PD CEN/TR 16998:2016

BSI Standards Publication

Ambient air — Report on nitro- and oxy-PAHs — Origin, toxicity, concentrations and measurement methods

National foreword

This Published Document is the UK implementation of CEN/TR 16998:2016.

The UK participation in its preparation was entrusted by Technical Committee EH/2, Air quality, to Subcommittee EH/2/3, Ambient atmospheres.

A list of organizations represented on this committee can be obtained on request to its secretary.

Published by BSI Standards Limited 2016

ISBN 978 0 580 91098 2
ICS 13.040.20

Compliance with a British Standard cannot confer immunity from legal obligations.

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 31 December 2016.

Amendments/corrigenda issued since publication

Date	Text affected

TECHNICAL REPORT
RAPPORT TECHNIQUE
TECHNISCHER BERICHT

CEN/TR 16998

November 2016

ICS 13.040.20

English Version

Ambient air - Report on nitro- and oxy-PAHs - Origin, toxicity, concentrations and measurement methods

Air ambiant - Rapport sur les nitro- et oxy-HAP - Origine, toxicité, concentrations et méthodes de mesure

Außenluft - Bericht über Nitro- und Oxy-PAHs - Herkunft, Toxizität, Konzentrationen und Messverfahren

This Technical Report was approved by CEN on 21 October 2016. It has been drawn up by the Technical Committee CEN/TC 264.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. CEN/TR 16998:2016 E

Contents

Page

European foreword

This document (CEN/TR 16998:2016) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

Introduction

Nitro-PAHs and oxy-PAHs are found in ambient air samples and there are strong indications that they are as harmful as PAHS. Several compounds are classified as probably carcinogenic for humans (see Table in Annex A) and nitro-PAHs are reported to be strongly mutagenic. Photooxidation of volatile PAHs gives rise to the formation of secondary aerosols (Chan et al. 2009, Kautzman et al. 2010, Shakya and Griffin, 2010).

1-Nitropyrene and 2-nitrofluorene are discussed as marker compounds for diesel exhaust and other combustion processes. 2-Nitropyrene and 2-nitrofluoranthene are good marker substances for the formation of nitro-PAHs by secondary reactions.

This Technical Report presents the state of the art of the oxy- and nitro-PAHS topics.

1 Scope

This Technical Report is focused on the presence of nitro- and oxy-PAHs in ambient air. It describes how nitro- and oxy-PAH are formed, what typical concentrations are found, what is known about their toxicity, and what sampling and measurement techniques are available.

The conclusions of this report are that nitro- and oxy-PAHs concentrations are present in the atmosphere in levels that are of concern regarding their high toxicity. Information on the presence of these compounds in ambient air is as relevant as information about PAHs. Validated techniques for the measurement of nitro- and oxy-PAHs are available.

2 Symbols and abbreviations

DNA	Deoxyribonucleic acid
EI	Electron ionization
CD	Chemiluminescence detection
FD	Fluorescence detection
GC-MS	Gas chromatography – mass spectrometry
GC-NICI-MS	Gas chromatography – negative ion chemical ionization – mass spectrometry
HPLC	High performance liquid chromatography
HPLC-FD	HPLC – fluorescence detection
HPLC-CD	HPLC – chemiluminescence detection
IARC	International Agency for Research on Cancer
LC	Liquid chromatography
MS	Mass spectrometry
NICI	Negative ion chemical ionization
Nitro-PAHs	Nitrated polycyclic aromatic hydrocarbons
Oxy-PAHs	Oxygenated polycyclic aromatic hydrocarbons
PAHs	Polycyclic aromatic hydrocarbons
SPE	Solid phase extraction
ToF-MS	Time of flight mass spectrometry

3 Literature overview

3.1 Nitro-PAHs

3.1.1 Sources

3.1.1.1 General

Nitro-PAHs in the atmosphere originate mainly from combustion sources and are produced from both gas and heterogeneous phase reactions of the parent PAHs with atmospheric oxidants such as NO_3, N_2O_5, O_3, OH and peroxide radicals (Arey et al., 1986; Atkinson et al., 1990; Keyte et al., 2013; Pitts et al., 1985; Pitts Jr et al., 1978) in the presence of nitrogen oxides.

3.1.1.2 Direct emissions

Nitro-PAHs from direct emissions are formed by high temperature electrophilic nitration of PAHs with NO_2 during combustion processes (Nielsen, 1984). Nitro-PAHs have been observed in vehicle exhaust (particularly diesel), industrial emissions, waste incinerator emissions (DeMarini et al., 1996) and emissions from domestic residential heating/cooking (Kinouchi et al., 1988; Van Houdt, 1990). Nitro-PAHs are also emitted by wood burning but in relative low amounts due to low emissions of NO_2 during this type of combustion process (Alfheim and Ramdahl, 1984, Orasche et al., 2012; Orasche et al., 2013; Shen et al., 2011; Shen et al., 2012a; Shen et al., 2012b), (Environmental Health Criteria (EHC) 229, 2003 and references therein).

Recently, nitro-PAHs have also been quantified in exhausts of modern biodiesel engines (Karavalakis et al., 2010a; Karavalakis et al., 2010b; Karavalakis et al., 2011). Additionally, several studies have shown the formation nitro-PAHs *in situ* on catalytic diesel particulate filters as they act as chemical reactors for the nitration of PAHs (Carrara et al., 2010; Carrara and Niessner, 2011; Heeb et al., 2008). In this case, nitro-PAHs would be considered as primarily emitted. Gasoline emissions have also been reported but at lower concentration levels (Alsberg et al., 1985; Hayakawa et al., 1994; IARC, 1989; Sera et al., 1994).

Overall, 1-nitropyrene, 2-nitrofluorene and 2-nitrofluoranthene are the most abundant nitro-PAHs in diesel and gasoline exhaust (gas and particulate phases) (Beije and Möller, 1988; Environmental Health Criteria (EHC) 229, 2003; Finlayson-Pitts and Pitts Jr, 2000; Paputa-Peck et al., 1983; Schuetzle and Perez, 1983).

3.1.1.3 Atmospheric formation

Gas-phase reactions of parent PAHs are initiated by OH radicals during the day and by NO_3 radicals at night in the presence of NO_x producing nitro-PAHs, with subsequent partitioning to or depositing on the particulate matter. (Arey et al., 1986; Atkinson et al., 1989a; Atkinson et al., 1989b; Atkinson et al., 1990; Atkinson and Arey, 1994; Environmental Health Criteria (EHC) 229, 2003; Helmig and Harger, 1994; Keyte et al., 2013; Sasaki et al., 1997; Vione et al., 2006).

Recently, research studies reported that heterogeneous reactions may be the dominant process for loss of atmospheric PAHs and a significant source for nitro-PAHs in the atmosphere (Keyte et al., 2013; Kwamena et al., 2007; Perraudin et al., 2007; Pöschl et al., 2001). These reactions may dramatically differ from the homogeneous reactions in their rates, mechanisms, and products. Numerous studies showed results obtained with model particles (soot, sea salt, organic aerosol, silica, graphite or azelaic acid particles) coated artificially with single or a mixture of PAHs and their reaction with various oxidants as OH, NO_3, O_3 or NO_2 (Cazaunau et al., 2010; Esteve et al., 2003; Kwamena et al., 2007; Miet et al., 2009; Perraudin et al., 2005; Zhang et al., 2011).

Few studies reported results obtained with natural soot particles laboratory generated (liquid carburant burners) (Bedjanian et al., 2010; Kwamena and Abbatt, 2008), with natural ambient air particles (Ringuet et al., 2012b; Zimmermann et al., 2013) or with diesel engine exhaust particles (Esteve et al., 2006; Kamens et al., 1990; Nguyen et al., 2009; Rattanavaraha et al., 2011).

Mechanistic reaction schemes for gas phase formation of nitro-derivatives of fluoranthene and heterogeneous formation of isomeric nitro-benzo[*a*]pyrenes are shown in Figure 1 and 2, respectively.

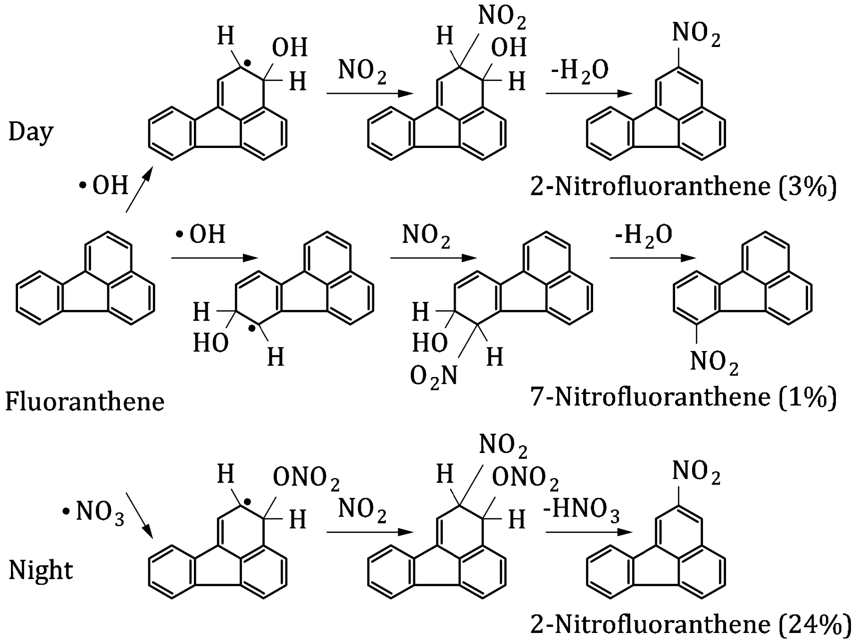


Figure 1 — Oxidation mechanisms of fluoranthene by OH during the day (Arey, 1998) and by NO_3 during the night (Atkinson and Arey, 1997)

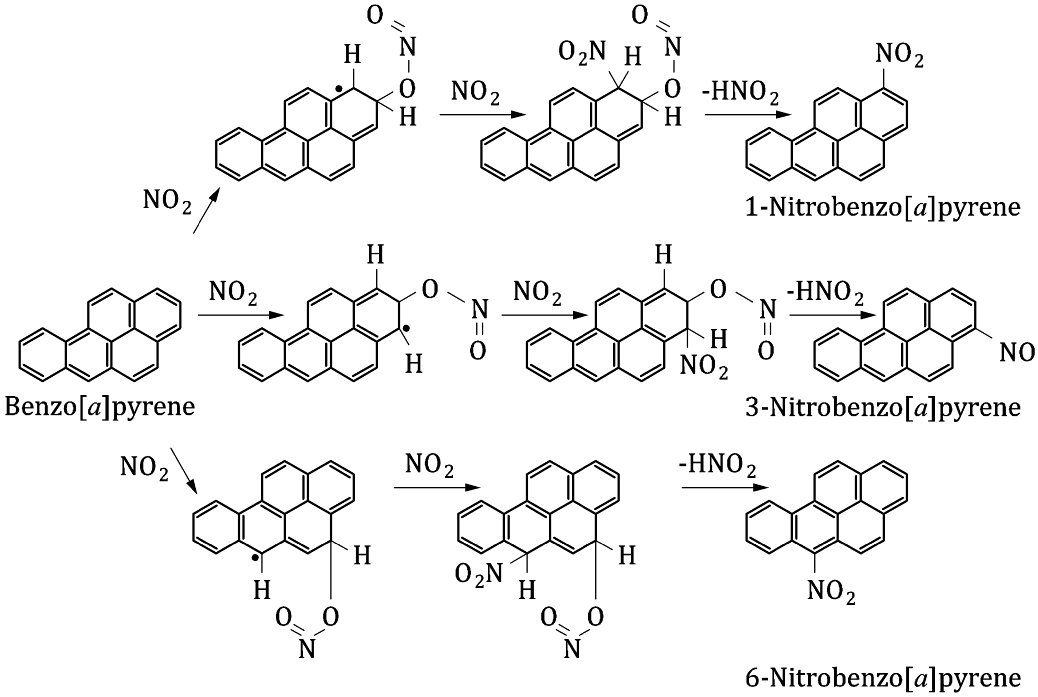


Figure 2 — Mechanism proposed for the nitration of benzo[a]pyrene (Cazaunau et al., 2010)

22-Nitrofluoranthene and 2-nitropyrene are the most abundant substances formed by gas phase reaction of PAHs with oxidants and oxides of nitrogen. A high 2-nitrofluoranthene/1-nitropyrene ratio is a good indicator for the secondary formation of nitro-PAHs (Albinet et al., 2007b; Albinet et al., 2008; Arey et al., 1989; Atkinson and Arey, 1994; Bamford and Baker, 2003; Reisen and Arey, 2005; Mariano et al., 2000; Ringuet et al., 2012a; Ringuet et al., 2012c; Zielinska et al., 1989; Zimmermann et al., 2012).

3.1.2 Concentrations, gas/particle partitioning and size distribution

Overall, in continental areas (urban, sub-urban and rural areas), nitro-PAHs atmospheric concentrations are one or two orders lower than PAHs atmospheric concentrations. Nitro-PAHs concentrations are in the range of 0,1 to 1000 pg·m^{-3} in both, gaseous and particulate phases (e.g. Albinet et al., 2007; Albinet et al., 2008a; Bamford and Baker, 2003; Ciccioli et al., 1995; Ciccioli et al., 1996; Feilberg et al., 2001; Feilberg and Nielsen, 2001; Hayakawa et al., 1995a; Hayakawa et al., 2002; Maria del Rosario Sienra, 2006; Valle-Hernandez et al., 2010; Wang et al., 2011). Nitronaphthalene isomers in gas phase and 2-nitrofluoranthene and 9-nitroanthracene in particulate phase are generally the most abundant nitro-PAHs and account for about 15 % to 50 % of the total nitro-PAHs concentrations.

Table 1 summarizes the reported concentration ranges of the most important nitro-PAHs.

Table 1 — List of concentration ranges of important nitro-PAHs in ambient air

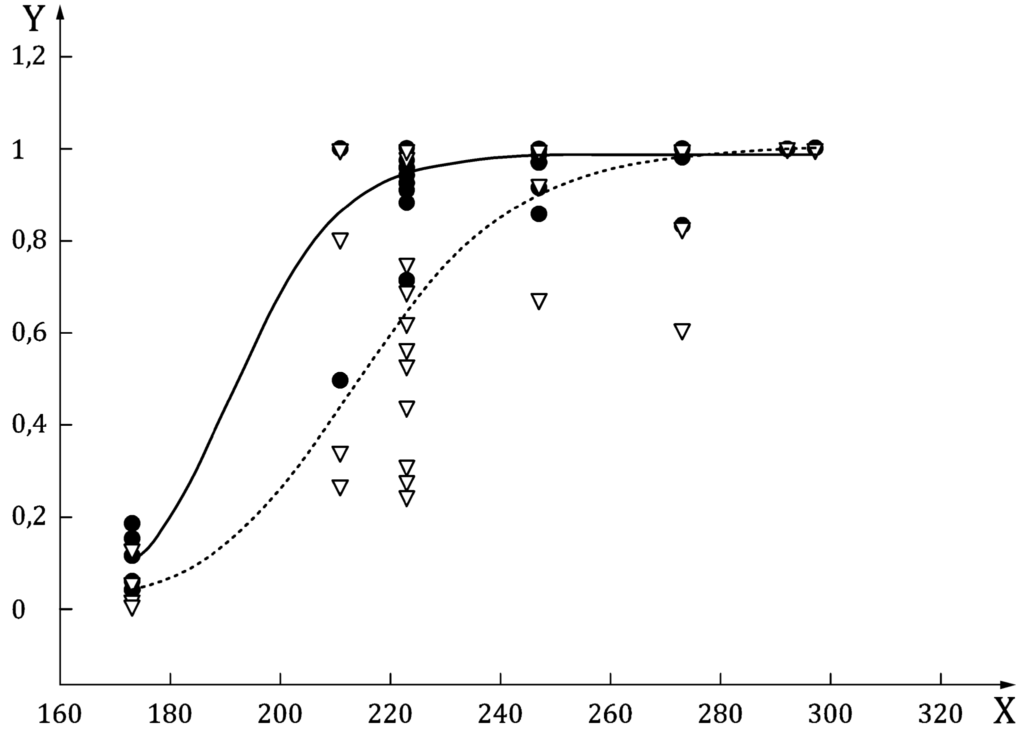
Substance	Concentration range ng/m^3		
	Traffic	Urban	Rural/remote
1-Nitronaphthalene	0,07 – 0,2 (n, o)	0,2 (h, n)	0,01 – 0,2 (h, n)
2-Nitronaphthalene	0,03 – 0,06 (n, o)	0,12 (h, n)	0,01 – 0,1 (h, n)
2-Nitrofluorene	0,001 – 0,021 (l, n)	0,05 – 0,4 (d, g, h, n)	0,001 – 0,005 (h, n)
9-Nitroanthracene	0,002 – 0,01 (n, o)	0,03 – 0,2 (a, c, d, g, h, j, l, n)	0,002 – 0,03 (g, h, n)
3-Nitrophenanthrene	0,007 – 0,1 (n, o)	0,001 – 0,02 (l, o)	0,0007 – 0,001 (o)
9-Nitrophenanthrene	0,005 – 0,05 (l, n)	0,01 – 0,3 (h, i, n)	0,0002 – 0,03 (h, n)
2-Nitrofluoranthene	0,03 – 0,2 (l, o)	0,03 – 2 (a, e, f, g, j, l, m, n)	0,02 – 0,03 (e, k, n)
3-Nitrofluoranthene	0,018 (i)	0,003 – 0,1 (d, j, l)	0,01 (e)
1-Nitropyrene	0,02 – 0,2 (l, o)	0,01 – 2 (a, b, e, f, g, h, j, l, n)	0,0006 – 0,01 (e, h, n, o)
2-Nitropyrene	0,007 – 0,2 (n, o)	0,01 – 0,04 (a, h, j, n)	0,001 – 0,08 (e, h, k, n)
4-Nitropyrene	0,02 – 0,03 (o)	0,001 (h, n)	0,0006 (h, n)
1,3-Dinitropyrene	0,0009 – 0,02 (n, o)	0,01 – 0,03 (d, h, n)	0,004 (n)
1,6-Dinitropyrene	up to 0,0002 (o)	0,01 (d, h, n)	0,0001 – 0,004 (n)
7-Nitrobenzo[*a*]anthracene	0,005 – 0,01 (n, o)	0,004 – 0,3 (a, h, l, m)	0,002 (h, n)
6-Nitrochrysene	0,003 – 0,004 (n, o)	up to 1,5 (b, h, j, l, n)	0,0003 – 0,002 (e, h, n)
6-Nitrobenzo[*a*]pyrene	0,007 – 0,01 (l, n)	0,001 – 0,01 (h, n)	0,0002 – 0,005 (n, o)
3-Nitrobenzanthrone	0,001 – 0,01 (l)	–	–

a) Atkinson et al. (1988)	Glendora (USA)
b) Matsushita and Ida (1986)	Tokio (Japan)
c) Hunt and Meisel (1995)	Fresno (USA)
d) Tokiwa et al. (1990a)	Sapporo (Japan)
e) Vasconcellos et al. (1998)	Alta Floresta (Brazil)
f) Wilson et al. (1995)	Houston (USA)
g) Berlincioni et al. (1995)	Florence (Italy)
h) Albinet et al. (2007)	Marseille (France)
i) Mücke et al. (2009)	Munich (Germany)
j) Di Filippo et al. (2010)	Rome (Italy)
k) Tsapakis et al. (2007)	Finokalia (Greece)
l) Valle-Hernandez et al. (2010)	Mexico City (Mexico)
m) Wang et al. (2011)	Bejing (China)
n) Albinet et al. (2008a, 2008b)	Chamonix, Maurienne (France)
o) Ringuet et al. (2012)	Paris (France)

Nitro-PAHs gas/particle partitioning is poorly documented (Albinet et al., 2007; Albinet et al., 2008a; Araki et al., 2009; Atkinson and Arey, 1994; Bamford and Baker, 2003; Dimashki et al., 2000; Huang et al., 2014; Reisen and Arey, 2005; Wilson et al., 1995). 2-Rings nitro-PAHs (nitronaphthalenes) are mainly associated to the gaseous phase. Nitro-PAHs with 4 or more rings are mainly bound to particles. 3-ring nitro-PAHs are partitioned in both gaseous and particulate phase. Due to their relative low vapour pressures ($<10^{-4}$ Pa at 20 °C, Yaffe et al., 2001), nitro-PAHs resulting from gas phase reactions condense immediately to ambient particles (Fan et al., 1995). Gas/particle partition is depending on their vapour pressure and the ambient conditions as temperature but also on their origin (primary or secondary) (Albinet et al., 2007; Albinet et al., 2008a; Wilson et al., 1995).

