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Application News

No. C187

LC/MS

LC/MS/MS Analysis of Alkylphenol Ethoxylates (APEO) and Alkylphenols (AP)

In recent years, the safety concern over textiles has been on a rise in addition to the environmental and food safety issues. Harmful substances in textiles are being regulated around the world, particularly EU region. Beside regional regulations, there are also strict regulations to ensure the safety of consumers. These include the adoption of independent inspection and certification on residual standard reference such as STANDARD 100 by OEKO-TEX® and chemical regulatory lists implemented by manufacturer.

Alkylphenol ethoxylates (APEOs) which are commonly used as textile surfactants are restricted by REACH regulation, especially nonylphenol ethoxylates (NPEOs). NPEOs can break down to nonylphenol (NP) which can cause endocrine disruption and other health issues.

"LC/MS/MS Method Package for Restricted Chemicals in Textiles" provides several types of methods for the various restricted chemicals for textiles. Here, we introduce the analysis of NPEOs and octylphenol ethoxylates (OPEOs), NP and octylphenol (OP) by using the method in them.

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LC-MS/MS Analysis (APEOs)

These analyses were performed by using the method contained in the Method Package. Fig. 1 shows each structure of the compound. APEOs are non-ionic surfactants that are synthesized by reactions between alkylphenols (APs) and ethylene oxide (EO). Each product is a mixture of different NPEOs or OPEOs with a variable number of ethoxylate (EO) groups. (Table 1) Therefore, the quantitation was performed by the sum of all APEOs. The ammonia adduct ions $[M+NH_4]^+$ were selected as the precursor ions. Table 2 shows the analytical conditions. The LC analysis conditions were according to the ISO-18254. On the other hand, the MS analysis conditions were optimized for the triple quadrupole mass spectrometer.

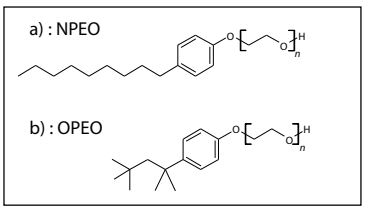

Fig. 1 Structure of a) NPEO, b) OPEO

Table 1 MRM transition

compounds	n	Molecular formula	Precursor ion (*m/z*)	Product ion (*m/z*)
NPEO	3	C15H24O(C2H4O)3	370.3	227.10
	4	C15H24O(C2H4O)4	414.3	271.15
	5	C15H24O(C2H4O)5	458.3	441.35
	6	C15H24O(C2H4O)6	502.4	485.30
	7	C15H24O(C2H4O)7	546.4	529.35
	8	C15H24O(C2H4O)8	590.4	573.35
	9	C15H24O(C2H4O)9	634.5	133.10
	10	C15H24O(C2H4O)10	678.5	133.00
	11	C15H24O(C2H4O)11	722.5	133.05
	12	C15H24O(C2H4O)12	766.5	133.00
	13	C15H24O(C2H4O)13	810.6	133.05
	14	C15H24O(C2H4O)14	854.6	133.00
	15	C15H24O(C2H4O)15	898.6	133.05
	16	C15H24O(C2H4O)16	942.6	132.80
	17	C15H24O(C2H4O)17	986.7	89.00
OPEO	3	C14H22O(C2H4O)3	356.3	226.70
	4	C14H22O(C2H4O)4	400.3	271.10
	5	C14H22O(C2H4O)5	444.3	427.30
	6	C14H22O(C2H4O)6	488.4	471.30
	7	C14H22O(C2H4O)7	532.4	515.40
	8	C14H22O(C2H4O)8	576.4	559.30
	9	C14H22O(C2H4O)9	620.4	133.05
	10	C14H22O(C2H4O)10	664.5	133.10
	11	C14H22O(C2H4O)11	708.5	133.05
	12	C14H22O(C2H4O)12	752.5	133.00
	13	C14H22O(C2H4O)13	796.5	133.05
	14	C14H22O(C2H4O)14	840.6	133.05
	15	C14H22O(C2H4O)15	884.6	89.05
	16	C14H22O(C2H4O)16	928.6	132.95

Table 2 Analytical Condition

LC conditions		
Column	:	Shim-pack™ FC ODS (75 mmL. × 2.0 mm I.D., 3 µm)
Mobile phase A	:	10 mM Ammonium Acetate – water (pH 3.6)
Mobile phase B	:	Acetonitrile
Time program	:	70 %B (0.0 mins to 1.0 mins) ➔ 95 %B (1.01 min to 5.00 min) ➔ 70 %B (5.01 min to 7.00 min)
Flow rate	:	0.25 mL/min
Column temp.	:	40 °C
Injection volume	:	5 µL
MS conditions (LCMS™-8045)		
Ionization	:	ESI (Positive)
Nebulizing gas flow	:	2.0 L/min
Drying gas flow	:	10.0 L/min
Heating gas flow	:	10.0 L/min
Interface temperature	:	300 °C
DL Temperature	:	250 °C
Block Temperature	:	400 °C

Results (APEO)

Fig. 2 shows each MRM Chromatogram of the NPEOs (n=3 to 16) and OPEOs (n=3 to 15). Fig. 3 shows each calibration curve. Each compound provides good linearity for the range of 1 to 100 ng/mL.

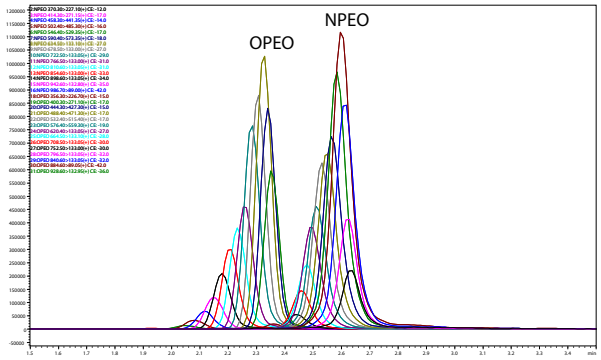

Fig. 2 MRM Chromatogram of the standards (50 ng/mL)

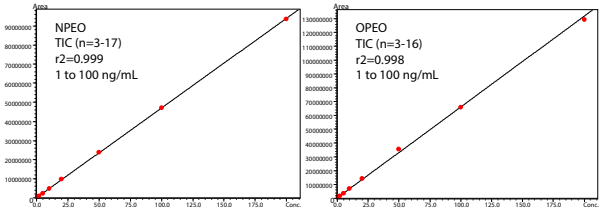

Fig. 3 Calibration curves of NPEO and OPEO

LC-MS/MS Analysis (AP)

When Alkylphenol (APs) are performed simultaneous analysis under the condition of APEOs analysis, the sensitivities of APs decrease. Therefore, the modification of the analytical conditions is needed.

Table 3 shows the MRM transitions. These deprotonated ions $[M-H]^-$ were selected as the precursor ions. Table 4 shows the analytical conditions for analysis for APs. As compared to the LC analysis conditions of the APEOs, all the conditions including column are similar except for mobile phase A. Hence, it can allow ease of analysis of APs by simply changing the mobile phase.

Table 3 MRM transition

Name	Abbreviation	Molecular formula	Precursor ion (*m/z*)	Product ion (*m/z*)
Nonylphenol	NP	C15H24O	219.2	133.10
4-n-Nonylphenol	4-n-NP	C15H24O	219.2	105.95
4-n-Octylphenol	4-n-OP	C14H22O	205.2	106.00
4-tert-Octylphenol	4-t-OP	C14H22O	205.2	133.05

Table 4 Analytical Condition

LC conditions		
Column	:	Shim-pack FC ODS (75 mmL. × 2.0 mm I.D., 3 µm)
Mobile phase A	:	Water
Mobile phase B	:	Acetonitrile
Time program	:	50 %B (0.0 mins to 0.50 mins) ➔ 95 %B (7.00 min to 9.00 min) ➔ 50 %B (9.01 min to 11.00 min)
Flow rate	:	0.4 mL / min
Column temp.	:	40 °C
Injection volume	:	10 µL
MS conditions (LCMS-8045)		
Ionization	:	ESI (Positive)
Nebulizing gas flow	:	2.0 L/min
Drying gas flow	:	10.0 L/min
Heating gas flow	:	10.0 L/min
Interface temperature	:	300 °C
DL Temperature	:	250 °C
Block Temperature	:	400 °C

Results (AP)

Fig. 4 shows each MRM chromatogram of APs and Fig. 5 shows the calibration curve for each compound. Each compound provides good linearity for the range of 1 to 100 ng/mL.

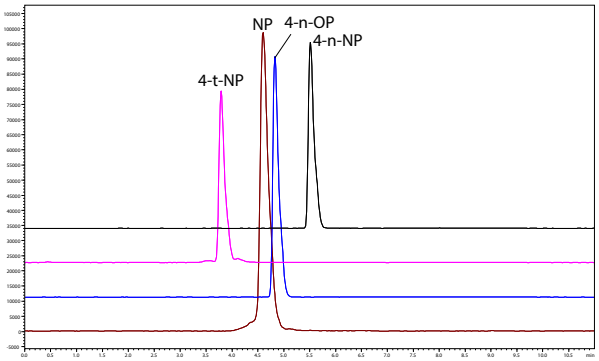

Fig. 4 MRM Chromatogram of the standards (20 ng/mL)

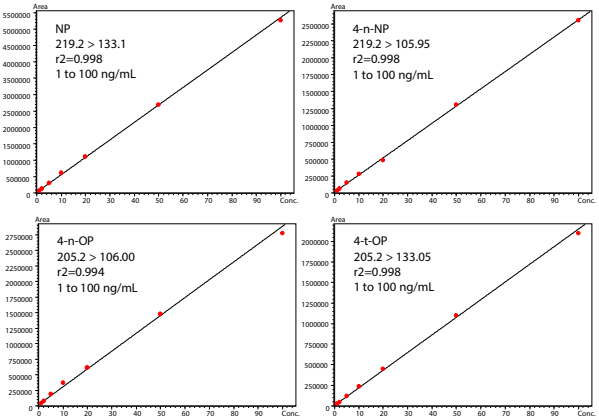

Fig. 5 Calibration curves of NP, 4-n-NP, 4-n-OP and 4-t-OP

Conclusion

The results of 2 APEOs and 4 APs analysis with LCMS-8045 provided good linearity and wide range of 1 to 100 ng/mL.

"LC/MS/MS Method Package for Restricted Chemicals in Textiles" provides several types of methods for not only APs and APEOs, but also PFCs, Azo dyes, and Aromatic Amines.

References
J. X. Lee, J. Xing, S. H. Chia and Z. Zhan, ASMS 2018, Poster Session WP 779.

First Edition: Feb. 2019

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