SAMPLE PRETREATMENT IN THE ANALYSIS OF THE TRACE ELEMENTS USING GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY (GFAAS)

ABSTRACT

Many methods have been proposed for the species pretreatment or extraction from the environmental water samples prior to the analytical measurement. Generally, separation and preconcentration methods can increase the accurate and precision of the species analysis by eliminating the matrix effects and lowering the detection limits (LOD) in many trace elements analysis. In this review, three different types of separation and preconcentration methods: cloud point extraction (CPE), solid phase extraction (SPE) and dispersive liquid-liquid microextraction (DLLME) were evaluated based on their different principles and efficiencies in the species analyzed by graphite furnace atomic absorption spectrometry with the aim of highlighting some of the important aspects like extraction time, pH, detection limit and their recoveries. Some advantages and problems arising from the three methods were also discussed and concluded in this review paper.

Keywords: Cloud Point Extraction, Solid Phase Extraction, Dispersive Liquid-liquid Microextraction, Graphite furnace atomic absorption spectrometry

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1.0 INTRODUCTION

1.1 Trace elements in water

Nowadays, water quality is an issue of concern for human health in most developing and developed countries like Malaysia, United States, France, China and Japan. This is because the polluted or contaminated water can lead to a serious problem for water quality and adversely affects human health and other living organisms.

Polluted or contaminated water contains chemical substances which can be divided to organic and inorganic elements. Pollutant that are classified to organic elements are such as detergents, disinfection by-products and volatile organic compounds while inorganic compounds are such as heavy and trace metals from vehicles, fertilizers from agriculture and industrial by-products. Through the investigation of World Health Organization (WHO), every year there are 1.6 million diarrhoeal deaths related to unsafe water especially for children under five years old. The WHO also estimated that safe water can prevent 1.4 million children death from diarrhoea.

Trace elements in water always cause numeral problems to human health and living organisms. Trace elements mainly occur in environmental water samples in the form of non-labile and inert elements. They are essential nutrients for mammals in trace amount but high amount of labile and toxic elements are hazardous and harmful to all organisms. Arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), zinc (Zn), nickel (Ni), copper (Cu) and iron (Fe) are the common trace elements found in the polluted seawater, tap water, river, lake and mineral water.

Cr(III) is essential for animals and plants at low concentrations for maintaining the glucose, lipid and protein metabolism in mammal body, while Cr(VI) is extremely toxic and carcinogenic for a variety of organisms. The main causes of excessive chromium exists in environment are due to the discharge from tanning factories, steel works, industrial electroplating and artificial fertilizers.

Besides chromium, arsenic is also a toxic and carcinogenic element that predominantly exists in inorganic form as As(III) and As(V) in water. In many parts of the world, arsenic-contaminated drinking water is caused by the natural occurrence in soils especially arsenopyrite and metal arsenates as well as anthropogenic activities such as agriculture and forestry. Inorganic arsenic causes cancers of the skin, lungs and bladder. Due to its toxicological effects, WHO has revised the maximum contaminant level to 10 ppb in order to provide safer water to people.

Since the concentrations of trace elements that exist in water are typically in the part per billion range, an efficient and simple analytical method or system is required to be developed in order to determine and analyze these trace heavy metals.

1.2 Graphite furnace atomic absorption spectrometry (GFAAS)

A variety of analytical sampling systems such as the flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) or electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma (ICP) technique, ICP mass spectrometry (MS) and hydride generation atomic absorption spectrometry (HG-AAS) can be used to determine and analyze the trace elements in environmental water samples. But among these analytical sampling systems, GFAAS is the obvious choice for the trace heavy metals analysis applications because it permits the determination of most trace heavy metals with high sensitivity and extremely low detection limit which is in the part per billion range. Because of the background correction techniques that have been developed to compensate the matrix interferences, its sensitivity and detection limit are better than flame atomic absorption from 20 to 1000 times. Besides high sensitivity, this advanced instrumentation and technique merely requires sample in micro-liter volume. The small volume of sample size can be a benefit when the amount of sample...
available for analysis is limited. The operational cost is also low compared to the ICP-MS. Due to these few advantages, GFAAS is considered as one of the most reliable and powerful analytical techniques in the determination of trace heavy metals in water\textsuperscript{7,8}.

1.3 Separation and preconcentration methods

Even though GFAAS is one of the most reliable and powerful analytical techniques for determination of trace elements in water, separation and preconcentration methods are still required to be used in some situations before the analytical measurement. This is because the separation and preconcentration methods can increase the accuracy and precision of the species analysis by eliminating the matrix effects and lowering the detection limits (LOD) of many trace elements\textsuperscript{9}. As a result, high recoveries of the species can be obtained by these preconcentration methods.

Many methods have been proposed for the species pretreatment or extraction from the environmental water samples prior to the analysis. Liquid-liquid extraction is the most classical extraction method that has been used in the sample pretreatment. Against this classical extraction method, other more recent approaches such as cloud point extraction (CPE), solid phase extraction (SPE), solid phase microextraction (SPME), dispersive liquid-liquid microextraction (DLLME), supercritical fluid extraction (SFE) and coprecipitation methods offer new choices and advantages in species treatment\textsuperscript{6,9,10}.

