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EXTRACTION AND PRECONCENTRATION OF MANY METALS IONS BY USING CPE TECHNIQUE

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ABSTRACT. Cloud point extraction is a simple, safe, and environmentally friendly technique for preparing many different kinds of samples. In this review, we discussed the CPE method and how to apply it to our environmental sample data. We also spoke about the benefits, problems, and likely developments in CPE. This process received a great deal of attention during preconcentration and extraction. It was used as a disconnection and follow-up improvement system before the natural mixtures (nutrients, polybrominated biphenyl ethers, pesticides, polycyclic sweet-smelling hydrocarbons, polychlorinated compounds, and fragrant amines) and inorganic mixtures were examined and many metals like (silver, lead, cadmium, mercury, and so on). We also find that combining CPE with various methods can yield good results by increasing the sensitivity of analysis and eliminating the effect of interference from the sample background.

KEY WORDS: Cloud point extraction, Preconcentration of metal ions, Surfactant, Medications, Biological matrix

INTRODUCTION

The cloud-point extraction (CPE) method was developed by Watanabe and Tanaka with the goal of preconcentrating metal ions from aqueous samples. It is commonly known that CPE-used surfactants can increase the solubility of hydrophobic compounds; this makes extraction technology environmentally friendly for many researchers and appealing to analytical chemists who are interested in alternative extraction systems [1]. Because CPE is easy to use, quick, and allows for convenient analyte extraction by adjusting experimental parameters such as salt addition, pH level, temperature, electrolyte type, extraction time, and surfactant concentration, it has attracted a lot of interest. The temperature at which two phases are created by stage partitioning of the surfactant: an aqueous phase and a surfactant-rich phase, above its critical temperature is referred to as the cloud point temperature. As a result, high preconcentration factor analyses are concentrated alongside [2]. CPE is a well-known effective extraction technique that just needs a small amount of solvent and a small amount of an environmentally safe not able to flame, and not volatile surfactant. A straightforward extraction approach, sample matrices riddance, and high extraction efficiency may all be achieved with this technology in a single step, according to our prior study on CPE [3]. Although there have been a few studies on the use of CPE in the study of organic compounds, ions of metal, medications, determined organic pollutants, and bioactive chemicals in the literature, none have addressed the use of CPE in environmental sample analysis. The successful extraction and preconcentration of the analyte by CPE were demonstrated in a recent work that used a water sample and combined CPE with second-order scattering (SOS) detection to analyze gold nanoparticles in ambient fluids.

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EXPERIMENTAL

Metal separation and preconcentration

The cloud point methodology is a simple method for metal determinations, which involves adding concentrated surfactant solution to an aqueous solution. Phase separation can be made easier by dissolving a chelating agent solution in water or an organic solvent and heating it over its cloud point [4]. After the micellar phase is separated, the bulk aqueous phase is removed as shown in Figure 1 by an ice bath due to increased viscosity of the surfactant-rich phase. To decrease the viscosity of the micellar phase and promote homogenization, small amounts of salting agent (such as alcohol) may be added after discarding the aqueous phase. The amount of organic solvent, metal concentration, and optimal viscosity must all be balanced when determining the salting agent quantity. The temperature is a highly experimentally changed condition for obtaining the cloud point. A diagram of the variations in surfactant concentration may be seen in a plot, which indicates the temperature at which the phase separation (cloud point temperature or just the cloud point) occurs [5]. Figure 2 shows the chemical structure of Triton X-114 commonly utilized surfactant for cloud point extraction. Figure 3 is split up into two areas. Only an isotropic phase appears in the aqueous solution for that specified by L. Nevertheless, a micellar phase and an aqueous phase separate at the region denoted by 2L, resulting in the formation of an anisotropic mixture that eventually splits into two isotropic phases.

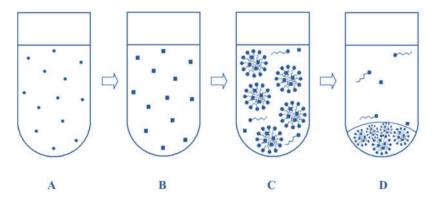


Figure 1. An illustration of a normal CPE to metal preconcentration is presented in the following ways: (A) the starter solution including low concentrations of metals (represented by circles); (B) metal chelates (represented by squares) created by adding a complexing reagent to the matrix solution; (C) adding a surfactant to the solution and trapping metallic chelates into micellar cores; and (D) micellar phase segregate following heating and separation following centrifugation.

