APPLICATION NOTE

Gas Chromatography /
Mass Spectrometry

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Measuring Alkylphenols in Textiles with Gas Chromatography / Mass Spectrometry

Introduction

Alkylphenols are nonionic surfactants widely used in detergent formulations both for industrial and household use. Additional industrial uses include manufacture of plastics, paper and textiles. Nonylphenol, a specific alkylphenol, is classified as an endocrine disruptor. It is known to bioaccumulate, especially in aquatic animals. Nonylphenol is classified as a 'priority hazardous substance' in Directive 2000/60/EC and 2003/53/EC of the European Parliament.[1] The maximum concentration has been limited to 0.1% in many materials, including textiles – as a result of this regulation, it is necessary to accurately determine the level of nonylphenol in textiles.

This application note will present a method to measure octyl- and nonylphenols at low levels using gas chromatography/mass spectrometry (GC/MS). It will also describe a simple and reliable procedure for extraction and purification of octyl- and nonylphenols from textile samples.

In addition to method optimization and calibration, a variety of textiles are analyzed and the level of alkylphenols determined.

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Experimental

Sample Preparation

0.5 g of the textile was cut into small (10 mm x 2 mm) pieces with a razor blade and placed into the glass centrifuge vial. Then it was extracted supersonically for 30 minutes with 10 mL of toluene. 1 mL of the extract was placed into a 2-mL plastic centrifuge tube with a purification matrix. This mixture was vortexed for 2 minutes. Five combinations of purification materials, including $MgSO_4$ combined with one of the following were tested: silica gel, aluminium oxide, polyamide, florisil, and primary secondary amine (PSA). Following cleanup, the extract was centrifuged for 2 minutes at 5000 rpm.

The evaluation of a cleanup procedure was performed on a brown leather sample. It was found that PSA, aluminium oxide, and florisil absorbed alkylphenols and achieved low recoveries of the matrix spike (Table 1). The cleanup with silica gel and anhydrous $MgSO_4$ removed the dye completely from the sample and had better than 75% recovery of both octyl- and nonylphenol (Table 1). This combination of 50 mg silica gel and 100 mg $MgSO_4$ was used for the remaining experiments.

Instrument Conditions

The alkylphenols in the extracted textile samples were identified and amount determined by GC/MS. The system used was a PerkinElmer® Clarus® 680 T GC/MS. Table 2 shows the complete instrumental-setup parameters for the GC/MS system.

***Table 1.* Matrix-Spike Recovery Using Different Purification Chemicals.**

Sample	Purification Chemicals	Color of the Extract	Compounds	Matrix-Spike Recovery (%)
Brown Leather	50 mg of silica gel and 100 mg of anhydrous $MgSO_4$	No color	4-tert-octylphenols Nonylphenols	78 92
	50 mg of aluminiun oxide and 100 mg of anhydrous $MgSO_4$	No color	4-tert-octylphenols Nonylphenols	1 20
	50 mg of polyamide and 100 mg of anhydrous $MgSO_4$	Pale	4-tert-octylphenols Nonylphenols	75 92
	50 mg of florisil and 100 mg of anhydrous $MgSO_4$	Pale	4-tert-octylphenols Nonylphenols	0 15
	50 mg of PSA and 100 mg of anhydrous $MgSO_4$	Brown	4-tert-octylphenols Nonylphenols	44 51

***Table 2.* Instrumental Parameters.**

Gas Chromatograph	PerkinElmer Clarus 680 GC
Inlet type	PSSI
Inlet temperature	280 °C
Oven program initial temperature	50 °C
Hold time 1	2 min
Ramp 1	25 °C/min to 300 °C
Hold time 2	3 min
Vacuum compensation	On
Column	PerkinElmer – Elite™-5ms 30 m x 0.25 mm x 0.25 µm
Carrier gas	Helium
Carrier flow	1 mL/min (Splitless 1.5 min)
Mass Spectrometer	**PerkinElmer Clarus 600 T MS**
Mass range	*m/z* 50-300
Solvent delay time	6 min
Scan time	0.20 sec
InterScan delay time	0.05 sec
Transfer-line temperature	280 °C
Source temperature	240 °C
Multiplier	400 V

SIM Mode

To increase the sensitivity of this analysis, a selected ion monitoring (SIM) method was created. Each compound had one quantifier ion and two qualifier ions, with a dwell time of 0.04 seconds each – the ions monitored for each compound are listed in Table 3. Nonylphenol is a multi-component mix that elutes as an unresolved group of peaks – as a result, the area of all isomers was integrated as a single compound.

Calibration Standards Preparation

A 10 µg/mL standard stock solution was prepared by diluting 0.1 mL of a 1000 µg/mL standard to 10 mL with toluene. From this stock solution, a working calibration standard set at 0.1, 0.2, 0.5, 1, 2, 4, 6 µg/mL was prepared. The calibration range extends well below the EU regulatory limit of 50 µg/mL (0.5 g sample to 10 mL solvent extraction), allowing laboratories to collect useful information about nonylphenol in samples, even if this amount is well below the regulatory limit.

Results

The calibration of the GC/MS system included seven standard levels. The response of the calibration was linear for both octylphenol and nonyphenol (Table 4 – Page 4). The precision of the GC/MS system was tested with five injections of a 0.2 ppm standard – for both analytes, the relative standard deviation of this analysis was less than 3%.

Following the calibration of the system, four textile samples were analyzed: dark cloth, red cloth, green towel and brown leather. The alkylphenol concentration was quantified in each (Table 4). Table 4 also shows that 1 µg/mL of alkylphenols was spiked into the samples and their matrix spike and matrix-spike duplicate recoveries were calculated. An example chromatogram from the analysis of the green towel sample is pictured in Figure 1.

