Journal of Chromatography A, 1217 (2010) 2306–2317

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Review

Separation and preconcentration of persistent organic pollutants by cloud point extraction

Shunping Xie[a], Man Chin Paau[a], Cheuk Fai Li[a], Dan Xiao[b,c,*], Martin M.F. Choi[a,**]

[a] Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon Tong, Hong Kong SAR, China
[b] College of Chemical Engineering, Sichuan University, Chengdu 610065, China
[c] College of Chemistry, Sichuan University, Chengdu 610065, China

ARTICLE INFO

Article history:
Available online 3 December 2009

Keywords:
Cloud point extraction
Persistent organic pollutants
Preconcentration
Detection

ABSTRACT

Persistent organic pollutants (POPs) are recognized as a class of poisonous compounds which pose risks of causing adverse effects to human health and the environment. Thus, it is very important to detect POPs in environmental and biological samples. The identification and determination of very low levels of POPs in complex matrices is extremely difficult. Recently a promising environmentally benign extraction and preconcentration methodology based on cloud point extraction (CPE) has emerged as an efficient sample pretreatment technique for the determination of trace/ultra-trace POPs in complex matrices. The purpose of this paper is to review the past and latest use of CPE for preconcentrating POPs and its coupling to different contemporary instrumental methods of analysis. First, the comparison of various extraction techniques for POPs is described. Next, the general concept, influence factors and other methods associated with CPE technique are outlined and described. Last, the hyphenations of CPE to various instrumental methods for their determination are summarized and discussed.

Contents

* Corresponding author at: Colleges of Chemistry and Chemical Engineering, Sichuan University, Chengdu 610065, China. Tel.: +86 28 8541 5029; fax: +86 28 8541 6029.
** Corresponding author at: Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon Tong, Hong Kong SAR, China. Tel.: +852 3411 7839; fax: +852 3411 7348.
E-mail addresses: xiaodan@scu.edu.cn (D. Xiao), mfchoi@hkbu.edu.hk (M.M.F. Choi).

0021-9673/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2009.11.075

1. Introduction

Persistent organic pollutants (POPs) are a heterogeneous group of natural or anthropogenic organic compounds including polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and several other industrial and agricultural chemicals such as pesticides, herbicides, and fungicides. They can persist in the environment, bioaccumulate through the food web, and pose adverse effects to human health and the environment. There are evidences of long-range transport of these pollutants to regions where they have not been used or produced. The international community has now, at several occasions called for urgent global actions to reduce and eliminate releases of these chemicals to minimize their threats to the global environment. The Stockholm Convention, a legally binding treaty on POPs, was signed in May 2001. Twelve POPs are officially registered by the United Nations Environmental Program; nine of them are organochlorine pesticides (OCPs) including aldrin, chlordane, dieldrin, endrin, heptachlor, toxaphene, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), hexachlorobenzene, and mirex. The other three include PCBs, PCDDs and PCDFs [1]. Besides these twelve POPs, some other organic pollutants such as chlorodecone, hexabromobiphenyl, hexachlorocyclohexane (α, β, and γ substitutes), PAHs, pentachlorobenzene, hexabromodiphenyl ether and heptabromodiphenyl ether, perfluorooctane sulfonic acid, perfluorooctane sulfonyl fluoride and its salts, tetrabromodiphenyl ether and pentabromodiphenyl ether are also listed [2,3]. More detailed information on POPs is available elsewhere [4,5]. Although strict legal controls are now imposed to regulate their production, usage and emission, considerable levels of POPs still exist in the environment and it is essential to detect and monitor POPs to ensure that they are within safe limits. Unfortunately, the identification and determination of trace and ultra-trace POPs in complex matrices still remains a challenge to analytical chemists.

Most recently, cloud point extraction (CPE) has been extended to the extraction/preconcentration and analysis of environmental organic pollutants. Although some reviews on CPE for analysis of metal ions, organic compounds, drugs and other bioactive compounds have appeared in literatures [6–11], there is no updated review on the CPE of POPs coupled with modern instrumental analysis. As such, this paper aims to summarize the recent progress of CPE and preconcentration of POPs and their coupling with contemporary instrumental methods. In view of the voluminous literature in this area, this review is meant to be illustrative and representative of the applications of CPE and not an exhaustive documentation of the literature. Nevertheless, we trust that this review can give readers an overall view of the current activities in CPE coupled with instrument and hopefully will catalyze further research on the use of CPE and modern analytical instrument for trace and ultra-trace determination of POPs in our environment. In this review, three main sections are included: (1) comparison of various extraction techniques for POPs, (2) principle of CPE, and (3) coupling CPE to instrumental analysis for determination of POPs.

2. Comparison of various extraction techniques for POPs

In general, for complex matrices, sample preparation is the first and most critical step in the whole analytical process and it determines the quality and credibility of the obtained results. Sample preparation involves analyte isolation and trace preconcentration prior to final analysis by instrumental methods. Many extraction techniques are used for sample pretreatment. Traditional extraction methods such as Soxhlet extraction and liquid-liquid extraction are both time- and solvent-consuming. They are somewhat tedious and unfriendly to both analysts and the environment because large volumes of toxic and volatile organic solvents are required. Therefore some new approaches such as ultrasonic-assisted extraction (UAE) [12], microwave-assisted extraction (MAE) [13], pressurized liquid extraction (PLE) or accelerated solvent extraction (ASE) [14], supercritical fluid extraction (SFE) [15], and subcritical water extraction (SWE) [16] have been developed in the past few decades. Table 1 summarizes and compares the characteristics, advantages and disadvantages of each extraction technique for POPs in solid samples.

Soxhlet extraction is the most widely used extraction method for organic pollutants strongly adsorbed in soil matrices. However, this technique requires large volume of usually toxic organic solvent (60–500 mL per sample) to be refluxed through the solid sample for 6–24 h. UAE uses about the same amount of solvent as Soxhlet extraction but it is faster (30–60 min per sample) and allows extraction of larger quantities of samples (ca. 10–30 g). Unfortunately, Soxhlet extraction and UAE is unable to couple online with most chromatographic instruments.

MAE is a very promising extraction technique which allows rapid extraction of solutes from solid matrices by employing microwave energy as heat source. MAE offers several advantages, such as short extraction times (20–30 min per sample), and small solvent consumption (10–40 mL). In addition, MAE can increase sample numbers through the use of multi-vessel systems that allow simultaneous extraction of multiple samples. However, in MAE, the extraction solvent must be polar, that is, the solvent has to be able to absorb microwaves, a clean-up procedure may be required before analysis, and the vessels need to be cooled down to room temperature after extraction. MAE is relatively difficult to online couple with chromatographic instrumentation.

PLE or ASE uses organic solvents to extract analytes from a range of sample matrix in a closed-vessel with control of temperature and pressure as the main factors. The higher temperature at which the extraction is conducted increases the capacity of the solvent to solubilize the analyte, and the higher pressure increases the diffusion rate into the pores of the matrix, thus facilitating the mass transfer of the analyte into the extracting solvent. This technique is attractive attributing to its relatively fast extraction time (ca. 15 min per sample), minimal use of solvent (10–60 mL), no filtration after extraction, and unattended operation of the instrument during extraction. It is possible for PLE to online couple with other chromatographic instruments. However, limited by high cost, its application is still not widespread.

SFE is a fast extraction technique which utilizes pure or modified carbon dioxide (CO_2) for extraction of analytes from samples. This technique is attractive as it is fast with extraction time of about 30–60 min per sample and uses small amounts of solvent (10–40 mL). CO_2 is a non-toxic, non-flammable, and environmental friendly extractant. Furthermore, the extraction selectivity can be tuned by varying the pressure and temperature of supercritical fluid CO_2 and by addition of modifiers, *e.g.*, methanol. Direct coupling of SFE with other chromatographic instruments can also be realized. However, the disadvantages of this technique include limited sample size, extraction efficiency is dependent on matrix type, analyte type and moisture content of the matrix, and high cost of the equipment.

SWE uses water as an extraction fluid to extract a variety of polar and non-polar organics from matrix samples based on the fact that the solubility of organic compound increases dramatically with temperature in liquid water. This technique is attractive as it is fast with extraction time of about 30–60 min per sample. Water is environmental friendly, readily available, non-toxic, and economical. Similar to SFE, it is possible to couple SWE with other chromatographic instruments. However, when the temperature and pressure of extraction vessel is cool down to room condition after extraction, some analytes can be

Table 1
Comparison of various extraction techniques for POPs in solid samples.

Extraction technique	Extraction solvent type	Sample size (g)	Extraction time	Solvent consumption	Temperature	Pressure	Cost	Advantages	Disadvantages
Soxhlet	Organic solvent	10–30	6–24 h	60–500 mL	Boiling point of solvent	Atmospheric pressure	Low	Large amount of sample, filtration not required, not matrix dependent, and easy to operate	Long extraction time, large consumption of organic solvent, exhaustive extraction, preconcentration of sample required after extraction, and difficult to online couple with most chromatographic instruments
UAE	Organic solvent	10–30	30–60 min	30–100 mL	30–35 °C	Atmospheric pressure	Low	Fast method, large amount of sample, not matrix dependent, easy to operate	Large amount of organic solvent, labor intensive, filtration required, risk of exposure to solvent vapor, and relatively difficult online connected to most chromatographic instruments
MAE	Organic solvent	2–5	20–30 min	10–40 mL	100–150 °C	Atmospheric pressure for open vessel and pressurized MAE for closed vessel	Moderate	Fast extraction, small amount of solvent, and full control of extraction parameters	Extracts must be filtered, polar solvent needed, exhaustive extraction, and relatively difficult online connected to most chromatographic instruments
PLE	Organic solvent	Up to 30	10–60 min	10–60 mL	100–150 °C	7–15 MPa	High	Fast technique, small solvent usage, no filtration needed, easy to use, and possibly online couple with some chromatographic instruments	Extraction efficiency is more matrix dependent
SFE	Carbon dioxide	1–10	30–60 min	10–40 mL	70–150 °C	15–50 MPa	High	Fast extraction, non-toxic, environmental friendly non-flammable extractant, selectivity can be tuned by varying pressure, temperature, and modifier, small amount of solvent, filtration not required, no solvent exposure, and can online coupled with some chromatographic instruments	Limited sample size, extraction efficiency depends on matrix and analyte
SWE	Water	1–50	30–60 min	30–60 mL	200–300 °C	5 MPa	Moderate	Fast method, water is non-toxic, non-flammable, environmental friendly, small amount of solvent, and possibly online connected to some chromatographic instruments	Required optimization of operating conditions
CPE	Surfactant solution	1–50	10–20 min	5–10 mL	CP of surfactant	Atmospheric pressure	Low	Fast extraction, surfactant is non-toxic, non-flammable, environmental friendly, small amount of solvent, and easy to online couple with HPLC	Required optimization of operating conditions

UAE: ultrasonic-assisted extraction; MAE: microwave-assisted extraction; PLE: pressurized liquid extraction; SFE: supercritical fluid extraction; SWE: subcritical water extraction; and CPE: cloud point extraction.

back-extracted into matrix samples; thus reducing the extraction efficiency.