Very few papers showed results about the particle size distribution of nitro-PAHs in ambient air (Albinet et al., 2008b; Cecinato et al., 1999; Di Filippo et al., 2010; Hayakawa et al., 1995a; Hayakawa et al., 1995b; Jinhui and Lee, 2000; Kawanaka et al., 2004; Kawanaka et al., 2008; Ringuet et al., 2012a; Teixeira et al., 2011). Overall, nitro-PAHs are mainly associated (>90 %) to the fine particle fraction ($D_p < 1$ µm) and about 20 % are associated to the ultrafine particle fraction ($D_p < 0,1$ µm). These results are important information regarding the risk assessment because nitro-PAHs can thus penetrate deeply into the lung.

Nitro-PAHs react with hydroxide and nitrate radicals, with ozone and they are decomposed by photolysis. As a result the atmospheric half life time of nitro-PAHs ranges from less than an hour to several days, depending on atmospheric conditions like temperature, sunlight intensity, on their structure and on the concentrations of reactive compounds in the air (Keyte et al. 2013).



Key

● Winter

▽ Summer

X Molecular weight in g/mol

Y Fraction in particulate phase

Figure 3 — Nitro-PAHs gas/particle partitioning according to their molecular weight (Albinet et al., 2008a)

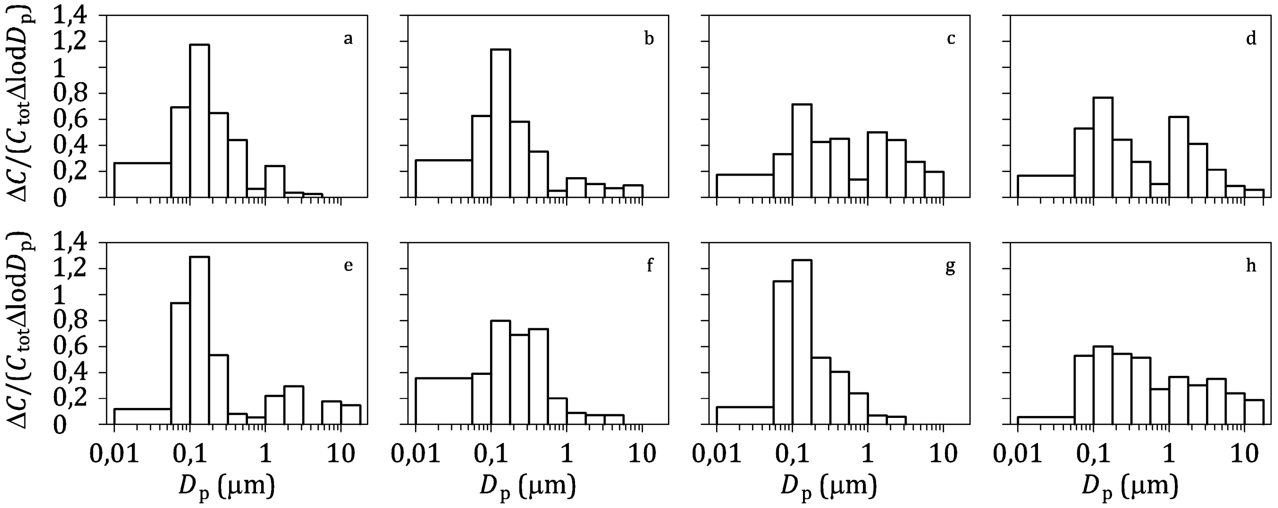


Figure 4 — Particle size distribution of 4 nitro-PAHs on a traffic (a – d) and suburban (e – h) site in the Paris region (France) (Ringuet et al., 2012c). a, e: 1-nitronaphthalene; b, f: 9-nitroanthracene; c, g: 2+3-nitrofluoranthene; d, h: 1-nitropyrene

3.1.3 Toxicity/mutagenicity

As they act as direct mutagens the mutagenic potential of nitro-PAHs can be 100 000 times greater than that of PAHs (Durant et al., 1996; Durant et al., 1998; Enya et al., 1997; Hannigan et al., 1998; Lewtas et al., 1990; Schuetzle, 1983; Landvik et al., 2007; Øvrevik et al., 2010). Four-ring nitro-PAHs seem to be the most toxic substances (Durant et al., 1996; Durant et al., 1998; Finlayson-Pitts and Pitts Jr, 1986). Overall, results from mutagenicity tests on bacteria (Ames test, *Salmonella typhimurium*) and on human cells (h1A1v2 cells) showed that 3,6-dinitrobenzo[*a*]pyrene, 3,7-dinitrofluoranthene, 3,9-dinitrofluoranthene, 6-nitrochrysene, 1- and 4-nitropyrene, 1,6-dinitropyrene and 1,8-dinitropyrene (the most powerful mutagens described in the literature) had the highest mutagenic activities (Environmental Health Criteria (EHC) 229, 2003; NTP, 2011; Enya et al., 1997; Pedersen et al., 2004; Pedersen et al., 2005).

Nitro-PAHs contributions to the mutagenic and/or carcinogenic activity of atmospheric inhalable particles were evaluated in the range 14 % to 50 % by different authors (Albinet et al., 2008a; Bandowe et al., 2014; Finlayson-Pitts and Pitts Jr, 2000; Kawanaka et al., 2008; Taga et al., 2005).

Substances with a coplanar nitro group are more carcinogenic than those with a perpendicular nitro-group. Dinitro-PAHs generally are more mutagenic than the mono-substituted compounds.

3.1.4 Carcinogenicity

Since the 1960s, evidence has increasingly supported the theory that chemical carcinogens (e.g. PAHs and nitro-PAHs) are metabolized via oxidative pathways to produce electrophilic reactive intermediates (e.g. nitrenium ions and epoxides) that react covalently with DNA and possibly with other cellular nucleophiles. Nitro-PAHs seem to be less carcinogenic than their parent PAHs (EHC 229, 2003; IARC, 2013; NTP, 2011; Benbrahim-Talaa et al., 2012). Different pathways seem to be possible for carcinogenic activity. If the nitro-PAHs contain a “bay region” similar to benzo[*a*]pyrene and benzo[*a*]anthracene their carcinogenicity is similar to the mechanisms described for the non-substituted substances: After formation of an dihydroepoxide in the “bay region” this reactive intermediate forms DNA adducts which are considered to be the first step causing carcinogenicity. If the nitro group of these substances is oriented parallel to the aromatic core of the substances, their carcinogenicity is not much lower than that of the non-substituted substances, but a perpendicular orientation of the nitro group largely attenuates the carcinogenicity of the compounds (Fu et al., 1994; Fu et al., 1998; Vogt et al., 2009; McDonald et al., 2004).

For some nitro-PAHs another pathway of carcinogenic action is postulated (Fu et al., 1994): The nitro group is partly reduced to a hydroxylamine derivative which after esterification (e.g. acetylation) forms a nitrenium ion, which reacts with DNA to form an adduct, which can cause carcinogenicity.

Additionally nitro-oxy-PAHs seem to be more toxic than oxy-PAHs or nitro-PAHs (Helmig et al., 1992a; Helmig et al., 1992b). For example, 3-nitrobenzanthrone is described as one of the the most potent mutagens and a potential carcinogen identified in diesel exhaust and ambient particulate matter (Arlt, 2005; Enya et al., 1997; Feilberg et al., 2002; Nagy et al., 2005; Phousongphouang and Arey, 2003). A list of the classification of the carcinogenicity of several nitro- and oxy-PAHs is given in Annex B.

3.1.5 Measurement

3.1.5.1 Sampling from ambient air

Nitro-PAHs with 4 rings or more are particle bound. For these substances sampling procedures for particulate matter (e.g. PM_{10} and $PM_{2,5}$, as described in EN 12341) are suitable. In order to collect more volatile compounds, a combination of a filter with, e.g. PUF as described in ISO 12884 is necessary.

Reaction of PAHs with oxidants in combination with nitrous oxides may lead to positive artefacts during sampling. Rearrangements of the nitro groups of the compounds during sampling are also possible.

The formation of nitro-PAHs via heterogeneous reactions with only nitrogen oxides has been shown to be unfounded in case of ambient air sampling (Arey et al., 1988; Dimashki et al., 2000). Only at elevated temperatures and extremely high concentrations of NO_2 direct nitration of PAHs is possible (Carrara et al., 2010; Carrara et al., 2011).

Studies delivered different results about the reactions of nitro-PAHs during sampling, possibly leading to artefacts, but until now no clear results about reactions of nitro-PAHs during sampling and about methods to inhibit these reactions have been published.

3.1.5.2 Analysis

A review paper on the analysis of nitro-PAHs in environmental samples was proposed by Zielinska and Samy (Zielinska and Samy, 2006). The analytical procedure of collected samples includes an extraction step prior to nitro-PAHs quantification. Several extraction procedures are reported (Soxhlet, microwaves, pressurized liquid extraction, sonication) using different solvents or solvent mixtures (dichloromethane, hexane, toluene, acetone). A purification step (e.g. SPE (solid phase extraction)) shall also be included. Alternatively to solvent extraction methods, SFE (supercritical fluid extraction) using pure CO_2 is also reported in numerous studies (Castells et al., 2003; Lewis et al., 1995). The use of solvent-free extraction techniques was also reported in different papers with thermal-desorption (TD) coupled with GC-ToF-MS or GC × GC-ToF-MS (Fushimi et al., 2012; Orasche et al., 2011) and laser desorption/ionization coupled to ToF-MS (LD-LI-ToF-MS) (Dotter et al., 1996). Finally, as an alternative to traditional procedures, recently Albinet et al. (2014) reported the use of QuEChERS-like (Quick Easy Cheap Effective Rugged and Safe) extraction approach for the analysis of nitrated and oxygenated PAHs.

Analysis of nitro-PAHs is generally achieved using GC-MS, GC-NICI-MS, HPLC-FD (fluorescence detection), HPLC-CD (chemiluminescence detection), LC-MS, LC-MS-MS.

Because of its great sensitivity and selectivity towards the nitro group, GC-NICI-MS using methane as the reactant gas minimizes the analytical interferences from co-eluted compounds by significantly improving signal-to-noise ratios (Bezabeh et al., 2003). Relative to GC-MS in EI ionization mode, a sensitivity improvement approaching two orders of magnitude could be obtained. Limits of detection in the lower picogram and femtogram ranges have been reported for this method (Albinet et al., 2006; Bezabeh et al., 2003). Actually, this analytical technique constitutes probably the best cost/performance compromise for the analysis of nitro-PAHs in ambient air samples. Maintenance requirement are mainly linked to the fouling of the MS source (due to the use of reagent gas for ionization) inducing a loss of sensitivity, but progress has been made enhancing the lifetime of the MS source.

HPLC-FD after reduction of the compounds to the corresponding amines or HPLC-CD is also widely used notably by Japanese research teams (e.g. Hayakawa et al., 1999; Hayakawa, 2000; Kawanaka et al., 2008; Nassar et al., 2011; Ohno et al., 2009; Tang et al., 2005, see also references in Zielinska and Samy, 2006). Greater precision and selectivity is obtained by increased automation of these kinds of analytical techniques. Limits of detection in the range of 1 pg to 10 pg injected have been reported for this method (Hayakawa et al., 1999; Hayakawa, 2000; Kawanaka et al., 2008; Ohno et al., 2009; Schauer et al., 2003; Tang et al., 2005; Zielinska and Samy, 2006 and references therein). The complexity and maintenance requirements of these kinds of systems (i.e. time automated switching valves, multiple plumbing components, and consumables), does implicate a need for highly specialized procedures with customized components and protocols.

The use of LC-MS and LC-MS-MS is also reported in several papers (e.g. Mirivel et al., 2010; Schauer et al., 2004; Zielinska and Samy, 2006 and references therein) but the sensitivity of this technique is still not optimal for nitro-PAHs analysis. Detection limits are 3 to 100 higher (5 pg to 100 pg injected) than those reported for GC-NICI-MS analytical systems. Only the possibilities of unknown species are a significant advantage of this method but the investment and working costs are really higher than for the other analytical techniques.

An example of an SOP dealing with sampling and analysis of nitro- and oxy-PAHs are given in Annex A.

3.2 Oxy-PAHs

3.2.1 Sources

3.2.1.1 General

Oxy-PAHs (ketones, aldehydes, hydroxy-PAHs) are both directly emitted from combustion processes and formed in the atmosphere as by-products of the photolysis of parent PAHs or photochemical reaction between parent PAHs and atmospheric oxidants (Vione et al., 2004; Yu, 2002).

3.2.1.2 Direct emissions

Major direct sources are diesel and gasoline combustions, biomass burning, waste combustion, coal and fuel burning, and production of charcoal (Abas et al., 1995; Akimoto et al., 1997; Cho et al., 2004; Choudhury, 1982; Leoz-Garziandia et al., 2000; Levsen, 1988; Orasche et al., 2012; Orasche et al. 2013; Ramdhal, 1983; Schauer et al., 1999, 2001, 2002; Schulze et al., 1984; Shen et al., 2011; Shen et al., 2012a; Shen et al., 2012b; Walgraeve et al., 2010 and references therein).

3.2.1.3 Atmospheric formation

Oxy-PAHs can be formed from PAHs via photochemical reactions and reactions with O_3, OH and NO_3 radicals Keyte et al., 2013). Given the partitioning of PAHs between the gaseous and particulate phases, transformation processes can take place in both phases. Reactions involving OH are considered to play a major role in gas phase reactions (Barbas et al., 1996; Bunce et al., 1997; Calvert et al., 2002; Vione et al., 2004; Wang et al., 2007). Additionally, several studies show the formation of Oxy-PAHs via heterogeneous reaction processes (Perraudin et al., 2007; Pöschl et al., 2001; Ringuet et al., 2012b). For example, major identified products of the reaction between ozone and anthracene adsorbed on silica particles were 1,1’-biphenyl-2,2’-dicarboxaldehyde, anthrone and 9,10-anthraquinone (Perraudin, 2004). Nevertheless, particle associated PAHs containing more than five rings are less susceptible to reaction with gaseous reactive radicals. Nevertheless, they can also undergo a wide variety of transformation processes, but often with slower kinetics than in the gas phase. Especially direct photolysis and photolysis in the presence of photosensitizers (e.g. ketones or aromatic carbonyls) play a significant role for these compounds (Yu, 2002). The wide electron delocalization of PAHs enables them to absorb sunlight, so that irradiation under atmospheric conditions may lead to photooxidation (Vione et al., 2004; Yu, 2002).

Examples of reaction pathways of benzo[*a*]pyrene with ozone and the photooxidation of anthracene are presented in Figures 5 and 6.

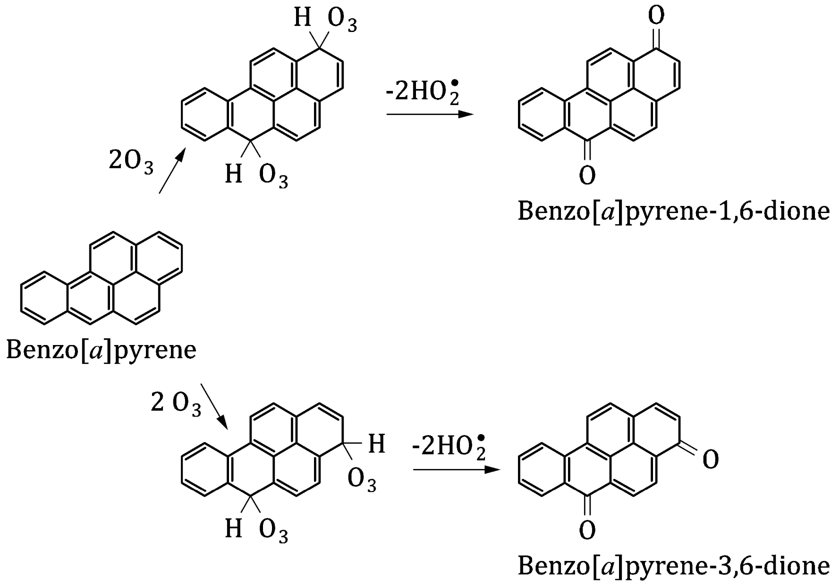


Figure 5 — Reaction pathways of benzo[*a*]pyrene with ozone (Vione et al., 2004)

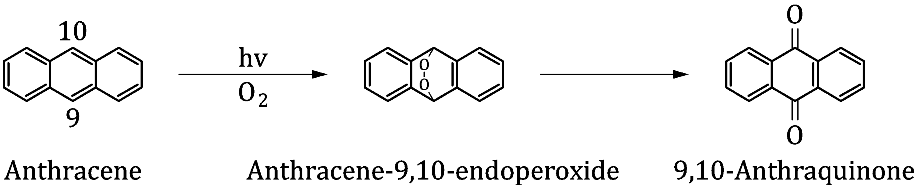


Figure 6 — Photooxidation of anthracene in aqueous solution (Yu, 2002)

3.2.2 Concentrations, gas/particle partitioning and size distribution

Oxy-PAHs atmospheric concentrations are in the same order as PAHs atmospheric concentrations in continental areas (urban, sub-urban and rural areas). Concentrations range from 10 to 10000 pg·m^{-3} in both, gaseous and particulate phases (e.g. Albinet et al., 2007; Albinet et al., 2008a; Allen et al., 1997; Barrado et al., 2012a; Barrado et al., 2012b; Barrado et al., 2012c; Eiguren-Fernandez et al., 2008a; Eiguren-Fernandez et al., 2008b; Enya et al., 1997; Feilberg et al., 2002; Fraser et al., 1998; Hawthorne et al., 1992; Kojima et al., 2010; König et al., 1983; Ligocki and Pankow, 1989; Liu et al., 2006; Niederer, 1998; Schnelle-Kreis et al., 2001; Wang et al., 2011; Wilson et al., 1995; Yassaa et al., 2001). Overall, ketones and quinones (specifically 9-fluorenone, 9,10-anthraquinone, 9,10-phenanthraquinone, benzanthrone) are the most abundant oxy-PAHs in ambient air. Hydroxy-PAHs were detected at lower concentration levels (10 pg·m^{-3} to 500 pg·m^{-3}) (Barrado et al., 2012a; Barrado et al., 2012b; Barrado et al., 2012c; Simoneit et al., 2007).

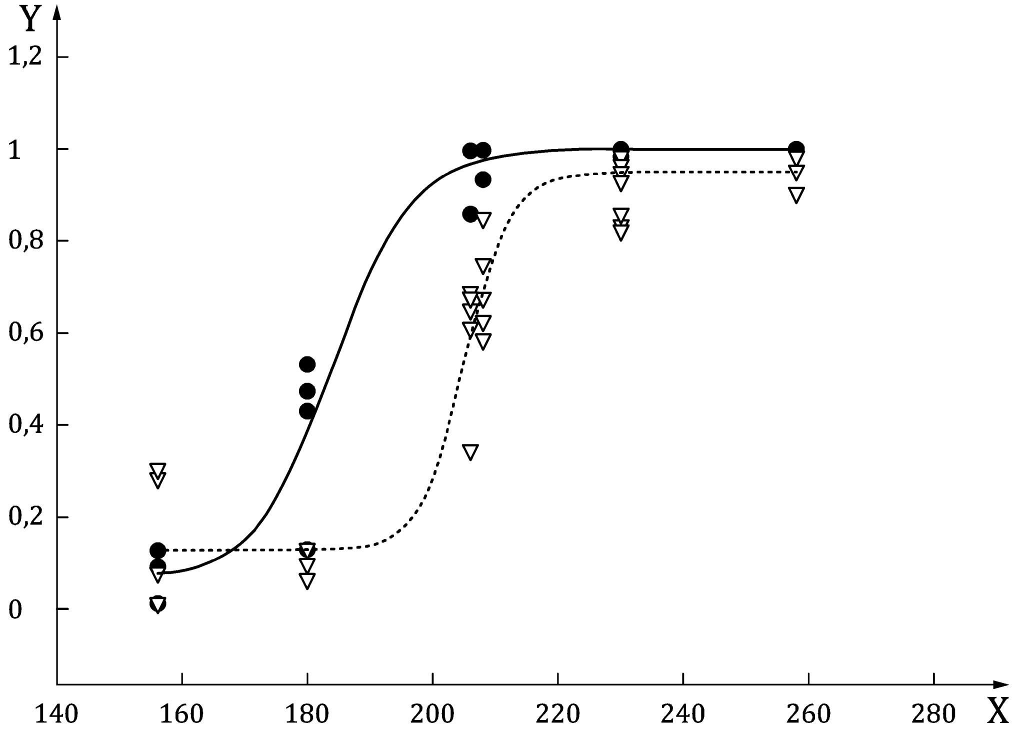
Oxy-PAHs gas/particle partitioning is poorly documented (Alam et al., 2013; Albinet et al., 2007; Albinet et al., 2008a; Eiguren-Fernandez et al., 2008b; Fraser et al., 1998; Huang et al., 2014; Leoz-Garziandia et al., 2000; Wilson et al., 1995). The fraction of oxy-PAHs associated with the particle phase is strongly dependent on the molecular weight and on the ambient conditions (temperature). The lightest compounds (number of aromatic rings ≤ 2) are detected mainly in the gas phase whereas the compounds with a number of aromatic rings ≥ 4 are detected in the particle phase; three-ring compounds can be found in both phases (Albinet et al., 2007; Albinet et al., 2008a).

