

Recent Trends for Separation and Preconcentration in Metal Ions and Organic Compounds Analysis after Cloud-Point Methodology: Developments and Analytical Applications – A review

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Abstract

In this article, various aspects of micelle-mediated extraction as a new tool for separation and enrichments in metals and organic analyses are scanned. The presented paper accentuates profitable information about start-of-the-art and potentialities offered by cloud-point extraction (CPE) as a simple alternative and yet an effective mean of extracting analytes into organic stationary phase comprises of the non-ionic surfactant micelles. The concept and mechanism of this model of extraction are also embodied. A concise survey of the literatures related to the applications of CPE coupled with different analytical instrumentations covering more than 120 reports submitted over the past decade have been compiled and the relevant analytical parameters such as methodology, matrix and detection limits are tabulated.

Keywords:

Cloud-point extraction; non-ionic surfactant micelles; extraction-preconcentration; metals ions; analytical instrumentations

1. Introduction

Despite several analytical instrumentations are now available for the determination of the analyte(s) in different matrices at trace levels with adequate sensitivity, the matrix effects and the presence of analyte(s) at very low concentration levels have been occasionally problematic thus creating an obstacle toward reliable and accurate analysis. Accordingly, the analytical chemists are often prospected for easy and simple pretreatment procedures to solve these dilemmas before taking action to carry out final measurement. Undoubtedly, the extraction-separation techniques are of superb solution due to their ability to isolate and enrich the target analytes from bulk sample. This paired action leads to reduce, control or even eliminate the interference effects and allow determining these analytes at ultra- trace levels.

The most popular and traditional methodology used for this assignment is the liquid-liquid extraction (LLE), but due to its drawbacks, such as the use of large amounts of toxic and flammable organic solvents, time-consuming (i.e. slow extraction speed) and high dilution factor (i.e. low concentration efficiency for solute), a considerable attentions have recently been paid towards the development of simple and rapid extraction methods together with the use of minimum of solvents, reducing the analysis step , increasing the sample throughput and improving the quality and the sensitivity of the analytical methods. These

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efforts brought about the appearance of novel domains of environmentally-clean extraction tools, allowing for versatility in the selection of the most suitable approach for any given analyte. The techniques, such as solid-phase extraction (SPE) or solid-phase microextraction (SPME), liquid-liquid microextraction (LLME), supercritical fluid extraction (SFE), supercritical water extraction (SWE), membrane extraction (ME) and others represent different replacements to the classical liquid-liquid extraction (LLE).

Currently, numerous reports have been displayed in chemical literatures related to the development and employment of the so-called cloud-point extraction (CPE) as an alternative to other techniques for both separation and pre-concentration of metal ions and organic compounds in most field of analytical instrumentations. The first use of the CPE methodology was pioneered by Watanabe and co-workers [1-2], and the potential of this theme in analytical chemistry were outlined by Watanabe in 1982 [3], followed by a review highlighted on the analytical applications of organized molecular assemblies in 1985 [4]. Thereafter, the concept of CPE have received wide acceptance by analytical scientists during the nineties, reflected on the appearance of large numbers of papers based on micelle-mediated separation (or CPE) in different fields of analytical chemistry which were then reviewed by Greece researchers [5-6].

This piece of article will highlight on the principle and theoretical aspects for the extraction-preconcentration of metal ions and organic species by using CPE based on micelle-mediation phenomena that described over the recently published papers. Also, more attentions are given to the analytical applications of this bride technique coupled with different spectrometric and chromatographic detection systems, for the determination of metal ions, biochemical and organic molecules in different matrices that were published in the last decade.

2. Basic concept of CPE

In CPE methodologies, the surfactants based-media (or surface-active agents) play a vital role in performing extraction/enrichment of the analyte(s) from bulk solution.

2.1. What is meant by micelle?

Surfactants are usually organic molecules that are amphiphilic; consist of two moieties with opposing properties: Hydrophilic polar head and hydrophobic hydrocarbon (nonpolar) tail. Therefore, they are typically sparingly soluble in both organic solvents and water. In contrast to purely polar or non-polar molecules, amphipathic molecules exhibit unique properties in water. Their polar group forms hydrogen bonds with water molecules, while the hydrocarbon chains (nonpolar) aggregate due to hydrophobic interactions. These properties allow surfactants to be soluble in water. In aqueous solutions, they form organized spherical structures called **micelles** (Fig. 1), each of which contains several surfactant molecules. Because of their amphipathic nature, surfactants are able to solubilize hydrophobic compounds in water at certain conditions [7].

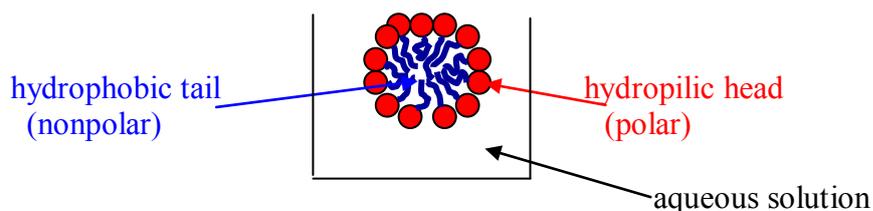


Fig 1. A surfactant-micelle in water (normal).

Also, other shapes such as ellipsoids, cylinders, and bilayers are possible (Fig.2). The shape and size of a micelle are a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength

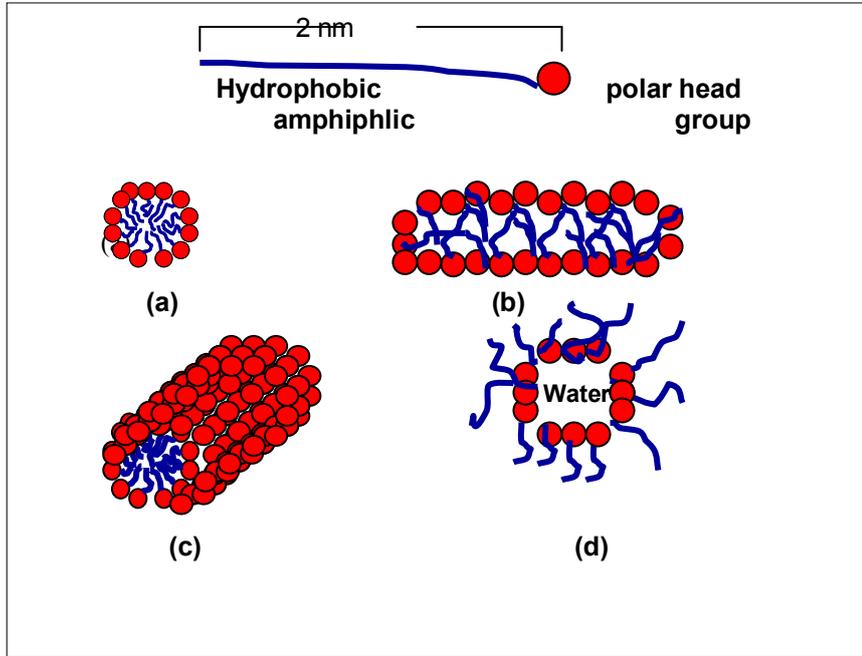


Fig 2 . Forms of an amphiphile and several forms of micelle:
 (a) spherical, (b) disk, (c) cylindrical, rod-like, and (d) reverse micelle.

Micelles are formed in nonpolar media such as benzene, where the amphiphiles cluster around small water droplets in the system, forming an assembly known as a **reversed micelle** (Fig. 2d). That is, the polar ends on the inside of the micelle, non-polar ends on the outside where they can come into contact with the nonpolar liquid and vice versa (Fig. 3).

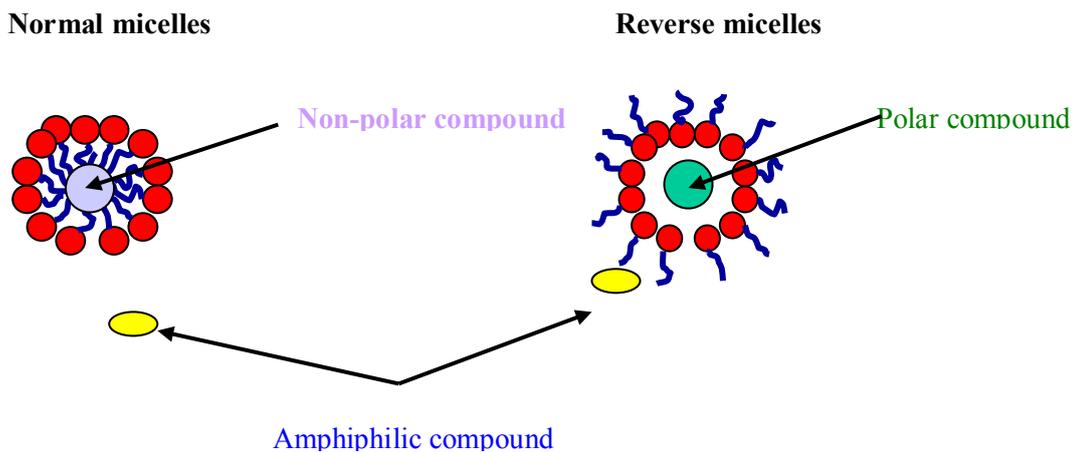


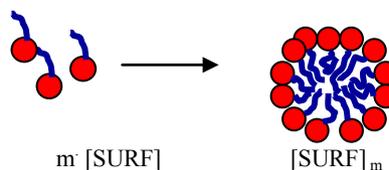
Fig 3. Spontaneous transfer of a compound insoluble in the bulk solvent into solution due to incorporation into the surfactant micelles

2.2. Why are micelles so important?

Generally, a polar (hydrophilic) solvent will dissolve polar materials (solutes), a non-polar (hydrophobic) solvent will dissolve non-polar materials. For example, water (a very polar solvent) will dissolve sodium chloride (an ionic or very polar solute) but not oil (a non-polar solute). The opposite is true with hexane, a very non-polar solvent. A micellar solution, however, is unique in that it allows non-polar solutes to dissolve in a polar medium. Because of the orientation of the surfactant molecules in a micelle in aqueous solution, there exists a hydrophobic region within the micelle. This hydrophobic regime will incorporate non-polar solutes, thus achieving solubility of oil in water. This leads directly to the use of surfactants as detergents as most soils encountered are non-polar [8].

2.3. How does micelle work in extraction?

When a non-ionic surfactant solution is heated over a critical temperature, namely cloud point (CP), the solution easily separates into two distinct phases. The first one is a surfactant phase, which consists a large hydrated micelles (surfactant-rich phase) of the small volume and the second one (aqueous phase) is an aqueous solution in which the concentration of the surfactant is approximately equal to the critical micelle concentration (CMC). The mechanism by which this separation occurs is attributed to the rapid increase in the aggregation number of the surfactant's micelles, as a result of the increase of temperature or to critical phenomena (defined as the cloud point) thereby the solution become turbid[9]. Hydrophobic species (metal ions after reaction with suitable hydrophobic ligand or hydrophobic organic compounds) present in sample solutions are in a position to interact with the micelles (i.e. favorably partitioned in non-polar microenvironment), thus being separated and concentrated in the small volume of the surfactant-rich phase [10]. The whole process similar to traditional liquid-liquid extraction (LLE), the only difference being the "organic" phase is generated within the aqueous phase, converting a previously homogeneous solution to heterogeneous one by simply gathering its previously scattered hydrophobic suspension [5]. The formation of micelles can be understood using thermodynamics: micelles can form spontaneously because of a balance between entropy and enthalpy. In water, the hydrophobic effect is the driving force for micelle formation, despite the fact that assembling surfactant molecules together reduces their entropy [11]. Explicitly, above the CMC, the entropic penalty of assembling the surfactant molecules is less than the entropic penalty of caging water molecules. Also important are enthalpic considerations, such as the electrostatic interactions that occur between the charged parts surfactants. This analysis of the thermodynamic parameters of the micelles formation is done for a nonionic surfactant. The enthalpy of micelle formation in aqueous solutions is usually small and can be negative. The main driving force for the micelle formation is the entropy changes due to aggregation of the alkyl tails of the surfactant ("hydrophobic interactions") [11].



$$K_{mic} = \frac{c_{mic}}{[SURF]^m} = \frac{c_{mic}}{[cmc]^m}$$

$$c_o = [cmc] + m \cdot c_{mic} \approx m \cdot c_{mic}$$

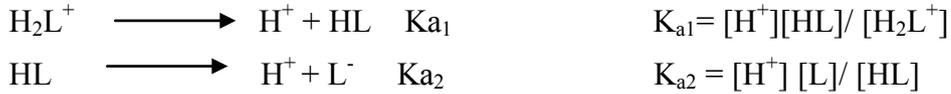
$\Delta G_{mic}^{\circ} \approx RT \ln cmc$ $\Delta H_{mic}^{\circ} \approx -RT \frac{2d \ln cmc}{dT}$ $\Delta S_{mic}^{\circ} = -R \ln cmc - RT \frac{2d \ln cmc}{dT}$

$$\Delta G_{mic}^o = \frac{\Delta G^o}{m} = \frac{RT}{m} = \ln K_{mic} = \frac{Rt}{m} \ln \frac{c_o}{m} + RT \ln cmc \approx RT \ln cmc \quad (m = 30 \div 100)$$

2.4. Distribution of metal chelate in two phases

To understand the mechanisms of distribution of metal ions in non-ionic surfactant systems, few papers have been described by Japanese researchers related to the distribution equilibria of metal chelate between surfactant phase and aqueous phases [12-15]. Through these articles, several examples were studied experimentally to derive mathematically the distribution of such metal chelates in two phases separated from micellar solution of non-ionic surfactant. Of these, the distribution equilibria of 2-(2-pyridylazo)-5-methylphenol (PAP-5-Me) and its zinc (II) chelate between two phases which were formed from a micellar solution of poly (oxylphenylene)-4-nonphenyl ether with 7.5 oxyethylene units (PONPE-7.5) [12].

