Journal of Chromatography A, 1530 (2017) 80–89

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Full length article

# Liquid chromatography coupled to quadrupole-Orbitrap high resolution mass spectrometry based method for target analysis and suspect screening of non-ionic surfactants in textiles

Xin Luo[a,1], Li Zhang[b,1], Zengyuan Niu[a,*], Xiwen Ye[a], Zhixu Tang[a], Shuwei Xia[b]

[a] Inspection and Quarantine Technical Center, Shandong Entry-Exit Inspection and Quarantine Bureau, Qingdao 266002, China
[b] College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

ARTICLE INFO

*Article history:*
Received 22 May 2017
Received in revised form 30 October 2017
Accepted 1 November 2017
Available online 7 November 2017

*Keywords:*
Alkylphenol polyethoxylates (APEOs)
Alcohol polyethoxylates (AEOs)
Orbitrap
High resolution mass spectrometry
Liquid chromatography
Textiles

ABSTRACT

In this study, we describe a high-throughput and sensitive method for textiles analysis, using liquid chromatography coupled to quadrupole-Orbitrap high resolution mass spectrometry (LC-Q-Orbitrap HRMS), for the simultaneously quantitative analysis of 40 target alkylphenol polyethoxylates (APEO) oligomers with reference standards and screening of 160 alcohol polyethoxylates (AEO) oligomers without standards in textiles. The APEOs contain nonylphenol ethoxylates (NPEOs) and octylphenol ethoxylates (OPEOs) with an EO number of ethylene oxide of 1–20, while AEOs focus on $C_{11}$EOs-$C_{18}$EOs with an EO number of 1–20. After ultrasonic extraction in methanol, the extract was directly separated using a core-shell CORTECS $C_{18}{}^{+}$ column and analyzed by Full MS/dd-$MS^2$ (data dependent acquisition) scan in ESI positive mode. Two best sensitivity experimental conditions for APEOs with short EO chains ($AP(EO)_{1-2}$) and long EO chains ($AP(EO)_{3-20}$) were investigated, respectively. Most APEO oligomers had wide concentration ranges and the correlation coefficients ($R^2$) were higher than 0.999. The limit of quantitation (LOQ) values for $NP(EO)_{3-20}$ oligomers ranges from 16.00 to 52.80 μg/kg and for $OP(EO)_{3-20}$ oligomers is from 2.40 to 8.00 μg/kg. LOQ for $NP(EO)_1$ and $NP(EO)_2$, $OP(EO)_1$ and $OP(EO)_2$ was 2.40 mg/kg and 0.24 mg/kg, 1.20 mg/kg and 0.16 mg/kg, respectively. The average recovery for each APEO oligomer in cotton and polyester matrix was between 78% and 110% at three spiked levels and the relative standard deviation (RSD%) was below 10%. As to AEOs suspects, a HRMS compound database containing 160 AEO oligomers was built and several parameters such as exact *m/z*, isotopic patterns, predicted product ions and predicted retention time were used for screening and confirmation. The established method was successfully applied for analysis of 40 commercial textile samples. Compared with OPEOs, NPEOs, especially $NP(EO)_{3-15}$ oligomers, were widely detected in samples and the total concentration ranged from 1.56 to 1376.31 mg/kg. AEOs were also found in most samples, among which $C_{12-14}$, $C_{16}$ and $C_{18}$ compounds appeared more frequently and the EO chains mainly ranged from 3 to 15.



## 1. Introduction

Non-ionic surfactants such as alkylphenol polyethoxylates (APEOs) and alcohol polyethoxylates (AEOs) are widely applied in textile industries in auxiliaries formulations (used in pretreatment operations) or in additives as detergents or wetting agents in wool scouring, hydrogen peroxide bleaching and dyeing processes [1,2]. For APEOs, nonylphenol ethoxylates (NPEOs) and octylphenol ethoxylates (OPEOs) are the most commonly used compounds. Around 80% of the market is composed of NPEOs and 15–20% is made up of OPEOs [1]. AEOs possess a chemical formula of $R\text{-}(OCH_2CH_2)_n\text{-}OH$ and compounds studied in previous reports mainly focus on $R = C_{11}–C_{18}$ and $n = 1–20$ [2,3]. Humans can be exposed to APEOs and AEOs through various sources, such as the environment, food or skin contact. The metabolites of APEOs such as nonylphenol (NP), octylphenol (OP) and short chain APEOs show estrogenic activity in vitro, which may increase the risk of testicular, prostate and breast cancer, and reproductive disorders in humans [4]. In the year 2011, the Greenpeace International commissioned an investigation on hazardous chemicals used in the production of high street fashion. NPEOs were found in 63% of clothes purchased from over 18 countries and the concentration ranged from above 1 mg/kg to 45,000 mg/kg, which raised wide concerns in

