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Sensitive and selective quantitative analysis of Nonyl phenol ethoxylates (NPEOs) in textile samples by LC/MS/MS

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Introduction

Surfactants have one of the highest production rates of all organic chemicals. Alkylphenol polyethoxylates (APEOs) are widely used as non-ionic surfactants in industrial formulations in the textiles, tannery, paper and metal working industries. They include octylphenol polyethoxylates (OPEOs), nonylphenol polyethoxylates (NPEOs) and dinonylphenol polyethoxylates (DNPEOs).

Nonyl phenol ethoxylates are non-ionic surfactants which have emulsifying and dispersing actions. They are used in detergents, waterproofing agents, adhesives, and dyes used in textile industry. They degrade by losing ethoxy groups and convert to non-degradable products. These compounds can affect the hormonal system, and are very toxic to aquatic organisms.

A highly sensitive and specific LC/TQ method was developed for the quantitation of NPEOs in textile products. Simple sample preparation is followed. After extraction, sample extracts are diluted to reduce matrix effects. By restricting analysis time to 5 minutes and by following simple sample preparation procedure, this method offers analysis of 15 compounds in a single run.

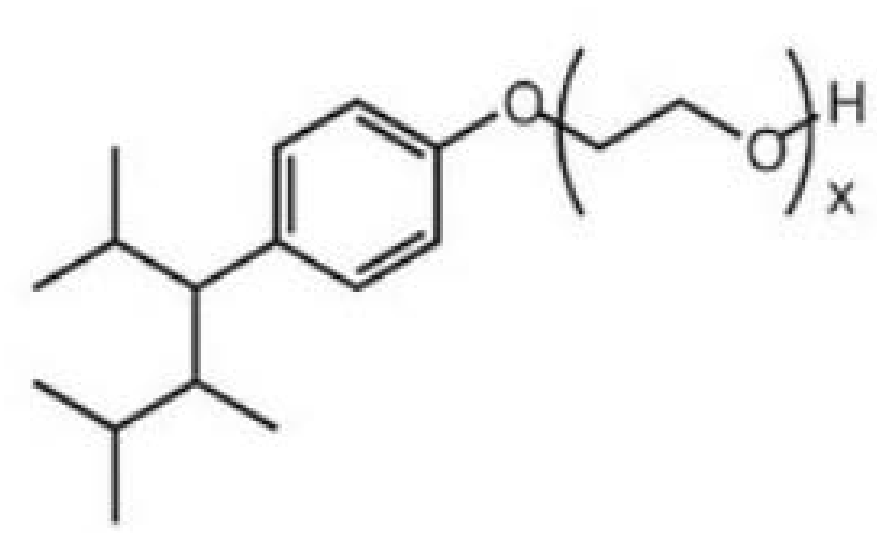

Figure 1: Representative structure of APEO

Chemical products containing nonylphenol ethoxylates concentrations equal to or greater than 0.1% are restricted within the EU for the specific uses, such as the processing of leather and textiles.

Experimental

Instrumentation.

A Agilent 6470 LC/MS/MS Triple Quadrupole mass spectrometer was operated in Multiple Reaction Monitoring (MRM) mode, employing an electrospray ionization source (ESI) in positive ionization mode for analysis of NPEOs.

