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Research article

Monitoring of selected non-ionic surfactants in river water by liquid chromatography–tandem mass spectrometry

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ABSTRACT

Alcohol ethoxylates (AEs) are a significant component of the non-ionic surfactant (NS) flux discharged into surface water. Due to the polydispersity of the majority of NS, they are easily recognizable by their 'fingerprints', i.e. a series of mass peaks which differ by $m/z = 44$, namely the m/z of a single oxyethylene subunit. Dodecanol ethoxylates ($C_{12}EO_x$) represent AEs from both renewable and petrochemical sources. Therefore, $C_{12}E_x$ are suitable fingerprints of NS in the aquatic environment.

The aim of this work was to develop an LC–MS/MS method suitable for AE monitoring in river water.

River water samples taken from the River Warta in Poznan (Poland) were extracted with ethyl acetate, evaporated, reconstituted in the mobile phase and processed by the LC – Multistage MS procedure (LC–MS/MS) using optimum multiple reaction monitoring (MRM). The method of multiple standard additions was used for the evaluation of each AE fingerprint concentration. The concentration of $C_{12}EO_x$ having 2–9 oxyethylene subunits was determined. Standards for higher $C_{12}EO_x$ are not yet available. The developed method offers an LOD of between 1 and 9 ng L^{-1}, and is suitable for the monitoring of NS fingerprints in river water.

The range of $C_{12}EO_{2-9}$ concentrations determined in the River Warta varied within two orders of magnitude in all cases. The lowest determined concentration was 17 ± 1 ng L^{-1}, while the highest was 2.6 ± 0.14 μg L^{-1}. The total concentration of $C_{12}EO_2$–$C_{12}EO_9$ homologues varied between 1.4 and 11.2 μg L^{-1}.

A relatively high concentration of short-chained homologues (2–5 oxyethylene subunits) was observed in the investigated river water. This provides evidence of a biodegradation pathway involving the gradual shortening of the AE oxyethylene chain. Distinct evidence was also obtained of unregulated NS discharges into the river.

1. Introduction

Surfactants are a significant anthropogenic component of the aquatic environment, being used in a huge number of household and industrial products, often typified by down-the-drain disposal. This degree of use is a consequence of the unique properties that result from their amphiphile structure. Non-ionic surfactants (NS) are a major component of the surfactant stream discharged into surface water (Zoller, 1994; Fuerhacker et al., 2001; Traczyk et al., 2006). In the EC, 1397 million tonnes of NS were manufactured in 2012, in addition to 1201 million tonnes of anionic surfactants (CESIO Statistics, 2012). Alcohol ethoxylates (AEs) are the major component of NS flux. Total AE production in the EC in 2012 was approximately 1 million tonnes. The ratio of AEs manufactured from renewable sources and from petrochemicals was approximately 3:4. Dodecanol ethoxylates ($C_{12}EO_x$) represent AEs from both renewable and petrochemical sources. Therefore, $C_{12}EO_x$ are suitable fingerprints of NS in the aquatic environment. Despite this huge flux of AEs directed into the aquatic environment via sewage, surprisingly little attention is paid to their monitoring.

Measurement of NS concentration in environmental samples is a problem due to the fact that NS is a mixture of homologues potentially composed of several hundred individual compounds (Brunner et al., 1988). Two approaches are used for this purpose: i. the determination of the total NS concentration, and ii. the determination of concentration of all components belonging to a specific

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NS group e.g. AE.

The total NS concentration may be determined by the Bismuth Active Substances (BiAS) (Fuerhacker et al., 2001), Cobalt Thiocyanate Active Substances (CTAS) (Zoller, 1994) or indirect tensammetric method (ITM) (Szymanski et al., 2001a). Using the BiAS method only non-ionic surfactants having more than five EO units per molecule can be determined, with an LOD in the range 0.01–0.05 mg L^{-1} (ECR, 1997). The CTAS procedure is best applicable to non-ionic surfactants having between 6 and 25 ethylene oxide groups (below 6 and above 25 the absorbance is not linear) with an LOD of 0.1 mg L^{-1} (Boyer et al., 1977; ECR, 1997). ITM is suitable for the determination of surfactants having more than 4 oxyethylene subunits, with an LOD of 10 μg L^{-1} (Traczyk et al., 2006). These three methods give closely similar results and are considered as equivalent. In model experiments the ITM results are 8% lower than BiAS results (Wyrwas et al., 1994), while in the case of river water and sewage they are 13–20% lower (Szymanski et al., 1995). All three methods are nonspecific; individual components of the NS mixture can be determined only using chromatographic methods. NS extraction from the water matrix is necessary prior to the final stage of determination. Due to the lack of chromophoric groups, derivatization of AEs is required in the case of HPLC with optical detection (UV, fluorescence) (Zanette et al., 1996; Zgola-Grzeskowiak et al., 2008). An alternative to this approach is the use of mass detection. The most popular solution is the hyphened technique LC–MS. NS are easily recognizable as a series of mass peaks which differ by $m/z = 44$, i.e. the m/z of a single oxyethylene subunit, due to the polydispersity of the majority of NS (Franska et al., 2003). Therefore, such a series of peaks is a specific NS fingerprint. Both the straight version of the technique (Gomez et al., 2011; Andreu et al., 2007) and the version with AE derivatization (Dunphy et al., 2001) are used. A more advanced technique than LC–MS is the LC–MS/MS technique.

