Development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates: A review

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Abstract

In the present work, the different sample collection, pretreatment and analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates is systematically reviewed, and the applications of these pretreatment and analytical methods for PAHs are compared in detail. Some comments on the future expectation are also presented.

Key words: polycyclic aromatic hydrocarbons (PAHs); airborne particulates; analytical methods; review

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of several hundred individual compounds defined to be composed of two or more fused aromatic rings. PAHs are of concern because certain of them are classified as probable human carcinogens (IARC, 1983; IPCS, 1998; UNECE, 1998; Vestreng and Klein, 2002) and show tumorigenic activity and endocrine disrupting activity in mammals (Cavalieri and Rogan, 1998). Recently the regulations of PAHs have been enacted or proposed in Europe and by the WHO (Bostroem et al., 2002; WHO, 2000; WHO/IPCS, 1998).

Unsubstituted PAHs are formed mainly by the incomplete combustion of organic materials (Baek et al., 1991; Mastral et al., 2000a). And the atmospheric photochemical PAH reactions cause to form many kinds of substituted PAHs, such as nitrated PAHs (NPAHs), hydroxylated PAHs (OH-PAHs), amino-PAHs (APAHs) and so on. For example, NPAHs are formed easily by the reaction of PAH with reactive species found in ambient air, such as dinitrogen pentoxide (N₂O₅) and oxygen radicals in the presence of nitrogen oxides and hydroxylated radicals. During the last three decades, a great deal of health research interest focused on the mutagenicity and carcinogenicity of PAHs and their derivatives (Ames et al., 1975; Finlayson-Pitts and Pitts, 1999; Mersch-Sundermann et al., 1993). And the results showed some of substituted PAHs may be more toxic than the parent PAHs. PAHs and their derivatives are directly emitted by diesel and petrol engines, industrial processes, coal combustion, cigarette smoke, and have also been found in carbon black and photocopier toners, fly ash, exhaust emission from waste incineration plants (Barzegar and Dasgupta, 1996; Cvacka et al., 1998; Jacob et al., 1991; Kirton and Crisp, 1990; Lee et al., 1998; Marr et al., 1999; Mastral et al., 1999; Moreira et al., 1999; Oanh et al., 1999; Wilhelm et al., 2000; Xu et al., 2006; Zimmermann et al., 1999). Hayakawa et al. (1995a, 1995b) reported that automobiles are a main source of atmospheric PAHs and NPAHs. PAHs and their derivatives need to be monitored in time, which is benefit to value the quality of air and infer the source of pollutants.

Due to the PAHs high volatility, PAHs from energy generation can be released both supported onto the particulate matter (PM) and in the gas phase (Mastral et al., 2000b, 2001). The most volatile compounds with two or three aromatic rings, are mainly released in the gas phase, while compounds containing more than three aromatic rings, are generally associated with the PM emission. The PAHs gas/solid partitioning is related to many different variables like the liquid vapor pressure, the ambient temperature and the size, chemical composition and surface area of the PM. These characteristics, together with the PAHs volatile character, will determine the way in which they are emitted to the atmosphere. The U.S. Environmental Protection Agency (EPA) promulgated a new size-specific air quality standard for environmental particulate matter in 1987 (EPA, 1987). This new standard
applies only to particulate with diameters smaller than or equal to 10 µm (PM_{10}) and replaces the original standard for total suspended particulate matter (TSP). Nowadays, PM_{2.5} and aerosols with 1.0 µm or less in diameter are being taken into account because they represent the particle fraction inhaled into the deeper respiratory tract regions. In addition, PAHs are concentrated in the submicro-PM due to gaseous PAHs condensation into the smallest particles.

