

ANALYTICAL DETERMINATION OF NONYLPHENOLS AND OCTYLPHENOLS IN SURFACE WATER SAMPLES

M. Bernardello^{1*}, M. Formalewicz¹, C. Gion¹, A. Feller¹ and C. Maggi²

¹ ISPRA - Istituto Superiore per la Protezione e la Ricerca Ambientale - Loc. Brondolo, 30015 Chioggia - marco.bernardello@isprambiente.it

² ISPRA - Istituto Superiore per la Protezione e la Ricerca Ambientale - via di Casalotti 300, 00166 Roma

Abstract

Decision N. 2455/2001/EC sets out the first list of 33 substances or groups of substances that have been prioritised for action at European Community level. Nonyl- and octylphenols are included in this list of priority and hazardous substances due to the risk to, or via, the aquatic environment, in accordance with the Article 16 of European Water Framework Directive 2000/60/EC (WFD) [1]. A method for the selective determination of 4-tert-octylphenol, 4-nonylphenol and 4-n-nonylphenol in surface water samples was developed and validated, based on solvent extraction and HRGC-ITMS (high resolution gas chromatography coupled with ion-trap mass spectrometry). Assessment of method performance gave good results in terms of accuracy, precision, selectivity and sensitivity.

Keywords: Chemical Analysis, Pollution, Monitoring

Introduction

The European Union (EU) Water Framework Directive 2000/60/EC (WFD) [1] sets up environmental objectives to achieve "good chemical status" for all European water bodies by 2015. "Nonylphenols" and "octylphenols" are listed as priority hazardous substances in Decision n. 2455/2001/CE [2]. The Directive 2008/105/EC [3] lays down environmental quality standards (EQS) for priority substances and certain other pollutants amending the WFD. EU Member States need to develop and to implement a quality-assurance/quality control (QA/QC) system to ensure that all monitoring results meet the levels of accuracy fixed by Directive 2009/90/EC of 31.07.2009. Nonylphenols and octylphenols are two groups of substances with general formulas HO-C₆H₄-C₉H₁₉ and HO-C₆H₄-C₈H₁₇, respectively. Alkylphenolic compounds in the aquatic environment originate primarily from the degradation of the industrially produced mixtures of alkylphenol polyethoxylates, resulting in complex mixtures of branched isomers which differs on the basis of branching and position of the alkyl chain with respect to the phenolic hydroxyl group [4]. The denomination of alkylphenols used in legislation, as well as in scientific literature, has proved sometimes ambiguous for identifying mixtures and single isomers. In this work a method was devised for analysing 4-tert-octylphenol (4-t-OP; 1,1,3,3-tetramethyl-4-butylphenol, single compound, CAS# 140-66-9), 4-n-nonylphenol (4-n-NP; linear-chain isomer, single compound, CAS# 104-40-5) and 4-nonylphenol (4-NP; mixture of para-substituted isomers, CAS# 84852-15-3 and CAS# 25154-52-3) in surface water samples. 4-NP is usually quantified in environmental samples by using technical mixtures of isomers, which can be resolved by HRGC-LRMS only at a group level [4,5].

Materials and methods

The method is based on extraction with toluene followed by clean-up on a silica-gel column. Qualitative and quantitative determination was carried out by means of HRGC-ITMS. ¹³C labelled 4-n-NP was used as internal standard and added to the sample before extraction. In order to determine precision and accuracy, the performance of the method was assessed by the analysis of spiked water samples, as no certified reference materials were available.

Results and discussion

The identification of analytes was performed on the basis of chromatographic retention time and by comparing Full Scan mass spectra of the analyte in the sample and in the calibration standards, after calculation of area ratios of characteristic ions as confirmation. 4-NP mixture eluted as a group of partially resolved peaks (5 to 11 depending on the selected ion) leading to distinctive chromatographic patterns. The quantitative determination was performed by means of the internal standard method. Calibration curves were calculated from the ratios of chromatographic areas of the analyte and the internal standard as a function of concentrations. 4-NP were quantified by the sum of areas of the identified peaks. Average recoveries of the analytes in spiked samples ranged between 89 % and 108 %. Good sensitivity was achieved. Limits of quantification were respectively 10 ng L⁻¹ for 4-t-OP and 4-n-NP and 100 ng L⁻¹ for 4-NP. The developed method has provided reliable analytical performance coupled with a relatively simple sample treatment.

References

1 - Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of

water policy. OJ L 327, 22.12.2000, p. 1.

2 - Decision n. 2455/2001/EC of the European Parliament and of the Council of 20.11.2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. OJ L 331, 15.12.2001, p.1.

3 - Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. OJ L 348, 24.12.2008, p. 84.

4 - Fries E. and Pittmann W., 2003. Occurrence and behaviour of 4-nonylphenol in river water of Germany. *J. Environ. Monit.* 5, 598-603.

5 - Espejo R., Valter K., Simona M., Janin Y. and Arrizabalaga P., 2002. Determination of nineteen 4-alkylphenol endocrine disruptors in Geneva municipal sewage wastewater. *J. Chromatogr. A* 976, 335-343.