THE APPLICATION OF CLOUD POINT EXTRACTION IN ENVIRONMENTAL ANALYSIS

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Abstract: The extraction method is cloud point extraction technique by phase separation which gives a convenient, a simple procedure, with minimal solvent usage and only needs a very discrete amount of relatively non-flammable and non-volatile surfactant which is ecofriendly. It has acknowledged usage for the extraction and preconcentration of species of extensively digress character and features likewise metal ions, proteins and other biomaterials, or organic compounds of strongly differing polarity. Here, we address the review about cloud point extraction (CPE) method as well as applications with this methodology to our environmental samples. We also discussed about the advantages, disadvantages and future trends of CPE. This technique received great attention in extraction and preconcentration by application as an isolation and trace enrichment procedure earlier to the analysis of organic compounds (polycyclic aromatic hydrocarbons, polychlorinated compounds, pesticides, phenolic derivatives, aromatic amines, vitamins and polybrominated biphenyl ethers), inorganic compounds and metal (copper, chromium, zinc, cadmium, nickel, cobalt), phthalates and parabens. These techniques are coupled with gas chromatography, liquid chromatography, capillary electrophoresis and spectrophotometry.

Keywords: Cloud point extraction (CPE), organic and inorganic pollutants, metal, phthalate, paraben, surfactant.

Introduction

Watanabe and Tanaka established the cloud-point extraction (CPE) technique in intention to preconcentrate metal ions from aqueous samples (Watanabe et al., 1978). It is well know that CPE used surfactant has the potential to intensify solubility of hydrophobic materials, extraction technology which is environment complaisant to many researchers and luring many analytical chemists as to other extraction system. CPE has received a great attention because the procedure are simple, fast and the extraction of the analytes can be handy by optimizing the experimental conditions likewise salt addition, pH value, temperature, type of electrolyte, time of extraction and surfactant concentration (Noorashikin Md Saleh et al., 2014; Zain et al., 2014).

The surfactant goes through a phase separation into surfactant-rich phase and surfactant aqueous phase, at greater temperature compared to its critical temperature is called cloud point temperature. Thus, analyses are concentrated alongside with high preconcentration factor (Liang et al., 2009; Santalad et al., 2009; Zhou et al., 2008). CPE is known as a fruitful extraction method uses minimal solvent and only needs diminutive amount of relatively non-flammable and non-volatile and ecofriendly surfactant. Based on our previous report in CPE, this technique CPE can produce high extraction efficiency, high preconcentration factor with a simple method of extraction and sample matrices riddance all in one step (Hunzicker et al., 2015; Noorashikin et al., 2014; Noorashikin et al., 2013).

In spite of few reviews on CPE for analysis of organic compounds, metal ions, drugs, persistent organic pollutants as well as bioactive compounds have materialized in literatures (Silva et al., 2006), there is no review on application of CPE in environmental samples. In recent study using water sample, combination of CPE with second-order scattering (SOS) detection succeeded for analysis of gold nanoparticles in environmental waters that proved the effectively of CPE to extract and pre-concentrate the analyte (Mandyla et al., 2016).

Principles of Cloud Point Extraction

It is prominent such surfactants are an amphiphilic molecule that contains a polar head group and a non-polar tail. Normally, the tail is a linear or branched hydrocarbon chain with diverse figure of carbon atoms which may consist aromatic rings, while the head is ionic or tenacious polar groups. These two moieties are hydrophilic and hydrophobic in an aqueous solution respectively. The hydrophobic tails gravitate to creates aggregates called micelles. Non-ionic surfactants build two phases beyond the cloud point temperature namely surfactant-rich phase (coacervate) and a dilute phase in an aqueous solution, when the concentration of the surfactant is proximate to its critical micelle concentration (CMC) (Silva et al., 2006). The solution becomes turbid at a temperature identified as cloud point (CP) due to deplete solubility of the surfactant in water when applicable modification on conditions such as temperature, addition of salt or additives carried out (Xie et al., 2010).

