Review

Latest approaches on green chemistry preconcentration methods for trace metal determination in seawater — A review

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ABSTRACT

Evaluation of trace metal levels in seawater samples is undertaken regularly by research groups all over the world, leading to a growing demand for techniques involving fewer toxic reagents, less time-consuming protocols and lower limits of detection. This review focuses on providing a brief but concise description of the latest methodologies developed to this end, outlining the advantages and disadvantages of the various protocols, chelating and dispersive agents and instruments used. Conclusions are drawn on the basis of the articles reviewed, highlighting improvements introduced in order to enhance the performance of the protocols.

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1. Introduction

Monitoring the presence of trace metals in seawater matrices is of great importance since they interact with most marine fauna, particularly in estuaries -unique ecosystems with complex and dynamic processes of ecological and environmental significance- and because of their effect on human development along the coast.

The determination of trace metals in seawater samples using conventional liquid—liquid extractions (LLE) requires the use of large volumes of samples, which are usually difficult to obtain. The procedure usually involves considerable amounts of potentially toxic organic solvents to achieve an efficient extraction and is furthermore considered to be a tedious, multistage operation. The adequate disposal and treatment of the generated waste is also a time-consuming process, thus increasing the cost of the analysis. In addition, organic solvents can be deleterious to some analytical techniques (e.g. Hari Babu et al., 2007; Stalikas, 2002), calling for an alternative approach to sample treatment.

Seawater samples are particularly difficult to study since the metal concentration within these solutions is usually quite low, often making it necessary to carry out preconcentration steps, and the saline matrix interferes with the determination. In order to overcome these difficulties it has been proposed that the traditional liquid—liquid extraction principle be miniaturized, options of this nature being safer and more environmentally friendly since they diminish the use of organic solvents and acids. The lower cost and lower risk of sample contamination implied by these novel techniques is also to their advantage.

Green chemistry principles aim at reducing hazardous impacts on human health and the environment. The techniques evaluated here are also designed to be less time-consuming, at the same time ensuring good recoveries and limits of detection.

Although numerous reviews have discussed miniaturized preconcentration techniques for trace metal determination or greener strategies for preconcentration, the present study is the first to focus on the applicability of these microextraction procedures exclusively to seawater samples. This article prioritizes strategies that minimize sample volume and avoid the use of toxic reagents

and solvents. A brief description is given of the techniques used for trace metal determination, with details of the properties and detection limits achieved. Different analytical methodologies are compared in terms of their ability to preconcentrate different analytes, highlighting their low cost and ease of acquisition for most laboratories.

2. CPE

Cloud-point extraction (CPE) was first reported by Watanabe et al. (1982, in Safavi et al., 2004), whose research was based on extracting and preconcentrating Ni with 1-(2-thiazolylazo)-2-naphtol (TAN) in a Triton X-100 micellar solution. This technique, fully described elsewhere (e.g. Bosh Ojeda and Sanchez Rojas, 2011;

Silva et al., 2006), is based on the use of non-ionic surfactants which are capable of producing micelles in aqueous solution and become turbid when heated at a temperature known as the cloud-point temperature (CPT). This is to be expected since at low temperatures polyoxyethylene surfactants show ethyl oxide segments in the micelle that repel each other. At higher temperatures, these segments attract each other and become a cloudy solution. Thus, at temperatures above the critical CPT a surfactant-rich phase separates from the mixture, in which the surfactant concentration is close to the critical micellar concentration (CMC).

The technique involves a reduction in solvent use, disposal costs and extraction time (Goudarzi, 2007) and is safe, rapid and easy to implement (Safavi et al., 2004). CPE offers many advantages over traditional liquid—liquid extraction, such as eliminating the need to

Table 1
CPE procedures for heavy metals preconcentration and determination in seawater samples. Reagents required for the procedures as well as limits of detection are also shown.

Analyte	Detection equipment	Extraction phase	Chelating agent	pH buffer solution	LOD (μg/L)	Recoveries (%)*	References
Cd	FAAS	Triton X-114	DPTH	5.4	0.95	106.5 (20)	Bosh Ojeda et al., 2010
Cd	FAAS	Triton X-114	TAN	8 to 10	0.099	102 (10)	Chen and Teo 2001b
Cd	FAAS	Triton X-114	Dithizone	7	0.31	98.6—100.3 (10—20)	Manzoori and Karim-Nezhad 2004
Cd	ICP OES	Triton X-114	TTA	6	0.1	90—110	Yamini et al., 2008
Co	FAAS	Triton X-114	1-PTSC	8 to 10	1	98—98 (10—20)	Citak and Tuzen 2010
Co	FAAS	Triton X-114	TAN	7	0.24		Chen and Teo 2001a
Co	FAAS	PONPE 7.5	1-nitroso-2-naphthol	2 to 6	1.22	99.1—96.1 (20—30)	Manzoori and Bavili-Tabrizi 2003
Co	UV-spectrophotometer	Triton X-114	ACDA	5	7.5	103.4 (20)	Safavi et al., 2004
Co	TLS	Triton X-114	PAN	7	0.03	100.9—100.3 (10—20)	Shemirani and Shokoufi 2006
Co	ICP OES	Triton X-114	TTA	6	0.3	90—110	Yamini et al., 2008
Cu	FAAS	Triton X-114	TAN	7 to 10	0.27	98.6 (10)	Chen and Teo 2001b
Cu	FAAS	Triton X-114	Cupron	6	0.04	99.5—101.8 (4—10)	Goudarzi 2007
Cu	FAAS	Triton X-114	1-PTSC	8 to 10	0.67	97—99 (10—20)	Citak and Tuzen 2010
Cu	ICP OES	Triton X-114	TTA	6	0.4	90—110	Yamini et al., 2008
Cu	FAAS	Triton X-114	ECR	6	0.57	103.1—99.6 (10—20)	Durukan et al., 2011
Cr	ICP OES	Triton X-114	TTA	6	0.2	90—110	Yamini et al., 2008
Cr (VI)	HPLC	Triton X-114	DDTC	7	5.2	97.3 (100)	Tang et al., 2004
Cr (III)	HPLC	Triton X-114	DDTC	7	3.4	97.1 (100)	Tang et al., 2004
Fe	ICP OES	Triton X-114	TTA	6	2.2	90—110	Yamini et al., 2008
Fe	FAAS	Triton X-114	ECR	4.5	0.33	98.8—102.4 (10—20)	Durukan et al., 2011
Mn	FAAS	Triton X-114	TAN	9.2	0.28	97.8—96.9 (10—20)	Teo and Chen 2001
Mn	ICP OES	Triton X-114	TTA	6	0.1	90—110	Yamini et al., 2008
Mo	GFAAS	Triton X-114	QA	3	0.0096	98—99 (5—10)	Filik et al., 2009
Ni	FAAS	Triton X-114	Dithizone	7	1.2	99.3—98.9 (10—20)	Manzoori and Karim-Nezhad 2004
Ni	UV-spectrophotometer	Triton X-114	ACDA	5	10	105.9 (20)	Safavi et al., 2004
Ni	FAAS	PONPE 7.5	1-nitroso-2-naphthol	6 to 9	1.09	100.8—97.2 (20—30)	Manzoori and Bavili-Tabrizi 2003
Ni	FAAS	Triton X-114	TAN	7	0.44		Chen and Teo 2001a
Pb	FAAS	Triton X-114	1-PTSC	8 to 10	3.42	96—98 (10—20)	Citak and Tuzen 2010
Pb	FAAS	Triton X-114	TAN	7 to 9	1.1	98.6 (10)	Chen and Teo 2001b
Pd	TLS	Triton X-114	PAN	4	0.04	102—100.3 (15—30)	Shokoufi et al., 2009
Zn	FAAS	Triton X-114	TAN	7 to 10	0.095	104 (10)	Chen and Teo 2001b

LOD: limits of detection; * spiked concentrations in μg/L are presented in parenthesis.

handle large volumes of volatile, toxic and flammable organic solvents (Bosh Ojeda et al., 2010).