The properties of surfactants and their formation in the microcellular medium

Organic compounds called surfactants are amphiphilic, involving an extremely tiny charged polar hydrophilic group and a lengthy hydrophobic hydrocarbon chain [6]. They have a R-X structure, with the hydrocarbon chain having 8-18 carbon atoms and the polar head group having X. Surfactants are classified into four groups: non-ionic, cationic, anionic, and amphoteric (Figure 4). The combination of hydrophilic and hydrophobic groups in a surfactant allows it to dissolve in water and other solvents. Surfactants also evaluate the structure of molecular aggregates that are organized microscopically by self-association in different solvents. Micellar media

applications in analytical chemistry include hydrophobic compounds become soluble in water and improve spectroscopic technique determination, enhanced effectiveness during nebulization and transport [7], in addition to catalysis of processes. Micelles are supramolecular structures with colloidal characteristics that naturally assemble in an aqueous solution upon reaching a critical micelle concentration (CMC). Molecules of surfactants generate micelles. The CMC of a surfactant depends on factors like molecular structure and experimental conditions. Micelles are not static structures but have a dynamic equilibrium with dissolved surfactant monomers. They may be damaged by water dilution when the surfactant concentration falls under its CMC, even though they are readily reproducible and thermodynamically inert [8] as show in Figure 5. The formation of a micelle decreases the entropy of the system, consuming free energy in its formation.

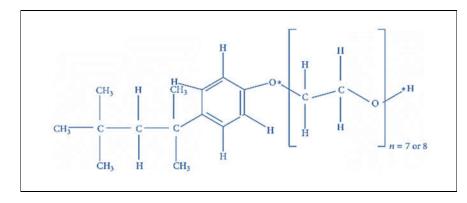


Figure 2. Chemical structure of Triton X-114.

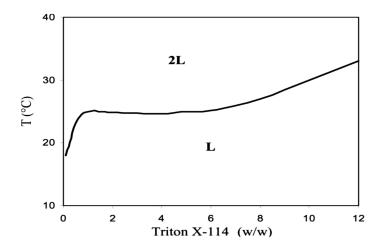


Figure 3. Phase diagram of the non-ionic surfactant Triton X-114 in an aqueous solution. L represents an area with just one isotropic phase, while 2L is an area where two isotropic phases coexist.

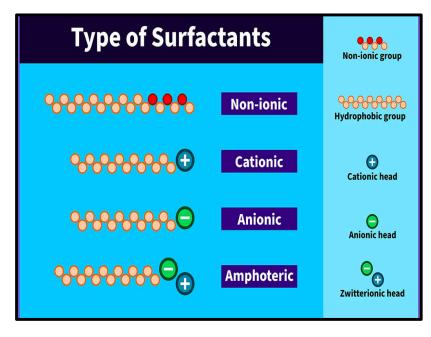


Figure 4. Types of surfactants.

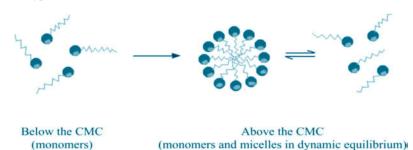


Figure 5. The micellar aggregate formation.

Micelles are organized structures that decrease the entropy of a system, allowing water molecules to attract themselves through hydrogen bonds [9]. In aqueous solutions, water molecules attract ionic or polar substances through hydrogen bonds, which are compensated by the hydration of dissolved species. Surfactants can be anionic, cationic, or zwitterionic, and their molecules present both anionic and cationic groups. When dissolved in aqueous solution above its CMC, the hydrophobic group distorts the water liquid structure, increasing free energy and compensating for the necessary work to create a surface area for micelle formation [10]. Micelles can dissolve chemical species with different polarities and sizes, with solubilization sites varying based on the characteristics of the surfactant and the solubilized substance. The binding site in a micelle is the hydrophobic core, and for the most modern techniques, the first stage is the generation of stable chelates. However, other micelle sites can iterate electrostatically with

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amphiphilic or charged substances like metallic ions, which is advantageous because iterating electrostatics with other substances is avoided. Examination methods like "Luconi and coworkers" extract lead with PONPE 7.5 surfactant without a chelating reagent, while extract copper in mixed micellar media of non-ionic surfactant OP-10 and monocarboxylic acids [11]. The surfactant-rich phase is another way to obtain copper. In the method of extraction, these surfactants function as both a micellar medium and a complex reagent at the same time.

