

Pre-concentration of Some Heavy Metals using cloud point extraction

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Abstract - eavy metals are usually present in trace amounts in real samples such as natural waters, soil and plants samples but many of them are toxic even at very low concentrations, therefore, cloud point extraction (CPE) used for heavy metal separation. The CPE usage comes back to the works of Watanabe and co-workers who recommended the application of CPE by employing the non-ionic surfactants as an alternative solvent for the extraction of metal ions. In principle, CPE depends on the separation of hydrophobic analyte (i.e. inorganic and/or organic analyte) between two phases generated from micellar of non-ionic surfactant solution when heated to its critical cloud point temperature-CPT. In this review, CPE approach and features elucidated. The mechanism phenomena of CPE explained in addition to the methodology of analytical procedure by this process. Then, the significant applications of this method listed for separation of some heavy metals such as (Cd, Cu and Co). Finally, this review, mentioned the factors that affected on the CPE approach and results. In general, using this kind of analytical process provides a most reliable and trustworthy results with almost simplicity approach.

Keywords—Cloud point extraction, pre-concentration, heavy metals.

Introduction

1: Basic of Cloud-Point Extraction (CPE):

The potential of micellar systems as an alternative to organic solvent was extensively introduced in the extraction and preconcentration of metal ions and organic compounds and became one of the most preferred preconcentration steps for enhancing the sensitivity in metal and organic analysis and an important practical application in the use of surfactants in analytical chemistry(1). This methodology was named “cloud point extraction” and abbreviated as CPE or “micelle- mediate extraction ”abbreviated as MME. Since its birth, CPE has been developed considerably in two parallel directions, both in term of CPE methodology and the analytical detection systems that accompanied the determination of analytes. The advancement in CPE methods has allocated among using various types of surfactants, chelating agents, electrolytes, etc. in order to improve the optimum conditions of the analytical CPE procedure and scoring a desirable enrichment factor of the analytes besides thermodynamic studies to understand the solubolization mechanism of hydrophobic analyte in the micelles. Also, the development involves the combination of CPE with various instrumental analytical techniques to achieve the best figures of merit of the analyte to be determined(2,3).

It is impossible to understand the action of micelles in a given analytical method or to accurately predict the results of incorporating micelles into a new method of analysis without understanding of micelles themselves. This includes effects arising from molecular structure of amphiphile from which the micelle is derived and possible effect of the various substrates which might be present in the solution. Furthermore, the catalytic abilities of micelles must be recognized by the analyst as so much of the observed benefits of the use of micelles in analytical chemistry come from these abilities.

There are many other properties of micelles which would be of some importance to researchers desiring to use them in analytical methods(4). Surfactants are amphiphilic molecules that are mean containing together hydrophobic group (tails) which is regularly extended chain of hydrocarbon or aromatic ring operates to reduce solubility in water, along with hydrophilic groups (heads) due to the occurrence of a number of nucleophilic or electrophilic groups which is often ionizable as well as has the differing effect of tail(5). Figure (1.1) viewing a plain structure of surfactant tiny part(6).

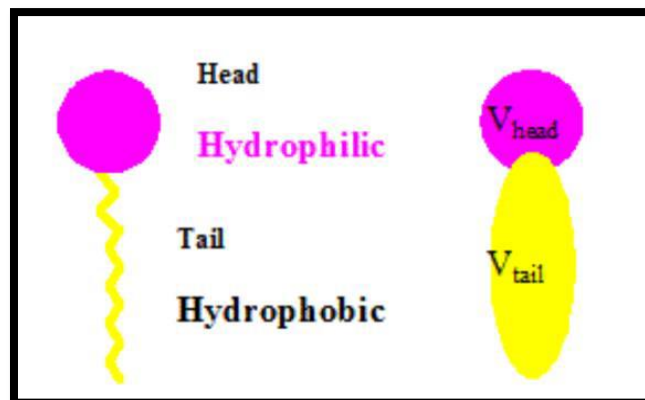


Figure (1.1): Simple structure of surfactant molecule

1.1: Selection and Properties of Surfactant:

