Trace Analysis of Alkylphenol Ethoxylates

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A method for quantitative determination of trace amounts of alkylphenol ethoxylates (APE) in environmental water is described. Levels of 1 to 3 μg/L can be detected and resolved into their complete oligomer distribution (1EO to 18EO) while maintaining integrity of the oligomer distribution. This is a major improvement over previous methods; for the first time distortion of oligomer distribution due to work-up conditions of earlier methods has been prevented.

Isolation of the APE from water is achieved using a simple and rapid dual-column procedure. The first column removes interfering ionic materials, the second traps the APE on alkyl-bonded silica. Assay of the extract employs HPLC with a fluorescence detector.

The method was used for analyzing treated wastewater and river water. A much better picture of the biodegradation behavior of APE in the environment has emerged as a result of keeping APE oligomer distribution intact during sample extraction. There is no accumulation of alkylphenol and the low EO oligomers during wastewater treatment, although the oligomer distribution may become skewed toward these species.

Concentrations in the receiving waters examined were very low, in the range of 1-2 μg/L total APE species (OEO to 18EO).

For decades the biodegradation and environmental fate of alkylphenol ethoxylate (APE) nonionic surfactants have been subjects of intense debate and research (1). Since APE, in particular nonylphenol ethoxylates (NPE), are widely used in industrial and household detergents—about 450 MM lb in the U.S. in 1988 (2)—their environmental levels need to be measured reliably in order to assess any risk to the environment.

Our goal was to simplify the extraction of environmental water samples so that NPE could be measured quantitatively by HPLC at ppb to sub-ppb levels, both cheaply and rapidly. A crucial requirement was maintaining the integrity of the NPE oligomer distribution as it moved from dilute aqueous solution through extraction into concentrated organic solution and injected onto the chromatographic column.

This goal has been accomplished through streamlining earlier extraction methods and attention to the details of sample protection during extraction. The method as now described may be used routinely; analysis time from water sample extraction and chromatography is as little as three hours, compared with up to 12 hr for the earlier procedures. Detection limit is about 0.1 μg/L for each oligomer.

Analytical methodology has been evolving rapidly in recent years for detecting APE at low levels. The first reported efforts to quantify APE in sewage by chromatography were cumbersome, slow and incomplete (3,4); gas chromatography and mass spectrometry could detect and quantitate the lowest molecular weight species NP (nonylphenol), NPE1, and NPE2 (detection limit 10 micrograms per liter or parts per billion [μg/L or ppb]) for each species, only after laborious clean-up procedures involving solvent extraction and column chromatography through alumina. Ease of analysis and detection limits were greatly improved when high pressure liquid chromatography was applied to these species. No clean-up was needed after extractive steam distillation through cyclohexane (5); the extract, containing NP and the lower ethoxylates, could be injected directly into the HPLC. Detection limit was 0.5 μg/L. Higher ethoxylates were now accessible (6), since NPE have UV absorption, but only with the use of complex extractions and clean-up prior to HPLC injection; detection limit was 1-3 μg/L for each oligomer. Sensitivity was increased enormously with the use of HPLC fluorescence detection (7,8). This new method was used to measure die-away of NPE by biodegradation in river water (9). A lengthy extraction procedure was still required with sewage samples, but detection limit for individual NPE oligomer was lowered to 2 nanograms (8,10). Two German sewage treatment plants were studied for efficiency of NPE removal using the extraction and HPLC fluorescence detection procedures (10).

A big step toward replacing the solvent extraction procedures was percolation of water solutions through octadecysilica (11). Alkylphenol ethoxylates and alkylbenzene sulfonates could be analyzed together in raw sewage using this technique. This method, however, lacked sensitivity (detection limit 4 μg/L total APE) and precision.

Methods specific for nonylphenoxyethoxy carboxylates, intermediates in the degradation of NPE, were also developed by Giger (12). This report described the performance of several treatment plants for removing nonylphenol-based species in the Zurich, Switzerland, vicinity. Assays using the cumbersome extraction procedures (6) provided the first data on treatment plant efficiency.