Recently, cloud point extraction (CPE) is considered as an alternative separation and preconcentration method for trace heavy metals determination when compared to other separation techniques due to the benefits such as simple experimental procedures with high recoveries and high concentration factors, low cost and environmental safety\textsuperscript{6}. The CPE procedure is based on the property of non-ionic surfactants in aqueous solutions to form micelles and become turbid when heated to cloud point temperature\textsuperscript{9}. Surfactants are amphiphilic molecules with long hydrophobic hydrocarbon chain and small charged group or polar hydrophilic\textsuperscript{11}. In aquatic solutions, low concentrations of surfactant molecules mainly present as monomers. These monomers will spontaneously accumulate to form colloidal-sized clusters which are known as micelles when their concentration increases above critical micellar concentration (cmc)\textsuperscript{6}. The micellar formation is used to trap the analyte chelates in the micellar cores.

Besides cloud point extraction, solid phase extraction (SPE) is also a separation method in which the sorbent is used to preconcentrate analytes or to separate them from a wide variety of matrices such as water, blood, urine and soil. SPE can preserve the original speciation of the sample and offer good preconcentration factors as well as to lower the limit of detections. The concept of SPE is based on the affinity of dissolved or suspended solutes in a liquid (mobile phase) to a solid (stationary phase), which the sample is passed through, to separate the interest compound and impurities. Most stationary phases are a packed of syringe-shaped cartridge, a 96 well plate, a 47- or 90-mm flat disk or silica that has been bonded to a specific functional group\textsuperscript{12}. Generally, SPE can be divided to four types, which are reversed phase SPE, normal phase SPE, ion exchange SPE and adsorption SPE. In most cases, water samples are used with reversed phase or ion exchange SPE\textsuperscript{13}.

Dispersive liquid-liquid microextraction (DLLME) is a separation and preconcentration method that based on a ternary component solvent system. This method involves the interaction between the extraction solvent and disperser solvent with the aqueous sample\textsuperscript{14}. The extraction solvents with high density like tetrachlorometane, chloroform, carbon disulfide, nitrobenzene and bromobenzene are usually used in DLLME, while for disperser solvents, they are methanol, ethanol, acetonitrile and acetone\textsuperscript{15}.

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Therefore, the aim of this review paper is to discuss CPE, SPE and DLME based on their efficiency in the species analysis by highlighting some of the important aspects like extraction time, pH, detection limit and their recoveries.

2.0 EFFICIENCY OF CLOUD POINT EXTRACTION (CPE)

2.1 Effect of the surfactant system

In the surfactant system, the amount and concentration of non-ionic surfactant are the two important factors influencing extraction efficiency. Since the temperature corresponding to cloud point is correlated with the hydrophilic property of non-ionic surfactants, an appropriate surfactant must be chosen correctly. Generally, the surfactant’s cloud point should be controlled under 100 °C. The surfactants which have too high or too low cloud point are not suitable for the CPE preconcentration of trace elements. Some CPE conditions for the trace element analysis are summarized in Table 1. Triton X-100, Triton X-114 and PONPE 7.5 are the three common types of non-ionic surfactants that had been studied by the researchers to extract Cr(III), Cr(VI), Al(III), Ni(II), Sn(IV), Ag, As(III) and (V), Mo(VI) and Bi.

According to Zhu et al., Triton X-100 was the best among the three surfactants (Triton X-100, Tween-80 and Span-20) that were used to extract Cr(VI)-Br-PF complex from tap and lake water. Their studies showed that the solution could be separated easily into two phases and the bulk aqueous phase could be decanted after centrifugation, while for the Tween-80 and Span-20, a poor phase separation was found. This was attributed by high recovery of the analyte when Triton X-100 was used.

Moreover, in the further study carried out by Zhu et al., Triton X-100 was used to extract the Sn(IV) from tap and lake water. Their investigation showed that the solution could be separated easily into two phases and the bulk aqueous phase could be decanted after centrifugation, while for the Tween-80 and Span-20, a poor phase separation was found. This was attributed by high recovery of the analyte when Triton X-100 was used.

Recent studies have shown that PONPE 7.5 may form a complex with Ag ion and act as both extracting and complexing agents in surfactant-rich phase. Due to its low cloud point temperature, the phase separation can be facilitated by centrifugation without heating the micellar solutions. As a result, this makes CPE procedure becomes simple and increases the extraction efficiency.

2.2 Effects of chelating agents and pH

Apart from the selection of appropriate surfactant, selection of the chelating agent and pH is the most critical factor regulating the partitioning of the target analyte in the micellar phase in order to control the extraction efficiency. The formation of metal chelate complex and its chemical stability are dependent on the pH. The effective pH range for Cr(III) and Cr(VI) was investigated and the results showed that the yield is constant and near quantitative recovery (recovery > 95%) for Cr(III) in the pH range of 3.0 to 7.0. This is the suitable pH range for Cr(III) to react with the chelating agent: 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP) to form Cr-PMBP complex in a stable condition. Therefore, it is possible to separate Cr(III) from Cr(VI) easily and the extraction of...
Cr(VI) was negligible in this pH range. The same application was used in Zhu et al.\textsuperscript{17} study.