To date, the majority of the applications of CPE for metal and organic analysis focused on employing non-ionic surfactants type mainly, polyoxyethylenated alkylphenols ranging from the triton family to PONPE series. This is because they are all commercially available of high purity grade, low cost, stable, non-volatile, non-toxic, balanced hydrophobicity and environmentally friendly(7). Surfactants belong to a group of association or amphiphilic organic substances. Amphiphilic molecules consist of an ionic or nonionic polar head group and a hydrophobic portion. The

formation of micelles or surfactant aggregates is primarily operated by three forces: the hydrophobic repulsion between the hydrocarbon chains and aqueous solution, the charge repulsion of ionic head groups, and the van der Waals attraction between the hydrocarbon tails(8). There are four types of general surfactants that are classified according to their charge on head group; non-ionic, cationic, anionic, and amphoteric (or zwitterions)(9). A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide and called polyethoxylated (POE or R-OCH₂CH₂O-) nonionics .

The cloud-point temperature depends on the structure of the surfactant and on its concentration. For ethoxylated nonionics which shows a peculiar behaviour with regard to temperature in a given temperature range, their solubility decreases with a temperature increase leading to surfactant precipitation at the “cloud point”. This anomalous behaviour of ethoxylated nonionics as well as the possibility to fine-tune the hydrophilic-lipophilic balance (HLB) makes them especially useful for bringing complex surfactant compositions to the phase-inversion temperature (PIT) conditions .

These surfactants are often referred to as polymeric ethers since they all contain common hydrophilic moiety of molecules, polyethylene oxide or polyethylene glycol, which has the repeated (CH₂CH₂O) n ether structure with n generally in a range of 10 to 100 units(10) .

1.2 : Separation Mechanism in CPE :

In fact, the mechanism of separation for the CPE process is some what similar to that of conventional liquid-liquid extraction which separates the desired analytes by their affinity in two immiscible (homogeneous) liquid phases. But, in CPE process, the only difference being the “organic” phase (micelles) is generated within the aqueous phase, converting a previously homogeneous solution to heterogeneous one by simply gathering its previously scattered hydrophobic suspension(11).

CPE is a simple and straightforward extraction procedure (figure 1.2). A surfactant typically nonionic is added to an aqueous solution containing the species of interest. The concentration of the surfactant must be above the critical micelle concentration (CMC) of the surfactant which allows the surfactant to organize and form micelles.

For metal ion extraction, a suitable chelating agent is added. In principle, the complexant should facilitate partitioning of the metal ion into the micelle by forming a hydrophobic complex with the metal. The properties of the aqueous solution are changed to reach the cloud point temperature (CPT),

this can be done by addition of salt or other surfactants or with heating. Upon reaching the CPT, the solution becomes cloudy and eventually separates into two phases: the aqueous phase and the surfactant rich phase (SRP). The aqueous phase contains surfactant at a concentration less than or equal to the CMC, while the SRP contains the majority of the surfactant. The SRP is significantly smaller in volume than the aqueous phase, allowing for pre-concentration of the target analyte. The phase separation is reversible upon mixing and cooling below the CPT, these two phases merge to form a clear phase again(12) .

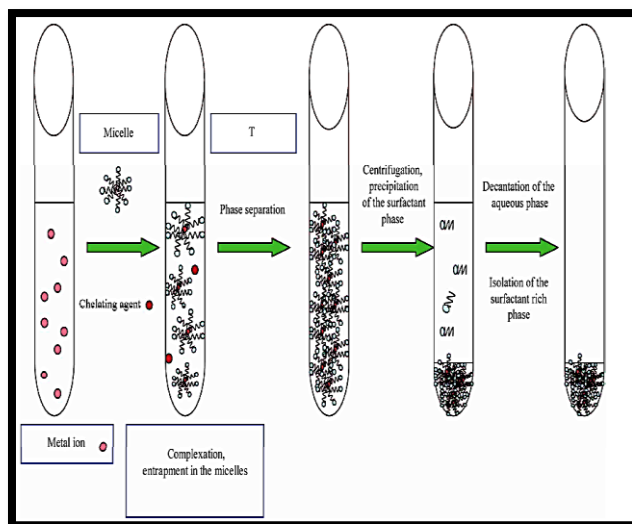


Figure (1.2): Separation mechanism in CPE process(13)

2: Thermodynamic Approach of CPE:

In fact, the clouding and separation mechanism phenomena in CPE are still to be defined exactly, several studies have shown that such phase separations result from the competition between entropy (which favours miscibility of micelles in water) and enthalpy (which favours separation)(14). An accurate explanation about cloud point phenomenon is still a controversy in the scientific literature. developed a model for explaining the phases separation in systems formed by non-ionic surfactants and water , at lower temperatures each surfactant’s molecules are evolved by a highly organized water layer, which forms hydrogen bonds with the polar head groups and with the polyoxyethylene units of non-ionic surfactants. When the temperature is increased, there is also an increase in the entropy, which causes the dehydration of polyoxyethylene chains and destroys the water molecules layer. From this point, the weak Van der Waals forces among the molecules make important contributions to micellar agglomerate formation and consequentially, the phase separation occurs(15). The formation of aggregates of micelles at the cloud point is obviously guided by thermodynamic principles.

At the phase separation temperature, the clouding components release their solvated water molecules and separate out from solution this can be considered as bthe limit of solubility . As phase separation is a reversible process, the chemical potential of species should be equal between surfactant-rich and surfactant-poor phases(16,17).

3: General Analytical Procedure for CPE:

CPE is a simple and straightforward extraction procedure and takes not more than half an hour to be accomplished after establishing the optimum conditions for the analyte determined. In fact, the experimental steps of CPE for metal and organic determination do not quite differ except in most cases the step of addition of chelating agent to metal ion to form hydrophobic complex to make easy extraction in the surfactant phase . But both producers engage in three simple main steps as follows; (1) solubilisation of the analytes in the micellar aggregates; (2) clouding; (3) phase separation for analysis(17).

In general, a typical CPE procedure for transition metal separation starts with an aqueous solution containing the

metal. Ligand and surfactant are added to the aqueous solution in suitable quantities. Depending on the solubility of the ligand, it may be added pre-dissolved in the neat surfactant or to the aqueous solution. The solution is mixed to homogenize and then heated above the cloud point temperature to promote phase separation. Once removed from heat, the sample is either placed on ice to increase the viscosity of the SRP or centrifuged to enhance phase separation. The SRP is typically on the bottom and the aqueous phase can be easily removed from the SRP for analysis.

High performance liquid chromatography, flame atomic absorption spectroscopy and UV-visible spectroscopy have all been used to analyze in CPE(18). Due to its viscosity the SRP is difficult to analyze and must be diluted for analysis with ICP or HPLC(18). The general CPE procedure in metal analysis can be implemented via experimental steps as shown in figures (1.3) and (1.4).

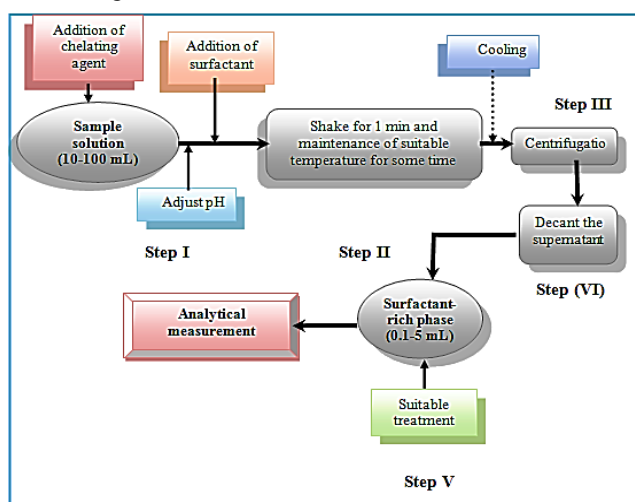


Figure (1.3): Flow chart of general systematic CPE procedure⁽¹⁹⁾

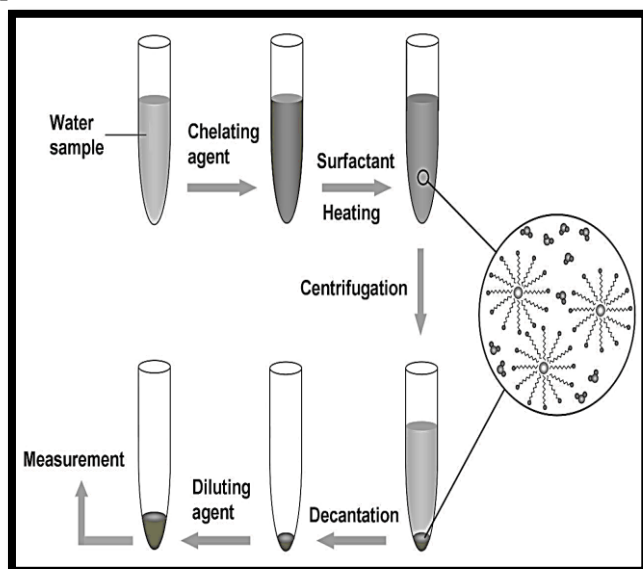
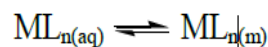
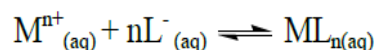
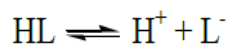