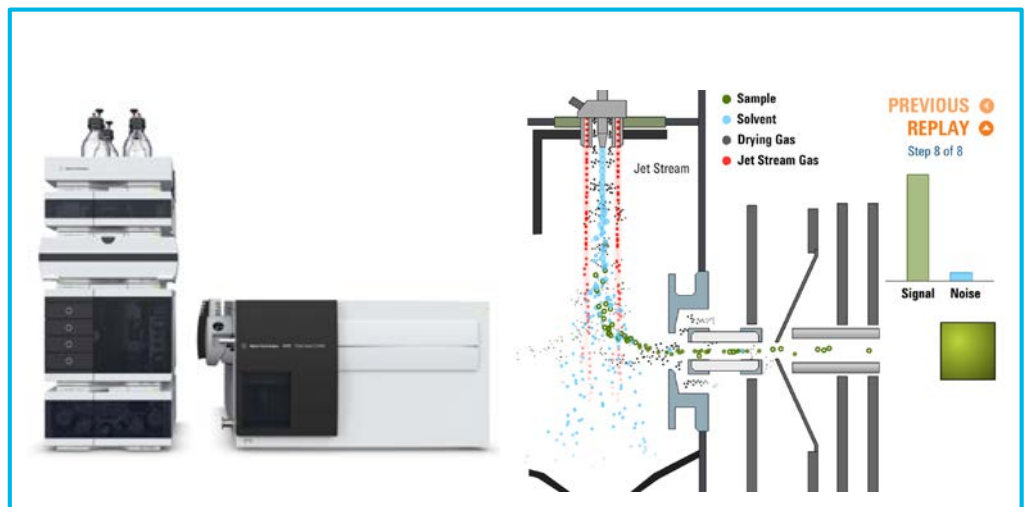

Figure 2: 6470 LC/TQ coupled to 1290 Infinity II UHPLC

LC separation was achieved using the reverse-phase C18 column with a gradient of 5 mM ammonium acetate in water (pH 3.6) and acetonitrile at a flowrate of 0.25 mL/min. Because of the sensitivity of 6470 QQQ system, the injection volume was set to 2 µL. Ammonium acetate mobile phases were chosen because of the preferential formation of the ammonium adducts $[M+NH_4]^+$ of the ethoxylate species.

Compound Name	ISTD?	Precursor Ion	MS1 Res	Product Ion	MS2 Res
NPEO 16	☐	942	Unit	89.1	Unit
NPEO 15	☐	898	Unit	133.1	Unit
NPEO 14	☐	854	Unit	89	Unit
NPEO 13	☐	810	Unit	89.1	Unit
NPEO 12	☐	766	Unit	89.1	Unit
NPEO 11	☐	722	Unit	89.1	Unit
NPEO 10	☐	678	Unit	89	Unit
NPEO 9	☐	634	Unit	89.1	Unit
NPEO 8	☐	590	Unit	573.4	Unit
NPEO 7	☐	546	Unit	529.3	Unit
NPEO 6	☐	502	Unit	485.3	Unit
NPEO 5	☐	458	Unit	441.3	Unit
NPEO 4	☐	414	Unit	271.1	Unit
NPEO 3	☐	370	Unit	227	Unit
NPEO 2	☐	326	Unit	183	Unit

