Review Article

Cloud point extraction as a sample preparation technique for trace element analysis: An overview

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ABSTRACT

Sample preparation is an important step in chemical analysis process. The present article gives an overview about the Cloud point extraction as a technique for sample preparation for trace element analysis. Cloud point extraction steps, mechanism, advantages, disadvantages and some applications have been discussed.

Keywords: Cloud point extraction, Sample preparation, Separation, Pre-concentration.
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INTRODUCTION

Sample preparation was probably the single most neglected area in analytical chemistry relatively to the great interest in instruments. While the level of sophistication of the instrumentation for analysis has increased significantly, a comparatively low technical basis of sample preparation often remains. [1]

Cloud-point temperature (CPT), or equivalently the lower critical consolute temperature, is the specific temperature at which the clear micellar solution of a weekly polar surfactant, such as nonionic or zwitterionic surfactant, becomes turbid upon heating or cooling. Explicitly for nonionic surfactants, at temperatures above the cloud point, the homogeneous surfactant solution separates into two immiscible phases with well defined composition, one of which contains much of surfactant, called surfactant-rich phase, whereas the other, called water phase, is almost free of micelles and has a surfactant concentration near its critical micelle concentration (CMC).[2-5]

Cloud point extraction (CPE) is an attractive technique that reduces the consumption of the solvent, extraction time and the disposal costs. Cloud point methodology has been used for the extraction and pre-concentrations of metal ions after the formation of sparingly water soluble complexes.[6-9]

The cloud point extraction in comparison with other enrichment techniques has some advantages such as low cost, speed, good concentration efficiency, environmentally lower toxicity and safety.[10,11]

CPE is a simple procedure with a high capacity to concentrate a wide variety of metal with quantitative recoveries and high pre-concentration factors, since the metal can be collected in small volumes (0.2–0.5 ml) of the surfactant phase. This allows pre-concentration factors identical to those of other techniques without an additional re-extraction step.

The CPE of metal ions involves the formation of sparingly water soluble chelates with suitable reagents. The technique is based on the property of most non-ionic surfactants that form micelles in aqueous solution. They become turbid when heated to the appropriate cloud point temperature. Above the cloud point temperature, the

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micellar solution separates into a small, surfactant rich phase and a larger diluted aqueous phase. In the aqueous phase, the surfactant concentration remains near the critical micelle concentration. Any analyte solubilised in the hydrophobic core of the micelle in the unheated solution, will be concentrated in the surfactant- rich phase following the cloud point extraction.[8,9,12-19]

DISCUSSION

Practically, the cloud point methodology used for metal determinations is relatively simple: a few milliliters of concentrated surfactant solution are added into the aqueous solution (this volume is in the range of tens of hundreds of milliliters). When necessary, a chelating agent solution is dissolved in an organic solvent or directly in water, depending on its solubility. This solution is then heated above its cloud point and the phase separation occurs, which can be accelerated by centrifugation. The discard of bulk aqueous phase after separation of micellar phase is facilitated after an ice bath, because the viscosity of the surfactant-rich phase is increased. Before the determination process, it may be necessary to add small amounts of a salting agent (such as alcohol) after the discard of aqueous phase in order to decrease the viscosity of micellar phase and to promote its homogenization. The salting agent content must be a compromise between the ideal viscosity, the metal concentration, and the quantity of organic solvent that some atomizers can support.[20]

There are many factors affecting cloud point extraction efficiency, such as pH of sample solution, salt concentration, effect of equilibration temperature and time, Kraft point temperature, centrifuge time, selection of the surfactant, and surfactant concentration.

Effect of pH
The effect of pH on the sensitivity and extraction parameters has to be tested. In the case of metal chelates, the optimal pH range frequently matches the range of the most favorable complex formation. The pH plays an important role in improving the extraction efficiency in CPE of metals without the addition of a chelating agent, since it affects the overall charges of the analyte, thus affecting the formation of the complex between the metal and the surfactant active functional groups.[21]

Effect of centrifugation time
The centrifugation time plays an important role in phase separation after the formation of the cloud. The effect of centrifugation time phase separation was studied in the range of 2–20 min at 3500 r/min for the determination of trace levels of Phthalate esters in water by CPE using Triton X-114 as the extraction solvent. The results showed 5 min is available for a complete phase separation.[22] The shorter centrifugation time is considered as advantage for CPE.