Figure (1.4): Schematic diagram of metal ion extraction in CPE procedure prior to its detection⁽¹⁹⁾

The extraction process involves several equilibrium and chemical species. Simply, the acid dissociation step of chelating reagent and the formation of a hydrophobic

chelate followed by its transference into a micellar phase can be represented by equations:



where $M^{n+}_{(aq)}$ and $L^-_{(aq)}$ are the metal and the ligand, respectively, in the aqueous phase, $ML_{n(aq)}$ is the complex in the aqueous phase, and $ML_{n(m)}$ is the complex in the surfactant phase. The distribution constant, K_d , the total formation constant, β_n , for the extracted species and the acid dissociation constant of HL , K_a , in aqueous phase is given by the following equations:

$$K_d = [ML_n]_m / [ML_n]_{aq} \text{ -----(1)}$$

$$\beta_n = [ML_n]_{(aq)} / [M^{n+}] [L^-]^n \text{ -----(2)}$$

$$K_a = [H^+] [L^-] / [HL] \text{ -----(3)}$$

Combining Eqs. (1)-(3) and rearranging gives:

$$[ML_n]_m / [ML_n]_{aq} = K_d \beta_n K_a [HL]^n [H^+]^{-n} \text{ -----(4)}$$

Since the distribution coefficient, D is given by:

$$D = \frac{(C)_m}{(C)_{aq}} = \frac{[ML_n]_m}{[M^{n+}]_{aq} + [ML_n]_{aq}} \text{ ----- (5)}$$

assuming that $[Mn]_{aq} > [ML_n]_{aq}$, and combining Eqs. (4) and (5) results in:

$$D = K_d \beta_n K_a^n [HL]^n [H^+]^{-n} \text{ ----- (6)}$$

Equation (6) shows that the distribution coefficient, D , is influenced by magnitudes of formation constant to specific cations with the complexing, by acid dissociation constant, the complexing reagent concentration, and the solution pH. These factors can be used to control the metallic ions extractions and must be evaluated to improve a method(9).

4: Heavy metals:

The term Heavy Metals refer to any metallic element that has a relatively high density and it is toxic or poisonous at low concentration(20).

Heavy metals are naturally occurring elements that a high atomic weight and a density at least 5 times more than that of water(21). Metals are vital for a huge number of physiological processes in the human body, But they can also destroy health when the concentration is not within the physiologically favorable range. Heavy metals are important environmental pollutants and many of them are toxic even at very low concentrations(22). Even essential trace elements can cause damage to health or even death at increased concentrations.

However, if the levels of these metals are higher than the levels of healthy life, the roles of these metals change to a negative dimension. The main sources of the heavy metal ions directly are food and water and, indirectly, industrial

activities and traffic(23). The form in which an element is ingested also plays a major role in its toxicity(24). Metals can directly influence the behaviour by impairing mental and neurological function, influencing neurotransmitter production and utilization, and altering numerous metabolic body processes(25). Copper, cadmium and cobalt are metals with known toxic properties(26).

Because of the serious effect of these metals on human life massive research was conducted in this field. Basim Y. Al-Khafaji et al.(27) were determined heavy metals Cd, Pb and Cu for river water samples which were collected from river of Euphrates close to the city center of Al-Nassiriya/southern of Iraq and the results showed that the mean of these elements was lower than the WHO values. Mohsin Azeed Mashkhood(28) estimated the heavy metals Cd, Pb, Cu and Ni of water samples from Marsh of Al-Chibayish in province of Thi-qar and the concentration of all heavy metals were not considered dangerous or significantly hazardous. AlKhafaji et al. (29) worked on some heavy metals Cu, Cd and Pb Bioaccumulation of in common carp related to their water concentration in and Al-Masab Alamm sediment for city of Al-Nassiriya and the results showed that the permissible Cu level of higher level accumulating in muscles and liver, whereas lowest was Cd. MustafaTüzen(30)was determined of heavy metals Cd and Cu in mushroom, plant, soil and samples via spectrometry of atomic absorption in Turkey and the results were high plants ratio to concentration of soil Cu and Cd indicating that mushrooms accumulating this element.