An overview of the main characteristics, recovery percentages and limitations of the technique are presented in Table 1. A schematic representation of the discussed procedure is shown in Fig. 1.

In 2001, Chen and Teo (2001a, 2001b) and Teo and Chen (2001) studied trace metals preconcentration within a CPE technique, in all cases using seawater for testing the reliability of a procedure that included the use of TAN (Lancaster Synthesis, Morecambe, UK) as the complexing agent and Triton X-114 (Sigma, St. Louis, MO, USA) as the non-ionic surfactant. TAN was directly prepared in Triton X-114, thus avoiding the use of harmful reagents. Phase separation required a centrifugation step (5000 rpm-15 min) and solidification was subsequently achieved by cooling in an ice-bath. The final solution was observed at the bottom of the tubes and obtained by inversion. A drawback of the procedure is the use of a harmful reagent like methanol for the dissolution of the analytes solution.

Manzoori and Bavili-Tabrizi (2003) proposed a cloud point procedure to preconcentrate Co and Ni from aqueous matrices but employing an unconventional non-ionic surfactant: polyethylene glycol-p-nonylphenylether, PONPE 7.5 (Tokyo Kasei Industries, Tokyo, Japan). This reagent was chosen since it gave rise to better cloud point temperatures and extraction efficiencies than other tested surfactants. A lower CPT assured no back extraction during centrifugation. These authors also tested seawater samples for the validation of the method.

The main steps of the preconcentration procedure involved heating the mixture in a 35 °C thermostated bath for 15 minutes followed by centrifugation (3200 rpm-10 min) and then cooling in an ice-acetone mixture. The final phase separation was carried out with the aid of a syringe. In order to facilitate handling, a dilution was made prior to introducing the final solution and the addition of methanol gave rise to better analytical signal results than nitric acid and ethanol.

Co and Ni recoveries were almost quantitative in the presence of other species with tolerance limits (error < 5%). The marked lack of interference effects could be attributed to the use of 1-nitroso-2-naphthol as complexing agent, which is a more selective ligand than those used by others researchers (Chen and Teo, 2001a, 2001b; Teo and Chen, 2001). The designed methodology involved the use of a flame atomic absorption spectrometer (FAAS) available in most laboratories, thus offering a simple, rapid, sensitive, low cost and non-polluting alternative compare to other separation-preconcentration techniques.

Manzoori and Karim-Nezhad (2004) proposed a CPE procedure to analyse Cd and Ni in combination with a FAAS detection system,
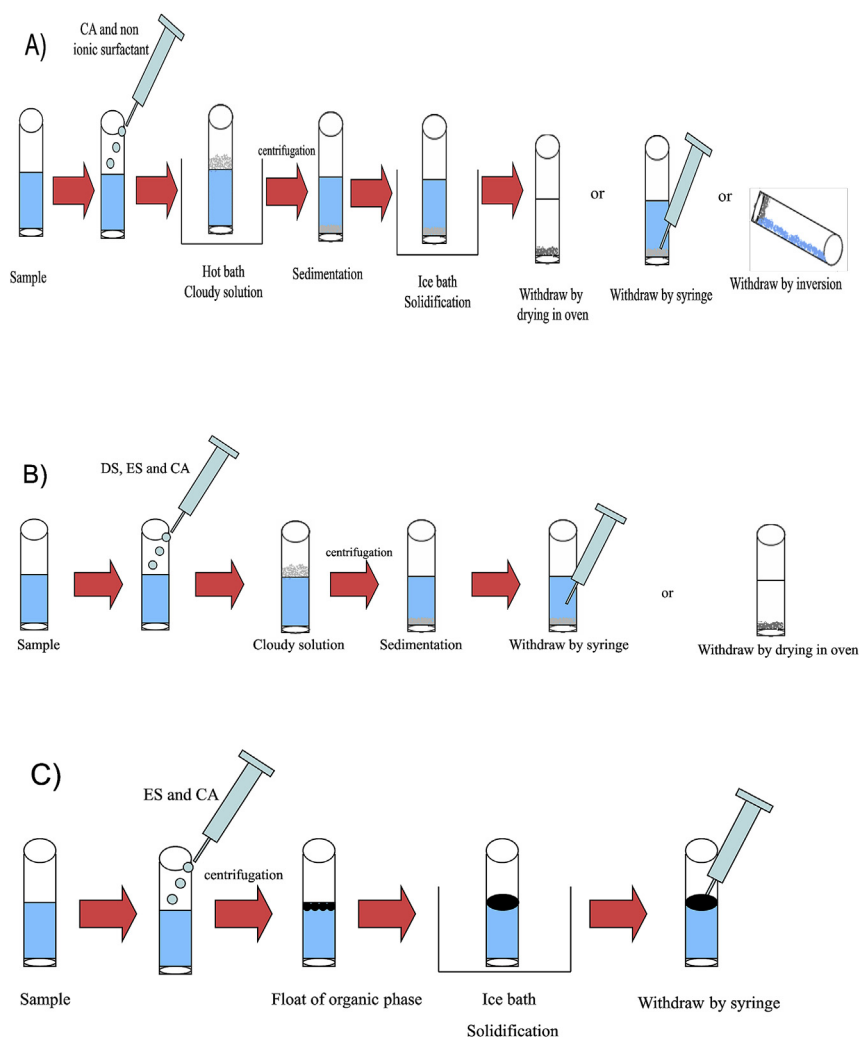

Fig. 1. Schematic representation of the steps involved in the different liquid−liquid preconcentration procedures until the final extract is obtained. A) Cloud point extraction (CPE); B) Dispersive liquid−liquid microextraction (DLLME); C) Solidified floating organic drop microextraction (SFODME). CA: chelating agent; DS: dispersive solvent; ES: extraction solvent.

choosing dithizone (E. Merck, Darmstadt, Germany) as the chelating agent since it is strong, stable and is commonly used. In order to facilitate its solubility and stability in water, tetrahydrofuran (THF) (E. Merck) was previously added to the solution. The procedure steps were similar to Manzoori and Bavili-Tabrizi (2003), being Triton X-114 and a pH 7 solution adequate for Cd and Ni recovery.

Safavi et al. (2004) developed a CPE technique combined with an UV-spectrophotometer for the determination of Ni and Co from natural and waste water samples. In order to validate the proposed methodology, seawater samples were tested. 2-amino-cyclo-pentene-1-dithiocarboxylic acid (ACDA) was the complexing agent and the non-ionic surfactant Triton X-114 (Fluka Chemie AG, Switzerland) was chosen due to its commercial availability in a highly purified homogeneous form, low toxicological properties and cost. Phase separation by centrifugation was facilitated due to the high density of the surfactant-rich phase.