Selection of the Surfactant
To date, non-ionic surfactants (mainly polyoxyethylenated alkylphenols, from the Triton and PONPE series) are those most widely employed for CPE metal analysis. They are all commercially available of high purity grade, stable, non-volatile, non-toxic and environmentally friendly [23-25]. Non-ionic surfactants do not contain a specific fixed number of ethylene oxide units, but instead consist of a statistical distribution of homologues (ethoxamer distribution).[24]

Salt Concentration
The addition of salt to the solution may influence the extraction process. In the case of most non-ionic surfactant, the presence of salts may facilitate phase separation since it increases the density of the aqueous phase [26].

Equilibration temperature and time
The greatest analyte pre-concentration factor is reached when the CPE process is conducted with equilibration temperatures well above the cloud point temperature of the system [27,28]. It was observed that the volume of the surfactant-rich phase decreased by a factor of 5 when the temperature was increased from 25 to 90 C° working at a surfactant concentration of 1% (w:w) [29]. Nevertheless, for thermally labile metal chelates, the use of elevated temperatures could result in a decreased recovery due to decomposition. Equilibration times within the range of 4 – 15 min at 60–70 C° are often selected as optimal.[30]

Krafft point temperature
Krafft point of a surfactant is the temperature above which the solubility of the surfactant increases dramatically in an aqueous solution, and is interpreted as the melting point of a hydrated solid surfactant. The concept of Krafft point has been applied extensively to ionic surfactants, but has rarely been observed for nonionic surfactants [31]. At the Krafft point, the solubility of the surfactant is equal to its critical micelle concentration (CMC). Above the Krafft

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point, the total solubility of the surfactant increases dramatically because of the formation of micelles. However, only surfactant monomers are presented and the solubility is drastically limited at a temperature below Krafft point. Thus, a solution containing surfactant is cloudy below its Krafft point, but becomes clear at temperatures above its Krafft point.[32]

Surfactant concentration
When the concentration of a surfactant is increased, its structure may change from single molecules to spherical, rod- and lamellar-shaped micelles. Spherical micelles are formed at the first critical micellar concentration (CMC). The second CMC indicates the structural transition from spherical micelles to rod-like ones. Many methods such as surface tension, conductivity, solubilization, and light scattering [28], have been used to determine the first CMC. These methods are simple and easily utilized. However, few techniques have been applied to determine the second CMC. Miural et al. determined the second CMC of SDS by several methods: conductivity, viscosity and light scattering [33-36]. Ma et al. [37] determined the second CMC of several surfactants by adsorptive voltammetry experiments. Li et al. [38] determined the second CMC of surfactants by the fluorescence probe technique.

Surfactants are amphiphilic organic substances. Their molecules present a long hydrophobic hydrocarbon chain and a small charged group or polar hydrophilic. A typical surfactant has a R-X structure, where R is a hydrocarbon chain, which can have between 8 and 18 atoms of carbon, and X is the polar or ionic head group. The most usual chemical classification of surfactant is based on the hydrophilic group nature. The four general groups of surfactants are defined as non-ionic, cationic, anionic, and amphoteric (or zwitterionic).[39,40]

The main parameter to attain a surfactant monomer agglomeration in a micelle-rich phase is the surfactant concentration at the cloud point temperature. The temperature-concentration phase diagram is specific for each surfactant. The effect of additives such as salts and other surfactants also has to be considered. The first application of cloud point extraction for analytical purposes described the micelle aggregation of hydrophobic anionic metal complexes.[6,41]

The main limitation of CPE is the relatively low partition coefficients of several metal species with determinate chelates. However, it can be circumvented with the use of highly hydrophobic ligands.[42,43]