4.1: CPE for Cadmium Cd(II):

Cadmium is highly toxic even at very low concentrations causing damages to organs such as kidneys, liver and lungs (31). One of the pathways that cadmium enters human body is through daily intake of food and water, thus the monitoring of cadmium concentrations in food and water samples is of significant importance. The maximum contaminant level allowed by the American Environmental Protection Agency (US EPA) in standard drinking water is 10 µg.l⁻¹ to provide ample protection of human health. Monitoring trace element concentrations in biological materials, particularly biological fluids, might be considered a difficult analytical task (32), mostly due to the complexity of the matrix and the low concentration of these elements, which requires sensitive instrumental techniques and often a pre-concentration step. Concretely, spectrometric techniques for the analysis of trace cadmium have developed rapidly due to the increasing need for accurate measurements at extremely low levels of this element in diverse matrices(33). The major route of cadmium exposure for the general population is via food. An increase in soil cadmium content generally results in an increase of plant uptake of cadmium although some soil and plant factors may influence cadmium accumulation by plants.

Crops grown in cadmium contaminated areas have been found to contain elevated cadmium content compared with normal levels. Therefore, human cadmium exposure via food in contaminated areas can be many times above normal intakes and cadmium is known to be toxic for living and lead to cadmium toxicity organism even if it is present in low levels(34). Some techniques extraction have offered proper extraction proficiency and high pre-concentration factor. Be that as it may, they have introduced some of

impediments related to test pollution, moderately tedious or high cost, unbending control of the conditions, require an extensive volume of natural solvents and generally poor precision. In this manner the separation and pre-concentration of cadmium or other metal particles, after the arrangement of chelate, in view of cloud point extraction (CPE) as an option pre-concentration strategy to elective extraction strategies, in the light of its effectiveness, effortlessness ease, industrially accessible surfactant, velocity and security(35).

Countless manuscript have been available in the chemical literatures on the separation and pre-concentration of cadmium in unusual matrices through CPE methodology previous to its determination by means of different instrumental techniques as exposed in table (1.1).

Table(1.1): Cloud point extraction of Cadmium in different matrixes^(12,20,27)

Sample type	Chelating agent	Surfactant type	Detection system	PF	EF	LOD
Tap water	IDPI	Triton X-114	FAAS	26	31	0.15 µg.ml ⁻¹
soil, water and vegetables	CV	Triton X-100	Spectrophotometry	125	150	0.042 µg.ml ⁻¹
Milk and cigarette	IPAI	Triton X-114	FAAS	30	33	2.4 ng.ml ⁻¹
Natural water	PPT	Triton X-114	FAAS	100	-	0.38 µg.L ⁻¹

4.2: CPE for Copper Cu(II):

Copper is an essential element not only for life in mammals but also for plants, and it plays an important role in carbohydrate and lipid metabolism. It has many biological effects as an essential element as well as a toxic one(36). In general, a daily copper intake of 1.5-2 mg is essential for adults and copper at nearly 40 ng.ml⁻¹ is required for normal metabolism of many living organisms(36,37).

Copper is a moderately toxic element as compared to other transition metals(38). But, copper(II) at higher levels is toxic and severe oral intoxication will affect mainly the blood and kidneys. So, the trace copper(II) content in foods must be controlled on a daily basis and the European Commission has fixed the limit of 2µg.ml⁻¹ for copper(II) in drinking water and the allowed limit of copper(II) is set to 1.3µg.ml⁻¹ in the USA similar to that in Canada (1.0µg.ml⁻¹)(39). Therefore, there is an increasing need to monitor copper(II) levels in food samples at ever decreasing concentrations.

For this purpose, very sensitive, simple, rapid and inexpensive methods are necessary(40). Much interest and effort have been devoted on the studies for copper determination in water and biological matrices because it is a good tool for environmental and toxicological monitoring. The removal of copper from aqueous medium such as effluents also is of great interest for environmental and human health purposes(41). The determination of trace copper in biological samples is particularly difficult because

of the complex matrix and the usually low concentration of copper, which requires sensitive instrumental techniques and frequently a pre-concentration step(42).