The influence of the ionic strength on the cloud point phenomenon was examined and no appreciable effect was observed after increments in $NaNO_3$ concentrations, in agreement with previous discussed articles (Asadollahi et al., 2010; Chen and Teo, 2001a, 2001b; Teo and Chen, 2001). Cd^{2+}, CrO^{4-}, Cu^{2+}, V^{4+} and V^{5+} were found to interfere in the determination of Co at a concentration of 50 μg/L.

Tang et al. (2004) introduced a CPE procedure for Cr species determination in seawater and snow water. The typical steps for preconcentration were followed (Manzoori and Bavili-Tabrizi, 2003; Manzoori and Karim-Nezhad, 2004). A pH 7 solution was selected for the simultaneous extraction of both analytes with good efficiency recoveries. Triton X-114 was the non-ionic surfactant and diethyldithiocarbamate (DDTC) (Tianjin Chemicals, Tianjin, China) the chelating agent because it forms highly hydrophobic complexes with trace metal ions.

A high-performance liquid chromatography (HPLC) instrument was used for metal speciation and since the use of the non-ionic surfactant might interfere with the UV absorbance, a mixture of methanol, water and acetonitrile was selected as the optimal composition for the mobile phase. Additionally, methanol was added to the surfactant-rich phase after phase separation to reduce the mobile phase viscosity just before HPLC separation.

Shemirani and Shokoufi (2006) proposed a new approach when working with a CPE procedure. They employed a cloud point extraction in combination with thermal lens spectrometry (TLS) for the determination of Co. The single laser TLS is simple both in the setup and alignment of the optical system. Moreover, the operational costs of this detection system are lower than those of other methods such as FAAS and inductively coupled plasma optical emission spectrometry (ICP OES).

Briefly, the scheme for Co determination involved the use of 1-(2-pyridylazo)-2-naphthol (PAN) (E. Merck) dissolved in pure ethanol as the chelating agent. The thermal lens signal was evaluated as a function of the complexing agent concentration, so a five-fold excess of PAN over the Co molar concentration was selected to obtain the maximum thermal lens signal. After the addition of the non-ionic surfactant, Triton X-114, a pH 7 solution was heated in a water bath at 100 °C up to the cloud point temperature so as to remove the remaining water. The complex exhibited absorption in the wavelength range of 540—650 nm whereas Triton X-114 and PAN showed no absorption in this range.

Shemirani and Shokoufi recommended the combined use of CPE and TLS since in both cases only a low volume of sample is required and Cu^{2+}, Pd^{2+}, Zn^{2+} and Rh^{3+} only showed interferences at a concentration ten times higher than Co. On the contrary, organic solvents were used since they have better thermo-optical properties than water, so might improve the sensitivity of the TLS method after CPE.

Goudarzi (2007) introduced a CPE procedure using low toxicity reagents to determine Cu in seawater samples. Optimization of the parameters included a pH 6 solution for maximum extraction efficiency, the non-ionic surfactant Triton X-114, Cupron (Fluka Chemie AG) as the chelating agent and a temperature above 50 °C for a good clouding behaviour. On the down side, a toxic reagent, acidic methanol, was used for a final dissolution of the micellar phase before introduction into a FAAS.

Yamini et al. (2008) designed an on-line preconcentration CPE procedure with an ICP OES equipped with a radial view configuration torch coupled to a V-groove nebulizer. Cd, Co, Cr, Cu, Fe and Mn in pH 6 seawater samples were simultaneously determined with 1-(2-thenoyl)-3,3,3-trifluoraceton (TTA) (E. Merck), selected as the chelating agent as it can complex all the trace elements. Off-line CPE involves a series of elaborate and time-consuming procedures (e.g. incubation, centrifugation) which may result in poor reproducibility and a low preconcentration factor (Yamini et al., 2008). Thus, these authors evaluated the feasibility of an on-line procedure where chelates of metal ions plus TTA were heated up to 65 °C with the addition of Triton X-114 and then trapped in a suitable in-line filter. The trapped phase was then eluted and introduced into an ICP OES nebulizer.

In the cited study, a home-made column was used to carry out phase separation. In trials using a cigarette filter and a glass wool-packed column to fill the in-line filter, the columns exhibited poor capability and precision for collecting the micelles. Finally, commercial cotton turned out to be highly efficient in retaining the surfactant-rich phase. The size of the column was also relevant: it was found that a longer column gave rise to high retention efficiencies but increase resistance to the passage of the solution, thus reducing precision, whereas a shorter column improved precision but reduced the filter capacity. A suitable degree of sensitivity and precision was accomplished using a column with an effective length of 4 cm. Prior to carrying out the analyses, the cotton column was cleaned with a methanol-nitric acid solution. Distilled water, methanol, ethanol and propanol in nitric acid were evaluated as eluents for the cotton column, on the basis of which the latter was selected for the elution step.

Yamini et al. also tested the volume of sample required to obtain higher enrichment factors. Their results indicate that 50 mL of sample achieved recoveries of Cd, Cr, Cu and Mn close to 100%, whereas for Co and Fe the require volume was 75 mL and 100 mL, respectively. The advantage of on-line preconcentration is that it only requires approximately 6 minutes for 25 mL of sample and yet the results are comparable to those of off-line CPE procedures in terms of precision, detection limits and linear ranges. The procedure maximizes simplicity and sensitivity, reducing to one step the heating of sample, trapping and elution of the entrapped analytes.

Filik et al. (2009) determined Mo in seawater samples, using surfactants instead of volatile organic solvents, thus avoiding laboratory contamination and generating less impact on the environment. The experimental conditions involved the use of 1,2,5,8-Tetrahydroxyanthracene-9,10-dione (QA) (Friederich Bayer & Co., Germany), highly selective for chelating Mo(VI) at pH 3 and the non-ionic surfactant Triton X-114 (E. Merck). The addition of ammonium fluoride was employed as a masking agent for Fe(III) and Al(III), both extracted along with Mo. The final surfactant-rich phase was diluted with tetrahydrofuran (THF) to gain homogeneity and reduce viscosity, compatible with a good sample introduction into the graphite furnace atomic absorption spectrometry (GFAAS) flame.

Shokoufi et al. (2009) combined the use of a cloud point extraction for the determination of Pd with TLS, for being a sensitive and inexpensive detection instrument. For the palladium—chelate complex formation, a pH 4 solution with PAN (E.

Merck) and Triton X-114 was selected. The surfactant-rich phase was heated in a 100 °C thermostated water bath in order to remove the remaining water. The researchers then dissolved the final extract with organic solvents since they gave rise to better thermo-optical properties than aqueous ones. Chloroform, THF, cyclo-hexane dimethyl sulfoxide (DMSO) and carbon tetrachloride were evaluated on the basis of which the latter was chosen.

The absorption spectrum of the palladium-PAN complex exhibited absorption in the wavelength range of 600—680 nm whereas Triton X-114 and PAN showed no absorption in this range. Cu^{2+}, Fe^{3+} and Ni^{2+} showed interferences at a concentration twenty times higher than Pd levels, while Co^{2+} showed interferences at equal values. The limit of detection of the procedure was comparable with ETAAS and ICP MS analytes determination.

Bosh Ojeda et al. (2010) proposed the use of a CPE procedure for the preconcentration of Cd in different matrices, including seawater for validation of the method. 1, 5-bis (di-2-pyridylmethylene) thiocarbonohydrazide (DPTH) prepared in dissolution with a possible carcinogenic reagent: dimethylforma-mide (DMF), was used as the chelating agent in a 5.4 pH solution. Triton X-114 (E. Merck), due to its recognized physicochemical characteristics, was chosen for the surfactant-rich phase. The solution was heated in a 50 °C thermostated water bath for a maximum recovery of analytes and then centrifuged (3800rpm-5 min). A HNO_3/methanol mixture was finally added to the solution before introduction into the flame to reduce surfactant-phase viscosity and facilitate its handling.