Sensitive, rapid, simple and accurate methods have been developed to determine PAHs and their derivatives in the atmospheric particles. As high efficient separation tools, GC and HPLC have been used for determining all kinds of samples containing complex components. GC-FID, GC-MS, HPLC-FL (Silvestre et al., 1986; Wilhelm et al., 2000) are the conventional analytical methods to determine the unsubstituted PAHs. And the substituted PAHs, such as NPAHs, most of these compounds are low volatile and unstable, are mainly determined by HPLC. And the continuing use of LC methods for the determination of NPAHs is documented by the increase in the number of published paper (Cvacka et al., 1998). Method of the combination of HPLC with fluorescence (Tejada et al., 1986), chemiluminescence (Hayakawa et al., 1995a) and electrochemical detection (Jin and Rappaport, 1983; Kuo et al., 2003) have been developed. GC-NPD and GC-NICIMS (David et al., 1982) are also used for determining the 2- or 3-rings NPAHs and have good selectivity and sensitivity.

The direct determination of extremely trace PAHs and their derivatives by modern high efficient chromatographic techniques is still very difficult. The limitations are associated not only with the insufficient sensitivity of these techniques but with matrix interference. For this reason, the separation and preconcentration techniques are often required. For the atmospheric particulates sample, extraction methods of PAHs and their derivatives include traditional Soxhlet extraction, ultrasonic extraction, supercritical fluid extraction, microwave-assisted extraction and accelerated solvent extraction. Solid phase extraction is often followed for clean-up the interference of the extraction liquid.

But the analysis of atmospheric PAHs faces many problems: the airborne particulate samples are extremely complex, and often contain many different classes of compounds in varying amounts; many studies are incompatible due to differences in results caused by differences in analysis techniques: very low concentration required more sensitive analytical methods which are not suitable for larger quantities; the most common atmospheric PAHs sampling uses filters or adsorbents, which are not proper for the most volatile species and can be lost before detection and/or other species cannot be totally extracted once adsorbed; PAHs deposition with the PM greater than 3–5 µm and/or gas PAHs re-volatilisation once deposited; strong influence of the meteorological conditions; strong influence of the ambient contaminants, and so on.

Researchers in many countries have made much effort to the analysis of PAHs in airborne particulates. This paper summarizes the PAHs data in airborne particulates to help understand the sample collection, pretreatment and analytical methods of PAHs.

1 Analytical methods for PAHs in airborne particulates

1.1 EPA standard analytical method for atmospheric PAHs

Under the sponsorship of EPA, Method TO-13 was originally published in March of 1989 as one of a series of peer-reviewed methods in the second supplement to “compendium of methods for the determination of toxic organic compounds in ambient air”, EPA 600/4-89-018. In an effort to keep these methods consistent with current technology, Method TO-13 has been revised and updated as Method TO-13A “determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography/mass spectrometry (GC/MS)”. This compendium incorporates new or improved sampling and analytical technologies. The summary of Method TO-13A is as following (EPA, 1999):

1. Filters and sorbent cartridges (containing PUF or XAD-2) are cleaned in solvents and vacuum dried. The filters and sorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or other species cannot be totally extracted) before careful installation on the sampler.

2. Approximately 300 m³ of air is drawn through the filter and sorbent cartridge using a high-volume flow rate air sampler or equivalent.

3. The amount of air sampled through the filter and sorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and sorbent cartridges to the analytical laboratory for analysis.

4. The filters and sorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by Kuderna-Danish (K-D) evaporator, followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by GC/MS.

5. The eluent is further concentrated by K-D evaporation, then analyzed by GC/MS. The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions.

6. A preliminary analysis of the sample extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If the preliminary analysis indicates nonperformance, then recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, and so on.