CPE separation, high enrichment factor, low consumption of organic solvents, detection techniques, much more environmentally friendly properties and it is safer because small volumes of noxious surfactants are used instead of toxic organic solvents(43). Separation and pre-concentration based on CPE is becoming an important and practical application of surfactants in analytical chemistry. Table(1.2) compresses the uses of CPE for assurance of Cu(II) in various matrices.

Table (1.2): Cloud point extraction of Copper in different matrixes^(20,45,46)

Sample type	Chelating agent	Surfactant type	Detection system	EF	LOD
environmental, water and biological samples	ANPAP	Triton X-114	Spectrophotometry	250	1.2 ng.ml ⁻¹
Tap, stream and rain water	SPAR	Triton X-100	FAAS	31	1.64 µg.L ⁻¹
milk powder and mineral water	DDTC	Triton X-114	FAAS	-	1.1 ng.ml ⁻¹
rice flour and water samples	MPMP	Triton X-114	FI-FAAS	81	15 µg.l ⁻¹

4.3: CPE for Cobalt Co(II):

Cobalt is an essential trace element which is present in most body tissues, with the highest concentrations typically found in the liver. It is a component of vitamin B12 (cyanocobalamin), which is involved in the production of the blood red cells and the prevention of pernicious anemia. Cobalt toxicity is quite low compared to many other metals. However, high exposure to this element can cause several health problems such as asthma and skin irritation. Therefore, quantitative determination of cobalt at low concentrations plays an important role in different fields such as environmental analysis, process control and medicine(44).

Some of heavy metals like cobalt is necessary for human life(45). Most of spectrophotometric methods developed for the determination of cobalt are, unfortunately, not practically usable due to poor sensitivity and partly poor selectivity. Routine spectrophotometric methods are not often sensitive enough to determine low concentrations of cobalt ions in environmental samples only at the µg/l level.

Consequently, a pre concentration step is usually required. In spite of recent advances in instrumental analysis, a direct determination of trace elements in complex matrixes, such as environmental, biological, mineral, ore and high purity materials, seems still to be difficult because of insufficient sensitivity and selectivity of the methods. Thus, enrichment and separation of the analytes are important for the determination of Co(II), because of its extremely low concentration in natural water. Cobalt determination at trace levels in real samples has been frequently difficult because of low concentration of the metal and matrix interferences

(46). Flame atomic absorption spectrometry (FAAS) is one of the techniques most extensively used for determining various elements with a significant precision and accuracy. This analytical technique is remarkable for its selectivity, speed and fairly low operation cost. However, in some cases it is rather difficult to determine traces of heavy metals in environmental samples due to insufficient sensitivity or matrix interferences. Thus, a pre-concentration and/or separation step is necessary(47).

Table (1.3): compresses the uses of CPE for assurance of Co(II) in various matrixes.

Table (1.3): Cloud point extraction of Cobalt in different matrixes^(27,45,54)

Sample type	Chelating agent	Surfactant type	Detection system	PF	LOD
Water and B12,B-complex vitamins	MPMP	Triton X-114	FI-FAAS	-	0.21 µg. L ⁻¹
Water samples	BTANP	Triton X-114	FAAS	50	1.5 ng.ml ⁻¹
Water samples	MOSDAA	Triton X-114	FAAS	19	0.47 ng.ml ⁻¹
Tap, sea ,fish , black tea	1-PTSC	Triton X-114	FAAS	25	1 µg.L ⁻¹

5: Factors Affecting Cloud Point Extraction:

The performance of a CPE process is influenced by many factors, such as surfactant type and its concentration, ionic strength and equilibration temperature and time .