Saim et al. [17] compared the extraction of PAHs from contaminated soil using Soxhlet extraction, pressurized and atmospheric MAE, SFE and PLE. Their results indicate that the recovery of PAHs is dependent on the extraction techniques. The total 16 PAHs content is 1623 mg/kg for Soxhlet extraction (RSD of 5–23%), 1578 mg/kg for pressurized MAE (RSD of 7–19%), 1492 mg/kg for atmospheric MAE (RSD of 5–22%), 1544 mg/kg for SFE (RSD of 4–12%), and 1537 mg/kg for PLE (RSD of 4–16%). Among the above extraction techniques, Soxhlet extraction gave the highest recoveries of individual PAHs consistently. In general, the organic extraction solvent volume required is: Soxhlet (150 mL) > atmospheric MAE (70 mL) > pressurized MAE (40 mL) > PLE (25 mL) > SFE (12 mL). For extraction time the order is: Soxhlet (24 h) > SFE (1 h) > atmospheric MAE (20 min) > PLE (12 min) > pressurized MAE (20 min per four samples or 5 min per sample). The relative order for sample weight is: Soxhlet (10 g) > PLE (7 g) > MAE (2 g) > SFE (1 g).

Hawthorne et al. [18] have described the extraction of a PAHs-contaminated soil from a former manufactured gas plant site with four different extraction techniques: Soxhlet extraction (18 h), PLE (50 min at 100 °C), SFE (1 h at 150 °C with pure CO_2), and SWE (1 h at 250 °C). The total 17 PAHs contents are 7025 mg/kg (RSD of 10–15%) for Soxhlet extraction, 7359 mg/kg (RSD of 1–18%) for PLE, 6407 mg/kg for SFE (RSD of 2–12%), and 6936 mg/kg for SWE (RSD of 3–20%). There were some minor differences in recoveries for some PAHs in these four methods. In addition, the extract quality varied with the extraction methods. The organic solvent extracts (Soxhlet and PLE) were much darker, the extracts from subcritical water (collected in toluene) were orange, and the extracts from SFE (collected in CH_2Cl_2) were light yellow. It is obvious that the extraction efficiencies of these extraction methods are different with different PAHs.

The extraction efficiency of 16 PAHs from contaminated soils and sediments with UAE and Soxhlet extraction was studied by Song et al. [19]. For highly polluted soils, the extraction efficiency of UAE (45.7–103.9% recovery) is higher than Soxhlet extraction (37.4–96.3% recovery). Also, Sun et al. [20] described the use of Soxhlet extraction and UAE techniques to determine the speciation and concentration of PAHs on lime spray dryer ash samples collected from the baghouse of a spreader stoker boiler. The average matrix spike recoveries ranged from 20 to 80% for the 13 lowest molecular weight PAHs tested. But Soxhlet extraction achieved a higher percentage of recoveries than UAE.

The simultaneous extraction of PAHs and OCPs from soils using Soxhlet extraction, MAE and PLE were investigated by Wang et al. [21]. The recoveries of PAHs obtained from Soxhlet extraction, MAE and PLE were 69.07–115.95% (RSD of 0.92–11.55%), 60.73–126.11% (RSD of 1.55–13.49%), and 70.35–112.14% (RSD of 1.44–11.44%), respectively. The recoveries of HCHs and DDTs obtained from Soxhlet extraction, MAE and PLE were in the range of 86.79–105.12% (RSD of 0.61–13.12%), 84.98–104.06% (RSD of 0.52–9.3%), and 82.90–105.40% (RSD of 3.11–12.08%), respectively. In their work, PLE had the best extraction efficiency compared to MAE and Soxhlet extraction, and that the extraction efficiencies of MAE and Soxhlet extraction were influenced by the properties of the studied compounds and soils.

Itoh et al. [22] analyzed the PAHs in lake sediment samples by using Soxhlet extraction, MAE and PLE in combination with gas chromatography (GC) and isotope dilution mass spectrometry (MS). These techniques showed good repeatability for the five PAHs examined. The results from the three techniques were different and the recoveries decreased in the order PLE > MAE > Soxhlet extraction.

Barco-Bonilla et al. [23] used UAE and PLE for the analysis of PAHs soil samples by GC coupled to tandem MS. There were no significant differences between the two extraction methods although PLE had better extraction efficiencies. The recoveries of PAHs from UAE and PLE were in the range of 29.2–82.5% (RSD of 6.0–39.3%) and 32–104.4% (RSD of 0.6–20.6%), respectively.

In essence, the extraction efficiency of the above techniques is influenced by factors such as type and volume of solvent, extraction time, and temperature. For Soxhlet extraction and UAE, both solvent and extraction time have significant impact on the extraction efficiency of analytes. Extraction efficiency by MAE is dependent on solvent, temperature, microwave energy, and time. For PLE and SFE, the extraction efficiency relies on temperature, pressure, time, sample size, matrix, and analyte. For SWE, temperature, pressure, and time have influence on the extraction efficiency of analyte while CPE is dependent upon the type and amount of surfactant and additive, time and temperature. In general, all the above techniques have good extraction efficiency for POPs. Unfortunately, Soxhlet extraction, UAE, MAE and PLE use toxic organic solvent as extractant which is not so environmental friendly. Although SFE and SWE employs an environmental friendly solvent (CO_2 for SFE and H_2O for SWE), the cost of equipment is relatively high, especially SFE. In addition, as CO_2 is non-polar, its polarity has to be adjusted with organic modifiers such as acetone and methanol to more efficiently extract moderate polar POPs. As such, organic solvents are still required.

To date CPE, as a new promising environmentally benign extraction technology, is much more attractive to analytical chemists as compared to the above extraction methods. Its advantages over other extraction techniques are high extraction efficiency, high preconcentration factor, low-cost, and usage of non-toxic surfactants instead of organic solvents. So far it has been successfully applied to the extraction and/or preconcentration of inorganic and organic species with wide varieties before instrumental determinations [6,7]. Historically, the first application of CPE for the extraction of metal ions forming complexes sparingly soluble in water was introduced by Watanabe and Tanaka [24]. Later, the application scope of CPE was extended by Bordier [25] for the extraction of hydrophobic biomolecules. In the following sections, the basic principle of CPE, factors affecting the extraction efficiency of POPs and hyphenation of CPE to instrumental analysis of POPs are described.

3. Cloud point extraction

3.1. Principle of cloud point extraction

CPE is a new promising environmentally benign extraction technique which is based upon phase separation behavior exhibited by aqueous solutions of certain surfactant micelles. It is well known that surfactants are amphiphilic molecules which contain a polar head group and a non-polar tail. In general, the tail is a linear or branched hydrocarbon chain with different numbers of carbon atoms, and may contain aromatic rings; whereas the head is ionic or strongly polar groups. In aqueous solutions, these two moieties are hydrophobic and hydrophilic, respectively. The hydrophobic tails tend to form aggregates called micelles. The minimum concentration of surfactant required for this phenomenon to occur is called the critical micellar concentration (CMC). Upon appropriate alteration of the conditions such as temperature or pressure, addition of salt or other and additives, the solution becomes turbid at a temperature known as cloud point (CP) due to the diminished solubility of the surfactant in water. CP varies widely with temperature from one surfactant to another. Hinze and Pramauro [26] have summarized the CP temperatures of various non-ionic and zwitterionic surfactants. Above the CP, the single isotropic micellar phase separates into two isotropic phases: the small volume “surfactant-rich phase” is separated from the bulk aqueous solution; and the “aqueous phase” which contains the surfactant at a concentration close to

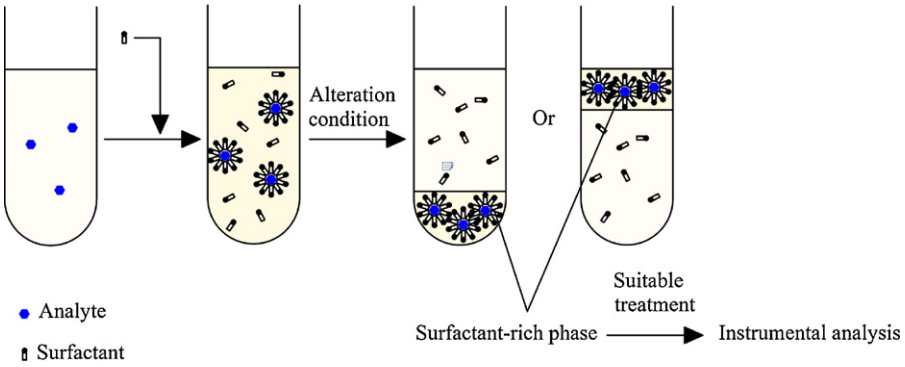

Fig. 1. Schematic representation of the cloud point extraction. I: the initial solution containing the analyte; II: solubilization of the analyte in the micellar aggregates after the addition of a surfactant solution (concentration of surfactant > CMC); III: the phase separation into two phases after appropriate alteration of the conditions (temperature change or adding salt). Finally, analyte is preconcentrated into a small volume of the surfactant-rich phase after a suitable treatment step and is submitted to instrumental analysis.

the CMC. This phenomenon is reversible and the re-establishment of the initial solution conditions drives the micelles to merge with the aqueous to form a single isotropic phase again. However, the mechanism of phase separation is still the subject of debates. The common interpretation is that the CP is formed due to the sharp increase in the aggregation of the micelles and the decrease in inter-micellar repulsions resulting from the decreased hydration of the polar group of surfactant with an increase in temperature [27,28]. Blankschtein et al. [29,30] have proposed that the phase separation behavior is a result of the competition between the internal-energy effects which promote separation of micelles from water and entropic effects together with the miscibility of micelles in water. Kjellander et al. [31,32] have also proposed that the phase separation results from the competition between entropies. Degiorgio et al. [33] explain that the phase separation at the lower consolution point is driven by the effective inter-micellar interaction potential which is repulsive at low temperature but becomes attractive at high temperature.

