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Isolation and analysis of polycyclic aromatic hydrocarbons from natural water using accelerated solvent extraction followed by gas chromatography–mass spectrometry

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Abstract

An innovative analytical procedure for the analysis of polycyclic aromatic hydrocarbons (PAHs) from large-volume water samples is presented. It involves sample preparation, sampling and the elution process in an automated continuous procedure involving the ASE technique. Prior to sampling, a XAD-2 resin column is prepared on the basis of a commercial accelerated solvent extraction (ASE) cartridge so that the resin bed is permanently fixed. Then, the XAD column inside the ASE cartridge is cleaned and conditioned. The sampling procedure involves conventional filtration with subsequent isolation of dissolved PAHs on an XAD-2 resin contained in the ASE cartridge. After sampling, the XAD-2 resin content inside the cartridge is eluted by ASE without any further sample preparation and subsequently reused. In order to validate the procedure, the PAHs were isolated from water samples from the Lake Maggiore (North of Italy) using both XAD-2 resin adsorption and hexane liquid–liquid extraction according to the International Standard Methodology ISO 17993. The mean percentages of deviation between concentrations obtained by both methodologies range from 6% for benzo(*a*)pyrene to 15% for fluoranthene and benzo(*b*,*k*)fluoranthene. Compared to the traditional techniques, this procedure offers numerous practical advantages: easy to perform, fast, savings in solvent volume and in time, all steps are fully automated thus avoiding any XAD-2 resin manipulation during and between steps and moreover, low detection limits were provided (0.001 ng l^{-1} for chrysene, benzo(*b*,*k*)fluoranthene, benzo(*a*)pyrene, dibenz(*a*,*h*)anthracene, benzo(*g*,*h*,*i*)perylene and indeno(1,2,3-*cd*)pyrene, and 0.01 ng l^{-1} for acenaphthylene and fluoranthene).

This procedure was developed in the frame of a project aimed at evaluating the diffuse input of organic contaminants in the Lake Maggiore.

Keywords: XAD-2; Dissolved phase; ASE; PFE; PAHs; ISO 17993; Lake Maggiore

1. Introduction

The trace determination of polycyclic aromatic hydrocarbons (PAHs) in environmental samples has been an ongoing challenge for several years. Many PAHs have been described as mutagenic, carcinogenic, and teratogenic [1,2] and are therefore listed as priority substances in the Water Framework Directive [3].

XAD-2 resin is used as solid phase extraction material for applications in water and air sampling and analysis of environmental contaminants such as PAHs, PCBs and pesticides [4–10]. In order to detect these analytes at trace levels (ng l^{-1}), the resin must be extremely clean prior to sampling, and eluted efficiently afterwards. Current cleaning methods involve days of extraction using liters of high-quality organic solvents. Manipulation of XAD during the cleaning procedure, column preparation, sampling, elution and also between steps (e.g. removal of XAD from the sampling to the elution) is usually performed on traditional methodologies, making the process lengthy tedious, prone to contamination and to sample loss.

Extraction and isolation of trace quantities from water is often the most time consuming and error-prone step in quantifying semivolatile organic compounds (SOCs).

Classical methods for determination of trace pollutants in water samples are usually laborious and time-consuming. Soxhlet extraction is the EPA method most commonly used for eluting organic pollutants from solid matrixes (method 3540)

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[11]. Soxhlet extraction achieves good extraction efficiencies, but requires long extraction times and large volumes of solvent.

In the past few years, various attempts have been made to replace this classical extraction technique. Ultrasonic extraction (method 3550) is a US EPA approved alternative [11] which is faster than Soxhlet extraction and uses less solvent but requires substantial sample handling with the risk for sample loss and exposure to solvents. Microwave extraction and supercritical fluid extraction have been successfully applied to sediment extraction [12,13]. Although these techniques reduce the volume of elution solvent required and shorten the sample preparation time, compared to Soxhlet extraction, all these procedures involve multiple sample manipulations, thus making them time consuming and labor intensive.

The liquid–liquid extraction (LLE) technique has proven to be effective for the quantitative determination, in aqueous phase, of a broad spectrum of trace organic compounds [14–19]. LLE is applicable to compounds of low to medium polarity and low to medium volatility. Under optimum operation conditions, XAD resins can absorb similar types of compounds as LLE, and therefore both methodologies can be compared for analyzing aqueous SOCs [20,21]. However, LLE is expensive, cumbersome, time-consuming and it is less effective for aqueous samples containing large numbers of volatile organic compounds.

Solid phase extraction is a widely used technique which provides a simple, fast method for extraction and fractionation of organic compounds from environmental samples [22–27].