The extraction recovery of trace elements can be affected when the pH is too high or too low. According to Shemirani et al.\textsuperscript{18}, at low pH level, the complex formed is decomposed. Furthermore, some complexes do not form completely at lower and higher pH values, which cause the low extraction efficiency\textsuperscript{19}. In addition, several buffer agents such as sodium hydroxide, carbonate, phosphate and borax can be added for the pH adjustment. In a study carried out by Manzoori et al.\textsuperscript{20}, they found that carbonate buffer solution is suitable for the pH adjusting upon the extraction of silver ions. This is because GFAAS gives the highest absorbance signal of silver ions after adding of carbonate buffer solution.

For the selection of chelating agent, several chelating agents such as PMBP, Br-PF, PAN, APDC, molybdate, QA and dithizone have been listed in Table 1. These chelating agents are utilized in order to produce sufficiently hydrophobic complexes to be isolated in the surfactant-rich phase of a micellar solution. The extraction efficiency is determined by their reactivity and formation constants with the target analyte species. Therefore, with the aid of suitable pH condition, the formation of hydrophobic metal complex is stable and this leads to the high extraction efficiency of the CPE.

### 2.3 Effects of equilibration temperature and time

The lowest possible equilibration temperature and the shortest incubation time are desired to compromise the completion of the reaction and efficient separation of the phases\textsuperscript{3,17,18,22,25,27}. Table 1 shows the optimum equilibration temperatures and incubation times that had been obtained in each study. The overall equilibration temperatures obtained in all studies listed in table 1 vary from 35 to 85 °C except studies carried out by Zhu et al.\textsuperscript{19} and Manzoori et al.\textsuperscript{20}. The former and later researchers used equilibration temperature at 0 °C and room temperature, respectively. The incubation time required to obtain an acceptable recovery varies from 5 to 30 minutes. According to Zhu et al.\textsuperscript{17}, the turbidity does not occur when the temperature is lower than 65 °C (cloud point). However, it begins to be turbid when the temperature is higher than 65 °C and up to 85 °C. The maximum intensity was achieved and remained constant during the temperature of 85 °C to 100 °C. This indicates that the Cr(VI)-Br-PF complex are able to be quantitatively extracted into surfactant-rich phase within this temperature range.

### 2.4 Accuracy and precision of CPE

In order to examine the accuracy and precision of the CPE method, the lowest R.S.D. and LOD as well as the highest recovery are required to be achieved during the speciation of trace elements analysis. R.S.D, LOD and percentage recoveries of a few methodologies that had been carried out by other researchers are listed in Table 1. Domestic tap water, lake, canal and seawater were studied by these groups of researcher and the elements tested in the water samples were chromium, aluminium, nickel, stanum, silver, arsenic, molydenuum and bismuth. The obtained results showed that the methodology precision is within 2-5% and all of the percentage recoveries obtained are more than 95%. Besides the good recovery, the overall R.S.D values of trace elements analysis pretreated with CPE show good agreement and satisfaction when compared to the R.S.D. values without go through CPE pretreatment. The R.S.D values obtained from the analysis with CPE pretreatment is higher than the analysis without CPE pretreatment only observed in the studies carried out by Manzoori et al.\textsuperscript{20} and Shemirani et al.\textsuperscript{23}. However, the values still within the acceptable range and just slightly higher than the analysis after CPE pretreatment. The very obvious LOD is the analysis of Ag in tap water, subterranean canal, underground and river water samples after CPE pretreatment, in which the LOD is 0.0012 ng/mL. This value is extremely low and approximately one thousand times lower than the other LODs which were determined by other researchers. In the studies carried out by

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Manzoori et al.\textsuperscript{20} and Shemirani et al.\textsuperscript{18,23}, LOD of the studied element is very much significant lower when the water samples were pretreated with CPE than the samples without CPE pretreatment. This shows that CPE pretreatment is a very powerful pretreatment technique which is able to pre-concentrate water sample to approximately 100 to 700 times from the original concentration. Based on the result shown in the table 1, CPE pretreatment is a reliable method, which can be applied effectively for the determination of trace elements in environmental water samples.

3.0 EFFICIENCY OF SOLID PHASE EXTRACTION (SPE)

3.1 Effect of pH on adsorption

The pH value is very important in the adsorption of different ions onto the surface of a sorbent\textsuperscript{26}. Some SPE conditions for the trace element analysis are illustrated in Table 2. A few types of sorbents such as immobilized nanometer TiO\textsubscript{2}, Cyanex 301, Diaion HP-2MG, MCI GEL CHP 20Y and Amberlite XAD-2000 resins were used to develop the new methods for separation and preconcentration of trace elements based on SPE prior to GFAAS determination.