In aqueous solution, the unique structure of surfactant allows sparingly soluble or water-insoluble substances to be solubilized because they can associate and bind to the micellar assembly [34]. The interaction between surfactant and analyte may be electrostatic, hydrophobic or a combination of both [10]. CPE mainly depends on the solubilization of surfactant solution and phase separation for the extraction and preconcentration of analytes [35]. In essence, CPE technique offers a simple, safe, inexpensive, and non-polluting approach for extraction/preconcentration and analysis of inorganic and organic analytes.

3.2. Influential factor

The extraction process of CPE technique is very simple and is shown in Fig. 1. First, the surfactant or a concentrated surfactant solution is added to the aqueous solution containing the analytes to be extracted/preconcentrated. The final surfactant concentration must exceed its CMC in order to ensure formation of micelle aggregates. Analytes can remain referentially in the hydrophobic domain of the micelles in a surfactant-rich phase, thus being extracted and preconcentrated [9]. Next, the conditions are altered by raising or lowering the temperature and/or adding salt or other additives to obtain phase separation. After demixing of the biphasic system, either by gravity settling or centrifugation, the analytes are preconcentrated in a small volume of surfactant-rich phase. Depending on the density of the surfactant-rich phase, it can be either at the bottom or the top. The preconcentrated analytes in surfactant-rich phase is so viscous that it cannot be injected directly into instrument for analysis; thus, it needs to be diluted with aqueous or organic solvent [34].

In CPE, extraction needs to be carried out under optimal conditions in order that the preconcentration factor can be maximized to achieve 100% extraction efficiency. The preconcentration factor (C_F) is a parameter for comparing the extraction capability of micellar systems for analytes. It is defined as the ratio of analyte concentration in the surfactant-rich phase (C_s) to that in the original aqueous solution before the preconcentration step (C_{aq}), *i.e.*, $C_F = C_s/C_{aq}$. In general, the C_F is dictated by V_{aq}/V_s, *i.e.*, the volume ratio of the original aqueous phase (V_{aq}) to that of the surfactant-rich phase (V_s) after phase separation. This depends on the phase relationship, *i.e.*, the distribution coefficient (K_d) of the analyte between the phase and the surfactant concentration. Several factors must be taken into account in order to obtain the maximum C_F. It is well known that the extraction/preconcentration process can be altered by the types and concentration of surfactant and additive, pH, equilibration temperature and time, and centrifugation conditions [34].

3.2.1. Surfactant type and concentration

Depending on the nature of the hydrophilic group, surfactants are classified as non-ionic, zwitterionic, cationic, and anionic. Up to now, non-ionic, zwitterionic and anionic surfactants are most widely used for CPE of inorganic metal ions, drugs, biomaterials, and organic compounds. However, the application of cationic surfactants in CPE is scarce [36]. It is very important to select an appropriate surfactant for a successful CPE analysis since it can directly affect the extraction and preconcentration, and accuracy of the final analytical results.

Some water always remains in the surfactant-rich phase after separation. The water content in the surfactant-rich phase (W_s) is commonly around 80 wt% even when the phase separation is strengthened by high speed centrifugation [37,38]. The high W_s limits the performance of CPE to a large extent and causes difficulty in further increase of C_F or K_d [38]. Triton X-114 is a widely used non-ionic surfactant which produces a high-density surfactant-rich phase with low W_s after CPE [39]. Recently Yao and Yang [38] have found that PEG/PPG-18/18 dimethicone surfactant also offers lower W_s compared with conventional non-ionic surfactants. The resulting C_F and K_d are as high as 30–40 and 2.5–2.9 ($\log(K_d)$), respectively, and they are almost independent of the surfactant concentration. The small surfactant-rich phase volume obtained by the PEG/PPG-18/18 dimethicone is attributed to the high flexibility of the polysiloxane chain in the silicone surfactant which enables it to acquire more conformations to form a more compact micelle structure. If target analytes are trapped in the surfactant-rich phase,

excellent enrichment would be expected using the CPE system with two silicone surfactants. This ability to lower the W_s is also proved to be useful for large-scale water treatment [40,41]. In addition, the surfactant concentration in solution is a very important factor influencing the efficiency of CPE. The C_F depends on the V_s which varies with the surfactant concentration. Research shows that the smaller the surfactant concentration, the higher the C_F. In addition, when the V_s is too small, the extraction process becomes difficult, and accuracy and reproducibility will probably suffer [42]. Therefore, a balance between the surfactant concentration required for a maximum C_F and an adequate volume V_s for subsequent volume manipulation is critical.

3.2.2. Effect of ionic strength

The addition of salt to the solution can influence the extraction/preconcentration process since it can alter the density of the aqueous phase for most non-ionic surfactants and remarkably facilitate phase separation [26,43,44]. Also, it can change the CP temperature of non-ionic surfactant. The salting-in and salting-out effects can be used to interpret the effects of the electrolyte on the CP of non-ionic surfactant [26]. In most studies, it was found that increases in the ionic strength do not appreciably affect V_s [45–48]. However, to date, some research found that salt can increase the incompatibility between the water structures in hydration shells of ions and surfactant macromolecules which can reduce the concentration of "free water" in surfactant-rich phase thus reduce its volume [49,50]. It was previously shown that C_F increased significantly with the increase in salt content [51–53]. On the other hand, the salt concentration does appear to influence the recovery of analyte. The recovery increases with the salt concentration up to saturation. Zhu et al. [54] have chosen four salts (NaCl, Na_2SO_4, Na_2CO_3, and $Na_3C_6H_5{\cdot}2H_2O$) to investigate their effects on CPE. The recovery is enhanced with salt concentration and Na_2CO_3 shows the highest recovery. In summary, the CPE system behaves differently with salt type and concentration.

3.2.3. Effect of pH

The pH effect on CPE depends on the characteristics of both surfactants and analytes. In most studies, the influence of pH on extraction efficiency and recovery are not crucial for those neutral or non-ionized compounds such as PAHs, PCBs, PCDFs, and PCDDs. However, a few notable exceptions have been reported [55]. For analytes possessing an acidic or a basic moiety, pH plays an important role for their CPE. The ionic form of a molecule formed upon deprotonation of a weak acid or protonation of a weak base normally does not interact and bind as strongly as its neutral form with the surfactant aggregate. As a result, the lesser ionized form of an analyte is extracted [56].

In general, the CP of zwitterionic surfactant is independent of solution pH except in very acidic media. Saitoh and Hinze [57] reported that the CP for a 5% 3-(nonyldimethylammonio)propyl sulfate (C_9-$APSO_4$) solution is independent on pH range 4–10. However, under the more acidic condition, the CP of the solution dramatically decreased as acidity increased until a completely clear homogeneous solution at pH 0 and temperature above 0 °C. This is due to the sulfate group of the zwitterionic C_9-$APSO_4$ surfactant being protonated at very low pH. Thus, one is converting the zwitterionic surfactant to a cationic surfactant, $C_9H_{19}(CH_3)_2N^+$–$(CH_2)_3OSO_3H$, in this region. As such, for cationic and anionic surfactants, pH is a very important parameter for CPE. It is known that anionic surfactants separate into two isotropic phases in an acid medium at room temperature. The C_F can be altered by pH. It has been reported that C_F for sodium dodecyl sulfate (SDS) and sodium dioctylsulfosuccinate (Aerosol OT) decrease with the increase in HCl concentration by one unit. By contrast, an identical increase in acid concentration results in an increase in C_F when sodium dodecanesulfonic acid (SDSA) and sodium dodecylbenzenesulfonic acid are used [58].

So far the application of cationic surfactants in CPE is still very few. Man and coworkers [36] have developed a new method for the determination of cyanobacterial toxins and microcystins in natural waters based on the electrostatic interaction between the charged head groups of Aliquat-336 and anionic species in aqueous media. At pH 6–7, CPE is very efficient in preconcentrating anionic microcystin variants. It was proposed that ion-pairing between the anionic toxin species and the cationic head group of surfactant molecules was initially formed and followed by the extraction of these much more hydrophobic ion-pairs into the surfactant-rich phase.

3.2.4. Equilibration temperature and time

The kinetics of extraction of analytes from the aqueous phase to surfactant micelles is very rapid; as a result, partition equilibrium is achieved in about 2 min [59]. Optimal equilibration temperature and time are necessary to achieve easy phase separation and efficient preconcentration. Theoretically, the optimal equilibration temperature of CPE occurs when the temperature is 15–20 °C higher than the CP temperature of the surfactant [50,60]. If the temperature is lower than the CP, two phases cannot be formed. But too high temperature may lead to the decomposition of analytes. It has also been demonstrated that the analyte C_F and recovery in the CPE increase as the equilibration temperature for phase separation is progressively increased to above the CP temperature [56,61]. Similarly, as the equilibration temperature increases, the V_s decrease because the hydrogen bonds are disrupted and dehydration occurs [55].