Determinations made with the traditional FAAS instrument were comparable with high sensitive ones, such as ETAAS. Influence of ionic strength in the extraction efficiency was examined for NaCl concentrations in the range 0.5—3%. The aforementioned authors concluded that ionic strength had no significant effect upon percentage recoveries and sensitivities of the method, highlighting no complications when complex matrices were tested.

Citak and Tuzen (2010) designed a CPE procedure for Co, Cu and Pb determination in different matrices, including seawater samples for testing the accuracy of the method. The technique involved the chelating agent 1-phenylthiosemicarbazide (1-PTSC) dissolved in methanol—water and the non-ionic surfactant Triton X-114 (E. Merck). The remaining surfactant-rich phase was dissolved in HNO_3/methanol and determined by FAAS.

In similar trials undertaken by Asadollahi et al. (2010), changes in the ionic strength of the samples up to 0.5 M had no appreciable effect on extraction efficiency and sensitivity. In the case of Triton X-114, the aforementioned authors concluded that due to an increase in the volume and viscosity of the surfactant phase, concentrations above 0.05% generated a decrease in the analytical signal as well as in the extraction efficiency (Goudarzi, 2007).

Durukan et al. (2011) proposed an online system in combination with FAAS for the determination of Cu and Fe in food and seawater samples. These authors aimed to avoid the multistage operations involved in an offline determination by working with an online procedure that offers advantages such as high velocity, analytical reproducibility, reduction in sample and solvent consumption and matrix contamination.

Eriochrome Cyanine R (ECR) (Fluka Chemie AG) was selected as the chelating agent since the complex formed was fast and with good selectivity. Triton X-114 was then added as the non-ionic surfactant to a pH 4.5 solution for Fe(III) determination and to a pH 6 solution for Cu(II) determination. The technique involved the use of a mini column as in Yamini et al. (2008). After trials using glass, wool, cotton, and silica gel, cotton turned out to be highly accurate for the entrapment of the analytes. An appropriate column size of an effective length of 2.8 cm was used to obtain suitable sensitivity and precision.

3. DLLME

Dispersive liquid—liquid microextraction (DLLME) is a technique based on the introduction of a mixture of disperser and extraction solvents into an aqueous sample. This mixture is capable of producing a cloudy solution. It consists of droplets of the extraction reagent which are able to attach analytes (e.g. heavy metals). The technique involves a centrifugation step to cause the sedimentation of the extraction phase. The removal of the phase containing the extracted analytes is then measured with appropriate detection instruments.

DLLME was first reported by Rezaee et al. (2006), whose aim was to develop a less time-consuming method with a reduction in the amounts of sample and solvents used. The cloudy solution is almost immediately formed and the equilibrium state is achieved (Andruch et al., 2012), thus having short extraction times. The use of microliters of organic solvents also makes it an environmentally friendly method for analytes determination. Detailed descriptions of the technique and applications have already been reviewed (Al-Saidi and Emara, 2014; Rezaee et al., 2010). An overview of the main characteristics of the protocols described below is presented in Table 2 and a schematic representation of the procedure is shown in Fig. 1.

The application of DLLME for trace metal determination in seawater samples was first introduced by Jahromi et al. (2007). These researchers reported the determination of Cd coupled to a GFAAS instrument. Ammonium pyrrolidine dithiocarbamate (APDC) (E. Merck) was selected for complexing Cd ions at pH 3.3. Chloroform, carbon disulfide and carbon tetrachloride were evaluated as extraction solvents with density higher than water and low solubility in the aqueous phase. The latter reagent was selected as it achieved a stable cloudy solution and a sedimentation phase that could be easily removed. Since miscibility between both the sample solution and the extraction phase is of great importance when selecting the disperser solvent, acetone, acetonitrile, methanol and ethanol were tested. Even though all solvents were efficient, methanol turned out to be the best choice. Disperser solvents additionally achieved high extraction efficiency by decreasing the adsorption of the analytes on the test tube (wall effect) caused by the presence of salts (Baghdadi and Shemirani, 2009).

Naseri et al. (2008) designed a DLLME protocol for the determination of Pb in seawater samples in combination with a GFAAS detection instrument. 5 mL sample without filtration and stored in a dark place at 4 °C was analyzed within 24 h of collection. As in Jahromi et al. (2007), the extraction procedure involved the use of carbon tetrachloride (E. Merck) as extraction solvent. Acetone (E. Merck) was the best option as the disperser solvent and diethyldithiophosphoric acid (DDTP) (E. Merck) was selected as the chelating agent. The aqueous solution of DDTP was almost acidic, thus no pH buffer solution was needed.

Anthemidis and Ioannou (2009) developed an automated sequential injection technique with a FAAS detection instrument for Cu and Pb determination. Coastal seawater was evaluated to test the reliability of the method. The scheme included pH 1.4 seawater with ammonium diethyldithiophosphate (DDPA) (Sigma) as the chelating agent, with high selectivity and stability at low pHs compared to the other commonly dithiocarbamate reagents employed. DDPA also forms strong complexes with metal ions, being resistant against hydrolysis, thus no buffer solution was needed and a possible source of contamination avoided.

Briefly, the main steps involved the on-line merger of the sample (aqueous phase) with the stream containing the dispersive (e.g. methanol) and extraction solvents, resulting in a cloudy solution. Extraction reagents should be immiscible with the aqueous phase and they should have high extraction efficiency, selectivity

Table 2
SFODME, DLLME and DLLME-SFO procedures for heavy metals preconcentration and determination in seawater samples. Reagents required for the procedures as well as limits of detection are also shown.

Analyte	Technique	Detection equipment	Extraction phase	Disperser solvent	Chelating agent	pH buffer solution	LOD (µg/L)	Recoveries (%)*	References
Cd	SFODME	FAAS	1-Undecanol		Potassium iodide-MTOA	1.2	0.0079	98 (15)	Dadfarnia et al., 2009
Cd	DLLME	GFAAS	Carbon tetrachloride	Methanol	APDC	3.3	0.0006	95 (0.005)	Jahromi et al., 2007
Co	SFODME	GFAAS	1-Undecanol		PAN	7	0.0004	99 (0.001)	Bidabadi et al., 2009
Co	DLLME-SFO	ICP OES	1-Undecanol	Acetone	TTA	6	0.2	93 (10)	Yamini et al., 2010
Cu	DLLME	FAAS	Xylene	Methanol	DDPA	1.4	0.04	100.3 (2)	Anthemidis and Ioannou 2009
Cu	DLLME	ICP OES	Carbon tetrachloride	Methanol	Na-DDTC	6.7	0.23	91.7 (100)	Sereshti et al., 2011
Cu	DLLME-SFO	ICP OES	1-Undecanol	Acetone	TTA	6	0.2	91 (10)	Yamini et al., 2010
Cr	DLLME	ICP OES	Carbon tetrachloride	Methanol	Na-DDTC	6.7	0.27	93 (100)	Sereshti et al., 2011
Cr	DLLME-SFO	ICP OES	1-Undecanol	Acetone	TTA	6	0.1	89.5 (10)	Yamini et al., 2010
Mn	DLLME-SFO	ICP OES	1-Undecanol	Acetone	TTA	6	0.3	96 (10)	Yamini et al., 2010
Ni	DLLME	ICP OES	Carbon tetrachloride	Methanol	Na-DDTC	6.7	0.4	90.5 (100)	Sereshti et al., 2011
Ni	SFODME	GFAAS	1-Undecanol		PAN	7	0.0003	95 (0.001)	Bidabadi et al., 2009
Pb	DLLME	FAAS	Xylene	Methanol	DDPA	1.4	0.54	95 (10)	Anthemidis and Ioannou 2009
Pb	DLLME	GFAAS	Carbon tetrachloride	Acetone	DDTP	–	0.02	93.3–105 (0.20–0.40)	Naseri et al., 2008
Pb	SFODME	GFAAS	1-Undecanol		Dithizone	6	0.0009	near 100 (0.001)	Dadfarnia et al., 2008
V	DLLME-SFO	GFAAS	1-Undecanol	Acetone	BPHA	3	0.007	105%-96 (0.20–0.25)	Asadollahi et al., 2010
Zn	DLLME	ICP OES	Carbon tetrachloride	Methanol	Na-DDTC	6.7	0.55	93 (100)	Sereshti et al., 2011