i. The acid dissociation of PAP-5-Me in water (ionic strength of 0.1M NaCl) occurs in two steps:



ii. The formation constant of metal chelate:



The overall formation constants



PAP-5-Me reacts with zinc (II) to form a stable chelate above pH=6

iii. Distribution equilibria of PAP-5-Me between surfactant and aqueous phases:



Where the concentration terms of counter ions in the expression for K_{d1}' and K_{d3}' are omitted and "s" refers to the surfactant phase. The distribution ratio (q) of PAP-5-Me can be written as follows:

$$q = \frac{K_{d1}'[H^+]K_{a1} + K_{a2} + K_{d3}'K_{a2}[H^+]}{[H^+]K_{a1}^{-1} + 1 + K_{a2}[H^+]^{-1}} \quad (1)$$

The $[\text{L}^-]$ in two phase will be low below pH=3; thus Eqn.(1) is simplified to

$$q = (K_{d2} - q) K_{a1} [H^+]^{-1} + K_{d1}' \quad (2)$$

Likewise, $[\text{H}_2\text{L}^+]$ will be extremely low above pH=8, therefore Eqn. (3) is obtained:

$$q = (K_{d2} - q) [H^+] K_{a2}^{-1} + K_{d3}' \quad (3)$$

A plot of q against $(K_{d2} - q) [H^+] K_{a2}$ in Eqn. (2) gives a straight line, with a slope and intercept from which the values of K_{a1} and K_{d1}' are evaluated. The values of K_{a2}^{-1} and K_{d3}' are also obtained as a slope and an intercept of a plot for q vs. $(K_{d2} - q) [H^+]$ in Eqn. (3).

iv. Distribution equilibria of zinc (II) between surfactant and aqueous phases:

The distribution ratio (q) of metal ion is pH dependent. The values of q become constant above pH=6.5; thus the uncharged species (ML_2) is extracted predominately. Below pH=6.5, the formation of ML^+ in aqueous phase and/ or simultaneous extraction of ML^+ with ML_2 may be occurred. The partition constants of the metal chelates are expressed as follows:



As a result, the distribution ratio of zinc (II) is expressed in terms of the equilibrium concentration for L^- in the aqueous phase

$$q = (K'_{D1} \beta_1 [L^-] + K_{D2} \beta_2 [L^-]^2) (1 + \beta_1 [L^-] + \beta_2 [L^-]^2)^{-1} \quad (4)$$

By rearrangement of Eqn.(4) we get :

$$q (\beta_1 [L^-]^{-1} + 1 + \beta_2 \beta_1^{-1} [L^-]) = K'_{D1} + K_{D2} \beta_1^{-1} \beta_2 [L^-] \quad (5)$$

As the values of β_1 and β_2 in water are already known, a linear plot of the left-hand term in Eqn. (5) vs. $\beta_2 \beta_1^{-1} [L^-]$ allows evaluation of K'_{D1} (the intercept) and K_{D2} (the slope). The equilibrium concentration of L^- in the aqueous phase was calculated by the following equation, which derived from material balance for PAP-5-Me:

$$[L^-]_t = \frac{v_s ([H_2L^+]_s + [HL]_s + [L^-]_s) + v_w ([H_2L^+] + [HL] + [L^-])}{v_s + v_w}$$

Where $[L^-]_t$ is the total concentration of PAP-5-Me taking as being entirely in the initial solution ($v_s + v_w$). In the material balance the amount of PAP-5-Me bound to the metal ions in the two phases were assumed to be practically negligible. This is reasonable, as the metal ions are extracted by adding 30-fold excess of PAP-5-Me in relation to the metal concentration [13]. It was found that K'_{D1} close to zero and concluded the extraction of ML^+ (ZnL^+) to be negligible. Since $K'_{D1} = 0$, Eqn. (4) is simplified to Eqn. (6).

$$q = K_{D2} \beta_2 ([L^-]^{-2} + \beta_1 [L^-] + \beta_2)^{-1} \quad (6)$$

2.5. Distribution of organic compounds in two phases

Separation and preconcentration by using micelle-mediated extraction methodology, together with the determination by different instrumental techniques for organic species in different matrices, had also proved itself as promising alternative procedure and have been given considerable attention by many researchers in the last decade. This method is based mainly on partitioning of non-polar organic solutes between the micellar (hydrophobic core) and aqueous phases. The efficiency of this procedure depends on the magnitude of analyte solubilization into the micellar (non-polar core and polar micelle-water interface), analyte polarity and solution composition [6]. Theoretically, extremely hydrophobic analytes show very favorable distribution constants between the micellar and aqueous phases, resembling

those observed with organic solvents. It is therefore estimated that maximum preconcentration factors that can be achieved coincide numerically with phase ratio [16]. In practice, the hydrated nature of the surfactant-rich phase leads to a smaller partition coefficient than those reported for organic solvents [17].

As with the traditional LLE, there are also many experimental factors that affect the partition of organic species between surfactant-rich and aqueous phases such as, surfactant concentration, time, acidity, additives and temperature to achieve high extraction efficiency by CPE [18-20]. In an attempt to study the equilibrium partition of PAHs, Li et al [21] derived some formulas that control separation/preconcentration processes and defined that the phase-volume ratio, R_V , as the ratio of the volume of the surfactant-rich phase (V_S) to that of the water phase (V_W), where the volume of the two phases were measured using graduated centrifuged tube,

$$R_V = \frac{V_S}{V_W} \quad (7)$$

The preconcentration factor, f_C , of each analyte as the ratio of the measured concentration of an analyte in surfactant-rich phase (C_S) to its initial concentration in bulk solution before phase separation (C_o), i.e.

$$f_C = \frac{C_S}{C_o} \quad (8)$$

The equilibrium partition coefficient K_P of an analyte in the CPE process is described as:

$$K_P = \frac{C_S}{C_W} \quad (9)$$

Where C_W is the analyte concentration in water phase after separation. The recovery efficiency, R , can be characterized as the percentage of an analyte extracted from bulk solution into the surfactant-rich phase,

$$\begin{aligned} R &= \frac{C_S V_S}{C_o V_t} \times 100\% = \frac{C_o V_t - C_W (V_t - V_S)}{C_o V_t} \times 100\% \\ &= \left(\frac{C_W}{C_o} \left(\frac{1}{1 + R_V} \right) \right) \times 100\% \end{aligned} \quad (4)$$

Where V_t is the total volume of the solution

2.6. Experimental procedure of CPE in metal analysis

Fig.4 represents the general steps that used in metal determination by combined CPE and any appropriate instrumental technique while Fig.(5) shows the experimental procedure for CPE in metal which revealed to the separation and preconcentration processes.

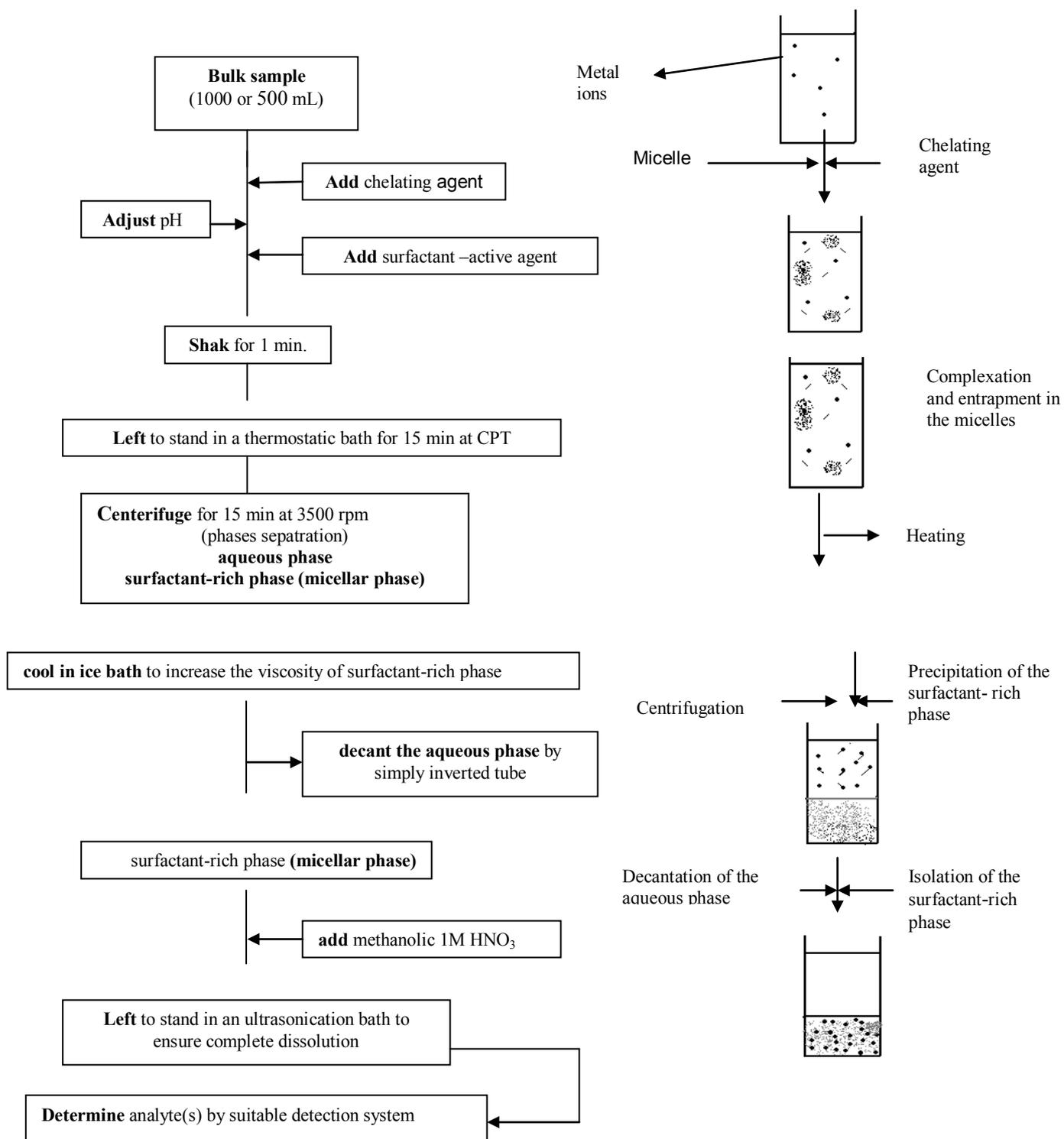


Fig 4. Flow chart of general systematic procedural

Fig.5. shows the experimental procedure steps for implementation of cloud-point extraction / preconcentration for metal ions determination for CPE in metal separation.

3. Applications of CPE in Atomic Spectrometry

The presence of metal ions at very low concentration levels in such complex matrices as natural, river, wastewaters, biological fluids, foods and environmental samples require pretreatments to release metals from these matrices and to enrich them prior determination. The CPE (or sometime called micelle-mediated extraction MME) coupled with atomic spectrometric techniques such as, atomic absorption spectrometry (AAS), Inductively-coupled plasma atomic emission spectrometry (ICP-AES) and Inductively-coupled plasma mass spectrometry (ICP-MS), can achieve the above-exigent demands and permit to design of extraction systems and analyses that are simple, cheap, of high efficiency, reducing in extraction time and environmentally-clean methodology due to low consumption of a solvent, apart from the results that comparable to those obtained with other separation procedures. This section will design to give some applications of specific cases of CPE in relation to the atomic spectrometric techniques that published in the last decade.

3.1. Flame Atomic Absorption Spectrometry (FAAS)

CPE technique has been successfully employed for the preconcentration of micro amounts of several metals in different matrices, as prior step before their determinations by FAAS. Table (1) synopsised the applications of PCE methodology when used with FAAS published through 1998-2008. During this period, the diversity of the applications of coupled CPE-FAAS has become extremely distinguished in the analysis of elements in different real samples, crossing the more complex matrices such as, biological, geological, environmental and food samples. In one paper of Brazilian researchers [22], CPE with Triton X-114 and *O,O*-diethyldithiophosphoric acid (DDTP) as hydrophobic chelating agent were used for perconcentration and separation of analytes in aqueous solution, allowing the determination, by FAAS, of ppb levels of Au and Ag in geological materials, after their acid dissolution. The technique gave an enhancement factor of 91 for Ag and 130 for Au with 0.05% m/v Triton X-114 and 100 μL of methanol, yielding the LODs of 0.46 and 0.53 ng mL^{-1} with linear ranges of 0-20 and 0-15 ng mL^{-1} for Ag and Au respectively. These authors have also described the extraction mechanism in CPE in way similar to the traditional LLE and found that the distribution ratio (*D*) depends mainly on ligand concentration in the aqueous phase which can be practically calculated from the normalized absorbance values. Germanium was successfully determined at trace levels in aqueous solutions by CPE methodology prior to HG-FAAS. Ge as quercetin complex was extracted at pH 6.4 into non-surfactant (Triton X-114), the surfactant-rich phase acidified with HCl and anti-foam solution added in order to quench foaming of surfactant during hydride generation [23]. This method gave an enhancement factor of 200 for Ge and under optimized conditions, the LOD and sensitivity of the CPE-HGAAS system were 0.56 and 0.0620 ng mL^{-1} respectively. A cloud point method allows for a new analytical potential of using surfactants for metal speciation, making FAAS is more selective, sensitive and inexpensive. In this respect, Paleologos and co-workers have been great devotees in this technique, in that they published three papers. In the first [24], the speciation of Cr was preformed using Triton X-114 as surfactant and, as chelating agents, ammonium pyrrolidinedithiocarbamate (APDC) for Cr (VI) and 8-hydroxyquinoline (8-HQ) for Cr (III). This method was based on separation and preconcentration of Cr(VI)-APDC system at pH 2.0 and Cr(III)-HQ system at pH 8.0 from bulk aqueous mixture by Triton X-114 and subsequently the surfactant-rich phase solutions of each species was aspirated directly into the flame of the AAS. A 30-mL solution containing both species gave an enhancement factor of 75 for Cr(III) and 120 for Cr(VI), yielding the LOD of 1.4 and 0.65 ng mL^{-1} and the calibration curves were rectilinear up to 130 and 85 ng mL^{-1} for Cr(III) and Cr(VI) respectively with good precision. In the second paper [25], they exploited the CP