Since longer equilibration times (>30 min) do not have any significant effect on the extraction [56], the equilibration time of 10–20 min is sufficient to obtain good extraction in most work [62]. In addition, centrifugation can accelerate equilibration time. If the equilibration temperature is too high to conduct CPE easily by centrifugation, phase separation can be accomplished by gravity settling [42]. In general, centrifugation time hardly affects micelle formation but accelerates phase separation in the same sense as in conventional separation of a precipitate from its original aqueous environment. Centrifugation times around 5–10 min are usually sufficient for most CPE procedures [63].

3.3. Other technologies associated with CPE

To date CPE is assisted with common technologies including microwave [64–67], ultrasonic [67–69] and stirring [41]. The combination of these technologies with CPE allows the extraction of different POPs from water, solid, and biological samples more efficiently. Microwave-assisted cloud point extraction (MA-CPE) has been reviewed in detail in literature [10]. MA-CPE combines the advantages of MAE and CPE, so the extraction efficiency is improved and the analysis time is shortened. Generally, various parameters such as extraction temperature, power and time, nature and volume of surfactant, and characteristics of analytes can influence the extraction/preconcentration process of analytes during MA-CPE. In some cases, analytes can be decomposed or volatilized due to high temperature and long extraction time [10]. Therefore, these parameters have to be carefully optimized.

Ultrasonic-assisted cloud point extraction (UA-CPE) has been developed by performing the CPE process in an ultrasonic environment and has drawn wide attention due to lower W_s (*i.e.*, higher C_F), high recovery and feasibility for continuous and scaling-up of the operation [68]. A pilot-scale continuous UA-CPE of anthracene, phenanthrene and pyrene is shown in Fig. 2 [69]. In addition, Yao and Yang [41] firstly introduced a stirring system into the CPE process using silicone surfactant (PEG/PPG-18/18 dimethicone). Their

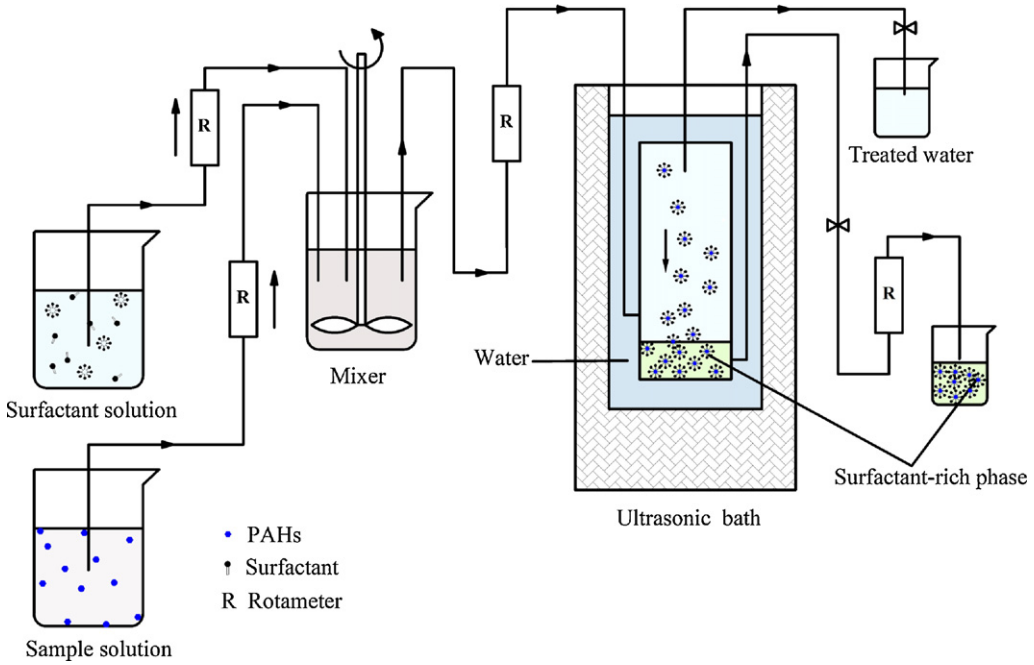

Fig. 2. Diagram of a pilot-scale ultrasonic-assisted cloud point extraction. The PAHs sample and surfactant solutions are pumped into a container and mix by stirring. Then the mixed solution is pumped into a purpose-made glass column fixed in the ultrasonic pool and incubates at a prescribed temperature. After a half of the glass column is filled with the mixed solution, the ultrasonic effect starts at a certain power until the accelerated phase separation of the mixed solution occurs in the glass column. The surfactant-rich phase is pumped through the bottom outlet slowly, and the aqueous phase in the upper is discharged from the top outlet.

stirring operation is feasible for scaling-up. Fig. 3 displays the process of the stirring-assisted cloud point extraction (SA-CPE). It is probable that both UA- and SA-CPE can be applied to extract POPs from water at large scale.

4. Determination of POPs by coupling CPE to instrumental analysis

4.1. Hyphenation of CPE to high-performance liquid chromatography

Most analytical applications of CPE for the extraction of POPs are coupled with reversed-phase high-performance liquid chromatography (RP-HPLC). The surfactant-rich phase obtained in the extraction process is compatible with the hydro-organic phase which is usually employed in RP-HPLC [10]. The solubilization of POPs in the hydrophobic micellar core is an inherent property of all surfactant systems; thus, it was widely exploited for the extraction/preconcentration of POPs from complex matrices such as environmental samples (soil, sediment, sludge, coal, and wood ash) [70], biological fluids [71] and organism [72]. The efficiency of extraction/preconcentration relies on the magnitude of analyte solubilization into the micelle (non-polar core and polar micelle–water interface), analyte polarity and solution composition. Therefore, any experimental approach should focus on these parameters to ensure maximum extraction efficiency [63].

Table 2 summarizes some of the recent applications of CPE for POPs coupling to HPLC. The CPE technique has been successfully exploited for the extraction/preconcentration of POPs as a sample pretreatment step prior to their determination by HPLC using a variety of non-ionic surfactants, such as Triton X [70,71,73–75], Brij

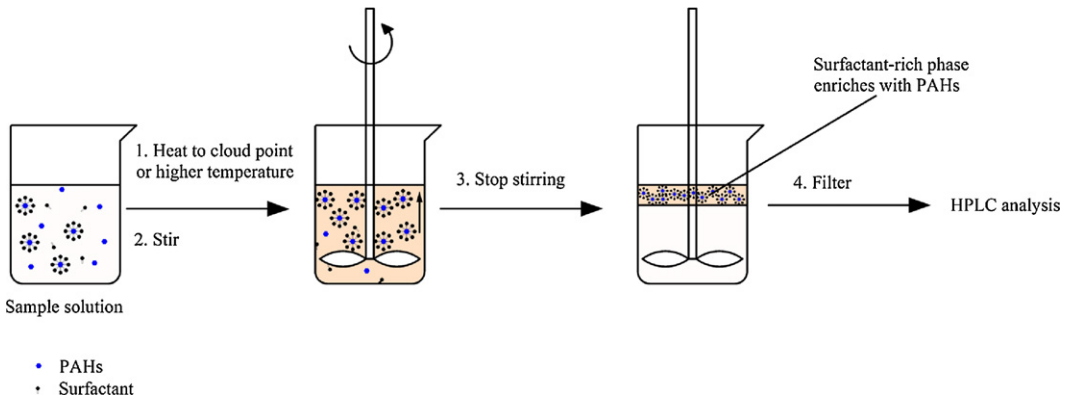

Fig. 3. Pictorial steps involved in the stirring-assisted cloud point extraction. A certain amount of surfactant is added into PAHs solution to form a micelle solution. Then the solution is heated to cloud point or higher temperature and is stirred by a stirring set. The surfactant aggregates are formed and both volume and number of aggregates increase with stirring time. Finally, they rise to the top layer of the solution. After the stirring operation, all the surfactant aggregates combine into one large continuous phase as the surfactant-rich phase and the water phase turns clearer. Two phases are easily separated by filtering. Then the continuous surfactant aggregates phase is collected in the strainer, dissolved in acetonitrile and injected into the HPLC.

Table 2
Detection of POPs coupling CPE to HPLC.

