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Rapid liquid chromatography–tandem mass spectrometry-based method for the analysis of alcohol ethoxylates and alkylphenol ethoxylates in environmental samples

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ABSTRACT

A sensitive and selective method for the determination of alcohol ethoxylates (AEOs) and alkylphenol ethoxylates (APEOs) using solid-phase extraction (SPE) and LC–MS/MS was developed and applied to the analysis of water samples. All AEO and APEO homologues, a total of 152 analytes, were analyzed within a run time of 11 min, and the MS allowed for the detection of ethoxymers containing 2–20 ethoxy units (n_{EO} = 2–20). The limits of detection (LOD) were as low as 0.1 pg injected, which generally increased as n_{EO} increased (e.g., as high as 300 pg for n_{EO} = 20). Additionally, the responses of the various ethoxymers varied by orders of magnitude, with ethoxymers with n_{EO} = 3–5 being the most sensitive and those with n_{EO} > 15 producing the least response in the MS. Absolute extraction recoveries of the analytes ranged from 37% to 69% in ultrapure water (RSD ≤ 20%), with the recovery depending on the length of the alkyl chain. Abiotic stability studies were performed, and $C_{14–18}$ ethoxylates showed significant degrees of degradation. Water samples from the Colorado River were then analyzed for AEOs and APEOs, with absolute extraction recoveries ranging from 33% to 45% (RSD ≤ 12%). The predominant species observed in most samples were the octylphenol (OP) and nonylphenol (NP) ethoxylates, which contained total concentrations that were greater than 100 ng/L APEOs in a couple samples. Other AEO homologues were identified in the river water samples, including C_{13}, C_{15}, C_{16}, and C_{18} ethoxylates, but these compounds were generally present at much lower levels (i.e., <50 ng/L total concentration).

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1. Introduction

The predominance of surfactant compounds in industrial and household cleaning products over the past four decades has led to environmentally relevant concentrations of alcohol ethoxylates (AEOs) and alkylphenol ethoxylates (APEOs) in ground and surface waters [1–6]. AEOs and APEOs are a class of nonionic surfactants that are common components of detergent formulations and household and industrial cleaning products. AEOs and APEOs are also used as surfactants during oil and gas extraction [7]. They are high-production volume chemicals, with estimates of 275,000 tons of AEOs being used in the year 2002 in European household detergents [8]. In the U.S., the consumption of nonylphenol ethoxylates (NPEOs) has been estimated at between 300 and 400 million lbs per year [9]. AEOs possess a chemical formula of $CH_3–(CH_2)_y–(OCH_2CH_2)_x–OH$, with values of y typically ranging from 11 to 17 and values of x ranging from 0 to 20 (Fig. 1). The alkyl portion of the molecule can be either linear or branched. In this work, APEOs refer to either octylphenol ethoxylates (OPEOs) or NPEOs.

NPEOs are considered toxic to many aquatic species and are a major contributor to nonylphenol (NP) in the environment, a persistent endocrine-disrupting compound [10,11]. AEOs biodegrade more rapidly and are considered less ecotoxic than APEOs; hence, NPEOs are gradually being phased out and replaced with AEOs. The European Union has banned NPEOs for household use due to their toxicity, but the U.S. has not prohibited their use. The U.S. Environmental Protection Agency (EPA) has, however, added $NPEO_1$, $NPEO_2$, $NPEO_3$, and $NPEO_4$ (i.e., the mono-, di-, tri-, and tetraethoxylates of NP, respectively) to the Toxic Substances Control Act (TSCA) Section 4(e) Priority Testing List [12]. Additionally, many detergent manufacturers in the U.S. are voluntarily replacing NPEOs with AEOs. While considered safe to humans [8], AEOs are not completely environmentally benign themselves, and many studies have investigated the ecotoxicity of alcohol ethoxymer species in various organisms, including estimating the quantitative

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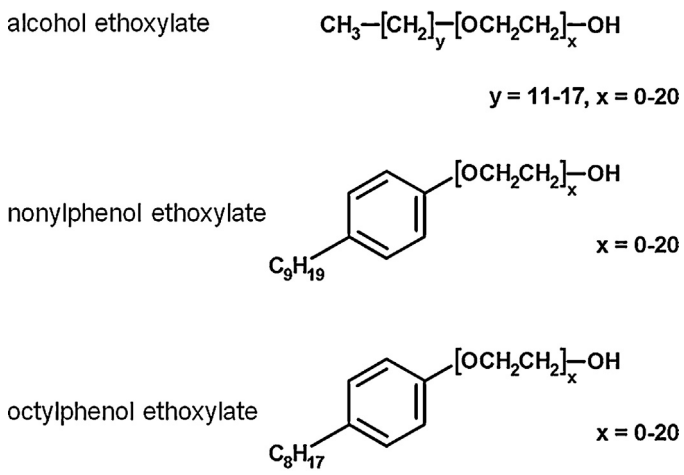

Fig. 1. Chemical structures of the alcohol ethoxylates and alkylphenol ethoxylates investigated in this study.

structure–activity relationships and no-observed-effect concentrations in algae, Daphnia, and various fish species [8,13–15]. Cardellini et al. [16] studied the teratogenic and toxic effects of AEOs in frog embryos and tadpoles and determined median lethal concentrations (LC_{50}) of 4.59 mg/L. The biodegradation rates of AEOS vary among the different isomers of the same chemical formula, e.g., AEOs with branched 2-alkyl chains were previously shown to degrade slower than linear AEOs [17]. Surveys of wastewater treatment plant (WWTP) effluents have shown that WWTPs typically remove >99% of AEOs from the influent [1,18]; however, often the more toxic species, i.e., the high-carbon alkyl chain and low-ethoxylate ethoxymers, are less efficiently removed [18]. Due to the ubiquity of AEOs and APEOs in both household and industrial detergents and surfactants, it may be particularly challenging to pinpoint the sources of ethoxylated compounds in environmental waters and sediments, e.g., whether they are due to residential down-the-drain disposal or from nearby industrial processes. However, the determination of AEOs and APEOs in environmental waters is necessary to assess potential risks to aquatic life.