In order to evaluate the effects of pH on the adsorption, it is necessary to adjust the pH of the sample solution to an optimal range to make the adsorption of the analyte ions onto the sorbent surface as efficient as possible. This is because each sorbent requires an appropriate pH medium to increase their surface ability of binding cations or anions\textsuperscript{26,27}. According to Liu and Liang\textsuperscript{28}, the OH functional group on TiO\textsubscript{2} surface possesses the ability of binding cations at high pH condition. At low pH condition, this OH functional group on the oxide surface is displaced and the surface charge is neutralized. Thus, this decreases the adsorption of cations onto the TiO\textsubscript{2} surface. On the other hand, when the pH of the solution is higher than the isoelectric point (IEP) of the oxide, cations adsorb onto titania surface due to the changing of surface characteristic to negatively charged. At pH below IEP, titania surface adsorbs anions\textsuperscript{29}.

In addition, Raoufi et al.\textsuperscript{30} stated that higher pH values are possible to cause the hydrolysis of octadecyl silica in the disks and therefore, the relatively high acid-base characteristic of the anthraquinone derivative is used. Hence, in their study, the higher pH values were not studied and the recovery of Pb ions was observed within the pH range of 2 to 7.

3.2 Eluent type and concentration

The effects of eluent type are an important factor on retaining the interest analyte ions in the SPE. A few types of eluent in different concentrations that had been studied are listed in Table 2. In order to choose a proper eluent, some recovery tests based on the different eluents are needed to be carried out to prove the elution efficiency. In the study carried out by Saygi et al.\textsuperscript{31}, the effects of various eluents on the Se(IV)-Diaion HP-2MG system were studied and the efficiency of hydrochloric acid, nitric acid and nitric acid in acetone were evaluated as eluent in the system. Their results showed that by using 1 mol/L of HNO\textsubscript{3} in acetone, the highest recovery percentage (97 ± 3) for Se(IV) was obtained. Besides Se(IV), the recoveries of Fe(III), Pb(II) and Cr(III) by using different types of eluent were studied by Elci et al.\textsuperscript{32}. Their results showed that 0.5 mol/L of HNO\textsubscript{3} is the most suitable eluent to be used to elute the three species retained on Amberlite XAD-2000 column in the presence of DPC.
3.3 Accuracy and precision of solid phase extraction (SPE)

The R.S.D. and recovery indicate the accuracy and precision of the SPE method in the speciation of trace elements analysis. Some of the R.S.Ds and recoveries that had been obtained by other researchers in their studies are listed in Table 2. These researchers used SPE method to study various types of element in mineral, domestic tap, river, lake and sea water. Most of the R.S.Ds obtained in their studies are less than 5% except studies carried out by Narin et al. and Chwastowska et al. In most of the single element studies, percentage recoveries higher than 95% can be obtained. Multi element studies carried out by Yang et al. had a wider range of the percentage recovery. Based on the recovery and R.S.D results shown in table 2, SPE method can be considered as a developed and reliable pre-concentration method, which can produce an accurate and precise analysis result.

4.0 EFFICIENCY OF DISPERSIVE LIQUID-LIQUID MICROEXTRACION (DLLME)

4.1 Effects of extraction solvent and its volume

The selection of an appropriate solvent is a very essential key parameter for the DLLME method. The type of extraction solvent used must have three special characteristics; it should have the extraction capability of the interested compounds, higher density than water, low solubility in water and non-volatile to prevent solvent loss during extraction. Some of the conditions for the trace elements analysis are listed in Table 3. As could be seen, carbon tetrachloride (CCl₄) and chlorobenzene (C₆H₅Cl) are the two most common extraction solvents for DLLME method.

For the purpose of acquiring the most suitable extraction solvent, Jiang et al. investigated three types of solvents which were carbon tetrachloride, chlorobenzene and bromobenzene. According to their results, these three types of solvents gave almost the same analytical absorbance. But due to the higher solubility of PAN (Chelating agent) in carbon tetrachloride, it was chosen as an extraction solvent in their further studies. However, the study carried out by Shamsipur and Ramezani showed that the chlorobenzene was the best extraction solvent when compared to carbon tetrachloride and chloroform. This is because the density of chlorobenzene (1.107g/mL) is closer to the water and it can form a very stable fine cloudy solution in the study. In order to examine the effect of extraction solvent volume on Au (III), the solutions containing different volumes of chlorobenzene were examined with the DLLME method. The results showed that high enrichment factor could only be achieved at low extraction solvent volume and the removing of sedimented phase was preferred at high extraction solvent volume.

4.2 Effects of dispersive solvent and its volume

Some of the common disperser solvents such as acetone, ethanol and methanol are listed in Table 3. The main criterion for the selection of an appropriate dispersive solvent in DLLME method is the mutual miscibility of disperser solvent in extraction solvent and aqueous solution. For this purpose, three different kinds of disperser solvents: acetone, acetonitrile and methanol were investigated by Jiang et al. The results showed that the acetone was the most suitable disperser solvent due to the highest absorbance response of the Co and Ni. Moreover, acetone is low in toxicity and low cost.

