

Analysis of Surfactants in Water by SPME/HPLC

Nonionic surfactants of the nonylphenol ethoxylate class are relatively nonvolatile analytes typically analyzed by liquid-liquid extraction and HPLC or, after derivatization, GC. With the development of an SPME/HPLC interface and a Carbowax/templated resin-coated SPME fiber, these surfactants can now be analyzed more easily. This publication describes an SPME/HPLC method for the analysis of Triton X-100 stock solution using the CWX/TR fiber. We observed excellent agreement of the ethoxamer distributions for direct injection analyses and after SPME extraction.

Key Words:

- alkylphenol ethoxylates • ethoxamer distribution
- nonionic surfactants • SPME

Due to environmental and human health concerns, alkylphenol ethoxylates are scheduled to be phased out of industrial and institutional (I & I) cleaning products by the year 2000. These nonionic surfactants are currently found in many influent and effluent streams of sewage treatment plants, and consequently in river waters and sediment.

Traditionally, nonionic surfactants have been separated by liquid-liquid extraction (LLE) or solid-phase extraction (SPE) and analyzed by HPLC or GC. These methods can have limitations, such as the inability to maintain the same oligomer distribution as the original sample, the use of large volumes of toxic solvent, the need to concentrate analytes for better sensitivity, and the plugging of cartridges or low breakthrough volumes in SPE. A more efficient and accurate method of analyzing ethoxylates in water will be needed to meet the upcoming testing demand.

Originally, solid phase microextraction[®] (SPME) was exclusively coupled with GC, and nonionic surfactants are not sufficiently volatile for GC analysis without derivatization. However, with the development of our SPME/HPLC interface, analytes from an SPME fiber can be directly desorbed into mobile phase and transported to an HPLC column, thereby making it possible to analyze ethoxylates via SPME/HPLC and eliminating the problems associated with other sample preparation techniques.

SPME is a simple, cost-effective, time-saving extraction technique developed at the University of Waterloo, Ontario, Canada. In SPME, a phase-coated fused silica fiber contained within a syringe

is exposed to the sample, allowing the analytes to adsorb to the fiber coating. Adsorption equilibrium typically is attained in 2 to 30 minutes. After sample adsorption, the fiber is removed from the sample vial and introduced into the SPME/HPLC Interface, where the analytes are desorbed and analyzed. It is quick, highly sensitive, and versatile. Solvent use is greatly decreased, and no complicated apparatus is needed.

The SPME/HPLC interface consists of a 6-port injection valve (both Rheodyne[®] and Valco[®] valves are available) and a fiber desorption chamber, which replaces the injection loop. After sample extraction, the needle is inserted into the desorption chamber and the fiber is exposed. Mobile phase contacts the fiber, desorbs the analytes, and delivers them to the HPLC column. A moving stream of mobile phase can remove the analytes (dynamic desorption) or, when the analytes are more strongly adsorbed, the fiber can be soaked in mobile phase or other solvent before the injection is made (static desorption).

SPME/HPLC was used to analyze Triton[®] X-100 (a reference nonionic surfactant) for ethoxylates. Of the various fibers tested, the Carbowax[®]/templated resin (CWX/TR) proved to be the best choice for extracting the ethoxylates.

To extract the analytes at the 100mg/L level using SPME, salted (25% NaCl) solutions of Triton X-100 were used. Salt will often increase analyte recovery by SPME (request Application Note 95 for information on optimizing SPME performance). In this application, it improved agreement between the ethoxamer distribution of the extracted sample and the standard.

The CWX/TR fiber was exposed to the Triton X-100 sample for 50 minutes, with vigorous stirring. After extraction, the fiber was inserted into the SPME/HPLC Interface and exposed to the mobile phase for static desorption. A similar analysis at the University of Waterloo showed that most of the ethoxamers were completely desorbed within the first minute, although slightly more analyte was desorbed in 50 minutes, for a total desorption of approximately 90% (1). (To remove residual analytes, the fiber should be desorbed a second time between analyses).

