

Oxidized forms of polycyclic aromatic hydrocarbons (Oxy-PAHs): determination in suspended particulate matter (SPM)

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Abstract

Smog is a serious problem of many cities in the world. The main component of smog is suspended particulate matter (SPM). Suspended particulate matter is defined as a solid or liquid particles as well natural (for example aerosols of sea salts) as unnatural which are mainly a contamination. SPM is classified in many ways, of which division by size of particles is best known. Two main types of SPM are distinguished: PM10 (particles with size less than 10 micrometers) and PM2.5 (particles with size less than 2.5 micrometers). The health threat caused by SPM is twofold. Dust, as an aerosol of solid particles with very small size, is a threat to the respiratory system. The second most serious threat to the health are substances adsorbed on SPM's surface. SPM is a carrier of many hazardous substances also coming from incomplete combustion of various fuels, more or less contaminated. SPM contains, between else, heavy metals and substances belonging to the broad spectrum of polycyclic aromatic hydrocarbons (PAH). Recently many studies have begun to pay attention to oxidized form of PAHs, especially nitro-PAHs, oxy-PAHs and hydroxy-PAHs, which are considered more harmful than 'original' ones. The state of the art concerning its determination in suspended particulate matter oxidized form of PAHs was the aim of presented paper.

Keywords: PAHs, nitro-PAHs, oxy-PAHs, hydroxy-PAHs, determination

1. Introduction

A serious problem of many cities in the world is a smog. Smog (the word comes from a bunch of two words: smoke and fog) is an unnatural occurrence which is caused by emission of product of incomplete combustion of different types of fuel which cause a poisonous fog at windless weather. The main component of smog is suspended particulate matter (SPM). Suspended particulate matter is defined as a solid or liquid particles as well natural (for example aerosols of sea salts) as unnatural which are mainly a contamination. SPM is classified in many ways, of which division by size of particles is best known. Two

main types of SPM are distinguished: PM10 (particles with size less than 10 micrometers) and PM2.5 (particles with size less than 2.5 micrometers). Various studies report also two other types: PM4 and PM0.1 (particles with size respectively less than 4 and 0.1 micrometers). The health threat caused by SPM is twofold. Dust, as an aerosol of solid particles with very small size, is a threat to the respiratory system. Accordingly, PM10 is defined as a 'chest fraction' because of its harmfulness to the thoracic organs – heart, bronchi; PM2.5 whose particles is small enough to penetrate deep into the lung structure, is a serious threat to the functioning of the alveoli and is therefore defined as 'respiratory fraction'. The second most serious threat to the health are substances adsorbed on SPM's surface. SPM is a carrier of many hazardous substances also coming from incomplete combustion of various fuels, contaminated in lesser or heavier degree. Heavy metals ions (for example ions of arsenic, cadmium, nickel etc.) are deposited mainly on PM2.5 fraction, penetrate the blood and cause serious havoc in the body, typical for exposures to these metals. SPM contains also substances belonging to the broad spectrum of polycyclic aromatic hydrocarbons (also known as polynuclear aromatic hydrocarbons - PAH). The extensive list of substances included in this group have a common strong and negative impact on health – its carcinogenicity, teratogenicity, mutagenicity and the persistence inherited DNA damages by metabolites of PAHs are shown in many studies.

2. PAHs and theirs oxidized forms

Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 200 compounds, which are consisted of condensed carbon rings. PAHs are a one of main components of smog, embedded on suspended particulate matter. A lot of research reports carcinogenicity and influence on the occurrence of many other diseases. 16 compounds included in this group are considered as especially dangerous. PAHs are produced by the process of incomplete combustion of many types of fuel. A content of PAHs in the air is a main criterion for the assessment of air quality, therefore analyses of these compounds are well

known. Both US EPA and European environmental agencies recognized as a necessity to monitor a content of PAHs in air because of their toxicity. Already in the 80s American experts made a division into carcinogenic and not carcinogenic PAHs and took benzo[a]pyrene as a standard of monitoring air pollution, nowadays US EPA mentions sixteen compounds belonging to PAH as significantly affecting on health and recommends detailed measurement of them, European agencies still recommends only benzo[a]pyrene's content control because benzo[a]pyrene remains the most dangerous PAH (Sapota,

1998). Recently many studies have begun to pay attention to oxidized form of PAHs, especially nitro-PAHs, oxy-PAHs and hydroxy-PAHs. Much more harmful of oxidized form of PAHs has been proven in many studies. Oxidized form of PAHs can be formed in two ways directly by nitration or oxidation of PAHs in combustion process or indirectly by reactions with nitrogen, nitrogen oxide or ozone in atmosphere. PAHs concentration observed in air ranged from 7 to 307 ng/m³, contrary to oxy-PAHs concentration ranged from 5 to 22 ng/m³ (Bandowe *et al.* (2014)). The figures below show ways of PAHs' oxidizing.