When the results indicate that there is no significant statistical difference among the different disperser solvents, other factors such as the solubility of chelating complex in the particular disperser solvent should be considered. For instance, ethanol was selected as disperser solvent in the study carried out by Liang and Sang. This solvent was chosen because it is less toxic and PMBP has higher solubility in this solvent. Moreover, the enrichment factor can be enhanced by increasing the solubility of chelating complex. The same condition can also be observed in the study...
After choosing the suitable disperser solvent, it is necessary to optimize its volume. The effect of the volume of acetone on the recovery of Au(III) in DLLME was studied by Shamsipur and Ramezani. It could be seen that the extraction efficiency increases with increasing the volume of acetone until 1.0 mL. This is because low volume of disperser solvent (acetone) is not able to cause the extraction solvent (chlorobenzene) to disperse properly into the sample solution. Proper dispersion can be seen when cloudy solution is formed. But high volume of disperser solvent can increase the solubility of the complex in aqueous sample solution. Therefore, extraction efficiency can be improved by adjusting the disperser solvent volume. However, further increasing the disperser solvent volume will decrease the extraction efficiency of DLLME method. The decreased extraction efficiency is caused by the increased solubility of complex adduct in aqueous solution which can reduce the extraction recovery.

4.3 Effects of chelating agents and pH

The selection of suitable pH in DLLME is also an important factor to regulate the metal-chelate formation and the subsequent extraction. This is because the formation of metal-chelate complex and its chemical stability depend on the sample pH. The extraction recovery of trace elements can be affected when the pH is too high or too low. The effect of pH on the DLLME of lead element in the sample solution was carried out by Liang and Sang. It was found that the highest absorbance signal was obtained at pH 4 and low absorbance signal was obtained at pH 2 and pH 8. Low absorbance signal obtained at pH 2 is due to the decomposition of its complex, which normally occurs at low pH values. Furthermore, some complexes do not form completely at extremely low and high pH conditions and cause the low extraction efficiency.

Some of chelating agent such as PMBP, PAN, APDC, DDTC, diethyldithiophosphoric acid and VBR are listed in Table 3. These chelating agents are utilized in order to produce sufficiently hydrophobic complexes to be extracted in DLLME method. The extraction efficiency is determined by their reactivity and formation constants with the target analyte species. The effect of the amount of APDC on the absorbance of cadmium and selenium respectively from DLLME was studied by Jahromi et al. and Bidari et al. Based on their results, the absorption increases by increasing the APDC amount and slightly decreases in high concentration of APDC. This is because at high concentration of APDC, the extraction of APDC itself occurs, which can easily saturate the small volume of extraction solvent. Hence, this causes the slight reduction on its extraction efficiency.

4.4 Effect of extraction time

Extraction time is the interval time between the injection of the mixture of disperser solvent and extraction solvent before the starting of the centrifugation. The dependence of extraction efficiency upon extraction time was investigated by various groups of researcher and their obtained results showed that the extraction time has no significant influence on extraction efficiency. This indicates that the surface area between extraction solvent and aqueous phase is infinitely large. Hence, the complex formation of trace element and its transition from aqueous phase to extraction solvent is fast. As a result, the extraction is very short and equilibrium state can be achieved in a very short period of time.
4.5 Accuracy and precision of DLLME

The precision of the DLLME methodology is based on the R.S.D values obtained in the studies carried out by the researchers. Most of the R.S.D results shown in table 3 are less than 5% except the study carried out by Jiang et al. The R.S.D values obtained by them are 7.5% for Co and 8.2% for Ni in lake and river water samples using PAN chelating agent and extracted to carbon tetrachloride before dispersed to acetone. This may be due to the high volatility of the extraction and dispersive solvents that had been chosen to be used in their method. However, same extraction and dispersive solvents were used by Naseri et al. to determine Pb in tap, well and sea water produced R.S.D less than 5%. The differences in these two studies are the type of chelating agent that was used and the elements that were studied. Most of the recovery results shown in table 3 have at least 90% or more except the study carried out by Jahromi et al., which the lower range recovery is merely 87%. In their study, carbon tetrachloride was used as extraction solvent to extract chelated Cd(II) in ammonium pyrrolidine dithiocarbamate. Chelated Cd(II) was then dispersed in methanol. This technique is able to enrich up to 125 times compared to the original concentration and the detection limit can go down to 0.0006 ng/mL. However, the difference between the lower and higher recovery ranges is quite high, which is 21%; whereas other differences between the lower and higher recovery ranges produced by other researchers are merely less than 10%. This is because three types of water, that are tap, sea and river waters were chosen to be used to determine the recoveries of this method. Same methodology was used by Rivas et al. to determine the concentrations of As(III) and Sb(III) in water samples. However, the recovery percentage was not reported and the R.S.D. obtained is approximately same as the R.S.D. obtained in the study carried out by Jahromi et al.

5.0 COMPARISON OF CLOUD POINT EXTRACTION (CPE), SOLID PHASE EXTRACTION (SPE) AND DISPERSIVE LIQUID-LIQUID MICROEXTRACTION (DLLME)

Table 4 shows that the overview of the advantages and limitations of CPE, SPE and DLLME. The presented data show that these three methods produced high recoveries (>87%) for the trace elements analysis in environmental water samples. This shows that the accuracy of these three methods is acceptable generally. Moreover, the lower values of R.S.D. are observed in all these three methods. These show that these three methods are comparable to each other in their precision in trace elements analysis. Among these three methods, DLLME has a highest enrichment factor, that is 70-388. Besides high enrichment factor, DLLME needs short extraction time compared to the other two methods due to the fast transition of analyte from aqueous sample to extraction phase. The equilibrium state can also be achieved immediately and therefore, it need very short extraction time for equilibrium. Short extraction time is a remarkable advantage for DLLME while CPE and SPE need longer extraction time than DLLME. The costs and reagents for these three methods are cheap and environmentally safe because it involves low amount of organic solvents in the separation process. Therefore, this definitely will not cause serious pollution in environment.