7. The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculate the concentration of PAHs in the air sample.

1.2 Some analytical methods for atmospheric PAHs

With the development of technology, the analytical methods for PAHs are growing. It is probably true to
say that advances in environmental analyses have more or less occurred concomitantly with those in the analytical methods. A cursory examination of accepted and certified methods of analysis of many environmental pollutants indicates that chromatographic techniques play a significant role, and may well be the most widely used procedures in this area of application. More specifically, chromatography is a principal technique in the analysis of air pollutants; the continued advent of new or improved instrumentation and novel column technologies have meant that chromatography has remained at the forefront in this area of research, and its preeminent position appears unchallenged in the foreseeable future. A wide number of techniques have been developed for the determination of PAHs in the airborne particulate matter, such as thin-layer chromatography (TLC), gel-permeation chromatography (GPC), gas chromatography (GC), gas chromatography-mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC), etc. Chromatographic techniques such as GC or HPLC coupled with fluorescence, UV, FID and MS detectors are the most frequently used now. As reported, HPLC has been successfully used to analyze PAHs for more than twenty years. It has become one of the most effective methods for monitoring PAHs. Compared with GC method, HPLC, especially reverse phase HPLC (RP-HPLC), can analyze the compounds without the considering of volatility and molecular weight, moreover, it shows good selectivity and high sensitivity. HPLC with ultraviolet absorption detector or fluorescence detector was used to determine atmospheric PAHs by many groups (Lee and Lee, 2004; Li and Ro, 2000; Venkataraman et al., 1999; Yutaka et al., 2005; Zhu and Wang, 2003). GPC was found to be good for PAHs isomers and derivations (Fernandez and Bayona, 2005; Zhu and Wang, 2003). GC/MS was also widely used in the determination of PAHs according to its superiority in qualitative and quantitative analysis (Allen et al., 1996; Chen et al., 2005; Gigliotti et al., 2005; Lee et al., 1995, 2001; Ochsenkuhn-Petropoulou et al., 2003; Possanzini et al., 2004).

In addition, some biologic methods also have been applied in the determination of PAHs. Li et al. (1999) developed sensitive enzyme-linked immunosorbent assays (ELISAs) for multianalyte detection of PAHs. The haptons with different lengths of carboxylic acid spacers at various positions were derived from PAHs. And these haptons were coupled with bovine serum albumin to form competitor conjugates. All of the haptons were recognized to different extents by monoclonal antibodies 4D5 and 10C10. Cigamek et al. (2004) realized a combined chemical and bioassay analysis of traffic-emitted PAHs. And Angerer et al. (1997) reviewed biological monitoring and biochemical effect monitoring of exposure to PAHs.

1.3 Analytical methods for nitro-PAHs and other PAHs derivatives

Oxygenated and nitro-substituted polycyclic aromatic hydrocarbons (oxy- and nitro-PAHs, respectively) are formed in the combustion of fuel, natural gas, wood, coke and in residue incineration. They are present in tobacco smoke and also in the ambient air due to chemical reactions of PAHs with different atmospheric pollutants, such as NOx or O3 (Alebic-Juretic et al., 1990; Fan et al., 1995; Pitts et al., 1978; Xu and Burlingame, 1988). The direct mutagenic activity of tobacco smoke or atmospheric extracts has been mainly correlated with the presence of oxy- and nitro-PAHs (Bayona et al., 1994; Casellas et al., 1995; Yu et al., 2002). While PAHs have proved to be indirect mutagens, nitro-PAHs are direct-acting mutagens.

Analytical techniques which have high resolution and specificity are required for the determination of a large number of NPAHs and related compounds in environmental samples. GC is used for determining nitro compounds because of its high resolution, sensitive and selective detection. Many types of detectors have been developed for nitro compounds. These include electron capture detector (ECD), nitrogen and phosphorus selective detector (NPD), thermionic ionization detector (TID) operated in a nitrogen atmosphere, chemiluminescence detector (CLD) and mass spectrometry (MS) (Marino et al., 2000; Schnelle-Kreis et al., 2001). The most selective and sensitive techniques for the detection of oxy- and nitro-PAHs are based on electron capture processes occurring in the gas phase, due to the electronegative character of the nitro and oxy groups conjugated with the aromatic rings. This allows the detection of low concentrations and a higher degree of selectivity than in other types of common detectors. Thus, negative ion chemical ionization mass spectrometry (NICI-MS) (Bezabeh et al., 2003; Dusek et al., 2002; Randahl and Urdal, 1982; Siegmund et al., 2003) and ECD (Xu and Lee, 2000) are the most widely used techniques for the analysis of oxy- and nitro-PAHs, showing the lowest limits of detection. Xu and Lee (2000) also developed a derivatization-GC/ECD analytical method to identify and quantify NPAHs in atmospheric particulate matter.