Mechanism of metal extraction

Cloud point extraction (CPE) is a method used to extract metals from organic and aqueous phases [12]. The efficiency of CPE depends on the interaction of metallic species with micellar structures, which includes the phase transference of metallic substances or chelates into a micellar medium, the kinetics of the complexation reaction, and the creation constant of metallic complexes. The distribution of metallic chelates in CPE is different from conventional solvent extraction due to the hydrated nature of the surfactant phase. Chelating reagents are extracted due to a specific interaction between functional groups on the chelating reagents and ether oxygen or terminal OH group of non-ionic surfactants and chelates. Ionic strength is another aspect related to extraction efficiency, as it does not significantly modify the extraction efficiency [13]. A typical distribution coefficient, D, indicates the amount of metal division in CPE from the aqueous solution to the surfactant-rich phase. The extraction factor, E, is given by the expression Vs/Vw, where Vs/Vw is the phase volume ratio. Frankwick and Hinze studied the extraction factor, distribution coefficient, and phase volume ratio of hydrophobic substances extracted by two series of poly (oxyethylene glycol) monoesters surfactants. They came to the conclusion that a suitable nonionic surfactant should be highly hydrophobic and have a modest phase volume ratio to maximize its capacity to concentrate substances in cloud points.

Lead

Developed a CPE-FI-FAAS method for lead determination, using a surfactant-rich phase collected in a mini-column packed with cotton wool and eluted using an ethanolic solution. The flow system includes a peristaltic pump, tygon tubes, a thermostatic bath, and a four-way valve, presented an on-line CPE-coupled method for Pb determination, using USN to enhance sensitivity. This approach removes the require for heating equipment or salting-out agents, uses PONPE 7.5 without the need for a complexing reagent, and achieves separation straight in a PTFE mini column, skipping the centrifugation and freezing stages of a typical CPE technique. All of these features improve the analytical process. These two concepts offer advantages over batch procedures and simplify the analytical process [14].

Manganese

Azevedo and Teixeira report the construction of an online preconcentration system with CPE for the detection of Mn. Using FAAS, the system was utilized to calculate the Mn levels in food samples. From reagent mixing to detection, every stage of the CPE process was carried out online, which provided some advantages over batch CPE [15]. A combination of the reagent and surfactant complexes Mn(II). To allow further identification, the components are first desorbed with eluent acid while still on a mini-column as in table1 represent extraction of many transitions' element by different reagent and technique.

Silver

Silver nanoparticles (AgNPs) were selectively concentrated from environmental water samples using a method that did not alter their size or shape [16] The process involved adjusting the AgNP

sample solution to pH 3.0 with diluted HNO₃, adding 0.1 M Na₂S₂O₃ or 3.5 M NaNO₃ and 0.4 mL Triton X-114, incubating at 40 °C for 30 min, and centrifuging at 2,000 rpm for 5 min, following microwave digestion, the Triton-114-rich phase containing (AgNPs) was taken away for identification or characterization by TEM/SEM energy dispersive spectrometer/UV-VIS spectrum and ICP-MS.

Mercury

Cold vapor atomic fluorescence spectrometry was used to discover a cloud point extraction process for the combination preconcentration of Hg(II), methylmercury (MeHg), ethyl mercury (EtHg), and phenylmercury (PhHg) for fish speciation analysis [17]. The four different mercury species were heated to 40 °C to concentrate them in the surfactant-rich phase after mixing with ammonium pyrrolidine dithiocarbonate (APDC) in an aqueous non-ionic surfactant solution named Triton X-114. The enhanced complexes were separated using an RP-C18 column and a mobile phase consisting of a 65:15:20, v/v combination of methanol, acetonitrile, and water with 200 mmol L⁻¹ acetic acid (pH 3.5). The initial step towards the best probable cold vapor generation of mercury species was an online oxidation of the HPLC effluent in with the presence of K₂S₂O₈ in HCl. We evaluated the factors influencing the processes of complexation and separation. The results of the preconcentration of 10 mL of solution using 0.08% w/v Triton X-114 and 0.04% w/v APDC at pH 3.5 were MeHg, EtHg, PhHg, and Hg(II) enrichment factors of 29, 43, 80, and 98, respectively. The created technique was effectively used for recognizing the species of mercury in true fish samples.

