Microchemical Journal 110 (2013) 158–168

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Multi-residue method for the analysis of commonly used commercial surfactants, homologues and ethoxymers, in marine sediments by liquid chromatography-electrospray mass spectrometry

B. Oliver-Rodríguez [a], A. Zafra-Gómez [a,*], F.J. Camino-Sánchez [a], J.E. Conde-González [b], J.P. Pérez-Trujillo [b], J.L. Vílchez [a]

[a] Research Group of Analytical Chemistry and Life Sciences, Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Campus of Fuentenueva, E-18071 Granada, Spain
[b] Department of Analytical Chemistry, University of La Laguna, E-38204 Tenerife, Spain

ARTICLE INFO

Article history:
Received 23 January 2013
Accepted 12 March 2013
Available online 20 March 2013

Keywords:
Surfactants
Ultrasound extraction
LC-ESI-MS/MS
Environmental analysis
Marine sediments pollution

ABSTRACT

A simple, sensitive and accurate multi-residue method has been developed for simultaneous determination of the main types of surfactants (linear alkylbenzene sulfonates [LAS], alkyl sulfates [AS], alkyl ethoxysulfates [AES], and alcohol polyethoxylates [AEO]). Ultrasound-assisted extraction was used for the extraction of surfactants. Liquid chromatography with tandem mass spectrometry with an electrospray interface (LC-ESI-MS/MS) was used for identification and quantification of the target compounds. The mass spectrometric conditions in positive and negative ionization mode were individually optimized for each analyte to obtain the maximum sensitivity. The selection of specific fragmentation reactions for LAS, AS and AES allowed simultaneous quantification and identification in one run, ensuring the high specificity of the method. For AEO determination, the triple quadrupole mass spectrometer was operated in the Q1 multiple ion mode (Q1 MI) with positive ionization due to the absence of fragmentation. The analytes were separated in less than 15 min. The limits of detection found ranged from 0.02 to 7.00 μg kg^{-1} in marine sediments. Due to the absence of certified materials, the method was validated using matrix-matched calibration and a recovery assay with spiked samples. Recovery rates were close to 100% in all cases and ranged from 94.1% to 113.3%. Precision was also evaluated in terms of %RSD. The values obtained, expressed as inter-day variability, fell between 2.0% and 8.2% for all the analyzed surfactants. Finally, after validation, the proposed method was applied for the simultaneous determination of all the target compounds in samples taken from Tenerife Island, Spain. For each family of analyzed compounds, the homologues or ethoxymers found at the highest concentration levels were LAS C_{13}, AS C_{16}, AES C_{14} EO_1 and AEO C_{18} EO_{14} with values up to 1136, 130, 61 and 9.4 μg kg^{-1} respectively.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, research in the field of environmental pollution has extended beyond the study of classical contaminants – pesticides, biocides, PAH, PCB or dioxins – to other families of compounds, which are starting to be considered as "emerging contaminants" when they are released into the environment. Among these pollutants, surfactants constitute one of the most relevant categories [1]. Surfactants are widely used for both industrial and domestic purposes, accounting for over 3 million tonnes per year in Western Europe [2]. Due to their surface-active properties, they are used in a wide variety of applications. Surfactants market is a complex industry with several producers, numerous product lines and a broad spectrum of end applications, including household detergents, industrial washing products and conditioners, laundry additives, cosmetics, lubricants, coatings and paints [4]. Surfactants are mainly of two types according to the charge of the hydrophilic moiety: anionic and non-ionic [5]. Linear alkylbenzene sulfonates (LAS) are the main component of anionic surfactants, with an estimated annual production of 0.4 million tonnes in Europe [4], followed by alcohol ethoxysulfates (AES) and alcohol sulfates (AS). Alcohol polyethoxylates (AEO) have also an important production worldwide [6, 7].