Oxy-PAHs particle size distribution in ambient air was only reported by few authors (Albinet et al., 2008b; Allen et al., 1997; Allen, 1997; Ladji et al., 2009; Ringuet et al., 2012a). Oxy-PAHs are mainly associated (>90 %) to the fine particle fraction ($D_{\mathrm{p}} < 1$ µm) that penetrates deeper into the organism.

Table 2 — List of concentration ranges of important oxy-PAHs in ambient air

Substance	**Traffic** ng/m^3	**Urban** ng/m^3	**Rural/remote** ng/m^3
1-Naphthaldehyde	0,006 – 7 (a, b, d, n)	up to 2 (b, c)	0,15 – 0,6 (d)
Naphthalene-1,2-dione	–	up to 1,1 (e, f)	–
Naphthalene-1,4-dione	–	up to 4 (c, e, f, g, h)	–
Benzophenone	–	0,2 – 0,5 (j, h)	–
9*H*-Fluoren-9-one	0,07 – 3,6 (a, b, d, n)	0,01 – 4 (b, c, h, k)	0,2 – 11 (c, d)
1*H*-Phenalen-1-one	–	0,4 – 2,5 (i, l, m, q)	0,03 (i)
10*H*-Anthracen-9-one (Anthrone)	–	0,3 – 0,8 (h, i)	–
Anthracene-9,10-dione	0,6 – 3,6 (d, n)	0,01 – 3,6 (d, i, k, m)	0,18 (d)
Phenanthrene-9-carboxaldehyde	0,1 – 7,2 (a, b, d, n)	0,3 (b, h)	0,01 – 0,5 (c, d)
11*H*-Benzo[*a*]fluoren-11-one	0,16 – 1,6 (b, d, n)	0,2 – 2,7 (b, i)	0,02 – 0,03 (c, d)
11*H*-Benzo[*b*]fluoren-11-one	0,15 – 1,5 (b, d, n)	0,2 – 1,7 (b, i)	0,01 – 0,5 (c, d)
7*H*-Benz[*de*]anthracen-7-one (Benzanthrone)	0,05 – 2 (b, d, n)	up to 2,6 (b, o, p, q)	0,02 – 1,7 (c, d)
Benzo[*a*]anthracene-7,12-dione	0,04 – 0,55 (d, n)	0,1 – 1,3 (b, e, h, l, q)	0,01 – 0,6 (c, d)
Chrysene-1,4-dione	–	up to 0,5 (e)	–
Chrysene-5,6-dione	–	0,001 – 0,8 (r)	–
Pyrene-1-carboxaldehyde	–	2,6 – 4,7 (h)	–
Pyrene-4,5-dione	–	0,3 – 0,7 (e)	–
Cyclopenta[*def*]phenanthren-4-one	–	0,01 – 0,3 (l)	–
6*H*-benzo[*cd*]pyren-6-one	–	up to 2 (h, l)	–
Benzo[*a*]pyrene-1,6-dione	–	0,001 – 0,08 (r)	–
Benzo[*a*]pyrene-3,6-dione	–	0,001 – 0,08 (r)	–
Benzo[*a*]pyrene-6,12-dione	–	0,001 – 0,08 (r)	–
a) Oda et al. (2001)	Kurashaki (Japan)		
b) Albinet et al. (2007a)	Marseille (France)		
c) Bandowe et al. (2014)	Xián (China)		
d) Albinet et al. (2008a)	Chamonix, Maurienne (France)		
e) Chung et al. (2006)	Fresno (USA)		
f) Valavanidis et al. (2006)	Athens (Greece)		
g) Tsapakis et al. (2002)	Santiago, Temuco (Chile)		
h) Sienra (2006)	Santiago (Chile)		
i) Delhomme et al. (2008)	Tempe (USA)		

j) Neusuess et al. (2000)	Melpitz (Germany)
k) Castells et al. (2003)	Barcelona (Spain)
l) Schnelle Kreis et al. (2005)	Munich (Germany)
m) Liu et al. (2006)	Augsburg (Germany)
n) Ringuet et al. (2012a)	Paris (France)
o) Yassaa et al. (2001)	Algier (Algeria)
p) Sklorz et al. (2007a)	Munich (Germany)
q) Park et al. (2000)	Seoul (Korea)
r) Lintelmann et al. (2006)	Munich (Germany)



Key

● Winter

▽ Summer

X Molecular weight in g/mol

Y Fraction in particulate phase

Figure 7 — Oxy-PAHs gas/particle partitioning according to their molecular weight (Albinet et al., 2008a)

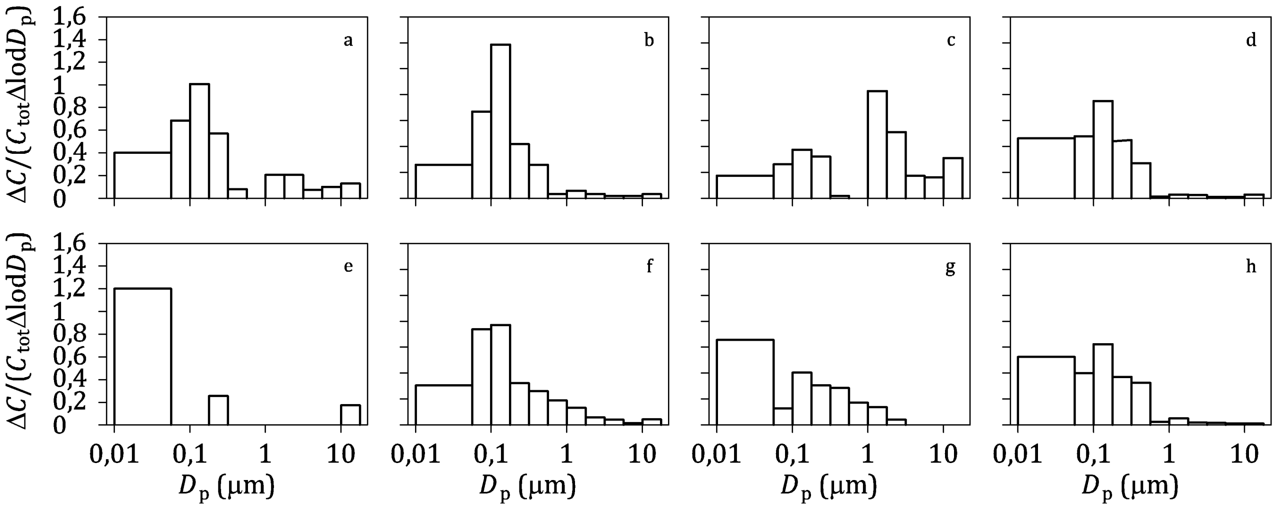
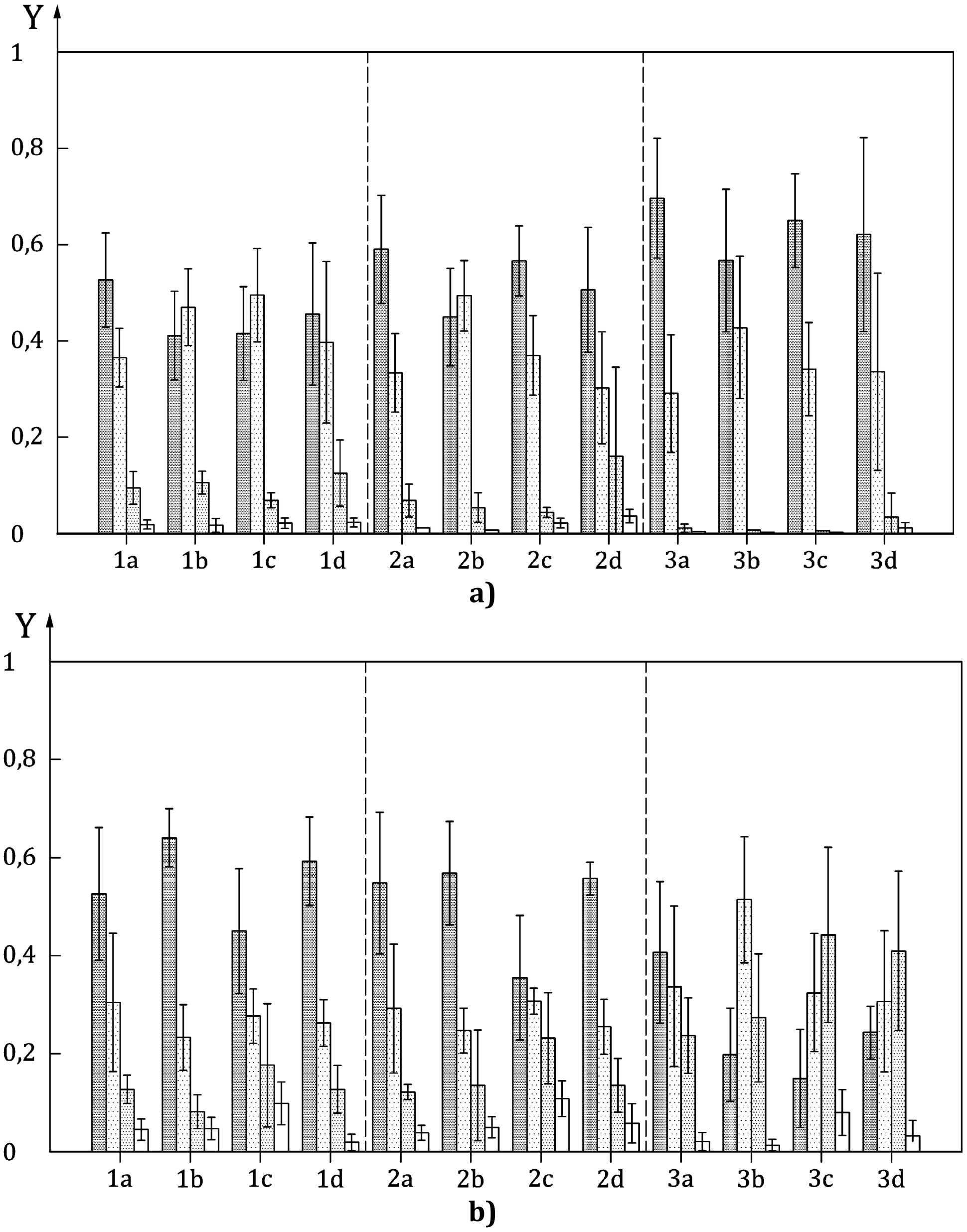


Figure 8 — Particle size distribution of 4 oxy-PAHs on a traffic (a – d) and suburban (e – h) site in the Paris region (France) (Ringuet et al., 2012c). a, e: 9,10-Anthraquinone; b, f: Benzo[*a*]fluorenone; c, g: Benzo[*b*]fluorenone; d, h: Benz[*a*]anthracene-7,12-dione



Key

1a, 1b	PAHs Chamonix valley
1c, 1d	PAHs Maurienne valley
2a, 2b	oxy-PAHs Chamonix valley
2c, 2d	oxy-PAHs Maurienne valley
3a, 3b	nitro-PAHs Chamonix valley
3c, 3d	nitro-PAHs Maurienne valley
Y	Fraction in size class

▓	0,01 µm – 0,39 µm
░	0,39 µm – 1,3 µm
▒	1,3 µm – 4,2 µm
☐	4,2 µm – 50 µm

Figure 9 — Average PAHs, oxy-PAHs and nitro-PAHs concentration fractions in the different particle size classes for different sampling site typologies located in the French Alpine valleys (upper figure: winter 2002/2003, lower figure: summer 2003). The error bars show the standard deviation from the weekly average of the sampling campaign (*n* = 7) (Albinet et al., 2008b)

3.2.3 Toxicity

Only few toxicological impacts of oxy-PAHs are documented. Studies mainly focus on compounds used for industrial or medical applications. The mechanisms underlying their toxicity are complex and far from fully understood (Lundstedt et al., 2007; Walgraeve et al., 2010 and references therein; Xia et al., 2004). Data on mutagenic effects mainly resulted from tests on bacteria (Ames test) and human cells (h1A1v2) (Durant et al., 1996; Durant et al., 1998; Pedersen et al., 2004; Pedersen et al., 2005). With respect to their human health effects, oxy-PAHs are considered to be more acute-toxic than their parent PAHs because of their direct mutagenic potency, whereas PAHs require first an enzymatic activation (Durant et al., 1996; Durant et al., 1998; Pedersen et al., 2004; Pedersen et al., 2005; Yu, 2002). Among the studied oxy-PAHs, ketones, quinones and three-ring oxy-PAHs seemed mutagens (e.g. benzanthrone, benzo[*a*]fluorenone, benzo[*b*]fluorenone). Tests on human cells showed that 6*H*-benzo[*cd*]pyren-6-one and anthanthrenequinone seemed highly mutagenic (Pedersen et al., 2004; Pedersen et al., 2005). 9,10-Anthraquinone is classified as possibly carcinogenic to humans (2B, IARC, 2012).

Some nitro-oxy-PAHs are known as strong mutagenes such as 3-nitrobenzanthrone.

Nitro-oxy-PAHs seem to be more toxic than nitro-PAHs or oxy-PAHs (Helmig et al., 1992a; Helmig et al., 1992b). As for example, 3-nitrobenzanthrone was described as one of the most potent mutagens and a potential carcinogen identified in diesel exhaust and ambient particulate matter (Arlt, 2005; Enya et al., 1997; Feilberg et al., 2002; Nagy et al., 2005; Phousongphouang and Arey, 2003). However, 3-nitrobenzanthrone itself undergoes extensive atmospheric rearrangements to the less mutagenic isomer 2-nitrobenzanthrone. Thus the level of 3-nitrobenzanthrone is highest near the source of emission, but only relatively low in general ambient air (Phousongphouang and Arey, 2003). A list of the classification of the carcinogenicity of several nitro- and oxy-PAHs is given in Annex B.

3.2.4 Measurement

A recent review on the analysis of oxy-PAHs in environmental samples was published by Walgraeve et al. (Walgraeve et al., 2010). As for nitro-PAHs, oxy-PAHs analytical procedures are generally solvent based methods including extraction and purification steps. Various extraction methods have been reported (Soxhlet extraction, microwave extraction, pressurized liquid extraction, sonication) with different solvents or solvent mixtures (dichloromethane, methanol, acetone, hexane).

The use of thermal desorption (TD) methods for extraction, coupled to chromatographic methods for separation and analysis of oxy-PAHs, was also reported in the literature. Advantages are reduced extraction times, the elimination of solvent use, which fits within the concept of green analytical chemistry and the elimination of the sample preparation steps (Orasche et al., 2011; Fushimi et al., 2012). Recently Albinet et al. (2014) report the use of QuEChERS-like extraction approach as an alternative procedure for the analysis of nitrated and oxygenated PAHs.

Analysis is generally achieved using GC-MS (e.g. Allen et al., 1997; Kojima et al., 2010), GC-NICI-MS, LC-MS or LC-MS-MS analytical systems) and includes a purification step on solid phase extraction or by HPLC. HPLC-Fluorescence detection analytical procedures are also reported in the literature (e.g. Barrado et al., 2008). For gas chromatography methods, higher sensibility and selectivity is obtained using negative chemical ionization in mass spectrometry (GC-NICI-MS) (Albinet et al., 2006; Wang et al., 2011). Femtograms injected (0,03 pg to 0,07 pg) have been reported as limits of detection for this method (Albinet et al., 2006). For GC-MS using electron impact ionization, a derivatization step (e.g. using BSTFA reagent (*N*,*O*-bis-trimethylsilyltrifluoroacetamide)) could be included in order to improve the sensitivity and the separation of hydroxy-PAHs (Simoneit et al., 2007). Identification of unknown species could be achieved using GC-MS in electron impact mode (with or without derivatization step procedure) while it is not possible using a soft ionization technique as chemical ionization. Compared to GC-MS techniques, LC-MS and LC-MS-MS offer several advantages, especially if the target compounds are thermally labile, have low vapour pressures or have highly polar functional groups (e.g. Delhomme et al., 2008; Mirivel et al., 2010; Schauer et al., 2004; Walgraeve et al., 2012). Limits of detection reported for these methods are 10 to 1000 higher than those for GC-NICI-MS analytical technique (10 pg to 1500 pg injected). As for Nitro-PAHs, the possibilities of unknown species are an advantage of these methods but the investment cost is quite significant. Finally, as for nitro-PAHs, GC-NICI-MS analytical technique constitutes probably the best compromise cost/performance for the analysis of oxy-PAHs in ambient air samples.

An example of an SOP for the analysis of nitro- and oxy-PAHs is given in Annex A.

4 Conclusions

Nitro-PAHs are about as carcinogenic as their parent PAHs. They are also known as strong mutagens. The concentrations of nitro-PAHs in ambient air are a magnitude lower than those of the parent PAHs. A lot of data for ambient air concentrations of these compounds have been published (see Tables 1 and 2), but adequate systematic long-term studies at different types of stations (traffic, urban background, rural) are still missing.

Nitro-PAHs can be directly formed by combustion processes, 1-nitropyrene and 2-nitrofluorene being the most abundant compounds. Thus these two compounds are good markers for diesel exhaust and diesel soot in PM (see 3.1.1.2). Emission factors for these substances in diesel exhaust and in other combustion aerosols should be established.

The nitration of three- and four-ring PAHs by oxidative agents in the presence of nitrogen oxides is an important reaction for the formation of secondary atmospheric aerosol. 2-Nitrofluoranthene and 2-nitropyrene are the most abundant substances formed by gas phase reaction of PAHs with oxidants and oxides of nitrogen.

The main nitro-PAHs formed by combustion processes and secondary reactions are different. Therefore the ratios 1-nitropyrene/2-nitrofluoranthene and 1-nitropyrene/2-nitropyrene are a good measure for the relation of primary versus secondary aerosols. 2-Nitrofluoranthene and 2-nitropyrene are good tracer substances for secondary formation of nitro-PAHs and probably for secondary aerosol formation (see 3.1.1.3).

Few is known about sources and reactions of oxy-PAHs. As for nitro-PAHs combustion processes are direct sources of the substances, but they are also formed by the reaction of PAHs with oxidative agents. The oxy-PAHs concentrations are in the same range as the concentrations of PAHs. Only few studies about the toxicity of oxy-PAHs are published. 9,10-Anthraquinone is classified as possibly carcinogenic for humans (IARC, group 2B). The nitrated oxy-PAHs 3-nitrobenzanthrone is a strong mutagen and classified as possibly carcinogenic (IARC, group 2B). More information about the occurrence, the formation and the behaviour of oxy-PAHs in organisms is necessary.

Nitro- and oxy-PAHs can, for example, be sampled and analysed according to the SOP in the Annex A. For two- and three-ring compounds a combination of filter and adsorbent (e.g. polyurethane foam) is necessary for sampling.

5 Recommendations

More investigations about chemical reactions of nitro-PAHs, oxy-PAHs and non-substituted PAHs, the degradation and rearrangements of the substances during sampling are encouraged.

An update of published emission factors for 1-nitropyrene in diesel and gasoline exhaust (IARC (1989)) should be made. Additionally, emission factors for other sources, e.g. biomass and coal burning, should also be established.

In order to identify the geographical variation and long-term trends of nitro-PAHs and oxy-PAHs the most relevant compounds of these substance groups should be determined together with the PAH compounds specified in Directive 2004/107/EC. The measurements shall be performed at different types of stations (traffic, urban background, rural) for a long period (at least several years). The data can also be used in order to obtain information about the sources of particles (traffic versus secondary aerosol formation). It is not necessary to analyse the whole spectrum of nitro- and oxy-PAHs, the selection of about 5 substances is considered adequate. The most important substances are:

- 1-Nitropyrene
- 2-Nitropyrene
- 2-Nitrofluoranthene
- 9,10-Anthraquinone
- Nitro-PAHs and oxy-PAHs species occurring in the highest concentrations (e.g. 6-nitrochrysene, benzofluorenones)

Consequently, European Standards for the measurement of selected nitro- and oxy-PAHs in ambient air should be established, accompanied by a comprehensive validation study, including i.a. methods to minimize formation, rearrangement and decomposition reactions of nitro-PAHs during sampling, and optimization of sampling conditions.