5.1: Type and concentration of surfactant:

Surfactant concentration plays an important role in phase separation as lower concentration makes the separation to be incomplete while higher concentration than the desired amount enhances the surfactant rich phase's viscosity which concurrently decreases its volume. Increasing the concentration of the surfactant also increases a number of surfactant aggregate complexes (48). Explicitly, surfactant plays a vital role in the CPE process. Thus, proper selection of surfactant could leads to satisfactory performance of the CPE process. There are several types of surfactants used in the CPE processes include Triton series and PONPE series (polyethylene glycol mono-4-nonylphenyl ethers). However, these surfactants contain alkyl phenyl groups in their hydrophobic moiety, leading to some environmental concerns. To overcome this problem, biodegradable surfactant, mainly polyethylene glycol or silicone surfactant without phenyl group is proposed(49). The main requirements for a surfactant to be selected as being suitable for the CPE experiments are associated mainly with its physicochemical characteristics: high density, which facilitates phase separation, low cloud point temperature, below or near room temperature in a narrow concentration range, for thermo labile molecules, balanced hydrophobicity, commercial availability and low cost(50). Depending on the nature of the hydrophilic group, surfactants are classified as non-ionic, zwitter ionic, cationic, and anionic. Nowadays, non-ionic, zwitter ionic and anionic surfactants are most widely used in the CPE

process for organic compounds, drugs, biomaterials and inorganic metal ions. However, the application of the cationic surfactants in the CPE is scarce. Since, it can directly affect the extraction and pre-concentration, and accuracy of the final analytical results, it is very important to select an appropriate surfactant for a successful CPE analysis(51).

5.2: Effect of ionic strength:

Generally, clouding is a phenomenon detected in non-ionic surfactants when the solution is heated to a threshold temperature which is known as clouding point temperature (CPT). The clouding phenomenon is uncommon with the ionic surfactants, presumably because of the large electrostatic repulsion between the aggregates that prevents phase separation in most cases. The phase separation occurs within a narrow temperature range into surfactant rich phase and aqueous phase, because of density difference due to a sharp increase in aggregation number of the micelles and the decrease in inter micellar repulsion. The CPT has been found extremely dependent on the presence of additives(8). Usually, the CPT of a non-ionic surfactant can be altered in the addition of additives, such as inorganic salt and organic compounds, into an aqueous solution. This phenomena is known as salting-out effect where the addition of neutral salts depresses the CPT of a nonionic surfactant aqueous solution in proportion to their concentration(52). Several factors have been considered to be responsible for the CPT phenomenon additives in the such as surfactant molecule and its system of CPE. However, CPT is very sensitive to the presence of additives used in the CPE system, even at a very low concentration.

The additives modify the surfactant-solvent interactions, change the CMC, size of micelles and phase behavior in the surfactant solutions. Many efforts has been made to investigate the effect of various additives e.g. inorganic electrolytes, organic compounds, ionic surfactant, cationic surfactant and zwitter ionic surfactants on the cloud point of a nonionic surfactant(53).

5.3: Equilibration temperature and time:

The optimum incubation time and equilibrium temperature are necessary to achieve an easy and efficient phase separation with Pre-concentration. The buildup of surfactant-rich phase are solely subjected by demeanor of the employed surfactant(54).

Theoretically, the phase separation can be achieved once the optimal equilibration temperature of the CPE which is higher than the CPT of the surfactant. If the temperature is lower than the CPT, two phases cannot be formed. However, too high temperature may lead to the decomposition of analytes. It has also been demonstrated that the analyte extraction efficiency and pre-concentration in the CPE increase as the equilibration temperature for phase separation is progressively increased to above the CPT. Similarly, as the equilibration temperature increases; the volume of surfactant rich phase decrease because the hydrogen bonds are disrupted and dehydration occurs. Based on a physical point of view, the increase of temperature provokes the dehydration of the hydrophilic groups of the surfactant molecules, an increase of the aggregation number and the swelling of the micelles until the micellar solution become turbid and the separation of the

surfactant rich phase takes place(55). Since longer equilibration times (> 30 min) do not have any significant effect on the extraction, the equilibration time of 10 – 20 min is sufficient to obtain good extraction in most work(51).
Conclusions:

Heavy metals contamination is becoming a serious issue of concern around the world as it has gained momentum due to the increase in the use and processing of heavy metals during various activities to meet the needs of the rapidly growing population. Therefore, Cloud-point extraction (CPE) methodology has constituted an important theme in the analytical chemistry as dependable procedure for the separation and pre-concentration for the metal ions from the complex matrices samples. Nowadays, it begins to take a large noteworthy position among the other modern separation methods in scientific research and application on a high level due to its simplicity, rapidity, more precise and cheapness beside an environmentally-friendly method.

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