# **SHIMADZU**

# Specific determination of non-ionic surfactants in drinking-, waste- and surface water with high resolution mass spectrometry

<u>Dennis JA VAN DEN HEUVEL<sup>1</sup>, Johan SCHOLTENS<sup>1</sup>, Tamara HAAGSMA<sup>1</sup>, Stephane MOREAU<sup>2</sup></u> 1 Shimadzu Benelux, 's-Hertogenbosch, The Netherlands 2 Shimadzu GmbH, Duisburg, Germany

### . Overview

This semi-automatic dataprocessing approach describes a cost effective and time saving systematic screening, identification and semi-quantification of non-ionic surfactants in drinking-, waste and surface water.

## 2. Introduction

Nonionic surfactants are surface-active compounds with hydrophobic and hydrophilic moieties. These surfactants do not ionize in aqueous solutions. Nonionic surfactants such as alkylphenol polyethoxylates (APEO), alcohol polyethoxylates (AEO) and alkanolamides are widely used in consumer products like, e.g., laundry detergents, cleaning and dishwashing agents, and personal care products. Nonionic surfactants are also widely used in cleaning agents formulated for the industrial and institutional sector. Surfactants released into the environment are biodegraded to short-chain ethoxylates, which are more toxic and more persistent than their parent compounds. Metabolites also exhibit estrogenic properties due to their structural similarity to estrogens. Therefore, there is a considerable interest and public concern about the potential negative impacts of surfactants, however, to better elucidate the potential risk in environmental samples, methods need to take into account a range of surfactant chemistries. Current surfactant monitoring methodologies tend to focus on a specific surfactant. Here, we have developed the simultaneous analysis method for typical non-ionic surfactant using high resolution LC-MS/MS.



Figure 1 Structure of non-ionic surfactants

### 3. Methods

To 10 mL of drinking-, surface- or wastewater is 10 mL acetonitrile added, followed by a filtration over a 0.45 µm membrane filter. From this mixture 5 µL is injected onto a C18 column (temperature 50 °C) and gradient analysis (with high resolution mass spectrometry (NexeraX3/LCMS-9050, Shimadzu Corporation, Japan) was performed



High Resolution Mass Spectrometer

Trusted mass accuracy < 1 ppm, internal Ultra-stable polarity switching 0.8 sec (< 5 ppm) Truly versatile with flexible extensions

#### **MS** conditions

MS Scan: 100 – 1000 Da Speed: 10 Hz ESI positive Interface: +4.5kV Interface: 350 °C External calibration

Calibration curves were created from the automated summation of 16 XIC's for Tergitol NP-9 (APEO C9) and Tergitol TMN 10 (AEO C12). The group calibration curve from APEO C9 and AEO C12 (31.8 – 1000  $\mu$ g/L) were used for semi-quantification of all short chain ethoxylates in the samples. For each surfactant the XIC was extracted and summarized according to the spectrum (regular mass distribution of 44 Da, corresponding to ethyleneoxide) and the total area was calculated. Quadratic regression was used for calculation and semi-quantification of the short-chain ethoxylates. Both compounds showed good linearity ( $r^2 > 0.999$ )

Figure 2 LCMS-9050 QTOF mass spectrometer

A positive electrospray ionization scanning method (100 – 1000 Da, 10

Hz) was performed followed by automated data-analysis. For each

surfactant, a summation of XIC's with mass difference of 44 Da,

## 4. Results

#### 4-1 Surfactants analysis

To 10 mL of drinking-, surface- or wastewater 10 mL of acetonitrile is added followed by a filtration over a 0.45  $\mu$ m membrane filter. From this mixture 5  $\mu$ L in is injected onto a C18 column thermostated at 50 °C. Gradient analysis was performed with 5mM ammonium acetate in water and acetonitrile. High resolution mass spectrometry was performed in the positive electrospray scanning mode (100 - 1000 Da, 10 Hz).

The following surfactants were analysed; Alkylphenol polyethoxylate: C6 – C19 and Alcohol ethoxylate C10 - C15, C10 – C15 branched, C16 and C18. For each surfactant, a summation of XIC's with mass difference of 44 Da, corresponding to a single AEO or APEO was reported.

#### **UHPLC** conditions

Column: C18 150 mm × 2.1 mm, 1.7 um Mobile phase A: 5 mM Ammonium acetate in water B: 5 mM Ammonium acetate in Acetonitrile Flow rate: 0.4 mL/min Time program: B conc.50%(0 min) - 100%(0-9min) - 50%(11-11.1min) Injection vol.: 5 µL Column temperature: 50 °C

Nebulizing gas 3 L/min Heating gas 10 L/min Drying gas 10 L/min DL temperature 250 °C Heat block temperature 400 °C

#### **4-2 Surfactants calibration**







Figure 4 Mass spectrum of typical non-ionic surfactant, showing typical mass difference of 44 Da, corresponding to ethyleneoxide



#### 4-3 Quantitative Analysis of real world sample



Figure 6 A; Total Ion Chromatogram real world surface water sample and corresponding B; mass spectrum for APEO C6 at 1.08 ppb

#### 5. Conclusions

With this semi-automatic data processing approach a cost effective and time saving systematic screening, identification and semi-quantification is developed.

diagnostic procedures.

The addition of acetonitrile to the water sample prevents adsorption of the non-ionic surfactants to the membrane filter or debris in the water.

Method performance was evaluated with different samples at different concentration levels for several surfactants resulting in positive identification.

For each surfactant, the XIC was extracted and automatically summarized according to the spectrum (regular mass distribution of 44 Da, corresponding to ethelenoxide) and the total area was calculated. The concentration of the found surfactant was then automatically back calculated to the corresponding calibration curve of AEO C9 or APEO C12.