Annex A
(informative)

Sampling and analysis by GC-MS of some nitro- and oxy-PAHs associated to ambient particulate matter

NOTE This standard operating procedure is applicable for the sampling and analysis of particle-bound nitrated and oxygenated PAHs in ambient air.

A.1 Sampling

For sampling, a similar procedure as for PAH measurements in ambient air should be used (EN 15549 and CEN/TS 16645). The sampling volume should be > 50 m^3.

NOTE For sampling of volatile compounds a sampling system according to ISO 12884 can be used.

A.2 Analytical materials

A.2.1 Glassware and sample handling

- Laboratory vessel (beakers, funnels, etc.)
- Micro-pipettes
- Micro-syringe (or equivalent)

Glassware should be rinsed with acetone and cleaned using a surfactant before rinsing using deionised or ultrapure water. All the non-volumetric glassware should be heated at 500 °C for a minimum of 8 h).

A.2.2 Reagents and Solvents

- Dichloromethane, HPLC grade or equivalent
- Acetonitrile, HPLC grade or equivalent
- Toluene, HPLC grade or equivalent
- Isooctane (2,2,4-Trimethylpentane), HPLC grade or equivalent
- n-Hexane, HPLC grade or equivalent
- n-Pentane, HPLC grade or equivalent

- Surrogate and internal standards: deuterium labelled nitro-PAHs or oxy-PAHs (purity > 99 %):

Substance	CAS number	molecular ion (m/e)
1,4-Naphthoquinone-d6	26473–08–5	164
9,10-Anthraquinone-d8	10439–39–1	216
9-Fluorenone-d8	137219–34–2	188 (internal standard)
9-Nitroanthracene-d9	220381–38–4	232
1-Nitropyrene-d9	93487–20–8	256 (internal standard)
3-Nitrofluoranthene-d9	350820–11–0	256
6-Nitrochrysene-d11	203805–92–9	284
2-Nitrofluorene-d9	128008–87–7	220

- Authentic nitro-PAHs and oxy-PAHs standards (purity > 95 %):

Substance	CAS number	molecular ion (m/e)
9-Fluorenone	486–25–9	180
9,10-Anthraquinone	84–65–1	208
Benzanthrone	82–05–3	230
11*H*-Benzo[*a*]fluoren-11-one	479–79–8	230
11*H*-Benzo[*b*]fluoren-11-one	3074–03–1	230
Benzo[*a*]anthracene-7,12-dione	2498–66–0	258
2-Nitrofluorene	607–57–8	211
9-Nitroanthracene	602–60–8	223
2-Nitrofluoranthene	13177–29–2	247
1-Nitropyrene	789–07–1	247
2-Nitropyrene	789–07–1	247
1,3-Dinitropyrene	75321–20–9	292
1,6-Dinitropyrene	42397–64–8	292
1,8-Dinitropyrene	42397–65–9	292
6-Nitrochrysene	7496–02–8	273
6-Nitrobenzo[*a*]pyrene	63041–90–7	297

- Nitrogen 99,999 % purity or higher
- Helium 99,9999 % purity or higher
- Methane 99,9995 % purity or higher

A.2.3 Extraction apparatus and materials

- Pressurized liquid extraction, or

- Centrifuges glass tubes (*D* = 16 mm, *L* = 100 mm, screw cap with PTFE septum face) for QuEChERS-like extraction procedure (Quick Easy Cheap Effective Rugged and Safe).

A.2.4 Evaporation apparatus and materials

- Concentration evaporator system using a nitrogen stream

A.2.5 Clean-up Material

- Ultra clean silica (neutral), SPE (solid phase extraction): 3 ml, 500 mg. The material shall be checked for blank levels of nitro-PAHs and oxy-PAHs.

- Multiposition SPE vacuum manifold

A.2.6 Weighting Apparatus

- Analytical balance with 0,01 mg precision.

A.2.7 Analytical system

- Gas chromatograph system equipped with a pulsed splitless injector.

- Mass spectrometer simple quad equipped with EI and CI sources. EI mode is suitable for oxy-PAHs analysis and NICI (negative ion chemical ionization) mode is used for the simultaneous quantification of oxy-PAHs and nitro-PAHs or nitro-PAHs alone. An automatic regulation of the reagent gas (CH_4) and Autotune setup in NICI are recommended.

A.3 Extraction

Using PLE, sand may be used to reduce the volume of required solvent. The filter is placed in the extraction cell (11 ml to 33 ml, depending of the filter size) and is extracted with dichloromethane (or toluene) at 120 °C (or 100 °C), 140 bar (or 100 bar), for 6 min; extraction is carried out three times (flush 90 % and purge 120 s). The resulting extracts are automatically combined. Extracts are then reduced near to dryness under a nitrogen stream and dissolved into a small volume of dichloromethane or acetonitrile (100 µl to 200 µl).

Using QuEChERS-like extraction procedure, samples (filter punches of 47 mm diameter) are placed in centrifuge glass tubes and immerged in 7 ml of acetonitrile and shaken/vortexed using a multi-position vortex for 30 s to 5 min. The agitation time is 1,5 min. Samples are next centrifuged for 5 min at 4500 rpm. 5,5 ml of supernatant are collected, reduced near to dryness under a gentle nitrogen stream and dissolved in a small volume of acetonitrile (100 µl to 200 µl).

For both, PLE and QuEChERS, samples are spiked with known amounts of labelled (deuterated) nitro-PAHs and oxy-PAHs surrogates prior to extraction (5 µl of a surrogate standard mixture of deuterated nitro-PAHs and oxy-PAHs at about 1 µg/ml concentration in acetonitrile. Same solution used for the preparation of calibration solutions).

A.4 Clean-up

The clean-up of the extracts is performed on first neutral alumina SPE and second neutral silica SPE cartridge.

The alumina SPE cartridge is first conditioned using 3 ml of methanol, 3 ml of acetonitrile and 3 ml of dichloromethane. The sample extract is added on the top of the cartridge. The vial containing the extract is rinsed using 1 ml of methanol and 1 ml of acetonitrile, added on the top of the cartridge.

Elution is performed using 4 ml of acetonitrile and 5,5 ml of dichloromethane. The extract is then reduced under nitrogen flow to a volume of about 100 µl or less.

The silica SPE cartridge is first conditioned using 1 ml of dichloromethane followed by 3 ml of n-pentane (or n-hexane). The previously purified sample extract is added on the top of the cartridge. Alkanes are eluted with 1 ml of n-pentane (or n-hexane) and discarded. Nitro-PAHs and oxy-PAHs are eluted with 6 ml of n-pentane/dichloromethane mixture (65/35, v/v) or n-hexane/dichloromethane mixture (same proportion). After reduction, near to dryness, under a gentle nitrogen stream, residues are dissolved into about 100 µl of acetonitrile.

A.5 Analysis

Prior to analysis, purified samples are spiked with known amounts of 2 labelled internal standards (1-nitropyrene-d9 and 1,4-naphthoquinone-d6; 5 ng added: 5 µl of an internal standard mixture of deuterated nitro-PAHs and oxy-PAHs at about 1 µg/ml concentration in acetonitrile) in order to evaluate the recovery rates of labelled nitro-PAHs and oxy-PAHs surrogates.

First, calibration solutions (from the lowest concentrations to the highest concentrations) are injected then, samples. After every 10 samples, solutions for quality control are injected (1 or 2). These solutions are independent (different stock solutions or at least, different diluted solutions) of the calibration solutions but are prepared in the same way (concentrations from 2 ng/ml to 500 ng/ml).

According to this procedure, a second calibration curve could be set up and combined with the first one.

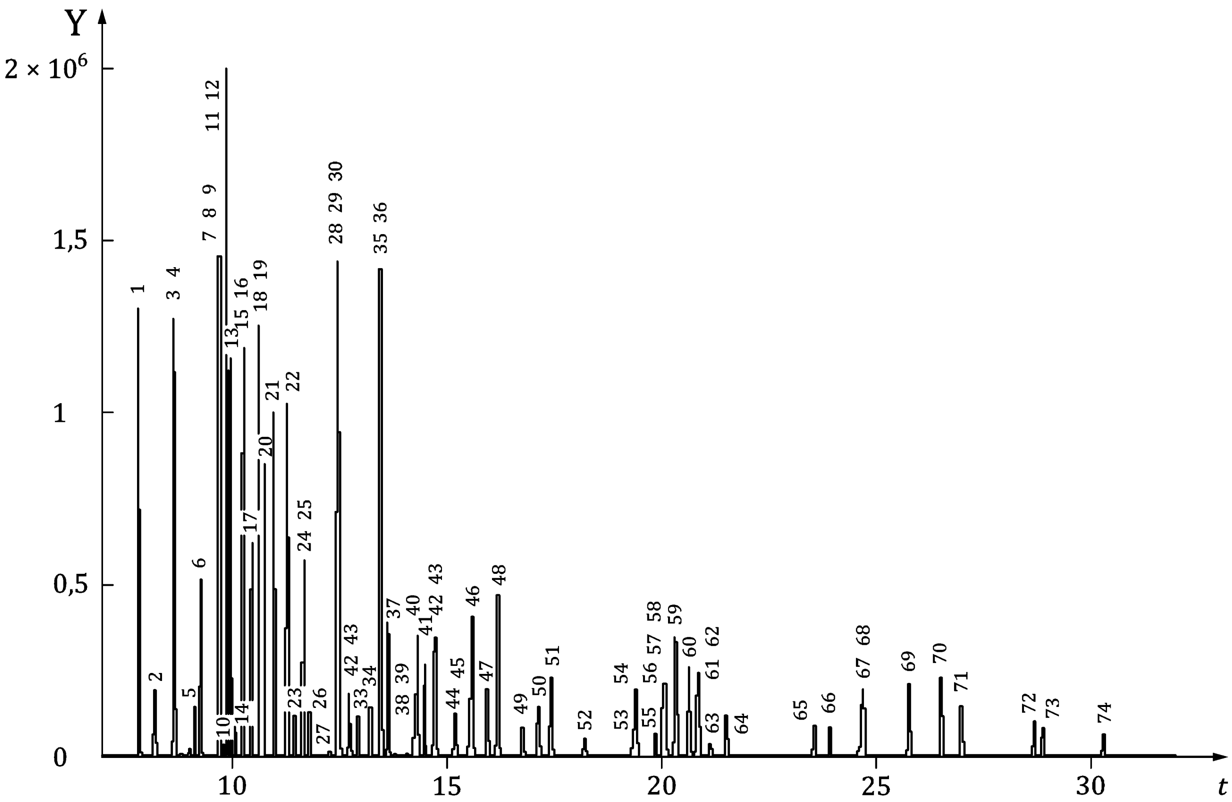
A.6 Results

The quantification of each target nitro- or oxy-PAHs is based on internal calibration. Nitro-PAHs and oxy-PAHs response factors are determined using calibration curves (first calibration or combination with results from the solutions of quality control) set up using the response ratio (peak areas) of target oxy-PAHs or nitro-PAHs with their corresponding surrogate standards.

Calibration curves can be obtained by the chromatographic software or calculated using spreadsheet software.

As quality control, the surrogate recoveries can be determined using 1-nitropyrene-d9 and 1,4-naphthoquinone-d6 as internal standard of injection for nitro-PAHs and oxy-PAHs surrogates, respectively.

Figure A.1 shows the chromatogram of a standard solution (Albinet et al., 2014). For the identification of the peaks, see Table A.1.



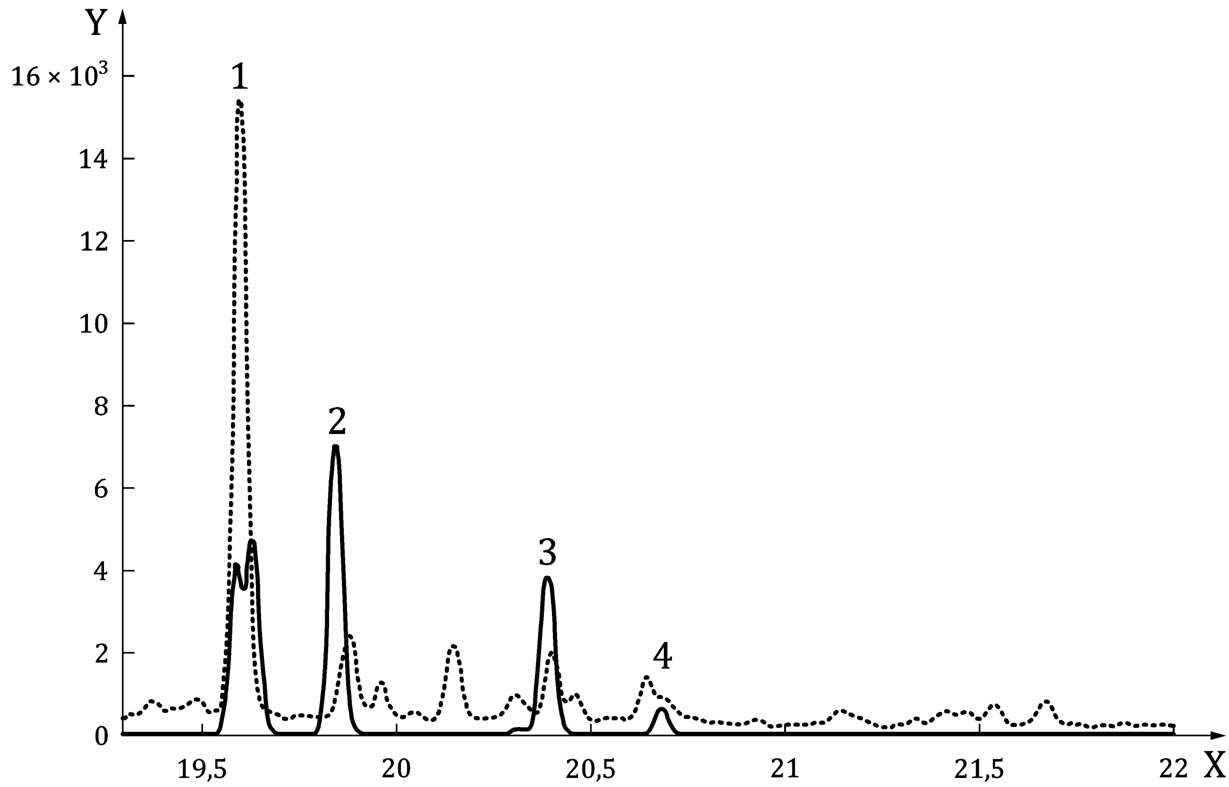
Key

t Time in min

Y Abundance (a.u.)

Figure A.1 — Chromatogramm of a mixture of reference materials

Figure A.2 shows the chromatogram of a real ambient air aerosol sample.



Key

1 2+3-Nitrofluoranthene

2 4-Nitropyrene

3 1-Nitropyrene

4 2-Nitropyrene

X Time in min

Y Abundance (a.u.)

Figure A.2 — Chromatogram of a real ambient air aerosol sample (.........) and a mixture of reference materials (———). Extraction of 247 m/z ions. Focus on nitrofluoranthene and nitropyrene derivatives

Table A.1 — List of compounds of the standard solution

Compound	**Peak number**	**Monitored ions (m/z)**	**Retention time (min)**
Oxy-PAHs and oxygenated compounds			
1,4-Naphthoquinone-d_6	***3***	***164***	***8.62***
Phthaldialdehyde	1	134	7.81
1,4-Naphthoquinone	4	158	8.63
1-Naphthaldehyde	5	156	9.12
9,10-Anthraquinone-d_8	***31***	***216***	***12.70***
Phthalic anhydride	2	148	8.17

2-Formyl-*trans*-cinnamaldehyde	6	160	9.25
1,2-Naphthoquinone	9	158	9.70
Benzophenone	10	182	9.78
1-Acenaphthenone	14	168	10.06
9-Fluorenone-d_8	*18*	*188*	*10.59*
9-Fluorenone	19	180	10.62
1,2-Naphthalic anhydride	23	198	11.45
Biphenyl-2,2'-dicarboxaldehyde	24	210	11.65
Xanthone	25	196	11.65
Acenaphthenequinone	26	182	11.77
2,3-Naphthalenedicarboxylic anhydride	27	198	12.28
Anthrone	29	194	12.54
6*H*-Dibenzo[*b*,*d*]pyran-6-one	30	196	12.54
9,10-Anthraquinone	32	208	12.75
1,8-Naphthalic anhydride	35	198	13.45
1,4-Anthraquinone	36	208	13.45
4,4'-Biphenyldicarboxaldehyde	37	210	13.62
2-Methylanthraquinone	39	222	14.27
Phenanthrene-9-carboxaldehyde	41	206	14.48
9,10-Phenanthrenequinone	44	208	15.19
2-Nitro-9-fluorenone	45	225	15.53
Benzo[*a*]fluorenone	51	230	17.42
Benzo[*b*]fluorenone	52	230	18.21
Benzanthrone	53	230	19.35
Pyrene-1-carboxaldehyde	54	230	19.42
Aceanthrenequinone	55	232	19.88
Benzo[*a*]anthracene-7,12-dione	60	258	20.64
1,4-Chrysenequinone	64	258	21.52
5,6-Chrysenequinone	66	258	23.89
Nitro-PAHs			
1-Nitronaphthalene-d_7	***7***	***180***	***9.67***
1-Nitronaphthalene	8	173	9.70
2-Methyl-1-nitronaphthalene + 1-methyl-5-nitronaphthalene	11, 12	187	9.86
2-Nitronaphthalene	13	173	9.95
2-Methyl-4-nitronaphthalene	17	187	10.43

1-Methyl-4-nitronaphthalene	20	187	10.77
1-Methyl-6-nitronaphthalene	21	187	10.95
1,5-Dinitronaphthalene	28	218	12.44
2-Nitrobiphenyl-d_9	***15***	***208***	***10.20***
2-Nitrobiphenyl	16	199	10.24
3-Nitrobiphenyl	22	199	11.26
3-Nitrodibenzofuran	33	213	12.91
5-Nitroacenaphthene	34	199	13.20
2-Nitrofluorene-d_9	***38***	***220***	***14.23***
2-Nitrofluorene	40	211	14.31
9-Nitroanthracene-d_9	***42***	***232***	***14.66***
9-Nitroanthracene	43	223	14.72
9-Nitrophenanthrene	46	223	15.61
2-Nitrodibenzothiophene	47	229	15.95
3-Nitrophenanthrene	48	223	16.19
2-Nitroanthracene	49	223	16.78
9-Methyl-10-nitroanthracene	50	237	17.14
3-Nitrofluoranthene-d_9	***57***	***256***	***20.04***
2-Nitrofluoranthene	56	247	20.02
3-Nitrofluoranthene	58	247	20.10
4-Nitropyrene	59	247	20.32
1-Nitropyrene-d_9	*61*	*256*	*20.80*
1-Nitropyrene	62	247	20.86
2-Nitropyrene	63	247	21.14
6-Nitrochrysene-d_{11}	***67***	***284***	***24.61***
7-Nitrobenzo[*a*]anthracene	65	273	23.56
6-Nitrochrysene	68	273	24.71
1,3-Dinitropyrene	69	292	25.77
1,6-Dinitropyrene	70	292	26.51
1,8-Dinitropyrene	71	292	26.99
1-Nitrobenzo[*e*]pyrene	72	297	28.68
6-Nitrobenzo[*a*]pyrene	73	297	28.88
3-Nitrobenzo[*e*]pyrene	74	297	30.30

A.7 Quality assurance

Selected important issues are:

- The extraction and clean-up procedure shall be validated using SRMs such as NIST 1650 (Diesel Particulate Matter) or NIST 2975 (Diesel Particulate Matter (Industrial Forklift)).
- An extremely clean GC-MS system is needed for the quantitative determination of dinitro-PAHs. Therefore, the system shall be heated for a longer period at a high temperature and the deactivated glass liner shall be frequently purified.
- 3-Nitrobenzanthrone is a very reactive compound and it is not stable during sampling on filters.

Annex B
(informative)

Carcinogenicity and references to nitro- and oxy-PAHs

A number of nitro- and oxy-PAHs is present on the IARC list (classification as carcinogenic, probably carcinogenic or possibly carcinogenic to humans). Recently IARC published the latest findings on diesel soot, resulting in its classification in the most harmful group 1 (carcinogenic to humans) due also to the presence of a mixture of PAHs including nitro-PAHs (classification group 2A and 2B). Table B.1 summarizes recent knowledge.