Figure 3: MRM transitions used

QC data generated from the method developed

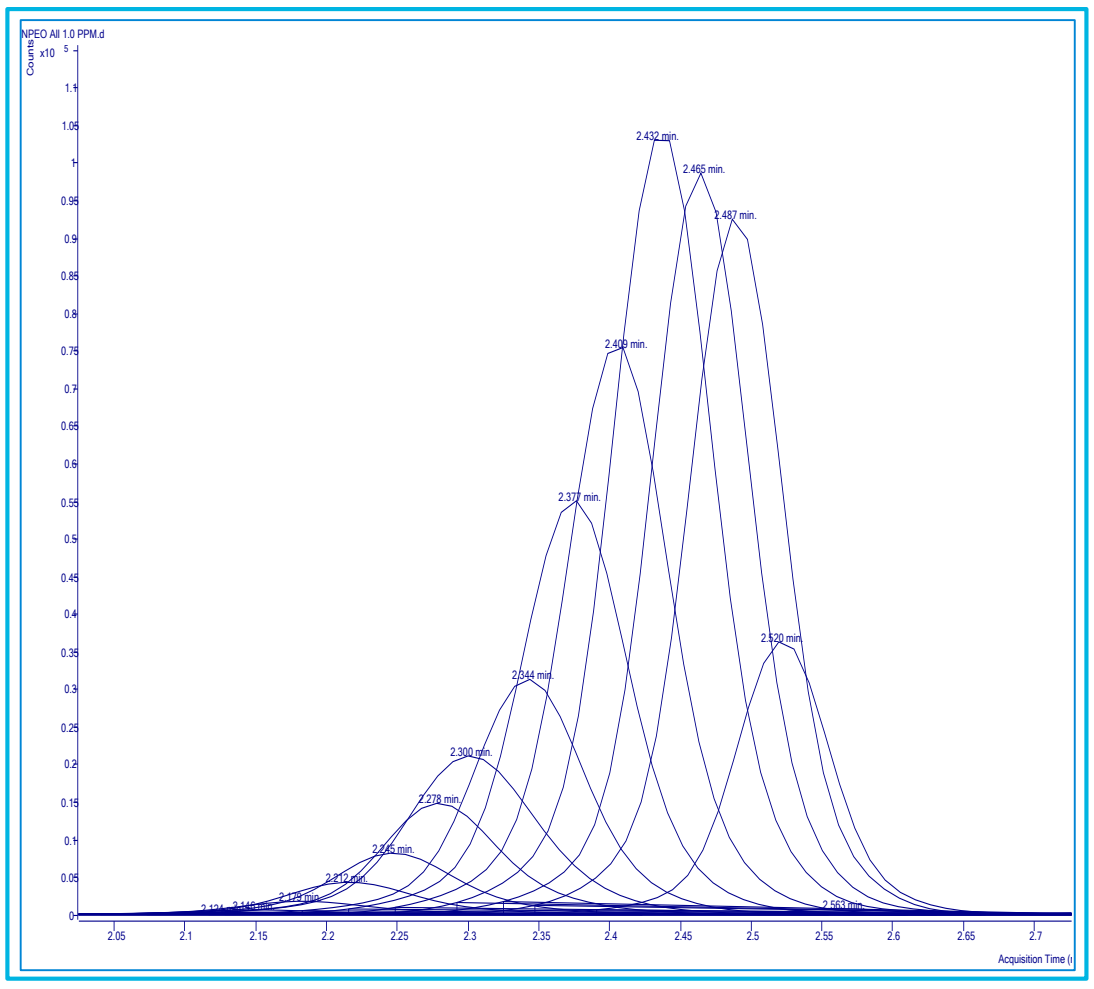

Figure 4: Composite Chromatogram of APEOs

Evaluation of Linearity

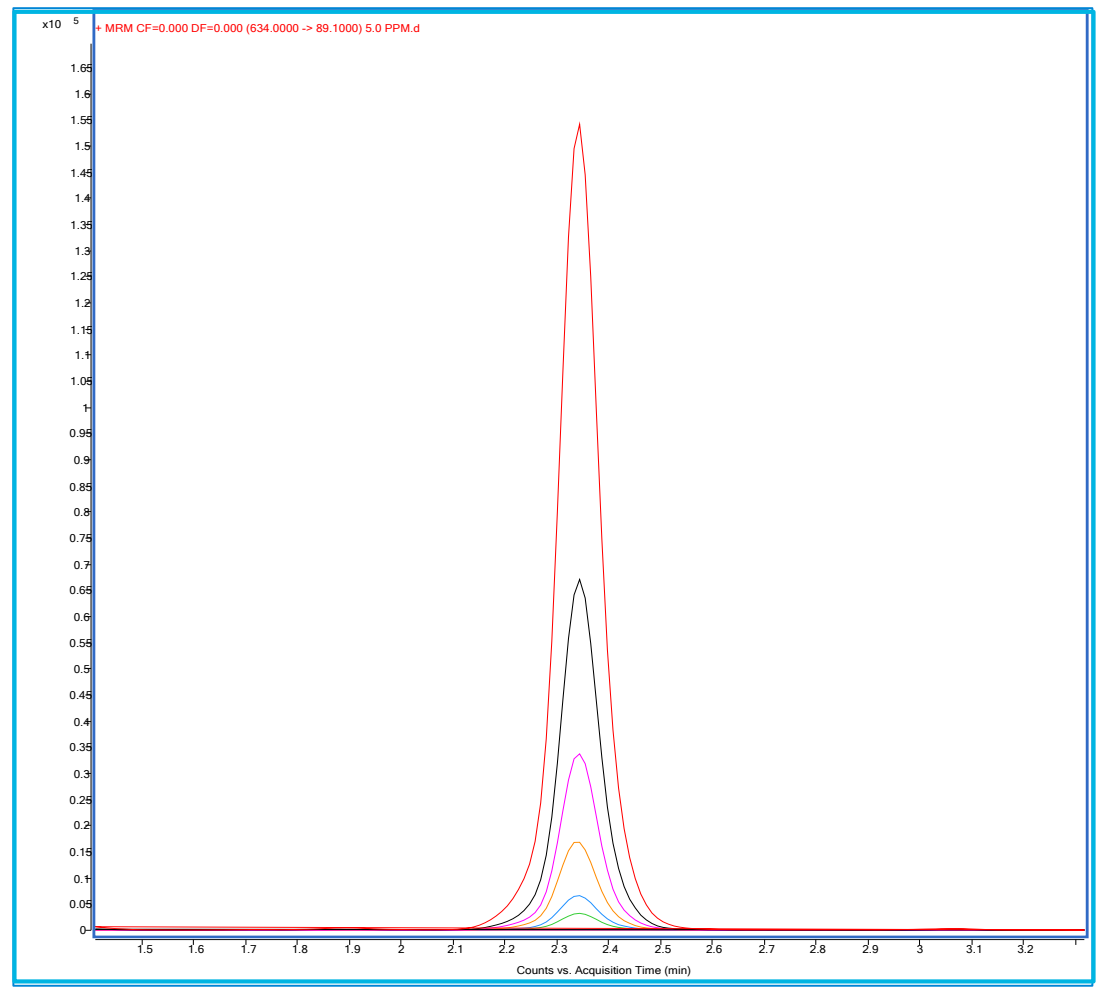

Figure 5: Overlaid Chromatograms of different concentration levels of NPEO 9 used to assess linearity

The MRM optimizer tool helped to adjust compound parameters such as, fragmentor voltage and collision energy. The source optimizer tool optimized all source parameters such as gas flow, source temperature and capillary voltage.

Aqueous linearity was made from set of standard dilutions from 0.1 mg/L to 5 mg/L. Limit of quantitation (LOQ) was found to be 0.1 ppm. However, the final calculation is made with a single calibration curve by plotting the average response of all analytes against concentration using the 'Compound Math' functionality in MassHunter Quant software. The calibration curve was linear for average response of all analytes against its concentration in the above range with minimum regression co-efficient (R^2): 0.9982 using linear regression and weighing factor of 1/X. Individual calibration curves were also made to quantify individual analytes in the sample. Accuracy of the standard levels used in the linearity curve were found to be between 80-120%.

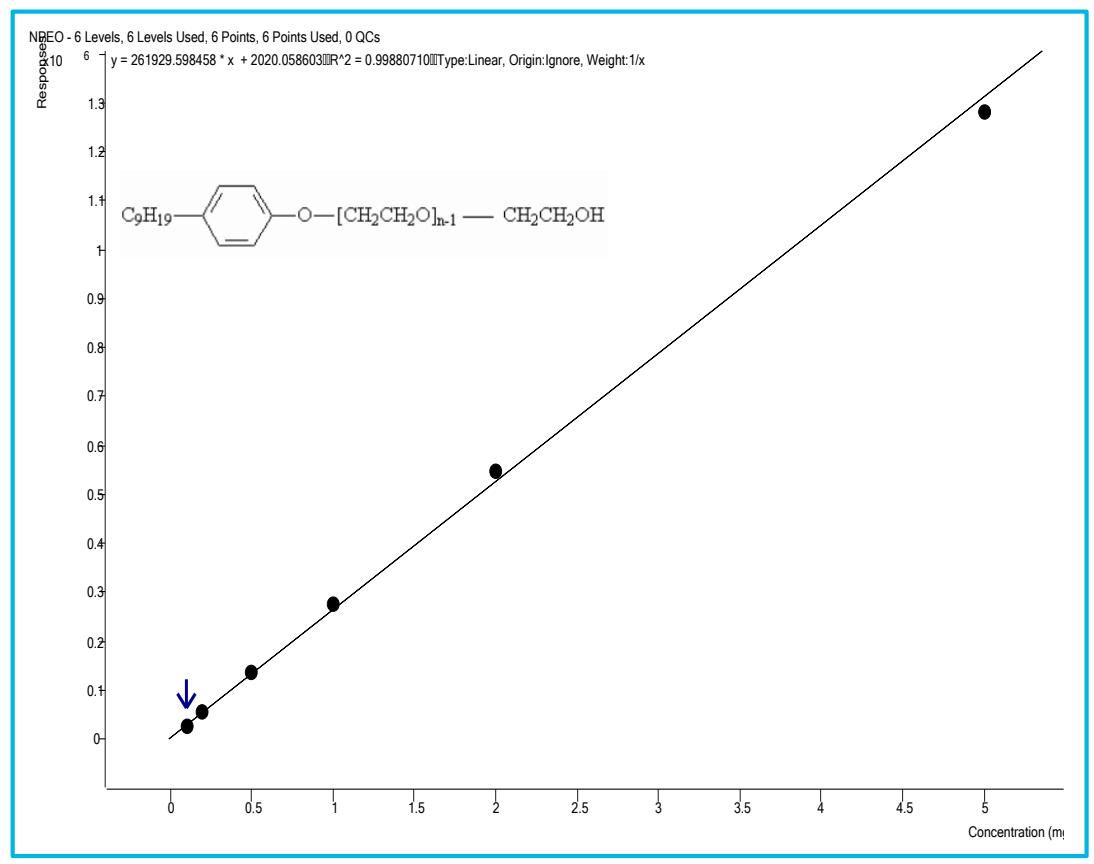

Figure 6: Calibration curve from 0.1 ppm to 5 ppm

Results and Discussion

Repeatability

Repeatability of the experiment was evaluated by analyzing 6 quality control samples spiked at 0.1 mg/L.