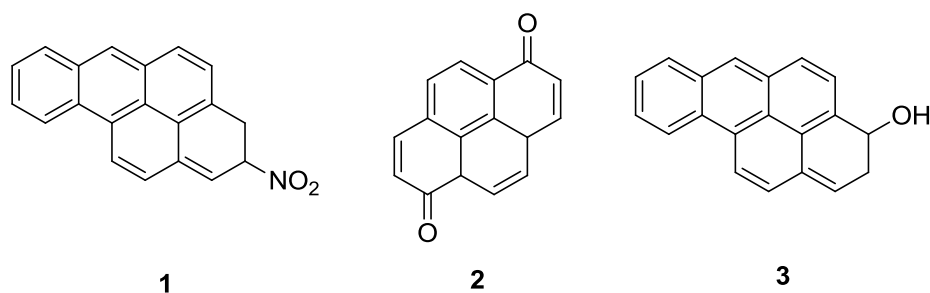


Figure 1. Examples of molecules of nitro-PAH (1), oxy-PAH (2) and hydroxy-PAH (3) (Cordeiro *et al.* (2009), Lu *et al.* (2011))

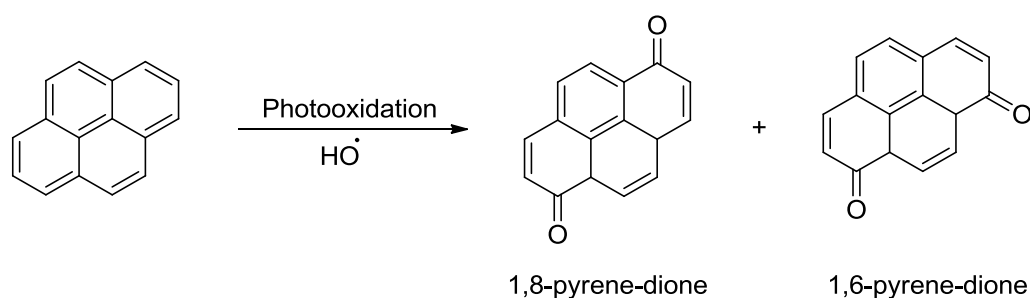


Figure 2. Possible way of photochemical oxidation of pyrene (Cordeiro *et al.* (2009))