Zuhair et al. (2014) stated that CPE is a mature and densely exploited technique with a very little perspective for substantial findings or for significantly new application. Based on our literature, although CPE has been explored for 34 years with more than 500 publications but these techniques are still popular, interesting to study and received improvement and modification on the method from the researchers to ensure that CPE is a useful to their research. Since 1999, CPE has been received great attention and huge

perspective to extraction of various analyses for example PAHs (Alibrahim, 2014; El-Shahawi et al., 2015), other organic compounds (Alias Saravanan et al., 2014; Haddou et al., 2006) and in the systems having minimal concentrations of metal ions (Citak et al., 2010; Şahin et al., 2010; Wang et al., 2010).

Parameters Used in Cloud Point Extraction

Type of Surfactants

Non-ionic, zwitterionic, cationic and anionic are the classes of surfactants. Nowadays, non-ionic surfactants are extensively used for CPE in inorganic metal ions, biomaterials and drugs as well as organic compounds. Phase separation is effortlessly acquired through modification of the solution properties such as temperature or additives. Moreover, an ubiquitous idea of hydrophobic interaction of non-ionic micelles is used for all these CPE procedures to workout (Meeravali et al., 2009).

However, there are inadequate application of cationic surfactant in CPE method (Guerrieri et al., 2010). Choosing an appropriate surfactant is very crucial for a victorious CPE analysis since it can directly affect the extraction and preconcentration as well as the accuracy of the final analytical results. Finite tenor to micellization and respective phase separation using analogous schemes were shown by cationic surfactants, therefore, it is been bombed-out in usage for cloud point extraction operations.

Large hydrophobic counterion (tosylate or salicylate) needed as sheer rationale (Guerrieri et al., 2010), anionic surfactant (Seebunrueng et al., 2011), a co-surfactant (Pourreza et al., 2007) in extremely large amount of common salts to induce micellar growth (Guerrieri et al., 2010). However, cationic surfactants with promising micellization properties are restricted and unavailable commercially (Guerrieri et al., 2010). Cetylpyridinium bromide (HPyBr) and cetyltrimethylammonium bromide (CTAB) are adequately used cationic surfactants together with more than 2 or 3 M of salt was added for phase separation occur. Immediate analytical

applications are deficient for this rationale (Amin et al., 2015).

CPE technique has been widen to utilize zwitterionic and anionic surfactant. In many outcomes, zwitterionic or anionic/cationic surfactant was habituated as cloud point extractant to overwhelm the strong UV/visible absorbing interference of non-ionic surfactants. Hence, petite attention has been shown to the potent benefaction of the charged head groups of these surfactants to analyse extraction (Guerrieri et al., 2010).

Time and Temperature

The optimum incubation time and equilibrium temperature are necessary, to achieve an easy and efficient phase separation also with preconcentration. The buildup of surfactant-rich phase are solely subjected by demeanor of the employed surfactant. Shah et al., (2010) reported that the brief heating time are supposed to avoid the loss of mercury in vapors because of its inherent volatility (Shah et al., 2010). In their study, the equilibrium temperature obtained was 35 ˚C and equilibrium time of 5 minutes in ultrasonic water bath was adequate to achieve quantitative extraction. Similar study conducted by Ezoddin et al., (2010) observed that 10 minutes and temperature of 25 ˚C is enough to obtain quantitative extraction of analyse. Longer extraction time shows no appreciated improvement of the separation. In certain cases show inconsistency of extraction

with interruption of salt in surfactant- rich phase. Meanwhile, lower extraction time than 5 minutes are not encouraged as phase separation said to be incomplete and just started to take place. Hence, for this method, the optimum extraction time would be in range of 5 minutes to 10 minutes. Temperature exceeding 40 ℃ causes evaporation of the solution, and results in lose in desired analytes. Lower temperature (below room temperature) causes the separation to be very less, as the analytes would be immobile at low temperature. Surfactant could not perform well at this moment.