6.0 CONCLUSION

The use of CPE, SPE and DLLME versus classical liquid-liquid extraction represents an improvement for sample treatment. These three different kinds of method have been evaluated for the extraction efficiency of trace elements with low experimental errors. Even though they show excellent results for the multi-elemental analysis, selection of the most suitable method still depends on several factors such as the optimal extraction and reaction conditions such as pH, concentration, temperature, extraction and centrifugation time. Therefore, further works need to be carried out to improve the efficiency of the separation and pre-concentration techniques in these methods in order that they can cover a wider range of elements.
### Abbreviations:

- APDC, ammonium pyrrolidine
- Br-PF, dibromophenylfluorone
- PAN, 1-(2-pyridylazo)-2-naphthol
- PMBP, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone
- PONPE 7.5, polyethylene glycol mono-p-nonylphenyl ether
- QA, quinalizarine
- SRP, surfactant-rich phase
- R.S.D., Relative Standard Deviation
- EF, Enrichment Factor
- DL, Detection Limit
- THF, tetrahydrofuran
- SDS, sodium dodecyl sulfate
- Equil.Temp., Equilibrium Temperature
- Incub. Time, Incubation Time
- Ref., References

Note: 
- a with CPE
- b without CPE
- c in refrigerator
- d room temperature

### Table 1 Cloud point extraction conditions for trace elements analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>Species</th>
<th>Surfactant System</th>
<th>Chelating Agent</th>
<th>SRP Diluting Agent</th>
<th>DL (ng/mL)</th>
<th>pH</th>
<th>Equal.Temp (°C)</th>
<th>Incub. Time (min)</th>
<th>EF</th>
<th>R.S.D.(%)</th>
<th>Recovery (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap &amp; lake water</td>
<td>Cr(III)</td>
<td>Triton X-114</td>
<td>PMBP</td>
<td>0.1 mol/L HNO₃</td>
<td>0.021</td>
<td>5</td>
<td>40</td>
<td>20</td>
<td>42</td>
<td>3.5</td>
<td>97-102</td>
<td>[16]</td>
</tr>
<tr>
<td>Tap &amp; lake water</td>
<td>Cr(VI)</td>
<td>Triton X-100</td>
<td>Br-PF</td>
<td>Methanolic solution with 1 mol/L HNO₃</td>
<td>0.01</td>
<td>4.5</td>
<td>85</td>
<td>15</td>
<td>30</td>
<td>2.6</td>
<td>98.9-105.3</td>
<td>[17]</td>
</tr>
<tr>
<td>Tap &amp; lake water</td>
<td>Ag</td>
<td>Triton X-114</td>
<td>PMBP</td>
<td>Methanol with 0.1 mol/L HNO₃</td>
<td>0.09</td>
<td>7</td>
<td>40</td>
<td>20</td>
<td>37</td>
<td>4.7</td>
<td>95-99</td>
<td>[22]</td>
</tr>
<tr>
<td>Tap &amp; lake water</td>
<td>Ni(II)</td>
<td>Triton X-100</td>
<td>PMBP</td>
<td>Methanol with 0.1 mol/L HNO₃</td>
<td>0.12</td>
<td>5</td>
<td>80</td>
<td>25</td>
<td>27</td>
<td>4.3</td>
<td>98.1-106</td>
<td>[24]</td>
</tr>
<tr>
<td>Tap water &amp; lake water</td>
<td>Sn(IV)</td>
<td>Triton X-100, SDS &amp; NaCl</td>
<td>PAN</td>
<td>2.0 mol/L HNO₃</td>
<td>0.51</td>
<td>6.0-8.5</td>
<td>0°</td>
<td>30</td>
<td>50</td>
<td>3.6</td>
<td>98.8-100.7</td>
<td>[19]</td>
</tr>
<tr>
<td>Tap, canal, underground &amp; river water</td>
<td>Ag</td>
<td>PONPE 7.5</td>
<td>-</td>
<td>Methanol/water (3:1) solution</td>
<td>0.0012±0.076±3</td>
<td>9</td>
<td>RT±</td>
<td>20</td>
<td>60</td>
<td>4.2±</td>
<td>97.5-101.7</td>
<td>[20]</td>
</tr>
<tr>
<td>River &amp; lake water</td>
<td>As(III)</td>
<td>Triton X-114</td>
<td>APDC</td>
<td>0.1 mol/L HNO₃ in methanol</td>
<td>0.04</td>
<td>4.2</td>
<td>35</td>
<td>9</td>
<td>36</td>