The nitro-group of NPAHs is electrochemically, chemically or metal-catalytically reduced to a nitros group forming the nitro-PAHs. And these haptens were different extents by monoclonal antibodies 4D5 and 10C10. Cigamek et al. (2004) realized a combined chemical and bioassay analysis of traffic-emitted PAHs. And Angerer et al. (1997) reviewed biological monitoring and biochemical effect monitoring of exposure to PAHs. NPAHs in atmospheric particulate matter.
effluent from the reducer column to increase the water concentration. After all APAHs were eluted from the clean-up column and concentrated on the concentrator column completely, the APAHs were separated on the separator column and detected by chemiluminescence. And as mentioned above, NPAHs are not fluorescent but most APAHs are strongly fluorescent. So in order to apply HPLC/FLD to NPAHs, NPAHs must be reduced. Both off-line and on-line reduction methods have been reported (Hayakawa et al., 1993, 2002; Murayama and Dasgupta, 1996). In addition, only a few studies have been reported concerning LC-MS of NPAHs (Bonfanti et al., 1996). But the sensitivity of LC-MS is not enough for NPAHs at trace levels in environmental samples. A few studies concerned the analysis of PAHs and NPAHs by low-temperature Shpol’skii fluorescence/luminescence spectroscopy (Kozin et al., 1996; Matsuzawa et al., 1995).

2 Sampling and pretreatment methods for PAHs in airborne particulates

2.1 Sampling methods for PAHs

The sampling techniques for PAHs have been improved in last two decades. A number of researches showed that the main sampling modes for atmospheric PAHs are active sampling and passive sampling. The samplers used mainly are high-volume sampler and impingement cascade sampler. Sorbent, filter, impingement collector, etc. are usually used to collect target compounds in active sampling. And passive sampling is due to the migration of target compounds through concentration gradient. Passive sampling has been successfully applied to environmental monitoring, particularly in the analysis of gaseous PAHs and other little organic compounds in the air. It is a popular sampling technique because it is portable, noiseless and lower cost. Semi-permeable membrane devices (SPMDs) used as passive samplers have been reported (Soderstrom and Bergqvist, 2004; Soderstrom et al., 2005). A standard semi-volatile sampling train with a filter was also used to collect PAHs (Sheu et al., 1997).

In many applications, filters were used to collect the particle-bound PAHs while solid sorbent was used to collect gaseous volatile PAHs. As reported, glass fiber filter (Bi et al., 2003; Lin et al., 2002; Simcik et al., 1999; Tsai et al., 2002), quartz fiber filter (Gigliotti et al., 2005; Okuda et al., 2002), cellulose filter (Ochsenkuhn-Petropoulou et al., 2003) were the filters mostly used to collect particle-bound PAHs. And the choice of sorbent is very important in the collection of gaseous volatile PAHs. The sorbent should has high collection efficiency, large adsorb capacity and chemical stability. Most sorbent used to collect gaseous PAHs were Tenax, XAD-2, polyurethane form (PUF), Florisil, Seppar-C, and so on. Thereinto PUF and XAD-2 are mostly used due to their advantages of low-cost and tractable.

For different size particles, there are some different methods to collect them. PM_{10} and PM_{2.5} samples can both be collected by high-volume samplers. But for data comparison, low-volume sampler with 10 or 2.5 µm inlet was used to collect PM_{10} and PM_{2.5} samples, respectively (Guo et al., 2003). In addition, airborne particles were collected and size-fractionated using a sampler that combined a minipump with a three-stage cascade impactor. Different kinds of filters were used to collect different size particles (Ohura et al., 2004).

It should be noted that it is better to reduce the sampling time especially in the collection of gaseous PAHs. Until now, both high-volume and low-volume samplers
can collect the particle-bound PAHs, but they have still
needed some improvements to monitor the gaseous PAHs
exactly. How to avoid the volatilization and loss of PAHs
in the sampling, the reaction between PAHs and other
compounds and the redistribution among different size
particles still need more effort. A modified high-volume
sampling—with an oxidant denuder system added, in order
to minimize the PAH degradation during air sampling, was
reported recently (Tsapakis and Stephanou, 2005a, b).