The generation of the metal chelates is a main step in the process of CPE. Several ligands, have been listed by Sun et. al. such as 1-(2- thiazolylazo)-2-naphthol (TAN), ammonium pyrrolidinedithiocarbamate (APDC), 8-hydroxyquinoline (Oxine), dithizone, diethyldithiocarbamate (DDTC), 2-(5-bromo-2- pyridylazo)-5-diethylaminophenol (5-Br-PADAP),18 and 1-(2- pyridylazo)-2-naphthol (PAN), have been used in cloud point extraction of metal ions.[44]

In the following some example for the application of cloud point extraction of metal ions in different samples prior to different analytical techniques will be presented.

N_2O_2-type Schiff base ionophore, named N,N'-bis(2-hydroxyacetophenone)-1,2-propanediimine has been used for extraction of Cu(II) from water samples prior to FAAS determination with a limit of detection of 0.06 ng ml^{-1}. [45]

After complexation with p-nitrophenylazoresorcinol (Magneson I), nickel and manganese have been extracted in a surfactant octylphenoxy polyethoxyethanol (Triton X-114) and then determined by FAAS in water and food samples.[46]

CPE was used for the extraction of cadmium(II), lead(II), palladium(II) and silver(I) from complicated matrix such as radiology waste, vegetable, blood and urine samples. The analytical procedure involved the formation of metals complex with bis((1H-benzo [d] imidazol-2yl)ethyl) sulfane (BIES), and quantitatively extracted to the phase rich in octylphenoxypolyethoxyethanol (Triton X-114) after centrifugation. Methanol acidified with 1 mol L^{-1} HNO3 was added to the surfactant-rich phase prior to its analysis by flame atomic absorption spectrometry (FAAS).[47]

Simultaneous pre-concentration has been also achieved for determination of Zn(II), Co(II), Ni(II) and Pb(II) by Flame Atomic Absorption Spectrometry. The cations were complexed with 2-guanidinobenzimidazole at pH 9. Triton X-114 was added as a non-ionic surfactant. After the phase separation at 40°C, the surfactant-rich phase was diluted to 1.5 ml using an ethanolic solution of HNO_3 and the analytes were determined by flame atomic absorption spectrometry. Many metal ions have also been determined by atomic absorption spectrometry such as Pb, Mn, Fe, Ag, Ni, Cu, Zn, Pd, Cr and Cd, after CPE in different kinds of samples.[49-55]

Rojas et. al. proposed a sensitive methodology for the pre-concentration and determination of nickel by UV/Vis spectrophotometry using tha cloud point extraction. Nickel ion was complexed with 1,5-bis(di-2-pyridylmethylene) thiocarbonohydrazide (DPTH) at pH 5.4 in buffer acetate medium and quantitatively extracted into a small volume of surfactant-rich phase of Triton X-114 after centrifugation. Their method was applied to the determination of nickel in different samples. [56]

Madrakian et al. proposed a method for spectrophotometric determination of uranium in different types of water samples. The method is based on the color reaction of uranium with pyrocatechol violet in the presence of potassium iodide in hexamethylenetetramine buffer media and mixed micelle mediated extraction of complex. Linearity was obeyed in the range of 0.20–10 $ngmL^{-1}$ of uranium (VI) ion and the detection limit of the method is 0.06 $ng.mL^{-1}$.[57]

Molybdenum(VI) was determined spectrophotometrically in steels and tap water and well water samples after cloud-point extraction process using micelle of the cationic surfactant CTAB with detection limit of 0.1 ng mL^{-1}.[58]

Molybdenum(VI) was also extracted using bromopyrogallol red/ acetyltrimethylammonium/ nonylphenoxypolyethoxy- ethanol mixed medium.[59]

Extraction and Spectrophotometric determination of mercury from aqueous solutions was investigated. The method is based on the complexation reaction of Hg(II) with Thio-Michler's Ketone (TMK) and micelle-mediated extraction of the complex using the nonionic surfactant Triton X-114. The detection limit of the method was 0.83 ng mL^{-1} of Hg(II) ion. The method was applied to the determination of mercury in water samples.[60]