The application of multiple reaction monitoring (MRM) in tandem MS (MS/MS) allows the selection and fragmentation of the parent ion followed by selective monitoring of the product ion. These so-called transitions enable very specific detection and sensitive quantification of compounds, because there is virtually no background (Zembrzuska et al., 2014a). LC–MS/MS has been successfully used for alkylphenol ethoxylate (APhE) determination in environmental samples (Houde et al., 2002; Jahnke et al., 2004; Loos et al., 2007; Loyo-Rosales et al., 2007; Lara-Martin et al., 2012). The technique is only marginally used for AE determination, frequently jointly with APhE determination (Lara-Martin et al., 2012; De Armond and Di Goregorio, 2013).

There are only two publications concerning AEs in water samples (Zgola-Grzeskowiak and Grzeskowiak, 2012; De Armond and Di Goregorio, 2013), while another is devoted to AE determination in bottom sediments (Lara-Martin et al., 2012). Therefore, in the present work, an attempt is made to verify the applicability of LC–MS/MS in monitoring AEs as NS fingerprints in river water, with a different approach than in previous studies. The present work used homogeneous standards and a standard addition method for evaluation of AE concentration, as well as straight determination without derivatization.

Separation of AEs from the water matrix is necessary prior to determination by LC–MS/MS. Solid phase extraction (SPE) with divergent filing is usually used for this purpose. SPE separation exhibits an advantage over liquid–liquid extraction in terms of AE recovery (LLE) under model conditions. However, LLE with ethyl acetate gives significantly better results in the case of AE extraction from real river water samples (Zembrzuska et al., 2014b). Recovery rates were obtained ranging from 74% to 95% for different homologues. Therefore, the conditions for AE separation and determination described in that paper were used in the present work. This method, considered jointly with LLE separation, ensures limits of detection of the order of a single ng L^{-1}, which is quite suitable for AE monitoring in river water. The incomplete AE separation can be compensated by standard addition at the stage of evaluation of the results. The incomplete extraction is compensated when the standard spike is present during the whole measuring cycle. Multiple standard addition was used in this work in order to enhance the accuracy and precision of measurement.

A significant problem in the application of LC–MS/MS is the availability of standards. Some AE homologues are available as relatively poor substances (97–99%). Scattered homologues of the series $C_{10}EO_x$, $C_{14}EO_x$, $C_{16}EO_x$, $C_{18}EO_x$ are offered (Sigma–Aldrich 2015 www.sigmaaldrich.com). Only representatives of the $C_{12}EO_x$ series having 1–9 oxyethylene subunits are available; longer homologues cannot yet be obtained. This represents a significant limitation on the expanded use of LC–MS/MS. To overcome this problem, De Armond and Di Goregorio (2013) used commercial polydispersal Neodol 25-9 having C_{12-15} alkyl chains and approximately 9 oxyethylene subunits on average. The concentration of a particular homologue in the mixture was presumed to be equal to its share in the MW distribution pattern. Due to the problems with standard availability, the scope of the present work was limited to $C_{12}EO_x$ series homologues having 2–9 oxyethylene subunits. The $C_{12}EO_1$ homologue was excluded because of its poor LC–MS/MS signal.

2. Experimental

2.1. Reagents and materials

All individual alcohol ethoxylates $C_{12}EO_x$ (x = 2; 3; 4; 5; 6; 7; 8; 9) used as standards were supplied by Sigma–Aldrich (St. Louis, MO, USA). All standards were of high purity grade (>98%). MS-grade acetonitrile was provided by Sigma–Aldrich (St. Louis, MO, USA). The ammonium acetate used as an addition to mobile phase was purchased from Sigma–Aldrich (St. Louis, MO, USA). Water was prepared by reverse osmosis in a Demiwa system followed by double distillation from a quartz apparatus. Only freshly distilled water was used. The reagents used for liquid–liquid extraction were of analytical grade. Ethyl acetate, sodium chloride and sodium hydrogen carbonate were obtained from POCh (Gliwice, Poland). Sodium chloride was purified of potential surfactant impurities by heating at 600 °C.

A stock standard solution of each compound was prepared in acetonitrile. The solution was stored at 4 °C.

The blank of the reagents was below the detection limit.

2.2. LC–MS/MS

The analytical method used in this study was developed previously by Zembrzuska et al. (2014b). Samples were analysed using high performance liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS). LC analysis was performed using the chromatographic system UltiMate3000 RSLC from Dionex (Sunnyvale, CA, USA) connected in series with a 4000 QTRAP Hybrid Triple Quadrupole Linear Ion Trap mass spectrometer equipped with a Turbo Ion Spray source (Applied Biosystems-Sciex, Foster City, CA, USA). The chromatographic separations were obtained in temperature 35 °C on a 150 × 1.9 mm id, particle size 3 μm, TSK gel Amide-80 analytical column with guard column, both supplied by TOSOH Bioscience (Stuttgart, Germany). The mobile phase was a mixture of 5 mM aqueous ammonium acetate (A) and acetonitrile (B). The flow rate was 0.1 mL min^{-1}, the injection volume was 5 μL. The following gradients were used: 0 min 99% B, 0.5 min 98% B, 10 min 65% B. The ESI interface was implemented in