LOD: limits of detection; * spiked concentrations in µg/L are presented in parenthesis.

and hydrophobicity. Hydrophobicity is the main factor affecting the retention of the extraction droplets (organic phase). Therefore, phase separation is based on retention and not on centrifugation. Additionally, density higher than water is not a requirement for the extraction reagent. Xylene achieved the highest extraction efficiency and Isobutyl methyl ketone (IBMK) was also added through the microcolumn in order to elute the analytes.

These researchers highlighted the improvements introduced by working with an automated technique, describing the importance of the size of the droplets. The best preconcentration factor was achieved with a decrease in the size, resulting in a better volume-ratio rate. The volume of the extraction solvent also affected the retention process and the flow rate of the disperser solvent of up to 0.36 mL/min improved the sedimentation of the extraction solvent (fine droplets formation) and the retention in the microcolumn.

Sereshti et al. (2011) studied a DLLME technique to preconcentrate Cr, Cu, Ni and Zn from pH 6.7 seawater samples. Sodium diethyldithiocarbamate (Na-DDTC) (Hopkin & Williams, UK) was selected as the chelating agent and methanol and carbon tetrachloride were chosen as the solvent pair with the maximum recovery for the cloudy solution. The remaining phase was then dried at 90 °C, dissolved in HNO₃ and introduced in an ICP OES nebulizer.

3.1. SFODME

Zanjani et al. (2007) introduced a technique based on the modification of the liquid−liquid microextraction one that was

termed solidified floating organic drop microextraction (SFODME). It is based on the partitioning of analytes of sufficient hydrophobicity between the aqueous phase and an organic extraction solvent with a melting point close to room temperature (10−30 °C). The organic phase floats on the surface of the stirred aqueous solution for a known amount of time and the solution is then cooled in an ice bath. After the organic solvent solidifies, it is easily separated from the bulk solution and melted for analytes determination.

The technique offers many advantages such as simplicity, short extraction time, low cost, minimum organic solvent consumption, achievement of high enrichment factor and efficiency for the removal of interfering matrices. Detailed information is provided by Dadfarnia et al. (2010). Table 2 includes the differential characteristics of the protocols described and the schematic representation of the procedure is shown in Fig. 1.

Dadfarnia et al. proposed the application of a SFODME technique in two different studies. One of them (Dadfarnia et al., 2008) reported the preconcentration of Pb in pH 6 seawater samples. Dithizone and 1-undecanol (E. Merck) were selected as the chelating and extraction solvents respectively. These researchers highlighted that the achievement of a state of equilibrium between the phases (aqueous and organic) and a maximum extraction of analytes relied on the extraction time (Bidabadi et al., 2009). A state of equilibrium was achieved after a centrifugation step (5000 rpm-5 min), this amount of time being appropriate for the solidification of the organic solvent after cooling the sample. The remaining phase was diluted with ethanol and determined by GFAAS.

In similar trials undertaken in 2009 (Dadfarnia et al., 2009), water samples were fixed at pH 1.2 with potassium iodide in order to convert Cd ions into the CdI_4^{2-} form. In order to fulfill the extraction of Cd, the analytes need to be part of a lipophilic complex and a way to increase their lipophilicity was by neutralizing their charge through an ion-pair formation with a large cation. For the ion-pair formation, methyltrioctylammonium chloride (MTOA) (E. Merck) was chosen. The main steps of the procedure involved the addition of 1-undecanol as extraction solvent, that due to its low volatility and water solubility gave rise to better analytical signal results than 2-dodecanol, 1,10-dichlorodecane and n-hexadecane. Stirring the solution (1200 rpm-15 min) before solidification was also necessary. A final dilution was made with ethanol prior to its introduction in a flow injection FAAS.

Bidabadi et al. (2009) designed a SFODME procedure for Co and Ni determination. They employed PAN (E. Merck), an organic re-agent commonly used for metal determination as the complexing reagent. A pH 7 seawater sample was stirred (1000 rpm- 30 min) including PAN and the organic extraction solvent, 1-undecanol, to assure a quantitative recovery of both analytes. 1-undecanol achieved higher extraction efficiency and produced lower background than 1,10-dichlorodecane and n-hexadecane. After the solution stood still for 5 minutes, the organic drop solidified and a final dilution in ethanol was made for a further determination by GFAAS.

In trials comparing different laboratory work temperatures, the range between 20 and 30 °C turned out to be highly efficient in quantitative extractions. Higher temperatures reduced recovery percentages due to an increment in the solubility of the organic phase and degradation of complexes, whereas temperatures below 20 °C reduced the correct dispersion of the extraction phase with consequently improper extractions. Cd, Cu and Zn interfered in analytes recovery but were eliminated upon addition of EDTA, as has been reported by other researchers (Shokoufi et al., 2007).

3.2. DLLME-SFO

In 2008, Leong and Huang reported a novel microextraction technique: the dispersive liquid−liquid microextraction based on the solidification of a floating organic drop, aiming to overcome several drawbacks of the former preconcentration procedure.

The preconcentration steps involved the introduction of a mixture of extraction and disperser solvents into the water sample by means of a syringe. Agitation is needed to maximize the contact area between the mixed solution and the analytes, thus creating a cloudy solution. The droplets at the top of the solution are then collected and solidified in an ice bath (Asadollahi et al., 2010; Yamini et al., 2010).

DLLME-SFO offers many advantages over DLLME, such as using extraction solvents compatible with the ICP detection system and working with lower amounts of and less toxic organic solvents. Also, it is no longer a requisite to use fragile and hard to clean conical bottom glass tubes. The droplet phase is easier to collect and there are no requirements for the extraction solvent to be high-density water immiscible (Asadollahi et al., 2010), thus differentiating from the DDLME technique. Even though DLLME-SFO and SFODME share the simplicity, high efficiency and low cost and need simple extraction apparatus, DLLME-SFO has shorter extraction times. The extraction equilibrium is rapidly achieved (Asadollahi et al., 2010) since the surface area between the extraction solvent and the aqueous phase is infinitely large. The differential characteristics of the protocols are described in Table 2 and the schematic representation of the procedure is shown in Fig. 2.

