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Meet Stringent Detection Requirements for All 13 4-Nonylphenol Isomers in Water using GCMS-SIM and a High Efficiency Ion Source

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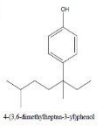
Introduction

Nonylphenol (NP) compounds are classified as endocrine-disruptors and listed as priority hazardous substances under the Water Framework Directive due to their potential impact upon the aquatic environment. NPs are used to manufacture nonylphenol ethoxylates (NPEs), which are nonionic surfactants found in household and industrial products such as textiles, paints and coatings, and those related to personal care and agriculture. NPEs degrade in the environment to NPs, which have been detected in surface and ground water, wastewater effluent, and food. Estrogenic effects can occur at concentrations as low as 10 µg/L and are isomer-dependent.

We describe a method for complete separation and detection of 13 isomers of 4-NP below 0.02 µg/L (or 20 ng/mL after final extraction) as regulated by the Japan Ministry of the Environment (2012).

The superior sensitivity of the HES source affords that the legislated detection limits of 20 ng/mL at injection (20 ng/L in water), are exceeded by more than 10 fold for all isomers but NP12, which is exceeded by 7 fold. The improved detection limits implies that **the sample size could be decreased *at least by* 5-fold** (200 ml instead of 1L) which also leads to lower transport, handling, solvent and waste disposal costs.

Structure example of 4-nonylphenol:
4-(3,6-dimethylheptan-3-yl)phenol



Experimental

Platform	**7890B GC and 5977B MS with HES**
Oven	**50°C (1.0min); 8°C/min; 280°C (5min)**
Column	**HP-5MSUI, 30m x 0.25mm i.d.x 0.25µm (p/n 19091S-433UI)**
Injection mode	**pulsed splitless (30 psi, 1min)**
SSL Inlet temperature	**250°C**
Injection volume	**1 µL**
Inlet liner	**Ultra Inert, Splitless, Single taper, Glass Wool (p/n 5190-2293)**
Column flow	**He 1.2mL/min (constant flow mode) (holdup time 1.2524 min)**
Run time	**20 min**
Acquisition Mode	**SIM**
Tune File	**HES tune**
Ion source	**350°C (optimized)**
Quad temperature	**150°C**
Transfer line	**280°C**
Solvent Delay	**10 min**
Gain Factor	**15 (optimized using NP11, *m/z* 135.0)**
Surrogate	**13C-labled 4-(3,6-dimethyl-3-heptyl) phenol**
ISTD	**4-n-nonylphenol-2,3,5,6 - d4**

Experimental, cont.

SIM Table

Group #	Time	Gain	Cycle /sec	Ions								
1	10.0	15	5	107	113	121	135	149	155	163	191	220
2	19.2	15	5	111	224							

High Efficiency Ion Source (HES): Generates > 10x ion intensity compared to traditional EI ion sources

High system sensitivity is required to detect 0.02 µg/L 4-NPs in water, which are "low responders" in EI mode

A high degree of instrument sensitivity is required to achieve the detection limit for 4-NPs in water of 0.02 µg/L (20 ng/mL, concentrated 1000x for injection), which was set by the Japan Ministry of the Environment in 2012. Higher sensitivity benefits laboratories in that less sample is required. In addition, it is necessary to detect the lowest responding isomer, NP12, which has 30-fold lower peak height than isomer NP11 (the tallest isomer peak).

A high level standard was run in full scan in order to optimize the GC separation of all 13 4-NP isomers, which elute from 18.1 to 19.1 minutes. Extracted ion chromatograms (EIC) for *m/z* 107, 121, 135, 149, 163, 191, and 220 were studied for optimization as they are indicative of the analytes. This optimization of mass spectral parameters included: detector gain, which was set to 15 (to achieve the best linear working range for NP11) and ion source temperature (350°C for greater response and analytical robustness).

Repeatability %RSD and Instrument Detection Limit

Repeatability RSD% (n=10) at 10 ng/mL and 100 ng/mL (1-2 µL injection)

Repeatability for 10 injections (%RSD, n=10) of 10 ng/mL and 100 ng/mL spiked 4-NP standards (concentration in vial) yielded acceptable results even at the lower concentration. For isomers NP1-NP13, area %RSDs uncorrected for the ISTD at 100 ng/mL ranged from 1.5 to 4.3. Applying the ISTD and quantitating the isomers concentration gave %RSDs ranging from 1.2 to 4.0 ng/mL. At 10 ng/mL, and using a 2 µL rather than a 1 µL injection volume, %RSDs in the concentrations range from 2.2 to 9.8, with the highest uncertainty resulting from the low responding NP12 isomer.