phenomenon for the determination of free and tannin-bound iron in wine samples via a sequential extraction scheme by FAAS. The method was based on precipitation of tannins and related compounds, in NS mixture (TX-100 and TX-45) upon increase of the solution temperature. The surfactant-rich phase containing the tannins and the insoluble Fe fraction was directly aspirated into nebulizer of FAAS spectrometer after its take up with a methanolic solution of HNO_3 . The free Fe was determined in supernatant after CPE procedure using ammonium pyrrolidine dithiocarbamate (APDC) as a chelating agent. In this methodology, the calibration graph was rectilinear up to $0.35 \text{ mg Fe L}^{-1}$, with detection limits of $0.02 \text{ } \mu\text{g mL}^{-1}$ and RSD of 2.4%. In third article [26], they presented CPE –FAAS procedure for the determination of free and organically complexed Cu species in natural waters. The method was based on the neutralization of the electrostatic charge of the humate-metal complexes using a positively charged-surfactant in a high ionic strength solution. The resulting complexes were then dissolved in the micelles of a NS and were thus separated from the bulk aqueous phase. The free metal species were determined after complexation with APDC, and they reported that the procedure was easy, rapid, and free from interference and enabled LODs of 8.5 and $0.9 \mu\text{g L}^{-1}$ for bound and labile species to be obtained. Shemirani and his group [27] have also exploited the coupling of the CPE-FAAS for the analysis of the oxidation states of Cr in tap and river waters. They used Schiff base (N, N'-bis-(α -methyl salicylidene) propane-1, 3-diimine) as a chelating agent for CPE for the first time. The method was based on the reaction of Cr (III) with Schiff base for the formation of a hydrophobic complex, which was subsequently entrapped in the micelle phase (Triton X-114), and was thus separated from the bulk water sample for the determination of Cr (III) by FAAS. In the separated experiment, Cr(VI) was reduced to Cr (III) by addition of H_2SO_4 and methanol to sample solution; Cr (III) subsequently reacts with chelating agent and the total Cr was determined in a similar manner and thus the Cr(VI) concentration was determined from the difference between total Cr and Cr(III). The method gave the preconcentration factor of 67.5 yielding LOD of 0.1 ng mL^{-1} , linear range of $0.1\text{-}75 \text{ ng mL}^{-1}$ with relative standard deviation of 2.3% for both species. The method was validated by analyzing the certified reference material (BCR544). Recently, Kiran and co-workers [28] have developed the CPE procedure for speciation determination of Cr (III) and Cr (VI) in various environmental samples with FAAS. This method was rested on the complexation of Cr (III) with bis-[2-hydroxynaphthaldehyde] thiourea which was subsequently entrapped by the surfactant micelle (Triton X-100) and quantitatively extracted to the surfactant-rich phase after centrifugation, giving LOD around 0.18 ng mL^{-1} , with RSD of 2.13%. The application of CPE–FAAS for simultaneous multielements determination was plentifully utilized in recent years, in different types of samples [29-33]. The preconcentration of heavy nine cations at trace levels from water samples was successfully demonstrated by using CPE prior to FAAS [29]. Cations were taken into a complex with 8-quinolinol in an aqueous non-ionic surfactant, Triton X-114 medium and concentrated in the surfactant-rich phase by bringing the solution to the cloud-point temperature. The preconcentration of only 100-mL of the solution with 1% Triton X-114 and 10^{-3} M 8-quinolinol at pH 7.0, gave a preconcentration factor higher than 100 for most cations with LODs of 25, 75, 105, 33, 167, 16, 4.5, 130 and 35 ng L^{-1} for Cu^{2+} , Cr^{3+} , Fe^{3+} , Mn^{2+} , Pb^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} , respectively. In more recent article, Ghaedi and coworkers [33] have described the CPE procedure for the preconcentration of Cu, Ni, and Co ions in various samples. This procedure was depended on the complexation of the analyte ions with methyl-2-pyridylketon oxime (MPKO) in basic medium, quantitatively extracted to the phase rich in Triton X-114, following centrifugation and the metal ions were directly aspirated into nebulizer of FAA spectrometer after adding of 1.0 M HNO_3 in methanolic solution. At optimum conditions, the LODs (3SDb/m) of 1.6, 2.1 and 1.9 ng mL^{-1} for Cu^{2+} , Co^{2+} and Ni^{2+} with preconcentration factor of 30 and enrichment factor of 65, 58 and 67 for

Cu^{2+} , Co^{2+} and Ni^{2+} , respectively were obtained. The proposed procedure was applied to the analysis of biological, natural and wastewater, soil and blood samples. In conclusion, CPE opens a new avenue to widen FAAS applications in metals analysis due to increase the detection power, thus allowing that metal concentration at $\mu\text{g L}^{-1}$ or ng L^{-1} could be accurately determined in complex matrices.

Table 1. Cloud-Point Separation and Extraction with FAAS

Analyte	Sample	Chelating agent(s)	Surfactant material	Limit of Detection	Ref.
Ni	sea, river and	PAN	Triton X-1	6 ng mL ⁻¹	[34]
Zn	mineral water			8 ng mL ⁻¹	
Cd	tap water;	TAN	Triton X-114	0.099 ng mL ⁻¹	[35]
Cu	sea water;			0.27 ng mL ⁻¹	
Pb	river water;			1.1 ng mL ⁻¹	
Zn				0.095 ng mL ⁻¹	
Co	tap water;	TAN	Triton X-114	0.24 ng mL ⁻¹	[36]
Ni	river water			0.44 ng mL ⁻¹	
Mn	water	TAN	Triton X-114	0.28 ng mL ⁻¹	[37]
Cu	rain water; blood serum; human hair	DDTP	Triton X-100	0.94 ng mL ⁻¹	[38]
Cd	human hair	DDTP	Triton X-114	0.62 ng mL ⁻¹	[39]
Pb				2.86 ng mL ⁻¹	
Cu^{2+}	tap water	capric acid+octylamine	OP-10	0.01 $\mu\text{g mL}^{-1}$	[40]
Co	urine	TAN	Triton X-114	0.38 ng mL ⁻¹	[41]
Ag	waste water, rain , tap, river water	dithizone	Triton X-114	0.56 ng mL ⁻¹	[42]
Mn^{2+}	natural waters	PAR and PAN	OP-7	5 ng mL ⁻¹	[43]
Cd	water samples and cigarettes samples	dithizone	Triton X114	0.3 ng mL ⁻¹	[44]
Ni				1.2 ng mL ⁻¹	
Co	pharmaceutical samples	PAN, PAR 5-Br-PADAP	Triton X-114 + SDS	1.1 and 1.6 ng mL ⁻¹	[45]
Cd,Pb Cr, Cu, Zn,Ni	environmental samples	APDC	Triton X-100	WD*	[46]
Cd	mineral water and lake water	DDTP	Triton X-114	0.9 ng mL ⁻¹	[47]
Cd,Pb,Cu Cr,Zn,Fe Zn^{2+}	river water	APDC	Triton X-114	WD* 130 ngL ⁻¹	[48]
Mn(II)	natural water	PMBP	Triton X-100	1.45 ng mL ⁻¹	[49]
Mn	milk and water	PAN	Triton X-114	0.39 ng mL ⁻¹	[50]
Co				4.9 $\mu\text{g L}^{-1}$	
Ni				7.8 ng mL-1	
Pb				11 ng mL-1	
Pb	water and biological samples	PMBP	Triton X-114	1.49 ng mL-1	[51]

(Table 1 continued)

Analyte	Sample	Chelating agent(s)	Surfactant material	Limit of Detection	Ref.
Cu	enviornmental samples	NDTT	Triton X-114	0.22 ng mL ⁻¹	[52]
Cu	river and sea water	Cupron	Triton X-114	0.04 ng mL ⁻¹	[53]
Cu	food samples	BDAP	Triton X114	0.1 µg g ⁻¹	[54]
Ni				0.4 µg g ⁻¹	
Cd	drinking water	TAC	Triton X-114	0.077 ng mL ⁻¹	[55]
Pb				1.05 ng mL ⁻¹	

PAN [1-(2-Pyridylazo)-2-naphthol], **APDC** [ammonium pyrrolidinedithiocarbamate], **TAN** [1-(2-thiazolylazo)-2-naphthol], **PAR** [4-(pyridylazo)-resorcinol monosodium], **DDTP** ([*O,O*,-diethylthiophosphate]), **5-Br-PADAP** [2-(5-bromo-2pyridylazo)-5-diethylaminophenol], **PMBP** [1-phenyl-3-methyl-4-benzoyl-5-pyrazolone], **NDTT** [6-(2-naphthyl)-2,3-dihydro-as-triazine-3-thione], **TAC** [2-(2-thiazolylazo)-p-cresol], **WD**(without datum).

3.2. Electrothermal Atomic Absorption Spectrometry (ETAAS)

Although the coupling of CPE with FAAS has offered the spectacular results in relation to the sensitivity and detection limits in metal analysis, improvements would continue toward higher figures of merits for several analytes. In this sense, electrothermal atomic absorption spectrometry (ETAAS) is an efficient alternative, particularly because the organic matrix, consisting of the surfactant and residual organic substances from the digested material, can be eliminated at least in part during the gradual increase in temperature prior to the atomization of the analyte [56], thus reducing the risk of a potential spectral interferences and making the ETAAS more selective and efficient. Also, the presences of surfactants offer an excellent benefit to liquid sample drop deposited on graphite tube to be spread evenly on the graphite surface before analysis. Table (2) summarized the applications of CPE methodology when used with ETAAS published in recent years. Speciation analysis by CPE-ETAAS has also raised a great challenge to the sophisticated instrumentation and approaches that are employed in this domain, and encompass tedious analytical steps. Hu et al [57] have been proposed a new method for the determination of Cr species in different water samples. The method was based on the complexation of Cr (VI) with dibromophenylfluoride (Br-F) which could enter surfactant-rich phase (Triton X-100) after centrifugation, whereas Cr (III) remained in aqueous phase. Thus, an in-situ separation of Cr (VI) and Cr (III) could be realized Cr (VI) in surfactant-rich phase was analyzed by ETAAS and Cr(III) calculated by subtracting of Cr(VI) from the total Cr which was directly determined by ETAAS. A 10-mL water sample gave the quantitation limit for Cr (VI) as low as 0.01 ng mL⁻¹, relative standard deviation (n=6 at C= 2.0 µg L⁻¹) was 2.6% and recoveries in the range of 98.9-105.3% under optimized conditions. A cloud point method for the ETAAS determination of As (III) and As (V) in tap water and biological samples has also been presented [58]. The method was relied on the reaction of As (V) with molybdate to form a yellow heteropoly acid complex in H₂SO₄ medium and upon increasing the temperature to 55 °C; analytes are quantitatively extracted to the non-ionic surfactant-rich phase (Triton X-114) after centrifugation. A 100-µL of this solution plus 10-µL of 0.1% *m/v* Pd (NO)₃ were injected into the graphite tube. Total inorganic arsenic (III, V) was extracted similarly after oxidation of As (III) to As (V) and As (III) calculated by difference. This procedure yielded a preconcentration factor of 52.5 for only 10-mL of sample, giving linear range of 0.02-0.35 ng mL⁻¹ with LOD of 0.01 ng mL⁻¹ and RSD of 5%. The polyethyleneglycolmono-*p*-nonphenylether (PONPE 7.5) was used as nonionic surfactant for the preconcentration and

determination of mercury after complexation with 2-(5-bromo-2-pyridylazo)-5-(diethyl amino)-phenol (5-Br-PADAP) in biological samples by ETAAS with Pd as chemical modifier [59]. All significant variables for both the separation and determination steps were studied, including pH of extraction, surfactant, chelating concentration, pyrolysis and atomization temperatures, different modifiers and also the furnace aging. Under optimized conditions, the LOD was 0.01 ng mL^{-1} and $0.001 \text{ } \mu\text{g g}^{-1}$, calibration graph was linear with correlation coefficient of 0.9994 at levels near the LOD up to at least 10 ng mL^{-1} and RSD at 2.0 ng mL^{-1} Hg was 4.0%. Tatian et al [60] have published two papers related to the determination of Pb and Cd in biological sample using CPE-ETAAS [60-61]. In one paper, they exploited the multivariate optimization using factorial and Box-Behnken design to achieve optimum values of experimental parameters and the possibility to evaluate the interaction between variables with reduced number of experiments [61]. The use of *O, O* diethyl dithiophosphate (DDTP) as chelating agent and Triton X-114 and the graphite tube with platform treated with $500 \text{ } \mu\text{g}$ Ru as permanent modifier, allowed a satisfactory enrichment factor (16 for both analytes), detection limits (40 and 2 ng L^{-1} for Pb and Cd, respectively) and recoveries ranged from 97 to 118%.

Table 2. Cloud-Point Separation and Extraction with ETAAS

Analyte	Sample	Chelating agent(s)	Surfactant material	Detection limit	Ref.
Pb	water samples	5-Br-PADAP	Triton X-114	$30 \text{ } \mu\text{g L}^{-1}$	[62]
Bi	biological and water	dithizon	Triton X-114	$0.02 \text{ } \mu\text{g L}^{-1}$	[63]
As ³⁺	water samples	APDC	Triton X-114	$0.04 \text{ } \mu\text{g L}^{-1}$	[64]
Fe ³⁺	water samples	8-quinolinol derivatives	Triton X-100	WD	[65]
V ⁵⁺	water samples	8-quinolinol derivatives	Triton X-100	WD	
Ni ²⁺	water samples	PMBP	Triton X100	$0.12 \text{ } \mu\text{g L}^{-1}$	[66]
Mn ²⁺	water samples	PMBP	Triton X-100	$0.02 \text{ } \mu\text{g L}^{-1}$	[67]
Fe ³⁺	water samples	PMBP	Triton X-100	$0.08 \text{ } \mu\text{g L}^{-1}$	
Cu ²⁺	water sample	PAR	Triton X-114	5 ng L^{-1}	[68]

PAN[1-(2-Pyridylazo)-2-naphthol], PAR [4-(pyridylazo)-resorsinol monosodium], 5-Br-PADAP[2-(5-bromo-2pyridylazo)-5-diethylaminophenol], DDTP [*O,O*, -diethyldithiophosphate], APDC [ammonium pyrrolidinedithiocarbamate], PMBP [1-phenyl-3-methyl-4-benzoyl-5-pyrazolone], WD(without datum).