Methods for the detection and quantitation of AEOs and APEOs from water samples typically utilize an extraction step followed by LC–MS [2,3] or LC–MS/MS [19–21]. The quantitation of AEOs and APEOs has been challenging due to a lack of certified standards, and assumptions are often made about instrument response for the various ethoxymers or about the concentrations of ethoxymers in the technical mixtures used as standards. The LC conditions often require long (i.e., 30 min to 1 h) run times to separate the homologues [3,22]. Deuterated $C_{13}EO_x$ [23] and ^{13}C-labeled $NPEO_x$ [4] have been synthesized for more accurate quantitation, but these compounds are not commercially available. Additionally, derivatization with 2-fluoro-*N*-methylpyridinium *p*-toluensulfonate (Pyr+) has been used to increase MS sensitivity [24], especially for mono- and diethoxylate species of the alcohols, but the derivatization process is subject to the purity and moisture content of the Pyr+ reagent and is time-consuming [24].

In this work, we developed an analytical method for the rapid determination and quantitation of individual alcohol and alkylphenol ethoxymers that does not require the use of derivatization reagents for quantitation. The method utilized solid-phase extraction (SPE) followed by a short LC–MS/MS run. The use of scheduled multiple-reaction monitoring (sMRM) mode was crucial for monitoring more than 100 MRM transitions in 11 min. We also show that the responses of the AEOs and APEOs vary considerably as a function of ethoxymer and that it is necessary to know the concentrations of each ethoxymer in the standard for accurate quantitation. We demonstrate the applicability of this approach by measuring AEOs and APEOs in river water samples. While only C_{12}–C_{16} and C_{18} AEOs and APEOs were investigated in this work, this method is potentially applicable to the analysis of C_8–C_{11} AEOs, providing appropriate standards can be obtained.

2. Materials and methods

2.1. Standards and reagents

Neodol 25-9, a commercial formulation of AEOs composed of C_{12}–C_{15} homologues, with an average ethoxylation of 9 units, was obtained as a white, waxy solid from Shell Chemical Company (Houston, TX) for use as AEO standards. The composition of the Neodol 25-9 was approximately C_{12}: 20%, C_{13}: 30%, C_{14}: 30%, and C_{15}: 20%, and the mol% of each ethoxymer was provided and is shown in Table S1. The Neodol 25-9 was "essentially linear", but approximately 20% of the ethoxymers were 2-alkyl branched [24]. Hexaethylene glycol monodecyl ether ($C_{10}EO_6$) and Triton X-100, a common laboratory detergent used as an $OPEO_x$ standard, were purchased from Sigma (St. Louis, MO). Polyoxyethylene (POE) (20) nonylphenol, POE (10) cetyl alcohol ether ($C_{16}EO_x$), and POE (10) stearyl alcohol ether ($C_{18}EO_x$) were obtained from Chem Service (West Chester, PA). Tergitol NP-10 was purchased from Fisher Scientific (Pittsburgh, PA). HPLC-grade methanol (MeOH) was purchased from Fox Scientific (Alvarado, TX), and HPLC-grade isopropanol (IPA) was obtained from J.T. Baker (Center Valley, PA). HPLC-grade methyl tert-butyl ether (MTBE), dichloromethane (DCM), and acetonitrile (ACN) were received from Burdick and Jackson (Honeywell International, Muskegon, MI). Ultrapure water was generated in-house from a Barnstead NANOpure water purification system. Stock solutions (0.5–1 mg/mL) of individual standards and standard mixtures were prepared by dissolving accurate amounts of the standard compounds in MeOH. Working standard solutions were obtained by further dilution of stock solutions with MeOH.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2013.07.017.

The choice of laboratory detergent is critical when cleaning glassware, as many detergents contain AEOs or APEOs. All glassware was cleaned with Alconox powdered detergent, which does not contain ethoxylates.

2.2. SPE extraction of target analytes

Samples were extracted using an Autotrace SPE Workstation (Dionex, Sunnyvale, CA). Various types of SPE extraction cartridges were evaluated, including Oasis HLB cartridges (200 mg, 6 cm^3) (Waters, Milford, MA), Enviro-Clean divinylbenzene (endcapped, 500 mg, 6 cm^3) (United Chem Service, Bristol PA), Enviro-Clean C18 (endcapped, 500 mg, 6 cm^3) (United Chem Service), Enviro-Clean C18 (unendcapped, 500 mg, 6 cm^3) (United Chem Service), and Enviro-Clean C8 (endcapped, 500 mg, 6 cm^3) (United Chem Service). The SPE cartridges from United Chem Service were constructed with glass. The cartridges were first conditioned with 5 mL MeOH and 5 mL water at a flow rate of 5 mL/min. After conditioning, 500 mL of sample was passed through the cartridges at 5 mL/min. To ensure quantitative recovery, the sample flasks were then rinsed with 50 mL water, and the rinsate was loaded onto the cartridges. The SPE cartridges were rinsed with 2 mL water before drying with N_2 gas for 30 min. The analytes were eluted off the cartridges with 10 mL of various solvents, including 90:10 MTBE/MeOH, MeOH, DCM, and 60:40 ACN/IPA, at 3 mL/min. The eluate was then concentrated and solvent exchanged with a TurboVap Concentrator (Biotage, Charlotte, NC) to 0.5 mL in MeOH and transferred to HPLC