Journal of Chromatography A, 1362 (2014) 75–88

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Liquid chromatographic–tandem mass spectrometric method for the simultaneous determination of alkylphenols polyethoxylates, alkylphenoxy carboxylates and alkylphenols in wastewater and surface-water

L. Ciofi[a], C. Ancillotti[a], U. Chiuminatto[b], D. Fibbi[c], L. Checchini[a], S. Orlandini[a], M. Del Bubba[a,*]

[a] Department of Chemistry, University of Florence, Via della Lastruccia, 3, 50019 Sesto Fiorentino, Florence, Italy
[b] ABSciex, Viale Lombardia, 218, 20047 Brugherio, Monza Brianza, Italy
[c] GIDA S.p.A., Via di Baciacavallo, 36, 59100 Prato, Italy

ARTICLE INFO

Article history:
Received 30 May 2014
Received in revised form 10 July 2014
Accepted 7 August 2014
Available online 15 August 2014

Keywords:
HPLC–MS/MS
Alkylphenols polyethoxylates
Alkylphenoxy carboxylates
Alkylphenols
Surface water
Wastewater

ABSTRACT

Four different pellicular stationary phases (i.e. octadecylsilane, octasilane, Phenyl-Hexyl and pentafluorophenyl) were investigated for the chromatographic resolution of alkylphenols (APs), alkylphenols polyethoxylates (AP*n*EOs) and alkylphenoxy carboxylates (APECs) using mixtures of water and organic solvents (i.e. methanol, acetonitrile and tetrahydrofuran) as eluents, in order to obtain their determination by a single LC–MS/MS run. In fact, alkylphenols and alkylphenoxy carboxylates must be analysed in negative ion mode, whereas alkylphenols polyethoxylates undergo ionisation only in positive ion mode, and therefore, two distinct LC–MS/MS analysis are commonly adopted. The best resolution among the aforementioned target analytes was achieved on the pentafluorophenyl column, eluting with an acidified water–acetonitrile–tetrahydrofuran mixture and using the post column addition of an ammonia solution in methanol for the detection of positively ionisable compounds. Under these optimized chromatographic conditions the investigated compounds were determined via a single chromatographic run, with only one polarity switch, in 15 min, achieving the following instrumental detection limits: 600 pg for AP1EOs, 0.8–14 pg for AP2EOs, 10.4–150 pg for APs and 4.4–4.8 pg for APECs. The chromatographic method was coupled with solid-phase extraction and clean-up procedures and successfully applied to the analysis of wastewater and surface water samples, highlighting mean concentration ranging from 6 ng/L for 4-t-OP1EC to 1434 ng/L for 4-$NP_{1,1,2}$1EC, depending on the sample analysed.

1. Introduction

Alkylphenols polyethoxylates (AP*n*EOs), with an average number of ethoxylic units (*n*) included between 3 and 10 and an alkyl chain length of eight (OP*n*EOs) or nine (NP*n*EOs) carbon atoms, have been widely used as non-ionic surfactants (mainly in textile, tannery and chemical industry) or antioxidants (e.g. in plastic manufacturing processes) in a number of industrial applications [1].

Many evidences of the presence of AP*n*EOs and their biodegradation derivatives have been reported in literature for different fresh water ecosystems, as a consequence of an incomplete removal in wastewater treatment plants (WTPs) or uncontrolled discharged in surface water [2–4].

Most persistent AP*n*EO aerobic degradation metabolites are AP1EOs, AP2EOs, the corresponding alkylphenoxy carboxylates (AP*n*ECs) and alkylphenols (APs), the last being the final result of the degradation of the ethoxylate chain [5].

Several literature studies have shown that AP*n*EOs, AP*n*ECs and APs exhibit varying degrees of estrogenicity; in particular, Jobling and Sumpter [6] evaluated the estradiol equivalent potency factors for 4-nonylphenol nonaethoxylate (4-NP9EO), 4-nonylphenol diethoxylate (4-NP2EO), 4-nonylphenoxycarboxylic acid, 4-nonylphenol (4-NP) and 4-tert-octylphenol (4-t-OP), evidencing relative potencies that increased in this order and were included between 2.0×10^{-7} and 3.7×10^{-5}. Ahel et al. [7] confirmed the results of Jobling and Sumpter [6] by the evaluation of the acute LC/EC50 value of these compounds,

* Corresponding author. Tel.: +39 0554573326; fax: +number: +39 0554573385.
E-mail address: delbubba@unifi.it (M. Del Bubba).

http://dx.doi.org/10.1016/j.chroma.2014.08.026
0021-9673/