Accelerated solvent extraction (ASE; also referred to as pressurized fluid extraction, PFE) is a new extraction technique, which offers faster sample processing and the potential of automated, unattended elution of multiple solid samples [28]. The US EPA has accepted the PFE as an official extraction method for several groups of organic micropollutants (PAHs, pesticides, PCBs, PCDD/DF) [29].

Some comparative studies carried out between ASE and conventional techniques, such as supercritical fluid extraction (SFE) and Soxhlet extraction show that the performance of ASE was consistently equivalent or better than the traditional methods [30–34].

Most literature on extraction of PAHs compounds by ASE is related to their levels in soils, sediments and biological samples [30,35–39]. In addition, ASE is well known for the extraction of other organic compounds from solid samples such as soils, sediments, suspended matter, residues [34,40–42], biological tissues and food [43–46].

So far, however nothing is reported on the development of an ASE procedure for the extraction of organic compounds from aqueous samples using XAD resin as adsorbent.

In this paper, a new procedure involving fully automated steps, from XAD-2 resin cleaning to sample elution is presented. The main advantage is that the same ASE commercial cartridge can be used for the sampling in situ, and subsequently for the elution, by reducing time and avoiding the XAD-2 resin manipulation associated with the traditional procedures.

SOCs examined in this study were 14 EPA-PAHs, a class of organic contaminants composed of numerous compounds that span a range of physical–chemical properties (e.g. solubility, vapor pressure, octanol/water partition coefficient [K_{ow}]). We also evaluated the effect of ASE conditions on the recovery of PAHs from XAD-2 resin. This procedure was validated with water samples from the Lake Maggiore by comparison of the PAHs concentrations obtained by the new procedure with those extracted by the hexane liquid–liquid extraction method described in the International Standard Methodology ISO 17993 [47].

2. Experimental procedure

2.1. Standards and chemicals

The surrogate standards (SA) contained 25 ng μl^{-1} each of PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}). The 15 EPA-PAHs mixture contained 2000 $\mu g\ ml^{-1}$ of each compound. The internal standard (IS) contained 25 ng μl^{-1} of terphenyl-d_{14}. All these standards were purchased from Supelco (Bellefonte, PA, USA).

Solvents used were methanol, acetone, hexane of *Suprasolv* quality (Merck KGaA, Germany) and Milli-Q water. XAD-2 resin was provided from Supelco (Bellefonte, PA, USA). The XAD-2 resin properties were surface area: 354 $m^2\ g^{-1}$; porosity 0.42 $cm^3\ cm^{-3}$; pore volume 0.68 $cm^3\ g^{-1}$.

Abbreviations of 14 EPA-PAHs compounds used were: acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benz(*a*)anthracene (BaA), chrysene (CHR), benzo(*b*)fluoranthene and benzo(*k*)fluoranthene 'quantified together' (BbkF), benzo(*a*)pyrene (BAP), dibenz(*a*,*h*)anthracene (DBA), benzo(*g*,*h*,*i*) perylene (BGP), indeno(1,2,3-*cd*)pyrene (IND).

2.2. Sampling procedure

2.2.1. Sampling equipment

The sampling device used in this study consisted of a stainless steel in-line filter holder, i.d. = 142 mm (Sartorius SM16275 GmbH, Germany) with a glass fiber filter (Whatman GF/F, 0.7 μm nominal pore size, diameter 130 mm) to remove the particulate matter, connected to a commercial ASE cartridge of 100 ml containing the resin to isolate the dissolved fraction; a pump (KNF, Neuberger, diaphragm NF 31). Fig. 1 shows a schematic view of the all equipment involved. The ASE cartridges were connected after the stainless steel filter holder and at the bottom with the pump, using two steel adapters (Fig. 2). Two Teflon rings (6 mm thickness) were adapted to both fitting adapters to keep the system sealed (Fig. 2). The pump provided a flow rate of 300 l min^{-1}, suction head of 60 Pa and a pressure head of 99 Pa. The flow rate through the system was maintained at 80–120 ml min^{-1}.

2.2.2. Column preparation

The bottom of the 100 ml ASE cartridge was closed with the adapter shown in Fig. 2b and filled with XAD-2 resin. Fig. 3a, shows how the XAD-2 resin bed (about 130 mm) was prepared:

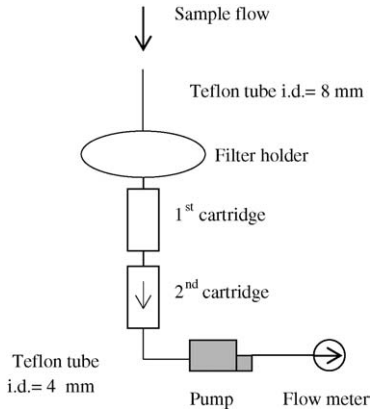

Fig. 1. Schematic view of the all equipment involved.

the resin was permanently packed between one glass fiber filter (Whatman GF/B, 1.3 μm pore size, diameter 30 mm) on top and one stainless steel frit (Dionex, P/N 056775) at the bottom of the ASE, which were supported by two steel rings (13.2 mm height, 2 mm thickness) opened 1 mm to be adapted to the cartridge (Fig. 3b). This distribution ensured that the bed resin remained fixed inside the cartridge during the cleaning procedure, sampling and elution process by avoiding any XAD-2 resin manipulation during and between steps. Sampling directly onto XAD-2 resin, already packed inside an ASE cartridge with subsequent elution from the same cartridge makes the process much easier, faster and easily reproducible.

