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APPLICATION NOTE 72509

Determination of linear alkylbenzene sulfonate in textile using online solid-phase extraction followed by HPLC with UV detection

Author

Thermo Fisher Scientific

Keywords

Online solid-phase extraction, HPLC, UV, textile, linear alkylbenzene sulfonate, surfactant, automated online SPE, cotton, LAS

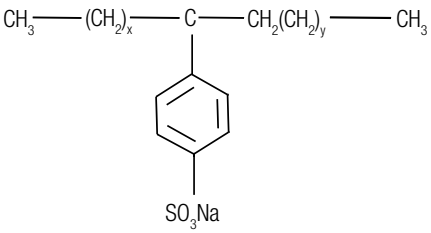

Figure 1. General structure of linear alkylbenzene sulfonate. For most textile samples, x+y = 10, 11, 12 and 13.

Goal

This work strives to transfer the Chinese Standard GB/T 23325-2009 method for the detection of linear alkylbenzene sulfonate (LAS), which requires an expensive LC-MS/MS system, to a lower cost LC-UV system. This work also aims to achieve a lower detection limit than the provided Chinese Standard guidelines by increasing the injection volume and using online SPE to enrich textile extracts.

Introduction

Linear alkylbenzene sulfonates in textiles are often assayed using cost-intensive LC-MS methods. Linear alkylbenzene sulfonate (LAS) generally refers to a mixture of homologs possessing a linear alkyl carbon number from 10 to 13. Its structural formula is shown in Figure 1.

A high-cost LC-MS/MS method is used in Chinese Standard GB/T 23325-2009 detection of LAS, and the detection limit, 2 mg per kg of textile sample, is relatively high[1]. In this application note, we use a the Thermo Scientific™ UltiMate™ 3000 Dual Gradient HPLC system to employ online solid-phase extraction (online SPE) for HPLC detection after the online enrichment of textile sample extracts (Figure 2). Injecting 100 µL of sample can boost the detection limit to 0.15 mg/kg, and the detection limit can be further reduced by increasing the injection volume accordingly.

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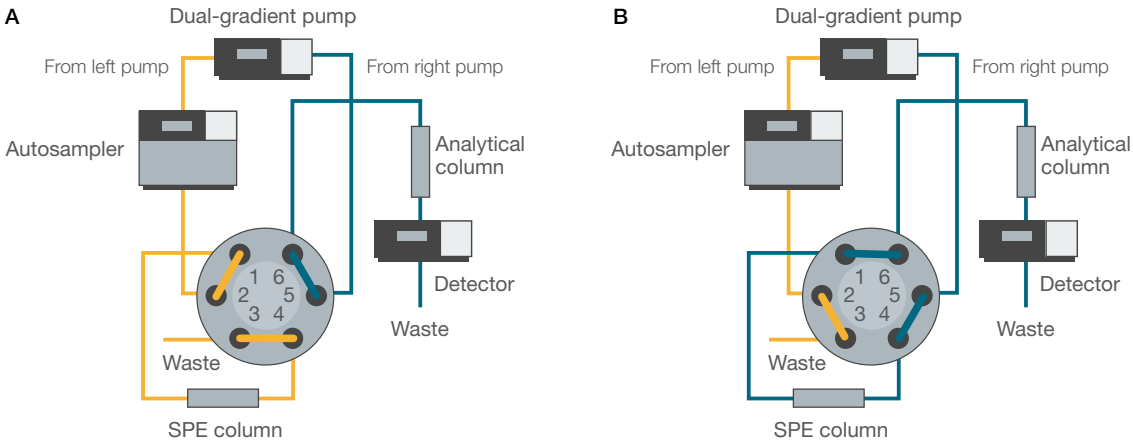

Figure 2. Instrument configuration. When valve is in position 1-2, sample is loaded onto the SPE-column (A). When the valve is in position 6-1, the sample is being transferred and separated on the analytical column (B).

The method described here achieves baseline separation of LAS with different carbon numbers, allowing LAS to be directly detected by an UV detector without the need for mass spectrometry. This method incorporates the automated matrix removal of sample extracts delivering high sensitivity and good recovery rates. The online SPE column can be reused, which greatly reduces analysis costs. In addition, automating the online SPE part of the assay reduces result variation caused by manual preparation of the samples.

Experimental

Equipment and software

The Thermo Scientific™ UltiMate™ 3000 Dual Gradient Standard LC system was used, which includes:

- Thermo Scientific™ UltiMate™ 3000 SRD-3600 Integrated Solvent and Degasser Rack (P/N 5035.9230)
- Thermo Scientific™ UltiMate™ 3000 DGP-3600SD Dual Gradient Standard Pump (P/N 5040.0061)
- Thermo Scientific™ UltiMate™ 3000 WPS-3000SL Semi-Preparative Split-Loop Autosampler (P/N 5822.0018)
- Thermo Scientific™ UltiMate™ 3000 TCC-3000RS Rapid Separation Thermostatted Column Compartment (P/N 5730.000) with one 2p-6p switching valve
- Thermo Scientific™ UltiMate™ 3000 DAD-3000 Diode Array Detector (P/N 5082.0010), equipped with analytical flow cell (stainless steel, 13 µL, P/N 6082.0100)
- Thermo Scientific™ Chromeleon™ Chromatography Data System software 6.8 or equivalent version 7.2