3.3. Inductively-coupled Plasma Atomic Emission Spectrometry (ICP-AES)

The versatility of ICP-OES makes it a good analytical technique for a wide variety of applications. This versatility is due not only to the large number of elements that can be determined rapidly at trace levels but also to the wide variety of sample types that can be analyzed using this technique [69]. Although, the possession of ICP-AES these features, but the separation and enrichment processes of metals from the complex samples are still demanded as an essential steps prior the final determination. Recently, CPE procedure was found to be increasingly compatible with ICP-AES technique, as a good tool of choice, due to it's successful in the separation /preconcentration of metals from different matrices and the surfactants used have shown little or modest effects on the and analytical sensitivity and sample transport into the plasma. Ortega et al [70-71] have used the non-ionic surfactant PONPE 7.5 to determine Gd and Dy by FI-ICP-EAS. In these two papers, both analytes were complexed with 2-(5-bromo-2pyridylazo)-5-diethylaminophenol (5-Br-PADAP). After phase separation, at 25 and $30 \text{ } ^\circ\text{C}$ for Gd [70] and Dy [71], respectively, the surfactant-rich phase was retained at pH 9.2 on micro-column packed with cotton. The analytes were then eluted

using 4 M HNO₃ at a flow rate of 1.5 mL min⁻¹ directly into the nebulizer of the plasma. Enhancement factor of 20 (for Gd) and 50 (for Dy) were obtained, giving LODs of 40 and 30 ng L⁻¹ respectively. Wuilloud and coworkers [72] used PONPE 5.0 for the determination of vanadium in parenteral solutions by FI-ICP-EAS. The vanadium was extracted as the V-(5-Br-PADAP) complex at pH 3.7 mediated by micelles of the PONPE 5.0. The extracted surfactant-rich phase (100-μL) was mixed with 100-μL of ethanol and this final volume injected into ICP-EAS. Under optimum conditions, the 50-mL sample solution preconcentration allowed raising an enrichment factor of 250-folds, giving LOD of 16 ng L⁻¹ and precision of 2.3% for 10 replicate determinations at the 2.0 ng L⁻¹ levels. The Brazilian researches [73] have developed a procedure for the simultaneous determination of traces amounts of Cd, Cr, Cu, Mn, Ni and Pb from saline oil-refinery effluents and digested vegetable samples by ICP-AES based on CPE. All metals were complexed with 5-Br-PADAP and extracted into a micellar phase of non-ionic surfactant type Triton X-114. Optimization of the procedure was performed by response surface method using Doehlert design and the principal components (PC) were used to simplify the multiple response analysis. Improvement factors of 22, 36, 46, 25, 65 and 39, along with limit of detection ($3\sigma_B$) of 0.081, 0.79, 0.38, 0.83, 0.28 and 0.69 ng L⁻¹, and precision (RSD% n=8 at 20.0 ng L⁻¹ levels) of 1.5, 2.2, 3.5, 2.6, 2.5 and 2.5 were obtained for Cd, Cr, Cu, Mn, Ni and Pb, respectively. A paper by Li and Hu [74], who employed the sequential CPE, combined with ICP-AES for the speciation of mercury in seafood. The method based on Hg²⁺ was complexed with I⁻ to form HgI₄²⁻ and the HgI₄²⁻ reacted with the methyl green (MG) cation to form hydrophobic ion-associate complex, then extracted into a micellar phase of non-ionic surfactant type Triton X-114, which sequentially formed methylmercury(MeHg⁺) in the initial solution by centrifugation. The surfactant-rich phase containing Hg (II) was diluted with 0.5 M HNO₃ for ICP-AES determination. The supernatant was also subjected to the similar procedure for the preconcentration of MeHg⁺ by the addition of a chelating agent (APDC) in order to form water-insoluble complex with MeHg⁺ which was then directly analyzed as described above. Under the optimized conditions, the extraction efficiency was 93.5% for Hg (II) and 51.5% for MeHg⁺, with enrichment factor of 18.7 for Hg (II) and 10.3 for MeHg⁺, respectively. The LODs were 65.3 ng L⁻¹ for Hg (II) and 94.6 ng L⁻¹ for MeHg⁺ (as Hg) with RSDs of 3.6% and 4.5%, respectively. Tavakoli et al [75] used 1,8-diamino-4,5-dihydroxy anthraquinone as chelating agent and Triton X-114 as non-ionic surfactant for simultaneous determination of Au and Pd in mine stones samples. After phase separation, the surfactant-rich phase was diluted with concentrated HNO₃ (65% w/w) and the analytes concentrations were determined by ICP-AES. The variables affecting the complexation and extraction condition were optimized and under these conditions, quantitative extraction of Au (III) and Pd (II) from 100-mL of the aqueous solution was performed. The calibration graphs were linear in the range of 0.5-1000 ng mL⁻¹ with LODs 0.5 and 0.3 ng L⁻¹ and enrichment factors were 8.6 and 20.2 for Au and Pd, respectively.

4. Applications of CPE in UV-Visible Spectrophotometry

UV-Vis. Spectrophotometry is still the most attractive and popular method that employ in different fields of chemical analysis, especially in quality control because of the simplicity of procedure, speed, precision and accuracy of the technique. The combination of spectrophotometric detection with cloud-point extraction was first proposed by Watanabe and co-workers [1-2] who studied the extraction for the preconcentration of Mn and Zn in water samples after complexation with 1-(2-Pyridylazo)-2-naphthol (PAN) using PONPE 7.5 as a micelle-mediated extracting. Since then, a number of articles have been published related to

the applications of CPE-spectrophotometry in metal ions and organic analysis in various samples.

Table 3. Cloud-Point Separation and Extraction with ICP-AES

Analyte	Sample	Chelating agent(s)	Surfactant material	Detection limit	Ref.
La ³⁺ Gd ³⁺	aqueous	HQ and Kelex 100	Triton X-114	WD*	[76]
Zr	water and alloy samples	quinalizarine	Triton X-114	0.26 µg L ⁻¹	[77]
Hf	saline media	dithizone	Tritone X-114	0.31 µg L ⁻¹	[78]
Cd				0.093 µg L ⁻¹	
Co				0.20 µg L ⁻¹	
Cr				1.2 µg L ⁻¹	
Mn				0.73 µg L ⁻¹	
La ³⁺ Eu ³⁺ Lu ³⁺	aqueous solution	HDEHP	Triton X-100	WD*	[79]
Be	tap, sea, mineral waters	1,8-dihydroxyanthrone	Triton X-114	0.001 ng L ⁻¹	[80]

HQ [8-hydroxyquinoline], **Br-PADAP** [2-(5-bromo-2-pyridylazo)-5-diethylaminophenol], **HDEHP** [di(2,4,4'-hexyl)phosphoric acid mono-2-ethylhexylester, DW: without datum

The extraction of Er(III) through CPE procedure with 2-(3,5-dichloro-2-pyridylazo)-5-dimethylamonophenol as chelating agent and PONPE 7.5 as non-ionic surfactant prior to spectrophotometric measurement was developed in 1997 by Sliva et al [81]. Under the optimal experimental conditions, the molar absorptivity was $1.27 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$, calibration plot of absorbance ($\lambda_{\text{max}} = 584 \text{ nm}$) vs. concentration was linear within the range $0.02\text{-}2 \text{ mg L}^{-1}$ with LOD of $1.48 \times 10^{-7} \text{ mol L}^{-1}$. Gd (III) in urine was determined by extraction methodology based on the formation of complexes with 2-(3, 5-dichloro-2-pyridylazo)-5-dimethylamonophenol, extraction of Gd (III) in the surfactant-rich phase of non-ionic surfactant (PONPE 7.5) and its determination by spectrophotometric technique at 592 nm [82]. This study reported that the preconcentration factors were 3.33, 10 and 25 for the standard, semi-micro and micro-scales with LODs of 4, 35×10^{-8} , 1.45×10^{-8} and $5.80 \times 10^{-9} \text{ mol L}^{-1}$, respectively. The method was applied successfully for the determination of total and free Gd (III) contents in real urine samples of patients. Simultaneous determination of Ni and Co in water samples was reported by Safavi et al [83]. The combined CPE- spectrophotometry was based on the complexation of both metal ions with 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA) and latter analysis by spectrophotometry using Triton X-114 as surfactant. Under optimal conditions, the calibration curves for Ni and Co were linear from 20 to 500 and 20 to 200 ng L⁻¹ with LODs of 10 and 7.5 ng L⁻¹, respectively. The main advantage of the method was simultaneous determination of traces of Ni and Co without the need for any chemometric method. Russian workers have introduced some water-soluble calixarenes derivatives as chelating agent in cloud point extraction of La (III), Gd (III) and Y (III) ions using Triton X-100 as nonionic surfactant [84]. They concluded that calix [4] resorcinarene phosphonic acid found to be the most efficient chelating agent exhibiting different pH-selectivity within La (III), Gd (III) and Y (III) in CPE. Shkoufi et al [85] have newly designed and constructed the fiber optic-linear array detection spectrophotometry (FO-LADS) using a cylindrical micro cell which exploited for simultaneous preconcentration and determination of cobalt and nickel after cloud point extraction. The method was rested on the chromogenic reaction of metal ions with PAN as

chelating agent and the preconcentration of formed complexes using Triton X-114 as nonionic surfactant. The remained phase after CPE was transferred into cylindrical micro cell located at the cell holder of FO-LADS where the spectra of Co and Ni complexes were collected and processed for ordinary and first derivative spectrophotometry. Under optimal conditions, the enhancement factor (for 10 mL of sample solution) were 198 and 199, yielding LODs of 0.2 and 0.04 ng mL⁻¹ and linearity in the range of 0.6-15.0 and 0.1-15.0 ng mL⁻¹ for Co and Ni, respectively. In this review period, Madrakian and Ghazizadeh [86] have reported the use of cationic surfactant CTAB to extract Mo (VI) from aqueous solution. The method was based on color reaction of Mo with bromopyrogallol red in the presence of KI at pH 1.0 glycine/HCl buffer media and micelle-mediated extraction of complex. Several analytical factors affecting the determination were studied and the figures of merits of the method were obtained. Under optimal conditions, linearity was obeyed in the range of 0.3-320.0 ng mL⁻¹ of Mo (VI), LOD of 0.1 ng mL⁻¹. The RSD and relative error for five replicate measurements of 65.0 ng mL⁻¹ were 1.1% and 1.9%, respectively. The interference effect of some anions and cations was also tested and the authors said that the method could be applied to the measurement of the Mo (VI) in steel and tap water and well water samples.

The applications of CPE with spectrophotometry for the analysis of organic compounds have also emerged in three articles. In one paper, the cloud point preconcentration of Vitamin K₃ (2-methyl-1, 4-naphthoquinone) and 1, 4-naphthoquinone after the reaction with aniline and later spectrophotometric simultaneous analysis by chemometric methods using Triton X-114 as surfactant was reported [87]. Several multivariate calibration methods were tested, including PLS, GA-PLS, PC-ANN and ITTFA. The authors claimed that the GA-PLC method was more accurate to model the considered chemical system for spectrophotometric determination of Vitamin K₃ and 1, 4-naphthoquinone after CPE. Results have shown that the preconcentration of 15-mL of sample solution permitted the detection of 0.05 and 0.08 µg L⁻¹ for Vitamin K₃ and 1, 4-naphthoquinone, respectively with linear calibration range of 0.25-10.00 µg L⁻¹ for 1, 4-naphthoquinone and 0.35-20.00 µg L⁻¹ for Vitamin K₃ measured at 425 nm and 330 nm and evaluated by linear regression. In another paper, a novel method for the spectrophotometric determination of malachite green in fish farming water samples after CPE has been described by Pourreza and Elhami [88]. The method was simply based on the extraction of malachite green mediated by micelles of nonionic surfactant (Triton X-100), dissolving the surfactant-rich phase in ethanol and measuring its absorbance by spectrophotometry at 630 nm. The effect of different variables such as pH, TritonX-100 concentration, CP temperature, and diverse ions were studied to establish the optimum conditions. Under the optimum conditions, calibration graph was linear in the range of 4-500 ng mL⁻¹ with LOD of 1.2 ng L⁻¹ and RSD of 1.48% and 1.13% (n=8) for 20 and 300 ng mL⁻¹ of malachite green, respectively. The application of least-squares support vector machines method (LS-SVM) in conjunction with CPE-spectrophotometric procedures has allowed for the efficient determination of nitroaniline isomers simultaneously in complex environmental samples. This methodology was developed by Niazi and co-workers [89] who managed to exploit the cloud-point phenomenon for quantitatively extract and preconcentrate the nitroaniline isomers (*m*-, *o* and *p*-nitroaniline) using Triton X-100 as surfactant and later simultaneous spectrophotometric determination by the application of LS-SVM in synthetic and real matrix samples. The absorbencies were measured at 251, 226 and 382 nm against blank, yielding the calibration graphs in the linear range of 0.2-20.0, 0.1-15.0 and 0.1-17.0 µg mL⁻¹ with detection limits of 0.08, 0.05 and 0.06 µg mL⁻¹ *m*-nitroaniline, *o*-nitroaniline and *p*-nitroaniline, respectively.