The steel tools (frits and adapters) and the Teflon rings were firstly rinsed with Milli-Q water and then cleaned by sonication in acetone for 10 min. They are left to dry under fume hood and wrapped in aluminium foil.

The pore size of the filters (frits and glass fiber filters) and their internal distribution were selected to obtain the optimum flow rate. Thus, the flow rate is a key parameter: too high flow rates could provide and inadequate water-sorbent contact time by reducing the effectiveness of the adsorption; too low flow rates, the organic compounds can react to form secondary reactions. The volume of XAD-2 resin versus the flow rate was determined based on a compilation of literature data (Table 1).

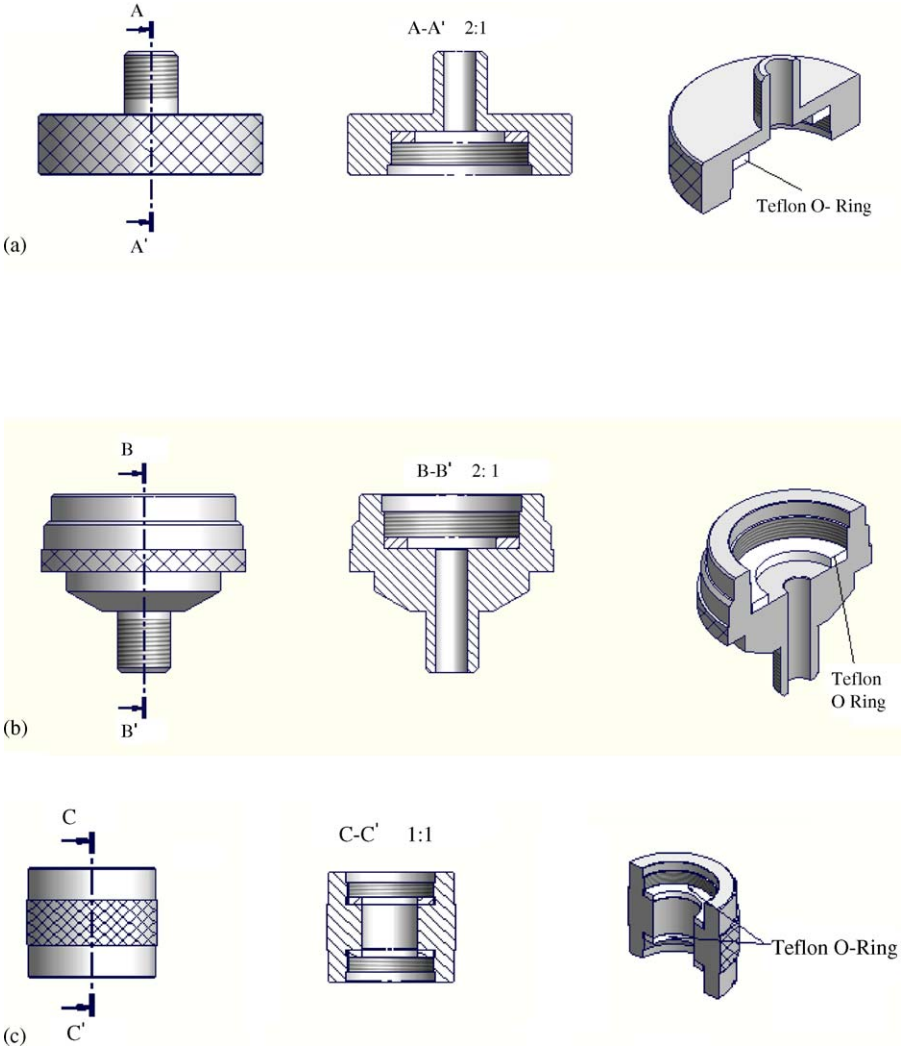

Fig. 2. (a) Adapter on top of the ASE cartridge connected with the stainless filter holder (thread: M 12 × 1). (b) Adapter at the bottom of ASE cartridge connected with the pump (thread: 1¼ inch; 28 thread/inch). (c) Detail of the fitting adapter to the second cartridge.