2.2 Preservation and pretreatment of air samples

2.2.1 Preservation of samples

Volatilization and loss of PAHs may occur on the filter
and sorbent. So the preservation of samples should be
very careful. Usually, each filter should be folded with
the adsorbed particulate matter on the inner side, wrapped
in an aluminum foil to protect them from light and kept
under refrigeration at low temperature (about -18°C) until
extraction and analysis (Dallarosa et al., 2005a; Sanderson
and Farant, 2005; Wu et al., 2006).

2.2.2 Pretreatment of samples

The air matrix is complicated and the concentration
of PAHs in the air is very low, so the pretreatment of
samples is a very important step for the determination
of PAHs. Song and Lin (2005) reviewed sample pre-
treatment techniques for PAHs in environmental matrix.
Dichloromethane, acetonitrile, benzene, toluene, cyclo-
hexane and their mixture are usually used as extraction
solvent. Solvent extraction (such as Soxhlet extraction,
ultrasonic extraction, supercritical fluid extraction (SFE),
microwave-assisted extraction (Lee et al., 2001), accelerat-
ed/pressurized solvent extraction), concentration (such as
K-D evaporator (Bae et al., 2002; Cecinato et al., 1999;
Zhang et al., 2005) and rotary evaporator concentration
(Chetwittayachan et al., 2002)) and clean-up with columns
(Hafner and Hites, 2005) are three mostly applied pretreat-
ment methods for PAHs samples. And subcritical water
extraction has also been applied as pretreatment of air
samples (Romero et al., 2002).

Soxhlet extraction is a classical method due to its
high extraction efficiency. Yang et al. (1999) determined
polycyclic aromatic hydrocarbon concentrations in extract
solvent of airborne particulate in different steps of Soxhlet
extraction, and drawn out the Soxhlet extraction curves,
then found the extract efficient mainly depended on extract
cycle numbers, did not depend on extract soak time. By
comparing Soxhlet extract efficient of eleven kinds of
extract solvents to adding standard reference matter and
research reference matter, they found cyclohexane and
benzene as extract solvents most in use were not so well ef-
cient extract solvents. The order of extract efficient of the
extract solvents is as follow: quinoline-ethanol, pyridine-
ethanol, acetone, ethanol, dichloromethane, benzene, cy-
clohexane, petroleum ether, acetone-ethanol-cyclohexane,
trichloromethane, and tetrahydrofuran. Dallarosa et al.
(2005b) used Soxhlet extraction technique to identify and
quantify the main sources of PAHs associated with aerosols (PM$_{10}$) collected at three different sampling sta-
tions. Fang et al. (2004) used dichloromethane/hexane
as solvent to Soxhlet extract PAHs and simultaneously
measured PAHs from 2002–2003. But it is time-consuming
(about several hours) for the extraction of PAHs and further
concentration need to do because of the large amount of
solvent.

Ultrasonic extraction is a popular method for PAHs
because it is time-saving, solvent-saved and high efficiency.
Park et al. (2002) applied ultrasonic extraction for PAHs
and followed by GC/MS determination. They analyzed the
concentrations of PAHs in different sites in Korea. Some
authors such as Hayakawa et al. (2002), Tang et al. (2005),
Bi et al. (2005), Duan et al. (2005) all applied ultrasonic
extraction technique.

Supercritical fluid extraction (SFE) also has been ap-
plied in the analysis of atmospheric PAHs. It has high
extraction efficiency, good selectivity. It is time-saving and
can not induce secondary pollution. What’s more, it can
be easily coupled with GC, GC-MS, HPLC, etc. Shimmo
et al. (2004) analyzed the PAHs by on-line SFE-LC-GC-
MS. The operation was simple and largely reduced the
loss of targets. The solvent used in SFE usually are CO$_2$,
NH$_3$, ethylene, ethane, N$_2$O, propane, propylene and H$_2$O.
Castells et al. (2003) reported on the applicability of SFE
for the analysis of oxy- and nitro-PAHs in particulate mater-
using a simultaneous extraction and clean up procedure.
The developed SFE method was applied to the analysis
of PAH derivatives using GC-ECD and GC-MS. It need
not to purify compared with other methods. Yang et al.
(1995) studied the effect of temperature and modifier on
the supercritical CO$_2$ extraction. They found that properly
increasing the temperature and the addition of modifier can
increase the recovery of PAHs. The most additive used is
methanol. Peltonen and Kalajukka (1995) compared some
different pretreatment methods for PAHs and found that
SFE has much higher extraction efficiency than Soxhlet
extraction.