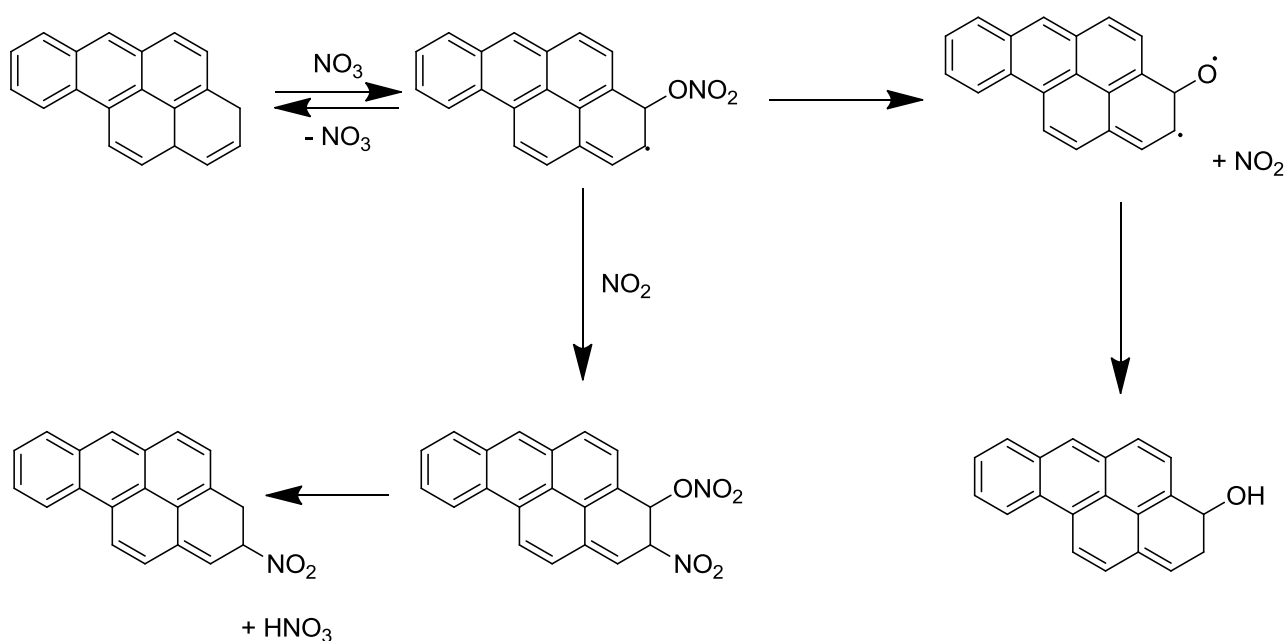


Figure 3. Different ways of nitration and oxidation of PAH (Lu *et al.* (2011))

3. Analytical procedures for PAHs and oxy-PAHs determination in air

3.1 PAHs

The sampling may be performed with a variety of samplers, both low- and high-volume sampling rates and even passive samplers. Sampling media include quartz-fiber, glass fiber, Teflon-coated glass fiber, and Teflon-membrane filters (Szulejko *et al.*, 2014). Glass and quartz-fiber filters are commonly annealed at high temperatures for several hours to lower blank levels associated with the new filters and weighed before the sampling. After the sampling, the filters were weighed again and preserved and stored at a low temperature (below -15°C). Such a sampling procedure is being applied in almost all studies. Gas chromatography-mass spectrometry (GC-MS) is the most commonly used analytical technique however (ultra) high performance chromatography liquid chromatography((U)HPLC) coupled with different detectors (for example fluorescence, photo diode array and mass spectrometer) as an analytical technique is also applied. Some differences can be observed in the way of extraction of samples. Barrado *et al.* (2012 and 2013) proposed extraction using a microwave oven following a 40 minutes program with temperature gradation to final grade 120°C and power 900W. Dichloromethane was used as an extraction solvent in this study. Yield of PAHs' extraction was more than 80%. Crimmins and Baker (2006) applied a sonic supported extraction. Dichloromethane also was used as an extraction solvent. Samples were sonicated for 30 minutes in dichloromethane and then stored at -20°C for 48h. After that, extracts were concentrated under N_2 to 200 microliters and analyzed using GC-MS. Umbuzeiro *et al.* (2008) used dichloromethane as a solvent in a Soxhlet extractor at temperature 40°C for 20h. Then, extract was evaporated until N_2 to almost dryness and re-dissolved in small amount of dichloromethane. Albinet *et al.* (2006) propose using pressurized liquid extraction (ASE) with dichloromethane as a solvent. Samples enriched with standards was extracted twice using ASE, and then dried on Na_2SO_4 . Also Wilcke *et al.* (2014) and Bandowe *et al.* (2014) used this method of extraction in their study.

3.2. Nitro-PAHs

Sampling collection is not different from PAH's sampling collection. Both PAHs and nitro-PAHs can be sampled simultaneously. Similarly to PAH analysis, nitro-PAHs can be analyzed by the GC-MS or (U)HPLC coupled with different detectors. Different studies utilized different ionization methods like electron impact (EI), negative ion chemical ionization (NICI), atmospheric pressure ionization (APCI) and atmospheric pressure photoionization (APPI) with instruments operated in selective ion monitoring (SIM) or multiple reaction monitoring mode (MRM). Besides mass spectrometry, fluorescence, chemiluminescence and photodiode array detection methods were also used. The main advantage of the (U)HPLC system relative to the GC-MS is that measurements can be carried out at room temperature, at which nitro-PAHs are more stable. Both small, volatile