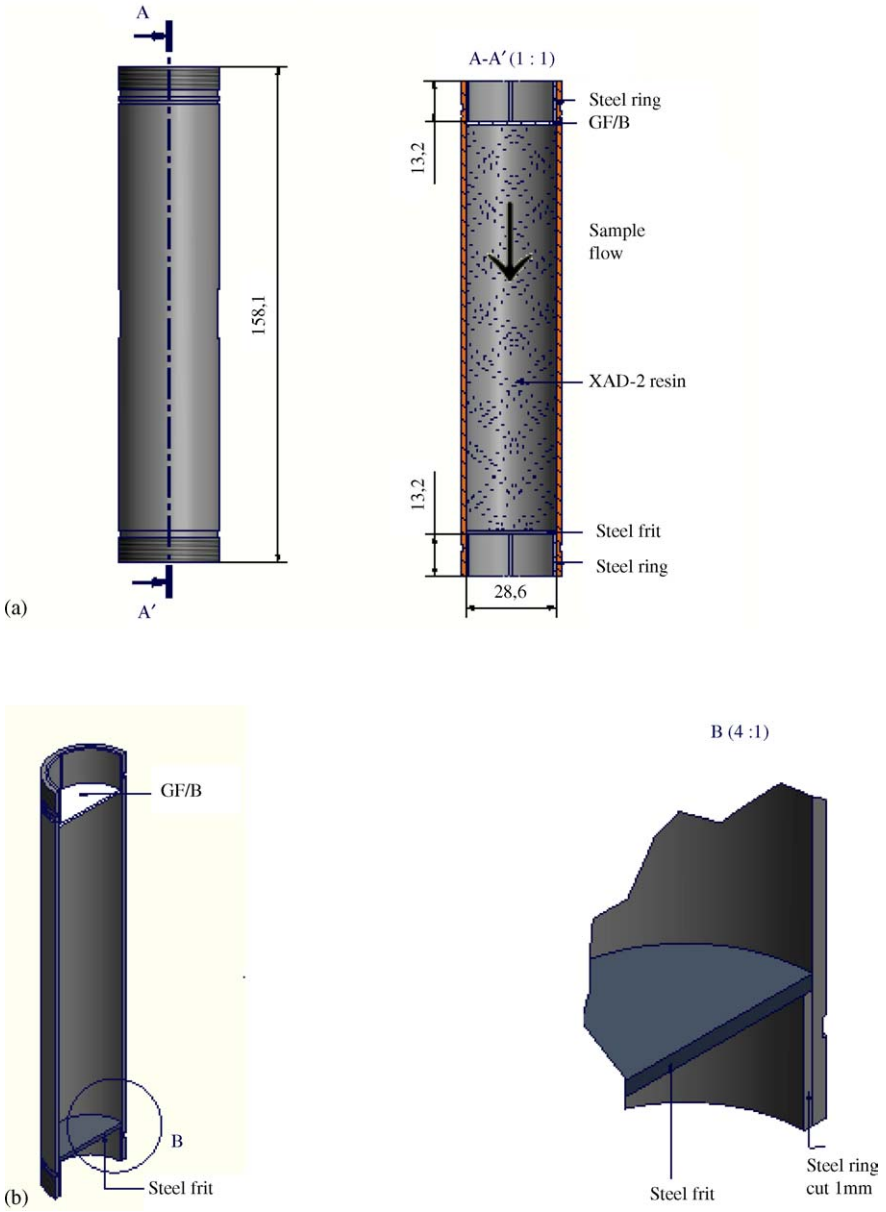

Fig. 3. (a) ASE cartridge (158.1 mm long × 28.6 mm i.d.) with XAD-2 resin column preparation (dimensions in mm). (b) Detail of the steel frits and steel rings in ASE cartridge.

For the analysis of environmental samples, in order to optimize the number of cartridges, two cartridges were connected in series through a fitting adapter (Fig. 2c) with two Teflon rings (6 mm thickness) to keep the system sealed.

Table 1
Dimensions (volume, diameter and length) of the XAD-2 resin columns and flow rates reported in literature

Flow rate (ml/min)	Volume ($\times 10^3$ mm^3)	Diameter (mm)	Length (mm)	Reference
200	133	22	350	[48]
100–200	98.2	25	200	[49]
250	98.2	25	200	[50]
80–120	81.3	28	132	This study

2.3. Cleaning procedure and conditioning

Once the XAD-2 resin bed had been prepared, it was cleaned automatically by the ASE instrument (Dionex Co., Milano, Italy). This cleaning procedure consisted of eight sequential elutions with methanol, acetone, hexane, acetone and methanol under standard conditions recommended by US EPA method 3545 [29] (method 1, Table 2). It should be note that this cleaning procedure was only performed for the new XAD-2 resin cartridges because when resins are received from manufacturer contain contaminants that make them unsuitable for immediate analytical use.

