Automated SPE Disk Extraction Method for the Analysis of Nonyl Phenol and Bisphenol A in Water Samples

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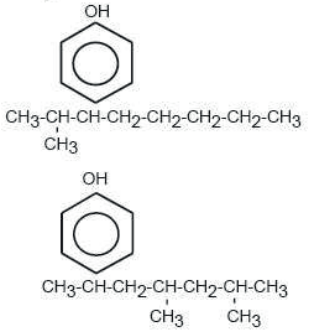
Introduction

Nonyl phenol and Bisphenol A are both of great environmental concern as they have been classified as endocrine disruptors. Endocrine disruptors are those compounds that mimic estrogen and thus could induce hormonal responses. Nonyl phenol has been banned in the European Union as a hazard to both human and environmental safety because of this concern.

NONYL PHENOL

Nonyl phenol is an organic compound formed during the alkylation process of phenols. Because of their man-made origins, nonyl phenol is classified as xenobiotic. Nonyl phenol is not a single chemical compound, but rather a term used to refer to a family of compounds, all of which have a central aromatic (or benzene) ring and a nine carbon side chain. See Figure 1 for the chemical structure.

Figure 1: Nonyl Phenol Chemical Structure



several common isomers of p-nonyl phenol (also known as 4-nonyl phenol)

One use of nonyl phenol is as a surfactant, which reduces the surface tension of water forming a bridge between two compounds that normally do not mix. This is one reason nonyl phenol is commonly found in water samples. It is also used in pesticide products as "inert" ingredients, with the purpose of increasing the amount of spray solution that remains on leaf surfaces and in general to make the pesticide product more potent.

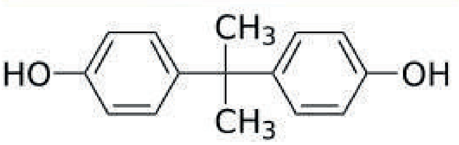
The Horizon Technology SPE-DEX® 4790 Automated Extraction System, Envision® Platform Controller, and DryVap® Automated Drying and Concentrating System.

BISPHENOL A

Bisphenyl A was first synthesized in 1891 and evidence of its estrogenicity came from experiments in the 1930s. However, the use of bisphenyl A was shelved for this role as an estrogen mimic when diethylstilbestrol was invented. Both nonyl phenol and bisphenyl A are now deeply imbedded in consumer products and the concern of these compounds to mimic hormonal responses has raised the need for adequate testing of these compounds. This application note will discuss the sample preparation method used to analyze for these compounds in drinking and waste water.

Currently, bisphenyl A has many uses. It is used in the synthesis of polyesters, polysulfones, and polyether ketones, as an antioxidant in some plasticizers, and as a polymerization inhibitor in PVC. It is also a key monomer in production of polycarbonate plastic, which is used to make a variety of consumer products including baby bottles, water bottles, sports equipment, medical devices, CD's, and household electronics. See Figure 2 for the chemical structure and IUPAC name.

Figure 2: Bisphenol A Chemical Structure



Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extractor System
  - Envision® Platform Controller
  - Atlantic™ DVB SPE disk (47 mm)
  - DryDisk® Separation Membrane
  - DryVap® Automated Concentrator System
- Agilent 5890/5971 GC/MS
- Column: 30M x 0.25 mm x 0.5um HP-5ms
- Injection Liner: Splitless, double gooseneck

Method Summary

1) 1000 mL water samples were spiked to a concentration of 5 ug/L.
2) The sample was placed onto the SPE-DEX® 4790 Automated Extractor System and the system was started using the method in Table 1.
3) The SPE-DEX® 4790 extracted 1000 mL samples in 25 minutes with a final extract volume of 25 mL.
4) The extract was poured into the DryDisk® Separation Membrane reservoir on the DryVap® Concentrator System to remove the residual water in the organic solvent extract.
5) The DryVap® Concentrator System concentrated the solvent extract to a final volume of 1.0 mL.
6) The sample was analyzed by GC/MS using Selected Ion Monitoring (SIM) mode and the conditions and methods listed in Tables 2, 3, and 4.

Table 1: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	$MeCl_2$	1:00 Min	30 s
Prewet 2	Acetone	1:00 Min	30 s
Prewet 3	DI water	1:00 Min	30 s
Prewet 4	DI water	0 sec	0 sec
Process Sample			
Air Dry 30 sec			
Rinse 1	Acetone	3:00 Min	10 s
Rinse 2	$MeCl_2$	3:00 Min	10 s
Rinse 3	$MeCl_2$	1:00 Min	10 s
Rinse 4	$MeCl_2$	1:00 Min	10 s
Rinse 5	$MeCl_2$	1:00 Min	30 s

Table 2: GC/MS Conditions

Solvent Delay	3.7 min
Inj. Vol.	2 uL
Inj. Temp.	280 C
Transfer Line Temp.	300 C
Ions Monitored	107, 213, 244

Table 3: GC/MS Pressure Program

Initial p.	12 psi (const. flow)	
Initial Time	0 min	
Level 1	Rate	99 psi/min
	Final p.	50 psi
	Hold	0.13 min
Level 2	Rate	99 psi/min
	Final p.	12 psi
	Hold	0.0 min
Total Time	0.90 min	
Remainder of run at const p.		