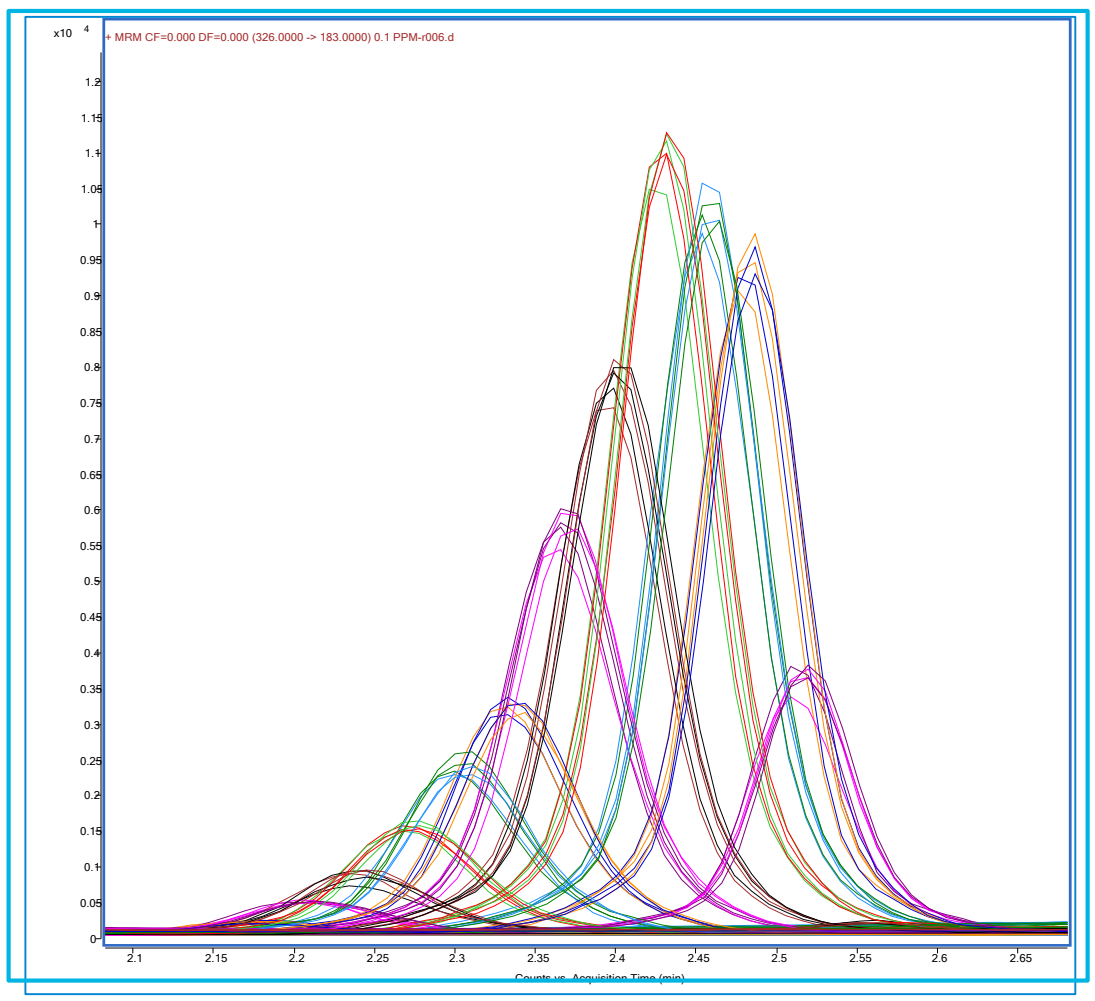

Figure 7: Overlaid extracted ion Chromatograms of 6 QC samples at LOQ level.

% Relative standard deviation for the obtained results found to be less than 5%.

Total NPEOs		
# Inj	RT	Area
1	2.33	26688.6
2	2.33	26650.5
3	2.33	26579.0
4	2.33	26789.1
5	2.33	26673.4
6	2.33	26455.0
Mean	2.3	26639.3
SD	0.0	112.9
%RSD	0.0	0.4

Figure 8: % CV data of the area response of 0.1 ppm

Sample analysis.

Simple sample preparation is followed. Approximately 1 g sample is accurately weighed to the nearest 10 mg. The sample is ultrasonicated with 10 mL of methanol at a temperature of 70 °C. After extraction, sample extracts are diluted to reduce matrix effects.

For the dyes sample, 10 mg of the sample is used. Spiked concentration of 0.1 mg/L extracted from matrix sample showed a recovery of above 90%. A few textile samples and two textile dyes were also analyzed to assess the suitability of the method. NPEO content in the analyzed samples were found to be lower than the lowest point in the calibration curve, and hence reported as 'not detected'

Characteristic MS chromatogram profile of the NPEOs help to screen these compounds in the Softline products such as textiles and leather.

Conclusions

- High-throughput MRM based method found to be sensitive and selective for screening and quantitation of NPEOs in textile samples.
- Method found to linear from 0.1 mg/L to 5 mg/L.
- Limit of quantitation is calculated as 0.1 ppm
- Recovery of NPOEOs at 0.1 mg/L showed recovery of 90%
- Presence of the characteristic MS chromatogram profile can be used to screen the presence or absence of NPEOs in the sample.

References

Textiles - Method for the detection and determination of alkyl phenol ethoxylates (APEO) -Part 1: Method using HPLC-MS; ISO 18254-1

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