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Review

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



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enhance the performance of the protocols.

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ABSTRACT

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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 significanceand 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.

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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. Conclu-

sions are drawn on the basis of the articles reviewed, highlighting improvements introduced in order to

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



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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	$\text{LOD}~(\mu\text{g}/\text{L})$	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
Со	FAAS	Triton X-114	1-PTSC	8 to 10	1	98-98 (10-20)	Citak and Tuzen 2010
Со	FAAS	Triton X-114	TAN	7	0.24		Chen and Teo 2001a
Со	FAAS	PONPE 7.5	1-nitroso-2-naphthol		1.22	99.1-96.1 (20-30)	Manzoori and Bavili-Tabrizi 2003
Со	UV-spectrophotometer		ACDA	5	7.5	103.4 (20)	Safavi et al., 2004
Со	TLS	Triton X-114	PAN	7	0.03	100.9-100.3 (10-20)	Shemirani and Shokoufi 2006
Со	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	0.23	90–110	Yamini et al., 2008
IVIII		Inton X-114	11/1	0	0.1	50 110	Tamini et al., 2000
Мо	GFAAS	Triton X-114	QA	3	0.0096	98-99 (5-10)	Filik et al., 2009
WIO	GIAAS	111011 A-114	QA	5	0.0090	38-33 (3-10)	Flik et al., 2005
NG	FAAS	Triton V 114	Dithizone	7	10	00.2 08.0 (10 . 20)	Mangoogi and Karim Northad 2004
Ni	FAAS	Triton X-114		5	1.2	99.3–98.9 (10–20)	Manzoori and Karim-Nezhad 2004
Ni	UV-spectrophotometer		ACDA		10	105.9 (20)	Safavi et al., 2004 Manzoori and Pavili Tabrizi 2002
Ni	FAAS	PONPE 7.5	1-nitroso-2-naphthol		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
Db	FAAS	Triton V 114	1 DTSC	8 to 10	2.42	06 08 (10 20)	Cital and Turan 2010
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
Dd	TLS	Triton V 114	PAN	4	0.04	102 100 2 (15 20)	Shekeyf et al. 2000
Pd	1123	Triton X-114	FAIN	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
Z11	гллэ	111t011 X-114	IAN	/ 10/10	0.095	104 (10)	Chen and 160 2001D

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