molecules and large, unstable molecules can be separated well on C18- (Schauer *et al.* (2004); Mirivel *et al.* (2010); Garcia-Alonso *et al.* (2012) or phenyl-hexyl column (Nyiri *et al.* (2016). Different approaches were used in sample preparation. Zielinska and Samy (2006) reported conventional methods of preparation such as Soxhlet extraction, sonication and pressurized fluid extraction (PFE) with dichloromethane, toluene or benzene as a more commonly used extraction solvent. Furthermore, they point advantages of PFE because of time saving, reduction of solvent consumption and ease of use. Bamford *et al.* (2002) also proposed using PFE with dichloromethane as a solvent. Also Ringuet *et al.* (2012) used this method of extraction. Bandowe *et al.* (2014) report simultaneously analysis both PAHs and nitro-PAHs with the same procedure of extraction using pressurized liquid extraction and dichloromethane as a extraction solvent. In turn, Schauer *et al.* (2004) indicate the need for separation PAHs and nitro-PAHs before analysis using glass column with silica. PAHs were eluted with cyclohexane fraction (first eluate) and nitro-PAHs were eluted with cyclohexane/dichloromethane (in 1:1 ratio) fraction. Also, Bamford *et al.* (2002) postulate a separation PAHs and nitro-PAHs using SPE and mixture of hexane and dichloromethane. Following this research, Cochran *et al.* (2012) proposed the same method of separation PAHs and nitro-PAHs. Nyiri *et al.* (2016) applied ultrasonic assisted extraction of PAHs and their oxy- and nitro- derivatives with hexane as a solvent. Tang *et al.* (2016) and Fujiwara *et al.* (2014) applied dichloromethane as their solvent of choice used in the ultrasonic assisted extraction of PAHs and nitro-PAHs. 3.3. O-PAHs

To properly describe analytical procedures for OPAHs, we need to divide this group into hydroxy-PAHs and oxy-PAHs. Containing of hydroxyl group in molecule requires a little different treatment. Cochran *et al.* (2012) report necessity of derivatization of sample for GC-MS analysis of hydroxy-PAHs. If both PAHs, nitro-PAHs and oxy-PAHs can be analysed without a derivatization, hydroxyl groups in hydroxy-PAHs need to be inactivated before GC-MS analysis. This process relied on derivatization with BSTFA and TMCS at 70°C for 6h(!). Long duration of this process provides, according to authors' experience, complete transformation of hydroxyl groups. Derivatization of hydroxy-PAHs is not necessary when the LC-MS method can be applied. Barrado *et al.* (2013) report using low temperature ultrasonification with methanol as an extraction solvent and then evaporation the extract almost to dryness under nitrogen flow. The last step appear also in other research. O'Connell *et al.* (2013) developed ethyl acetate based extraction procedure which in combination with GC and LC-MS techniques allowed for quantification of 250-PAHs Oxy-PAHs need no derivatization, and can be analyzed together with nitro-PAHs and PAHs (Albinet *et al.* (2006)). Measurement of oxy-PAH needs only slightly different conditions (the main differences are in temperature program; Souza *et al.* (2014). There is no more differences in extraction of oxy-PAHs

process and oxy-PAHs can be analyzed simultaneously with nitro-PAHs and PAHs.

4. Adverse health effect.

The PAHs incorporated into the human body are converted to phenols and dihydrodiols by cytochrome P450-dependent monooxygenases. In addition, one part of the dihydrodiols is converted to dihydrodiol epoxides by additional oxidation. The PAH metabolites have been determined as biomarkers to evaluate the exposure of humans to PAHs. Among them, urinary 1-hydroxypyrene has been frequently used as a biological indicator for evaluating PAH exposure. Recently, 1-hydroxypyrene and naphthol isomers have been identified amongst the antiandrogenic chemicals present in the wastewater effluent (Rostkowski et al. (2011)). Inhalation, oral ingestion and dermal contact are the main routes of nitro-PAH intake from the environment by humans and animals. The carcinogenicity, mutagenicity/genotoxicity of nitro-PAHs in environmental media (soil, sediments, atmospheric particulates) have been extensively studied with several test systems eg. bacterial strains (Ames test using Salmonella), mammalian cell lines, fish cell lines, biological molecules (DNA), plants and in-vivo studies using rats and mice. Based on published scientific studies, the IARC Working Group on the Evaluation of Carcinogenic Risks to Humans has classified several nitro-PAHs into carcinogenic groups (Bandowe et al. (2017)). Some of them have been assigned Toxicity Equivalence Factor (TEF) values some of which are much higher than those of benzo[a]pyrene (Collins et al. (1998)).

5. Conclusions

Analytical procedures of PAH and its oxidized form are well known. A lot of research has allowed to develop a comprehensive procedures of quantitative and qualitative analyses. Despite the differences in molecular structure between PAH and its oxidized form, analytical procedures are similar because both PAHs and oxidized form of PAHs have very similar structure. It only occur a little differences in samples preparation. All groups can be successfully analyzed by the same analytical techniques. If GC-MS is being used, then the most serious difference appears only in hydroxy-PAHs analysis, demanding derivatization. But we need to remember, than different ranges of concentration of PAHs and theirs oxidized forms forces using different limits of detection. However, it doesn't make a problem for used analytical methods with wide range of detection.

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