Salt

Table 1 shown summarizes some of the parameters used in CPE systems. The CPE techniques have been flourishing feat for preconcentration or extraction of many compounds as a sample pretreatment step right before their diagnosis by various instruments using a diverse nonionic surfactants like Triton X, PONPE, Cetrimide, and PEG/PPG. Development of cloud point in ionic surfactants is generally invoked by increasing ionic strength of the aqueous media, such as "salting-out". Mirzaei et al. (2011) have approach the use of sodium chloride to acquire clouding of cetrimide but could not able to bring a clear phase separation unless a co-surfactant, 1-octanol was introduced into. Cloud point phase separation for aliquat-336 is willingly accomplished with addition of sodium sulphate (Mirzaei et al., 2011). With presence of sulphate, phase separation of non-ionic surfactants

Table 1: Parameters optimized in CPE systems

Type of Surfactant	Temperature	Salts	pH	Surfactant system	Ref.
Triton X-114	40˚C -80˚C	NaOH or HCl	pH 4	0.3% (v/v) Triton X114	(Khan et al., 2010)
Triton X-114	40˚C	none	pH 5.5	1.25% (v/v) Triton X-114	(Wang, L.-L. et al., 2010)
PEG600MO	45˚C	Na_2SO_4	none	2 wt% PEG600MO	(Tang et al., 2010)
C13E10	70˚C	NaCl	none	1wt% of $C_{13}E_{10}$	(Didi et al., 2011)
PONPE 5.0	70˚C	NaCl	pH 5.8	50% (v/v) of PONPE 5.0	(Santarossa et al., 2016)

increases in a aqueous solution (Kulichenko et al., 2010).

Salt plays major role in the separation with combination of surfactant as it accelerates the separation. However, too much amount or concentration of salt decreases the efficiencies of surfactant and directly reduces the recovery, as higher salt concentration makes the surfactant more soluble in the sample solution, which subsequently decreases the effectiveness (Dong et al., 2014). In most of the experiments carried out, the concentration of salt should not be too less (less than 1.0 M) of too high (more than 2.0 M). Lower salt concentration do not help the surfactant to completely carry out the separation, while higher concentration of certain salts such as sodium sulphate forms precipitate which interrupts the separation as well as the extraction.

Usage of salt also induces the drop of temperature of the CPE system. The temperature drops to 25 $^{\circ}$C with the introduction of 1.5 M salt into CPE system, which results better separation and also the less need of instruments such as sonicator to increase the temperature. A salt that are commonly used for CPE and phase separation is sodium sulphate, tri-potassium phosphate, potassium hydroxide sodium hydroxide. Of these salts, often observation is that salts with higher ionic number forms better separation. For example, SO_4^{2-} ions gives better separation as it has stronger interaction with water compared to water-water interaction. On the other hand, 'salting out' effect Na^+ is significantly high compare to other studied cation, which also possesses large Gibbs' free energy of hydration (Noorashikin, Md. Saleh. et al., 2014).

pH

The pH has function on metal-chelate development and extraction, also proven to be an important parameter in CPE method (Liang et al., 2010). So pH was a first parameter optimized in extraction procedure before proceed to other parameters. Yilmaz et al. (2015) selected a pH 5 for their study on metal ion which corresponds with the literature resulting in R.S.D. values

ranging from 1.7% to 2.9% (Yılmaz et al., 2015). The extraction of phenols showed that pH value should be as low as it can in first CPE for phenol extractions in theory due to protonated phenols which is hydrophobic hence may be extracted into surfactant-rich phase. pH 5 chosen as the optimal pH value (Yin et al., 2010).