Yamini et al. (2010) coupled DLLME−SFO with ICP OES for the simultaneous determination of Cr, Co, Cu and Mn in a pH 6 seawater solution. The procedure included TTA (E. Merck) as the chelating agent since it can complex all the metal ions. Acetone, a commonly used disperser solvent for DLLME (Khani et al., 2011; Naseri et al., 2008), was chosen due to its higher intensity signal compared to acetonitrile and methanol. The extraction solvent of choice was 1-undecanol since it satisfied the requirements when selecting the extraction solvent: low volatility and water solubility, high solubility in the dispersive solvent, the ability to form a cloudy solution in the presence of dispersive solvent, a melting point near room temperature (10−30 °C) and density lower than water. A final dilution with 1-propanol was made before ICP OES determinations, coupled to a V-groove nebulizer and a Scott spray chamber.

Asadollahi et al. (2010) employed the DLLME-SFO technique working with 25 mL pH 3 sample solution. N-benzoyl-N-phenyl-hydroxylamine (BPHA) complexed V as the analyte of interest and a mixture of 1-undecanol and acetone (E. Merck) was selected for the cloudy solution since it showed a sharper signal than 2-dodecanol, 1,10-dicholorodecane and n-hexadecane. The influence of the ionic strength on the DLLME-SFO performance was studied. A concentration of salt up to 0.5 M had no effect on the extraction efficiency. Above this concentration, there might be a decrease in the extraction solvent solubility in the aqueous phase, thus reducing the signal absorbance in the GFAAS detection instrument.

4. RTILs

Room temperature ionic liquids (RTILs) are of great interest since they are environmentally friendly solvents for metal determinations, with good qualities arising from their lack of vapour pressure, high conductivity, high stability and low viscosity as well as solvent solubility and miscibility (Dadfarnia et al., 2010). They are organic salts comprising an organic cation with delocalized charge and organic or inorganic anions liquid at room temperature. Information has been already published concerning ionic liquid (IL) techniques applied to metal analysis (Martinis et al., 2010) and an overview of the main characteristics, recovery percentages and limitations are presented in Table 3. The schematic representations of the procedures are shown in Fig. 2.

Dadfarnia et al. (2010) developed a liquid−liquid extraction technique based on RTILs for Ni determination in water and seawater samples. The procedure involved the dissolution of the chelating reagent PAN in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4MIM]$ $[PF_6]$ (E. Merck), being capable of extracting Ni from a pH 7 aqueous solution. After phase separation by centrifugation (3500 rpm- 5 min), analytes were back-extracted into an acidified aqueous phase and they were determined by FAAS.

The equilibrium time between the aqueous phase and ionic liquids was a parameter influencing extraction capacity. An increase in the recovery of the analytes was observed with an increment in extraction time of up to 15 minutes. The findings were similar to those previously shown by Baghdadi and Shemirani (2008).

Ionic liquids tend to interact with conical bottom glass tubes used for decantation of the solution. In order to avoid the sticking of the IL phase onto the wall of the tubes, even after centrifugation at high rpm, polypropylene tubes were used.

4.1. CIAME

Baghdadi and Shemirani (2008) designed a procedure termed cold induced aggregation microextraction (CIAME) for Hg determination, introducing the use of RTILs towards heavy metal preconcentration. CIAME is the modification of a homogeneous liquid−liquid microextraction (HLLME) technique but without an interface between water and the extractant phase.
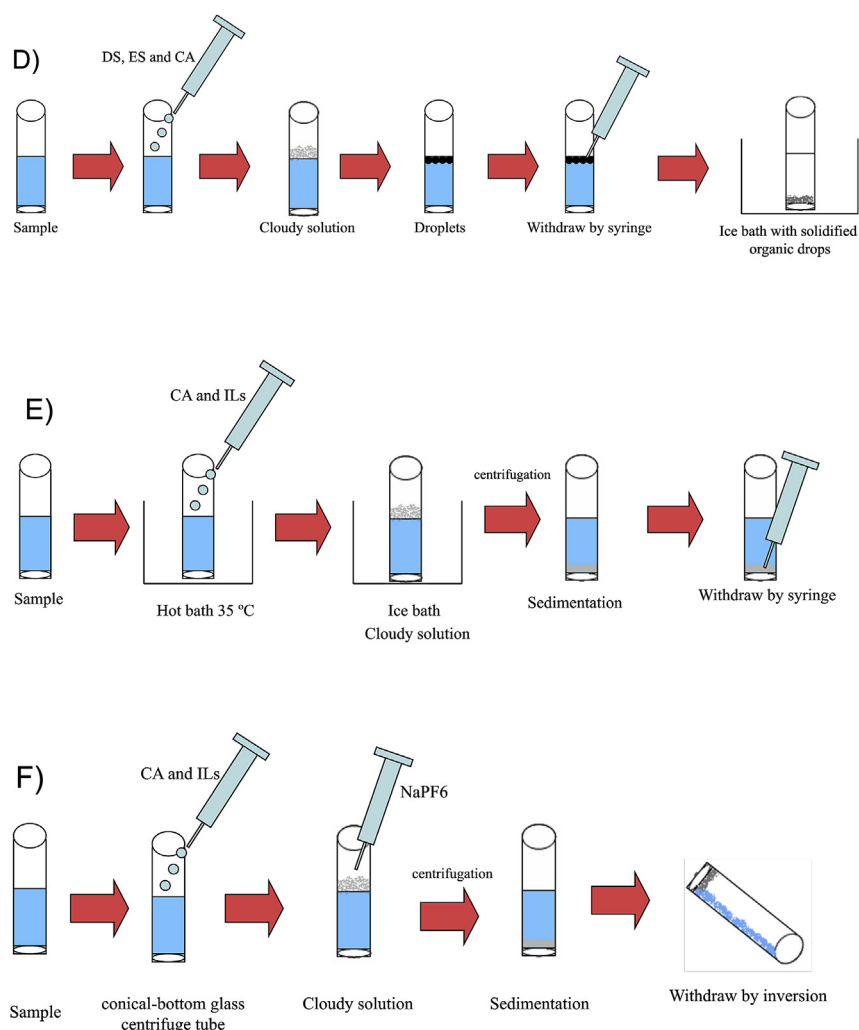
Fig. 2. Schematic representation of the steps involved in the different liquid–liquid preconcentration procedures until the final extract is obtained. D) Dispersive liquid–liquid microextraction-solidification of a floating organic drop (DLLME-SFO); E) Cold induced aggregation microextraction (CIAME); F) In-situ solvent formation microextraction (ISFME). CA: chelating agent; DS: dispersive solvent; ES: extraction solvent.

In the procedure, a pH 4 sample was kept at 35 °C with michler thioketone (TMK) (E. Merck) as the chelating agent and a mixture of 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim] [PF_6] and 1-hexyl-3-methylimidazolium bis (tri-fluoromethylsulfonyl) imide [Hmim] [Tf_2N] (E. Merck) as ionic liquids. Temperature was not critical between 20 °C and 50 °C. At higher temperatures, absorbance slightly decreased because of the degradation of TMK and the complex previously generated. Thus, an ice bath was further used to form a cloudy solution. After centrifugation (5000 rpm- 5 min), the fine droplets of IL settled at the bottom of the tube and were easily separated from the bulk sample solution.