Table 4: GC/MS Temperature Program

Initial T.	60 C	
Initial Time	1.0 min	
Level 1	Rate	20 C/min
	Final T.	270 C
	Hold	0.0 min
Level 2	Rate	6 C/min
	Final T.	300 C
	Hold	0.0 min

Results

A standard was prepared in acetone at a concentration of 100 ug/mL. Of this standard, 50 uL was added to one liter of sample to give a concentration of 5 ug/L. A volume of internal standard solution of 10 uL at a concentration of 500 ug/mL (terphenyl-d14) was also added to the sample. The sample bottle was capped and mixed for 1 minute. The sample was loaded onto the SPE-DEX® 4790 extractor and the system was started. For this work, 47 mm Atlantic™ disks containing 0.35 g of divinyl benzene (DVB) were used. All steps of the extraction process are automated.

On average, it took about 15 minutes to process (filter) the one liter sample. The total run time, including all prewet, air dry, and solvent elution times was roughly 25 minutes per sample. If dirty waste water samples are to be processed, the Atlantic™ glass fiber prefilter should be used. The prefilter is simply placed on top of the SPE disk and the 4790 extractor is run as normal.

Upon completion, the collection vessel containing approximately 25 mL of solvent was removed. The solvent extract was poured into the DryDisk® separation membrane holder and the DryVap® was started.
Vacuum was used to pull the solvent through the DryDisk® membrane, while the membrane retains the residual water. The retention of the residual water is beneficial as the residual water can be manually washed with organic solvent, typically methylene chloride, to ensure that all

organics are removed from the holder and the transfer line.

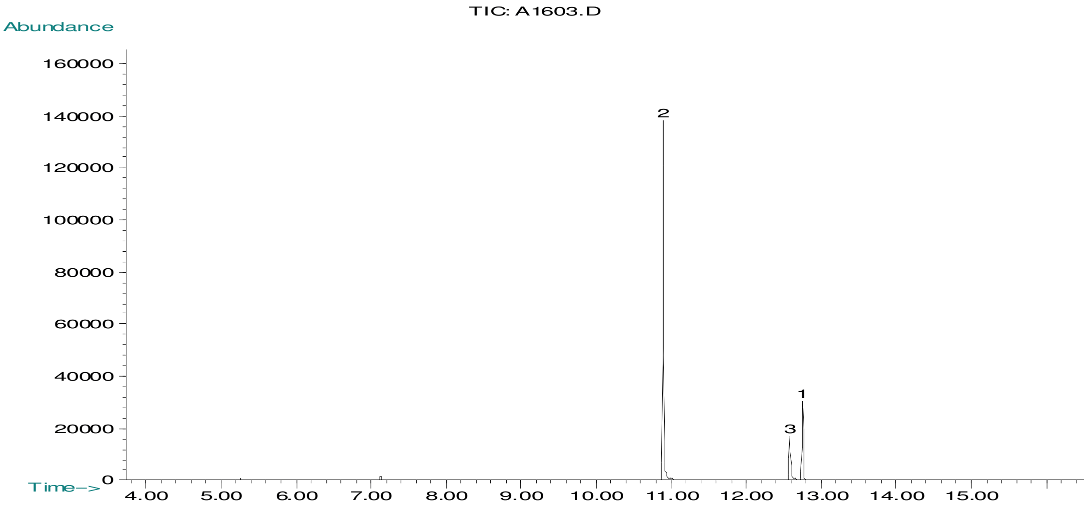
Once the DryVap® was finished concentrating the extract, which took on average 25 minutes, the final volume was brought up to 1.0 mL and the extract was transferred into a GC vial and run on the GC/MS.

The recoveries shown in Table 5 were obtained from three runs, using the technique described. The data indicates that these compounds can be adequately and quickly extracted from water samples using SPE disk technology. Figure 3 shows a typical chromatogram for these compounds.

Table 5: Recoveries

Runs	Nonyl Phenol (%)	Bisphenol A (%)
1	117.2	109.8
2	100.0	104.8
3	117.6	120.8
Ave	111.6	111.8
SD	10	8
%RSD	9.0	7.3

Figure 3: Typical Chromatogram
1 Terphenyl-d14
2. Nonyl phenol
3. Bisphenyl A



Conclusions

This study shows that the SPE-DEX® 4790 Automated Extractor system, along with the Atlantic™ DVB disk, the DryDisk® separation membrane, and the DryVap® Concentrator System can be successfully used to analyze for Nonyl Phenol and Bisphenyl A in water samples. This sample preparation process is fully automated, requiring minimal human intervention, and allowing for reductions in sample processing costs.

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