Consumables

- Thermo Scientific™ Acclaim™ Surfactant LC analysis column (5 µm, 4.6 × 250 mm, P/N 063203)
- Acclaim Surfactant LC guard column (5 µm, 4.6 × 10 mm, P/N 069701)
- Thermo Scientific™ IonPac™ NS1 enrichment column (10 µm, 4 × 35 mm, P/N 039567)

Chromatographic conditions		
Enrichment Pump Mobile Phase	A: Acetonitrile B: Water	
Analysis Pump Mobile Phase	A: Acetonitrile B: 100 mmol/L NH_4OAc (pH = 5, adjusted with HCl)	
Enrichment Pump Gradient	Time (min)	Enrichment Pump (%B)
	0	100
	5	100
	10.2	100
	11	0
	22	0
	23	100
	30	100
Analysis Pump Isocratic Gradient	Time (min)	Pump (%B)
	0	30
	30	30
Valve Position	Time (min)	Valve position
	0	1-2
	5	6-1
	10.2	1-2
Injection Volume	100 µL	
Flow Rate	1.0 mL/min	
Temperature:	30 °C	
Detection Wavelength:	225 nm	

Sample preparation

To extract the sample textile with methanol, cut 5 × 5 mm pieces from representative places throughout the textile. Then accurately weigh 0.25 g of cut samples into a sample container, add 5 mL of methanol and seal with a stopper or container cap. Place the sample container into an ultrasonic bath for 30 minutes at 75 °C. After cooling down the sample to ambient temperature, filter and extract using a 0.22 µm pore size nylon membrane filter. After optional dilution with more methanol (dependent on calibration curve range), the filtrate is ready for analysis.

Results and discussion

Standard chromatogram

The standard chromatogram for a typical LAS mixture is shown in Figure 3. Linear alkyl chains of LAS generally range from C10 to C13 with an average carbon chain of about 11.6. Commercially available LAS products contain over 20 kinds of chemical compounds, including homologs with different carbon chain lengths and isomers at different positions. Therefore, the peak shape and retention times for the C10 to C13 peaks are irregular. Despite the peak shapes, all peak pairs are baseline-separated, and the resolution is about 30 for all peak pairs.

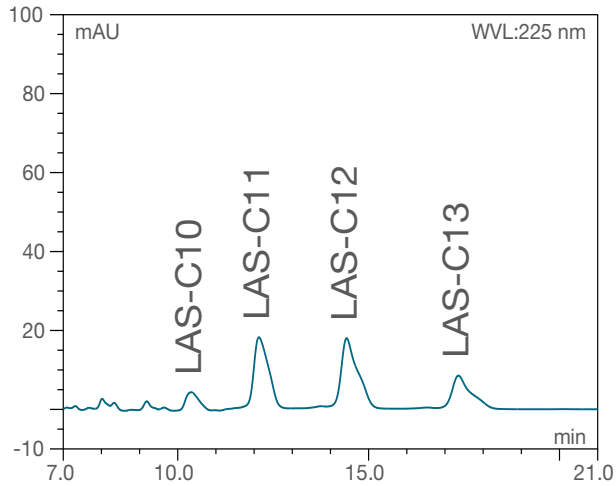

Figure 3. Chromatogram of a mixed standard solution (the total concentration of LAS is 10 µg/mL).

Sensitivity and linearity

Under the above chromatographic conditions, the quantitation was performed by processing the total peak area of the LAS peaks. The linearity was good within a concentration range from 5 µg/mL to 100 µg /mL, and the linear correlation coefficient was $r^2 > 0.9991$. Using signal-to-noise based determination for the limit of detection (3 × S/N), the LAS limit of detection for this method was found to be 0.15 mg/kg. If necessary, the sample concentration and injection volume can be increased to further reduce the detection limits.

Sample analysis

Chromatograms for spiked and unspiked samples of cotton, denim, non-woven fabric and silk are shown in Figure 4. Typical recovery rates are shown in Table 1.

Table 1. Recovery test of LAS in Textile Sample Extracts (recovery calculated using total LAS).

Sample name	Measured value (µg/g)	Added standard (µg/g)	Measured value for added standard (µg/g)	Recovery (%)
Cotton	95.1	10	105.2	101.3
Denim fabric	52.3	10	63.2	109.3
Non-woven fabric	7.8	20	31.6	118.9
Silk	2.8	20	25.6	113.7

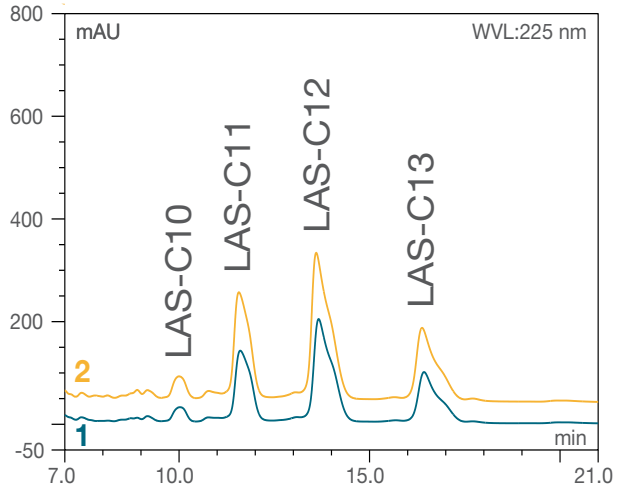

Figure 4A. Cotton sample extract (1) and same extract, spiked with LAS mixed standard (20 µg/g) (2).