Cmpd.	100 ng/mL (1 µL)		10 ng/mL (2 µL)
	Area (%RSD)	Conc. (%RSD) (corrected to ISTD)	Conc. (%RSD) (corrected to ISTD)
NP1	1.5	1.2	5.1
NP2	2.2	1.8	7.3
NP3	2.1	1.8	3.9
NP4	3.1	3.1	4.7
NP5	3.4	3.0	2.2
NP6	3.9	4.0	4.1
NP7	2.1	1.9	3.9
NP8	3.2	2.1	3.5
NP9	2.2	2.0	3.8
NP10	2.5	2.5	5.7
NP11	4.1	3.6	3.9
NP12	4.3	3.5	9.8
NP13	1.9	1.2	5.1
Min	**1.5**	**1.2**	**2.2**
Max	**4.3**	**4.0**	**9.8**

Instrument Detection Limit Calculations for the 10 replicate injections of 2 µL at the 10 ng/mL concentration:

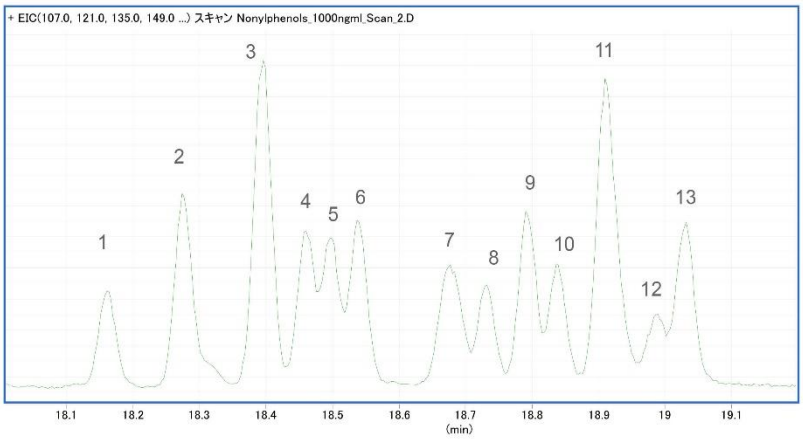
- IDL = t0.99 · SD = t0.99 · (%RSD / 100) · 10 ng/mL
- t0.99 = 2.821 for 9 degrees of freedom

*NP12 (highlighted) is the isomer with lowest response

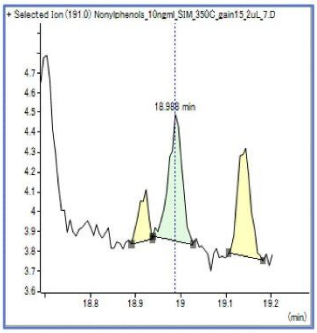
Cmpd.	IDL (ng/mL)
NP1	1.4
NP2	2.1
NP3	1.1
NP4	1.3
NP5	0.6
NP6	1.2
NP7	1.1
NP8	1.2
NP9	1.1
NP10	1.0
NP11	1.1
NP12	1.6
NP13	1.1

Complete isomer separation with excellent sensitivity

Scan data (1000ng/mL): EIC (*m/z* 107,121,135,149,163,191,220)



EIC for lowest responding isomer, NP12 SIM *m/z* 191.0, 10ng/mL, 2µL injection



Conclusions

The legislated detection limits of 20 ng/mL at injection (20 ng/L water), are exceeded by more than 10 fold for 12 of the 13 isomers. NP12 is exceeded by 7 fold. This suggests that ***at least*** a 5-fold decrease in sample size is possible: instead of a liter of sample, only 200 mL of water need be extracted and concentrated to 1 mL. This would be a considerable savings in transport, handling, solvent and waste disposal costs. Of course, combining the HES sensitivity with large volume injection would produce further improvements.

This work demonstrates the rapid and sensitive detection of these difficult compounds and suggests upstream, bench-chemistry improvements to lower laboratory costs. The HES makes this a generally applicable approach for rethinking many existing similar analyses.

Reference

Ministry of the Environment Government of Japan (2012) *https://www.env.go.jp/en*