There are important items to consider for an adequate ILs election. They must be water-immiscible: ILs containing BF_4, Cl^- and $CF_3SO_3^-$ are water-miscible and ILs containing PF_6^-, $(CF_3SO_2)^2N^-$ are water-immiscible. ILs must be inexpensive: those containing PF_6^- are fairly inexpensive. Also, the effects of the high content of salt in ILs should be evaluated when selecting the extractant solvent. Even though at high salt concentrations the solubility of [Hmim] [PF_6] increase preventing phase separation, ILs with a common ion (e.g. [Hmim] [Tf_2N]) decrease solubility and enable phase separation. CIAME benefits include the low background levels in saline solutions due to the low solubility of water in ILs and the simplicity of removing the bulk aqueous phase due to the high viscosity of ILs.

Possible ion interference was evaluated, with Ag^+, Au^{3+}, I^-, Pd^{2+} and Pt^{4+} interfering at the same concentration as Hg, and NO_2^- needing a concentration ten times greater than that of Hg to generate an adverse effect on the absorbance. Consequently, interferences were eliminated with the addition of EDTA. Due to the sticking of the droplets on the centrifugation tubes, a non ionic surfactant (Triton X-114) was added to the solution. Molecules of the surfactant surround the fine droplets of IL diminishing interactions with the wall of the centrifuge tube. The IL-phase was then dissolved in an ethanol solution in agreement with Mahpishanian and Shemirani (2010a).

Gharehbaghi et al. (2009) developed a procedure for the determination of Co in seawater samples. According to Baghdadi and Shemirani (2008), the procedure involved similar steps, although working with PAN (E. Merck) as chelating agent and Triton X-114 (Fluka Chemie AG) as anti-sticking agent. As for ILs, they prioritize ILs containing imidazolium cation. Imidazolium ionic liquids with PF_6^- as anions are hydrophobe, inexpensive and remain liquid at the experimental conditions, so being suitable for liquid–liquid extractions. [Hmim] [PF_6] and [Hmim] [Tf_2N] (E. Merck) were the ILs of election. Also, pH 1 was selected for the

Table 3
DLLME, ISFME, CIAME and M-CIAME procedures for heavy metals preconcentration and determination in seawater samples. Reagents required for the procedures as well as limits of detection are also shown.

Analyte	Technique	Detection equipment	Extraction phase	Disperser agent	Chelating agent	pH buffer solution	LOD (μg/L)	Recoveries (%)*	References
Cd	ISFME	FAAS	[Hmim] [BF$_4$]		DDTP	2	0.07	98.6 (5)	Mahpishanian and Shemirani 2010b
Co	CIAME	FO-LADS	[Hmim] [PF$_6$] [Hmim] [Tf$_2$N]		PAN	1	0.14	103.0–101.6 (10–25)	Gharehbaghi et al., 2009
Cu	DLLME	FAAS	[Hmim] [Tf$_2$N]	Acetone	TMK	5.5	0.45	85 (10)	Khani et al., 2011
Hg	CIAME	UV–Vis spectrometer	[Hmim] [PF$_6$] [Hmim] [Tf$_2$N]		TMK	4	0.3	97.5 (25)	Baghdadi and Shemirani 2008
Hg	ISFME	UV–Vis spectrometer	[Hmim] [BF$_4$] (NaPF$_6$)		TMK	4	0.7	104 (40)	Baghdadi and Shemirani 2009
Mo	DLLME	FO-LADS	[Hmim] [Tf$_2$N]	Acetone	CTAC-PR	4	1.43	104.3–102.5 (30–55)	Gharehbaghi and Shemirani 2011
Ni	Novel microextraction	FAAS	[C$_4$MIM] [PF$_6$]		PAN	10	12.5	100.8–97.2 (60–100)	Dadfarnia et al., 2010
Pd	M-CIAME	UV–Vis spectrometer	[Hmim] [BF$_4$] (NaPF$_6$)		TMK	4	0.2	103.2 (50)	Vaezzadeh et al., 2010
Au	M-CIAME	UV–Vis spectrometer	[Hmim] [BF$_4$] (NaPF$_6$)		TMK	4	0.7	98.2%–97.4 (50–100)	Mahpishanian and Shemirani 2010a

LOD: limits of detection; * spiked concentrations in μg/L are presented in parenthesis.

determinations since absorbance decreased by increasing pH as cations are more likely to precipitate.

Cu^{2+}, Fe^{3+} and Pd^{2+} ions prevent an adequate determination of Co^{2+} ions and so were eliminated with proper masking agents, like ascorbic acid and iodide for masking Cu^{2+} ions, oxalate for Fe^{3+} and acetylacetone in the case of Pd^{2+}. CIAME exhibited advantages including rapidity (extraction procedure of less than 20 minutes) and a decrease in the use of toxic and high purity solvents. CIAME proved to be a robust procedure against high salt content and water-miscible organic solvents and it could be operated in continuous mode.

Vaezzadeh et al. (2010) employed a modified CIAME technique to determine Pd in seawater samples. In this procedure the extractant phase had high density ILs, so samples of up to 40% salt concentration could be used. The solvent sodium hexa-fluorophosphate (NaPF$_6$) (ACROS, Geel, Belgium) was added to the sample solution already containing 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim] [BF$_4$] (E. Merck). The chelating agent selected was TMK (E. Merck) and the measurement was carried out at pH 4 with a UV–Vis spectrometer. The researchers avoided the use of the non-ionic surfactant, even though it was not explained how to solve the problem of the sticking to the wall of the centrifuge tubes.

The CIAME method was selected due to its simplicity and rapidity for extracting and preconcentrating metal ions. The technique is considered to be in agreement with the use of "Green Solvents" since small amount of ILs are needed instead of organic solvents.

Mahpishanian and Shemirani (2010a) also preconcentrated Au from water matrices employing a modified CIAME technique. In

M-CIAME, to a pH 4 sample solution, NaPF$_6$ (ACROS) was added as an ion pairing agent. A hydrophilic IL such as [Hmim] [BF$_4$] (E. Merck) instead of [Hmim] [PF$_6$] was selected since it can be dissolved easily without the need for Triton X-114. The chelating agent of election was TMK (E. Merck) with a UV–Vis spectrometer as detection instrument. M-CIAME is a useful tool when working with saline solutions since phase separation occurred successfully up to 40% NaNO$_3$ concentration. Finally, interferences with Pd^{2+} were eliminated with the addition of acetylacetone.

4.2. DLLME

In 2011, Gharehbaghi and Shemirani developed a DLLME procedure with the addition of ionic liquids to determine Mo. ILs containing an imidazolium cation were selected, since under laboratory conditions they behave as liquids with greater hydrophobicity than others containing a shorter alkyl chain. ILs also need to be immiscible with the sample solution to reduce the consumption of the extraction solvent and produce a settled phase at appropriate amounts.

Briefly, pyrogallol red (PR) (E. Merck), employed as the complexing agent, was added to the pH 4 solution containing the analytes and CTAC (sensitizing agent) (Sigma). Afterwards, a violet-bluish ternary complex of Mo–PR–N-cetyl-N-N-N-trimethyl ammonium ions (CTA) was formed. Then, the extraction solvent [Hmim] [Tf$_2$N] (E. Merck) together with the acetone as the disperser solvent were rapidly injected into the sample solution by means of a syringe. Thus, a stable cloudy solution was obtained and the ternary complex of Mo extracted into the fine droplets of IL. A centrifuge phase (4 min) was necessary to settle the fine droplets at

the bottom of the centrifuge tube and the extracted phase was then diluted with pure ethanol. A colorimetric detection system, fiber optic-linear array detection spectrophotometry (FO-LADS), was used for the determination of Mo in water samples.