Surfactants are typically highly water soluble and surface active, which confer them with partition to suspended particles that become incorporated into sediments in the environment, where the highest exposure to these compounds is expected [8]. Biodegradation rates and pathways of organic compounds, including some detergent ingredients, are known to depend strongly on the anoxic conditions occurring in sediments, leading to a potential increase in exposure secondary to their accumulation in sediments [9, 10]. In addition, in some situations, the continued input into the environment of

* Corresponding author. Tel.: +34 958 243326; fax: +34 958 243328.
E-mail address: azafra@ugr.es (A. Zafra-Gómez).

0026-265X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.microc.2013.03.006

compounds (e.g., via wastewater treatment plant effluents, other known and unknown point sources, runoff) may result in chronic exposure. However, little is known about the bioavailable fraction of these compounds, up- and downstream of wastewater treatment plants on a homologue specific basis [11].

Despite the numerous studies that report the almost total elimination of these substances in wastewater treatment plants [12, 13], their high production makes that a high part of surfactants may escape elimination and enter the environment [14–16]. The structure of surfactants allows them to adsorb to the surface of solid particles or to droplets of water vapor, thus moving through different environmental compartments [17]. When released into the environment, surfactants undergo a variety of physical and chemical changes [18–20]. In order to gain a more detailed understanding of the environmental distribution, behavior and fate of surfactants, it has become necessary to monitor their levels and evaluate their impact on the ecosystems. While the environmental performance of LAS has been extensively studied, the same cannot be said for AS, AES or AEO [2, 3]. In this respect, several studies have been recently conducted that examine the environmental behavior of anionic surfactants, most of them included in the review by Ying (2006) [21].

Although a number of multi-residue methods for the analysis of surfactants in different environmental compartments have been published in the literature [22], little data are available regarding surfactants at homologue and ethoxymer levels. For that reason, we aim to develop a simple, accurate and sensitive multi-residue method for the identification and quantification of the homologues and ethoxymers of the most commonly used commercial surfactant (LAS, AS, AES, and AEO) in marine sediments. The proposed method involves an ultrasound assisted extraction (USE) procedure followed by a liquid chromatographic-tandem mass spectrometric (LC-ESI-MS/MS) analysis. The use of mass spectrometry allows the identification and quantification of target homologues and ethoxymers without the need of a previous derivatization process or complex clean-up of sample extracts.

The natural samples were collected from Tenerife Island, Spain. This island is located in the Canary Archipelago, in the Atlantic Ocean, and about 300 km from the coast of Africa. It is the largest island of the archipelago with a surface area of 2034 km^2, a coastline amounting to 342 km, and a population of 906,854 inhabitants [23]. Agriculture and tourism are the main economic resources. Some small industrial areas and one oil refinery are the main sources of industrial wastewaters. Due to its geographic location, climatic conditions and limited industrial activity, pollution levels are expected to be very low. Almost 50% of its area is environmentally protected; therefore, there is a need for more effective methods to fight pollution.

2. Experimental

2.1. Chemical and reagents

All reagents were analytical grade unless otherwise specified. Water (18.2 MΩ cm) was purified using a Milli-Q system from Millipore (Bedford, MA, USA). Commercial LAS, AS and AES mixtures and LAS-2∅C_{16} were kindly supplied by Cepsa Química S.A. (Madrid, Spain). AEOs mixtures (Brij 56 and Brij 76) and N,N-dimethyltetradecylamine were purchased from Sigma-Aldrich (Madrid, Spain). LC grade methanol and formaldehyde were purchased from Merck (Darmstadt, Germany). LC-MS grade ethanol; acetic acid and triethylamine were also purchased from Sigma-Aldrich. Stock solutions of LAS (500 mg L^{-1}), AES (100 mg L^{-1}), Brij 56 (100 mg L^{-1}), Brij 76 (100 mg L^{-1}), LAS 2-∅C_{16} (1000 mg L^{-1}) and N,N-dimethyltetradecylamine (1000 mg L^{-1}) were prepared in methanol and stored at 4 °C in the dark. The solutions were stable for at least six months. All glassware was washed with chromic mixture to minimize contamination. Working standards were prepared diluted in LC grade methanol immediately before use.