<td>3</td>
<td>97-108</td>
<td>[25]</td>
</tr>
<tr>
<td>Tap water</td>
<td>As(V)</td>
<td>Triton X-114</td>
<td>Molydate</td>
<td>Methanol</td>
<td>0.01±1.08±3</td>
<td>2</td>
<td>55</td>
<td>5</td>
<td>52</td>
<td>4.5±</td>
<td>98</td>
<td>[23]</td>
</tr>
<tr>
<td>Seawater</td>
<td>Mo(VI)</td>
<td>Triton X-114</td>
<td>QA</td>
<td>THF &amp; 1 mol/L HNO₃</td>
<td>0.0007</td>
<td>3.6</td>
<td>50</td>
<td>10</td>
<td>25</td>
<td>3.7-3.9</td>
<td>98-102</td>
<td>[21]</td>
</tr>
<tr>
<td>Tap water</td>
<td>Bi</td>
<td>Triton X-114</td>
<td>Dichloroacetic</td>
<td>THF</td>
<td>0.02±1.2±3</td>
<td>3.0-3.5</td>
<td>50</td>
<td>5</td>
<td>196</td>
<td>4.3±</td>
<td>98.7</td>
<td>[18]</td>
</tr>
</tbody>
</table>
### Table 2: Solid phase extraction conditions for trace elements analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>Species</th>
<th>Sorbent</th>
<th>Chelating Agent</th>
<th>Elution</th>
<th>DL (ng/mL)</th>
<th>pH</th>
<th>EF</th>
<th>R.S.D. (%)</th>
<th>Recovery (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral waters &amp; salinas</td>
<td>Cr(III)</td>
<td>Dilution HP-2MG resin</td>
<td>APDC</td>
<td>Concentrated HNO₃</td>
<td>0.03</td>
<td>4</td>
<td>-</td>
<td>9</td>
<td>94-98</td>
<td>[34]</td>
</tr>
<tr>
<td>Tap &amp; river water</td>
<td>Al(III)</td>
<td>XAD-1180-PV</td>
<td>-</td>
<td>2 mol/L HCl</td>
<td>0.021</td>
<td>8.0-9.0</td>
<td>150</td>
<td>&lt;10</td>
<td>95-105</td>
<td>[33]</td>
</tr>
<tr>
<td>Tap &amp; lake water</td>
<td>As(III)</td>
<td>Immobilized nanometer TiO</td>
<td>-</td>
<td>0.5 mol/L NaOH</td>
<td>0.024</td>
<td>9.5-10.5</td>
<td>50</td>
<td>4.8</td>
<td>96-105</td>
<td>[26]</td>
</tr>
<tr>
<td>Tap &amp; lake water</td>
<td>Mo</td>
<td>Immobilized TiO nanoparticles</td>
<td>-</td>
<td>0.5 mol/L NaOH</td>
<td>$6 \times 10^{-4}$</td>
<td>1</td>
<td>100</td>
<td>3.4</td>
<td>95-103</td>
<td>[27]</td>
</tr>
<tr>
<td>Tap &amp; lake water</td>
<td>Po</td>
<td>Immobilized nanometer TiO</td>
<td>-</td>
<td>1 mol/L HCl</td>
<td>0.01</td>
<td>4.0-7.0</td>
<td>50</td>
<td>3.2</td>
<td>96-104</td>
<td>[28]</td>
</tr>
<tr>
<td>Spring water</td>
<td>Po</td>
<td>1,8-dihydroxy-2,7-bis(2,3,6-trisubstituted anthraquinone)</td>
<td>-</td>
<td>1 mol/L HNO₃</td>
<td>5</td>
<td>2.0-7.0</td>
<td>-</td>
<td>1.8</td>
<td>98.5</td>
<td>[30]</td>
</tr>
<tr>
<td>Spring water</td>
<td>Bi</td>
<td>Cyanoex 301</td>
<td>-</td>
<td>3.0 mol/L HNO₃</td>
<td>0.01</td>
<td>-</td>
<td>20</td>
<td>1.0-1.5</td>
<td>98.5-100.0</td>
<td>[44]</td>
</tr>
<tr>
<td>Tap, river &amp; sea water</td>
<td>Se(IV)</td>
<td>Dilution HP-2MG resin</td>
<td>APDC</td>
<td>1 mol/L HNO₃ in acetone</td>
<td>0.01</td>
<td>2</td>
<td>100</td>
<td>1.8-9.1</td>
<td>98-101</td>
<td>[31]</td>
</tr>
<tr>
<td>Pure, well, tap &amp; lake water</td>
<td>Ni, Ag, Co, Cu, Cd &amp; Pb</td>
<td>MCI GEL CHP 20V</td>
<td>QAMDHB</td>
<td>1.0 mol/L HNO₃</td>
<td>0.001 (Ag), 0.0005 (Cu), 0.0005 (Co), 0.0005 (Cd), 0.0001 (Pb)</td>
<td>8</td>
<td>300</td>
<td>&lt;3.2</td>
<td>89-104</td>
<td>[35]</td>
</tr>
<tr>
<td>Hot spring &amp; drinking water samples</td>
<td>Fe(III), Pb(II) &amp; Cr(III)</td>
<td>Anambact XAD-2000 resin</td>
<td>DPC</td>
<td>0.5 mol/L HNO₃</td>
<td>0.32 (Fe); 0.51 (Pb); 0.31 (Cr)</td>
<td>9</td>
<td>50-100</td>
<td>&lt;2</td>
<td>100±1 for Fe; 99±1 for Pb; 93±2 for Cr</td>
<td>[32]</td>
</tr>
</tbody>
</table>