Wu et al. (2006) applied accelerated solvent extraction
and analyzed particle size distributions of PAHs in Tianjin,
China. Perrasdin et al. (2005) analyzed particle-bound
PAHs using pressurized fluid extraction followed by GC-
MS recently. Zhou et al. (2005b) also developed a micro
pressurized liquid extraction device for the determination
of PAHs on PM$_{10}$ samples.

In addition, Koziel et al. (2001) improved a needle trap
device and commercial poly (dimethylsiloxane) (PDMS)
7-µm film thickness solid-phase microextraction (SPME)
fibers for the sampling and analysis of air samples. The
air volumes ranged from 0.1 to 50 ml and the sampling
times varied from 10 s to 16 min. Results suggested the
method should be a simple, fast, reusuable and cost-effective
screening tool. Kolar et al. (2004) also used SPME for
atmospheric PAHs and estimated distribution coefficients
between air and PDMS coated fiber. But until now, SPME
has not been popularly used for the PAHs in the air.

The applications of pretreatment and analytical meth-
ods for PAHs in airborne particulates since 2000 are sum-
marized and compared in Table 1. It can be concluded
from the table that GC-MS and HPLC are the analytical
Table 1: Applications of pretreatment and analytical methods for PAHs in airborne particulates since 2000

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Pretreatment method</th>
<th>Analytical method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 PAHs</td>
<td>Soxhlet extraction (dichloromethane/acetone = 5 : 1), column chromatography on Al2O3, elute with dichloromethane</td>
<td>GC-MS</td>
<td>Cecinato et al., 2000</td>
</tr>
<tr>
<td>5 PAHs</td>
<td>Soxhlet extraction (dichloromethane/acetone = 3 : 1), column chromatography on Al2O3, elute with dichloromethane</td>
<td>GC-MS</td>
<td>Cecinato et al., 2003</td>
</tr>
<tr>
<td>14 EPA-PAHs</td>
<td>Dialysis in cyclopentane/dichloromethane for 48 h, rotary evaporation, GPC and silica gel column clean-up</td>
<td>GC-MS</td>
<td>Soderstrom and Bergqvist, 2004</td>
</tr>
<tr>
<td>15 EPA-PAHs</td>
<td>Dialysis in cyclopentane/dichloromethane for 48 h, rotary evaporation, GPC and silica gel column clean-up</td>
<td>GC-MS</td>
<td>Soderstrom et al., 2005</td>
</tr>
<tr>
<td>22 PAHs</td>
<td>Soxhlet extraction by dichloromethane for 8 h, evaporation concentration</td>
<td>HPLC-FLD</td>
<td>Kameda et al., 2005</td>
</tr>
<tr>
<td>15 PAHs</td>
<td>Dialysis in hexane for 48 h, silica gel/alumina column clean-up, elute with dichloromethane/hexane, GC clean-up</td>
<td>GC-MS</td>
<td>Lohmann et al., 2001</td>
</tr>
<tr>
<td>21 PAHs</td>
<td>Soxhlet extraction (n-hexane/dichloromethane, v : v=1 : 1) for 24 h, concentration, clean-up, recombination</td>
<td>GC-MS</td>
<td>Tsai et al., 2002</td>
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<tr>
<td>12 PAHs</td>
<td>Ultrasonic extraction with dichloromethane/acetonitrile, evaporate concentration</td>
<td>HPLC-FLD</td>
<td>Zhu and Wang, 2003</td>
</tr>
<tr>
<td>15 PAHs</td>
<td>Ultrasonic extraction with dichloromethane/hexane, rotary evaporation</td>
<td>RP-HPLC-FLD</td>
<td>Li and Ro, 2000</td>
</tr>
<tr>
<td>7 PAHs</td>
<td>Ultrasonic extraction with dichloromethane, column chromatography</td>
<td>GC-MS</td>
<td>Schnelle-Kreis et al., 2001</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Ultrasonic extraction 3 times with dichloromethane, rotary evaporation, silica-alumina column clean-up, elute with dichloromethane/hexane</td>
<td>GC-MS</td>
<td>Guo et al., 2003</td>
</tr>
<tr>
<td>18 PAHs</td>