Table B.1 — Carcinogenicity of nitro- and oxy-PAHs

Compound	**Group**	**Reference**
Diesel engine exhaust	1	1
Gasoline engine exhaust	2B	1
1,3-Dinitropyrene	2B	1, 4, 8
1,6-Dinitropyrene	2B	1, 4, 8
1,8-Dinitropyrene	2B	1, 4, 8
1-Nitrobenzo[*a*]pyrene		2
1-Nitronaphthalene	3	1, 6, 7, 8, 9,
1-Nitropyrene	2A	1, 6, 7, 8, 9
2-Nitrobenzanthrone		2
2-Nitrofluoranthene		8
2-Nitrofluorene	2A	1, 6, 7, 8, 9
2-Nitronaphthalene	3	1, 6, 7, 8, 9
2-Nitropyrene	3	1, 8, 9
3,6-Dinitrobenzo[*a*]pyrene		2
3,7-Dinitrofluoranthene	2B	1, 4
3,9-Dinitrofluoranthene	2B	1, 4
3-Nitrobenzanthrone	2B	2
3-Nitrobenzo[*a*]pyrene		2
3-Nitrodibenzo[*a,c*]anthracene		2
3-Nitrofluoranthene	3	3, 6, 7, 9
3-Nitroperylene	3	1, 2
3-Nitrophenanthrene		8, 9
4-Nitrobiphenyl		6, 7
4-Nitropyrene	2B	1, 8, 9

6-Nitrobenzo[*a*]pyrene	3	1, 2, 7, 8, 9
6-Nitrochrysene	2A	1, 2, 6, 7, 8, 9
7,12-Dinitrobenzo[*a*]pyrene		2
7-Nitrobenzo[*a*]anthracene	3	1, 2, 8, 9
9-Nitroanthracene	3	3, 7, 8, 9
9-Nitrophenanthrene		8, 9
1,2-Acenaphthenequinone		7
1,4-Anthraquinone		8
1,4-Naphthoquinone		6, 7
1,8-Naphthalic anhydride		7
1-Naphthaldehyde		6, 7, 8
Pyrene-1-carboxaldehyde		6, 7
9,10-Anthraquinone	2B	5, 6, 7, 8, 9
9,10-Phenanthrenequinone		7
9-Fluorenone		6, 7, 8, 9
Phenanthrene-9-carboxaldehyde		8, 9
Anthrone		7
Benzo[*a*]anthracene-7,12-dione		5, 6, 7, 8
Benzanthrone		6, 7, 8, 9
Benzo[*a*]fluorenone		8, 9
Benzo[*b*]fluorenone		8, 9
Benzo[a]anthracene	2A	3
Benzo[*a*]pyrene	1	3
Benzo[*b*]fluoranthene	2B	3
Benzo[*j*]fluoranthene	2B	3
Benzo[*k*]fluoranthene	2B	3
Dibenzo[*a,h*]anthracene	2A	3
Indeno[1,2,3-*cd*]pyrene	2B	3

Groups

1	Carcinogenic to humans
2A	Probably carcinogenic to humans
2B	Possibly carcinogenic to humans
3	Not classifiable as to its carcinogenicity to humans
4	Probably not carcinogenic to humans

References

[1] IARC (2013)

[2] Environmental Health Criteria (2003)
[3] BALL-POP (2007)
[4] IARC Monograph 105 (2012)
[5] IARC Monograph 101 (2012)
[6] TNO (2009)
[7] TNO (2011)
[8] Albinet et al. (2006)
[9] Albinet et al. (2007b)

Annex C
(informative)

Mutagenicity of nitro-PAHs

Table C.1 summarizes mutagenicity data of nitro-PAHs as cited in Environmental Health Criteria 229: Selected Nitro- and Nitro-Oxy-Polycyclic Aromatic Hydrocarbons, EEHC 229, 2003

Table C.1 — Mutagenicity of nitro-PAHs

Substance	**Mutagenicity**
2-Nitrofluoranthene	+
3-Nitrofluoranthene	++
2,4-Dinitrofluoranthene	++
3,4-Dinitrofluoranthene	++
3,7-Dinitrofluoranthene	+++
3,9-Dinitrofluoranthene	+++
1-Nitropyrene	+
2-Nitropyrene	++
4-Nitropyrene	++
1,3-Dinitropyrene	++
1,6-Dinitropyrene	+++
1,8-Dinitropyrene	+++
2-Nitrochrysene	++
6-Nitrochrysene	+
1-Nitrobenzo[*a*]pyrene	+
2-Nitrobenzo[*a*]pyrene	++
3-Nitrobenzo[*a*]pyrene	+
3,6-Dinitrobenzo[*a*]pyrene	+++
3-Nitrobenzanthrone	++++
+ > 100, < 1000 revertants per mmol in *Salmonella typhimurium* cells without metabolic activation ++ > 100, < 100 000 revertants per mmol in *Salmonella typhimurium* cells without metabolic activation +++ > 100 000 revertants per mmol in *Salmonella typhimurium* cells without metabolic activation ++++ strongest mutagen of nitro- and oxy-PAHs	

Annex D
(informative)

Diesel exhaust data

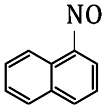
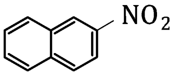
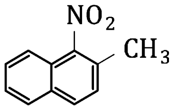
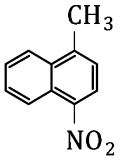
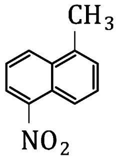
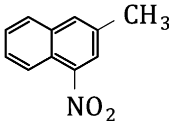
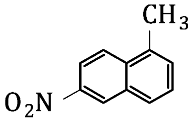
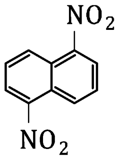
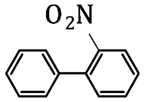
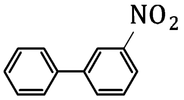
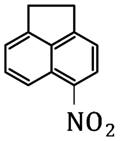
The concentrations of nitro-PAHs in diesel exhaust and other materials are listed in Table 1. Thus the content of nitro-PAHs in the exhaust of a large diesel engine and an industrial forklift as certified by NIST (NIST 1650b, NIST 2975) and data cited in the IARC monograph on diesel and gasoline exhaust and some nitroarenes (IARC, 2013) can be compared with their concentration in urban dust (NIST 1649b). The concentrations of benzo[*a*]pyrene and 2-nitrofluoranthene are higher in urban dust, but the concentration of 1-nitropyrene is by far higher in the diesel exhaust samples.

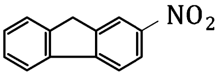
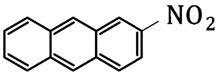
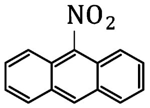
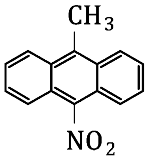
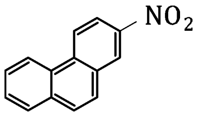
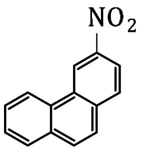
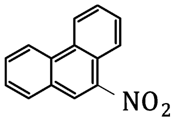
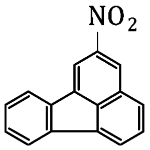
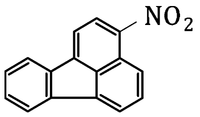
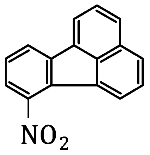
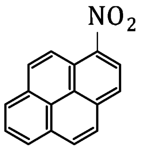
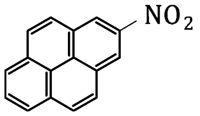
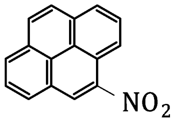
Table D.1 — Concentrations of selected nitro-PAHs and BaP in SRMs and in urban particulate matter (IARC, 2013), in mg/kg

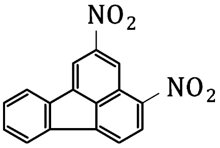
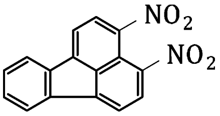
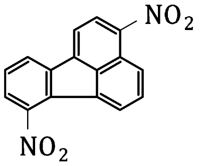
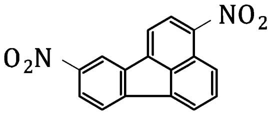
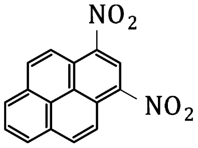
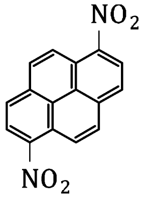
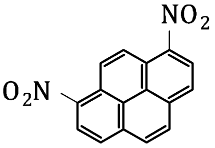
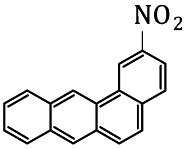
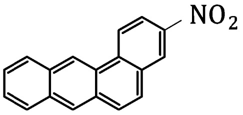
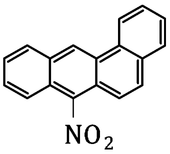
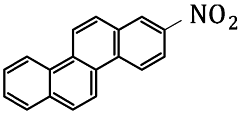
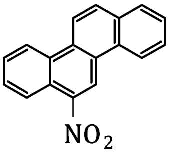
Substance	NIST 1650**b (Diesel Particulate Matter)**	NIST 2975 **(Diesel Particulate Matter (Industrial Forklift))**	**IARC data**	NIST 1649**b (Urban Dust)**
1-Nitropyrene	18,4 [a)]	35,2 [a)]	2 – 90	0,072 [b)]
4-Nitropyrene	0,13 [b)]	0,17 [b)]	0,07	0,006 [b)]
2-Nitrofluoranthene	0,21 [a)]	0,23 [a)]	–	0,311 [b)]
6-Nitrochrysene	0,05 [a)]	2,45 [a)]	0,8	0,004 [b)]
1,6-Dinitropyrene	–	2,3 [b)]	0,7 – 1,2	–
Benzo[*a*]pyrene	1,25 [a)]	0,7 [b)]	–	2,47 [a)]
[a)] Certified value in SRM [b)] Reference value in SRM				

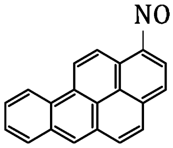
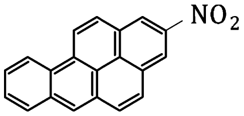
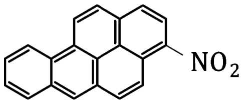
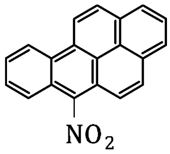
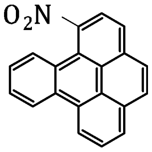
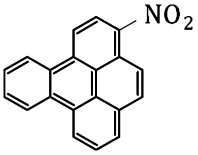
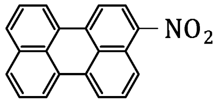
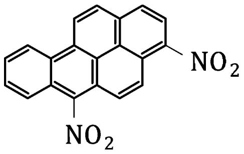
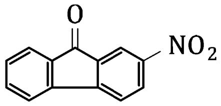
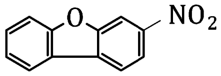
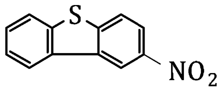
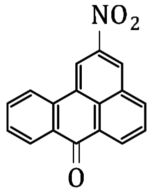
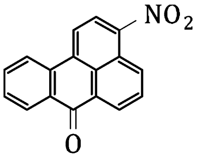
Annex E
(informative)

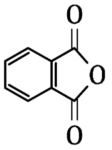
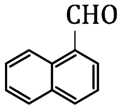
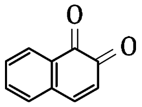
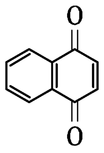
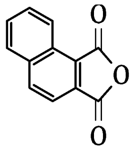
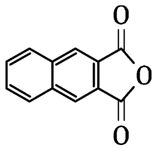
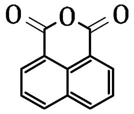
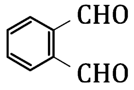
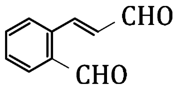
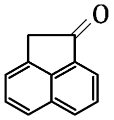
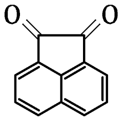
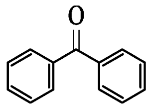
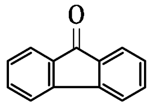
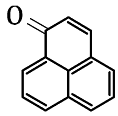
Structures of nitro- and oxy-PAHs referred in this Technical Report

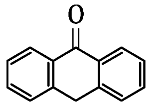
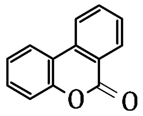
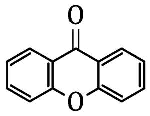
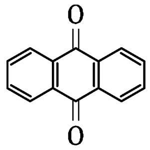
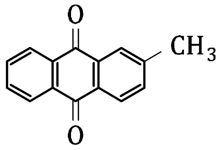
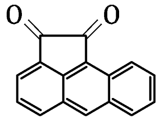
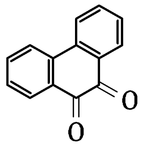
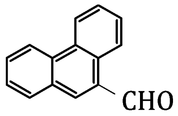
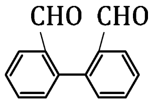
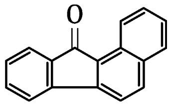
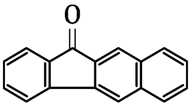
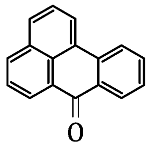
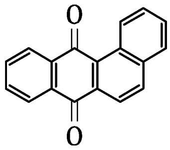
Substance	**Formula**	**Molecular weight** g/mol	**Structure**
1-Nitronaphthalene	$C_{10}H_7NO_2$	173,17	
2-Nitronaphthalene	$C_{10}H_7NO_2$	173,17	
2-Methyl-1-nitronaphthalene	$C_{11}H_9NO_2$	199,20	
1-Methyl-4-nitronaphthalene	$C_{11}H_9NO_2$	199,20	
1-Methyl-5-nitronaphthalene	$C_{11}H_9NO_2$	199,20	
2-Methyl-4-nitronaphthalene	$C_{11}H_9NO_2$	199,20	
1-Methyl-6-nitronaphthalene	$C_{11}H_9NO_2$	199,20	
1,5-Dinitronaphthalene	$C_{10}H_6N_2O_4$	218,16	
2-Nitrobiphenyl	$C_{12}H_9NO_2$	199,21	
3-Nitrobiphenyl	$C_{12}H_9NO_2$	199,21	
5-Nitroacenaphthene	$C_{12}H_9NO_2$	199,21	

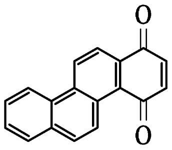
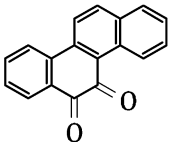
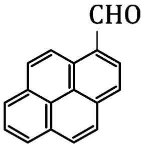
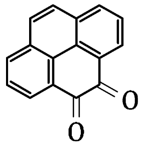
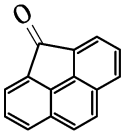
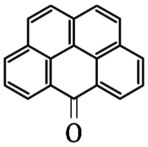
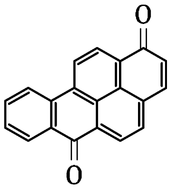
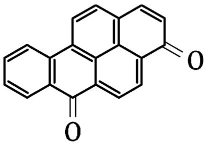
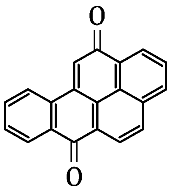
2-Nitrofluorene	$C_{13}H_9NO_2$	211,22	
2-Nitroanthracene	$C_{14}H_9NO_2$	223,23	
9-Nitroanthracene	$C_{14}H_9NO_2$	223,23	
9-Methyl-10-nitroanthracene	$C_{15}H_{11}NO_2$	237,25	
2-Nitrophenanthrene	$C_{14}H_9NO_2$	223,23	
3-Nitrophenanthrene	$C_{14}H_9NO_2$	223,23	
9-Nitrophenanthrene	$C_{14}H_9NO_2$	223,23	
2-Nitrofluoranthene	$C_{16}H_9NO_2$	247,25	
3-Nitrofluoranthene	$C_{16}H_9NO_2$	247,25	
7-Nitrofluoranthene	$C_{16}H_9NO_2$	247,25	
1-Nitropyrene	$C_{16}H_9NO_2$	247,25	
2-Nitropyrene	$C_{16}H_9NO_2$	247,25	
4-Nitropyrene	$C_{16}H_9NO_2$	247,25	

2,4-Dinitrofluoranthene	$C_{16}H_8N_2O_4$	292,3	
3,4-Dinitrofluoranthene	$C_{16}H_8N_2O_4$	292,3	
3,7-Dinitrofluoranthene	$C_{16}H_8N_2O_4$	292,3	
3,9-Dinitrofluoranthene	$C_{16}H_8N_2O_4$	292,3	
1,3-Dinitropyrene	$C_{16}H_8N_2O_4$	292,3	
1,6-Dinitropyrene	$C_{16}H_8N_2O_4$	292,3	
1,8-Dinitropyrene	$C_{16}H_8N_2O_4$	292,3	
2-Nitrobenzo[*a*]anthracene	$C_{18}H_{11}NO_2$	273,2	
3-Nitrobenzo[*a*]anthracene	$C_{18}H_{11}NO_2$	273,2	
7-Nitrobenzo[*a*]anthracene	$C_{18}H_{11}NO_2$	273,2	
2-Nitrochrysene	$C_{18}H_{11}NO_2$	273,2	
6-Nitrochrysene	$C_{18}H_{11}NO_2$	273,2	

1-Nitrobenzo[*a*]pyrene	$C_{20}H_{11}NO_2$	297,31	
2-Nitrobenzo[*a*]pyrene	$C_{20}H_{11}NO_2$	297,31	
3-Nitrobenzo[*a*]pyrene	$C_{20}H_{11}NO_2$	297,31	
6-Nitrobenzo[*a*]pyrene	$C_{20}H_{11}NO_2$	297,31	
1-Nitrobenzo[*e*]pyrene	$C_{20}H_{11}NO_2$	297,31	
3-Nitrobenzo[*e*]pyrene	$C_{20}H_{11}NO_2$	297,31	
3-Nitroperylene	$C_{20}H_{11}NO_2$	297,31	
3,6-Dinitrobenzo[*a*]pyrene	$C_{20}H_{10}N_2O_4$	342,29	
2-Nitro-9-fluorenone	$C_{13}H_7NO_3$	225,20	
3-Nitrodibenzofurane	$C_{12}H_7NO_3$	213,19	
2-Nitrodibenzothiophene	$C_{12}H_7NO_2S$	229,26	
2-Nitrobenzanthrone	$C_{17}H_9NO_3$	275,26	
3-Nitrobenzanthrone	$C_{17}H_9NO_3$	275,26	

Phthalic anhydride	$C_8H_4O_3$	148,11	
1-Naphthaldehyde	$C_{11}H_8O$	156,18	
Naphthalene-1,2-dione	$C_{10}H_6O_2$	158,15	
Naphthalene-1,4-dione	$C_{10}H_6O_2$	158,15	
1,2-Naphthalic acid anhydride	$C_{12}H_6O_3$	198,18	
2,3-Naphthalic acid anhydride	$C_{12}H_6O_3$	198,18	
1,8-Naphthalic acid anhydride	$C_{12}H_6O_3$	198,18	
1,2-Phthalic dialdehyde	$C_8H_60_2$	134,13	
2-Formyl-*trans*-cinnamaldehyde	$C_{10}H_8O_2$	160,17	
Acenaphthen-1-one	$C_{12}H_8O$	168,18	
Acenaphthene-1,2-dione	$C_{12}H_6O_2$	182,17	
Benzophenone	$C_{13}H_{10}O$	182,22	
9*H*-Fluoren-9-one	$C_{13}H_8O$	180,19	
1*H*-Phenalen-1-one	$C_{13}H_8O$	180,19	

10*H*-Anthracen-9-one (Anthrone)	$C_{14}H_{10}O$	194,23	
6*H*-Dibenzo[*b,d*]pyran-6-one	$C_{13}H_8O_2$	196,19	
Xanthone	$C_{13}H_8O_2$	196,19	
Anthracene-9,10-dione (Anthraquinone)	$C_{14}H_8O_2$	208,22	
2-Methyl-9,10-anthraquinone	$C_{15}H_{10}O_2$	222,23	
Aceanthrenequinone	$C_{16}H_8O_2$	232,22	
Phenanthrene-9,10-dione	$C_{14}H_8O_2$	208,22	
Phenanthrene-9-carboxaldehyde	$C_{15}H_{10}O$	206,24	
Biphenyl-2,2´-dicarbaldehyde	$C_{14}H_{10}O_2$	210,23	
Benzo[*a*]fluorenone	$C_{17}H_{10}O$	230,26	
Benzo[*b*]fluorenone	$C_{17}H_{10}O$	230,26	
Benzo[*de*]anthracen-6-one (Benzanthrone)	$C_{17}H_{10}O$	230,26	
Benzo[*a*]anthracene-7,12-dione	$C_{18}H_{10}O_2$	258,27	