Element	Reagent	Sample type	Method of detection	Ref.
detection				
Cu	I) 00,0-diethyldithiophosphate, Triton X-100	Drinking water,	FAAS	[18]
		blood serum,		
		human hair		
	II) N,N ⁰ -bis(2-hydroxyacetophenone)-1,2	Water, food and	Spectrophotometry	[19]
	propanediimine (L)	water samples		
	III) Amino acid (chelating agent), Triton X-	Certified defatted	Atomic absorption	[20]
	100	milk powder and	<u>^</u>	
		tea		
	IV) Triton X-100, octanol (cloud point	Water samples	Spectrometry (AAS)	[21]
	revulsion and synergic reagent)	<u>^</u>	· · · · ·	
	V) Monocarboxylic acids and their mixtures	Synthetic samples	Spectrophotometry	[22]
	with amines		· · ·	
	VI) N,N ⁰ bis(salicylideneaminoethyl) amine		Spectrophotometry	[23]
	(H ₂ L), Triton X-100		· · ·	
Zn	2-Methyl-8-hydroxyquinoline (quinaldine), 1-	Herbal remedies	FAAS	[24]
	(2-pyridylazo)-2-naphthol (PAN), Triton X-	and patient		
	114	samples of blood		
		with liver cancer		
Co	Polyethyleneglycolmonopnonyl phenylether	Drinking water	Electrothermal	[25]
	Triton X-100 and sodium dodecyl sulfate	sample tablets	atomic absorption	
	(SDS), pyridyl azo compounds 1-(2-	from various	spectrometry	
	pyridylazo)-2-naphthol (PAN),	medical products	(ETAAS), FAAS	
	octylphenoxypolyethoxyethanol (Triton X-	that have vitamin	Laser induced	
	114)	B12 tap, river, and	thermal lens	
		ocean water	spectrometry	
Zn	8-Hydroxyquinoline, Triton X-114	Mineral water in	Spectro- fluorimetry	[26]
	• • • • •	bottles		
		and food stuffs		

Cr	1-(2-Pyridilazo)-2-naphtol (PAN),	Water sample	Flame atomic	[27]
	Triton X-114	contaminated with	absorption	
	chelating agents, ammonium	leather Effluents	spectrometry	
	pyrrolidinedithiocarbamate for Cr(+6) and 8-	river and sea water	flame atomic	
	hydroxyquinoline for Cr(+3),		absorption	
	Triton X-114		spectrometry	
V	1-(2-Pyridylazo)-2-naphthol (PAN) and	Water samples,	FAAS	[28]
	hydrogen peroxide in acidic medium, Triton X-100	geological samples		
Hg(II)	HgI4 reacted with methyl green (MG) cation,	Sea food sample	ICP-OES	[29]
	octylphenoxypolyethoxyethanol	Tap water	ICP-OES	
	(Triton X-114)	Water samples	Spectrophotometry	
	Ammonium O,O-	Natural water and	IĈP-MŜ	
	Diethyldithio phosphate (DDTP), Triton X-	tilapia muscle	CVAAS	
	114,	samples	ETAAS	
		Human hair,		
		dogfish		
Fe(II)	2-(5-Bromo-2-pyridylazo)-5-	Beer sample	Spectrophotometry	[30]
	diethylaminophenol (5-Br-PADAP)	1	1 1 2	
Mn	Laboratory made reagent 4-(5-bromo2-	Food (corn flour,	Flame atomic	[31]
	thiazolylazo) orcinol (Br-TAO) and the	rice flour, and	absorption	
	surfactant Triton X-114	baby formula) and	spectrometry	
		biological (tomato	(FAAS)	
		leaves) samples	· /	
Mn and	1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone	Water sample	Graphite furnace	[32]
Fe	(PMBP), p-octylpolyethylene		atomic absorption	
	glycolphenylether (Triton X-100)		spectrometry	