Table 3. **Calibration Table for Alkylphenols.**

Name	Retention Time	Quantifier Ion	Qualifier Ion 1	Qualifier Ion 2	%RSD	r^2	MDL (µg/mL)
4-tert-octylphenols	7.63	135	136	107	2.8	0.9981	0.023
Nonylphenols	9.26 to 9.55	135	121	107	1.7	0.9994	0.015

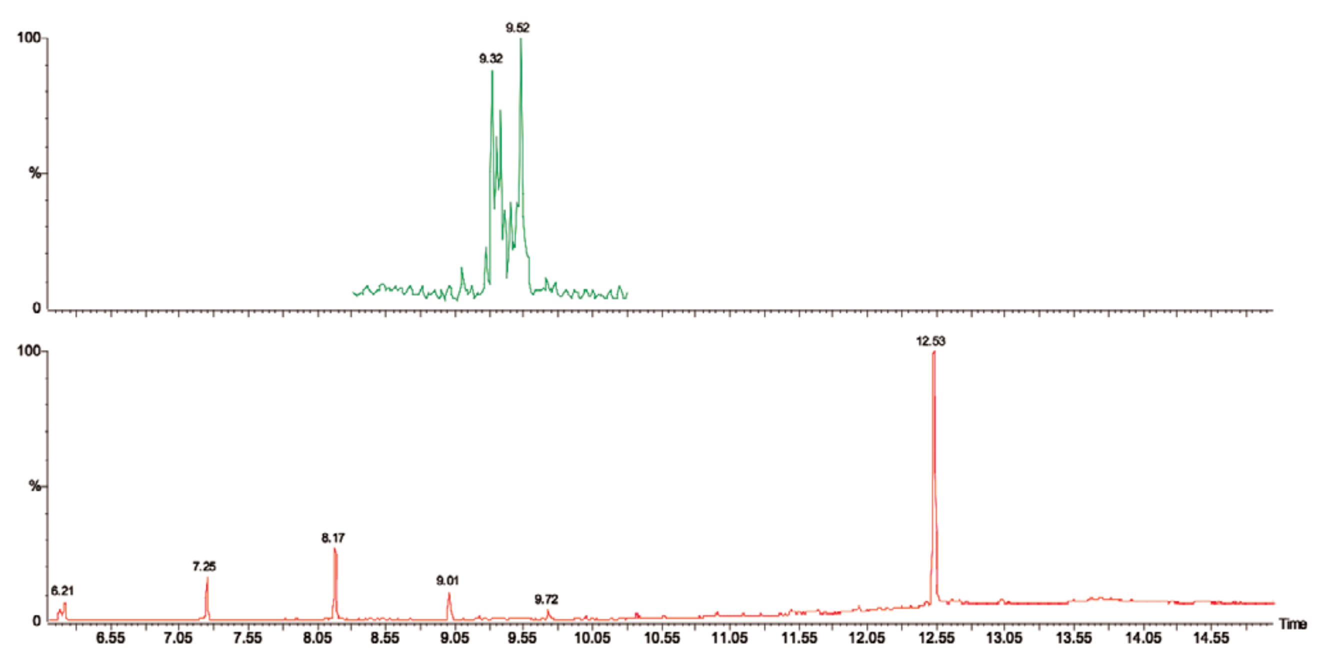

Figure 1. Total ion chromatogram (TIC – bottom) and selected ion monitoring chromatogram (SIM – top) of 0.05 g of green-towel sample.

Table 4. **Sample Analysis and Matrix-Spike Recovery.**

Sample	Compounds	Concentration (µg/mL)	Matrix-Spike Recovery (%)	Matrix-Spike Duplicate Recovery (%)
Dark Cloth	4-tert-octylphenols	0	105	107
	Nonylphenols	0.11	99	107
Red Cloth	4-tert-octylphenols	0	115	101
	Nonylphenols	0.16	106	92
Green Towel	4-tert-octylphenols	0	98	105
	Nonylphenols	1.44	96	93
Brown Leather	4-tert-octylphenols	0	86	87
	Nonylphenols	0.18	80	81

Discussion

The European guidelines limit the concentration of nonylphenols in textiles to 0.1%. This method is able to quantitate nonylphenols down to a level 100 times lower than the regulatory limit. This will provide laboratories sufficient capability to measure with confidence the amount of nonylphenols in a sample that meets the regulatory guidance. This is very useful because it will allow the manufacturers of textiles to monitor their process and have advanced notice of changes in the levels of nonylphenols that may eventually exceed the regulations. If the sensitivity requirements of this analysis are at the regulatory limit – 50 µg/mL – rather than 10 times lower, 1 mL of sample extract can be diluted to 10 mL. This will make the effective regulatory limit – 5 µg/mL – within the calibration range presented here. This dilution approach will further reduce co-extracted material introduced by each injection, keeping the system cleaner over the long term.

Conclusion

This application note demonstrates a precise and accurate method to quantitate the amount of alkylphenols in textile samples. The Clarus 680 GC/MS system has demonstrated to be linear across the calibration range of 0.1 to 6 ppm, meeting and exceeding the analytical requirements for Directive 2003/53/EC of the European Parliament and of the Council of 18 June 2003.

In addition to calibration, a fast and reliable extraction technique with sample cleanup was developed and applied to textile samples. The precision of the extraction was verified by the analysis of textile samples spiked with known levels of nonylphenols.

Acknowledgements

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References

1. Directive 2003/53/EC of the European Parliament and of the Council of 18 June 2003.

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