Chrysene-1,4-dione	$C_{18}H_{10}O_2$	258,27	
Chrysene-5,6-dione	$C_{18}H_{10}O_2$	258,27	
Pyrene-1-carboxaldehyde	$C_{17}H_{10}O$	230,26	
Pyrene-4,5-dione	$C_{16}H_8O_2$	232,23	
Cyclopenta[*def*]phenanthren-4-one	$C_{15}H_8O$	204,2	
6*H*-Benzo[*cd*]pyren-6-one	$C_{19}H_{10}O$	254,3	
Benzo[*a*]pyrene-1,6-dione	$C_{20}H_{10}O_2$	282,29	
Benzo[*a*]pyrene-3,6-dione	$C_{20}H_{10}O_2$	282,29	
Benzo[*a*]pyrene-6,12-dione	$C_{20}H_{10}O_2$	282,29	

Bibliography

[1] ABAS M.R.B., SIMONEIT B.R.T., ELIAS V., CABRAL J.A., CARDOSO J.N. Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in Amazonia. *Chemosphere*. 1995, **30** pp. 995–1015

[2] ADAMS K.M., JAPAR S.M., PIERSON W.R. Development of a MnO_2-coated, cylindrical denuder for removing NO_2 from atmospheric samples. *Atmos. Environ.* 1967, **1986** (20) pp. 1211–1215

[3] AKIMOTO Y., AOKI T., NITO S.I., INOUYE Y. Oxygenated polycyclic aromatic hydrocarbons from MSW incinerator fly ash. *Chemosphere*. 1997, **34** pp. 263–273

[4] ALAM M.S., DELGADO-SABORIT J.M., STARK C., HARRISON R.M. Using atmospheric measurements of PAH and quinone compounds at roadside and urban background sites to assess sources and reactivity. *Atmos. Environ.* 2013, **77** pp. 24–35

[5] Albinet, A., Leoz-Garziandia, E., Budzinski, H. and Villenave, E. Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation. *J. Chromatogr. A*. 2006, **1121** pp. 106–113

[6] ALBINET A., LEOZ-GARZIANDIA E., BUDZINSKI H., VILLENAVE E. Sampling precautions for the measurement of nitrated polycyclic aromatic hydrocarbons in ambient air. *Atmos. Environ.* 2007a, **41** pp. 4988–4994

[7] ALBINET A., LEOZ-GARZIANDIA E., BUDZINSKI H., VILLENAVE E. Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources. *Sci. Total Environ.* 2007b, **384** pp. 280–292

[8] ALBINET A., LEOZ-GARZIANDIA E., BUDZINSKI H., VILLENAVE E., JAFFREZO J.L. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys. Part 1: Concentrations, sources and gas/particle partitioning. *Atmos. Environ.* 2008a, **42** pp. 43–54

[9] ALBINET A., LEOZ-GARZIANDIA E., BUDZINSKI H., VILLENAVE E., JAFFREZO J.L. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys. Part 2: Particle size distribution. *Atmos. Environ.* 2008b, **42** pp. 55–64

[10] ALBINET A., NALIN F., TOMAZ S., BEAUMONT J., LESTREMAU F. A simple QuEChERS-like extraction approach for molecular chemical characterization of organic aerosols: application to nitrated and oxygenated PAH derivatives (NPAH and OPAH) quantified by GC–NICIMS. *Anal. Bioanal. Chem.* 2014, **406** pp. 3131–3148

[11] ALBINET A., PAPAICONOMOU N., ESTAGER J., SUPTIL J., DRAYE M., BESOMBES J.-L. A new ozone denuder for aerosol sampling based on an ionic liquid coating. *Anal. Bioanal. Chem.* 2010, **396** pp. 857–864

[12] ALFHEIM I., RAMDAHL T. Contribution of wood combustion to indoor air pollution as measured by mutagenicity in *Salmonella* and polycyclic aromatic hydrocarbons. *Environ. Mutagen.* 1984, **6** pp. 121–130

[13] ALLEN J.O., DOOKERAN N.M., TAGHIZADEH K., LAFLEUR A.L., SMITH K.A., SAROFIM A.F. Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. *Environ. Sci. Technol.* 1997, **31** pp. 2064–2070

[14] ALLEN J.O. *Atmospheric partitioning of polycyclic aromatic hydrocarbons (PAH) and oxygenated PAH. Massachusetts Institute of Technology*. MIT, 1997, 345 p.

[15] ALSBERG T., STENBERG U., WESTERHOLM R., STRANDELL M., RANNUG U., SUNDVALL A. et al. Chemical and biological characterization of organic material from gasoline exhaust particles. *Environ. Sci. Technol.* 1985, **19** pp. 43–50

[16] ARAKI Y., TANG N., OHNO M., KAMEDA T., TORIBA A., HAYAKAWA K. Analysis of atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in gas/particle phases separately collected by a high-volume air sampler equipped with a column packed with XAD-4 resin. *J. Health Sci.* 2009, **55** pp. 77–85

[17] AREY J., ZIELINSKA B., ATKINSON R., WINER A.M., RAMDHAL T., PITTS J.N. JR. The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_x. *Atmos. Environ.* 1986, **20** pp. 2239–2345

[18] AREY J., ZIELINSKA B., ATKINSON R., ASCHMANN S.M. Nitroarene products from the gas phase reactions of volatile polycyclic aromatic hydrocarbons with the OH radical and N_2O_5. *Int. J. Chem. Kinet.* 1989, **21** pp. 775–799

[19] AREY J., ZIELINSKA B., HARGER W.P., ATKINSON R., WINER A.M. The contribution of nitrofluoranthenes and nitropyrenes to the mutagenic activity of ambient particulate organic matter collected in Southern California. *Mutat. Res.* 1988, **207** pp. 45–51

[20] AREY J. Atmospheric reactions of PAHs including formation of nitroarenes. In: *The handbook of environmental chemistry, PAHs and related compounds, 3*. Springer-Verlag, Berlin, 1998, pp. 347–85.

[21] ARLT V.M. 3-Nitrobenzanthrone, a potential human cancer hazard in diesel exhaust and urban air pollution: a review of the evidence. *Mutagenesis*. 2005, **20** pp. 399–410

[22] ATKINSON R., AREY J., WINER A.M., ZIELINSKA B., DINOFF T.M., HARGER W.P. et al. (1988) A survey of ambient concentrations of selected polycyclic aromatic hydrocarbons (PAH) at various locations in California. Riverside, California, University of California, Statewide Air Pollution Research Center, May, 181 pp. (Report A5-185-32)

[23] ATKINSON R., ASCHMANN S.M., AREY J., CARTER P.L. Formation of ring-retaining products from the OH radical-initiated reactions of benzene and toluene. *Int. J. Chem. Kinet.* 1989a, **21** pp. 801–827

[24] ATKINSON R., ASCHMANN S.M., AREY J., ZIELINSKA B., SCHUETZLE D. Gas-phase atmospheric chemistry of 1- and 2-nitronaphthalene and 1,4-naphtoquinone. *Atmos. Environ.* 1989b, **23** pp. 2679–2690

[25] ATKINSON R., AREY J., ZIELINSKA B., ASCHMANN S.M. Kinetics and nitro-products of gas-phase OH and NO_3 radical-initiated reactions of naphthalene, fluoranthene and pyrene. *Int. J. Chem. Kinet.* 1990, **22** pp. 999–1014

[26] ATKINSON R., AREY J. Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: formation of atmospheric mutagens. *Environ. Health Perspect.* 1994, **102** pp. 117–126

[27] Atkinson R., Arey J. Lifetimes and fates of toxic air contaminants in California's atmosphere. In: *Final report to the California air resources board*. Contract N, 1997, pp. 93–307.

[28] Bamford H.A., Baker J.E. Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region. *Atmos. Environ.* 2003, **37** pp. 2077–2091

[29] Bandowe B.A.M., Meusel H., Huang R.-J., Ho K., Cao J., Hoffmann T. et al. $PM_{2.5}$-bound oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: Seasonal variation, sources and cancer risk assessment. *Sci. Total Environ.* 2014, **473–474** pp. 77–87

[30] Barbas J.T., Sigman M.E., Dabestani R. Photochemical oxidation of phenanthrene sorbed on silica gel. *Environ. Sci. Technol.* 1996, **30** pp. 1776–1780

[31] Barrado A.I., García S., Pérez R.M., Pindado O. Measurements of hydroxylated polycyclic aromatic hydrocarbons in atmospheric aerosols from an urban site of Madrid (Spain). In: Nucleation and Atmospheric Aerosols, 2008, pp. 517-521

[32] Barrado A.I., García S., Barrado E., Pérez R.M. $PM_{2,5}$ bound PAHs and hydroxyl PAHs in atmospheric aerosol samples: Correlations with season and with physical and chemical factors. *Atmos. Environ.* 2012a, **49** pp. 224–232

[33] Barrado A.I., García S., Castrillejo Y., Barrado E. Exploratory data analysis of PAH, nitro-PAH and hydroxyl-PAH concentrations in atmospheric PM_{10} bound aerosol particles. Correlations with physical and chemical factors. *Atmos. Environ.* 2012b, **67** pp. 385–393

[34] Barrado A.I., García S., Castrillejo Y., Pérez R.M. Hydroxy-PAH levels in atmospheric PM10 aerosol samples correlated with season, physical factors and chemical indicators of pollution. *Atmos. Pollut. Res.* 2012c, **3** pp. 81–87

[35] Benbrahim Tallaa L., Baan R.A., Grosse Y., Lauby-Secretan B., El Ghissassi F., Bouvard V. et al. Carcinogenicity of Diesel-engine and gasoline-engine exhausts and some nitroarenes. *Lancet Oncol.* 2012, **13** pp. 663–664

[36] Bedjanian Y., Nguyen M.L., Le Bras G. Kinetics of the reactions of soot surface-bound polycyclic aromatic hydrocarbons with the OH radicals. *Atmos. Environ.* 2010, **44** pp. 1754–1760

[37] Beije B., Möller L. 2-nitrofluorene and related compounds prevalence and biological effects. *Mutat. Res.* 1988, **196** pp. 177–209

[38] Berlincioni M., Croce G., Ferri F., Iacovella N., La Rocca C., Lolini M. et al. Priority organic microcontaminants in selected environmental and food matrices. *Fresenius Environ. Bull.* 1995, **4** (3) pp. 169–174

[39] Bezabeh D.Z., Bamford H.A., Schantz M.M., Wise S.A. Determination of nitrated polycyclic aromatic hydrocarbons in diesel particulate-related standard reference materials by using gas chromatography/mass spectrometry with negative ion chemical ionization. *Anal. Bioanal. Chem.* 2003, **375** pp. 381–388

[40] Brown M.A., Ashby P.D., Ogletree D.F., Salmeron M., Hemminger J.C. Reactivity of ozone with solid potassium iodide investigated by atomic force microscopy. *J. Phys. Chem. C*. 2008, **112** pp. 8110–8113

[41] BUNCE N.J., LIU L., ZHU J., LANE D.A. Reaction of naphthalene and its derivatives with hydroxyl radicals in the gas phase. *Environ. Sci. Technol.* 1997, **31** pp. 2252–2259

[42] CALVERT J.G., ATKINSON R., BECKER K.H., KAMENS R.M., SEINFELD J.H., WALLINGTON T.J. et al. *The mechanisms of atmospheric oxidation of aromatic hydrocarbons.* Oxford University Press, New York, 2002

[43] CARRARA M., WOLF J.-C., NIESSNER R. Nitro-PAH formation studied by interacting artificially PAH-coated soot aerosol with NO_2 in the temperature range of 295 - 523 K. *Atmos. Environ.* 2010, **44** pp. 3878–3885

[44] CARRARA M., NIESSNER R. Impact of a NO_2-regenerated diesel particulate filter on PAH and NPAH emissions from an EURO IV heavy duty engine. *J. Environ. Monit.* 2011, **13** pp. 3373–3379

[45] CASTELLS P., SANTOS F.J., GALCERAN M.T. Development of a sequential supercritical fluid extraction method for the analysis of nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in urban aerosols. *J. Chromatogr. A*. 2003, **1010** pp. 141–151

[46] CAZAUNAU M., LE MÉNACH K., BUDZINSKI H., VILLENAVE E. Atmospheric heterogeneous reactions of benzo(a)pyrene. *Z. Phys. Chem.* 2010, **224** pp. 1151–1170

[47] CHAN A.W.H., KAUTZMAN K.E., CHHABRA P.S., SURRATT J.D., CHAN M.N., CROUNSE J.D. et al. Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: Implications for oxidation of intermediate volatile organic compounds (IVOCs). *Atmos. Chem. Phys.* 2009, **9** pp. 3049–3060

[48] CECINATO A., MARINO F., DI FILIPPO P., LEPORE L., POSSANZINI M. Distribution of n-alkanes, polynuclear aromatic hydrocarbons and nitrated polynuclear aromatic hydrocarbons between the fine and coarse fractions of inhalable atmospheric particulates. *J. Chromatogr. A*. 1999, **846** pp. 255–264

[49] CEN/TS 16645:2014, *Ambient air - Method for the measurement of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene*

[50] CHO A.K., DI STEFANO E., YOU Y., RODRIGUEZ C.E., SCHMITZ D.A., KUMAGAI Y. et al. Determination of four quinones in diesel exhaust particles, SRM 1649a, an atmospheric $PM_{2.5}$. *Aerosol Sci. Technol.* 2004, **38** pp. 68–81

[51] CHOUDHURY D.R. Charaterization of polycyclic ketones and quinones in diesel emission particulates by Gas Chromatography / Mass Spectrometry. *Environ. Sci. Technol.* 1982, **16** pp. 102–106

[52] CHUNG M.Y., LUZARO R.A., LIM D., JACKSON J., LYON J., RENDULIC D. et al. Aerosol borne quinones and reactive oxygen species generation by particulate matter extracts. *Environ. Sci. Technol.* 2006, **40** pp. 4880–4886

[53] CICCIOLI P., CECINATO A., BRANCALEONI E., FRATTONI M., ZACCHEI P., DE CASTRO VASCONCELLOS P. The ubiquitous occurence of nitro-PAH of photochemical origin in airborne particles. *Ann. Chim.* 1995, **85** pp. 455–469

[54] CICCIOLI P., CECINATO A., BRANCALEONI E., MASSIMILIANO F., ZACCHEI P., MIGUEL A.H. et al. Formation and transport of 2-nitrofluoranthene and 2-nitropyrene of photochemical origin in the troposphere. *J. Geophys. Res.* 1996, **101** pp. 19567–19581

[55] COUTANT R.W., BROWN L., CHUANG J.C., RIGGIN R.M., LEWIS R.G. Phase distribution and artifact formation in ambient air sampling for polynuclear aromatic hydrocarbons. *Atmos. Environ.* 1967, **1988** (22) pp. 403–409

[56] DELHOMME O., MILLET M., HERCKES P. Determination of oxygenated polycyclic aromatic hydrocarbons in atmospheric aerosol samples by liquid chromatography/tandem mass spectrometry. *Talanta*. 2008, **74** pp. 703–710

[57] DEMARINI D.M., SHELTON M.L., BELL D.A. Mutation spectra of chemical fractions of a complex mixture: role of nitroarenes in the mutagenic specificity of municipal waste incinerator emissions. *Mutat. Res.* 1996, **349** pp. 1–20

[58] DI FILIPPO P., RICCARDI C., POMATA D., BUIARELLI F. Concentrations of PAHs, and nitro- and methyl-derivatives associated with a size-segregated urban aerosol. *Atmos. Environ.* 2010, **44** pp. 2742–2749

[59] DIMASHKI M., HARRAD S., HARRISON R.M. Measurements of nitro-PAH in the atmospheres of two cities. *Atmos. Environ.* 2000, **34** pp. 2459–2469

[60] DING Y., PANG Y., EATOUGH D.J. High-Volume diffusion denuder sampler for the routine monitoring of fine particulate matter: I. Design andoptimization of the PC-BOSS. *Aerosol Sci. Technol.* 2002a, **36** pp. 369–382

[61] DING Y., PANG Y., EATOUGH D.J., EATOUGH N.L., TANNER R.L. High-volume diffusion denuder sampler for the routine monitoring of fine particulate matter: II. Field evaluation of the PC-BOSS. *Aerosol Sci. Technol.* 2002b, **36** pp. 383–396

[62] DOTTER R.N., SMITH C.H., YOUNG M.K., KELLY P.B., JONES A.D., MCCAULEY E.M. et al. Laser desorption/ionization time-of-flight mass spectrometry of nitrated polycyclic aromatic hydrocarbons. *Anal. Chem.* 1996, **68** pp. 2319–2324

[63] DURANT J.L., BUSBY W.F. JR., LAFLEUR A.L., PENMAN B.W., CRESPI C.L. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. *Mutat Res-Gen Tox*. 1996, **371** pp. 123–157

[64] DURANT J.L., LAFLEUR A.L., PLUMMER E.F., TAGHIZADEH K., BUSBY W.F., THILLY W.G. Human lymphoblast mutagens in urban airborne particles. *Environ. Sci. Technol.* 1998, **32** pp. 1894–1906

[65] EATOUGH D.J., OBEIDI F., PANG Y., DING Y., EATOUGH N.L., WILSON W.E. Integrated and real-time diffusion denuder sample for PM2.5. *Atmos. Environ.* 1999, **33** pp. 2835–2844

[66] EIGUREN-FERNANDEZ A., MIGUEL A.H., LU R., PURVIS K., GRANT B., MAYO P. et al. Atmospheric formation of 9,10-phenanthraquinone in the Los Angeles air basin. *Atmos. Environ.* 2008a, **42** pp. 2312–2319

[67] EIGUREN-FERNANDEZ A., MIGUEL A.H., DI STEFANO E., SCHMITZ D.A., CHO A.K., THURAIRATNAM S. et al. Atmospheric distribution of gas- and particle-phase quinones in southern California. *Aerosol Sci. Technol.* 2008b, **42** pp. 854–861

[68] EN 12341:2014, *Ambient air — Standard gravimetric measurement method for the determination of the PM10 or PM2,5 mass concentration of suspended particulate matter*

[69] EN 15549:2008, *Air quality — Standard method for the measurement of the concentration of benzo[a]pyrene in ambient air*

[70] Environmental Health Criteria (EHC) 229. Selected nitro- and nitro-oxy-polycyclic aromatic hydrocarbons. WHO Library, 2003, 464 http://whqlibdoc.who.int/ehc/WHO_EHC_229.pdf.

[71] ENYA T., SUZUKI H., WATANABE T., HIRAYAMA T., HISAMATSU Y. 3-nitrobenzanthrone, a powerful bacterial mutagen and suspected human carcinogen found in diesel exhaust and airborne particulates. *Environ. Sci. Technol.* 1997, **31** pp. 2772–2776

[72] ESTEVE W., BUDZINSKI H., VILLENAVE E. Heterogeneous reactivity of OH radicals with phenanthrene. *Polycycl. Aromat. Compd.* 2003, **23** pp. 441–456

[73] ESTEVE W., BUDZINSKI H., VILLENAVE E. Relative rate constants for the heterogeneous reactions of NO_2 and OH radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a. *Atmos. Environ.* 2006, **40** pp. 201–211

[74] FAN Z., CHEN D., BIRLA P., KAMENS R.M. Modeling of nitro-polycyclic aromatic hydrocarbon formation and decay in the atmosphere. *Atmos. Environ.* 1995, **29** pp. 1171–1181

[75] Feilberg, A. B., Poulsen, M. W., Nielsen, T. and Henrik Skov. Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark. *Atmos. Environ.* 2001, **35** pp. 353–366

[76] FEILBERG A., NIELSEN T. Photodegradation of nitro-PAHs in viscous organic media used as models of organic aerosols. *Environ. Sci. Technol.* 2001, **35** pp. 108–113

[77] FEILBERG A., OHURA T., NIELSEN T., POULSEN M.W.B., AMAGAI T. Occurrence and photostability of 3-nitrobenzanthrone associated with atmospheric particles. *Atmos. Environ.* 2002, **36** pp. 3591–3600

[78] FICK J., POMMER L., ANDERSSON B., NILSSON C. Ozone removal in the sampling of parts per billion levels of terpenoid compounds: an evaluation of different scrubber materials. *Environ. Sci. Technol.* 2001, **35** pp. 1458–1462

[79] FINLAYSON-PITTS B.J., PITTS J.N. JR. *Atmospheric Chemistry: Fundamental and experimental techniques*. Wiley-Interscience, 1986, 1097 p.

[80] FINLAYSON-PITTS B.J., PITTS J.N. JR. *Chemistry of the upper and lower atmosphere*. Academic Press, 2000, 969 p.