Using the ASE for the cleaning of the XAD resin has numerous advantages compared to the traditional techniques: (1) savings in solvent volume and (2) in time, (3) the process is fully

Table 2
List of ASE methods used in the developed procedure

Methods	Temperature (°C)	Static time (min)	Flush (%)	Purge (s)	Cycles	Solvent
1	100	5	60	125	1	Methanol or acetone or hexane
2	Off	0	100	60	1	Milli-Q water
3	Off	0	0	180	–	No solvent
4	120	5	60	125	2	Hexane

automated and (4) avoids the problem of multiple sample manipulations associated with Soxhlet and sonication extractions.

The next step consisted of replacing methanol with Milli-Q water by using the ASE method 2 (Table 2) twice. Then, cartridges containing XAD-2 resin were stored under Milli-Q water until the next sampling.

Resin cleaned and conditioned as described above is suitable for immediate use in the field.

2.4. Elution and analysis

2.4.1. ASE procedure

All methods summarized in Table 2 were carried out using an automated Dionex-ASE 300 system.

After sampling, most of the water content in XAD-2 resin cartridge was removed by purging under a nitrogen stream for 3 min (ASE method 3, Table 2).

Silicone taps from ASE bottles (250 ml) were replaced with aluminium foil to avoid contamination with siloxane compounds (m/z 73).

ASE elutions were performed at a constant standard operating pressure of 1500 psi. The reason for the use of pressure is to maintain the solvents in the liquid state above their atmospheric boiling points, and to rapidly move the fluids through the system. The pressures used in ASE are well above the thresholds required to maintain the solvents in their liquid states, so pressure adjustments for changing solvents were not required.

Temperature is the most important factor affecting the kinetics of mass transfer in ASE. In ASE, the elution temperature was above the normal boiling point of the solvent, while that of Soxhlet extraction was limited to the boiling point of the solvent used. As a result of increasing the temperature of the elution, the diffusion of the components from XAD-2 particles to their surface is enhanced and the transfer from the surface of the particles into the eluted solvent is accelerated [28]. Thus, the capacity of solvents to solubilize analytes improves at increased temperatures [28]. The elution temperature, however, should not be above the melting point of the XAD-2 resin. Unfortunately, information on the melting point of XAD-2 resin was not available under ASE conditions. However, as tested, the XAD-2 resin had good thermal stability under ambient pressure and stable at temperatures as high as 200 °C [51].

To determine the effect of temperature on elution performance, pre-cleaned XAD-2 resin was spiked with the PAH standard mix and eluted at 80, 100 and 120 °C and at a constant pressure of 1500 psi, 5 min of static time and 1 cycle. Once the temperature was optimized the number of cycles was also evaluated.

As a final step, the cartridge was purged with gaseous nitrogen. The total amount of elution solvent was ∼85 ml per elution and cartridge. In this study, a total volume of 60% fresh solvent and purge time of 125 s were used for the elution of the analytes. Elution was performed with hexane.

After elution, the cartridge containing the XAD resin was cleaned with acetone and methanol at 100 °C, 5 min of static time and 1 cycle and subsequently conditioned by replacing methanol with Milli-Q water as explained above (see Section 2.3, cleaning procedure and conditioning). Then, the cartridge is kept in a bottle containing Milli-Q water, ready to be reused for the next sampling.

The extracts were frozen and then decanted from residual water. This step also prevents any potential contamination associated with the filtration through anhydrous sodium sulfate. Finally, extracts were concentrated to 500 μl at 30 °C in a TurboVap II Concentrator Workstation (Zymark, Hopkinton, MA, USA) under a nitrogen stream at a 0.2 bar operating pressure.

2.4.2. Gas chromatography–mass spectrometry (GC–MS) instrument

After evaporation the extracts were analysed with a Thermoquest MD800 GC–MS system, equipped with a Gerstel large volume programmable temperature injector, using helium as carrier gas (1.3 ml min^{-1}). Electron impact (EI) ionization a 70 eV was used. The GC separation was performed on a column SGE 25QC3/HT8 ((SGE Italy Srl.), 25 m × 0.32 mm i.d., film thickness 0.25 μm). The ion source temperature and interface temperature were adjusted to 200 and 300 °C, respectively. The temperature program was held at 60 °C for 1 min and ramped from 60 to 350 °C at 10 °C/min for 5 min. The Gerstel Cooled Injection System (CIS3) (Gerstel Gmbh, Germany) was operated using solvent vent and stop flow mode as follows: initial time, 0.6 min; rate, 12 °C/min; final temperature, 350 °C; final time, 4 min; cryo-off; equilibration time, 0.2 min (solvent vent with stop flow mode: purge time, 0.8 min; splitless time, 2 min). The total run time of the GC oven was 35 min. The sample volume injected was 7 μl. The mass spectrometer was operated in selected ion monitoring mode (SIM), detecting the following ion masses: m/z 164, 188, 240, 264, 244, 152, 153, 165, 178, 202, 228, 252, 278, 276.