* Corresponding author.
*E-mail addresses:* zyniuqd@163.com, rossi612@hotmail.com (Z. Niu).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.chroma.2017.11.001
0021-9673/

the public sphere. Widespread use of APEOs, coupled with their toxic characteristics, has led to the incorporation of 4-NPEOs, 4-tert-OPEOs, 4-NP and 4-tert-OP in the list of substances of very high concern (SVHCs) in the European REACH regulation; Moreover, according to Annex XVII of REACH, the limitation for NPEOs in textile articles can't exceed 100 mg/kg after 3rd February 2021 [5]. Related ecological textile regulations such as EU Ecolabel [6] and OEKO-TEX® Standard 100 [7] also limit the use of NPEO, OPEO, NP and OP, and the limitation was 25 mg/kg and 100 mg/kg, respectively. Due to the restriction of APEOs as well as the relatively rapid biodegradation characteristic of AEOs, APEOs are gradually being phased out and replaced by AEOs [3,8]. According to surveys of wastewater treatment plant effluents, although >99% of AEOs can be removed from the influent, the more toxic species, for example, the high-carbon alkyl chain and low-ethoxylate ethoxymers, are less efficiently eliminated [9]. In the case of insufficient biological degradation, they are potential sources of environmental pollution. While considered safe to humans, AEOs are not completely environmentally benign themselves, and they have proven to be toxic for certain aquatic species [8]. In recent years, AEOs have been detected and reported frequently in environmental samples, such as water and sediments [10,11].

Most analytical methods have been developed to detect APEOs and AEOs in various environmental matrixes, such as rivers, waste waters, sludge, sediments and food samples [1,11,12]. Methods mainly include GC–MS [13,14], LC–MS and LC–MS/MS [3,10,15]. GC–MS approaches are only appropriate for APEOs with short ethylene oxide (EO) chains, and however derivatization steps are required due to the physico-chemical properties of APEO analytes (moderate polarity, low volatility), which cause more analytical time and greater error [16]. Among LC based methods, LC–MS/MS in selected reaction monitoring (SRM) mode with triple-quadrupole (QqQ) mass analyzer have been widely accepted for the qualitative and quantitative analysis in recent years, due to their high sensitivity and selectivity [17,18]. However, since above MS technics are based on unit mass resolution, false positive identifications might be possible. Sample clean-up procedures such as solid phase extraction for some complex textile matrixes (silk, et al) are usually needed [19,20]. According to previous reports, highly ethoxylated NPEOs can generate doubly charged ions which have very similar $m/z$ with single charged ions of less ethoxylated NPEOs, such as $m/z$ of $[NP(EO)_5+NH_4]^+$ (458.34761) and $[NP(EO)_{15}+2NH_4]^{2+}$ (458.32179), etc. [4,20]. It is important to mention that recording MS with unit mass resolution is incapable to distinguish between these coeluting isobaric ions interferences accurately. On the other hand, with the improvement of health and environmental awareness, both the types and quantities of hazardous compounds have constantly increased due to related regulations. For example, the number of SVHCs has increased from 15 in the year of 2008 to 173 in 2017 [21]. The newest version of the OEKO-TEX® Standard 100 extended the regulation from some certain oligomers ($NP(EO)_{1\text{-}20}$ and $OP(EO)_{1\text{-}20}$) to all possible APEOs oligomers (NP(EO) and OP(EO)) [7]. Nevertheless, since non-ionic surfactants used in industry such as APEOs and AEOs are complex mixtures, reference standards for all oligomers are not available and the synthesis and characterization of the neat standards would be expensive, all data for target analysis of above compounds using unit mass resolution MS is limited [4].