Lower pH value (lower than pH 5), where the solution in acidic form, results in declining trend of extraction recovery. In acidic form solution, the analytes possesses ionic characteristics in hydrophobic micelles, which results in small amount of recovery of analyte. At higher pH value (more than pH 8), the analytes seems to be deprotonated due to the basic condition of the solution. Hence, separation do not occur at optimum level and the concentration of analytes in surfactant rich phase decreases (Noorashikin et al., 2013).

Surfactant Concentration

Surfactant concentration plays an important role in phase separation as lower concentration makes the separation to be incomplete while higher concentration than the desired amount enhances the surfactant- rich phase's viscosity which concurrently decreases its volume. Increasing the concentration of the surfactant also increases number of surfactant-aggregate complexes. According to Yang et al. (2017), Triton X-114's concentration used for determining Ag^+ ions using CPE is 0.35%, as it gives maximum recovery at this point, beyond 0.4%, the recovery drop significantly due to viscosity and increase of volume of the micellar phase (Yang et al., 2017).

Application of Cloud Point Extraction in Environmental Samples

Cloud Point Extraction in Persistent Organic Pollutants Analysis

Non-ionic surfactants that are commonly used like Triton X (polyoxyethylene-(n)-octylphenyl ether), PONPE (polyoxyethylene-(n)-nonylphenyl ether, Genapol X (oligoethylene glycol monoalkyl ether)

and brij (polyoxyethylene-10-akyl ether) have both hydrophobic and hydrophilic parts in its molecular structures. Extraction of polycyclic aromatic hydrocarbons (PAHs) polychlorinated biphenyls (PCBs) polychlorinated dibenzofurans (PCDFs) as well as dibenzo-p-dioxins (PCDDs) synthetic pesticides, hydroxyaromatic compounds also vitamins, hydrophobic membrane proteins and pharmaceuticals from natural waters, soils and sediments as well as complex biological fluids were done by using those surfactants (Guerrieri et al., 2010).

Table 2: Determination of Organic Pollutants using CPE

Compounds	Matrix	LOD	CPE method	Detection	Reference
Humic acid	Industrial effluent	-	Direct and back process of CPE	HPLC-UV	(Ghouas et al., 2010)
2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and 4 nitrophenol (4-NP)	Water	None	Conventional CPE	Spectrophotometry	(Zain et al., 2014)
Phenanthrene	Sand	None	Micellar solubilization-CPE	HPLC-UV	(Li, J.-L. et al., 2008)
Aurium (III)	Water	1.1 ngL^{-1}	Conventional CPE	ICP-MS (inductive coupled plasma-mass spectrometry)	(Chen et al., 2010)
Auxins	Leaves	2.5 nM	Dual CPE	CE-ECL(capillary electrophoresis-electrochemiluminesence)	(Yin et al., 2010)
Organophosphorus pesticides(Diazon)	Aqueous Samples	0.02 ng mL^{-1}	Conventional CPE	UV Sepctrophotometry	(M.R.Sohrabi et al., 2012)
Triazole fungicides	Water	6.8-34.5 ngL^{-1}	Conventional CPE	HPLC-UV	(Tang et al., 2010)
PAHs	Chinese medical herbs	0.01-0.05 ng/mL	Conventional CPE	HPLC- Fluorometric detection	(Shi et al., 2011)
Phenol	Waste water	None	Conventional CPE	UV-Vis Spectrophotometer	(Taechangam et al., 2009)
Bisphenol A and Naphtol	Water	0.67-1.67 µg l^{-1}	Preconcentration using CPE	Capillary Electrophoresis (CE)	(S.Zhong, 2011)
Hydrocarbons	Fuel spill	None	Conventional CPE	HPLC-UV, ELSD	(Ghouas et al., 2010)
polybrominated diphenyl ethers (PBDEs)	Aqueous Sample	1.71-5.82 ng/L	conventional GC	fluorescence spectroscopy	(Shan et al., 2015)
Polychlorinated dibenzofurus (PCDFs)	Sea water	0.5-27.5 ng/L	Conventional CPE	HPLC-FD	(Fernández et al., 1999)