Compounds	Matrix	Surfactant system	LOD	Cloud point extraction method	Detection	Ref.
PAHs	Water	1.0% PEG/PPG-18/18 dimethicone 1.0% PEG-12 dimethicone	–	–	UV	[40]
	Aqueous solution	1.0% PEG/PPG-18/18 dimethicone	–	Stirring-assisted CPE	UV	[41]
	Marine sediments	3.1% POLE	2.2–52.4 μg/L	Ultrasonic-/microwave-assisted CPE	UV	[42]
	Seawater	1.0% POLE	1.0–150 ng/L	–	FD	[45]
	Coal	5% C_9-APSO$_4$	–	–	UV	[57]
	Dried sewage sludge	1.0% SDS or SDSA, 4.2 M HCl	–	–	UV	[58]
	Soil, sediment, and sludge	2% SDS, 4.2 M HCl	0.1–5 μg/L	–	FD	[59]
	Marine sediments	0.02 M POLE	0.01–0.14 ppm	Microwave-assisted CPE	UV	[64]
	Marine sediments	0.02 M Brij 35 and polyoxyethylene$_{10}$dodecyl ether	–	Microwave-assisted CPE	FD	[65]
	Soil	1.0% Tergitol 15-S-7	0.101–0.456 μg/L	Ultrasonic-/microwave-assisted CPE	FD	[67]
	Water	2% Tergitol TMN-6	–	Ultrasonic-assisted CPE	UV	[68]
	Water	10% Tergitol TMN-6	–	Ultrasonic-assisted CPE	UV	[69]
	Water	0.1% Triton X-114	0.002–0.12 ppb	–	FD	[70]
	Smoke particulates	0.5% Triton X-114				
	Wood ashes	0.5% Triton X-114				
	Human serum	2.0% Triton X-100	–	–	UV	[71]
	Water	1.0% Triton X-114	0.3–11.6 ng/L	–	FD	[73]
	Water	5% Triton X-114	0.6–1.8 ng/L	–	FD	[74]
	Aqueous solution	Tergitol 15-S-5, LE-203 and Brij 30	–	–	UV	[76]
	Aqueous solution	3% Tergitol 15-S-7	–	–	FD	[82]
	Aqueous solution	1% Tergitol 15-S-5	–	–	FD	[83]
	Aqueous solution	Tergitol 15-S-9 Neodol 25-7 Tergitol 15-S-7	0.1 μg/mL	–	UV	[84]
	Water	0.1% SDSA, 4 M HCl	0.1–7.9 ng/L	–	FD	[85]
	Seawater	1.0% POLE/Brij 30	23.4–231 ng/L	–	FD	[86]
	Certified marine sediment	0.02 M POLE 0.1 M POLE	0.03–1.09 ng/mL	Microwave-assisted CPE Ultrasonic-assisted CPE	FD	[89]
	Marine sediments	0.1 M POLE	0.01–0.16 ppm	Ultrasonic-assisted CPE	UV	[90]
PCBs	Marine sediments	0.02 M Genapol X-080/POLE	–	Microwave-assisted CPE	FD	[66]
	Marine organisms	2% POLE	7.47–72.6 ng/mL	Microwave-assisted CPE	FD	[72]
	Seawater	2% Genapol X-080 2% Brij 56	0.7–12.8 ng/mL	–	FD	[77]
	Seawater	2% Brij 30 2% Brij 97	1.89–16.30 ng/mL 0.94–18.04 ng/mL	–	FD	[78]
	Marine sediments	0.02 M POLE 0.02 M Genapol X-080	0.89–4.89 ng/mL 0.7–3.61 ng/mL	Microwave-assisted CPE	FD	[80]
PCDDs	Water	5% POLE	0.05–12.80 ng/mL	–	UV	[62]
	Human serum	12% Triton X-100	–	–	UV	[71]
	Marine sediments	5% POLE 5% Genapol X-080	1.0–30.1 ng/mL 0.1–3.3 ng/mL	Microwave-assisted CPE	UV	[81]
PCDFs	Marine sediments	0.02 M Genapol X-080 0.02 M POLE	1.53–5.10 ng/mL 1.04–3.06 ng/mL	Microwave-assisted CPE	FD	[66]
	Marine organisms	2% POLE	8.98–104 ng/mL	Microwave-assisted CPE	FD	[72]
	Seawater	2% Genapol X-080/Brij 56	0.7–27.5 ng/mL	–	FD	[79]
OCPs	Soil	3%/5% Iegepal ICO-630 and Triton X-114 mixture	–	–	UV	[75]
	Soil	5% POLE	86.4–806.4 ng/g	Microwave-assisted CPE	UV	[91]

FD: fluorescence detection and UV: ultraviolet detection.

[65,76–79], Genapol [66,77,79–81], and Tergitol [67–69,76,82–84] series. Recently some zwitterionic surfactants such as C_9-APSO$_4$ [57] and anionic surfactants [58,59,85] such as SDS, SDSA and Aerosol OT have also been exploited for CPE and preconcentration of POPs. However, to our best knowledge, the analytical applications of CPE and/or preconcentration of POPs using cationic surfactants have never been reported.

The advantages of using CPE in separation techniques have been summarized in literature [57] and these include (i) the ability to concentrate a variety of analytes, (ii) safe and cost-effective, (iii) easy disposal of non-ionic surfactant, (iv) the surfactant-rich phase compatibility with micellar or hydro-organic mobile phases, and (v) the possibility of enhanced detection as the analytes are preconcentrated in the surfactant-rich micellar phase. However, one of the drawbacks of this methodology is the high background absorbance in the UV region and high fluorescence signals when an excitation wavelength in UV region is used by virtue of the aromatic moiety in surfactant structure, which mask all PAHs having low retention times [73]. This clearly limits the use of this methodology in chromatographic determination. One possible way of overcoming this problem is to use surfactants that do not absorb at the normal working wavelengths of HPLC [57,86]. Another way to circumvent this drawback is to use electrochemical detector [87] or to add clean-up procedure [73] prior to HPLC analysis. In addition, a general problem encountered by both zwitterionic and non-ionic surfactants in CPE is that the surfactant-rich phase is too viscous for convenient

sampling by a HPLC micro-syringe. Thus, in some applications, a relatively small volume of an appropriate solvent (diluent) such as water, methanol, ethanol, acetonitrile, and aqueous solution of another surfactant, has been added to dilute the surfactant-rich phase [57].

It is well known that the adsorption of PAHs onto containers of water samples during storage results in losses of these pollutants. To avoid this, it is recommended that organic solvents are added to the aqueous sample [88]. In addition, the use of non-ionic and anionic surfactants such as polyoxyethylene-10-lauryl ether (POLE), Triton X-114, Tergitol 15-S-5, and SDSA for the extraction/preconcentration of PAHs has the added favorable attribute of avoiding adsorption of PAHs onto the containers [45,70,83,85]; thus, no chemical reagents is required to prevent their adsorption. Moreover, the CPE and preconcentration of PAHs using surfactants can avoid interference from humic acids [45,70,85].

Delgado et al. [86] proposed the use of non-ionic surfactant mixtures (POLE and Brij 30) to modify and control the CP temperature required to extract and preconcentrate 13 PAHs from seawater samples. The limits of detection (LODs) ranged from 23.4 to 231 ng/L. The mean recoveries oscillated between 72.0 and 98.8%.

Recently the use of microwaves, ultrasound, or stirring techniques in the CPE process has been developed. The combination of microwave or ultrasound with CPE allows the extraction of different POPs from solid samples. Pino et al. [64] first proposed the extraction of PAHs from marine sediments by MAE with a micellar medium of POLE as a prior step to their determination by HPLC with UV detection. The LODs for the PAHs range from 0.01 to 0.14 ppm. Subsequently, Pino and coworkers [42,89,90] used UA-CPE or MA-CPE in the extraction of PAHs from marine sediments prior to liquid chromatographic analysis with UV or fluorimetric detection. To check feasibility of these analytical methods certified marine sediment has been used to validate both UA-CPE and MA-CPE [89]. Both sample pretreatment methods are credible for extraction/preconcentration of PAHs with more than three rings from solid samples. However, acenaphthene, fluorene, and phenanthrene are not included because their recoveries from UAE or MAE with micellar medium are very poor and have large relative standard deviations (RSDs) [64,90]. Possible attributes to the low recoveries of the more volatile PAHs and degradation of PAHs are excessive heating or the loss of these hydrocarbons during UAE or MAE [89]. Even so, the use of UA- or MA-CPE for PAHs has been reported by other authors [65,68].

The SA-CPE can probably be applied to separate PAHs from polluted water at a large scale. A pilot-scale UA-CPE of anthracene, phenanthrene and pyrene with Tergitol TMN-6 as the extractant in a purposely made 500 mL extraction column was proposed by Yao and Yang [69]. The treatment process operated continuously with pumps. The steady-state time of the continuous system was within 5 h. An excellent extractability was obtained in a 10 mg/L PAHs solution. Higher K_d of PAHs were achieved in a larger extraction column or lower total flow rate. Comparing with the batch operation of their previous work, the continuous process offered comparably higher performance. In essence, this process is feasible for the treatment of common PAHs in polluted water.

Besides PAHs, the determination of other POPs such as PCBs, PCDDs, PCDFs, and OCPs has also been investigated by HPLC coupling to CPE. Rodríguez and his coworkers have applied CPE to analyze POPs. They used several non-ionic surfactants in the extraction/preconcentration of PCDDs [62], PCBs [78] and PCDFs [79] from seawater samples prior to HPLC analysis with UV or fluorescence detection. The recoveries are more than 70%. The LODs are 1.89–16.3 ng/mL for PCBs, 0.05–12.8 ng/mL for PCDDs, and 0.7–27.5 ng/mL for PCDFs. In addition, they also used MA-CPE with two surfactants (POLE and Genapol X-080) to determine PCBs [66,80] and PCDFs [66] in marine sediments. The results show good recoveries with different analytes and are comparable to those obtained by Soxhlet extraction. The extraction/preconcentration of PCDDs from human serum has also been reported using non-ionic surfactant Triton X-100 [71]. OCPs such as DDT, dieldrin and aldrin have been determined in agricultural soils by using MA-CPE with two non-ionic surfactant mixtures (POLE/polyoxyethylene 10 cetyl ether and POLE/polyoxyethylene 10 stearyl ether) prior to their separation by HPLC with UV detection [91]. The recoveries largely depend on the type of surfactant mixture used and soil characteristics.

4.2. Hyphenation of CPE to gas chromatography

To date the use of CPE process as sample pretreatment technique for POPs prior to GC analysis is not so well developed due to risk of column blocking from the viscous and low volatile surfactant-rich phase. Therefore, after CPE and before GC injection, a supplemental stage is required in order to avoid clogging the injector and deterioration of the column. In general, two methods have been employed to overcome this problem. One is to extensively clean-up the surfactant by two columns [92] and the other is to back-extract the target analyte from the surfactant-rich phase as a preconcentration step prior to GC analysis [93,94]. Fig. 4 presents the experimental schemes of both the clean-up treatment and back-extraction methods.