Extraction and preconcentration of many metals ions by using CPE technique

RESULTS AND DISCUSSION

Principle of cloud point extraction

CPE is an environmentally friendly extraction technique that uses phase separation behavior to separate surfactant micelles from aqueous solutions. Surfactants are amphiphilic molecules with polar head groups and non-polar tails, which form micelles. The critical micellar concentration (CMC) [33] is the minimum concentration needed for this phenomenon to occur. When conditions like temperature, pressure, salt, and additives are altered, because the surfactant dissolves less readily in water, the mixture turns turbid at the cloud point (CP), CP varies in response to temperature, and varies between non-ionic and zwitterionic surfactants. Above the CP, the single isotropic micellar phase separates into two isotropic phases: the aqueous phase containing the surfactant at a concentration near the CMC and the surfactant-rich phase separated from the bulk aqueous solution. The micelles in a solution are driven to converge with the fluid by re-founding the initial arrangement conditions, resulting in the formation of a solitary isotropic stage that is reversible. The stage partition component is still being debated; some interpret it as a fast increase in micelle collection and a decrease in the intervals between micellar shocks due to decreased hydration of the polar group of surfactants with temperature increase [34]. Others propose that competition between internal-energy effects, entropic effects, and the miscibility of micelles in water leads to phase separation. Phase separation at the lower consolation point is driven by the effective inter-micellar interaction potential at that consolation point. The unique structure of surfactants allows for the solubilization of sparingly soluble or water-insoluble substances in aqueous solutions. Surfactant and analyte can interact electrostatically, hydrophobically, or a combination of the two. The CPE method extracts and preconcentrates analytes through phase separation and solubilization of surfactant solution. Figure 6 addresses schematic portrayal of the cloud point extraction.

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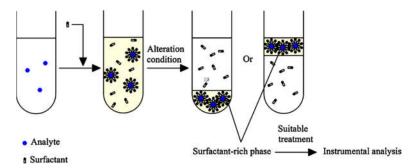


Figure 6. Schematic illustration of the extraction of cloud points. I: The first analyte containing solution; II: the analyte's solubilization in the micellar aggregating followed by the insertion of a surfactant solution (surfactant concentration > CMC); III: phase division into multiple phases followed by appropriate modification (temperature change or adding salt). After a suitable treatment stage, the analyte is preconcentrated A small amount of the surfactant-rich phase was sent for instrumental analysis.

Factors affecting on the efficiency of CPE

Surfactants are substances that reduce surface tension among binary phases, such as detergents, which lower the surface tension in greasy waste [35]. They are typically organic substances with hydrophilic heads and hydrophobic tails. When added to an oil-water mixture, the hydrophobic tail extends into the oil, disrupting the cohesive forces that hold water molecules together, resulting in a decrease in surface tension. Surfactant molecules create micelles to stabilize the contact between the two phases, physically separating them and reducing intermolecular interactions between water molecules. Surfactant concentration plays a crucial role in phase separation. If the concentration falls below a critical value, the separation is incomplete, while if it exceeds the critical value [36], the volume of the surfactant-rich phase decreases and its viscosity increases. The quantity of surfactant-aggregate complexes also increases with surfactant concentration. For example, the ideal concentration of Triton X-114 for measuring Ag⁺ ions using CPE is 0.35%, which yields the highest recovery.

Interaction of temperature and time

The ideal incubation period and equilibrium temperature are crucial for effective phase separation using preconcentration. The surfactant-rich phase formation is influenced by the surfactant's behavior, and short heating times are used to prevent mercury loss. Studies have shown that quantitative dissection can be achieved at temperatures of 25 °C in under 10 min. Extending extraction periods does not significantly improve separation, and inconsistent extraction can occur when salt is interrupted in the surfactant-rich phase [37]. The ideal extraction time for this approach is between five and ten minutes. When temperature rises over 40 °C, the solution evaporates, and the required analytes are lost. Separation is greatly reduced when the temperature is lower than room temperature, as the surfactant currently cannot function correctly.

Effect of salt

In the CPE process, the concentration of salt is very important. Because of the bulk aqueous phase becomes denser when salt is present, it can speed up phase separation in some nonionic surfactant systems. Moreover, accessible electrolytes can diminish the temperature of cloud point of

nonionic surfactant bringing about an extra effective removal. To concentrate because of the electrolyte, Na_2SO_4 was useful in fixations going from 0.3 to 0.8 M. As displayed in Figure 7, expanding the convergence of sodium sulfate salt $[Na_2SO_4]$ up to 0.5 M improves the extraction productivity. The extraction yield was nearly identical for " Na_2SO_4 " concentrations of 0.5 to 0.7 M. After 0.7 M, a conspicuous decline in the extraction effectiveness was noticed. The phenomenon known as the "salt-out effect," which intensifies the attraction between micelles and lastly causes surfactant molecules to precipitate, was the cause because of the increased extraction productivity that resulted from the expansion of 0.3- 0.5 M from same salt [38]. At the point when the concentrate is more than 0.7 M, the surfactant-rich stage will be on the outer layer of the arrangement, which makes it more troublesome, to isolate the extraction dissolvable into two stages, and the exactness and accuracy will endure appropriately. Considering the recently referenced discoveries, 0.5 M Na_2SO_4 was picked as the best to acquire the most noteworthy extraction proficiency [39].