5. Applications of CPE in Flow Injection Analysis

Fernández Laespada et al [90] were the first to perceive and employ the combining CPE with FIA for the preconcentration of uranium, prior to its determination by flow injection. The non-ionic surfactant used was Triton X-114 and the reagent chosen to form a hydrophobic chelate of uranium was 1-(2-pyridylazo)-2-naphthol. However, their combination CPE/FIA procedure was not in fully automated because the sample preconcentration using cloud point extraction was implemented off-line in their experiment. The full automation of coupling CPE/FIA system was proffered for the first time by Fang and co-workers in 2001 [91]. They presented some remedies to cope with the technical difficulties that associated with cloud point phenomenon, separating the surfactant-rich phase from aqueous phase and detection trace amounts of analyte(s) in the presence of the highly scattering medium in an on-line FIA system, mainly via the use of a salting out agent to induce the CP phenomenon as well as of a collection column (packed with cotton) to entrap the analyte-containing surfactant aggregates. The developed method was applied for the determination of coproporphyrin in pretreated urine samples, giving LOD of 2.0 mg mL^{-1} and the calibration curve was linear from 46 to 2319 mg mL^{-1} ($r = 0.9996$). In the same year, couple of articles from Greece workers [92-93] has been published which highlighted for determining metal ions rather than organic compounds. In one paper, the combined CPE/FIA system was exploited for the differentiation and the selective speciation analysis of Cr species in different waters and dietary supplement tablets [92]. The method was rested on the reaction of Cr (III) with 8-hydroxyquinoline (8-HQ) in nonionic-surfactant solution (Triton X-114) yielding a hydrophobic complex, which then entrapped 'in situ' in the surfactant micelles while the Cr (VI) assay was based on its reduction to Cr (III) by sodium sulfite which subsequently reacts with 8-HQ in the similar manner and determined by FIA-fluorimetry. The optimum working conditions were allowed the reliable determination of Cr (III) and / or Cr (VI) at levels as low as $0.2 \text{ } \mu\text{g L}^{-1}$, in various samples even in those with complex matrix (sea water, pharmaceuticals). The authors concluded that the method can easily be employed not necessarily for the analysis of both species but alternatively for the determination of either of them in the presence of the other. An other group from Greece researchers has also developed, for the first time, on-line CPE/FIA-chemiluminescence(CL) to extract and preconcentrate metal species rapidly, avoiding the formation of hydrophobic complexes, using a mixed micellar medium [94]. In detail, the metal species were trapped inside the micelles formed in a mixed surfactant medium consisting of an anionic sodium dodecyl sulphonate (SDS) and a non-ionic (Triton X-114) surfactant. This mixture was clouded with the addition of sodium sulphate and filtered through a cotton-packed mini column, which retained the micellar phase. The other micellar carrier containing Triton X-114 carried this metal-containing micellar phase away leading the extract to chemiluminescence detection. This on-line configuration allowed for the preconcentration and determination of metal species at ng L^{-1} levels in complex matrices. The developed procedure was applied successfully for the determination of Cr in sea and wastewater, with LOD and LOQ of 0.5 and 2.0 ng L^{-1} , and the calibration graph was rectilinear from 2 to 200 ng L^{-1} ($r = 0.9996$, $n = 6$). The Argentinean research workers having a great deal of the development for the on-line CPE using different detection systems, resulting in publishing several of articles [70-71, 95]. Of these, the on-line incorporation of CPE to FIA associated with capillary zone electrophoresis (CZE) for simultaneously determining Dy and Fe at ppb levels in urine was described by Ortega et al, for the first time [95]. The solution containing the analyte and a solution containing the chelating agent (5-Be-PADAP) plus micelles of nonionic surfactant (PONPE 7.5), buffered to pH 9.22 were mixed on-line, at flow rates of 8.0 and 2.0 mL min^{-1} , respectively. Subsequently, the surfactant-rich phase was retained in a microcolumn packed with cotton and then eluted with $50 \text{ } \mu\text{L}$ acetonitrile directly into the CE vial. A 10-mL of sample solution gave an enhancement factor

of 200, yielding the LODs of $0.20 \mu\text{g L}^{-1}$ for Dy, and $0.48 \mu\text{g L}^{-1}$ for Fe and the calibration graphs were linear at levels near the detection limits up to at least $500 \mu\text{g L}^{-1}$. The successes that achieved by coupling on-line CPE/FIA system in metal analysis have attracted considerable attention in organic analysis particularly in biological, clinical and environmental samples. Recently, the determination of total serum bilirubin by using the improved on-line CPE/FIA-CL was depicted by Chinese research team [96], who reported that the key difference/ improvement of the present on-line CPE/FIA system compared to all previously published works for on-line systems, was that the collection column served a dual function: (1) to entrap the analyte-containing surfactant aggregates and (2) to provide CL emission (i.e. the collection column was mounted directly adjacent to the detector). The present approach was contributed to the overall increase in CL intensity thus the enhancement factor of near or more than 1000 (when bilirubin in the concentration range of $5\text{-}500 \mu\text{g L}^{-1}$ preconcentrated under salt-induced CPE conditions) was achieved. Using the optimum conditions, a good linear relationship was obtained in the range of $5\text{ to }120 \mu\text{g L}^{-1}$ with a detection limit(S/N = 3) of $1.8 \mu\text{g L}^{-1}$ and RSD% was 2.6% (n = 30) for $20 \mu\text{g L}^{-1}$ bilirubin. Table (4) summarized some other applications of PCE methodology when used with FIA published in chemical literatures.

Table 4 . Cloud-Point Separation and Extraction with FIA

Analyte	Sample	Chelating agent(s)	Surfactant material	Detection limit	Ref.
Al	parenteral solutions	Chrome Azurol S	PONPE 7.5	$1.12 \times 10^{-7} \text{ M}$	[97]
Gd	urine	Br-PADAP	PONPE 7.5	40 ng L^{-1}	[70]
Dy	urine	Br-PADAP	PONPE 7.5	30 ng L^{-1}	[71]
	Humic and natural water	none	CTAB+	$5 \mu\text{g L}^{-1}$	[98]
	Fulic acid		Triton X-11		
Al	parenteral solutions	none	PONPE 7.5	$200 \mu\text{g L}^{-1}$	[99]
Hg	water	dithizone	Triton X-100	$0.014 \mu\text{g mL}^{-1}$	[100]
Sb	Environmental & Biological samples	PDC	Triton x-114	$0.09 \mu\text{g L}^{-1}$	[101]

Br-PADAP [2-(5-bromo-2pyridylazo)-5-diethylaminophenol] , **CTAB** (Hexadecyltrimethylammonium bromide), **PDC** (ammonium pyrrolidine dithiocarbamate)

6. Applications of CPE in Chromatography

Application of the micelle-mediated extraction (or CPE) in aqueous media for the determination of trace organic targets in different matrices has acquired increasing attention in the last decade. Most applications of this methodology with the chromatographic techniques have markedly been exploited for the extraction and preconcentration of organic compounds whether in the environmental or biological samples prior to high performance liquid chromatography (HPLC). This was obvious from the copious publications of the combining CPE-HPLC compared to the other chromatographic techniques such as, gas chromatography (GC) or capillary zone electrophoreses (CZE). In this sense, the surfactant-rich phase is compatible with micellar and aqueous-organic mobile phase in LC, which facilitates the application of this analytical method [102]. However, in each case, a lot of experimental work

was dedicated to cope with the problems arising from the viscosity of micellar phase, its adsorption on the analytical column, and the broad overlapping peaks when UV detection is employed. While the CPE has found very little applications as a preconcentration step prior to GC as a result of the viscous nature of surfactant, which endangered blocking the capillary column [103-104]. This section will design to give some applications of specific cases of CPE in relation to the chromatographic techniques, mainly in the analysis of organic compounds in the last ten years.

6.1. High Performance Liquid Chromatography (HPLC)

The use of coupling the cloud point extraction procedure with HPLC for the extraction/preconcentration and determination of organic species in various matrices has received more attention than the other chromatographic techniques in the last decade. This is obvious, because the separated surfactant-rich phase is quite convenient with micellar and aqueous-organic mobile phase in LC, which facilitates the application of this analytical method. Generally, the selection of surfactant type is of significant importance provided that has favorable spectroscopic characteristics and low chromatographic retention time to allow the determination of the more polar analytes without need of a clean-up step to remove the surfactant. The analysis of polyaromatic hydrocarbons (PAHs) in environmental samples by using the combining CPE-HPLC was paid more and more attention in the last ten years, because of their carcinogenic and mutagenic characteristics. In this direction, the two groups of Spanish workers have published four articles during this period. The first group have attempted to use an anionic surfactant sodium dodecane sulphonic acid (SDSA) to extract 16 PHAs from polluted water samples [105] and sodium dodecanesulphonate (SDoS) induced by an acid to extract of several PHAs from different environmental samples (soils, sediments and sludges) prior to chromatographic analysis [106]. They suggested sequential steps followed by acid-induced cloud point extraction (ACPE) for the extraction of PAHs from environmental materials via the formation of three phases in the centrifuge tube from which the surfactant-rich phase was separated by the lowering the temperature to 0 °C, then this phase turned gelatinous, dense enough to be separated from liquid phase. The gelatinous phase made liquid and diluted to 2 mL with acetonitrile prior to inject in the chromatographic system equipped with fluorescence detector. The authors claimed that several substantial advantages were raised with the use of ACPE for solid-liquid extraction; that is, easily biodegradable surfactant solutions are used as extractants, low volume extracts are obtained, wet samples can be analyzed and no special equipment is required. The second group has used single nonionic surfactant polyoxyethylene-10-lauryl ether "POLE" [107] and mixed surfactants POLE with Triton X-100 and Brij30 as the preconcentration step followed by HPLC with fluorimetric detection for the determination of several PAHs in seawater samples [108]. The principle purpose of using the mixed surfactants was to decrease the cloud-point temperature of the mixture, therefore preventing the losses of the more volatile PAHs and favouring increases in total recovery of PAHs. The optimized CP method using the mixture of POLE/Brij30 followed by HPLC /fluorimetric detection allowed for the determination of 13 PAHs from seawater with LODs ranging from 23 ng L⁻¹ for benzo (a) pyrene to 231 ng L⁻¹ for benzo (ghi) perylene compared to 0.26 to 2.56 µg L⁻¹ without using the preconcentration step. Chen and his group [21] have studied the equilibrium partition of PHAs in CPE process in the presence of sodium sulfate in an attempt to enhance the phase separation of Tergitol 15-S-7 micellar solution by decreasing the ambient temperature. In recent study, Chen and co-workers [109] have employed three nonionic surfactants with molecular similarity (Tergitol 15-S-9, Neodo 25-7 and Tregitol 15-S-7) to study the effect of these micelle solutions on the performance of the CPE processes in preconcentration trace amount of PAHs consisting of two to five fused rings from aqueous solution at 25 °C by addition of sodium sulfate and

sodium phosphate. They indicated that the preconcentration factor could be enhanced either by increasing the salt concentration or by decreasing the initial surfactant concentration present in the micellar solution. With CPTs regulated at around 15 and 18 °C with addition of Na₂SO₄ and Na₃PO₄, the preconcentration factors of 30 and 45 were obtained from 1% micellar solutions of these three surfactants. In the other trend, the Chinese workers have exploited of using a new generation of surfactants such as the silicon-type surfactants(DC-190 and DC-193) as the cloud point extractants in the preconcentration and treatment for the water polluted by three PAHs, anthracene, phenanthrene and pyrene [110]. They inferred that (1) the two surfactants, had little UV absorbance, so can be injected into the HPLC with UV detector directly without any pretreatment, (2) had a lower water content in the surfactant-rich phase comparing with Triton X-114, thus the two surfactants and their mixture offered much smaller V_s in the same surfactant concentration, (3) for the preconcentration process prior to HPLC to determine the three PAHs, DC-190 was a good selection, which offered a high recovery, high preconcentration factor, low cloud point, and without any clean-up treatment before HPLC and (4) satisfactory extraction of three PAHs was achieved with the mixture of two silicon surfactants as extracting solution, which offered both low cloud point and high phase separating speed at the same time. In this review period, the same Chinese group has essayed to employ other silicon surfactants (PEG/PPG-18/18 dimethicone) for studying the equilibrium partition of the above-mentioned three PAHs in the cloud point extraction in these media for the first time [111]. They proved that the higher concentrations of the three PAHs in surfactant-rich phase, and the resulting higher concentrations factors (as high as 30-40) distribution coefficients ($\log K_d = 2.5-2.9$) were able to be achieved at the same time due to the low surfactant-rich phase volume. Table 5 synopsised the other analytical applications of CPE /HPLC in organic analysis of the different matrices.

The Chinese workers have also applied the coupling of CPE/HPLC for metal speciation analysis for the first time, in an attempt to determine the Cr (III) and Cr (VI) simultaneously in aqueous solutions [123]. The method was based on using diethyldithiocarbamate (DDTC) as chelating agent and Triton X-114 as the extracting agent. The baseline separation of the DDTC chelates of Cr(III) and Cr(VI) was realized on a RP-C₁₈ column with the use of a mixture of methanol-water-acetonitrile (65:21:14, v/v) buffered with 0.05 M NaAC-HAc solution (pH 3.6) as the mobile phase at a flow rate of 1.0 mL min⁻¹. The analytical characteristic data of the proposed CPE/HPLC for Cr (III) and Cr (VI) revealed that the concentration factor was 65 for Cr (III) and 19 for Cr (VI), with linear concentration ranges were from 50 to 1000 µg L⁻¹ for Cr (III) and 50 to 2000 µg L⁻¹ for Cr (VI), yielding LODs (3σ) of 3.5 and 5.2 µg L⁻¹ for Cr (III) and Cr (VI), respectively. The repeatability for 8 replicate injections of a mixture of 100 µg L⁻¹ of Cr (III) and Cr (VI) were 0.6 and 0.5% for retention time, 4.1 and 4.6% for the peak area, respectively.