[81] FRASER M.P., CASS G.R., SIMONEIT B.R.T., RASMUSSEN R.A. Air quality model evaluation data for organics. 5. C6-C22 nonpolar and semipolar aromatic compounds. *Environ. Sci. Technol.* 1998, **32** pp. 1760–1770

[82] FU P.P., HERRENO-SAENZ D., VON TUNGELN L.S., LAY J.O., WU Y.-S. Lai, J.-S., Evans, F. E. DNA-Adducts and Carcinogenicity of nitro-polycyclic aromatic hydrocarbons. *Environ. Health Perspect.* 1984, **102** (suppl 6) pp. 177–184

[83] FU P.P., CHOU M.W., BELAND F.A. In: *Effects of nitro substitution on the in vitro metabolic activation of polycyclic aromatic hydrocarbon carcinogenesis: Structure-Activity relationships.* (YANG S.K., SILVERMAN B.D., eds.). CRC press, Florida, 1988, pp. 37–65.

[84] FUSHIMI A., HASHIMOTO S., IEDA T., OCHIAI N., TAKAZAWA Y., FUJITANI Y. et al. Thermal desorption – comprehensive two-dimensional gas chromatography coupled with tandem mass spectrometry for determination of trace polycyclic aromatic hydrocarbons and their derivatives. *J. Chromatogr. A*. 2012, **1252** pp. 164–170

[85] GORIAUX M., JOURDAIN B., TEMIME B., BESOMBES J.-L., MARCHAND N., ALBINET A. et al. Field comparison of particulate PAH measurements using a low flow denuder device and conventional sampling systems. *Environ. Sci. Technol.* 2006, **40** pp. 6398–6404

[86] HANNIGAN M.P., CASS G.R., PENMAN B.W., CRESPI C.L., LAFLEUR A.L., BUSBY W.F. JR. et al. Bioassay-directed chemical analysis of Los Angeles airborne particulate matter using a human cell mutagenicity assay. *Environ. Sci. Technol.* 1998, **32** pp. 3502–3514

[87] HAWTHORNE S.B., MILLER D.J., LANGENFELD J.J., KRIEGER M.S. PM_{10} high-volume collection and quantification of semi- and nonvolatile phenols, methoxylated phenols, alkanes, and polycyclic aromatic hydrocarbons from winter urban air and their relationship to wood smoke emissions. *Environ. Sci. Technol.* 1992, **26** pp. 2251–2262

[88] HAYAKAWA K., BUTOH M., HIRABAYASHI Y., MIYAZAKI M. Determination of 1,3-, 1,6-, 1,8-dinitropyrenes and 1-nitropyrene in vehicle exhaust particulates. *Jap. J. Toxicol. Environ. Health*. 1994, **40** pp. 20–25

[89] HAYAKAWA K., MURAHASHI T., BUTOH M., MIYAZAKI M. Determination of 1,3-, 1,6-, and 1,8-dinitropyrenes and 1-nitropyrene in urban air by high-performance liquid chromatography using chemiluminescence detection. *Environ. Sci. Technol.* 1995a, **29** pp. 928–932

[90] HAYAKAWA K., KAWAGUCHI Y., MURAHASHI T., MIYAZAKI M. Distributions of nitropyrenes and mutagenicity in airborne particulates collected with an Andersen sampler. *Mutat. Res.* 1995b, **348** pp. 57–61

[91] HAYAKAWA K., KIZU R., ANDO K. Study on atmospheric behavior and toxicity of carcinogenic nitroarenes by high-performance liquid chromatography using chemiluminescence detection. *Chrom J Sep Det Sci*. 1999, **20** pp. 37–43

[92] HAYAKAWA K. Chromatographic methods for carcinogenic/mutagenic nitropolycyclic aromatic hydrocarbons. *Biomed. Chromatogr.* 2000, **14** pp. 397–405

[93] HAYAKAWA K., TANG N., AKUTSU K., MURAHASHI T., KAKIMOTO H., KIZU R. et al. Comparison of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in airborne particulates collected in downtown and suburban Kanazawa, Japan. *Atmos. Environ.* 2002, **36** pp. 5535–5541

[94] HEEB N.V., SCHMID P., KOHLER M., GUJER E., ZENNEGG M., WENGER D. et al. Secondary effects of catalytic diesel particulate filters: conversion of PAHs versus formation of nitro-PAHs. *Environ. Sci. Technol.* 2008, **42** pp. 3773–3779

[95] HELMIG D., AREY J., HARGER W.P., ATKINSON R., LÓPEZ-CANCIO J. Formation of mutagenic nitrodibenzopyranones and their occurrence in ambient air. *Environ. Sci. Technol.* 1992a, **26** pp. 622–624

[96] HELMIG D., LOPEZ-CANCIO J., AREY J., HARGER W.P., ATKINSON R. Quantification of ambient nitrodibenzopyranones: further evidence for atmospheric mutagen formation. *Environ. Sci. Technol.* 1992b, **26** pp. 2207–2213

[97] HELMIG D., HARGER W.P. OH radical-initiated gas-phase reaction products of phenanthrene. *Sci. Total Environ.* 1994, **148** pp. 11–21

[98] HELMIG D., GREENBERG J. Artifact formation from the use of potassium-iodide-based ozone traps during atmospheric sampling of trace organic gases. *J. High Resolut. Chromatogr.* 1995, **18** pp. 15–18

[99] HELMIG D. Ozone removal techniques in the sampling of atmospheric volatile organic trace gases. *Atmos. Environ.* 1997, **31** pp. 3635–3651

[100] HIEN T.T., THANH L.T., KAMEDA T., TAKENAKA N., BANDOW H. Nitro-polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons in particulate matter in an urban area of a tropical region: Ho Chi minh Cyty, Vietnam. *Atmos. Environ.* 2007, **41** pp. 7715–7725

[101] HOIGNE J., BADER H., HAAG W.R., STAEHLELIN J. Rate constants of reaction of ozone with organic and inorganic compounds in water. *Water Res.* 1985, **19** pp. 993–1004

[102] HUANG B., MING L., BI X., CHAEMFA C., REN Z., WANG X. et al. Phase distribution, sources and risk assessment of PAHs, NPAHs and OPAHs in a rural site of Pearl River Delta region, China. *Atmos. Pollut. Res.* 2014, **5** pp. 210–218

[103] HUNT G.T., MAISEL B.E. Atmospheric concentrations of PCDDs/PCDFs, PAHs, and Nitro-PAHs in Fresno, California, during winter months. *Organ Comp*. 1995, **24** pp. 55–61

[104] IARC. *IARC Monogr. Eval. Carcinog. Risks Hum.* 1989, **46** p. ••• [Diesel and gasoline engine exhaust and some nitroarenes, Lyon]

[105] IARC. *IARC Monogr. Eval. Carcinog. Risks Hum.* 2012, **101** p. ••• [Some Chemicals present in Industrial and Consumer Products, Food and Drinking-water, Lyon]

[106] IARC. *IARC Monogr. Eval. Carcinog. Risks Hum.* 2013, **105** p. ••• [Diesel and gasoline engine exhaust and some nitroarenes, Lyon]

[107] ISO 12884:2000, *Ambient air — Determination of total (gas and particle-phase) polycyclic aromatic hydrocarbons — Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analyses*

[108] JINHUI X., LEE F.S.C. Quantification of nitrated polynuclear aromatic hydrocarbons in atmospheric particulate matter. *Anal. Chim. Acta*. 2000, **416** pp. 111–115

[109] KAMENS R.M., GUO Z.G., MCDOW S.R. Polynuclear aromatic hydrocarbon degradation by heterogeneous reactions with N_2O_5. *Atmos. Environ.* 1990, **24A** pp. 1161–1173

[110] KARAVALAKIS G., DEVES G., FONTARAS G., STOURNAS S., SAMARAS Z., BAKEAS E. The impact of soy-based biodiesel on PAH, nitro-PAH and oxy-PAH emissions from a passenger car operated over regulated and nonregulated driving cycles. *Fuel*. 2010a, **89** pp. 3876–3883

[111] KARAVALAKIS G., FONTARAS G., AMPATZOGLOU D., KOUSOULIDOU M., STOURNAS S., SAMARAS Z. et al. Effects of low concentration biodiesel blends application on modern passenger cars. Part 3: Impact on PAH, nitro-PAH, and oxy-PAH emissions. *Environ. Pollut.* 2010b, **158** pp. 1584–1594

[112] KARAVALAKIS G., BOUTSIKA V., STOURNAS S., BAKEAS E. Biodiesel emissions profile in modern diesel vehicles. Part 2: Effect of biodiesel origin on carbonyl, PAH, nitro-PAH and oxy-PAH emissions. *Sci. Total Environ.* 2011, **409** pp. 738–747

[113] KAUTZMAN K.E., SURRATT J.D., CHAN M.N., CHAN A.W.H., HERSEY S.P., CHHABRA P.S. et al. Chemicalo composition of gas- and aerosol-phase products from the photooxidatioon of naphthalene. *J. Phys. Chem. A*. 2010, **114** pp. 913–934

[114] KAVOURAS I.G., LAWRENCE J., KOUTRAKIS P., STEPHANOU E.G., OYOLA P. Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts. *Atmos. Environ.* 1999, **33** pp. 4977–4986

[115] KAWANAKA Y., MATSUMOTO E., SAKAMOTO K., WANG N., YUN S.-J. Size distributions of mutagenic compounds and mutagenicity in atmospheric particulate matter collected with a low-pressure cascade impactor. *Atmos. Environ.* 2004, **38** pp. 2125–2132

[116] KAWANAKA Y., MATSUMOTO E., WANG N., YUN S.J., SAKAMOTO K. Contribution of nitrated polycyclic aromatic hydrocarbons to the mutagenicity of ultrafine particles in the roadside atmosphere. *Atmos. Environ.* 2008, **42** pp. 7423–7428

[117] KEYTE I.J., HARRISON R.M., LAMMEL G. Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons - a review. *Chem. Soc. Rev.* 2013, **42** pp. 9333–9391

[118] KINOUCHI T., NISHIFUJI K., TSUTSUI H., HOARE S.L., OHNISHI Y. Mutagenicity and nitropyrene concentration of indoor air particulates exhausted from kerosene heater. *Jpn. J. Cancer Res.* 1988, **79** pp. 32–41

[119] KOJIMA Y., INAZU K., HISAMATSU Y., OKOCHI H., BABA T., NAGOYA T. Influence of secondary formation on atmospheric occurrences of oxygenated polycyclic aromatic hydrocarbons in airborne particles. *Atmos. Environ.* 2010, **44** pp. 2873–2880

[120] KÖNIG J., BALFANZ E., FUNCKE W., ROMANOWSKI T. Determination of oxygenated polycyclic aromatic hydrocarbons in airborne particulate matter by capillary gas chromatography and gas chromatography/mass spectrometry. *Anal. Chem.* 1983, **55** pp. 599–603

[121] KWAMENA N.O.A., STAIKOVA M.G., DONALDSON D.J., GEORGE I.J., ABBATT J.P.D. Role of the aerosol substrate in the heterogeneous ozonation reactions of surface-bound PAHs. *J. Phys. Chem. A*. 2007, **111** pp. 11050–11058

[122] KWAMENA N.O.A., ABBATT J.P.D. Heterogeneous nitration reactions of polycyclic aromatic hydrocarbons and n-hexane soot by exposure to $NO_3/NO_2/N_2O_5$. *Atmos. Environ.* 2008, **42** pp. 8309–8314

[123] LADJI R., YASSAA N., BALDUCCI C., CECINATO A., MEKLATI B.Y. Distribution of the solvent-extractable organic compounds in fine (PM_1) and coarse (PM_{10}) particles in urban, industrial and forest atmospheres of northern Algeria. *Sci. Total Environ.* 2009, **408** pp. 415–424

[124] LANDVIK N.E., GORRIA M., ARLT V.M., ASARE N., SOLHAUG A., LAGADIC-GOSSMANN D. et al. Effects of of nitrated polycyclic aromatic hydrocarbons and Diesel exhaust particle extracts on cell signalling related to apoptosis: Possible implications for their mutagenic and carcinogenic effects. *Toxicology*. 2007, **231** pp. 159–174

[125] LEOZ-GARZIANDIA E., TATRY V., CARLIER P. Sampling and analysis of polycyclic aromatic hydrocarbons (PAH) and oxygenated PAH in diesel exhaust and ambient air. *Polycycl. Aromat. Compd.* 2000, **20** pp. 245–258

[126] LEVSEN K. The analysis of diesel particulate. *Fresenius Z. Anal. Chem.* 1988, **331** pp. 467–478

[127] Lewis A.C., Robinson R.E., Bartel K.D., Pilling M.J. On-line coupled LC-GC-ITD/MS for the identification of alkylated, oxygenated, and nitrated polycyclic aromatic compounds in urban air particle extracts. *Environ. Sci. Technol.* 1995, **29** pp. 1977–1981

[128] Lewtas J., Nishioka M., Peterson B. Bioassay directed fractionation of the organic extract of SRM 1649 urban air particulate and ambient matter. *Int. J. Environ. Anal. Chem.* 1990, **39** pp. 245–256

[129] Ligocki M.P., Pankow J.F. Measurement of gas/particle distributions of atmospheric organic compounds. *Environ. Sci. Technol.* 1989, **23** pp. 75–83

[130] Liu Y., Sklorz M., Schnelle-Kreis J., Orasche J., Ferge T., Kettrup A. et al. Oxidant denuder sampling for analysis of polycyclic aromatic hydrocarbons and their oxygenated derivates in ambient aerosol: Evaluation of sampling artefact. *Chemosphere*. 2006, **62** pp. 1889–1898

[131] Lundstedt S., White P.A., Lemieux C.L., Lynes K.D., Lambert B., Oberg L. et al. Sources fate and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites. *Ambio*. 2007, **36** pp. 475–485

[132] Mader B.T., Schauer J.J., Seinfeld J.H., Flagan R.C., Yu J.Z., Yang H. et al. Sampling methods used for the collection of particle-phase organic and elemental carbon during ACE-Asia. *Atmos. Environ.* 2003, **37** pp. 1435–1449

[133] Maria del Rosario Sienra M. Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter. *Atmos. Environ.* 2006, **40** pp. 2374–2384

[134] Marino F., Cecinato A., Siskos P.A. Nitro-PAH in ambient particulate matter in the atmosphere of Athens. *Chemosphere*. 2000, **40** pp. 533–537

[135] Mastral A.M., Garcia T., Callen M.S., Navarro M.V., Galban J. Assessement of phenanthrene removal from hot gas by porous carbons. *Energy Fuels*. 2000, **15** pp. 1–7

[136] Mastral A.M., Garcia T., Murillo R., Callen M.S., Lopez J.M., Navarro M.V. Measurements of polycyclic aromatic hydrocarbon adsorption on activated carbons at very low concentrations. *Ind. Eng. Chem. Res.* 2003, **42** pp. 155–161

[137] Matsushita H., Iida Y. Application of capillary gas chromatography to environmental analysis. *J. High Resolut. Chromatogr.* 1986, **9** pp. 708–711

[138] Metts T.A., Batterman S.A. Effect of VOC loading on the ozone removal efficiency of activated carbon filters. *Chemosphere*. 2006, **62** pp. 34–44

[139] Miet K., Le Menach K., Flaud P.M., Budzinski H., Villenave E. Heterogeneous reactivity of pyrene and 1-nitropyrene with NO2: Kinetics, product yields and mechanism. *Atmos. Environ.* 2009, **43** pp. 837–843

[140] Mikuška P., Vecera Z., Broškovicová A. *In Artifact free denuder method for sampling of carbonaceous aerosols, EGU Joint Assembly, Nice (France), 2003*. Geophysical Research Abstracts, Nice, France, 2003, pp. 05873.

[141] Mirivel G., Riffault V., Galloo J.-C. Simultaneous determination by ultra-performance liquid chromatography–atmospheric pressure chemical ionization time-of-flight mass spectrometry of nitrated and oxygenated PAHs found in air and soot particles. *Anal. Bioanal. Chem.* 2010, **397** pp. 243–256

[142] MÜCKE W., HUBER W., HORNDASCH M., HUNSTEIN R., KOCH M. *Weindl., J., Huber, J., Constantin, A., Matuschek, G., Lintelmann, J. Analytik und Mutagenität von verkehrsbedingtem Feinstaub: PAK und Nitro-PAK*. Herbert Utz Verlag, München, 2009

[143] NAGY E., ZEISIG M., KAWAMURA K., HISAMATSU Y., SUGETA A., ADACHI S. et al. DNA adduct and tumor formations in rats after intratracheal administration of the urban air pollutant 3-nitrobenzanthrone. *Carcinogenesis*. 2005, **26** pp. 1821–1828

[144] NASSAR H.F., TANG N., KAMEDA T., TORIBA A., KHODER M.I., HAYAKAWA K. Atmospheric concentrations of polycyclic aromatic hydrocarbons and selected nitrated derivatives in Greater Cairo, Egypt. *Atmos. Environ.* 2011, **45** pp. 7352–7359

[145] NEUSUESS C., PELZING M., PLEWKA A., HERRMANN H. A new analytical approach for size resolved speciation of organic compounds in atmospheric aerosol particles, methods and first results. *J. Geophys. Res., D, Atmospheres*. 2000, **105** pp. 4513–4527

[146] NGUYEN M., BEDJANIAN Y., GUILLOTEAU A. Kinetics of the reactions of soot surface-bound polycyclic aromatic hydrocarbons with NO_2. *J. Atmos. Chem.* 2009, **62** pp. 139–150

[147] NIEDERER M. Determination of polycyclic aromatic hydrocarbons and substitutes (nitro-, oxy-PAHs) in urban soil and airborne particulate by GC-MS and NCI-MS/MS. *Environ Sci Pollut Res*. 1998, **5** pp. 209–216

[148] NIELSEN T. Reactivity of polycyclic aromatic hydrocarbons toward nitrating species. *Environ. Sci. Technol.* 1984, **18** pp. 157–163

[149] NIST NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY. *Certificate of Analysis: Standard Reference Material 1650b*. Diesel Particulate Matter, 2013a

[150] NIST NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY. *Certificate of Analysis: Standard Reference Material 2975*. Diesel Particulate Matter, Industrial Forklift, 2013b

[151] NIST NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY. *Certificate of Analysis: Standard Reference Material 1649b*. Urban Dust, 2009

[152] NTP. Report on Carcinogens, Twelfth Edition. Research Triangle Park, NC: U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, 2011, 499 p http://ntp.niehs.nih.gov/ntp/roc/twelfth/roc12.pdf.