Fröschl et al. [92] reported the use of Triton X-100 in the preconcentration of PCBs from water and extensive clean-up with two columns (silica gel and Florisi) prior to GC analysis with electron capture detector (ECD). After the preconcentration of PCBs from water, the surfactant-rich phase passes through a silica gel column and is eluted with *n*-hexane. Then a small volume of eluate is collected. The rest of Triton X-100 in the eluate is removed by a second column filled with Florisil. After the two clean-up procedures, the surfactant is eliminated completely and the final eluate is injected into GC-ECD for further analysis. The recoveries of PCBs obtained by CPE were compared with those obtained by liquid-liquid extraction. Both methods are comparable with recoveries ranging 86–116% for spiked ultra-pure and tap water samples. The micellar extraction for PCBs is superior to the liquid-liquid extraction for landfill seepage water.

Recently CPE using non-ionic and anionic surfactants (Triton X-114 and SDSA) for preconcentration of six PAHs from aqueous and soil samples prior to GC has been proposed by Sikalos and Paleologos [93]. The PAHs are back-extracted from the surfactant-rich phase into isooctane by microwave or sonication and are directly analyzed by GC-flame ionization detection without supplemental clean-up procedure. The recoveries of spiked water and soil samples range between 92 and 105%. The analysis of certified reference materials is in good agreement with the certified values. The LODs for the PAHs are 0.9–9.9 μg/L.

The extraction/preconcentration of PBDEs from water and soil samples by CPE coupled with UA back-extraction prior to GC-MS analysis has been developed by Fontana et al. [94]. It is based on the induction of micellar organized medium by a non-ionic surfactant (Triton X-114) to extract the target PBDEs. After extracting PBDEs from the water and soil samples into the surfactant-rich phase, the PBDEs are UA back-extracted into isooctane. The resulting isooctane phase is analyzed by GC-MS without clean-up. The LODs range from 1 to 2 pg/mL with RSDs $\leq$ 8.5% (n = 5). The analytical performance of this method for PBDEs in water samples is superior to previous analytical techniques such as solid-phase microextraction and GC-tandem MS, solid-phase microextraction and GC-ECD, dispersive liquid-liquid microextraction and HPLC with variable wavelength detection.

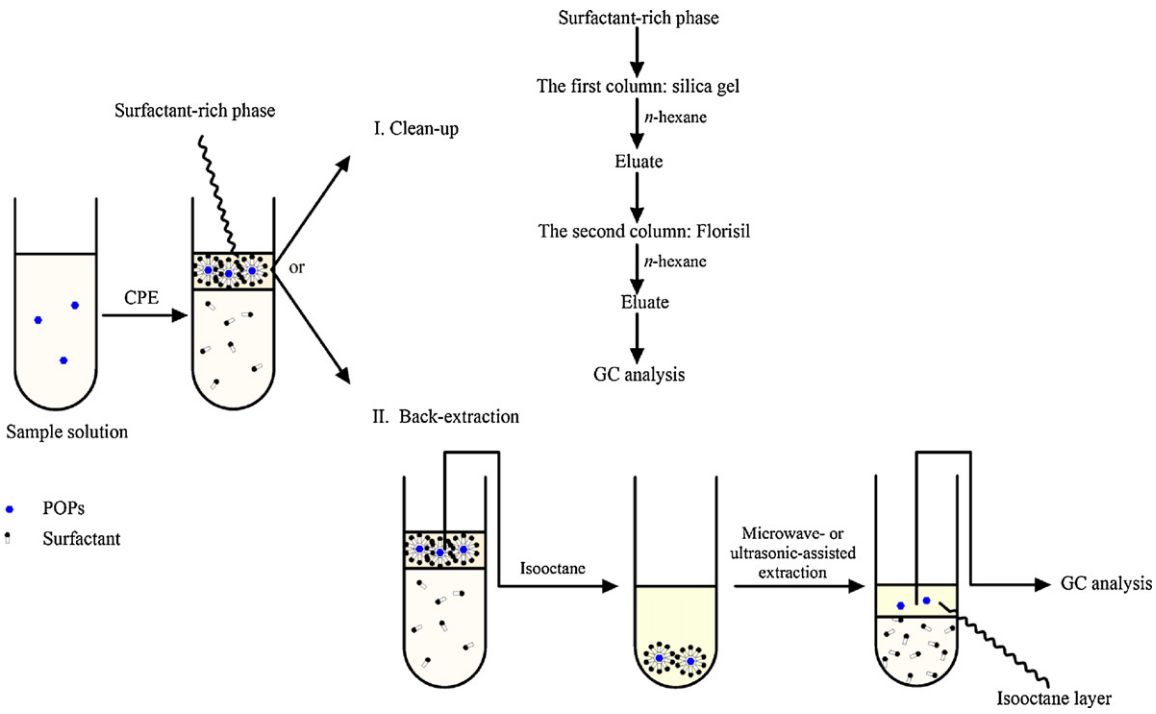

Fig. 4. Experimental schemes for preconcentration persistent organic pollutants (POPs) prior to gas chromatography.

Lately, a new CPE with Triton X-114 surfactant derivatization as an enrichment step for preconcentration of six PAHs prior to GC-MS analysis has been proposed by Takagai and Hinze [95]. The post-extraction derivatization step is employed where Triton X-114 in the surfactant-rich phase is reacted with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide prior to injection into GC. Such a derivatization step can improve the chromatographic performance yielding a fairly wide elution time window that is free of derivatized surfactant signals, reproducible analyte retention times and more quantitative results. Good agreement is observed in the mean retention times for each of the six PAHs. The RSDs for the CPE samples are slightly better than the standard PAHs solutions.

4.3. Hyphenation of CPE to capillary electrophoresis

The use of CPE as sample pretreatment techniques for POPs prior to capillary electrophoresis (CE) analysis has not been extensively investigated. The main problem of applying CPE to CE is that the surfactant-rich phase introduced into a bare fused-silica capillary using aqueous buffers would be adsorbed onto the wall of the

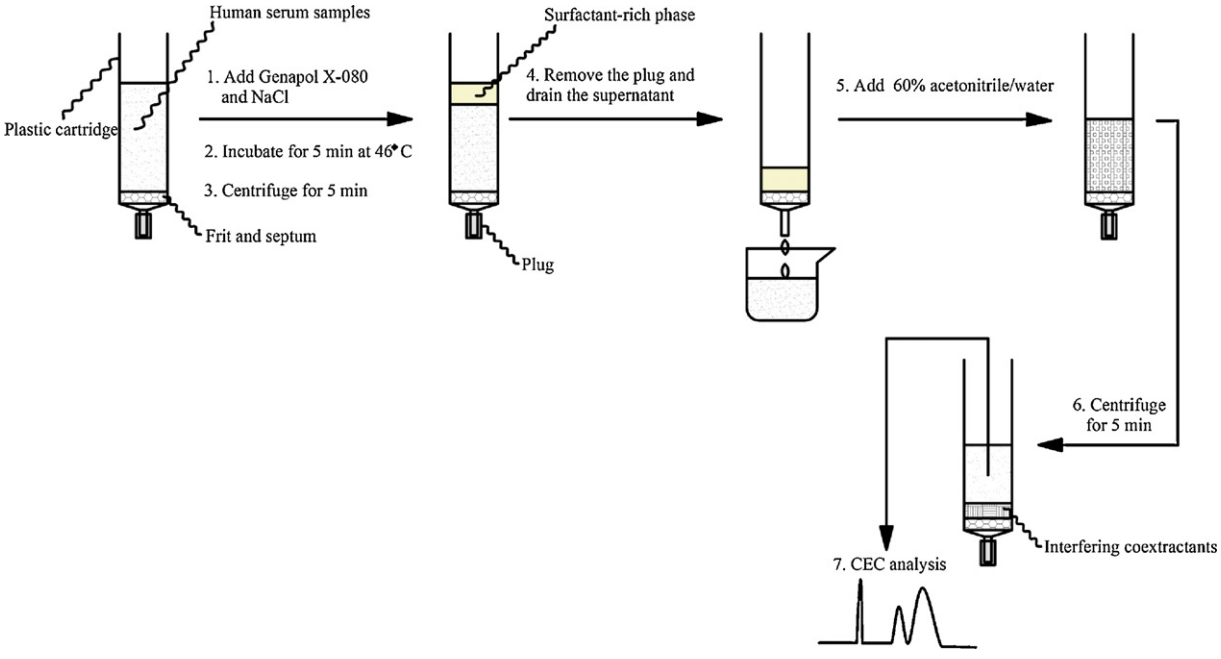

Fig. 5. Cloud point extraction for preconcentration of persistent organic pollutants in human serum prior to capillary electrochromatography.

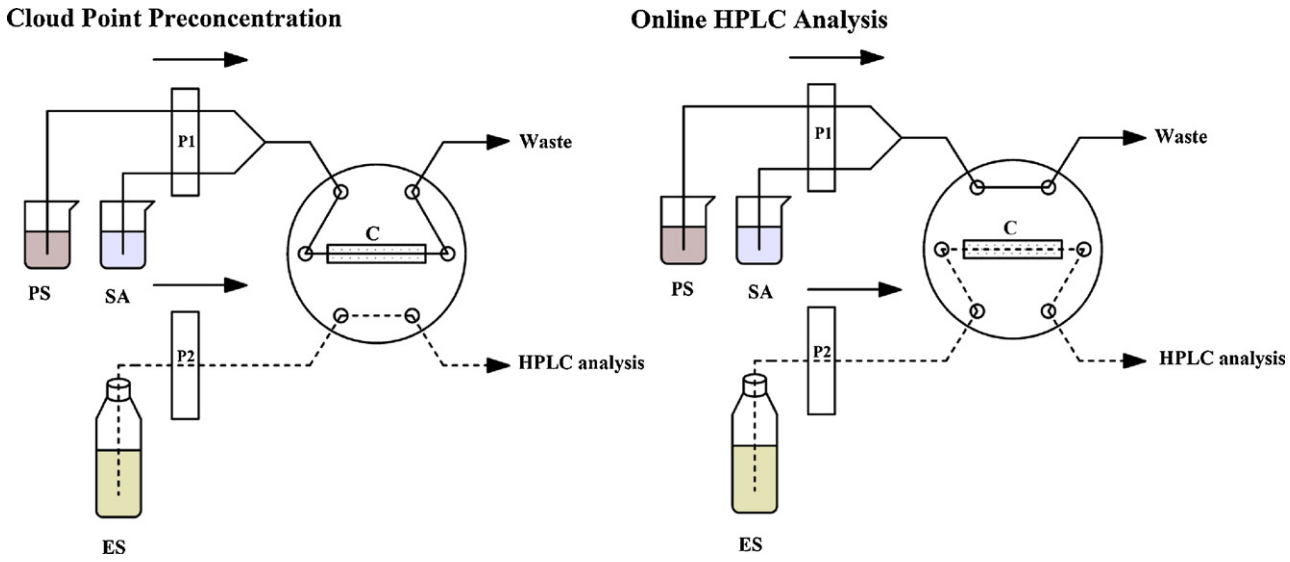

Fig. 6. Schematic diagram of the online flow injection-cloud point preconcentration-HPLC system. P1 and P2, peristaltic pumps; PS, PAHs sample solution; SA, salting-out agent; ES, eluting solvent (organic solvent and/or water); and C, preconcentration column.