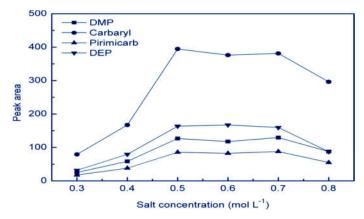


Figure 7. CPE impact of salt concentration. Surfactant concentration: 1% (v = v), equilibrium time: 30 min, equilibrium temperature: 40 °C, and sample pH: 5.0

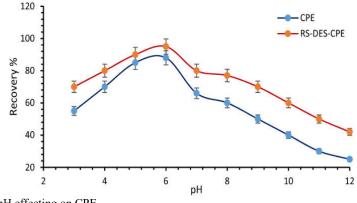


Figure 8. pH effecting on CPE.

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Effect of pH

The pH is a crucial parameter in the extraction process of metal-chelates, as it plays a significant role in the CPE approach [40]. A pH below 5 causes the recovery to decrease, as analytes in hydrophobic micelles with acidic solutions exhibit ionic characteristics, leading to negligible recovery. Higher pH values (above pH 8) cause analytes to deprotonate, preventing optimal separation and causing analyte concentration in the phase rich in surfactants to fall as shown in Figure 8.

Applications

Applications of cloud point extraction can be divided into eight general categories [41], separation of metal ions, including chromium, aluminum, and so forth, polycyclic aromatic hydrocarbon separation, polychlorinated compound separation, biological substances like proteins (casein, alpha-lactalbumin, etc.) being isolated, pesticide separation, extracting metal combinations and lanthanides from aqueous samples, distinguishing between fat-soluble vitamins, removing phenols, benzyl alcohols, and chlorophenols from aqueous samples.

Advantages of CPE

CPE is fascinating and provides several benefits. It has never been disregarded and is currently going strong with new environmental applications. Since these methods are the most straightforward and adaptable in order to get rid of hydrophobic species from solutions and perform preconcentration, they receive the most attention. CPE is promoted as a viable substitute due to its excellent fixation factor and recuperations; it is recommended for separation and preconcentration strategies [42]. In recent years, CPE works at room temperature as opposed to high temperature, and it is combined with a variety of instruments like gas chromatography flame photometric identification (GC-FPD). CPE is additionally employed with FAAS and Tween 80 to determine the trace quantities of ions such as Pb⁺², Ni⁺², Cu⁺², Cd⁺², and Cr⁺³. The formation of CPE has been widely employed in new studies to identify silver ions from water samples that have been pre-concentrated. The procedure has been combined with sodium diethyl dithiocarbonate as a chelating substance and Triton X-114, a non-ionic surfactant. Furthermore, CPE adheres to the "green chemistry" concept, which is a process for reducing the use of hazardous materials that are harmful to the public's health and the environment. Because it uses inexpensive, media-diluted extractor solutions as a surfactant, which produces less residues, it is regarded as a green technique.

Limitation of CPE

The complexity of surfactants in detecting PAHs can limit the number of analytes discovered, making it challenging to obtain specific compounds for a micellar system. Non-ionic surfactants extract polar molecules less efficiently, and temperature limits phase separation when extracting thermally labile parts. Some extracts must be further treated before measurement, and automation can be challenging. Surfactants can produce analytical interference and impact detection range, especially if the analyte is unable to properly separate from the surfactant [43]. The CPE technique has limitations due to increased absorbance in the UV area. Fluorometric signals are mainly derived from surfactants with double bond topologies, such as PONPE series, Gopal series, and Triton series. Other extracting agents, such as polymeric anionic surfactants and primary ethoxylated alcohols, have been experimented with to mitigate difficulties. Anionic surfactants are often used as effective extractants in CPE separation, but they can interfere with UV absorbance problems to overcome this, surfactants that are unable to absorb at the operating