Abbreviations: APDC, ammonium pyrrolidine; DPC, diphenylcarbazide; QAMDHB, 2-(2-quinolinilazo)-4-methyl-1,3; DL, Detection Limit; R.S.D., Relative Standard Deviation; EF, Enrichment Factor; Ref., References.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Species</th>
<th>Extraction Solvent</th>
<th>Dispersive Solvent</th>
<th>Chelating Agent</th>
<th>DL (ng/mL)</th>
<th>pH</th>
<th>R.S.D. (%)</th>
<th>Recovery (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>Au(III)</td>
<td>Chloroform</td>
<td>Acetone</td>
<td>VBR</td>
<td>0.005</td>
<td>3</td>
<td>4.2</td>
<td>98-101.5</td>
<td>[38]</td>
</tr>
<tr>
<td>Environmental samples</td>
<td>Cd(II)</td>
<td>Carbon tetrachloride</td>
<td>Methanol</td>
<td>Ammonium pyrroldine dithiocarbamate</td>
<td>0.0006</td>
<td>3</td>
<td>3.5</td>
<td>87-108</td>
<td>[37]</td>
</tr>
<tr>
<td>Water samples</td>
<td>As(III) &amp; Sb(III)</td>
<td>Carbon tetrachloride</td>
<td>Methanol</td>
<td>Ammonium pyrroldine dithiocarbamate</td>
<td>0.01 (As(III)) 0.05 (Sb(III))</td>
<td>1</td>
<td>2.9-4.5</td>
<td>-</td>
<td>[42]</td>
</tr>
<tr>
<td>River, lake &amp; tap water</td>
<td>Pd</td>
<td>Carbon tetrachloride</td>
<td>Ethanol</td>
<td>DDTC</td>
<td>0.0024</td>
<td>1</td>
<td>4.3</td>
<td>96-102</td>
<td>[39]</td>
</tr>
<tr>
<td>Tap water</td>
<td>Pb</td>
<td>Carbon tetrachloride</td>
<td>Ethanol</td>
<td>PMBP</td>
<td>0.039</td>
<td>4</td>
<td>3.2</td>
<td>94-95</td>
<td>[36]</td>
</tr>
<tr>
<td>Tap, well &amp; sea water</td>
<td>Pb</td>
<td>Carbon tetrachloride</td>
<td>Acetone</td>
<td>Dithyldithio phosphorylic acid</td>
<td>0.02</td>
<td>1</td>
<td>2.5</td>
<td>93-5-105</td>
<td>[43]</td>
</tr>
<tr>
<td>Tap, river water &amp; sea water</td>
<td>Se(IV)</td>
<td>Carbon tetrachloride</td>
<td>Ethanol</td>
<td>APDC</td>
<td>0.05</td>
<td>3</td>
<td>4.5</td>
<td>96-106</td>
<td>[41]</td>
</tr>
<tr>
<td>Lake &amp; river water</td>
<td>Co &amp; Ni</td>
<td>Carbon tetrachloride</td>
<td>Acetone</td>
<td>PAN</td>
<td>21 (Co&lt;sup&gt;+&lt;/sup&gt;) 32 (Ni&lt;sup&gt;2+&lt;/sup&gt;)</td>
<td>9.2</td>
<td>101 (Co) 200 (Ni) 7.5 (Co)</td>
<td>8.2 (Ni) 90-90</td>
<td>[40]</td>
</tr>
</tbody>
</table>

**Table 3: Dispersive liquid phase microextraction conditions for trace elements analysis**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Cloud extraction (CPE)</th>
<th>Solid phase extraction (SPE)</th>
<th>Dispersive liquid-liquid microextraction (DLLME)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trace elements with good recoveries (&gt;87%)</td>
<td>Cr, Al, Ni, Sn, Ag, As, Mo &amp; Bi</td>
<td>Cr, Al, Ni, Ag, As, Mo, Bi, Pb, Se, Co, Cu, Cd &amp; Fe</td>
<td>Ni, As, Pb, Se, Co, Cd, Au, Sb &amp; Pd</td>
</tr>
<tr>
<td>Enrichment Factor (EF) (%)</td>
<td>25-196</td>
<td>20-300</td>
<td>70-388</td>
</tr>
<tr>
<td>Relative Standard Deviation (R.S.D.) (%)</td>
<td>2.6-4.7</td>
<td>1.0-&lt;0.0</td>
<td>2.5-8.2</td>
</tr>
<tr>
<td>Extraction Time (h)</td>
<td>Medium</td>
<td>Medium</td>
<td>Fast</td>
</tr>
<tr>
<td>Reagent and costs</td>
<td>Environmentally safe and cheap</td>
<td>Environmentally safe and cheap</td>
<td>Environmentally safe and cheap</td>
</tr>
</tbody>
</table>

**Table 4: An overview of advantages and limitations of CPE, SPE and DLLME methods.**
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