Internal standard calibration was used for quantification of the extracts. Quantification of PAHs was based on comparisons of the areas for the monitored molecular ions to that of the internal standard, with calibration response curves generated from four different concentrations (0.1, 0.05, 0.02, 0.005 ng μl^{-1}) of each target PAH. The calibration curves for the compounds were linear ($R^2 > 0.99$) over the established concentration range.

2.5. Analytical quality assurance

All data were submitted to rigorous control procedures. The sample was spiked with deuterated to compensate losses during sample elution and manipulation procedure. Prior to elution, the XAD-2 resin and filter samples were spiked with 10 μl of the standard solution containing 2.5 ng μl^{-1} of each of the deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}). Prior to injection, 5 μl of deuterated terphenyl-d_{14} containing 2.5 ng μl^{-1} was added to the sample extract to calculate the recovery of the deuterated standards.

Since no standard reference material (SRM) for PAHs in water is available, XAD-2 resin blanks, following exactly the same process as those for the samples, were analyzed with each set of samples. The blanks concentrations found were as follows: <0.06 ng l^{-1} for ACY, FLU, FLT, PHE and PYR; <0.003 ng l^{-1} for ACE, BaA, ANT; <0.001 ng l^{-1} for BbkF, BAP, CHR, DBA, BGP, IND.

Method detection limits were defined as the average plus three standard deviations of the XAD-2 blanks and ranged from 0.001 ng l^{-1} for CHR, BbkF, BAP, DBA, BGP, IND to 0.01 ng l^{-1} for ACY and FLT.

3. Validation experiments

The efficiency of the XAD-2 resin for isolating PAHs was tested in triplicate by spiking a standard PAH mix into 40 l of Milli-Q water. Afterwards, the water was passed through the ASE cartridge containing XAD-2 resin, then it was eluted by ASE and analyzed by GC–MS, as described above (Section 2.4).

Once the efficiency of the methodology was tested in the laboratory, the developed analytical procedure was applied for the analysis of PAHs from Lake Maggiore water.

The lake is situated at 194 m a.s.l., in a fluvial valley reshaped by glacier activity in the Alpine area of Northern Italy. It is the second largest (212 km^2) and deepest (370 m) of the Italian subalpine lakes [52]. Water was collected in a tank and processed in the laboratory. About 40 l of Lake Maggiore water was passed through two cartridges in series, each containing 50 g of XAD-2 resin and both connected through an adapter (Fig. 2c).

In order to have the same representative water sample from the steel tank and from the bottle of 3 l (for the liquid–liquid extraction), the spatial and time variation due to the tank emptying and sampling time were taken into account as follows: portions of water were taken periodically and poured into a bottle of 3 l wrapped in aluminium foil to protect the water from light.

The performance of the proposed procedure was validated by comparison with the extraction procedure described by the International Standard Methodology ISO 17993 [47]. Briefly, approximately 3 l of water sample was liquid–liquid extracted with hexane using a magnetic stirrer at 1000 min^{-1} for 1 h 45 min. The hexane was frozen and decanted from the residual water, concentrated to 500 μl and injected to the GC–MS using the same procedure as described above.

Prior to elution, water samples were spiked with 100 μl of the standard solution containing 0.05 ng μl^{-1} of surrogate analytes. Prior to injection, 5 μl of deuterated terphenyl-d_{14} containing 2.5 ng μl^{-1} was added to the sample extract to calculate the recovery of the deuterated standards.

4. Results and discussion

The schematic diagram of the entire procedure developed is shown in Fig. 4.

Particulate phase procedure is described elsewhere [53]. Briefly, prior to extraction, wet filter samples (~5 g moist weight) were well mixed with anhydrous sodium sulfate (1:5) and sand (1:3) and then packed into 100 ml ASE cartridges. It should also be noted that the mean suspended particulate matter concentration found in Lake Maggiore is among the lowest reported for European lakes [54]. Additionally, the partitioning between the dissolved and the particulate phases in water showed that dissolved—particle interactions for PAHs in surface waters are apparently at or near equilibrium [53].

4.1. Validation in the laboratory

The optimized elution conditions were at a temperature of 120 °C and two static cycles. Results are presented in Table 3.

Recoveries of the entire procedure obtained by spiking PAHs into Milli-Q water were 104% for BaA, 103% for PYR, 101% for FLT, 87% for PHE and 70% for FLU (Table 3).