6.2. Gas Chromatography (GC)

There is scanty articles appeared in the chemical literatures concerning the application of CPE as the preconcentration step prior to gas chromatographic analysis for the organic compounds. This is most probably ascribed to the viscous nature of surfactant-rich phase, which drive the separating column to work with low efficiency and/or the presence of the micelles type in surfactant-rich phase may interfere with the determination of the components of interest. Thus the clean-up step should be required prior to chromatographic analysis. In this sense, Ohashi et al [103] have developed a procedure for removing surfactants in a surfactant-rich phase before a GC measurement upon the determination of phenothiazine derivatives in spiked human serum. The method was rested on loading the sample solution obtained by CPE on a cation-exchange column conditioned with 2 mL of 0.5 M NH₃-CH₃OH,

2 mL of 0.1M HCl-CH₃OH and 2 mL of CH₃OH. After the column was washed with 6 mL of methanol, the adsorbed phenothiazine was eluted with 3 mL of a 0.2 M NH₃-CH₃OH solution. This elute was evaporated with a rotary evaporator then the resulting solution was taken into mini-vial and evaporated to dryness under reduced pressure. The residue was dissolved in 50 μ L of methanol containing an internal standard and the peak area ratio of the analyte and I.S. obtained from the gas chromatogram was determined against the amount of sample. The proposed method gave the linearity ranges from 12.3 to 82.1 nmol for pericyazine, from 9.0 to 90.2 nmol for chlorpromazine and from 14.9 to 37.3 nmol for fluphenazine with detection limit for three phenothiazine derivatives was about 2 nmol (1.5×10^{-6} M).

Table 5. Cloud-Point Separation and Extraction with HPLC

Analyte	Sample	Surfactant material	Detection system	Limit of Detection	Ref.
Phenol and Phenolic compounds water Polychlorinated	sea and waste	Genapol X-080	photodiode array	< 10 μ g L ⁻¹	112
dibenzo-p-dioxins	water samples	POLE	UV	0.26-16.84 ng L ⁻¹	113
Selected Herbicides	environmental samples	Genapol X-080	spectrophotometer	WD	114
Biogenic amine (benzoyl derivatives)	v trout samples	Triton X-114	Uv-Vis	0.01 mg L ⁻¹	115
Organophosphorus pesticides	aqueous samples	POLE and Genapole X-080	photodiode array	0.88-28.45 ng mL ⁻¹ 0.03-2.81 ng mL ⁻¹	116
Nodularin-R	natural waters	Aliquat-336	UV multi- wavelength	330 pg mL ⁻¹	117
Estrogens (four kinds)	wastewater treatment plant	Triton X-114	UV	0.25-5.0 ng mL ⁻¹	118
Arbidol	rat plasma	Triton X-114	UV	80 ng mL ⁻¹ LOQ)	119
Aesculin and aesculetin	Cortex fraxini	Genapol X-080	UV-Vis	WD	120
Sudan dyes	chilli powder	Triton X-114	UV	2.0-4.0 μ g kg ⁻¹	121
Osthole	rat plasma	Triton X-114	photodiode array	< 0.03 μ g mL ⁻¹	122

Genapol X-080 (oligoethylene glycol monoalkyl ether), **POLE** (polyoxyethylene 10 lauryl ether), **Aliquat-336** (tricaprylmethylammonium chloride), **WD** (without datum)

Recently, Sikalos and Paleologos [104] have proposed a technique based on microwave assisted back extraction of the analytes from the micellar extracts into a water immiscible solvent thus allowing for the first time the injection of micellar extracts into a GC apparatus. They applied the conventional CPE for nonionic surfactant (Triton X-114) and the acid-induced phase separation of anionic surfactant (sodium dodecanesulfonic acid [SDSA]) to preconcentrate a series of PAHs in aqueous and soil samples. The recommended method for

both nonionic and ionic extraction have achieved an enhancement factor of 70.1, 69.8, 67.5, 65.8, 70.5 and 71.2 with LODs (3σ) of 9.3, 9.9, 0.9, 1.6, 1.0 and 1.1 $\mu\text{g L}^{-1}$ for naphthalene, acenaphthene, fluorene, anthracene, fluoranthene and pyrene, respectively. In the other attempt, Zygoura et al [124] have applied the proposed technique of the microwave assisted back extraction to cloud point extracts [104] in order to enable combination with gas chromatographic determination of commercial plasticizers; diethylhexyladipate (DEHA) and acetyltributylcitrate (ATBC) in PVC food packaging film. The procedure was based on the isolation of the plasticizers DEHA and ATBC from aqueous simulants and their preconcentration into micelles of the nonionic surfactant (Triton X-114). The obtained surfactant-rich phase was treated with isooctane then the preconcentrated analytes were back extracted by short-term microwave application and the isooctane extract was subsequently injected into the GC with FID detection. The calibration curves obtained, following the suggested method offered the preconcentration factor of 60 for both DEHA and ATBC with calibration linearity from 50 to 2000 $\mu\text{g L}^{-1}$ for each analyte and LODs as low as 15 and 19 $\mu\text{g L}^{-1}$ for DEHA and ATBC, respectively. More recently, Shen and Shao [125] have testified the feasibility of employing CPE as a simple and effective alternative for recovery of alkaloids from much complex solid tobacco samples followed by GC-MS analysis. After dissolution of 35 mg of tobacco samples in 0.05% NaOH, 5 ml of filtrate (aqueous solution) was introduced to centrifugal tube, then certain amount of Triton X-114 stock solution and 100 μL of saturated NaCl were added, and the mixture was left to stand for 15 min in the water bath at 50 °C. The two phases were separated by a centrifugation for 10 min at 3500 rpm, and the surfactant-rich phase was back-extracted by addition certain amount of dichloromethane containing 0.365 g L^{-1} of the internal standard (n-heptadecane), the surfactant-rich phase was subsequently extracted by applying ultrasonication (80 W) for 10 min. The distinct layers were formed and 1 μL of the lower phase was injected into the GC. They reported that this procedure yielded recovery of nicotine of 80.4%, LOD of 7.1 $\mu\text{g g}^{-1}$ and RSD% for the seven alkaloids were in the range of 2.77-9.97.

6.3. Capillary Electrophoresis (CE)

The application of the CPE as a preconcentration step precedes the capillary electrophoresis analysis was first described by Spanish workers [126] who highlighted on the particular problems incorporated in its application in CE, particularly those concerning with the electrophoretic conditions in which the surfactant will not be adsorbed onto the capillary walls. In this trend, they studied the behavior of a surfactant-rich phase injected into a capillary electrophoresis system using different separation modes such as, micellar electrokinetic capillary chromatography (MECC) and capillary zone electrophoresis (CZE). They found that the surfactant content in the surfactant-rich phase injected into a bare fused silica capillary have markedly contributed in losing the efficiency and reproducibility both in the migration times and electrophoretic peak are. This dilemma was resolved by adding the cation surfactant CTAB to the separation buffer to form the dynamic coatings in the capillary and afforded reproducible results, although the half-life of the capillary was short. But the most satisfactory results were obtained by using nonaqueous media, acetonitrile-methanol, in the CZE mode, thus avoiding surfactant adsorption. The method was applied to the determination of triazines in tape and river water samples, giving good results. The same authors [16] have also studied the determination of concentration factors, recoveries and distribution coefficients for a set of triazine herbicides using cloud-point extraction coupled with capillary electrophoresis system equipped with a UV detector. They have deduced that the concentration factor of triazine herbicides decreases as the concentration of Triton X-114 increases, while extraction recovery was higher for solutions with a high concentration of

Triton X-114. The distribution coefficient between the Triton X-114 micelles and water K_c prior to CPE was also calculated for each triazine and related to the corresponding octanol-water partition coefficient K_{ow} . Recently, the application of combining of CPE / CE in the determination of trace metal ions has also demonstrated by Chinese workers and a couple of articles were appeared in chemical literatures. In this respect, Tang et al [127] have investigated the potential factors affecting the CPE preconcentration and subsequent CE separation of the PAN chelates of Co (II) and Cu (II). Non-aqueous buffer was used to avoid the adsorption of nonionic surfactant Triton X-114 and the metal-PAN complexes onto the capillary wall thus offering the reproducible electropherograms. The apparent concentration factor was 15.9 for Co (II) and 160.3 for Cu (II). The linear range was from 3 to 100 $\mu\text{g L}^{-1}$ for both Co (II) and Cu (II), yielding LODs of 0.12 and 0.26 $\mu\text{g L}^{-1}$ for Co (II) and Cu (II), respectively. This developed method was successfully applied to the determination of both ions in tap water, snow water, and flavor wines. More recently, Yin [128] has introduced a novel dual-cloud point extraction (dCPE) for sample pretreatment of capillary electrophoresis speciation analysis of mercury, in an attempt to overcome the drawbacks of traditional CPE. In dCPE, cloud point was carried out twice in a sample pretreatment. First, four mercury species, methylmercury (MeHg), ethylmercury (EtHg), phenylmercury (PhHg) and inorganic mercury (Hg (II)) formed hydrophobic complexes with 1-(2-pyridylazo)-2-naphthol (PAN). After heating and centrifuging, the complexes were extracted into the formed Triton X-114 surfactant-rich phase. Instead of the direct injection or analysis, the surfactant-rich phase containing the four Hg species was treated with 150 μL of 0.1% (m/v) L-cysteine aqueous solution and then back into aqueous phase by forming hydrophilic Hg-L-cysteine complexes. The obtained aqueous extract was injected in electrophoretic capillary as sample. Using 10 mL sample, 17, 15, 45 and 52 of preconcentration factors for MeHg, EtHg, PhHg and Hg (II) were obtained. The LODs were 45.2, 47.5, 4.1 and 10.0 $\mu\text{g L}^{-1}$ (as Hg) for MeHg, EtHg, PhHg and Hg (II), respectively. The method was validated by the analysis of the spiked natural water and tilapia muscle samples.

8. Future studies

The CPE has definitely opened new horizons in the development of contemporary analytical chemistry as a promising methodology in the separation and enrichment of metal ions and organic compounds in variety of matrices. In addition, it offers an eco friendly alternative to other separation/ preconcentration techniques and green chemistry concept can be employed here.

To increase the sensitivity and selectivity of the method, the extending in using the other and more efficient chelating agents are also required for metal ions assay in atomic spectrometry to obtain good enrichment factor and new detection limits, beside to make the simultaneous extraction and preconcentration of multi-elements in single sample experimental procedure as much efficient as possible. It appeared that without use of matrix modifiers in ETAAS analysis after CPE, high pyrolysis temperatures for some volatile elements were obtained. This status is clearly deserved an in-depth investigations of the matrix components and/or reagents that cause this stabilization. More efforts are also needed to automate the analytical procedure for metal analysis via the coupling of CPE with FIA-ETAAS in order to achieve more practical advantages.

On-line coupling of CPE with FIA have attained great progress in last few years. This approach offers new route of improving conventional analytical methods and makes the automated separation methods is feasible, easy and simple. However, more studies are desired to select new surfactants having structure free from chromophores to avoid interferences with analyte(s) determination when using UV / Visible detection system. In this sense, the silicon-

type surfactants as the cloud point extractants which have a little UV absorbance [109] could open for future researches, so the selected works in this area can be expected in near future to make the CPE methodology more versatile and benefits.

Expanding to metal speciation other than chromium will present substantial development in contemporary analytical chemistry and open the vast ways toward easy, simple and inexpensive routine analysis instead of using expensive instrumentations in this field.

The separation/preconcentration of low concentrations of medical drugs and pharmaceutical preparations, especially in biological, environmental and forensic matrices has not received any attention to date by using CPE. The contemplation in this topic will open up novel skylines in designing the procedural steps and widen the analytical applications of CPE in pharmacy, environment and forensic sciences.

The studies related to employment of reversed micelles are still scanty in dealing with extraction of whether metal ions or organic materials. In next years, I anticipate that the research workers will consecrate their efforts on the theoretical, practical approaches and capability of the reversed micelles for the separation/preconcentration of various types of compounds.

7. Conclusions

To draw conclusions of this review, the CPE methodology is providing an enormous number of advantages to those who practice extraction/preconcentration in analytical chemistry and research, presenting robustness, low cost, excellent extraction efficiencies and an exciting new green chemistry process can be employ here. In addition, the possibility of performing on-line analysis with most instrumental techniques which will open up an attractive alternative in the area of automated separation methods. Although many new coupling CPE with instrumental techniques have been developed so far, it is obvious that a far greater number of innovations in this domain of research will continue for the next years ahead. More theoretical backgrounds related to the mechanism of separation and preconcentration are also needed to go deeply in understanding the action of the factors controlling the behavior of micelle-mediated extraction.

References

1. Goto K, Fukue Y and Watanabe H (1977) Spectrophotometric determination of manganese with 1-(2-pyridylazo)-2-naphthol and a non-ionic surfactant. , *Talanta*, 24: 752.
2. Watanabe H and Tanaka H (1978) A non-ionic surfactant as a new solvent liquid-liquid extraction of zinc (II) with 1-(2-pyridylazo)-2-naphthol. *Talanta*, 25:585.
3. Watanabe H, in: Mitta K L, Fendler E J (Editors) (1982) *Solution behavior of surfactants*. Plenum Press, New York, USA, P. 1305-1316.
4. Pelizzetti E and Parmaura E (1985) Analytical application of organized molecular assemblies. *Anal Chem Acta*, 169:1.
5. Stalikas C D (2002) Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis. *Trends in Analytical Chemistry*, 21(1):343.