Prior work indicated that degraded NPE was largely composed of NP and the lower EO oligomers NPE1 and NPE2, the species least water-soluble and most toxic to aquatic fauna (6). Our improved sample handling procedures allow us to define NPE oligomer distribution in environmental samples with much greater accuracy and precision and to demonstrate that there is no substantial skewing of the oligomer distribution toward the low EO end.

It should be noted that the present method does not distinguish among the various alkylphenols and their ethoxylates. Nonylphenol is by far the major al-

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kylphenol in common use, so its ethoxylates were used as the reference standards during method development.

**EXPERIMENTAL**

**Water sample collection.** Raw and treated wastewater samples from remote locations were collected as 24-hr composites and preserved with 1% formalin. The filled glass containers, 1 quart to 1 gallon, were shipped by public carrier to the laboratory, and refrigerated when received.

Samples of river water were collected from the Colorado River downstream from Austin, Texas, as 1 gal grab samples. A boat was used to reach midstream. Preservatives, if any, were added to the jugs onshore. Samples were refrigerated to 4°C within three hours after collection.

**Extraction of NP and NPE from water—NP and low oligomers.** Steam distillation was performed on 1 L water samples in a modified Nielsen-Kryger apparatus (Ace Glass 6555-13). The sample was heated to reflux with 2 mL iso-octane for 1 hr. The resulting iso-octane solution could be injected directly into the HPLC without further handling.

**NPE.** Water samples up to 1 L were passed through a dual column apparatus consisting of four pieces of glassware mounted vertically in series. On top was a 1 L solvent reservoir charged with the sample with a valve in the bottom. The water flowed into a 10-inch decylsilica (Baker, 7031-0), which adsorbed organic material which removed all ionic species. (Adding 150 mL methanol was removed at 45°C under a stream of nitrogen just to dryness. Residue was taken up into a dichloromethane/hexane (25/75) mixture for HPLC analysis.)

At all times the sample was protected from air and dissolved oxygen.

**Loss of NPE spike (3 µg) in methanol occurred during simple solvent blow-down, apparently because of adsorption to the vial glass. The same effect was observed during methanol removal from NPE extracts when a new lot of octadecylsilica was used; the original lot (used for the entire present study) gave high (>90%) recoveries. The losses were minimized (>80% recoveries) when a small amount of alcohol ethoxylate (5 µL) was spiked into the methanol prior to blow-down. The analyte remained dissolved in the alcohol ethoxylate, which did not interfere with subsequent HPLC analysis. The preferred ethoxylate was C_{1214} alcohol-3EO (SURFONIC® L24-3 or equivalent).

**Standard NPE blend.** A mixture of NPE was used for method and instrument calibration (Table 1). From HPLC analysis of the NPE4 and NPE9 the blend was calculated to contain 3.0 wt% each of NP, NPE1, and NPE3, and 6.0% NPE2. HPLC analysis of the blend came close to these values, but was not exact because these low EO oligomers were incompletely resolved. Stock solutions were unstable so they were made fresh daily.

**HPLC procedures.** Apparatus included a Waters Associates liquid chromatograph with two Model 510 high pressure pumps. Model 680 solvent programmer, Rheodyne 7125 injector with 100 microliter loop, Hewlett Packard HP1046A fluorescence detector, and Waters 840 data system. The column used was Rainin Microsorb 250 mm × 4.6 mm 5 micrometer CN.

Solvents were the purest grades available. Elution solvent A (20/80 tetrahydrofuran/hexane, v/v) was passed through a 4.6 mm × 150 mm column, dry packed with alumina (activity 1), inserted between the A and B pumps to trap traces of peroxides. The trap was changed every 2 to 4 days. Elution Solvent B was 10/90 (v/v) water/isopropl alcohol.

Methanol used for sample extraction was checked for purity by blowing down 30 mL to dryness, taking up the residue in 25/75 dichloroethane/hexane and examining by HPLC. Some lots of methanol showed high background levels of NPE. Likewise water was a source of background NPE. Deionized water was further purified in a Milli-Q system of adsorbent cartridges. Frequent blank extractions using only reagent water were necessary. Sodium sulfite (100 ppm) was added to the degassed water to scavenge dissolved oxygen.

The elution gradient is presented in Table 2. Figure 1 illustrates the resulting chromatography using the NPE standard blend (Table 1) both unextracted (3 µg/mL stock solution) and extracted (3 µg/L spike).