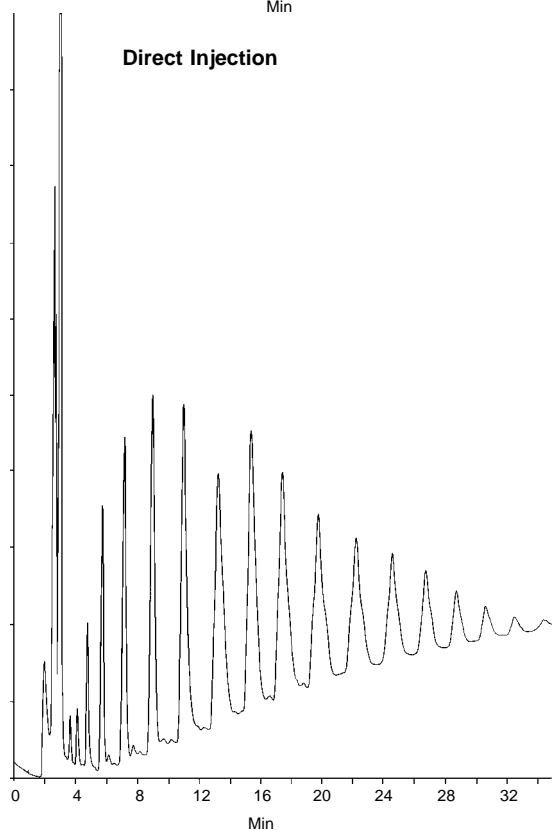
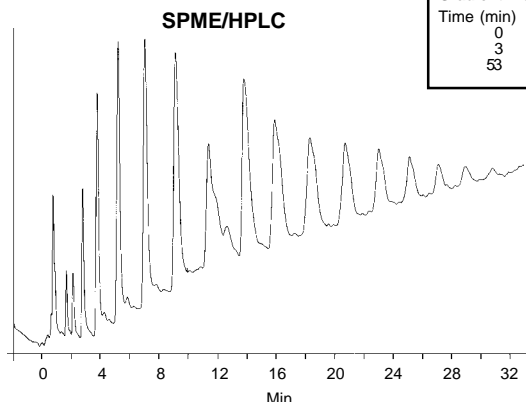
The integrity of the ethoxamer distribution after extraction is an important consideration in the analysis of surfactants. The CWX/TR fiber successfully maintained agreement of the ethoxamer distribution between direct injection and SPME/HPLC analysis of Triton X-100 (Figure A). Peak sharpness was maintained, indicating efficient transfer from the SPME fiber to the HPLC column.

Figure A. SPME/HPLC vs. Direct Injection

Sample: 500ppm Triton X-100
 SPME Fiber: Carbowax/templated resin, 50µm film
 Cat. No.: 57315
 Extraction: immersion, 50 min (rapid stirring)
 Desorption: static, 2min, 200µL mobile phase

Column: SUPELCOSIL™ LC-NH₂
 Cat. No.: 58338
 Mobile Phase: A = hexane:2-propanol (90:10)
 B = 2-propanol:water (90:10)
 Flow Rate: 0-1 min: 0.5mL/min
 2-53 min: 1.5mL/min
 Det.: UV, 220nm

Gradient Program	
Time (min)	%B
0	3
3	3
53	53



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Analysts at the University of Waterloo tested the precision of this method, using the CWX/TR fiber. The ethoxamers of Triton X-100 were extracted with variations in recovery ranging from $\pm 2\%$ to $\pm 15\%$. Even for ethoxamers that were less well extracted, this precision is much better than that required by the US Environmental Protection Agency (i.e., $\pm 30\%$).

Using SPME/HPLC with the CWX/TR fiber to extract nonionic surfactants from water will prove to be a time and cost savings for your lab. You can reduce solvent use and decrease the time and effort spent extracting analytes, while maintaining accuracy during analysis.

Ordering Information:

Description	Cat. No.
HPLC/SPME Interface with Valco valve	57350-U
with Rheodyne valve	57353
SPME Holder for HPLC/Varian AutoSampler	57331
SPME Fibers, Carbowax/Templated Resin, 50µm pk. of 3	57315
SUPELCOSIL LC-NH ₂ HPLC Column, 25cm x 4.6mm ID, 5µm particles	58338
Stirring/Hot Plate 110VAC	Z11,091-4
220VAC	Z26,200-7
Magnetic Stirring Bars, 10 x 3mm, pk. of 3	Z11,887-7
SPME Stand, 8 position, for 4mL vials	57333-U

Reference

- Boyd-Boland, Anna A., and Janusz B. Pawliszyn, *SPME Coupled with HPLC for the Analysis of Nonylphenol Ethoxylate Surfactants in Water*, *Anal. Chem.*, **68**: 1521-1529 (1996).

Reference not available from Supelco.

Trademarks

Carbowax, Triton — Union Carbide Corp.
 Rheodyne — Rheodyne, Inc.
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