6. Paleogos E K, Giokas D L and Karayannis M I (2005) "Micelle-mediated separation and cloud-point extraction" *Trends in Analytical Chemistry*, 24(5):426.
7. Bhairi S M (2001) *A guide to the properties and uses of detergents in biological systems*. Calbiochem-Novabiochem Corporation publication, UK, pp. 6.
8. Pilot Chemical Company, Technical Bulletin, RFF705.10.52, 2744 East Kampar Road, Cincinnati, OH45241.
9. Shinoda K, Nakagawa T, Bamamushi B and Isemura T (1963) *Colloidal Surfactants*. Academic Press, New York and London P.129.
10. Manzoori J L and Bavili-Tabrizi A (2002) The application of cloud point preconcentration for the determination of Cu in real samples by flame atomic absorption spectrometry. *Microchem J*, 72:1.
11. <http://en.wikipedia.org/wiki/Micelle>.
12. Kawamorta S, Watanabe H and Haraguchi K (1985) Distribution equilibria of 2-(2-Pyridylazo)-5-methylphenol and its Zn (II) chelate between two phases separated from a micellar solution of a nonionic surfactant. *Analytical Science*, 1: 41.
13. Watanabe H, Kamidate T, Kawamorta S, Haraguchi K and Miyajima M (1987) Distribution of nickel(II), cadmium(II) and copper (II) chelates of 2-(2-Pyridylazo)-5-methylphenol in two phases separated from a micellar solution of a nonionic surfactant. *Analytical Science*, 3:433.
14. Saitoh T, Kimura Y, Kamidate T, Watanabe H and Haraguchi K (1989) Distribution equilibria of metal chelates with thiazolyazo dyes between two phases formed from an aqueous micellar solution of a nonionic surfactant. *Analytical Science*, 5:577.
15. Tagashira S, Onoue K, Murakami Y and Sasaki Y (1992) Simultaneous kinetic determination of nickel(II) and cobalt (II) with 5-octyloxy methyl-8-quinolinol in nonionic surfactant micellar system. *Analytical Science*. 8:307.
16. Carabias-Martínez R, Rodríguez-Gonzalo E, Moreno-Cordero B, Pérez-Pavón J L, García-Pinto C, Fernández Laespada E (2000) Surfactant cloud point extraction and preconcentration of organic compounds prior to chromatography and capillary electrophoresis *J Chromatogr A*, 902 (1): 251.
17. Hinze W L and Pramauro E (1993) A critical review of surfactant-mediated phase separation (cloud point extraction): theory and applications. *Crit. Rev. Anal Chem*, 24:133.
18. Klotz W L , Schure M R and Folry J P (2001) Determination of octanol-water partition coefficients of pesticides by microemulsion electrokinetic chromatography", *J Chromatogr A* , 930: 145.
19. Tomlin C D S (Ed.) (1997) *The pesticide manual*. 11th ed. British Crop Protection Council, Surrey (UK).

20. Terabe S, Otsuke K and Ando T (1985) Electrokinetic chromatography with micellar solution and open-tubular capillary. *Anal Chem*, 57: 834.
21. Li J-L and Chen B-H (2003) Equilibrium partition of polycyclic aromatic hydrocarbons in a cloud-point extraction process. *J of Colloid interface Science*, 263: 625.
22. Da Silva M A N, Frescura V L A, Aguilera FJ N and Curtius A J (1998) Determination of Ag and Au in geological samples by flame atomic absorption spectrometry after cloud point extraction. *J Anal At Spectrom*, 13:1369.
23. B y kbayram E and Volkan M (2000) Cloud point preconcentration of germanium and determination by hydride generation atomic absorption spectrometry. *Spectrochim Acta B*, 55: 1073.
24. Paleologos E K, Stalikas C D, Tzouwara-Karayanni S M, Pilidis G A and Kayarannis M I (2000) Micelle-mediated methodology for speciation of chromium by flame atomic absorption spectrometry. *J Anal At Spectrom*, 15:287.
25. Paleologos E K, Giokas D L, Tzouwara-Karayanni S M and Kayarannis M I (2002) Micelle mediated methodology for the determination of free and bound iron in wines by flame atomic spectrometry. *Anal Chim Acta*, 458:241.
26. Giokas D L, Antelo J, Paleologos E K, Arce F and Kayarannis M I (2002) Copper fractionation with dissolved organic matter in natural waters and wastewater-a mixed micelle mediated methodology (cloud point extraction) employing flame atomic absorption spectrometry. *J Environ Monit*, 2:505.
27. Shemirani F, Abknenar S D, Kozani R R, Nisarari M S and Mirroshandel A (2004) The application of cloud point extraction for preconcentration and speciation of chromium by flame atomic absorption spectrometry. *Canadian J of Anal Sci and Spectro*, 49(1): 31.
28. Kiran K, Kumar K, Prasad B, Suvardhan K, Lekkala R B and Janardhanam K (2008) Speciation determination of chromium(III) and (VI) using preconcentration cloud point extraction with flame atomic absorption spectrometry(FAAS) *J of Hazardous Materials*, 150(3): 582.
29. Farajzadeh M A and Fallahi M R (2006) Simultaneous cloud point extraction of nine cations from water samples and their determination by flame atomic absorption spectrometry. *Analytical. Science*, 22:635.
30. Lemos V A, daFranca R S and Moreira B O (2007) Cloud point extraction for Co and Ni determination in water samples by flame atomic absorption spectrometry. *Separation and Purification Technology*, 54:349.
31. Dallali N, Zahedi M M and Yamini Y (2007) Simultaneous cloud point extraction and determination of Zn, Co, Ni and Pb by flame atomic absorption spectrometry, using 2-guanidinobenzimidazole as the complexing agent. *Scientia Irenics*, 14(4): 291.

32. Ahmadi F, Khanmohammadi Niknam K and Jafrapour J (2007) Micelle-mediated extraction for preconcentration and determination of copper and zinc in real samples. *Eurasian J of Anal Chem*, 2(3):118.
33. Geady M, Shokrollahi A, Ahmadi F, Rajabi H R and Soylak M (2008) Cloud point extraction for the determination of copper, nickel and cobalt ions in environmental samples by flame atomic absorption spectrometry. *J of Hazardous Materials*, 150(3): 533.
34. Oliveros M C C, deBlas O J, Pavon J L P and Cordero B M (1998) Cloud point preconcentration and flame atomic absorption spectrometry: application to the determination of nickel and zinc. *J Anal At Spectrom*, 13: 547.
35. Chen J and Toe K C (2001) Determination of cadmium, copper, lead and zinc in water samples by flame atomic absorption spectrometry after cloud point extraction. *Anal Chim Acta*, 450:215.
36. Chen J and Toe K C (2001) Determination of cobalt and nickel in water samples by flame atomic absorption spectrometry after cloud point extraction. *Anal Chim Acta*, 434:325.
37. Toe K C and Chen J (2001) Determination of manganese in water samples by flame atomic absorption spectrometry after cloud point extraction. *Analyst*, 126: 534.
38. Manzoori J L and Bavili-Tabrizi A (2002) The application of cloud point preconcentration for the determination of Cu in real samples by flame atomic absorption spectrometry. *Microchemical J*, 72:1.
39. Manzoori J L and Bavili-Tabrizi A (2002) Cloud point preconcentration and flame atomic absorption spectrometric determination of Cd and Pb in human hair. *Anal Chim Acta*, 470: 215.
40. Kulichenko S A, Doroschuk V O and Lelyushok S O (2003) The cloud point extraction of copper (II) with monocarboxylic acids into non-ionic surfactant phase. *Talanta*, 59: 767.
41. Manzoori J L and Karim-Nezhad G (2003) Sensitive and simple cloud point preconcentration flame atomic absorption spectrometry: Application to the determination of cobalt in urine samples. *Analytical Science*, 19:579.
42. Manzoori J L and Karim-Nezhad G (2003) Selective cloud point and preconcentration of trace amounts of silver as dithizone complex prior to flame atomic absorption spectrometric determination. *Anal Chim Acta*, 484:155.
43. Doroschuk V O, Lelyushok S O, Ishchenko V B and Kulichenko S A (2004) Flame atomic absorption determination of manganese(II) in natural water after cloud point extraction. *Talanta*, 64: 853.
44. Manzoori J L and Karim-Nezhad G (2004) Development of a cloud point extraction and preconcentration method for Cd and Ni prior to flame atomic absorption spectrometric determination. *Anal Chim Acta*, 521:173.

45. Nascentes C C and Arruda M A Z (2003) Cloud point formation based on mixed micelles in the presence of electrolytes for cobalt extraction and preconcentration. *Talanta*, 61:759.
46. Giokas D L, Eksperiandova L P, Blank A B and Karayannis M I (2004) Comparison and evaluation of cloud point extraction and low-temperature directed crystallization as preconcentration tools for the determination of trace elements in environmental samples. *Anal Chim Acta*, 505: 51.
47. Coelho L Arruda M A Z (2005) Preconcentration procedure using cloud point extraction in the presence of electrolyte for cadmium determination by flame atomic absorption spectrometry. *Spectrochim Acta part B*, 60: 743.
48. Giokas D L, Paleologos E P and Karayannis M I (2005) Optimization of a multi-elemental preconcentration procedure for the monitoring survey of dissolved metal species in natural waters. *Anal Chim Acta*, 537: 249.
49. Sun Z, Liang P, Ding Q and Cao J (2006) Cloud point preconcentration of manganese (II) from natural water samples using 1-phenyl-3-methyl-4-benzotriazol-5-pyrazolone and Triton X-100 and determination by flame atomic absorption spectrometry. *Analytical Science*, 22:911.
50. Rod A R Borhani S and Shemirani F (2007) Cloud point preconcentration and flame atomic absorption spectrometry: application to the determination of manganese in milk and water samples. *European Food Research and Technology*, 223(5):1438.
51. Manzoori J L and Abodlmohammad-Zadeh H (2007) Extraction and preconcentration of lead using cloud point technology: application to its determination in real samples by flame atomic absorption spectrometry. *Acta Chim. Slov*, 54: 378.
52. Biparva P and Hadjmohammadi M R (2007) Cloud point extraction using NDTT reagent for preconcentration and determination of copper in some environmental water samples by flame atomic absorption spectrometry. *Acta Chim Slov*, 54:805.
53. Goudarzi N (2007) Determination of trace amounts of copper in river and sea water samples by flame atomic absorption spectrometry (FAAS) after cloud-point preconcentration. *J Braz Chem Soc*, 18(7):1348.
54. Lemos V A, Santos M S, David G T, Maciel M V and Bezerra M D (2008) Development of a cloud-point extraction method for copper and nickel determination in food samples. *J of Hazardous Materials*, in press
55. Portugal L A, Ferreira H S, dos Santos W N L and Ferreira S L C (2007) Simultaneous pre-concentration procedure for the determination of cadmium and lead in drinking water employing sequential multi-element flame atomic absorption spectrometry. *Microchim J*, 87: 77.
56. Borges D L G, de Veiga N M M S, Frescura V L A, Welz B and Curtius A J (2003) Cloud-point extraction for the determination of Cd, Pb and Pd in blood by electrothermal atomic absorption spectrometry, using Ru as permanent modifiers. *J Anal At Spectrom*, 18: 501.

57. Hu X Z, Jiang Z and Li M (2005) Cloud point extraction for speciation of chromium in water samples by electrothermal atomic absorption spectrometry. *Water Research*, 39(4): 589.
58. Shemirni F, Baghdadi M and Ramezani M (2005) Preconcentration and determination of ultra trace of arsenic(III) and arsenic (V) in tap water and total arsenic in biological samples by cloud point extraction and electrothermal atomic absorption spectrometry. *Talanta*, 65:882.
59. Aranda P R, Gil R A , Moyano S , De Vito I E and Martinez L D (2008) Cloud point extraction of mercury with PONPE 7.5 prior to its determination in biological samples by ETAAS. *Talanta*, 75:307.
60. De A Maranhão T, Borges D L G, da Veiga M A M S and Curtius A J (2005) Cloud point extraction for the determination of cadmium and lead in biological samples by graphite furnace atomic absorption spectrometry. *Spectrochim Acta B*, 60:667.
61. de A Maranhão Martendal T E, Borges D L G ,Carasek E, Welz B and Curtius A J (2007) Cloud point extraction for the determination of lead and cadmium in urine by graphite furnace atomic absorption spectrometry with multivariate optimization using Box-Behnken design. *Spectrochim Acta B*, 62:1019.
62. Chen J, Xiao A. Wu X, Fang K and Lui W (2005) Determination of lead in water samples by graphite furnace atomic absorption spectrometry after cloud point extraction. *Talanta*, 67: 992.
63. Shemirani F, Baghdadi M, Ramezani M and Jamali M R (2005) Determination of ultra trace amounts of bismuth in biological and water samples by electrothermal atomic absorption spectrometry (ET-AAS) after cloud point extraction. *Anal Chim Acta*, 534:163.
64. Tang A, Ding G and Yan X (2005) Cloud point extraction for the determination of AS (III) in water samples by electrothermal atomic absorption spectrometry. *Talanta*, 67:942.
65. Ohashi Ito A H , Kanai C, Imura H and Ohashi K (2005) Cloud point extraction of iron(III) and vanadium (V) using 80quinolinol derivatives and Triton X-100 and determination of 10^{-7} mol dm⁻³ level iron(III) in river water reference by graphite furnace atomic absorption spectroscopy. *Talanta*, 65:525.
66. Sun Z, Liang P, Ding Q and Cao J (2006) Determination of nickel in water samples by cloud point extraction preconcentration coupled with graphite furnace atomic absorption spectrometry. *J of Hazardous Materials*, 137(2): 943.
67. Liang P, Sang H and Sun Z (2006) Cloud point extraction and graphite furnace atomic absorption spectrometry determination of manganese (II) and iron (III) in water samples. *Colloidal and Interface Science*, 304: 486.
68. Jian-guo C, Heng-wu C, Shao-hong C, Li Land Ying-ying Z (2007) Determination of ultratrace amounts of copper (II) in water samples by electrothermal atomic absorption spectrometry after cloud point extraction. *Chem Res. Chinese U*, 23(2): 143.