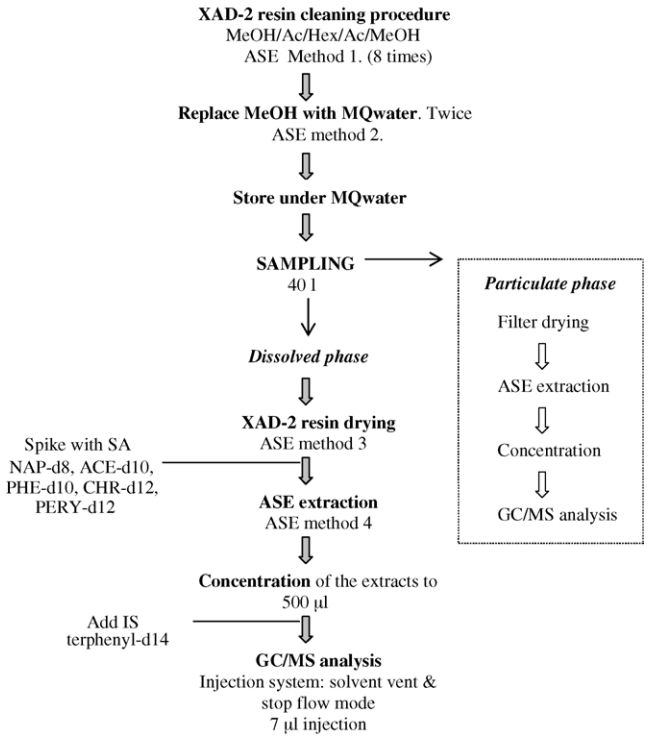

Fig. 4. Schematic diagram of the steps involved on the entire methodology developed in this work for the analysis of PAHs in dissolved phase. The dashed line block represents the particulate phase procedure, not described in this paper.

Table 3
Recoveries (%) of the PAHs from the spiked XAD-2 resin obtained with the ASE at a temperature of 120 °C and two static cycles (first column), recoveries (%) (second column), standard deviations (S.D.s) of PAHs spiked in 40 l of Milli-Q water (third column) and mean PAH concentrations in the dissolved phase of Lake Maggiore surface waters (fourth column)

Compounds	Dissolved phase			[PAHs] (ng l^{-1})
	T = 120 °C, 2 cycles	% Recovery	S.D.s (%), n = 3	
ACY	78	85	10.5	1.00
ACE	75	86	9.4	0.11
FLU	71	70	8.2	0.41
PHE	72	87	9.1	0.75
ANT	71	74	10.5	0.043
FLT	98	101	11.1	0.52
PYR	96	103	6.4	0.29
BaA	101	104	10.7	0.037
CHR	86	86	10.2	0.063
BbkF	100	90	5.9	0.042
BAP	82	80	0.1	0.009
DBA	85	86	8.1	0.006
BGP	82	81	6.3	0.013
IND	80	76	5.8	0.010
Mean	84	86		0.24

The overall precision of the analysis was satisfactory with the S.D. of triplicate measurements ranging between 0.1% and 11%. The average recovery of 86% verifies the use of this methodology for the quantification of PAHs in water. Recoveries for the whole analytical procedure based on surrogate data were: naphthalene-d_8 50 ± 4%, acenaphthene-d_{10} 66 ± 6%, phenanthrene-d_{10} 102 ± 10%, chrysene-d_{12} 92 ± 10% and perylene-d_{12} 101 ± 12% (n = 5). The lowest surrogate values might be attributed to the loss of volatiles during concentration and/or the purge processes, as for example when the remaining solvent is displaced with a purging gas through the vent for the needle assembly. The average recovery obtained by the methodology proposed was higher to that obtained using the traditional Soxhlet extraction [8,55] and similar to that obtained by sonication [56]. However, the method proposed shows clear advantages in terms of sample preparation, analysis time (15 min versus 24 h per sample for Soxhlet) solvent volume employed (from 250 to 500 ml versus 85 ml) and analysis cost. Compared to solid phase extraction, PAH recoveries at trace level (ng l^{-1}) ranged from 60% to 90% [22].

The following times (per cartridge) were estimated for each step involved in the methodology proposed: column preparation (20 min); XAD-2 resin cleaning (400 min); cartridge conditioning (10 min); elution (15 min); removal of remaining water (3 min); freezing (60 min) and concentration (60 min). In order to save time part of the cleaning procedure was performed off-line (overnight).

Furthermore, sampling directly onto the XAD-2 resin, already packed inside an ASE cartridge, with subsequent elution from the same cartridge makes it easier, faster and more reproducible by avoiding the problems of multiple washing procedures and long exposure to chemical agents associated with sonication and therefore faster and safer.