Table 2 shown summarizes some of the applications of CPE for organic pollutants analysis using several of instrumentation. Application of ultrasound or microwaves or stirring techniques and dual CPE process were formed. Microwave or ultrasound alliances with CPE permits extraction of a diverge organic pollutant from solid samples (Xie et al., 2010). Mahugo et al. (2009) suggest the extraction of PAHs in marine sediments by micellar assisted extraction with POLE as a early procedure to analysis using HPLC-UV (Mahugo Santana et al., 2009).

Fontana et al. (2009) studied the PBDEs in samples of soil and water using GC-MS. They were extracting target analyses from the aqueous bulk into surfactant-rich phase, the analyses were back-extracted into isooctane with ultrasound-assisted. A triumphant with high recoveries without decreasing the separation capability of the capillary column were seen when the back-extracted were introduced to GC-MS.The polychlorinated dibenzo-p-dioxins (PCDDs) comprising a bunch of organochlorinated, lipophilic also bioaccumulative substances are pertinacious in the environment. Over recent decades, a great coverage on social and scientific interest highly toxic. It have been detected in vast amount of samples like soils, sediments and water (Ssebugere et al., 2014).

Tang et al. (2010) formed a simple CPE process for determination of triazole fungicides (tricyclazole, triadimefon, tebuconazole and diniconazole) in environmental waters using non-ionic surfactant, which is polyethylene glycol 600 monooleate (PEG600MO) and analysis using HPLC/UV (Tang et al., 2010). Average recovery experiments were from 82% to 92% and RSDs were from 2.8% to 7.8% with samples spiked four fungicides in river water and tap water.

Pourreza et al. (2007) reported that malachite green was successfully detected in fish farming and river water samples with application pf CPE with Triton X-100 also analysis using UV-Visible spectrophotometer

with recoveries 95% to 102% (Pourreza et al., 2007).

Cloud Point Extraction in Phthalate and Paraben Analysis

Gas chromatography or high performances liquid chromatography are the most popular chromatographic methods for analysing phthalate esters (Net et al., 2015). However, selectivity and sensitivity limit their direct usage to determine these contaminants at very low level of concentration in environmental samples with complex matrix. Therefore, sample pre-treatment before chromatographic analysis solid-phase extraction and liquid-liquid extraction is usually necessary. However, these methods are time-consuming as well as requiring larger sample volume. On the other hand, liquid-liquid extraction method also toxic to our environment due to its usage in large amounts of volatile solvent. Hence, cloud point extraction (CPE) became the alternative in analytical chemistry to preconcentrate organic compounds (Hung et al., 2007; Wang et al., 2007).

Wang et al. (2007) reported that, the determination of di-ethyl-phthalate (DEP), 2-ethylhexyl-phthalate (DEHP) and di-cyclohexyl-phthalate (DCP) in spiked water samples (environmental samples) using HPLC/UV (Wang et al., 2007). It showed that, the recoveries of three compounds in between 85% to 103% and enrichment factors were between 35 to 111.

Noorashikin et al. (2014) investigated the performance of silicone non-ionic surfactant (DC193C) in CPE, determining parabens in water samples. Continuing on that research, they would like to improve the performance of non-ionic surfactant by using β-CD as a modifier for parabens determination from water samples (Noorashikin et al., 2014). The parameters such as pH value of the solution, temperature, salt concentration, surfactant concentration and β-CD concentration were screened to obtain optimum conditions for phase separation of parabens. This research has showed that modifier use like the CPE– β-CD-DC193C method using

a silicone surfactant and β-CD was an perfect method for the extraction of parabens from various water samples. Addition of CD as a modifier increases the capability to develop phase separation between the dilute aqueous and surfactant-rich phase. The introduction of b-CD into the method also reduces the water content percentage in surfactant-rich phase. The CPE– β-CD-DC193C method is economically viable with application of β-CD because it dramatically enhances the performance over the CPE–SNIS method and uses chemicals which are inexpensive and environmentally not toxic.

Cloud Point Extraction in Metal Analysis

Preconcentration and separation methods with CPE have been widely used to separate and preconcentrate metallic ions from different matrices (Bezerra et al., 2005). Few studies used a surfactant as quantification technique to determine trace metals after a preconcentration procedure by CPE and flame atomic absorption spectrometry (FAAS) (Şahin et al., 2010; Kiran et al., 2008; Lemos et al., 2007), electrothermal atomic absorption spectrometry (ET-AAS) (Ezoddin et al., 2010; Shemirani et al., 2005; Chen et al., 2005) or inductive coupled plasma optical emission spectroscopy (ICP-OES) (Shemirani et al., 2007; Tavakoli et al., 2008). ICP-OES is one of the supernal substitute method for analysis of toxic metals, providing an eloquent decrease in time analysis (Silva et al., 2009). Silva et al. (2009) developed a step for separation and preconcentration simultaneously of copper, cadmium, nickel and zinc to join the ability of simultaneous determination provided by ICP-OES with the advantages given by CPE (Silva et al., 2009). They found that proposed procedure using Triton X-114 and 4-(2-pyridylazo) resorcinol (PAR) as a chelating agent exhibits efficient, simple and safe method with LOD was 1.0-6.3 µgL^{-1}.

The usual accessibility of the instrumentation, the simple procedure, speed as well as accuracy and precision of the technique still make the spectrophotometric method appealing for copper determination. Procedure using CPE for preconcentration of metal ions has been based on the extraction of these metallic substances as water-soluble chelate complexes sparingly. Few ligands such as 8-hydroxyquinoline (oxine), diethyldithiocarbamate (DDTC), 1-(2-pyridylazo)-2-naphthol (PAN), 1-(2-thiazolylazo)-2-naphthol (TAN) and 4-(2-pyridylazo) resorcinol (PAR) applied for CPE of copper (Liang et al., 2010).

Donati et al. (2006) reported that, the combination of cobalt derivatization and CPE lead to an increase about 130-fold of sensitivity for cobalt measurement by thermo spray flame furnace atomic absorption spectrometer (TS-FF-AAS) and provides practicable determination of trace amounts of cobalt in food samples (Donati et al., 2006). Sensitivity increases around 670-fold when derivatization-CPE-TS-FF-AAS step and conventional FAAS are equated.

Ezoddin et al. (2010) studied a comparison technique so-called mixed micelle CPE with different preconcentration methods for speciation analysis chromium in water samples (Ezoddin et al., 2010). They claimed that mixed-micelle CPE has greater enhancement factor following a lower LOD (1 ngL^{-1}). It is the key interest in laboratories for trace metal ion analysis. Further, the proposed method anionic CPE procedure with the antecedent investigated CPE procedures for the speciation analysis of chromium shows the current procedure has the equatable or better LOD than those investigated before.

Maranhao et al. (2005) describes the application of microwave-assisted acid digestion with CPE to identify cadmium and lead in biological samples with ET AAS using Triton X-114 as the non-ionic surfactant and ammonium diethyldithiophosphate (DDTP) as the chelating agent (Maranhão et al., 2005). The phase separation can be acquired at relatively low temperatures and greater extraction efficiency, resulting low detection limits (6 and 40 ngL^{-1}) and high enrichment factor (129 and 18).

A similar studied has been carried out by Shah et al. (2010) using microwave assisted acid digestion procedure to obtain total mercury in

different tissues of broiler chicken by CPE and AAS (Shah et al., 2010). The concentration of mercury in the disparate tissues were identified in the range of 1.55-4.22 µgkg⁻¹. CPE has been selected as a method for preconcentration in this study because CPE is an relatively safe and easy as well as cheap method for the aqueous solution compared with other techniques. Table 3 shown some of CPE applications for metal pollutants determination.

Advantages of Cloud Point Extraction

CPE has immense advantages and becomes captivating (Ghouas et al., 2010; Haddou et al., 2006). CPE never been neglected and still continues with new applications to our environment. These techniques get the greatest attention because it is the most simple and versatile technique for preconcentration and hydrophobic species extraction from aqueous environment. Based on its high recoveries and concentration factor, CPE is claimed as a valid alternative for separation and preconcentration techniques (Bader et al., 2014). Nowadays, CPE has been used at ambient temperature rather than high temperature and has been combining with a various instruments such as gas chromatography flame photometric detection (GC-FPD) (Zhao et al., 2011), flow injection cloud point extraction with high performance liquid chromatography (FI-CPP-HPLC) (Li et al., 2008), capillary electrophoresis electrochemiluminesence (CE-ECL) (Yin et al., 2010), microwave-assisted CPE (Gao et al., 2010). In order to discover the trace amount of Bi(III), Cd(II), Cr(III), Cu(II), Ni(II) and Pb(II) ions, CPE also has been used with FAAS and Tween 80 (Mohammadi et al., 2016). In recent study, the development of CPE has been victoriously used for separation also pre-concentration of silver ion in water samples which this method was coupled with non-ionic surfactant, Triton X-114 and sodium diethyl dithiocarbamate as a chelating agent (Yang et al., 2017). In addition, CPE follows the principle of 'green chemistry' which its procedure for decreasing the utilise of toxic substances towards environment and human health (Gondim et al., 2016). It considered as green method due to the usage of media diluted extractor solutions as a surfactant that are low cost resulting to less production of residues (Nobuko et al., 2013).

Table 3: Determination of metal pollutants using CPE

Compounds	Matrix	LOD	CPE method	Detection	Reference
Mercury	Water	1.65 µg/L	Conventional CPE	UV Spectrophotometry	(Ulusoy et al., 2012)
Bismuth (III)	Water	None	Conventional CPE	Thermo system	(Didi et al., 2011)
Copper (II)	River water	None	Conventional CPE	Flame atomic absorbance spectrophotometry (FAAS)	(Nobuko et al., 2013)
Cadmium	Tap water and river water	0.2 ppb	Conventional CPE	Anodic stripping voltammetry (ASV)	(Cory et al., 2015)
Cobalt	River water	0.47 ng/mL	Conventional CPE	Flame Atomic Absorption Spectrometry (FAAS)	(Shangzhi et al., 2013)
Nickel	Water samples	1.7 ng/mL	Conventional CPE	Flame Atomic Absorption Spectrometry (FAAS)	(Hongbo et al., 2013)

Limitations of Cloud Point Extraction

The restriction of CPE methodology is greater absorbance exhibited immense surfactants in the UV region and fluorometric signals especially comes from surfactant that contain double-bond structures, likewise phenyl group in the surfactants of akylphenyl ether. Usual surfactant that containing double-bond structures applied in the separation include Triton series (Union Carbide), Igepal series (Rhodia) and PONPE series (polyethylene glycol) mono-4-nonylphenyl ethers).

To blunt the challenges, researchers tried other extractants including polymers anionic surfactants such as sodium dodecyl sulphate (SDS) (Carabias-Martínez et al., 2000; Casero et al., 1999) and primary ethoxylated alcohols such as Brij series (ICI) and Genapol series (Clariant) (Bai et al., 2001; Haddou et al., 2006; Ito et al., 2003; Padrón Sanz et al., 2004; Sosa Ferrera et al., 2004). However, just a minimal fortune has been obtained in using polymers as extractants to preconcentration PAHs (Bai et al., 2001). Furthermore, anionic surfactants usage as efficacious extractants in the CPE separation regularly needs salts addition and pH adjustments, generally to a petite value (Casero et al., 1999; Sicilia et al., 1999).

In most cases, the interferences in UV absorbance problem prevents usage of certain surfactant in procedure prior to chromatographic analysis unless the mobile phase used to accommodate high methanol content, where elution of the surfactant happens in short period of time and does not obstruct detection of the analytes (Casero et al., 1999; Shemirani et al., 2006; Yao et al., 2007). Ways to overrule this challenge is to utilize surfactants that would not absorb at the working wavelengths commonly applied in chromatography (Sicilia et al., 1999). Triton X-114 is famous for micelle formation, but its aromatic chromosphere has great UV absorbance or fluorescence signals in the detectors, resulting in masking of the PAHs signal in HPLC analysis, it is environmentally dangerous also forbidden to be applied in many countries (Yao et al., 2008).

Saitoh et al., (1991) utilized the zwitterionic surfactant, 3-(nonyldimethylammonium) propyl sulphate (C_9APSO_4) and 3-(decyldimethylammonium) propyl sulphate ($C_{10}APSO_4$) that do not absorb at the working wavelengths normally used in the chromatographic system (Saitoh et al., 1991). Garcia Pinto et al. (1995) used detection of analytes with electrochemical subjected to cloud point preconcentration open a modern perspective towards the methodology, whose main restrictions stays in the high absorbance background because of the surfactant interruption (Garcia Pinto et al., 1995).

Dual electrochemical detection (reductive-oxidative mode) was employed in their work for the liquid chromatographic analysis of organophosphorus pesticides after the cloud point with Triton X-114. The method gave high recoveries (85-100%) when using a high amount of surfactant in water samples. One of the disadvantages of this methodology is the high background absorbance in the UV region and high fluorescence signals whenever excitation wavelength in UV region employed by virtue of the aromatic moiety in surfactant structure, which masks all analytes having minimal retention times (Crick et al., 2000).

Conclusion and Future Trends

The explanation detailed above stipulates CPE methodology and application is a better diverse extraction technique for solid and liquid samples with gives a series of great appealing trump card from an analytical point of view like possibility of extracting and pre-concentrating the analytes of diverge polarities just in one step. The pre-concentration factor could be optimized by altering type, surfactant concentration and experimental conditions where extraction and phase separation are carried out. Surfactant is less toxic and inexpensive than the extractant used in liquid-liquid extraction. Generally used surfactants are available commercially and no analyte is lost in the process since it is unnecessary to evaporate the solvents off. The experimental procedures involved in

CPE methodology are unconditional and the surfactant-rich phase is compatible with the mobile phases used in HPLC. The CPE technique is easy to use and systems apparatus are cheaper than other modern techniques. Furthermore, the use of CPE reduces exposure to solvent vapours and wastes.

The study on the mechanism between CPE and analyte is inadequately understood and some CPE results were unpredictable. Only a little surfactants are frequently employed based on literature review on CPE application in environmental analysis, so that more exploration of other micelle-forming systems or mixed surfactant systems should be studied and considered, there is a vast mixed micelle-forming polymers in aqueous solution which has the potential to substitute organic solvents in a classical extraction methodologies. In addition, combining the use of surfactants with other extraction techniques may be great interest for the extraction and determination of organic components that are found in the environment in concentrations too small to be detected using conventional techniques. Amalgamation of different sample preparation step in the same experimental procedure has modernly obtained attention. Research on the issue is still restricted and concerns the blend use of CPE with dispersive solid phase extraction (DSPE), dispersive liquid-liquid microextraction (DLLME), matrix solid-phase dispersion (MSPD) and other techniques up to this date. It can be concluded that combined extraction methods are yielding in overrule certain limitations of each individual technique, proficiently extemporized selectivity, ameliorating enhancement factors and amending recoveries while alleviating time-consuming and laborious enrichment process of loading large sample volume.

Acknowledgements

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