capillary, leading to a marked loss of efficiency and reproducibility both in migration times and solute peak areas. To solve this problem, Carabias-Martínez et al. [96] used non-aqueous media in the separation buffer that can permit the electrophoretic separation of samples with high-surfactant contents, thus avoiding the adsorption of surfactant onto the wall of the capillary. But the life-time of the capillary was shortened.

Sirimanne et al. [97] reported a method for the determination of 16 PAHs and 8 PCDDs in spiked human serum based on CPE and capillary electrochromatography (CEC) as depicted in Fig. 5. Human serum samples spiked with PAHs or PCDDs are extracted using non-ionic surfactant Genapol X-080. Subsequently, the surfactant-rich phase is treated with acetonitrile to remove unwanted interfering co-extractants such as proteins to prevent capillary clogging. 16 PAHs or 8 PCDDs are well separated but both migration times are shifted slightly. This phenomenon may be attributed to the dynamic coating of the C_{18} stationary phase by the residual surfactant or co-extractants in the sample. But their results still prove to be feasible for analyses of PAHs and PCDDs using CPE-CEC.

4.4. Hyphenation of CPE to online flow injection analysis

The online incorporation of CPE to flow injection analysis (FIA) is proposed for the first time by Fang et al. [98]. Later, the use of CPE coupled with online FI with chemiluminescence analysis of benzo[*a*]pyrene in aqueous solution using Triton X-114 was reported by Song et al. [99]. The analytical capability of online FI-CPE, especially in terms of C_F, extraction efficiency, and analysis time, are considerably improved as compared to the traditional CPE method. The online incorporation of CPE with FIA and coupled with HPLC for the determination of five selected PAHs in soil samples has recently been developed [67]. The UA- and MA-CPE/preconcentration of PAHs from soil samples were accomplished using a non-ionic surfactant Tergitol 15-S-7. The FI-CPE-HPLC system as shown in Fig. 6 provides higher calibration sensitivity and lower LODs for PAHs than that of common HPLC methods.

4.5. Hyphenation of CPE to fluorescence analysis

The application of micellar extraction/preconcentration of PAHs (fluoranthene, benzo(*k*)fluoranthene, and benzo[*a*]pyrene) from aqueous solution and detection by synchronous fluorescence was developed by Böckelen and Niessner [100]. To avoid interference from self-fluorescence of surfactant, only surfactants possessing no aromatic ring, Genapol X-80 and 1:1 Genapol X-80/Brij 76 mixture, are applicable in the direct fluorimetric analysis of these PAHs. The recoveries are 79–104% with preconcentration of Genapol X-80 and 63–106% with preconcentration of 1:1 Genapol X-80/Brij 76 mixture. The LODs are in the range 5.3–190 ng/L and 2.6–93 ng/L with preconcentration of Genapol X-80 and 1:1 Genapol X-80/Brij 76 mixture, respectively. In addition, the desorption capability for soil particle-bound PAHs increases with increasing concentration of Genapol X-80 from 0.01 to 0.8% and lowering the soil/water ratio to 1:40.

Goryacheva et al. [101] successfully used the acid-induced CPE technique based on SDS micelles for preconcentration of 10 PAHs with subsequent fluorescence determination. Under optimal conditions, PAHs having high fluorescence intensities possess LODs from 0.6 μM chrysene to 1.0 pM pyrene. The proposed method was applied to tap water samples spiked with benzo[*a*]pyrene at 0.17–167 ng/mL and the recoveries are 98–125%. This method gives a rapid assay with a wider linear range than the traditional HPLC using fluorescence detection.

5. Conclusion

In the present review, some recent researches in CPE on the determination of POPs are covered. Currently most analytical applications of CPE for the extraction/preconcentration of POPs make use of RP-HPLC analysis. By contrast, the direct coupling of CPE as sample pretreatment of POPs with other instrumental methods such as GC, FI, and CE is still under development. So far only PAHs are relatively well studied while other POPs seem to be neglected. We anticipate that the online coupling of CPE with modern analytical instrument for the extraction-preconcentration-analysis of other POPs including PCBs, PCDDs, PCDFs, PBDEs, and OCPs should attract considerable interest as the whole analytical system becomes more automatic, has higher sample throughput, and achieves better sensitivity and lower LODs.

Finally, most of the past and current work seems to focus mainly on the extraction of POPs from soil and water samples. As it is possible to apply CPE to extract POPs from food and biological samples, we anticipate that more emphasis can be placed on these areas in

the forthcoming future. It is also our wish that the description of various extraction techniques for POPs, principle of CPE, coupling of CPE with various instrumentations, and the key references cited in this review will arouse the environmental community to develop and adopt online coupling methods of CPE to GC, HPLC or CE for ultra-trace determination of POPs in our environment.

Acknowledgement

MCP acknowledges the receipt of a postgraduate studentship from the Additional UGC-funded Research Postgraduate Places in the area of Environmental and Human Health Risk Assessment of Persistent Toxic Substances.