So far, ASE has only been applied to the extraction of terrestrial, biological and food samples but with the methodology proposed in this paper its application is also extended to aqueous samples with the potential future use also applied to aerial samples. Thus, the main advantage of this methodology is that not only the elution but sample preparation, sampling are integrated in one instrument, ASE, for the analysis of all kind of matrixes and organic compounds of interest.

4.2. Validation in the field

The average concentration for the 14 PAHs analyzed in the dissolved phase of Lake Maggiore surface waters was 0.24 ng l^{-1} (Table 3). The PAH distribution was mainly dominated by the low molecular weight compounds (ACY, PHE, FLT, FLU) with concentrations of 1, 0.75, 0.52 and 0.41 ng l^{-1}, respectively. Seasonal PAH data, in different environmental matrices, such as suspended material, surface water and rainwater are reported elsewhere [53].

The percentages of the total PAHs retained in the second cartridge for the five separate experiments carried out were: 3%, 1%, 5%, 5% and 3%. Therefore, more than 95% of the total PAHs were retained in the first cartridge. The average proportion of the individual PAHs found in the second cartridge in the total PAHs were: 1% for ACY, FLU; 0.5% PHE, BbkF; 0.2% FLT, CHR, BbkF, BGP, IND; 0.1% ANT, DBA; 0.05% PYR; 0.03% BaA. Two elutions were performed by each cartridge containing XAD-2 resin by using the ASE method 4 (Table 2) to ensure the complete elution of all compounds.

Simultaneously, Lake Maggiore water was extracted using the International Standard Methodology ISO 17993 [47]. Results are shown in Fig. 5. As it is shown, the ratio between concentrations obtained by both methodologies is close to one: the mean ratio is 1 for FLU, BaA and CHR; 1.1 for ACY and 0.9 for ACE, PHE, FLT, PYR, BbkF and BAP. Standard deviations for the five experiments performed are <0.1 for all compounds except for BaA and BbkF (0.2). Mean percentages of deviation between concentrations measured by both methodologies are found to be 6% for BAP, 7% for PYR, 9% for ANT, 10%

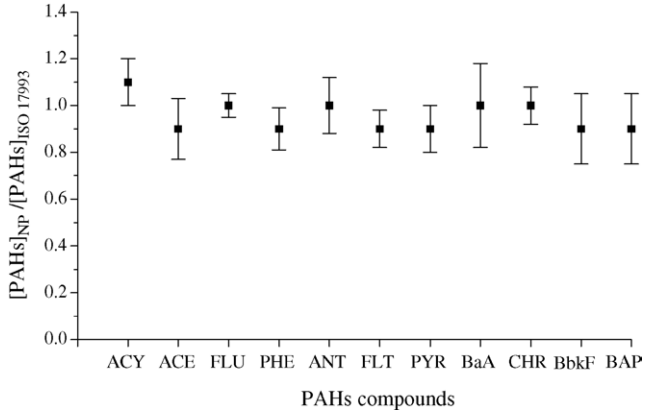

Fig. 5. Ratio between PAH concentrations in dissolved phase by the new procedure (NP) developed vs. PAH concentrations in dissolved phase by ISO 17993 method (n = 5) and their respective standard deviations.

for ACE and FLU, 12% for ACY and PHE, 15% for FLT and BbkF. These results prove the reliability of the methodology. The less soluble PAH compounds DBA, BGP and IND are not shown because they were below the limit of detection in the liquid phase.

Given the wide range of $\log K_{ow}$ of the PAH tested, it can be expected that their application need not be limited to PAHs but could also be applied for ultra trace analysis of other priority substances such as halogenated substances. Development of an ASE analytical strategy for sampling and elution of aerial samples is also planned.

5. Conclusions

A newly optimized procedure for the efficient sampling and fast elution of PAHs compounds from large-volume water samples was applied by using ASE followed by GC–MS.

The procedure was successfully validated with water samples from Lake Maggiore by comparing the PAH concentrations isolated using the new procedure and the hexane liquid–liquid extraction method, according the International Standard Methodology ISO 17993.

Overall, the reported methodology represents a new approach integrating sample preparation, sampling and elution as a continuous and easily reproducible procedure using ASE for analyzing organic compounds in aqueous samples. It offers the following advantages: (1) all steps are fully automated, (2) the same ASE cartridge can be used during the cleaning procedure, sampling and elution process, (3) no XAD-2 resin manipulation between steps is necessary, (4) savings in solvent consumption, as well as (5) in time, (6) filtration of the extracts through a sodium sulfate column was not required, (7) high percentages of recovery (R_m = 86%), and (8) low detection limits were obtained ($<0.01\ ng\ l^{-1}$).

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