The Orbitrap high resolution mass spectrometry used in present work is an attractive alternative. It has both high resolving power and excellent mass accuracy, providing greater confidence in identification and quantification, especially for complex matrix. Moreover, the full scan mode allows to record unlimited compounds, which makes it feasible for the retrospective analysis of any potential compounds of interest. The Orbitrap HRMS can also reduce method cost and development time by not having to purchase multiple standards or in performing manual method set up. To date, Orbitrap HRMS has been used extensively in lipids, proteomics, environment and food safety research for target and non-target analysis [22–25]. However, to the best of our knowledge, no studies have been reported on the analysis of non-ionic surfactants in textiles using Orbitrap.

In this work, a high-throughput and sensitive method for simultaneously quantitative analysis of 40 target APEOs and screening of 160 AEOs suspects in textiles was established by LC-Q-Orbitrap HRMS. Two chromatographic and mass spectrometric conditions were optimized for $AP(EO)_{1\text{-}2}$ and $AP(EO)_{3\text{-}20}$, respectively, to achieve the best sensitivities for all oligomers. The theoretical $m/z$ and assignments of MS/MS product ions for all APEOs oligomers were predicted and the fragment regularity was observed. The established method was validated by ways of the linearity, LOQ, recovery and precision for each APEOs oligomer. And a compound database with parameters of exact $m/z$, isotopic patterns and predicted product ions for screening and confirmation of AEOs suspects was built. Its applicability was demonstrated by measuring APEOs and AEOs in 40 textile samples.

## 2. Experimental

### 2.1. Materials and chemicals

Methanol and acetonitrile (LC–MS grade) were purchased from Merck (Darmstadt, Germany). Ammonium acetate and formic acid (LC–MS grade) was purchased from Sigma-Aldrich (St. Louis, MD, USA). Ultra-pure water with 18.2 MΩ cm was produced by Milli-Q Advantage A10 system (Millipore Corporation, Bedford, MA, USA). 4-Nonylphenyl-polyethylene glycol with an average ethoxylation of around 10 unites (CAS 9016-45-9, Part number 03853) and Triton™ X-100 BioXtra with an average ethoxylation of 9–10 unites (CAS 9002-93-1, Part number T9284) were purchased from Sigma-Aldrich (St. Louis, MD, USA). 4-*tert*-Octylphenol Monoethoxylate ($OP(EO)_1$, CAS 2315-67-5, 96%) and 4-*tert*-Octylphenol Diethoxylate ($OP(EO)_2$, CAS 2315-61-9, 98%) were purchased from Toronto Research Chemicals (Toronto, ON, Canada). Nonylphenol Monoethoxylate ($NP(EO)_1$, CAS 27986-36-3, 97.7%) and Nonylphenol Diethoxylate(tech) ($NP(EO)_2$, 98.6%), both of which were 2500 μg/mL in acetonitrile-methanol (90/10, v/v), were purchased from AccuStandard (New Haven, CT, USA).

Individual stock standard solutions of APEOs except $NP(EO)_1$ and $NP(EO)_2$ were prepared at a concentration of 1000 mg/L in methanol. Standard solutions were stored in the refrigerator at −18 °C. Standards can be used by diluting the stock standard solutions to the concentration needed with methanol/water (1/1, v/v).

### 2.2. Sample preparation

Cut the textile sample into pieces of approximately 5 mm × 5 mm and mix them homogeneously. Prepare (0.5 ± 0.01) g of the cut textile and then place it into the glass container. 20 mL methanol was added, the vessel was capped and extracted by an ultrasonic generator (40 KHz, KQ-500DE, Kun Shan, China) at 65 °C for 60 min. After cooling down to room temperature, a certain volume of supernatant was diluted with equal amount of water and filtered by a 0.22 μm PTFE membrane before analysis.

### 2.3. LC conditions

Analyses were performed using Dionex Ultimate 3000 UHPLC system (Thermo Scientific, Germering, Germany). The analytes were separated on a CORTECS $C_{18}^+$ column (2.1 mm × 100 mm, 2.7 μm) (Waters, Ireland). The injection volume was 10 μL and column temperature was 35 °C.