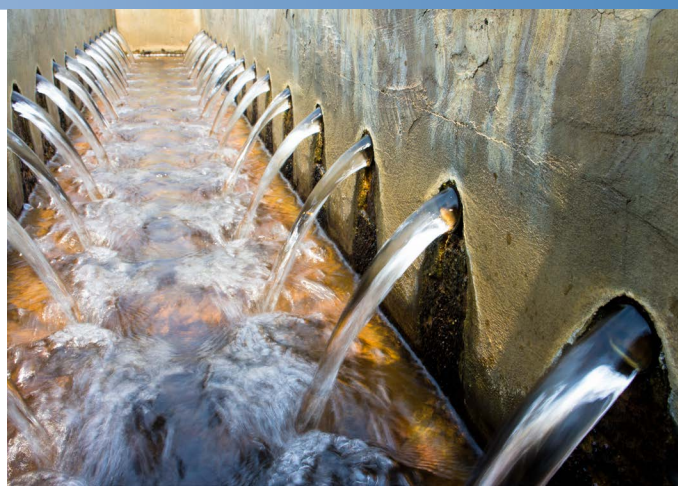
Automated Solid-Phase Extraction of Linear Alkylbenzene Sulfonate in Wastewater Using a Weak Anion-Exchange Cartridge Followed by HPLC with UV Detection

Jing Hong and Rosanne Slingsby
Thermo Fisher Scientific, Sunnyvale, California, USA

Application Note 1080

Key Words
Surfactant, Dionex SolEx SPE WAX Cartridges, Dionex AutoTrace 280, Recovery



Introduction

Surfactants are the major active ingredients of laundry detergents. Anionic surfactants account for 60% of surfactant used in the United States. Linear alkylbenzene sulfonate (LAS, CAS 68411-30-3) is an anionic surfactant. It is a mixture of closely-related isomers and homologues, each containing an aromatic ring sulfonated at the para position and attached to a linear alkyl chain.[1] The linear alkyl chain typically consists of 10–13 carbon units. LAS surfactants have a strong affinity for sorption to sediments. The concentration range of LAS in wastewater treatment plant effluent is 19,000–71,000 ng/L.[1] The method detection limits (MDLs) of LC techniques employing direct injection of samples are too high for the detection of the low levels. Therefore, solid-phase extraction (SPE) is used for sample enrichment. The Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction (SPE) instrument performs automated SPE of large-volume liquid samples for organic analysis. In this application, LAS is extracted from ASTM wastewater matrix by the Dionex AutoTrace 280 instrument using a weak anion-exchange (WAX) cartridge. The WAX stationary phase is comprised of a 22 µm medium surface area divinylbenzene resin particle grafted with carboxylate functionality. The ion-exchange capacity is about 1.2 mEq/g. This phase is mixed mode reversed-phase and cation-exchange.

Goal

Analysis of LAS in wastewater by automated SPE using the Dionex AutoTrace 280 instrument and a new polymeric sorbent Thermo Scientific™ Dionex™ SolEx™ SPE WAX cartridge.

Experimental

A substitute wastewater sample was prepared according to ASTM Designation D5905-98 (Standard practice for the preparation of substitute wastewater). Preparation procedures are as below.

Substitute Wastewater Preparation Procedure

1. Place 0.4 g flour, 2.0 g ocean salts, 0.08 g Kaolin, 20.0 mL Triton X-100 solution (1.20 g Triton X-100 to water and dilute to 1 L), and 120 mL beer (shake vigorously and loosen the cap. Allow the beer to dissipate carbonate by refrigerating for 24 hr followed by allowing the sample to reach room temperature.
2. Blend the mixture at the lowest setting for 30 sec. Allow most of the foam to subside before transferring. Transfer quantitatively to 2 L volumetric flask and dilute to 2 L with water.

Thermo SCIENTIFIC

System

- Dionex AutoTrace 280 6 mL SPE cartridge system
- Dionex SolEx SPE WAX cartridge, 3 mL barrel, 60 mg and 150 mg resin, 6 mL barrel, 100 mg and 200 mg resin
- Thermo Scientific™ Dionex™ UltiMate™ 3000 HPLC system including:
  - DGP 3600M dual gradient pump
  - SRD 3600 solvent rack with integrated vacuum degasser
  - TCC-3200 thermestatted column compartment
  - WPS-3000 autosampler equipped with 5 µL loop
  - PDA-3000
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, version 6.80 SP4 and higher

Solid-Phase Extraction Conditions

Dionex AutoTrace 280 Instrument Barrel:	Dionex SolEx SPE WAX cartridge, 3 mL barrel, 60 mg and 150 mg resin 6 mL Barrel, 100 mg and 200 mg resin
Flow Rate:	5 mL/min
Elution Solvent:	5 mL, 5% Ammonium Hydroxide in methanol

Dionex AutoTrace 280 Instrument Method:

No.	Method	SPE Steps
1	Wash syringe with 5.0 mL of water	
2	Condition cartridge with 5.0 mL of water into aqueous waste	Condition
3	Condition cartridge with 5.0 mL of Methanol into solvent waste	Condition
4	Dry cartridge with gas for 5.0 minutes	Dry
5	Condition cartridge with 5.0 mL of 1% v/v Formic Acid in water into aqueous waste	Equilibrate
6	Load 20.0 mL of sample onto cartridge	Load
7	Rinse cartridge with 5.0 mL of 1% v/v Formic Acid in water into aqueous waste	Wash 1
8	Rinse cartridge with 5.0 mL of 1% v/v Formic Acid in Methanol into solvent waste	Wash 2
9	Collect 5.0 mL fraction into sample tube using 5% v/v Ammonium Hydroxide in Methanol	Elute

Analytical Conditions

Column:	Thermo Scientific™ Dionex™ Acclaim™ Surfactant Plus column, 3 µm
Dimensions:	3.0 × 100 mm

Gradient:

Time (min)	Acetonitrile	0.1 M Ammonium Acetate, pH 5
–6.0	25%	75%
0.0	25%	75%
10.0	80%	20%

Temperature:	30 °C
Flow Rate:	0.6 mL/min
Inj. Volume:	5 µL
Detection:	UV at 225 nm
Peaks:	Linear alkylbenzene sulfonate (LAS)

Results and Discussion

The separation of LAS chromatogram is shown in Figure 1. WAX SPE sorbent was packed into six formats as listed in Table 1. Larger barrel sizes have larger diameters and higher bed weights than smaller barrels. The larger diameters are more rugged for samples containing particulates, colloids than small diameter. In the Dionex AutoTrace 280 SPE instrument method, WAX sorbent is pre-conditioned to low pH by 1% formic acid. WAX sorbent is positively-charged at low pH and is able to retain negatively-charged LAS during sample loading. LAS was later eluted from WAX sorbent by "turning off" the anion-exchange functionality at high pH by 5% ammonium hydroxide in methanol.

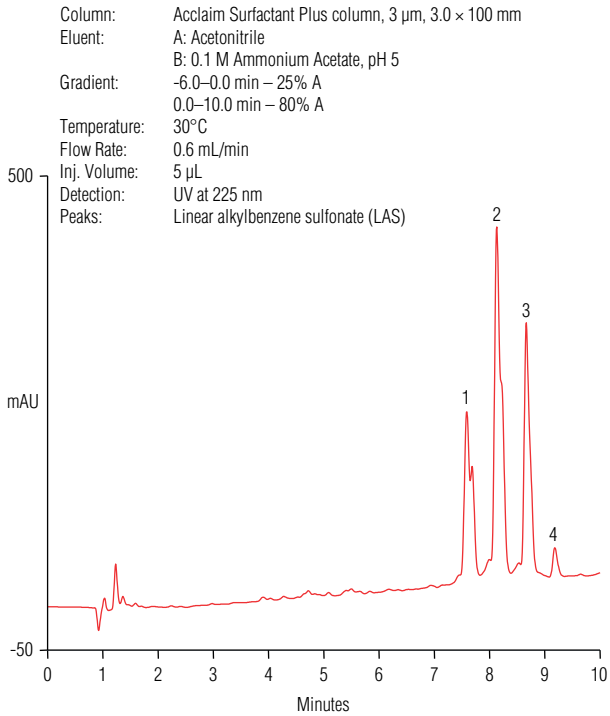


Figure 1. Chromatogram showing the separation of 0.1% LAS using a Dionex Acclaim Surfactant Plus Column, with sample prepared by automated SPE using the Dionex SolEx WAX phases.

The table below shows comparison of recoveries using several bed weights and barrel cartridge volumes. A recovery study was performed by spiking a low concentration sample with LAS and comparing UV absorbance area count of LAS standard to the concentrated sample after SPE.

Table 1. Recovery of LAS samples on six different WAX sorbent formats.

Bed Size	60 mg, 3 mL	150 mg, 3 mL	100 mg, 6 mL	200 mg, 6 mL
0.005% LAS, 20 mL (3 µEq)				106%
0.005% LAS, 30 mL (4.5 µEq)	81%	103% (10 mL/min loading)	90.5%	102%
0.005% LAS in wastewater, 20 mL (3 µEq)	91%	92.5%	100%	99%

When a total of 3 µEq LAS in D.I. water is pre-concentrated on Dionex SolEx SPE WAX sorbent, good recovery (> 90%) is obtained on even the smallest bed size (60 mg in 3 mL cartridge). When a total of 4.5 µEq LAS in D.I. water passed through WAX sorbent, bed weight should be over 100 mg to have a good recovery as shown on the second row of Table 1. When 3 µEq of LAS is extracted from wastewater matrix, all bed sizes give a good recovery ranging from 91% with the 3 mL barrel with 60 mg of resin to 100% for the 6 mL barrel with 100 mg resin.

Conclusion

The successful analysis of LAS in substitute wastewater demonstrates that automated SPE using the Dionex AutoTrace 280 SPE instrument and Dionex SolEx SPE WAX cartridge can determine the LAS without laborious sample preparation.

References and Acknowledgements

1. Application Note 219: Determination of linear alkylbenzene sulfonate in treatment plant wastewater streams using on-line solid-phase extraction followed by HPLC with fluorescence detection.

AN70883_E 08/16S