[153] ODA J., NOMURA S., YASUKARA A., SHIBAMOTO T. Mobile sources of atmospheric polycyclic aromatic hydrocarbons in a roadway tunnel. *Atmos. Environ.* 2001, **36** pp. 4819–4827

[154] OHNO T., TORIBA A., KAMEDA T., TANG N., HAYAKAWA K. Determination of 1-nitropyrene in low volume ambient air samples by high-performance liquid chromatography with fluorescence detection. *J. Chromatogr. A*. 2009, **1216** pp. 4625–4628

[155] ORASCHE J., SCHNELLE-KREIS J., ABBASZADE G., ZIMMERMANN R. Technical Note: In-situ derivatization thermal desorption GC-TOFMS for direct analysis of particle-bound non-polar and polar organic species. *Atmos. Chem. Phys.* 2011, **11** pp. 8977–8993

[156] ORASCHE J., SEIDEL T., HARTMANN H., SCHNELLE-KREIS J., CHOW J.C., RUPPERT H. et al. Comparison of emissions from wood combustion. Part 1: Emission factors and characteristics from from different small-scale residential heating appliances considering particulate matter and polycyclic

aromatic hydrocarbon (PAH)-related toxicological potential of particle-bound organic species. *Energy Fuels*. 2012, **26** pp. 6695–6704

[157] ORASCHE J., SCHNELLE-KREIS J., SCHÖN C., HARTMANN H., RUPPERT H., ARTEAGA-SALAS J.M. et al. Comparison of emissions from wood combustion – 2: The impact of combustion conditions on emission factors and characteristics of particle bound organic species and PAH related toxicological potential. *Energy Fuels*. 2013, **27** pp. 1482–1491

[158] ORTIZ R., HAGINO H., SEKIGUCHI K., WANG Q., SAKAMOTO K. Ambient air measurements of six bifunctional carbonyls in a suburban area. *Atmos. Res.* 2006, **82** pp. 709–718

[159] ØVREVIK J., ARLT V.M., ØYA E., NAGY E., MOLLERUP S., PHILLIPS D.H. et al. Differential effects of nitro-PAHs and amino-PAHs on cytokine and chemokine responses in human bronchial epithelial BEAS-2B cells. *Toxicol. Appl. Pharmacol.* 2010, **242** pp. 270–280

[160] PAPUTA-PECK M., MARANO R.S., SCHUETZLE D., RILEY T.L., HAMPTON C.V., PRATER T.J. et al. Determination of nitrated polynuclear aromatic hydrocarbons in particulate extracts by capillary column gas chromatography with nitrogen selective detection. *Anal. Chem.* 1983, **55** pp. 1946–1954

[161] PARK E.J., KIM D.S., PARK K. Monitoring of ambient particles and heavy metals in a residential area of Seoul, Korea. *Environ. Monit. Assess.* 2008, **137** pp. 441–449

[162] PEDERSEN D.U., DURANT J.L., PENMAN B.W., CRESPI C.L., HEMOND H.F., LAFLEUR A.L. et al. Human-cell mutagens in respirable airborne particles in the northeastern United States. 1. Mutagenicity of fractionated samples. *Environ. Sci. Technol.* 2004, **38** pp. 682–689

[163] PEDERSEN D.U., DURANT J.L., TAGHIZADEH K., HEMOND H.F., LAFLEUR A.L., CASS G.R. Human cell mutagens in respirable airborne particles from the northeastern United States. 2. Quantification of mutagens and other organic compounds. *Environ. Sci. Technol.* 2005, **39** pp. 9547–9560

[164] Perraudin, E. Réactivité des hydrocarbures aromatiques polycycliques (HAP) adsorbés sur des particules modèles d'intérêt atmosphérique: mesures cinétiques, développements analytiques et analyse des produits d'oxydation. Université de Bordeaux 1, 2004, 285p pp

[165] PERRAUDIN E., BUDZINSKI H., VILLENAVE E. Kinetic study of the reactions of NO_2 with polycyclic aromatic hydrocarbons adsorbed on silica particles. *Atmos. Environ.* 2005, **39** pp. 6557–6567

[166] PERRAUDIN E., BUDZINSKI H., VILLENAVE E. Identification and quantification of primary ozonation products of phenanthrene and anthracene adsorbed on silica particles. *Atmos. Environ.* 2007, **41** pp. 6005–6017

[167] PHOUSONGPHOUANG P.T., AREY J. Sources of the atmospheric contaminants, 2-nitrobenzanthrone and 3-nitrobenzanthrone. *Atmos. Environ.* 2003, **37** pp. 3189–3199

[168] PITTS J.N., SWEETMAN J.A., ZIELINSKA B., ATKINSON R., WINER A.M., HARGER W.P. Formation of nitroarenes from the reaction of polycyclic aromatic hydrocarbons with dinitrogen pentoxide. *Environ. Sci. Technol.* 1985, **19** pp. 1115–1121

[169] PITTS J.N. JR., VAN CAUWENBERGHE K.A., GROSJEAN D., SCHMID J.P., FITZ D.R., BELSER W.L.J. et al. Atmospheric reactions of polycyclic aromatic hydrocarbons. *Science*. 1978, **202** pp. 515–519

[170] PÖSCHL U., LETZEL T., SCHAUER C., NIESSNER R. Interaction of ozone and water vapor with spark discharge soot aerosol particles coated with benzo[*a*]pyrene: O_3 and H_2O adsorption,

benzo[*a*]pyrene degradation, and atmospheric implications. *J. Phys. Chem. A*. 2001, **105** pp. 4029–4041

[171] POSSANZINI M., FEBO A., CECCHINI F. Development of a KI annular denuder for NO_2 collection. *Anal. Lett.* 1984, **17** pp. 887–896

[172] RAMDHAL T. Polycyclic aromatic ketones in environmental samples. *Environ. Sci. Technol.* 1983, **17** pp. 666–670

[173] RATTANAVARAHA W., ROSEN E., ZHANG H.F., LI Q.F., PANTONG K., KAMENS R.M. The reactive oxidant potential of different types of aged atmospheric particles: An outdoor chamber study. *Atmos. Environ.* 2011, **45** pp. 3848–3855

[174] REISEN F., AREY J. Atmospheric reactions influence seasonal PAH and nitro-PAH concentrations in the Los Angeles basin. *Environ. Sci. Technol.* 2005, **39** pp. 64–73

[175] RINGUET J., LEOZ-GARCIANDIA E., BUDZINSKI H., VILLENAVE E., ALBINET A. Particle size distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs and OPAHs) an traffic and suburban sites of a European megacity: Paris (France). *Atmos. Chem. Phys.* 2012a, **12** pp. 8877–8887

[176] RINGUET J., LEOZ-GARCIANDIA E., BUDZINSKI H., VILLENAVE E. Reactivity of polycyclic aromatic hydrocarbons (PAHs, NPAHs and OPAHs) adsorbed on natural aerosol particles exposed to atmospheric oxidants. *Atmos. Environ.* 2012b, **61** pp. 15–22

[177] RINGUET J., ALBINET A., LEOZ-GARCIANDIA E., BUDZINSKI H., VILLENAVE E. Diurnal/nocturnal concentrations and sources of particulate-bound PAHs, NPAHs and NPAHs at traffic and suburban sites in the region of Paris (France). *Sci. Total Environ.* 2012c, **437** pp. 297–305

[178] RUBEL A.M., STEWART M.L., STENCEL J.M. Activated carbon for control of nitrogen oxide emissions. *J. Mater. Res.* 1995, **10** pp. 562–567

[179] RUIZ P.A., LAWRENCE J.E., FERGUSON S.T., WOLFSON J.M., KOUTRAKIS P. A counter-current parallel-plate membrane denuder for the non-specific removal of trace gases. *Environ. Sci. Technol.* 2006, **40** pp. 5058–5063

[180] SAMY S., ZIELINSKA B., SAGEBIEL J.C., MCDONALD J.D. Application for a newly developed high-capacity NO(x) denuder: low-NO(x) diesel transformation experiments. *J. Air Waste Manage. Assoc.* 2011, **61** pp. 319–323

[181] SASAKI J., ASCHMANN S.M., KWOK E.S.C., ATKINSON R., AREY J. Products of the gas-phase OH and NO_3 radical-initiated reactions of naphthalene. *Environ. Sci. Technol.* 1997, **31** pp. 3173–3179

[182] SCHAUER J.J., KLEEMAN M.J., CASS G.R., SIMONEIT B.R.T. Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty Diesel trucks. *Environ. Sci. Technol.* 1999, **36** pp. 1169–1180

[183] SCHAUER J.J., KLEEMAN M.J., CASS G.R., SIMONEIT B.R.T. Measurement of emissions from air pollution sources. 3. C-1 to C-29 organic compounds from fireplace combustion of wood. *Environ. Sci. Technol.* 2001, **35** pp. 1716–1728

[184] SCHAUER J.J., KLEEMAN M.J., CASS G.R., SIMONEIT B.R.T. Mesurement of emissions from air pollution sources. 5. C-1 to C-22 organic compounds from gasoline powered motor vehicles. *Environ. Sci. Technol.* 2002, **36** pp. 1169–1180

[185] SCHAUER C., NIESSNER R., POSCHL U. Polycyclic aromatic hydrocarbons in urban air particulate matter: decadal and seasonal trends, chemical degradation, and sampling artifacts. *Environ. Sci. Technol.* 2003, **37** pp. 2861–2868

[186] SCHAUER C., NIESSNER R., POSCHL U. Analysis of nitrated polycyclic aromatic hydrocarbons by liquid chromatography with fluorescence and mass spectrometry detection: air particulate matter, soot, and reaction product studies. *Anal. Bioanal. Chem.* 2004, **378** pp. 725–736

[187] SCHNELLE-KREIS J., GEBEFUGI I., WELZL G., JAENSCH T., KETTRUP A. Occurrence of particle-associated polycyclic aromatic compounds in ambient air of the city of Munich. *Atmos. Environ.* 2001, **35** pp. 71–81

[188] SCHNELLE-KREIS J., SKLORZ M., CYRYS J. Analysis of particle-associated semi-volatile aromatic and aliphatic hydrocarbons in urban particulate matter on a daily basis. *Atmos. Environ.* 2005, **39** pp. 7702–7714

[189] SCHUETZLE D. Sampling of vehicle emissions for chemical analysis and biological testing. *Environ. Health Perspect.* 1983, **47** pp. 65–80

[190] SCHUETZLE D., PEREZ J.M. Factor influencing the emissions of nitrated-polynuclear aromatic hydrocarbons (nitro-PAH) from diesel engines. *JAPCA J Air Waste Ma*. 1983, **33** pp. 751–755

[191] SCHULZE J., HARTUNG A., KRAFT J., LIES K.-H. Identification of oxygenated polycyclic aromatic hydrocarbons in diesel particulate matter by capillary gas chromatography and capillary gas chromatography/mass spectrometry. *Chromatographia*. 1984, **19** pp. 391–397

[192] SERA N., FUKUHARA K., MIYATA N. Detection of nitro-azabenzo[*a*]pyrene derivatives in the semivolatile phase originating from airborne particulate matter, diesel and gasoline vehicles. *Mutagenesis*. 1994, **9** pp. 47–52

[193] SHAKYA K.M., GRIFFIN R.J. Secondary aerosol from photooxidation of polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 2010, **44** pp. 8134–8139

[194] SHEN G., TAO S., WANG W., YANG Y., DING J., XUE M. et al. Emission of oxygenated polycyclic aromatic hydrocarbons from indoor solid fuel combustion. *Environ. Sci. Technol.* 2011, **45** pp. 3459–3465

[195] SHEN G., WEI S., ZHANG Y., WANG R., WANG B., LI W. et al. Emission of oxygenated polycyclic aromatic hydrocarbons from biomass pellet burning in a modern burner for cooking in China. *Atmos. Environ.* 2012a, **60** pp. 234–237

[196] SHEN G., TAO S., WEI S., ZHANG Y., WANG R., WANG B. et al. Emissions of parent, nitro, and oxygenated polycyclic aromatic hydrocarbons from residential wood combustion in rural China. *Environ. Sci. Technol.* 2012b, **46** pp. 8123–8130

[197] SHIMMO M., JUNTTI J., AALTO P., HARTONEN K., HYOTYLAINEN T., KULMALA M. et al. Identification of organic compounds by online supercritical fluid extraction-liquid chromatography gas chromatography mass spectrometry. *J. Chromatogr. A*. 2008, **1022** pp. 151–159

[198] SIENRA M.D. Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter. *Atmos. Environ.* 2006, **40** pp. 2374–2384

[199] SIMONEIT B.R.T., BI X. Oros, D. R., Medeiros, P. M., Sheng, G. and Fu, J. Phenols and hydroxy-PAHs (arylphenols) as tracers for coal smoke particulate matter: Source tests and ambient aerosol assessments. *Environ. Sci. Technol.* 2007, **41** pp. 7294–7302

[200] Sklorz, M., Briede, J. J., Schnelle-Kreis, J., Liu, Y., Cyrys, J., de Kok, T., M., Zimmermann, R. Concentration of oxygenated polycyclic aromatic hydrocarbons and oxygen free radical formation from urban particulate matter. Journal of Toxicology and Environmental Health – Part A- Current issues 70, (2007), 1866 – 1869

[201] SPAULDING R.S., FRAZEY P., RAO X., CHARLES M.J. Measurement of hydroxy carbonyls and other carbonyls in ambient air using pentafluorobenzyl alcohol as a chemical ionization reagent. *Anal. Chem.* 1999, **71** pp. 3420–3427

[202] SUBRAMANIAN R., KHLYSTOV A.Y., CABADA J.C., ROBINSON A.L. Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations. *Aerosol Sci. Technol.* 2004, **38** pp. 27–48

[203] TAGA R., TANG N., HATTORI T., TAMURA K., SAKAI S., TORIBA A. et al. Direct-acting mutagenicity of extracts of coal burning-derived particulates and contribution of nitropolycyclic aromatic hydrocarbons. *Mutat Res-Gen Tox En.* 2005, **581** pp. 91–95

[204] TANG N., HATTORI T., TAGA R., IGARASHI K., YANG X., TAMURA K. et al. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries. *Atmos. Environ.* 2005, **39** pp. 5817–5826

[205] TEIXEIRA E.C., GARCIA K.O., MEINCKE L., LEAL K.A. Study of nitro-polycyclic aromatic hydrocarbons in fine and coarse atmospheric particles. *Atmos. Res.* 2011, **101** pp. 631–639

[206] TNO (2009) Chemical characterisation of Biofuel emissions; TNO-034-UT-2009-01077_RPT-ML

[207] TNO (2011) De bepaling van nitro- en oxy-PAK met isotoopverdunning en GC-MS analyse; TNO-060-UT-2011-00953

[208] TOKIWA et al. The Role of Nitroarenes in the Mutagenicity of Airborne Particles Indoors and Outdoors. In: *Genetic Toxicology of Complex Mixtures*, (WATERS M.D., DANIEL F.B., LEWTAS J. et al., eds.). Plenum Press, New York, USA, 1990, pp. 165–72.

[209] TSAPAKIS M., STAPHANOU E.G. Diurnal cycle of PAHs, nitro PAHs and oxygenated PAHs in a high oxidation capacity marine background atmosphere. *Environ. Sci. Technol.* 1998, **41** pp. 8011–8017

[210] TSAPAKIS M., STEPHANOU E.G. Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling. *Atmos. Environ.* 2003, **37** pp. 4935–4944

[211] VALAVANIDIS A., FIOTAKIS K., VLANOGIANNI T., PAPADIMITROU M., PANTIKAKI V. Determination of selective quinones and quinoid radicals in airborne particulate matter and vehicular exhaust particles. *Environ. Chem.* 2006, **3** pp. 118–123

[212] VALLE-HERNANDEZ B.L., MUGICA-ALVAREZ V., SALINAS-TALAVERA E., AMADOR-MUNOZ O., MURILLO-TOVAR M.A., VILLALOBOS-PIETRINI R. et al. Temporal variation of nitro-polycyclic aromatic hydrocarbons in PM_{10} and $PM_{2.5}$ collected in Northern Mexico City. *Sci. Total Environ.* 2010, **408** pp. 5429–5438

[213] VAN HOUDT J.J. Mutagenic activity of airborne particulate matter in indoor and outdoor environments. *Atmos. Environ.* 1990, **24B** pp. 207–220

[214] VASCONCELLOS P.C., ARTAXO P.E., CICCIOLI P., CECINATO A., BRANCALCONI E., FRATTONI M. Chemical composition of aerosol collected in the Amazon forest. *Quim. Nova*. 1998, **21** pp. 385–393

[215] VIONE D., BARRA S., DE GENNARO G., DE RIENZO M., GILARDONI S., PERRONE M.G. et al. Polycyclic aromatic hydrocarbons in the atmosphere: monitoring, sources, sinks and fate. II: Sinks and fate. *Ann. Chim.* 2004, **94** pp. 257–268

[216] VIONE D., FALLETTI G., MAURINO V., MINERO C., PELIZZETTI E., MALANDRINO M. et al. Sources and sinks of hydroxyl radicals upon irradiation of natural water samples. *Environ. Sci. Technol.* 2006, **40** pp. 3775–3781

[217] VOGT R.A., RAHMAN S., CRESPO-HERNANDEZ C.E. Structure-Activity Relationships in Nitro-Aromatic Compounds. In: *Practical Aspects of Computational Chemistry. Methods, Concepts and Applications*, (LESZCZYNSKI J., SHUKLA M.K., eds.). Springer, Netherlands, 2009, pp. 217–40.

[218] WALGRAEVE C., DEMEESTERE K., DEWULF J., ZIMMERMANN R., VAN LANGENHOVE H. Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: Molecular characterization and occurrence. *Atmos. Environ.* 2010, **44** pp. 1831–1846

[219] WALGRAEVE C., DEMEESTERE K., DE WISPEAERE P., DEWULF J., LINTELMANN J., FISCHER K. et al. Selective accurate mass-based analysis of 11 oxy-PAHs on atmospheric particulate matter by pressurized liquid extraction followed by high-performance liquid chromatography and magnetic sector mass spectrometry. *Anal. Bioanal. Chem.* 2012, **402** pp. 1695–1711

[220] WANG L., ATKINSON R., AREY J. Formation of 9,10-phenanthrenequinone by atmospheric gas-phase reactions of phenanthrene. *Atmos. Environ.* 2007, **41** pp. 2025–2035

[221] WANG W., JARIYASOPIT N., SCHRLAU J., JIA Y., TAO S., YU T.-W. et al. Concentration and photochemistry of PAHs, NPAHs, and OPAHs and toxicity of $PM_{2.5}$ during the Beijing olympic games. *Environ. Sci. Technol.* 2011, **45** pp. 6887–6895

[222] WILLIAMS E.L., GROSJEAN D. Removal of atmospheric oxidants with annular denuders. *Environ. Sci. Technol.* 1990, **24** pp. 811–814

[223] WILSON N.K., MCCURDY T.R., CHUANG J.C. Concentrations and phase distributions of nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air. *Atmos. Environ.* 1995, **29** pp. 2575–2584

[224] XIA T., KORGE P., WEISS J.N., VENKATESAN M.I., SIOUTAS C., NEL A. Quinones and aromatic chemical compounds in particulate matter induce mitochondrial dysfunction: Implications for ultrafine particle toxicity. *Environ. Health Perspect.* 2004, **112** pp. 1347–1358

[225] YAFFE D., COHEN Y., AREY J., GROSOVSKY A.J. Multimedia analysis of PAHs and nitro-PAH daughter products in the Los Angeles basin. *Risk Anal.* 2001, **21** pp. 275–294

[226] YASSAA N., MEKLATI B.Y., CECINATO A., MARINO F. Organic aerosols in urban and waste landfill of Algiers metropolitan area: Occurrence and sources. *Environ. Sci. Technol.* 2001, **35** pp. 306–311

[227] YI F.Y., LIN X.D., CHEN S.X., WEI X.Q. Adsorption of VOC on modified activated carbon fiber. *J. Porous Mater.* 2009, **16** pp. 521–526

[228] YU H. Environmental carcinogenic polycyclic aromatic hydrocarbons: photochemistry and phototoxicity. *J. of Environ. Sci. Health,Part C*. 2002, **20** pp. 149–183

[229] ZHANG Y., YANG B., GAN J., LIU C., SHU X., SHU J. Nitration of particle-associated PAHs and their derivatives (nitro-, oxy- and hydroxy-PAHs) with NO_3 Radicals. *Atmos. Environ.* 2011, **45** pp. 2515–2521

[230] Zielinska, B., Ary, J., Atkinson, R., and McElroy, P. A., 1989. Formation of methylnitronaphthalenes from the gas-phase reactions of 1- and 2-methylnaphthalene with OH radicals and N_2O_5 and their occurrence in ambient air. *Environ. Sci. Technol*. 23 pp. 723 – 729

[231] ZIELINSKA B., SAMY S. Analysis of nitrated polycyclic aromatic hydrocarbons. *Anal. Bioanal. Chem.* 2006, **386** pp. 883–890

[232] Zielinska, B., Samy, S., McDonald, J. D. and Seagrave, J. Atmospheric transformation of diesel emissions. *Res. Rep. Health Eff. Ins.* 2010, **147** pp. 5 – 60

[233] ZIMMERMANN K., ATKINSON R., AREY J., KOJIMA Y., INAZU K. Isomer distributions of molecular weight 247 and 273 nitro-PAHs in ambient samples, NIST Diesel SRM, and from radical-initiated chamber reactions. *Atmos. Environ.* 2012, **55** pp. 431–439

[234] ZIMMERMANN K., JARIYASOPIT N., MASSEY SIMONICH S.L., TAO S., ATKINSON R., AREY J. Formation of nitro-PAHs from the heterogeneous reaction of ambient particle-bound PAHs with $N_2O_5/NO_3/NO_2$. *Environ. Sci. Technol.* 2013, **47** pp. 8434–8442

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Copyright in BSI publications

All the content in BSI publications, including British Standards, is the property of and copyrighted by BSI or some person or entity that owns copyright in the information used (such as the international standardization bodies) and has formally licensed such information to BSI for commercial publication and use.

Save for the provisions below, you may not transfer, share or disseminate any portion of the standard to any other person. You may not adapt, distribute, commercially exploit, or publicly display the standard or any portion thereof in any manner whatsoever without BSI's prior written consent.

Storing and using standards

Standards purchased in soft copy format:

- A British Standard purchased in soft copy format is licensed to a sole named user for personal or internal company use only.
- The standard may be stored on more than 1 device provided that it is accessible by the sole named user only and that only 1 copy is accessed at any one time.
- A single paper copy may be printed for personal or internal company use only.

Standards purchased in hard copy format:

- A British Standard purchased in hard copy format is for personal or internal company use only.
- It may not be further reproduced – in any format – to create an additional copy. This includes scanning of the document.

If you need more than 1 copy of the document, or if you wish to share the document on an internal network, you can save money by choosing a subscription product (see 'Subscriptions').

Reproducing extracts

For permission to reproduce content from BSI publications contact the BSI Copyright & Licensing team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email subscriptions@bsigroup.com.

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Useful Contacts

Customer Services
Tel: +44 345 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 345 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK