

## THE APPLICATION OF CLOUD POINT EXTRACTION IN ENVIRONMENTAL ANALYSIS

MD SALEH NOORASHIKIN<sup>1\*</sup>, NORSEYRIHAN MOHD SOHAIMI<sup>2</sup>, NURSYAZWANI SUDA<sup>2</sup>,  
HUSNIYAH ZAINAL AZIZ<sup>2</sup>, SITI RAHMAH MOHD ZAINI<sup>2</sup>, SANGEETHA KANDASAMY<sup>2</sup>  
AND KARTHI SURESH<sup>2</sup>

<sup>1</sup>Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia. <sup>2</sup>School of Marine Science and Environment, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.

\*Corresponding author: noorashikin@ukm.edu.my

**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 widened 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 °C 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, Cetrinide, 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 cetrinide 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

<b>Type of Surfactant</b>	<b>Temperature</b>	<b>Salts</b>	<b>pH</b>	<b>Surfactant system</b>	<b>Ref.</b>
Triton X-114	40°C -80°C	NaOH or HCl	pH 4	0.3% (v/v) Triton X114	(Khan <i>et al.</i> , 2010)
Triton X-114	40°C	none	pH 5.5	1.25% (v/v) Triton X-114	(Wang, L.-L. <i>et al.</i> , 2010)
PEG600MO	45°C	Na <sub>2</sub> SO <sub>4</sub>	none	2 wt% PEG600MO	(Tang <i>et al.</i> , 2010)
C13E10	70°C	NaCl	none	1wt% of C <sub>13</sub> E <sub>10</sub>	(Didi <i>et al.</i> , 2011)
PONPE 5.0	70°C	NaCl	pH 5.8	50% (v/v) of PONPE 5.0	(Santarossa <i>et al.</i> , 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) or 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 °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,  $\text{SO}_4^{2-}$  ions gives better separation as it has stronger interaction with water compared to water-water interaction. On the other hand, 'salting out' effect  $\text{Na}^+$  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% (Yilmaz *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  $\text{Ag}^+$  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 <i>et al.</i> , 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 <i>et al.</i> , 2014)
Phenanthrene	Sand	None	Micellar solubilization-CPE	HPLC-UV	(Li, J.-L. <i>et al.</i> , 2008)
Aurium (III)	Water	1.1 ngL <sup>-1</sup>	Conventional CPE	ICP-MS (inductive coupled plasma-mass spectrometry)	(Chen <i>et al.</i> , 2010)
Auxins	Leaves	2.5 nM	Dual CPE	CE-ECL(capillary electrophoresis-electrochemiluminescence)	(Yin <i>et al.</i> , 2010)
Organophosphorus pesticides(Diazon)	Aqueous Samples	0.02 ng mL <sup>-1</sup>	Conventional CPE	UV Sepctrophotometry	(M.R.Sohrabi <i>et al.</i> , 2012)
Triazole fungicides	Water	6.8-34.5 ngL <sup>-1</sup>	Conventional CPE	HPLC-UV	(Tang <i>et al.</i> , 2010)
PAHs	Chinese medical herbs	0.01-0.05 ng/mL	Conventional CPE	HPLC- Fluorometric detection	(Shi <i>et al.</i> , 2011)
Phenol	Waste water	None	Conventional CPE	UV-Vis Spectrophotometer	(Taechangam <i>et al.</i> , 2009)
Bisphenol A and Naphtol	Water	0.67-1.67 µg l <sup>-1</sup>	Preconcentration using CPE	Capillary Electrophoresis (CE)	(S.Zhong, 2011)
Hydrocarbons	Fuel spill	None	Conventional CPE	HPLC-UV, ELSD	(Ghouas <i>et al.</i> , 2010)
polybrominated diphenyl ethers (PBDEs)	Aqueous Sample	1.71-5.82 ng/L	conventional GC	fluorescence spectroscopy	(Shan <i>et al.</i> , 2015)
Polychlorinated dibenzofurus (PCDFs)	Sea water	0.5-27.5 ng/L	Conventional CPE	HPLC-FD	(Fernández <i>et al.</i> , 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 isoctane 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  $\beta$ -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  $\beta$ -CD concentration were screened to obtain optimum conditions for phase separation of parabens. This research has showed that modifier use like the CPE-  $\beta$ -CD-DC193C method using

a silicone surfactant and  $\beta$ -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  $\beta$ -CD into the method also reduces the water content percentage in surfactant-rich phase. The CPE- $\beta$ -CD-DC193C method is economically viable with application of  $\beta$ -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  $\mu\text{gL}^{-1}$ .

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  $\text{ngL}^{-1}$ ). 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  $\text{ngL}^{-1}$ ) 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  $\mu\text{gkg}^{-1}$ . 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 electrochemiluminescence (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

<b>Compounds</b>	<b>Matrix</b>	<b>LOD</b>	<b>CPE method</b>	<b>Detection</b>	<b>Reference</b>
Mercury	Water	1.65 $\mu\text{g/L}$	Conventional CPE	UV Spectrophotometry	(Ulusoy <i>et al.</i> , 2012)
Bismuth (III)	Water	None	Conventional CPE	Thermo system	(Didi <i>et al.</i> , 2011)
Copper (II)	River water	None	Conventional CPE	Flame atomic absorbance spectrophotometry (FAAS)	(Nobuko <i>et al.</i> , 2013)
Cadmium	Tap water and river water	0.2 ppb	Conventional CPE	Anodic stripping voltammetry (ASV)	(Cory <i>et al.</i> , 2015)
Cobalt	River water	0.47 ng/mL	Conventional CPE	Flame Atomic Absorption Spectrometry (FAAS)	(Shangzhi <i>et al.</i> , 2013)
Nickel	Water samples	1.7 ng/mL	Conventional CPE	Flame Atomic Absorption Spectrometry (FAAS)	(Hongbo <i>et al.</i> , 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 alkylphenyl 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 ( $C_9$ APSO<sub>4</sub>) and 3-(decyldimethylammonium) propyl sulphate ( $C_{10}$ APSO<sub>4</sub>) 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.

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### References

- Alias Saravanan, M. D., Shanmugapriya, D., Kalaichelvi, P., & Arunagiri, A. (2014). Cloud Point Extraction of Phenol Using TX-100 as Non-ionic Surfactant. *International Journal of Scientific & Engineering Research*, 5(12): 18-25.
- Alibrahim, M. (2014). Cloud Point Extraction of Polycyclic Aromatic Hydrocarbons in Aqueous Solution with Nonionic Surfactants. *Tenside Surfactants Detergents*, 51(4): 333-338. doi: 10.3139/113.110315
- Amin, A. S., Kassem, M. A., & Mohammed, T. Y. (2015). Utilization of Cloud-point Extraction for Colorimetric Determination of Trace Amounts of Thorium (iv) in Real Samples. *RSC Advances*, 5(64): 52095-52100. doi: 10.1039/C5RA08806B
- Bader, N. R., Edbey, K., & Telgheder, U. (2014). Cloud Point Extraction as a Sample Preparation Technique for Trace Element Analysis: An Overview. *Journal of Chemical and Pharmaceutical Research*, 6(2): 496-501.
- Bai, D., Li, J., Chen, S. B., & Chen, B. H. (2001). A Novel Cloud-point Extraction Process for Preconcentrating Selected Polycyclic Aromatic Hydrocarbons in Aqueous Solution. *Environ. Sci. Technol.*, 35(19): 3936-3940. doi: 10.1021/es0108335
- Bezerra, M. A., Arruda, M. A. Z., & Ferreira, S. L. C. (2005). Cloud Point Extraction as a Procedure of Separation and Pre-concentration for Metal Determination Using Spectroanalytical Techniques: A Review. *Appl. Spectrosc. Rev.*, 40: 269-299.
- Carabias-Martínez, R., Rodríguez-Gonzalo, E., Moreno-Cordero, B., Pérez-Pavón, J. L., García-Pinto, C., & Fernández Laespada, E. (2000). Surfactant Cloud Point Extrac-

- tion and Preconcentration of Organic Compounds Prior to Chromatography and Capillary Electrophoresis. *Journal of Chromatography A*, 902(1): 251-265. doi: 10.1016/s0021-9673(00)00837-2
- Casero, I., Sicilia, D., Rubio, S., & Pérez-Benito, D. (1999). An Acid-induced Phase Cloud Point Separation Approach Using Anionic Surfactants for the Extraction and Preconcentration of Organic Compounds. *Analytical Chemistry*, 71(20): 4519-4526. doi: 10.1021/ac990106g
- Chen, J., Xiao, S., Wu, X., Fang, K., & Liu, W. (2005). Determination of Lead in Water Samples by Graphite Furnace Atomic Absorption Spectrometry after Cloud Point Extraction *Talanta*, 67: 992-996.
- Chen, S., & Zhu, X. (2010). Simplified Cloud Point Extraction-inductively Coupled Plasma Mass Spectrometry for the Preconcentration/analysis of Ultra-trace Gold. *Minerals Engineering*, 23(14): 1152-1154. doi: 10.1016/j.mineng.2010.07.009
- Citak, D., & Tuzen, M. (2010). A Novel Preconcentration Procedure Using Cloud Point Extraction for Determination of Lead, Cobalt and Copper in Water and Food Samples Using Flame Atomic Absorption Spectrometry. *Food and Chemical Toxicology*, 48(5): 1399-1404.
- Cory, A. R., Adam, B., Ian, P., & William, R. H. (2015). Cloud Point Extraction for Electroanalysis: Anodic Stripping Voltammetry of Cadmium. *Analytical Chemistry*, 87: 6133-6140.
- Crick, E. W., & Conte, E. D. (2000). Alkyltrimethylammonium Surfactant-mediated Extractions: Characterization of Surfactant-rich and Aqueous Layers, and Extraction Performance. *Journal of Chromatography A*, 877(1-2): 87-93. doi: 10.1016/s0021-9673(00)00194-1
- Didi, M. A., Sekkal, A. R., & Villemin, D. (2011). Cloud Point Extraction of Bismuth (III) with Nonionic Surfactants in Aqueous Solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 375(1-3): 169-177.
- Donati, G. L., Nascentes, C. C., Nogueira, A. R. A., Arruda, M. A. Z., & Nóbrega, J. A. (2006). Acid Extraction and Cloud Point Preconcentration as Sample Preparation Strategies for Cobalt Determination in Biological Materials by Thermospray Flame Furnace Atomic Absorption Spectrometry. *Microchemical Journal*, 82(2): 189-195. doi: 10.1016/j.microc.2006.01.006
- Dong, J., Sharpless, K. B., Kwisnek, L., Oakdale, J. S., & Fokin, V. V. (2014). SuFEx-based Synthesis of Polysulfates. *Angew. Chem. Int. Ed.*, 53: 9466-9470. doi:10.1002/anie.201403758.
- El-Shahawi, M. S., Bashammakh, A. S., Alwael, H., Alsibai, A. A., & Dowaidar, A. M. (2015). Adsorption Characteristics of Polycyclic Aromatic Hydrocarbons from Non-aqueous Media Using Activated Carbon Derived from Phenol Formaldehyde Resin: Kinetics and Thermodynamic Study. *Environmental Science and Pollution Research*, 1-13. doi: 10.1007/s11356-015-4936-2
- Ezoddin, M., Shemirani, F., & Khani, R. (2010). Application of Mixed-micelle Cloud Point Extraction for Speciation Analysis of Chromium in Water Samples by Electrothermal Atomic Absorption Spectrometry. *Desalination*, 262(1-3): 183-187. doi: 10.1016/j.desal.2010.06.007
- Fernández, A. E., Ferrera, Z. S., & Rodríguez, J. J. S. (1999). Application of Cloud-point Methodology to the Determination of Polychlorinated Dibenzofurans in Sea Water by High-performance Liquid Chromatography. *Analyst*, 124(4): 487-491.
- Fontana, A. R., Silva, M. F., Martínez, L. D., Wuilloud, R. G., & Altamirano, J. C. (2009). Determination of Polybrominated Diphenyl Ethers in Water and Soil Samples by Cloud Point Extraction-ultrasound-assisted Back-extraction-gas Chromatogra-

- phy-mass Spectrometry. *J. Chromatogr. A*, 1216(20): 4339-4346. doi: 10.1016/j.chroma.2009.03.029
- Gao, S., You, J., Zheng, X., Wang, Y., Ren, R., Zhang, R., Zhang, H. (2010). Determination of Phenylurea and Triazine Herbicides in Milk by Microwave Assisted Ionic Liquid Microextraction High-performance Liquid Chromatography. *Talanta*, 82(4): 1371-1377.
- Garcia Pinto, C., Perez Pavon, J. L., & Moreno Cordero, B. (1995). Cloud Point Preconcentration and High-performance Liquid Chromatographic Determination of Organophosphorus Pesticides with Dual Electrochemical Detection. *Analytical Chemistry*, 67(15): 2606-2612. doi: 10.1021/ac00111a018
- Ghouas, H., Haddou, B., Bouabdesselam, H., Bouberka, Z., & Derriche, Z. (2010). Elimination of Fuel Spills from Effluent Using Cloud Point Extraction Methods. *Journal of Hazardous Materials*, 180(1-3): 188-196. doi: 10.1016/j.jhazmat.2010.04.012
- Gondim, T. A., Guedes, J. A. C., Ribeiro, L. P. D., Lopes, G. S., & Matos, W. O. (2016). Optimization of a Cloud Point Extraction Procedure with Response Surface Methodology for the Quantification of Dissolved Iron in Produced Water from the Petroleum Industry Using FAAS. *Marine Pollution Bulletin*, 114(2): 786-799.
- Guerrieri, P., Rumondor, A. C. F., Li, T., & Taylor, L. S. (2010). Analysis of Relationships between Solid-state Properties, Counterion, and Developability of Pharmaceutical Salts. *AAPS PharmSciTech*, 11(3): 1212-1222. doi: 10.1208/s12249-010-9499-4
- Haddou, B., Canselier, J. P., & Gourdon, C. (2006). Cloud Point Extraction of Phenol and Benzyl Alcohol from Aqueous Stream. *Separation and Purification Technology*, 50(1): 114-121. doi: http://dx.doi.org/10.1016/j.seppur.2005.11.014
- Hongbo, X., Wanping, Z., Xiaoshun, Z., Jing, W., & Jian, W. (2013). Simultaneous Preconcentration of Cobalt, Nickel and Copper in Water Samples by Cloud Point Extraction Method and Their Determination by Flame Atomic Absorption Spectrometry. *Procedia Environmental Sciences*, 18: 258-263.
- Hung, K.-C., Chen, B.-H., & Yu, L. E. (2007). Cloud-point Extraction of Selected Polycyclic Aromatic Hydrocarbons by Nonionic Surfactants. *Separation and Purification Technology*, 57(1): 1-10. doi: http://dx.doi.org/10.1016/j.seppur.2007.03.004
- Hunzicker, G. A., Hein, G. J., Hernández, S. R., & Altamirano, J. C. (2015). Cloud Point Extraction for Analysis of Antiretrovirals in Human Plasma by UFLC-ESI-MS/MS. *Analytical Chemistry Research*, 6: 1-8. doi: http://dx.doi.org/10.1016/j.ancr.2015.08.002
- Ito, A., Nii, S., Kawaizumi, F., & Takahashi, K. (2003). Separation of Clay Minerals Based on Phase Transition of Surfactant Followed by Cooling. *Separation and Purification Technology*, 30(2): 139-146. doi: 10.1016/s1383-5866(02)00141-7
- Khan, S., Kazi, T. G., Baig, J. A., Kolachi, N. F., Afridi, H. I., Wadhwa, S. K., Shah, F. (2010). Cloud Point Extraction of Vanadium in Pharmaceutical Formulations, Dialysate and Parenteral Solutions Using 8-hydroxyquinoline and Nonionic Surfactant. *J. Hazard. Mater.*, 182(1-3): 371-376. doi: 10.1016/j.jhazmat.2010.06.042
- Kiran, K., Kumar, K. S., Prasad, B., Suvardhan, K., Lekkala, R. B., & Janardhanam, K. (2008). Speciation Determination of Chromium(III) and (VI) Using Preconcentration Cloud Point Extraction with Flame Atomic Absorption Spectrometry (FAAS). *J. Hazard. Mater.*, 150(3): 582-586. doi: 10.1016/j.jhazmat.2007.05.007
- Kulichenko, S., Doroschuk, V., & Gonta, N. (2010). Phase Separation in Non-ionic Surfactant Triton X-100 Solutions in the Pres-



- ence of Phenol. *Chemical Papers*, (Vol. 64, pp. 91).
- Lemos, V. A., da França, R. S., & Moreira, B. O. (2007). Cloud Point Extraction for Co and Ni Determination in Water Samples by Flame Atomic Absorption Spectrometry. *Separation and Purification Technology*, 54(3): 349-354. doi: 10.1016/j.seppur.2006.10.004
- Li, C. F., Wong, J. W. C., Huie, C. W., & Choi, M. M. F. (2008). On-line Flow Injection-cloud Point Preconcentration of Polycyclic Aromatic Hydrocarbons Coupled with High-performance Liquid Chromatography. *Journal of Chromatography A*, 1214(1-2): 11-16. doi: 10.1016/j.chroma.2008.10.062
- Li, J.-L., & Chen, B.-H. (2008). Recovering Phenanthrene from Spiked Sand by a Combined Remediation Process of Micellar Solubilization and Cloud-point Extraction. *Journal of the Chinese Institute of Chemical Engineers*, 39(4): 337-342. doi: 10.1016/j.jcice.2008.01.005
- Liang, P., & Yang, J. (2010). Cloud Point Extraction Preconcentration and Spectrophotometric Determination of Copper in Food and Water Samples Using Amino Acid as the Complexing Agent. *J. Food Compos. Anal.*, 23(1): 95-99. doi: 10.1016/j.jfca.2009.01.015
- Liang, R., Wang, Z., Xu, J.-H., Li, W., & Qi, H. (2009). Novel Polyethylene Glycol Induced Cloud Point System for Extraction and Back-extraction of Organic Compounds. *Separation and Purification Technology*, 66(2): 248-256. doi: 10.1016/j.seppur.2009.01.001
- Mahugo Santana, C., Sosa Ferrera, Z., Esther Torres Padrón, M., & Juan Santana Rodríguez, J. (2009). Methodologies for the Extraction of Phenolic Compounds from Environmental Samples: New Approaches. *Molecules*, 14(1): 298-320.
- Mandyla, S. P., Tsogas, G. Z., Vlessidis, A. G., & Giokas, D. L. (2016). Determination of Gold Nanoparticles in Environmental Water Samples by Second-order Optical Scattering Using Dithiothreitol-functionalized CdS Quantum Dots after Cloud Point Extraction. *Journal of Hazardous Materials*, 323: 67-74.
- Maranhão, T. d. A., Borges, D. L. G., da Veiga, M. A. M. S., & Curtius, A. J. (2005). Cloud Point Extraction for the Determination of Cadmium and Lead in Biological Samples by Graphite Furnace Atomic Absorption Spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 60(5): 667-672. doi: 10.1016/j.sab.2005.02.004
- Meeravali, N. N., & Jiang, S.-J. (2009). A Novel Cloud Point Extraction Approach Using Cationic Surfactant for the Separation and Pre-concentration of Chromium Species in Natural Water Prior to ICP-DRC-MS Determination. *Talanta*, 80(1): 173-178. doi: 10.1016/j.talanta.2009.06.051
- Mirzaei, M., Behzadi, M., Abadi, N. M., & Beizaei, A. (2011). Simultaneous Separation/preconcentration of Ultra Trace Heavy Metals in Industrial Wastewaters by Dispersive Liquid-liquid Microextraction Based on Solidification of Floating Organic Drop Prior to Determination by Graphite Furnace Atomic Absorption Spectrometry. *Journal of Hazardous Materials*, 186(2-3): 1739-1743. doi: <http://dx.doi.org/10.1016/j.jhazmat.2010.12.080>
- Mohammadi, S. Z., Shamspur, T., Afzali, D., Taher, M. A., & Baghelani, Y. M. (2016). Applicability of Cloud Point Extraction for the Separation Trace Amount of Lead Ion in Environmental and Biological Samples Prior to Determination by Flame Atomic Absorption Spectrometry. *Arabian Journal of Chemistry*, 9: S610-S615.
- Net, S., Delmont, A., Sempéré, R., Paluselli, A., & Ouddane, B. (2015). Reliable Quantification of Phthalates in Environmental Matrices (Air, Water, Sludge, Sediment and Soil): A Review. *Science of the Total Environment*, 515: 162-180.



- Nobuko, S., Masanobu, M., & Hideyuki, I. (2013). Cloud Point Extraction of Cu (II) Using a Mixture of Triton X-100 and Dithizone with a Salting-out Effect and Its Application to Visual Determination. *Talanta*, 117: 376-381.
- Noorashikin, M., Mohamad, S., & Abas, M. (2014). Extraction and Determination of Parabens in Water Samples Using an Aqueous Two-phase System of Ionic Liquid and Salts with beta-cyclodextrin as the Modifier Coupled with High Performance Liquid Chromatography. *Analytical Methods*, 6(2): 419-425.
- Noorashikin, M. S., Raoov, M., Mohamad, S., & Abas, M. R. (2013). Cloud Point Extraction of Parabens Using Non-ionic Surfactant with Cyclodextrin Functionalized Ionic Liquid as a Modifier. *International Journal of Molecular Sciences*, 14(12): 24531-24548.
- Noorashikin, M. S., Roov, M., Mohamad, S., & Abas, M. R. B. (2014). Extraction of Parabens from Water Samples Using Cloud Point Extraction with a Non-ionic Surfactant with  $\beta$ -Cyclodextrin as Modifier. *Journal of Surfactants and Detergents*, 17(4): 747-758.
- Padrón Sanz, C., Halko, R., Sosa Ferrera, Z., & Santana Rodríguez, J. J. (2004). Micellar Extraction of Organophosphorus Pesticides and Their Determination by Liquid Chromatography. *Anal. Chim. Acta*, 524(1-2): 265-270. doi: 10.1016/j.aca.2004.06.024
- Pourreza, N., & Elhami, S. (2007). Spectrophotometric Determination of Malachite Green in Fish Farming Water Samples after Cloud Point Extraction Using Nonionic Surfactant Triton X-100. *Analytica Chimica Acta*, 596(1): 62-65.
- Şahin, Ç. A., Efeçinar, M., & Şatiroğlu, N. (2010). Combination of Cloud Point Extraction and Flame Atomic Absorption Spectrometry for Preconcentration and Determination of Nickel and Manganese Ions in Water and Food Samples. *Journal of Hazardous Materials*, 176(1): 672-677.
- Saitoh, T., & Hinze, W. L. (1991). Concentration of Hydrophobic Organic Compounds and Extraction of Protein Using Alkylammoniosulfate Zwitterionic Surfactant Mediated Phase Separations (Cloud Point Extractions). *Analytical Chemistry*, 63(21): 2520-2525.
- Santalad, A., Srijaranai, S., Burakham, R., Glennon, J., & Deming, R. (2009). Cloud-point Extraction and Reversed-phase High-performance Liquid Chromatography for the Determination of Carbamate Insecticide Residues in Fruits. *Analytical and Bioanalytical Chemistry*, 394(5): 1307-1317. doi: 10.1007/s00216-009-2663-6
- Santarossa, D. G., Talio, M. C., & Fernández, L. P. (2016). Aluminium Traces Determination in Biological and Water Samples Using a Novel Extraction Scheme Combined with Molecular Fluorescence. *Microchemical Journal*, 129: 274-280.
- Seebunrueng, K., Santaladchaiyakit, Y., Soisungnoen, P., & Srijaranai, S. (2011). Catanionic Surfactant Ambient Cloud Point Extraction and High-performance Liquid Chromatography for Simultaneous Analysis of Organophosphorus Pesticide Residues in Water and Fruit Juice Samples. *Analytical and Bioanalytical Chemistry*, 401(5): 1703. doi: 10.1007/s00216-011-5214-x
- Shah, A. Q., Kazi, T. G., Baig, J. A., Afridi, H. I., Kandhro, G. A., Arain, M. B., & Wadhwa, S. K. (2010). Total Mercury Determination in Different Tissues of Broiler Chicken by Using Cloud Point Extraction and Cold Vapor Atomic Absorption Spectrometry. *Food and Chemical toxicology*, 48(1): 65-69. doi: 10.1016/j.fct.2009.09.016
- Shan, H., Liu, C., Wang, Z., Ma, T., Shang, J., & Pan, D. (2015). A Fluorescence-based Method for Rapid and Direct Determination of Polybrominated Diphenyl Ethers in Water. *Journal of Analytical Methods in Chemistry*, 2015, 10. doi: 10.1155/2015/853085
- Shangzhi, W., Shuangming, M., & Yong, G. (2013). Cloud Point Extraction for the De-

- termination of Trace Amounts of Cobalt in Water and Food Samples by Flame Atomic Absorption Spectrometry. *Journal of Spectroscopy*, 1-7.
- Shemirani, F., Baghdadi, M., Ramezani, M., & Jamali, M. R. (2005). Determination of Ultra Trace Amounts of Bismuth in Biological and Water Samples by Electrothermal Atomic Absorption Spectrometry. *Analytica Chimica Acta*, 534: 163-169.
- Shemirani, F., Jamali, M., Kozani, R., & Niasari, M. (2006). Highly Selective Cloud Point Extraction and Preconcentration of Trace Amounts of Silver in Water Samples Using Synthesized Schiff's Base Followed by Flame Atomic Absorption Spectrometric Determination. *Journal of Analytical Chemistry*, 61(2): 124-128. doi: 10.1134/s1061934806020067
- Shemirani, F., & Yousefi, S. R. (2007). Selective Extraction and Preconcentration of Cerium (IV) in Water Samples by Cloud Point Extraction and Determination by ICP-OES. *Microchemical Acta*, 157: 223-227.
- Shi, Z., Yan, J., Ma, Y., & Zhang, H. (2011). Cloud Point Extraction HPLC Determination of Polycyclic Aromatic Hydrocarbons Residues in Traditional Chinese Medical Herbs. *Procedia*, 10: 1216-1221.
- Sicilia, D., Rubio, S., Pérez-Bendito, D., Maniasso, N., & Zagatto, E. A. G. (1999). Anionic Surfactants in Acid Media: A New Cloud Point Extraction Approach for the Determination of Polycyclic Aromatic Hydrocarbons in Environmental Samples. *Analytica Chimica Acta*, 392(1): 29-38.
- Silva, E. L., Roldan, P. d. S., & Giné, M. F. (2009). Simultaneous Preconcentration of Copper, Zinc, Cadmium, and Nickel in Water Samples by Cloud Point Extraction Using 4-(2-pyridylazo)-resorcinol and Their Determination by Inductively Coupled Plasma Optic Emission Spectrometry. *J. Hazard. Mater.*, 171(1-3): 1133-1138. doi: 10.1016/j.jhazmat.2009.06.127
- Silva, M. F., Cerutti, E. S., & Martinez, L. D. (2006). Coupling Cloud Point Extraction to Instrumental Detection Systems for Metal Analysis. *Microchemical Acta*, 155: 349-364.
- Sohrabi, M. R., Jamshidi, S., & Esmaeilifar, A. (2012). Cloud Point Extraction for Determination of Diazinon: Optimization of the Effective Parameters Using Taguchi Method. *Chemometrics and Intelligent Laboratory Systems*, 110: 49-54.
- Sosa Ferrera, Z., Padrón Sanz, C., Mahugo Santana, C., & Santana Rodríguez, J. J. (2004). The Use of Micellar Systems in the Extraction and Pre-concentration of Organic Pollutants in Environmental Samples. *Trac-Trend. Anal. Chem.*, 23(7): 469-479. doi: 10.1016/s0165-9936(04)00732-0
- Ssebugere, P., Sillanpää, M., Wang, P., Li, Y., Kiremire, B. T., Kasozi, G. N., Zhang, Q. (2014). Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polybrominated diphenyl ethers in Sediments and Fish Species from the Murchison Bay of Lake Victoria, Uganda. *Science of the Total Environment*, 500: 1-10.
- Taechangam, P., Scamehorn, J. F., Osuwan, S., & Rirksomboon, T. (2009). Effect of Nonionic Surfactant Molecular Structure on Cloud Point Extraction of Phenol from Wastewater. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 347(1-3): 200-209. doi: 10.1016/j.colsurfa.2009.04.005
- Tang, T., Qian, K., Shi, T., Wang, F., Li, J., & Cao, Y. (2010). Determination of Triazole Fungicides in Environmental Water Samples by High Performance Liquid Chromatography with Cloud Point Extraction Using Polyethylene Glycol 600 Monooleate. *Analytica Chimica Acta*, 680(1-2): 26-31. doi: 10.1016/j.aca.2010.09.034
- Tavakoli, L., Yamini, Y., Ebrahimzadeh, H., Nezhadali, A., Shariati, S., & Nourmohamadian, F. (2008). Development of Cloud Point Extraction for Simultaneous Extraction and

- Determination of Gold and Palladium using ICP-OES. *Journal Hazardous Material*, 152: 737-743.
- Ulusoy, H. I., Gurkan, R., & Ulusoy, S. (2012). Cloud Point Extraction and Spectrophotometric Determination of Mercury Species at Trace Levels in Environmental Samples. *Talanta*, 88: 516-523.
- Wang, L.-L., Wang, J.-Q., Zheng, Z.-X., & Xiao, P. (2010). Cloud Point Extraction Combined with High-performance Liquid Chromatography for Speciation of Chromium(III) and Chromium(VI) in Environmental Sediment Samples. *Journal of Hazardous Materials*, 177(4): 177-181.
- Wang, L., Jiang, G.-b., Cai, Y.-q., He, B., Wang, Y.-w., & Shen, D.-z. (2007). Cloud Point Extraction Coupled with HPLC-UV for the Determination of Phthalate Esters in Environmental Water Samples. *Journal of Environmental Sciences*, 19(7): 874-878. doi: 10.1016/s1001-0742(07)60145-4
- Watanabe, H., & Tanaka, H. (1978). A Non-ionic Surfactant as a New Solvent for Liquid-liquid Extraction of Zinc(II) with 1-(2-pyridylazo)-2-naphthol. *Talanta*, 25: 585-589.
- Xie, S., Paa, M. C., Li, C. F., Xiao, D., & Choi, M. M. F. (2010). Separation and Preconcentration of Persistent Organic Pollutants by Cloud Point Extraction. *J. Chromatogr. A*, 1217(16): 2306-2317. doi: 10.1016/j.chroma.2009.11.075
- Yang, X., Jia, Z., Yang, X., Li, G., & Liao, X. (2017). Cloud Point Extraction-flame Atomic Absorption Spectrometry for Pre-concentration and Determination of Trace Amounts of Silver Ions in Water Samples. *Saudi Journal of Biological Sciences*, 24(3): 589-594. doi: http://dx.doi.org/10.1016/j.sjbs.2017.01.030
- Yao, B., & Yang, L. (2008). Equilibrium Partition of Polycyclic Aromatic Hydrocarbons in Cloud Point Extraction with a Silicone Surfactant. *Journal of Colloid and Interface Science*, 319(1): 316-321. doi: http://dx.doi.org/10.1016/j.jcis.2007.11.033
- Yao, B., Yang, L., Hu, Q., & Shigendo, A. (2007). Cloud Point Extraction of Polycyclic Aromatic Hydrocarbons in Aqueous Solution with Silicone Surfactants. *Chinese J. Chem. Eng.*, 15(4): 468-473.
- Yılmaz, F. M., Karaaslan, M., & Vardin, H. (2015). Optimization of Extraction Parameters on the Isolation of Phenolic Compounds from Sour Cherry (*Prunus cerasus* L.) Pomace. *Journal of Food Science and Technology*, 52(5): 2851-2859. doi: 10.1007/s13197-014-1345-3
- Yin, X.-B., Guo, J.-M., & Wei, W. (2010). Dual-cloud Point Extraction and Tertiary Amine Labeling for Selective and Sensitive Capillary Electrophoresis-electrochemiluminescent Detection of Auxins. *Journal of Chromatography A*, 1217(8): 1399-1406. doi: 10.1016/j.chroma.2009.12.029
- Zain, N., Abu Bakar, N., Mohamad, S., & Saleh, N. M. (2014). Optimization of a Greener Method for Removal Phenol Species by Cloud Point Extraction and Spectrophotometry. *Spectrochim Acta A*, 118: 1121-1128.
- Zhao, W.-j., Sun, X.-k., Deng, X.-n., Huang, L., Yang, M.-m., & Zhou, Z.-m. (2011). Cloud Point Extraction Coupled with Ultrasonic-assisted Back-extraction for the Determination of Organophosphorus Pesticides in Concentrated Fruit Juice by Gas Chromatography with Flame Photometric Detection. *Food Chemistry*, 127(2): 683-688. doi: 10.1016/j.foodchem.2010.12.122
- Zhong, S., S. N. T., Ge, L., Wang, W., & Chen, J. (2011). Determination of Bisphenol A and Naphthols in River Water Samples by Capillary Zone Electrophoresis after Cloud Point Extraction. *Talanta*, 85: 488-492.
- Zhou, J., Wang, S. W., & Sun, X. L. (2008). Determination of Osthole in Rat Plasma by High-performance Liquid Chromatography Using Cloud-point Extraction. *Anal.*

*lytica chimica acta*, 608(2): 158-164. doi: 10.1016/j.aca.2007.12.029

Zuhair, A.-A.-K., & Hala, N. M. (2014). A Sequential Separation and Determination of Some Organic Reagent Dyes in Pollutant Samples by Using Cloud Point Extraction

Methodology Coupled with Spectrophotometry. *International Journal of Science and Research*, 3(9): 2133-2139. 1–3): 114-118. doi: <http://dx.doi.org/10.1016/j.jhazmat.2009.12.003>