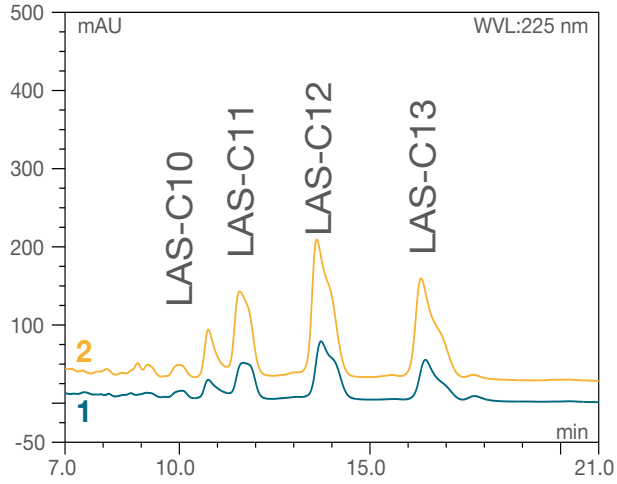

Figure 4B. Denim fabric sample extract (1) and same extract spiked with LAS mixed standard (20 µg/g) (2).

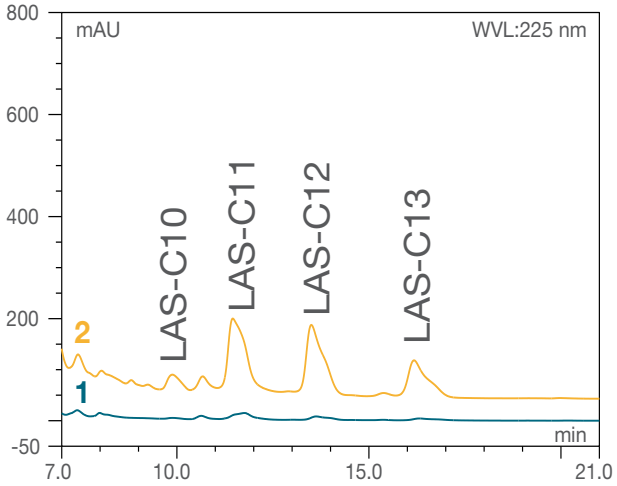

Figure 4C. Non-woven fabric sample (1) and same sample spiked with LAS (20 µg/g) (2).

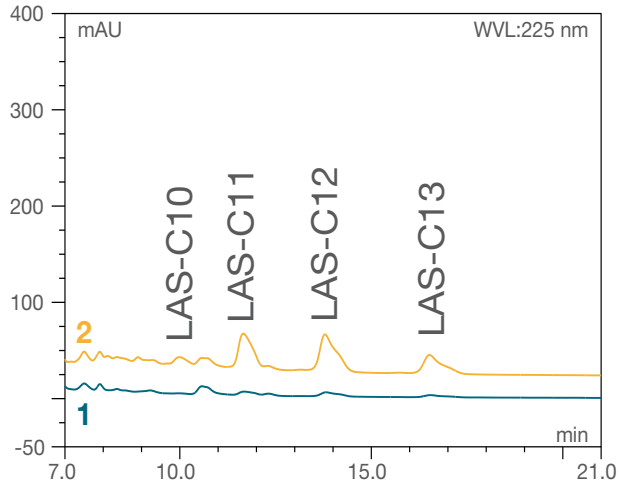

Figure 4D. Silk sample extract (1) and same extract spiked with LAS (20 µg/g) (2).

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Conclusions

This method shows the use of automated online solid-phase extraction technology (online SPE) to quantify linear alkylbenzene sulfonates in textile samples. A dual gradient pump was successfully used for sample enrichment and purification. The Acclaim Surfactant column achieves baseline separation of LAS mixtures with various carbon chain lengths and from various textile matrices. Levels of LAS in all four textiles tested could be quantified with UV detection with minimal sample preparation. Using the IonPac NS1 guard column as the online SPE column, the setup is compatible with 100% aqueous-phase for washing between samples with no carry-over between samples. The reusability of the SPE column reduces sample analysis costs, which is of benefit for labs who routinely analyze LAS in textiles.

The good recovery rates of between 101 and 114% and the low detection limit of 0.15 mg/kg, which is significantly lower than the method outlined under GB/T 23325-2009,[1] allow this method to be recommended for general practice.

References

1. National Standard of PRC, GB/T 23325-2009 Textiles—*The Determination of Surface Active Agent Linear Alkylbenzene Sulfonate*.

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