69. Boss C B and Fredeen K J (1997) Concepts, instrumentation and techniques in inductively coupled plasma optical emission spectrometry. Second Edition, The Perkin-Elmer Corporation, USA, P5-1.
70. Ortega C, Gomez M R, Olsina R A, Silva M F and Martinez L D (2002) On-line cloud point preconcentration and determination of gadolinium in urine using flow injection inductively coupled plasma optical emission spectrometry. *J Anal At Spectrom*, 17(5): 530.
71. Ortega C, Cerutti S, Olsina R A, Silva M F and Martinez L D (2003) On-line complexation/cloud point preconcentration for the sensitive determination of dysprosium in urine by flow injection inductively coupled plasma-optical emission spectrometry. *Anal. Bioanal Chem*, 375(2):270.
72. Wuilloud G M , de Wuilloud J C A, Wuilloud R G ,Silva M F , Olsina R A and Martinez L D (2002) Cloud point extraction of vanadium in parenteral solutions using a nonionic surfactant (PONPE 5.0) and determination by flow injection – inductively coupled plasma optical emission spectrometry . *Talanta*, 58(4): 619.
73. Bezerra M A, Burns R E and Ferreira S L C (2006) Statistical design-principal component analysis optimization of a multiple response procedure using cloud point extraction and simultaneous determination of metals by ICP-OES. *Anal Chim Acta*, 580:251.
74. Li Y and Hu B (2007) Sequential cloud point extraction for the speciation of mercury in seafood by inductively coupled plasma optical emission spectrometry. *Spectrochim Acta B*, 62:1153.
75. Tavakoli L, Yamini Y, Ebrahimzadeh H, Nezhadai A, Shariti S and Nourmohammadian F (2008) Development of cloud point extraction for simultaneous extraction and determination of gold and palladium using ICP-OES. *J of Hazardous Materials*, 152(2):737.
76. De Jong, N Draye M, Favre-Réguillon A, LeBuzit G, Cote G and Foos J (2005) Lanthanum (III) and Gadolinium (III) separation by cloud point extraction. *J of Colloid and Interface Science*, 291: 303.
77. Shariati S and Yamini Y (2006) Cloud point extraction and simultaneous determination of zirconium and hafnium using ICP-OES. *J of Colloid and Interface Science*, 298:419.
78. Bezerra M A, do Nascimento Maêda S M, Oliveira E P, de Carvalho M and Santelli R E (2007) Internal standardization for the determination of cadmium, cobalt, chromium and manganese in saline produced water from petroleum industry by inductively coupled plasma optical emission spectrometry after cloud point extraction. *Spectrochim Acta*, part B, 62:985.
79. Ohashi A, Hashimoto T, Imura H and Ohashi K (2007) Cloud point extraction equilibrium of lanthanum(III), europium(III) and lutetium(III) using di(2-ethylhexyl)phosphoric acid and Triton X-100. *Talanta*, 73: 893.

80. Beiraghi A and Babae S (2008) Separation and preconcentration of ultra trace amounts of beryllium in water samples using mixed micelle-mediated extraction and determination by inductively coupled plasma-atomic emission spectrometry. *Anal Chim Acta*, 607:183.
81. Silava M F, Fernandez L P, Olsina R A and Stacchiola D (1997) Cloud point extraction, preconcentration and spectrophotometric determination of erbium (III)-2-(3, 5-dichloro-2-pyridylazo)-5-dimethylaminophenol . *Anal Chim Acta*, 342(1-2):229.
82. Silva M F, Fernandez L P and Olsina R A (1998) Monitoring the elimination of gadolinium-based pharmaceuticals. Cloud point preconcentration and spectrophotometric determination of Gd (III) - 2-(3, 5-dichloro-2-pyridylazo)-5-dimethylaminophenol in urine. *Analyst*, 123:1803.
83. Safavi A, Abdollahi H, Nezhad M R H and Kamali R (2004) Cloud point extraction, preconcentration and simultaneous spectrophotometric determination of nickel and cobalt in water samples. *Spectrochim Acta part A*, 60: 2897.
84. Mustafina A, Elistratova J, Burilov A, Knyazeva I, Zairov R, Amirov R, Solovieva S and Konovalov A (2006) Cloud point extraction of lanthanide (III) ions via use Triton X-100 without and with water-soluble calixarenes as added chelating agents. *Talanta*, 68: 863.
85. Shokoufi N, Shemirani F and Memarzadeh F (2007) Fiber optic-linear array detection spectrophotometry in combination with cloud point extraction for simultaneous preconcentration and determination of cobalt and nickel. *Anal Chim Acta*, 601: 204.
86. Madrakian T and GHazizadeh F (2008) Cloud point preconcentration and spectrophotometric determination of trace amounts of molybdenum (VI) in steels and water. *J of Hazardous Materials*, 153(1-2):695.
87. Abdollahi H and Bagheri L (2004) Simultaneous spectrophotometric determination of Vitamin K₃ and 1,4-naphthoquinone after cloud point extraction by using genetic algorithm based wavelength selection-partial least squares regression. *Anal Chim Acta*, 514: 211.
88. Pourreza N and Elhami S (2007) Spectrophotometric determination of malachite green in fish farming water samples after cloud point extraction using nonionic surfactant Triton X-100. *Anal Chim Acta*, 596: 62.
89. Niazi A, Ghasemi J and Yazdanipour A (2007) Simultaneous spectrophotometric determinations of nitroaniline isomers after cloud point extraction by using least-squares support vector machines *Spectrochim Acta part A*, 86:523.
90. Fernández Laespada M F, Pérez Pavón J L and Moreno Cordero B (1993) Micelle-mediated methodology for the preconcentration of uranium prior to its determination by flow injection. *Analyst*, 118:209.
91. Fang Q, Du M and Huie W (2001) On-line incorporation of cloud point extraction to flow injection analysis. *Anal Chem*, 73:3502.

92. Paleologos E K, Stalikas C D, Tzouware-Karayanni S M and Karayannis M I (2001) Selective speciation of trace chromium through micelle-mediated preconcentration, coupled with micellar flow injection analysis-spectrofluorimetry. *Anal Chim Acta*, 436: 49.
93. Giokas D I, Paleologos E K, Tzouware-Karayanni S M and Karayannis M I (2001) Single-sample cloud point determination of iron cobalt and nickel by flow injection analysis flame atomic absorption spectrometry-application to real samples and certified reference materials. *J of Anal. At Spectrom*, 16: 521.
94. Paleologos E K, Vlessidis A G, Karayannis M I and Evmiridis N P (2003) On-line sorption preconcentration of metals based on mixed micelle cloud point extraction prior to their determination with micellar chemiluminescence-application to the determination of chromium at ng L⁻¹ levels. *Anal Chim Acta*, 477:223.
95. Ortega C, Cerutti S, Olsina R A, Martinez L D and Silva M F (2004) Simultaneous determination of dysprosium and iron in urine by capillary zone electrophoresis coupled to cloud point extraction. *J Pharm and Biomed Anal*, 36:721.
96. Lu C, Song G, Lin J-M and Huei C (2007) Enhancement in sample preconcentration by the on-line incorporation of cloud point extraction to flow injection analysis inside the chemiluminescence cell and the determination of total serum bilirubin. *Anal Chim Acta*, 590:159.
97. Sombra L L, Luconi M O, Silva M F, Olsina R A and Fernandez L P (2001) Spectrophotometric of trace aluminum content in parenteral solutions by combined cloud point preconcentration-flow injection analysis. *Analyst*, 126:1172.
98. de Wuilloud J C A, Wuilloud R G, Sadi B B M and Caruso J A (2003) Trace humic and fulvic acid determination in natural water by cloud point extraction/preconcentration using non-ionic and caionic surfactant with FI-UV detection. *Analyst*, 128:453.
99. Sombra L L, Luconi M O, Fernandez L P, Olsina R A, Silva M F and Martinez L D (2003) Assessment of trace aluminium content in parenteral solutions by combined cloud point preconcentration-flow injection inductively coupled plasma optical emission spectrometry. *J Pharm and Biomed Anal*, 30:1458.
100. Garrido M, Di Nezio M S, Lista A G, Palomeque M and Frenández Band B S (2004) Cloud-point extraction/ preconcentration on-line flow injection method for mercury determination. *Anal Chim Acta*, 502:173.
101. Li Y, Hu B and Jaing A (2006) On-line cloud point extraction combined with electrothermal vaporization inductively coupled plasma atomic emission spectrometry for the speciation of inorganic antimony in environmental and biological samples. *Anal Chim Acta*, 576: 2007.
102. Frenández A E, Ferrera Z S and Rodriguez 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: 487.

103. Ohashi A, Ogiwara M, Ikeda R, Okasa H and Ohashi K (2004) Cloud point extraction and preconcentration for gas chromatography of phenothiazine tranquilizers in spiked human serum. *Analytical Science*, 20:1353.
104. Sikalos T I and Paleologos E K (2005) Cloud point extraction coupled with microwave or ultrasonic assisted back extraction as a preconcentration step prior to gas chromatography. *Anal Chem*, 77: 2544.
105. Sicilia D, Rubio S, Pérez-Bendito D, Maniasso N and Zagatto E A G (1999) Anion surfactants in acid media: a new cloud point extraction approach for the determination of polyaromatic hydrocarbons in environmental samples. *Anal Chim Acta*, 392: 29.
106. Merino F, Rubio S, and Pérez-Bendito D (2002) Acid-induced cloud point extraction and preconcentration of polyaromatic hydrocarbons from environmental solid samples. *J chromatgr A*, 962:1.
107. Pino V, Ayala J H, Afonso A M and González V (2002) Determination of polyaromatic hydrocarbons in seawater by high-performance liquid chromatography with fluorescence detection following micelle-mediated preconcentration. *J chromatgr A.*, 949:291.
108. Delgado B, Pino V, Ayala J H, González V and Afonso A M (2004) Nonionic surfactant mixtures: a new cloud-point extraction approach for the determination of PAHs in seawater using HPLC with fluorimetric detection. *Anal Chim Acta*, 518:165.
109. Hung K C, Chen B H and Yu L E (2007) Cloud-point extraction of selected polyaromatic hydrocarbons by nonionic surfactants. *Separation and Purification Technology*, 57: 1.
110. Bingjia Y, Li Y, Qiong H and Akita S (2007) Cloud point extraction of polycyclic aromatic hydrocarbons in aqueous solution with silicon surfactants. *Chin J Chem Eng.*, 15: 468.
111. Bingjia Y and Li Y (2008) Equilibrium partition of polycyclic aromatic hydrocarbons in cloud point extraction with a silicone surfactant. *J of Colloid Interface Sci*, 319: 316.
112. Santanna C M, Ferrera Z S and Rodriguez J S (2002) Use of non-ionic surfactant solutions for the extraction and preconcentration of phenolic compounds in water prior to their HPLC-UV detection. *Analyst*, 127: 1031.
113. Sanz C P, Ferrera Z S and Rodriguez J J S (2002) Extraction and preconcentration of polychlorinated dibenzo-p-dioxins using the cloud-point methodology application to their determination in water samples by high-performance liquid chromatography. *Anal Chim Acta*, 470:205.
114. Hilko R and Hutta M (2002) Study of high-performance liquid chromatographic separation of selected herbicides by hydro-methanolic and micellar liquid chromatography using Genapol X-080 non-ionic surfactant as mobile phase constituent. *Anal Chim Acta*, 466:325.

115. Paleologos E K, Chytiri S D, Savvaidis I N and Kontominas M G (2003) Determination of biogenic amines as their benzoyl derivatives after cloud point extraction with micellar liquid chromatographic separation. *J of Chromatogr A*, 1010:217.
116. Sanz C P, Halko R, Ferrera Z S and Rodriguze J J S (2004) Micellar extraction of organophosphorus pesticides and their determination by liquid chromatography. *Anal Chim Acta*, 524: 265.
117. Yu H, Man B K-W, Chan L L-N, Lam M H-W, Lam P K-S, Wang L, Jin H and Wu R S S (2004) Cloud-point extraction of nodularin-R from natural water. *Anal Chim Acta*, 509:63.
118. Wang L, Cai Ya-Qi, He B, Yuan C-G, Shen Da-Z, Shao J and Jiang G-B (2006) Determination of estrogens in water by HPLC-UV using cloud point extraction. *Talanta*, 70:47.
119. Liu X, Chen X-H, Zhang Y-Y, Liu W-T and Bi K-S (2007) Determination of arbidol in rat plasma by HPLC-UV using cloud point extraction. *J of chromatogr B*, 856: 273.
120. Shi Z, Zhu X and Zhang H (2007) Micelle-mediated extraction and cloud point preconcentration for the analysis of aesculin and aesculetin in *Cortex fraxini* by HPLC. *J Pharm and Biomed Anal.*, 44: 867.
121. Liu W, Zhao W-J, Chen J-B and Yang M-M (2007) A cloud point extraction approach using Triton X-114 for the separation and preconcentration of Sudan dyes in chili powder. *Anal Chim Acta*, 605: 41.
122. Zhou J, Wang S W and Sun X L (2008) Determination of osthole in rat plasma by high-performance liquid chromatograph using cloud-point extraction. *Anal Chim Acta*, 608: 158.
123. Tang A-N, Jiang D-Q, Jiang Y, Wang S-W and Yan X-P (2004) Cloud point extraction for high-performance liquid chromatographic speciation of Cr (III) and Cr (VI) in aqueous solutions. *J Chromatogr A*, 1036:183.
124. Zygoura P D, Paleologos E K, Riganakos K A and Kontominas M G (2005) Determination of diethylhexyladipate and acetyltributylcitrate in aqueous extracts after cloud point extraction coupled with microwave assisted back extraction and gas chromatographic separation. *J of Chromatogr A*, 1093:29.
125. Shen J and Shao X (2006) Determination of tobacco alkaloids by gas chromatography-mass spectrometry using cloud point extraction as a preconcentration step. *Anal Chim Acta*, 516:83.
126. Carabias-Martinez R, Rodriguez-Gonzalo E, Dominguez-Alvarez J and Hernandez-Mendez J (1999) Cloud point extraction as preconcentration step prior to capillary electrophoresis. *Anal Chem*, 71: 2468.
127. Tang A-N, Jaing D-Q and Yan X-P (2004) Cloud point extraction preconcentration for capillary electrophoresis of metal ions. *Anal Chim. Acta*, 507:199.

128. Yin X-B (2007) Dual-cloud point extraction as a preconcentration and clean-up technique for capillary electrophoresis speciation analysis of mercury. *J of Chromatogr A*, 1154: 437