The researchers studied the aptitude of the technique to work in high saline content matrices. It was found that absorbance remained constant in samples containing up to 20% salt concentration, but at higher salt content the determination became difficult due to the high background levels. Moreover, in this study no non-ionic surfactants were added since CTAC also prevents sticking to the wall of the test tube. Interferences were investigated and eliminated using proper masking agents like EDTA for Bi^{3+} and Pb^{2+} and ascorbic acid for Cu^{2+} and V (V).

IL-DLLME had short extraction times, lasting less than 7 minutes compared to the 25 minutes that usually involves a CPE/spectrophotometry procedure. Also, removing the bulk aqueous phase was easier than the CPE method due to high viscosity of ILs. IL-DLLME exhibited less background levels compared to CPE, in which the background is increased because the enrichment phase has part of the aqueous sample. Consequently, IL-DLLME is a reproducible, rapid, simple and low cost technique.

Investigations carried out by Khani et al. (2011) introduced the use of RTILs in a DLLME preconcentration technique. The modification allowed the use of an environmentally friendly solvent as an alternative to the toxic organic ones commonly employed. A central composite full factorial was design in order to optimize the method.

A pH 5 aqueous solution was mixed with 4,4′-bis(dimethylamino) thiobenzophenone (TMK) (E. Merck) for Cu determination, in spite of previous addition of dithiocarbamate and diethyldithiophosphate compounds as complexing agents for Cu (Anthemidis and Ioannou, 2009; Jahromi et al., 2007). Acetone as the disperser solvent and the ionic liquid [Hmim] [Tf$_2$N] (E. Merck) as extraction solvent, were also chosen for the procedure. In order to reduce the volume of solvent needed for extraction, ionic liquids of election need to have low miscibility with the aqueous phase and should produce a settled phase in great amounts.

The final extraction phase was diluted with ethanol in order to generate a solution with good nebulization and burning characteristics, as well as a not too low boiling point and the capacity to be coupled to a FAAS detection instrument. No statistical differences were found in the results between FAAS and ICP OES detection systems.

4.3. ISFME

Baghdadi and Shemirani (2009) published a novel technique termed in situ solvent formation microextraction (ISFME) with the use of RTILs. The procedure was designed as a modification of HLLME based on ILs and was first focused on the analysis of Hg in water samples. In ISFME, the extractant molecules collect the hydrophobic species and the extraction process is complete after the formation of the droplets.

To sum up, a pH 4 aqueous solution was mixed with TMK (E. Merck) and the ionic liquid [Hmim] [BF$_4$] (E. Merck), then the mixture was transferred to a conical-bottom glass centrifuge tube. A cloudy solution was generated by the addition of NaPF$_6$ (ACROS) and after centrifuging (5000 rpm- 6 min) the fine droplets of IL settled at the bottom of the centrifuge tube. They were then extracted by simply inverting the tube and before determination by UV–Vis spectrometer, the sample was dissolved in a diluting agent. Even though the IL-phase exhibited maximum absorbance in the presence of acetone and methanol, it could not be dissolved completely. In the presence of ethanol, however, the sample solution became translucent and good absorbance was acquired.

The article highlighted the use of ILs to avoid analytes adsorption on test tubes, since ILs are structurally similar to ionic surfactants. ILs allow phase separation in the presence of a common ion and due to the high density, the fine droplets of the extractant phase can settle even in saturated solutions (40%, w/v). Furthermore, the use of syringes during the entire protocol avoided fuzzy steps and possible interferences of Ag^+, Au^{3+} and Pt^{4+} were eliminated with the addition of EDTA.

Mahpishanian and Shemirani (2010b) proposed the use of the ISFME technique, introducing the use of RTILs for Cd preconcentration, compatible with samples with high salt content (up to 40%, w/v).

Briefly, a pH 2 aqueous solution was mixed with DDTP (ACROS), a chelating agent that forms stable complexes with several transition metals and semi-metals in acidic media. The usual ionic liquid [Hmim] [BF$_4$] (E. Merck) was selected and phase extraction was accomplished with the aids of a microsyringe and finally dissolved in ethanol before determination by FAAS.

5. Conclusion

An overview of the different liquid–liquid microextraction methodologies employed to preconcentrate trace metal ions from seawater samples during the last decade was presented. This review focussed on the utilization of environmentally friendly techniques. These procedures have gained interest among scientists since they combine the use of reduced amounts of non-harmful reagents and small volumes of samples (Rocha et al., 2013). Direct comparison of the methodologies applied was not always achieved since analytes determined varied, thus preventing a rigorous discussion.

Among preconcentration techniques, CIAME proved to be a robust procedure against high content of salt and water-miscible organic solvents. Distinctively, in CPE, the presence of over 3% water-miscible organic solvents destroyed the extraction capacities. CIAME was usually combined with room temperature ionic liquids, thus analyses of saline samples showed little background and it was easy to remove the final phase from the bulk aqueous one. Furthermore, the CIAME technique was suitable for determining heat-sensitive species since temperatures required were not elevated. It also allowed the determination of Hg in seawater samples, Hg being a difficult metal ion to preconcentrate. Better limits of detection were achieved compared to the ISFME preconcentration method, even when they both employed the same detection equipment (UV–Vis spectrometer).

As drawbacks, sticking of the ionic liquids to the wall of the glass centrifuge tubes used in the CIAME technique was observed (Baghdadi and Shemirani, 2008; Gharehbaghi et al., 2009). To solve the problem, a non-ionic surfactant, usually Triton X-114, needed to be introduced in the solution, enlarging possible contamination. Additionally, due to the presence of Triton X-114 in the sample solution, the sizes of the ILs droplets decreased and they were not able to settle in solutions containing over 20% salt. Dilutions made with ethanol are also a disadvantage since it is a harmful reagent.

In comparison with CIAME, ISFME is free of volatile organic solvents because it uses ionic liquids as green extraction solvents; it is faster and simpler and it is applicable for high saline content matrices. All of these characteristics are of key interest for laboratories doing routine trace metal ion analysis.

Compared to DLLME, no pure disperser solvent that could reduce extraction recoveries was used in ISFME and due to the high density of ILs, the fine droplets of the extractant phase in ISFME could settle in saturated solutions up to 40%. There was no agreement if sticking of ILs on conical bottom glass vessels occurred or if ILs were able to avoid it since they are structurally similar to ionic

surfactants. In agreement with CIAME, ethanol for a final dilution was needed as well.

The CPE procedure was the leading technique for metal ions determination in seawater samples. CPE managed to achieve the lowest detection limits for the preconcentration of Co, Fe, Mn, Mo, Pd and Zn. A great variety of equipment also made possible their determination: UV-spectrometer, ICP OES, TLS, HPLC and GFAAS. A drawback was the use of organic solvents to dissolve the solution before its introduction in the equipment.

A common disadvantage for all of the methods was that the surfactant-rich phase always exhibits a little volume of aqueous sample, possibly containing residual salinity from the matrix. Consequently, due to the crystallization during surfactant-rich phase dissolution, serious problems may occur for spectrometers (Baghdadi et al., 2009).

In conclusion, it can be said that procedures aiming to preconcentrate small amounts of metals in seawater samples together with the use of environmentally friendly reagents are efficient tools demonstrating that good detection limits can be achieved while developing easy and less time-consuming procedures with the equipment available for most laboratories.

Acknowledgements

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