

Fully automated on-line solid phase extraction coupled to liquid chromatography–tandem mass spectrometry for the simultaneous analysis of alkylphenol polyethoxylates and their carboxylic and phenolic metabolites in wastewater samples

Lorenzo Ciofi¹ · Claudia Ancillotti¹ · Ugo Chiuminatto² · Donatella Fibbi³ ·
Benedetta Pasquini¹ · Maria Concetta Bruzzoniti⁴ · Luca Rivoira⁴ ·
Massimo Del Bubba¹

Received: 1 December 2015 / Revised: 30 December 2015 / Accepted: 8 February 2016
© Springer-Verlag Berlin Heidelberg 2016

Abstract Three different sorbents (i.e. endcapped octadecylsilane, octasilane and styrene-*N*-vinylpiperidinone co-polymer) were investigated in order to develop an on-line solid phase extraction–liquid chromatographic tandem mass spectrometric method (on-line SPE–LC–MS/MS) for the simultaneous analysis of alkylphenols polyethoxylate (AP_{*n*}EOs, *n* = 1–8) and corresponding monocarboxylate (AP₁ECs) and phenolic (APs) metabolites. The endcapped octadecylsilane was selected due to its full compatibility with a chromatographic approach, which allowed the elution of positively and negatively ionisable compounds in two distinct retention time windows, using a water–acetonitrile–tetrahydrofuran ternary gradient and a pellicular pentafluorophenyl column. On this SPE sorbent, the composition of the loading/clean-up solution was then optimized in order to achieve the best recoveries of target analytes. Under the best experimental conditions, the total analysis time per sample was 25 min and method detection limits (MDLs) were in the sub-nanograms

per litre to nanograms per litre range (0.0081–1.0 ng L⁻¹) for AP_{*n*}EOs with *n* = 2–8, AP₁ECs and APs, whereas for AP₁EOs, an MDL of about 50 ng L⁻¹ was found. Using the mass-labelled compound spiking technique, the method performance was tested on inlet and outlet wastewater samples from three activated sludge treatment plants managing domestic and industrial sewages of the urban areas and the textile district of Prato and Bisenzio valley (Tuscany, Italy); in most cases, apparent recovery percentages approximately in the ranges of 50–110 % and 80–120 % were found for inlet and outlet samples, respectively. The on-line SPE–LC–MS/MS analysis of wastewater samples highlighted the presence of target analytes at concentrations ranging from few nanograms per litre to thousands nanograms per litre, depending on the compound and matrix analysed. AP₂ECs were also tentatively identified in outlet samples.

Electronic supplementary material The online version of this article (doi:10.1007/s00216-016-9403-5) contains supplementary material, which is available to authorized users.

✉ Massimo Del Bubba
delbubba@unifi.it

- ¹ Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Florence, Italy
- ² Scix Italia, Viale Lombardia, 218, 20047 Brugherio, Monza Brianza, Italy
- ³ GIDA S.p.A., Via di Baciacavallo 36, 59100 Prato, Italy
- ⁴ Department of Chemistry, University of Turin, Via Pietro Giuria, 5, 10125 Turin, Italy

Keywords On-line solid phase extraction–liquid chromatography–tandem mass spectrometry · Alkylphenols polyethoxylates · Alkylphenoxy carboxylates · Alkylphenols · Wastewater

Introduction

Alkylphenols polyethoxylates (AP_{*n*}EOs) are a well-known class of non-ionic surfactants that have been used as emulsifiers, dispersive agents, surfactants and/or wetting agents [1]; within the AP_{*n*}EO class, branched ethoxylate nonylphenols (NP_{*n*}EOs) with a number of ethylene oxide (EO) units up to 9–10 have been commonly used in cleaning processes [2].