<td>Ultrasonic extraction with dichloromethane, centrifugation, evaporation under N2</td>
<td>HPLC-FLD</td>
<td>Ohura et al., 2004</td>
</tr>
<tr>
<td>51 PAHs</td>
<td>Soxhlet extraction with acetone for 24 h, rotary evaporation, silica gel column clean-up, elute with n-hexane/methylene chloride</td>
<td>GC-MS</td>
<td>Okuda et al., 2002</td>
</tr>
<tr>
<td>21 PAHs</td>
<td>Soxhlet extraction with dichloromethane/n-hexane for 24 h, concentration, clean-up, recombination</td>
<td>GC-MS</td>
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<tr>
<td>24 PAHs</td>
<td>Soxhlet extraction with n-hexane for 24 h, rotary evaporation, silica gel column clean-up, elute with n-hexane/toluene</td>
<td>GC-MS</td>
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<tr>
<td>16 EPA-PAHs</td>
<td>No pretreatment method</td>
<td>Pyrolysis/GC-MS</td>
<td>Ochenkou-Petropoulou et al., 2003</td>
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<tr>
<td>16 EPA-PAHs</td>
<td>Ultrasonic extraction 3 times with dichloromethane</td>
<td>GC-MS</td>
<td>Bi et al., 2005</td>
</tr>
<tr>
<td>14 PAHs</td>
<td>Soxhlet extraction with dichloromethane/petroleum ether for 24 h, rotary evaporation, alumina silica column clean-up, elute with dichloromethane</td>
<td>GC-MS</td>
<td>Vardar et al., 2004</td>
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<tr>
<td>21 PAHs</td>
<td>Soxhlet extraction with dichloromethane/methanol (9/1), K-D concentration</td>
<td>GC-MS</td>
<td>Possanzini et al., 2004</td>
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<tr>
<td>12 PAHs</td>
<td>Soxhlet extraction with methylene chloride for 20 h, fractionation</td>
<td>GC-MS</td>
<td>Vasconcellos et al., 2003</td>
</tr>
<tr>
<td>18 PAHs</td>
<td>Microwave-assisted extraction with dichloromethane, rotary evaporation</td>
<td>GC-MS</td>
<td>Lee et al., 2001</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Ultrasonic extraction 3 times with dichloromethane, rotary evaporation, silica alumina column, clean-up, elute with dichloromethane/hexane</td>
<td>GC-MS</td>
<td>Bi et al., 2003</td>
</tr>
<tr>
<td>11 PAHs</td>
<td>Ultrasonic extraction with dichloromethane, rotary evaporation</td>
<td>GC-MS</td>
<td>Chetwittayachan et al., 2002</td>
</tr>
<tr>
<td>15 PAHs</td>
<td>Soxhlet extraction with dichloromethane/petroleum ether for 24 h, K-D concentration, alumina silica column clean-up, elute with dichloromethane</td>
<td>GC-MS</td>
<td>Bae et al., 2002</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Extraction with methylene chloride, concentration</td>
<td>HPLC-UV</td>
<td>Lee and Lee, 2004</td>
</tr>
<tr>
<td>8 PAHs</td>
<td>Subcritical water extraction, transfer into dichloromethane, concentration</td>
<td>GC-MS</td>
<td>Romero et al., 2002</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Micro pressurized liquid extraction</td>
<td>GC</td>
<td>Zhou et al., 2005b</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Ultrasonic extraction with dichloromethane, evaporation</td>
<td>HPLC-FLD</td>
<td>Venkataraman et al., 2002</td>
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<td>16 EPA-PAHs</td>
<td>Ultrasonic extraction 3 times with dichloromethane, rotary evaporation, silica column clean-up</td>
<td>GC-MS</td>
<td>Duan et al., 2005</td>
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<tr>
<td>16 EPA-PAHs</td>
<td>Accelerated solvent extraction with dichloromethane, clean-up</td>
<td>GC-MS</td>
<td>Wu et al., 2006</td>
</tr>
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<td>16 EPA-PAHs</td>