2.2. Instrumentation and software

The analyses were performed using an Agilent 1200 series (Agilent Technologies Inc., Palo Alto, CA, USA) high-performance liquid chromatography system equipped with a vacuum membrane degasser, a binary pump, an autosampler, a thermostated column compartment and coupled to an API 2000 (Applied Biosystems, Foster City, CA, USA) triple quadrupole mass spectrometer system. The electrospray ionization (ESI) interface was used for the analyses. Analyst software version 1.4.2 was used for LC-MS/MS instrument control and for acquisition and analysis of data. A Kinetex C_{18} analytical column (100 Å pore size) of 100 mm × 2.10 mm and 2.6 μm particle diameter, and a Kinetex C_{18} analytical column (100 Å pore size) of 150 mm × 2.10 mm and 2.6 μm particle diameter (both from Phenomenex, Torrance, USA) were evaluated to obtain adequate chromatographic separation.

For the extraction procedure, a Branson digital sonifier model S-450D (Danbury, CT, USA) (20 kHz, 400 W) with a 102 converter, a standard 12.7 mm diameter titanium disruptor horn, a flat and replaceable 12.7 mm diameter titanium tip and a temperature probe was used.

For sample evaporation, a Stuart Block Heater and a Stuart Sample Concentrator (Stone, Staffordshire, UK) were used. An Ortoalresa Digicen 21 centrifuge (Madrid, Spain), an ultrasonic bath from P. Selecta (Barcelona, Spain) and a vortex-mixer (Yellow line, Wilmington, NC, USA) were also used. Statgraphics software package [24] was used for statistical and regression analysis (linear mode).

2.3. Sample collection and storage

Marine sediment samples were collected from nine marine outfalls located along the coast of Tenerife Island. The location of the outfalls was the following: *Los Silos* (LS, 28322360/3141336 UTM) and the sample was taken at a depth of 32 m; *Punta Brava,* in *Puerto de la Cruz* (PBR, 28345970/3144718 UTM) at a depth of 40 m; *Playa de San Juan* (PSJ, 28321436/3117924 UTM) at a depth of 46 m; *Punta Blanca, Guía de Isora* (PBL, 28319180/3122534 UTM) at a depth of 25 m; *Las Caletillas* (CLT, 28366983/3139268 UTM) at a depth of 29 m; *Punta Larga* (PLR, 28366757/3138455 UTM) at a depth of 19 m; *the industrial park of Güímar* (PIG, 28366635/3135395 UTM) at a depth of 30 m; *Santa Cruz, Los Llanos* (SCR, 28376703/3147755 UTM) at a depth of 38 m; and *Playa de Las Américas* (LAM, 28328883/3105599 UTM) at a depth of 26 m. All outfalls are discharge points of urban wastewater, sampling, except for the Güímar outfall that is industrial. Four sediment samples were taken from each outfall. The first sample was taken about 50 cm in front of the outfall and the other three samples were taken at a distance between 8 and 10 m around the outfall. All samples were placed in glass containers and kept at 4 °C during transport to the laboratory. Once in the laboratory the samples were preserved by immediate addition of 3 % (v/v) formaldehyde. The sediments were dried in an oven to constant weight, and then milled and strained through a 2 mm sieve to enhance the extractability of the analytes. Finally, the samples were stored in the dark at 4 °C until analysis.

2.4. Sample extraction procedure

The extraction was performed using four metallic capsules within the ultrasonic bath at the same time (Fig. 1). The capsules containing the marine sediment sample (5.00 ± 0.01 g) and methanol (20 mL) were arranged in the ultrasonic bath spaced 1 cm apart and 1 cm from the probe tip. The samples were sonicated for 20 min at 75% of amplitude. The ultrasonic bath was prepared with 1 L of distilled water.

The methanol was transferred to a glass vial. The sediment residues were then washed with 5.0 mL of methanol and centrifuged at 5000 rpm (3690 ×*g*) for 10 min. The two methanolic extracts were combined and evaporated to dryness at 50 °C under a nitrogen stream. The residues were re-dissolved in 1 mL of a methanol/

Download English Version:

https://daneshyari.com/en/article/7643557

Download Persian Version:

https://daneshyari.com/article/7643557

Daneshyari.com