particular, the US Environmental Protection Agency (US EPA) lists 16 PAH as priority pollutants as well as World Health Organization (WHO) further lists 17 PAHs, then summing up 33 PAHs likely to be subjected to regulations, the European ambient air legislation recommends 1 ng m^{-3} as guideline value to not be exceeded by benzo[a]pyrene as annual average concentration, due to its high carcinogenicity [9,30,31]. No regulation exists for nitro-PAHs nor quinones.

PAH are thermally stable with high boiling points and low vapor pressures, which favor their association with airborne particles. However, the lighter PAHs ($\text{MW} \leq 202 \text{ g mol}^{-1}$) are preferentially found in gas phase in the air. Since their concentration in air is relatively low (from pg m^{-3} to ng m^{-3}), sample collection of PAHs both in vapor and particulate phases requires quite large volumes of air on sorbent materials or on filters respectively [9,31]. Nitro-PAHs and quinones atmospheric levels are generally one or two orders of magnitude lower than PAH which makes their determination even more difficult.

The most widely employed techniques for PAH determination in airborne aerosol samples are high performance liquid chromatography coupled to fluorescence detector (HPLC–FLD) and gas chromatography coupled to mass spectrometry (GC–MS). Both methods present advantages and disadvantages. HPLC–FLD presents higher sensitivity and it is suggested to be used with low-volume air samples, such as those collected by cascade impactors (which work at $\sim 10\text{--}30 \text{ L min}^{-1}$) or other low volume samplers [9,16,32]. On the other hand, the use of GC–MS with selective ion monitoring (SIM) provides structural information and also a reduction of matrix effects and interference, which could happen with HPLC–FLD in some extension [11]. In turn, due to the quenching effects generated by electronegative heteroatoms present in their structures, nitro-PAHs and quinones are not fluorescent substances, and are practically not analyzable by HPLC–FLD.

The determination of quinones using gas chromatography coupled to mass spectrometry (GC–MS) has been mainly reported by adopting a derivatization step prior to analysis. In fact some quinones have low thermal stability, low vapor pressure and poor ionization efficiency, thus derivatization can bypass these problems and improve detection [33]. Nevertheless, a recent study performed by Sousa et al. [34] shows that the non-derivatized quinones (1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, 9,10-phenanthraquinone, and 9,10-anthraquinone) present distinct thermal stability up to $600 \text{ }^\circ\text{C}$, it also reports a GC–MS methodology for their determination in PM samples. These results indicate that the molecular structure strongly influences the thermal decomposition of these quinones, being a determining factor in their thermal stability. Despite that, the studied quinones could be directly analyzed by GC–MS without a prior derivatization step [35].

The main goal of this study was to develop a comprehensive, simple and green analytical method for simultaneous determination of PAHs, nitro-PAHs and oxy-PAHs in atmospheric particulate matter using GC–MS. It was also employed the Doehlert matrix and response surface methodology associated with a desirability function for optimizing simultaneous extraction of the studied substances in one single step. In this latter, a very simple and fast sample preparation was sought, requiring a very low extraction volume and bypassing pre-concentration, sample fractionation and clean-up prior to analysis. Chromatographic analyses were performed using a mass spectrometer in electron impact (EI) mode for simultaneous identification and quantification of 20 PAHs, 27 nitro-PAHs and 5 quinones in one only 38-min run. The method was validated by using the IUPAC criteria (e.g. calibration curve, linear range, linearity, limit of detection, limit of quantification, precision, accuracy, and test with real samples). In order to meet these

criteria, we used urban dust particulate matter SRM 1649b (NIST) and deuterated internal standards. The methodology was applied to real samples collected at a bus terminal in Salvador, BA, Brazil.