<td>Ultrasonic extraction 3 times with dichloromethane, rotary evaporation, silica column clean-up, elute with hexane/dichloromethane</td>
<td>GC-MS</td>
<td>Niu et al., 2005</td>
</tr>
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<td>13 PAHs</td>
<td>Pressurized fluid extraction</td>
<td>GC-MS</td>
<td>Ferraudi et al., 2005</td>
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<td>16 EPA-PAHs</td>
<td>Soxhlet extraction with dichloromethane and dimethylsulfoxide for 18 h, concentration, silica gel column clean-up</td>
<td>GC-MS</td>
<td>Dallara et al., 2005</td>
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<tr>
<td>12 PAHs</td>
<td>Ultrasonic extraction with acetonitrile, rotary evaporation</td>
<td>RP-HPLC-FLD</td>
<td>Terzi and Samara, 2005</td>
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<tr>
<td>9 PAHs</td>
<td>Ultrasonic extraction twice with benzene/ethanol (3/1), evaporation</td>
<td>HPLC-FLD</td>
<td>Tang et al., 2005</td>
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<td>Ultrasonic extraction 3 times with dichloromethane, K-D concentration</td>
<td>HPLC-FLD</td>
<td>Zhang et al., 2005</td>
</tr>
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<td>Supercritical fluid extraction</td>
<td>HPLC</td>
<td>Jonker et al., 2005</td>
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<td>Ultrasonic extraction</td>
<td>HPLC-FLD</td>
<td>Sanderson and Farant, 2005</td>
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<td>15 PAHs</td>
<td>Ultrasonic extraction 3 times with dichloromethane, column separation, rotary evaporation</td>
<td>GC-MS</td>
<td>Tan et al., 2005</td>
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<td>23 PAHs</td>
<td>Soxhlet extraction with dichloromethane/acetone (4/1), evaporation, alumina column chromatography, elute with dichloromethane</td>
<td>GC-MS</td>
<td>Yassae and Cecinato, 2005</td>
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<td>24 PAHs</td>
<td>Soxhlet extraction with n-hexane for 24 h, rotary evaporation, silica gel column clean-up, elute with n-hexane/toluene</td>
<td>GC-MS</td>
<td>Tsapakis and Stephanou, 2005b</td>
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<td>17 PAHs</td>
<td>Ultrasonic extraction with dichloromethane, rotary evaporation, silica gel column clean-up, elute with dichloromethane</td>
<td>GC-MS</td>
<td>Zhou et al., 2005a</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Soxhlet extraction with dichloromethane/n-hexane (1/1) for 8 h, rotary evaporation</td>
<td>GC-MS</td>
<td>Bourrotte et al., 2005</td>
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</table>
methods mostly used; Soxhlet extraction and ultrasonic extraction are the extraction methods mostly applied in the pretreatment.

3 Expectations

Atmospheric PAHs pollution has become a serious problem in the world. More and more researchers have put effort into this field. Though there are many reports on toxicity, concentration, distribution of PAHs and their derivatives, there are still many unknown mutagenic compounds of PAHs which are too low to be detected but have high mutagenicity. How to avoid the volatilization and loss of PAHs in the sampling, the reaction between PAHs and other compounds and the redistribution among different size particles; and how to develop new, noiseless and lower-volume sampler; to realize the pretreatment automatically, innocuously, rapidly, low-cost; to protect people’s health from PAHs; all these problems need further endeavors.

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