Trace quantity of vanadium ions in pharmaceutical formulations (PF), dialysate (DS) and parenteral solutions (PS) was extracted using 8-hydroxyquinoline (oxine) as complexing reagent and mediated by nonionic surfactant (Triton X-114). The extracted surfactant-rich phase was diluted with nitric acid in ethanol, prior to subjecting electrothermal atomic absorption spectrometry.[61]

Cloud point extraction (CPE) was applied by Hagarova et al. as a separation/preconcentration step for electrothermal atomic absorption spectrometric (ETAAS) determination of ultratrace Sb(III) in natural water samples. After complexation with ammonium pyrrolidine dithiocarbamate (APDC) in mildly acidic medium, the analyte was quantitatively extracted to the phase rich in the non-ionic surfactant octyl phenoxy polyethoxy ethanol (Triton X-114) after centrifugation. Then the surfactant-rich phase was diluted by 0.20 mol L^{-1} HNO_3 in methanol and the concentrated analyte was introduced into ETAAS. The linear concentration range was from 0.10 to 3.50 µg L^{-1} Sb(III). The detection limit of 0.03 µg L^{-1} Sb(III) was achieved.[62]

A cloud point extraction has been developed by Baig et al. for the determination of As in maize (Zea mays L.) and adjoining agriculture soil. The different parts of maize (grains, shoots and roots) and soil were subjected to microwave assisted digestion in a mixture of nitric acid and hydrogen peroxide (2:1 ratio). The trace amounts of As was pre-concentrated by cloud point extraction, as prior step to its determination by electrothermal atomic absorption spectrometry.[63]

Cloud point extraction and graphite furnace atomic absorption spectrometry (GFAAS) have been used for preconcentration and determination of platinum in aqueous solution with diethyldithiocarbamate (DDTC) as chelating agent and Triton X-114 as extraction medium. The limit of detection was 0.2 $ngmL^{-1}$.[64]

Beiraghi and Babaee have studied a cloud point extraction process using mixed micelle of the cationic surfactant cetyl-pyridinium chloride (CPC) and non-ionic surfactant Triton X-114 for extraction of beryllium from aqueous solutions. The extraction was performed in the presence of 1,8-dihydroxyanthrone as chelating agent in pH 9.5. After phase separation, the surfactant-rich phase was diluted with 0.4mL of a 60:40 methanol–water mixture containing 0.03mL HNO3. The enriched analyte in the surfactant-rich phase was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The calibration graph was linear in the range of 0.006–80 $ngmL-1$ with detection limit of 0.001 $ngmL^{-1}$.[65]

Molybdenum (VI) has been extracted by 8-hydroxyquinoline in the presence of the surfactant Triton X-100 and determined by ICP-MS.[66]

A flow injection (FI) cloud point extraction (CPE) method for the determination of iron and copper by flame atomic absorption spectrometer (FAAS) has been improved. The analytes were complexed with 3-amino-7-dimethylamino-

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2-methylphenazine (Neutral Red, NR) and octylphenoxypolyethoxyethanol (Triton X-114) was added as a surfactant. This method was successfully applied to determination of iron and copper in spice samples.[67-72]

The on-line incorporation of cloud point extraction (CPE) with/without 8-hydroxyquinoline (8-Ox) as chelating agent into flow injection analysis associated with inductively coupled plasma optical emission spectrometry (ICP-OES) for determining trace rare earth elements (REEs) has been presented by Li, Hu. The developed methods of online CPE–ICP-OES were validated by the analysis of certified reference material (tea leaves) and real biological samples of pig liver, Auricularia auricula and mushroom.[73]

CONCLUSION

Cloud point extraction is a simple analytical technique used for sample preparation to improve trace element analysis. It is a valid alternative for separation and pre-concentration procedures due to its high recoveries and concentration factors. The application of CPE offers an attractive alternative to classical extraction methods by reducing the consumption of and exposure to the solvent, disposal cost, and extraction time.

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