2. Experimental

2.1. Reagents and standards

A US Environmental Protection Agency (EPA) 610 PAH mix containing acenaphthene (ACE), acenaphthylene (ACY), anthracene (ANT), benz[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[ghi]perylene (BgP), benzo[k]fluoranthene (BkF), chrysene (CRY), dibenz[a,h]anthracene (DBA), fluoranthene (FLT), fluorene (FLU), indeno[1,2,3-d]pyrene (IND), naphthalene (NAP), phenanthrene (PHE), and pyrene (PYR) at $2000 \text{ } \mu\text{g mL}^{-1}$ each, in methanol:methylene chloride (1:1) was purchased from Supelco (St. Louis, USA). In addition, the individual standards of $50 \text{ } \mu\text{g mL}^{-1}$ coronene (COR) and $1000 \text{ } \mu\text{g mL}^{-1}$ perylene (PER) as well as two deuterated compounds, namely pyrene D10 (PYR d10) and fluorene D10 (FLU d10) were acquired from Sigma–Aldrich (St. Louis, USA). A $1.0 \text{ } \mu\text{g mL}^{-1}$ standard stock solution and the analytical standards containing all PAHs were prepared by successive dilutions in chromatographic and spectroscopic grade acetonitrile (JT Baker, USA).

The quinones investigated in this study were 1,4-benzoquinone (1,4-BQ) (98%), 9,10-phenanthraquinone (9,10-PQ) (95%) and 9,10-anthraquinone (9,10-AQ) (99.4%), purchased from Sigma–Aldrich (St. Louis, USA), and 1,2-naphthoquinone (1,2-NQ) (90%) and 1,4-naphthoquinone (1,4-NQ) (96.5%), purchased from Fluka (St. Louis, USA). All quinone standards were used without further purification. A $500 \text{ } \mu\text{g mL}^{-1}$ quinone mix stock solution was prepared by dissolving solid standards in tetrahydrofuran (THF) (JT Baker, USA).

Nitro-PAH certified standard solutions SRM 2264 (aromatic hydrocarbons nitrated in methylene chloride I) and SRM 2265 (polycyclic aromatic hydrocarbons nitrated in methylene chloride II) were purchased from the National Institute of Standards and Technology (NIST, USA). The SRM 2264 contains the following compounds: 1-nitronaphthalene (1-NNap), 2-nitronaphthalene (2-NNap), 1-methyl-4-nitronaphthalene (1-methyl-4-NNap), 1-methyl-5-nitronaphthalene (1-methyl-5-NNap), 1-methyl-6-nitronaphthalene (1-methyl-6-NNap), 2-methyl-4-nitronaphthalene (2-methyl-4-NNap), 2-nitrobiphenyl (2-NBP), 3-nitrobiphenyl (3-NBP), 4-nitrobiphenyl (4-NBP), 5-nitroacenaphthene (5-NAce), and 2-nitrofluorene (2-NFlu). In turn, the SRM 2265 is composed of the following analytes: 2-nitrophenanthrene (2-NPhe), 3-nitrophenanthrene (3-NPhe), 9-nitrophenanthrene (9-NPhe), 2-nitroanthracene (2-NAnt), 9-nitroanthracene (9-NAnt), 2-nitrofluoranthene (2-NFlt), 3-nitrofluoranthene (3-NFlt), 1-nitropyrene (1-NPyr), 2-nitropyrene (2-NPyr), 4-nitropyrene (4-NPyr), 6-nitrochrysene (6-NCry), 7-nitrobenz[a]anthracene (7-NBaA), 3-nitrobenzanthrone (3-NBA), 6-nitrobenzo[a]pyrene (6-NBaPyr), 1-nitrobenzo[e]pyrene (1-NBePyr), and 3-nitrobenzo[e]pyrene (3-NBePyr).

The standard reference material SRM 1649b was also purchased from NIST (Maryland, USA). According to NIST, the SRM 1649b is comprised of atmospheric particulate material collected in an urban area (Washington, DC).

2.2. Analytical instrumentation

The analyses were performed by means of a high-resolution gas chromatograph coupled with a high-resolution mass spectrometric detector, a GCMS-QP2010PLUS Shimadzu gas chromatograph/mass spectrometer (Shimadzu, Japan). This instrument was

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