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wavelengths commonly used in chromatography are used. Triton X-114, known for its ability to form micelles, is used for its ability to mask PAHs signals in HPLC analysis. However, its use is prohibited due to environmental concerns. Similarly, zwitterionic surfactants 3-(decyl dimethylammonium) propyl sulfate (C_{10} APSO₄) and 3-(nonyl dimethylammonium) propyl sulpate (C_{9} APSO₄) is used, which are not absorbent at the operating wavelengths typically used in chromatographic procedures used Triton X-114 for pesticides with organophosphorus via liquid chromatography analysis following the cloud point, utilizing dual electrochemical techniques (reductive-oxidative mode). However, this approach has significant extreme fluorescence signals when an excitation frequency is applied, and foundation assimilation in the UV region is employed, covering all analytes with low retention times in the ultraviolet region.

Newly developed in CPE techniques

CPE (chemical electrophoresis) is a popular and adaptable method for hydrophobic species removal from aqueous solutions and preconcentration environments. Its strong yields and concentration factor make it an attractive option for separation in conjunction with preconcentration processes. CPE has been used in various applications, including gas chromatography flame photometric identification, high performance liquid chromatography, and electrochemiluminescence capillary electrophoresis. It has also been successfully applied in detecting low amounts of Bi⁺³, Cd⁺², Cr⁺³, Cu⁺², Ni⁺², and Pb⁺² ions. In a recent study, CPE was successfully used to separate and pre-concentrate silver ions within water samples using sodium diethyl dithiocarbonates and Triton X-114 as a chelating agent. CPE conforms to the "green chemistry" idea by limiting the use of hazardous compounds and using inexpensive [44], media-diluted extraction solutions as a surfactant, producing lower residues. As a green technique, CPE uses inexpensive, media-diluted extraction solutions, producing lower residues. The latest CPE approaches for initial concentration of metal ions are detailed in Table 2.

Table 2. Summary of current CPE methods for metal ion preconcentration.

Metal ion	Detecting technique	Sample	Description of the preconcentration procedure	Sample volume (mL)	EF	LOD (µg L ⁻¹)	Linearity (µg L ⁻¹)	Ref.
Ag	FAAS	Water	Conventional CPE method employing Triton X-114 as a surfactant and DDTC as a complexing agent	10	33	0.3	1 – 500	[45]
Pb	FAAS	Environmental	Pb extraction into the rich phase of Triton X- 114 following PAN complexation	15	15.5	5.3	7.5-3500	[46]
Cd	ETAAS	Coal fly ash	By creating a negative ternary complex with Cl ⁻ and SDS, which then forms an ion pair complex with the positive surfactant CTAB, the metal ion was recovered	10	14.3	0.001588	0.5 - 4.75	[47]
Zr	ICP-MS	Rat liver, kidney	Compact working CPE that eliminates the need for a centrifugation phase. As a surfactant and a complexing agent, 8-hydroxyquinoline and	40	53	0.055	0.18-100	[48]

			Triton X-100 were utilized, respectively					
Sb	ICP-OES	Water and food	CPE with ultrasound assistance that uses Triton X-114 as a surfactant and PAN as a chelating agent	10	77.3	0.008	0.027-650	[49]
Ni	Spectrophoto metry	Water and coins	1-[(5-benzyl-1,3- thiazol-2-yl)diazenyl] naphthalene-2-ol, a synthetic ligand, is used to measure Ni ²⁺ via spectrophotometry and CPE	10	50	3.9	5.9-73.4	[50]
Pd	ICP-OES	Water	The cloud system composed of 2- mercaptobenzothiazole	50	100	0.525	5 - 100	[51]

LOD = limit of detection, ICP-OES = inductively coupled plasma optical emission spectrometry, ETAAS = electrothermal atomic absorption spectrometry, FAAS = flame atomic absorption spectrometry, EF = extraction efficiency.

CONCLUSION

This study demonstrates that the CPE process has proven valuable in the separation and preconcentration of several chemicals, including organic molecules, metal ions, and nanomaterials, in actual samples. When compared to other preconcentration techniques, it offers a lot of features, it is quick, effective, accurate, and exact. Because it uses fewer hazardous organic solvents, this process is considered environmentally benign. It's important to consider the procedure's minimal cost. Different techniques were created to enhance the selectivity and application of sensitivity. Despite the fact that certain anions are hazardous, it is evident that careless anions are extracted using CPE. As a result, using this technique for anion preconcentration may become commonplace in the future.

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