References

[1] Stockholm Convention on Persistent Organic Pollutants, http://chm.pops.int/Portals/0/Repository/convention_text/UNEP-POPS-COP-CONVTEXT-FULL.English.PDF.
[2] Protocol to the 1979 Convention on Long-range Transboundary Air Pollution on Persistent Organic Pollutants, http://www.unece.org/env/lrtap/full%20text/1998.POPs.e.pdf.
[3] Stockholm Convention on Persistent Organic Pollutants, Stockholm, 22 May 2001 Adoption of Amendments to Annexes A, B and C, Reference no.: C.N.524.2009. TREATIES-4. http://chm.pops.int.
[4] H. Fiedler, The Handbook of Environmental Chemistry, vol. 3, Part O. Persistent Organic Pollutants, Springer, Berlin, 2003.
[5] E. Mehmetli, B. Koumanova, The Fate of Persistent Organic Pollutants in the Environment, NATO Science of Peace and Security Series-C: Environmental Security, Springer, Netherlands, 2007.
[6] M.F. Silva, E.S. Cerutti, L.D. Martinez, Microchim. Acta 155 (2006) 349.
[7] R. Carabias-Martínez, E. Rodríguez-Gonzalo, B. Moreno-Cordero, J.L. Pérez-Pavón, C. García-Pinto, E.F. Laespada, J. Chromatogr. A 902 (2000) 251.
[8] H. Tani, T. Kamidate, H. Watanabe, J. Chromatogr. A 780 (1997) 229.
[9] C.D. Stalikas, Trends Anal. Chem. 21 (2002) 343.
[10] Z.S. Ferrera, C.P. Sanz, C.M. Santana, J.J.S. Rodríguez, Trends Anal. Chem. 23 (2004) 469.
[11] K. Madej, Trends Anal. Chem. 28 (2009) 436.
[12] F. Sun, D. Littlejohn, M.D. Gibson, Anal. Chim. Acta 364 (1998) 1.
[13] T. Pena, L. Pensado, C. Casais, C. Mejuto, R. Phan-Tan-Luu, R. Cela, J. Chromatogr. A 1121 (2006) 163.
[14] J.J. Ramos, C. Dietz, M.J. González, L. Ramos, J. Chromatogr. A 1152 (2007) 254.
[15] T. Nilsson, J. Häkkinen, P. Larsson, E. Björklund, Environ. Pollut. 140 (2006) 87.
[16] A.E. McGowin, K.K. Adom, A.K. Obubuafo, Chemosphere 45 (2001) 857.
[17] N. Saim, J.R. Dean, Md.P. Abullah, Z. Zakaria, J. Chromatogr. A 791 (1997) 361.
[18] S.B. Hawthorne, C.B. Grabanski, E. Martin, D.J. Miller, J. Chromatogr. A 892 (2000) 421.
[19] Y.F. Song, X. Jing, S. Fleischmann, B.-M. Wilke, Chemosphere 48 (2002) 993.
[20] P. Sun, L.K. Weavers, P. Taerakul, H.W. Walker, Chemosphere 62 (2006) 265.
[21] W. Wang, B. Meng, X. Lu, Y. Liu, S. Tao, Anal. Chim. Acta 602 (2007) 211.
[22] N. Itoh, M. Numata, Y. Aoyagi, T. Yarita, Anal. Chim. Acta 612 (2008) 44.
[23] N. Barco-Bonilla, J.L.M. Vidal, A.G. Frenich, R. Romero-González, Talanta 78 (2009) 156.
[24] H. Watanabe, H. Tanaka, Talanta 25 (1978) 585.
[25] C. Bordier, J. Biol. Chem. 256 (1981) 1604.
[26] W.L. Hinze, E. Pramauro, Crit. Rev. Anal. Chem. 24 (1993) 133.
[27] M.J. Rosen, Surfactants and Interfacial Phenomena, 2nd ed., John Wiley & Sons, New York, 1989.
[28] B. Lindman, H. Wennerström, J. Phys. Chem. 95 (1991) 6053.
[29] D. Blankschtein, G.M. Thurston, G.B. Benedek, J. Chem. Phys. 85 (1986) 7268.
[30] C.-L. Liu, Y.J. Nikas, D. Blankschtein, Biotechnol. Bioeng. 52 (1996) 185.
[31] R. Kjellander, E. Florin, J. Chem. Soc., Faraday Trans. 177 (1981) 2053.
[32] P.M. Claesson, R. Kjellander, P. Stenius, H.K. Christenson, J. Chem. Soc., Faraday Trans. 182 (1986) 2735.
[33] V. Degiorgio, R. Piazza, M. Corti, C. Minero, J. Chem. Phys. 82 (1985) 1025.
[34] F.H. Quina, W.L. Hinze, Ind. Eng. Chem. Res. 38 (1999) 4150.
[35] E. Pramauro, A.B. Prevot, Pure Appl. Chem. 67 (1995) 551.
[36] B.K.-W. Man, M.H.-W. Lam, P.K.S. Lam, R.S.S. Wu, G. Shaw, Environ. Sci. Technol. 36 (2002) 3985.
[37] J.-L. Li, B.-H. Chen, J. Colloid Interface Sci. 263 (2003) 625.
[38] B. Yao, L. Yang, J. Colloid Interface Sci. 319 (2008) 316.
[39] F. Shemirani, M.R. Jamali, R.R. Kozani, M.S. Niasari, J. Anal. Chem. 61 (2006) 124.
[40] B. Yao, L. Yang, Q. Hu, S. Akita, Chin. J. Chem. Eng. 15 (2007) 468.
[41] B. Yao, L. Yang, Ind. Eng. Chem. Res. 47 (2008) 3949.
[42] V. Pino, J.H. Ayala, A.M. Afonso, V. González, Fresen. J. Anal. Chem. 371 (2001) 526.
[43] S. Akita, H. Takeuchi, Sep. Sci. Technol. 30 (1995) 833.
[44] M. de, A. Bezerra, M.A.Z. Arruda, S.L.C. Ferreira, Appl. Spectrosc. Rev. 40 (2005) 269.
[45] V. Pino, J.H. Ayala, A.M. Afonso, V. González, J. Chromatogr. A 949 (2002) 291.
[46] L. Wang, Y.-Q. Cai, B. He, C.-G. Yuan, D.-Z. Shen, J. Shao, G.-B. Jiang, Talanta 70 (2006) 47.
[47] L. Wang, G.-B. Jiang, Y.-Q. Cai, B. He, Y.-W. Wang, D.-Z. Shen, J. Environ. Sci. 19 (2007) 874.
[48] J. Zhou, S.W. Wang, X.L. Sun, Anal. Chim. Acta 608 (2008) 158.
[49] W. Liu, W.-J. Zhao, J.-B. Chen, M.-M. Yang, Anal. Chim. Acta 605 (2007) 41.
[50] A. Santalad, S. Srijaranai, R. Burakham, J.D. Glennon, R.L. Deming, Anal. Bioanal. Chem. 394 (2009) 1307.
[51] Q. Fang, H.W. Yeung, H.W. Leung, C.W. Huie, J. Chromatogr. A 904 (2000) 47.
[52] Z. Shi, J. He, W. Chang, Talanta 64 (2004) 401.
[53] C. Sun, Y. Xie, Q. Tian, H. Liu, Phytochem. Anal. 19 (2008) 160.
[54] H.-Z. Zhu, W. Liu, J.-W. Mao, M.-M. Yang, Anal. Chim. Acta 614 (2008) 58.
[55] G. Jia, C. Lv, W. Zhu, J. Qiu, X. Wang, Z. Zhou, J. Hazard. Mater. 159 (2008) 300.
[56] R.P. Frankewich, W.L. Hinze, Anal. Chem. 66 (1994) 944.
[57] T. Saitoh, W.L. Hinze, Anal. Chem. 63 (1991) 2520.
[58] I. Casero, D. Sicilia, S. Rubio, D. Pérez-Bendito, Anal. Chem. 71 (1999) 4519.
[59] F. Merino, S. Rubio, D. Pérez-Bendito, J. Chromatogr. A 962 (2002) 1.
[60] X. Liu, X.-H. Chen, Y.-Y. Zhang, W.-T. Liu, K.-S. Bi, J. Chromatogr. B 856 (2007) 273.
[61] M.F. Silva, L. Fernandez, R.A. Olsina, D. Stacchiola, Anal. Chim. Acta 342 (1997) 229.
[62] C.P. Sanz, Z.S. Ferrera, J.J.S. Rodríguez, Anal. Chim. Acta 470 (2002) 205.
[63] E.K. Paleologos, D.L. Giokas, M.I. Karayannis, Trends Anal. Chem. 24 (2005) 426.
[64] V. Pino, J.H. Ayala, A.M. Afonso, V. González, J. Chromatogr. A 869 (2000) 515.
[65] A.B. Prevot, M. Gulmini, V. Zelano, E. Pramauro, Anal. Chem. 73 (2001) 3790.
[66] A.E. Fernández, Z.S. Ferrera, J.J.S. Rodríguez, Chromatographia 53 (2001) 375.
[67] C.F. Li, J.W.C. Wong, C.W. Huie, M.M.F. Choi, J. Chromatogr. A 1214 (2008) 11.
[68] B. Yao, L. Yang, Sep. Sci. Technol. 42 (2007) 1843.
[69] B. Yao, L. Yang, Sep. Sci. Technol. 43 (2008) 1564.
[70] C.G. Pinto, J.L.P. Pavón, B.M. Cordero, Anal. Chem. 66 (1994) 874.
[71] S.R. Sirimanne, J.R. Barr, D.G. Patterson Jr., L. Ma, Anal. Chem. 68 (1996) 1556.
[72] C.P. Sanz, A.E. Fernández, Z.S. Ferrera, J.J.S. Rodríguez, J. AOAC Int. 85 (2002) 44.
[73] R. Ferrer, J.L. Beltrán, J. Guiteras, Anal. Chim. Acta 330 (1996) 199.
[74] S. Pongpiachan, Southeast Asian J. Trop. Med. Public Health 40 (2009) 392.
[75] E. Evdokimov, R. von Wandruszka, Anal. Lett. 31 (1998) 2289.
[76] K.-C. Hung, B.-H. Chen, AIChE J. 53 (2007) 1450.
[77] A.E. Fernández, Z.S. Ferrera, J.J.S. Rodríguez, Quím. Anal. 16 (1997) S283.
[78] A.E. Fernández, Z.S. Ferrera, J.J.S. Rodríguez, Anal. Chim. Acta 358 (1998) 145.
[79] A.E. Fernández, Z.S. Ferrera, J.J.S. Rodríguez, Analyst 124 (1999) 487.
[80] A.E. Fernández, Z.S. Ferrera, J.J.S. Rodríguez, Anal. Chim. Acta 433 (2001) 237.
[81] C.P. Sanz, Z.S. Ferrera, J.J.S. Rodríguez, Anal. Lett. 37 (2004) 1385.
[82] D. Bai, J. Li, S.B. Chen, B.-H. Chen, Environ. Sci. Technol. 35 (2001) 3936.
[83] J.-L. Li, R. Bai, B.-H. Chen, Langmuir 20 (2004) 6068.
[84] K.-C. Hung, B.-H. Chen, L.E. Yu, Sep. Purif. Technol. 57 (2007) 1.
[85] D. Sicilia, S. Rubio, D. Pérez-Bendito, N. Maniasso, E.A.G. Zagatto, Anal. Chim. Acta 392 (1999) 29.
[86] B. Delgado, V. Pino, J.H. Ayala, V. González, A.M. Afonso, Anal. Chim. Acta 518 (2004) 165.
[87] C.G. Pinto, J.L.P. Pavón, B.M. Cordero, Anal. Chem. 64 (1992) 2334.
[88] A.L. García, E.B. González, J.I.G. Alonso, A. Sanz-Medel, Anal. Chim. Acta 264 (1992) 241.
[89] V. Pino, J.H. Ayala, A.M. Afonso, V. González, Int. J. Environ. Anal. Chem. 81 (2001) 281.
[90] V. Pino, J.H. Ayala, A.M. Afonso, V. González, Talanta 54 (2001) 15.
[91] D.V. Moreno, Z.S. Ferrera, J.J.S. Rodríguez, J. Chromatogr. A 1104 (2006) 11.
[92] B. Fröschl, G. Stangl, R. Niessner, Fresen. J. Anal. Chem. 357 (1997) 743.
[93] T.I. Sikalos, E.K. Paleologos, Anal. Chem. 77 (2005) 2544.
[94] A.R. Fontana, M.F. Silva, L.D. Martínez, R.G. Wuilloud, J.C. Altamirano, J. Chromatogr. A 1216 (2009) 4339.
[95] Y. Takagai, W.L. Hinze, Anal. Chem. 81 (2009) 7113.
[96] R. Carabias-Martínez, E. Rodríguez-Gonzalo, J. Domínguez-Alvarez, J. Hernández-Méndez, Anal. Chem. 71 (1999) 2468.
[97] S.R. Sirimanne, J.R. Barr, D.G. Patterson Jr., J. Microcol. Sep. 11 (1999) 109.
[98] Q. Fang, M. Du, C.W. Huie, Anal. Chem. 73 (2001) 3502.
[99] G.Q. Song, C. Lu, K. Hayakawa, J.-M. Lin, Anal. Bioanal. Chem. 384 (2006) 1007.
[100] A. Böckelen, R. Niessner, Fresen. J. Anal. Chem. 346 (1993) 435.
[101] I.Y. Goryacheva, S.N. Shtykov, A.S. Loginov, I.V. Panteleeva, Anal. Bioanal. Chem. 382 (2005) 1413.