New Stationary Phases for Solid-Phase Extraction

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Overview

Purpose: To develop five new polymer-based stationary phases for large volume SPE, which include a hydrophilic reversed phase (HRPHS), strong anion exchange (SAX), strong cation exchange (SCX), weak anion exchange (WAX), and weak cation exchange (WCX).

Methods: Large volume samples are pre-concentrated on a Thermo Scientific™ Dionex™ SolEx™ SPE cartridge, using Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction instrument followed by HPLC analysis. Recovery percentages are calculated with the separation and quantification of analytes.

Results: Recoveries are all greater than 95% for all the analytes. Successful recovery of analytes from matrices are shown here by automated SPE without laborious sample preparation.

Introduction

Five new polymeric stationary phases were developed for solid phase extraction (SPE) sample preparation of large sample volumes. The phase chemistries include a hydrophilic reversed phase material as well as mixed mode, strong and weak, anion and cation exchange. Base particles are derivatized with functional groups to achieve a useful balance between reversed phase and ion exchange capacities. The hydrophilic reversed phase material bears specific functionality to retain polyphenolic and azo-containing species through a charge transfer mechanism and H-bonding. This allows the retention of such species as humic acids along with the ability to elute other organic species using conventional reversed phase techniques. These new resins are formatted to be compatible with sample volumes larger than 20 mL in automated SPE instrumentation.

TABLE 1. Recommended applications of the five stationary phases.

Cartridge Type	Functional Group	Example Applications
HRPHS	Divinylbenzene (DVB)/ polyvinylpyrrolidone (PVP, high)	General reversed phase, polyphenolics, azo compounds
SAX	DVB-sulfonate	Ionizable (weak) anions, carboxylic acids
SCX	DVB-quaternary ammonium	Ionizable (weak) cations, amines
WAX	DVB-amine	Permanent anions, inorganic and organic, sulfonates, sulfates
WCX	DVB-carboxylate	Permanent cations, inorganic and organic, quaternary ammonium

Two applications will be shown. The targets include triclosan, a popular but very hydrophobic bacteriocide, and 14 explosives regulated in U.S. EPA Method 8330. The matrices include tap water and soap water.

Methods

Sample Preparation

TABLE 2. Sample preparation conditions.

Sample Prep Conditions	Method A: Analysis of Explosives	Method B: Analysis of Triclosan
Sample	100 mL, 2 ppb 14 explosive standard in tap water	100 mL 1/3000 liquid hand soap containing triclosan in Sunnyvale tap water
SPE barrel	6 mL cartridge, 500 mg HRPHS	6 mL cartridge, 200 mg HRPHS
Loading flow rate	5 mL/min	10 mL/min
Elution solvent	5 mL of acetronitrile	5 mL of methanol

Sample Preparation Instrument: Dionex AutoTrace 280 Solid-Phase Extraction instrument

Liquid Chromatography:

Thermo Scientific™ Dionex™ UltiMate™ 3000 HPLC system including:

- DGP 3600M Dual-Gradient Micro Pump
- SRD 3600 Integrated Solvent and Degasser Rack, 6 Channels
- TCC-3000 Thermostatted Column Compartment
- WPS-3000 Wellplate Sampler equipped with 5 µL loop
- PDA-3000 Photodiode Array Detector Data Analysis

Software: Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System, 6.80 SP4 and higher

FIGURE 1. Dionex AutoTrace 280 Solid-Phase Extraction instrument; a Dionex SolEx SPE cartridge and the fluid connections are shown.

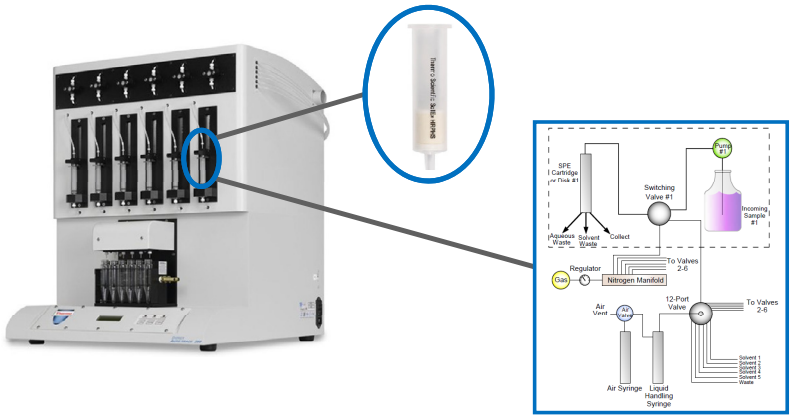


TABLE 3. Liquid chromatography conditions for Methods A and B.

Analytical Conditions	Method A: Analysis of Explosives	Method B: Analysis of Triclosan
Column	Thermo Scientific™ Acclaim™ Explosives columns E2, 3µm, 3.0×250 mm	Acclaim columns 120, 2.1×50mm
Flow rate	0.3 mL/min	0.21 mL/min
Eluent	48/52 v/v MeOH/H_2O	65/35 v/v acetonitrile/H_2O
Gradient	Isocratic	Isocratic
Temperature	25 °C	25 °C
Detection	UV 254 nm	UV 254 nm

Results

Method A: Automated solid-phase extraction of 14 explosives in tap water based on U.S. EPA Method 8330 using hydrophilic reversed-phase cartridge followed by HPLC with UV detection

Land and groundwater have been found to be laden with explosive residues such as 2,4,6-trinitrotoluene (TNT) and associated nitroamine impurities. Target compounds include nitroaromatics, nitramines, and nitrate esters, which present health concerns due to their carcinogenic, mutagenic, and toxic effects. The U.S. EPA Method 8330, first introduced in November 1990, is the most common method for the analysis of explosives. Used here are the Dionex AutoTrace 280 Solid-Phase Extraction instrument and the Dionex SolEx SPE HRPHS cartridge to concentrate the explosives, followed by HPLC analysis using Acclaim Explosives E2 column.

The HRPHS SPE phase was packed into a 6mL barrel with a bed weight of 500 mg. In the SPE steps, HRPHS sorbent is preconditioned by methanol followed by water. After drying under nitrogen for 5 min, 100 mL of sample was loaded at a flow rate of 10 mL/min. Hydrophilic matrix was removed by water rinse of the cartridge. The concentrated explosives were eluted in the final step by an organic solvent such as acetonitrile.

The separation of 14 explosives cyclotetramethylenetetraanitramine (HMX), cyclotrimethylenetrinitramine(RDX),1,3,5-trinitrobenzene,1,3-dinitrobenzene, nitrobenzene, 2,4,6-trinitrobenzene, tetryl, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 2-nitrotoluene, 4-nitrotoluene, 3-nitrotoluene, 4-amino-2,6-dinitrobenzene, 2-amino-4,6-dionitrotoluene are shown in the chromatogram in Figure 2. Most of the explosives are well separated with the exception of RDX and 1,3,5 trinitrobenzene as well as 2,4,6 trinitrobenzene and tetryl.

TABLE 4. Automated SPE conditions for 14 explosives in tap water using the Dionex SolEx SPE HRPHS cartridge and Dionex AutoTrace 280 Solid-Phase Extraction instrument.

Step No.	Step Description	SPE Function
1	Condition cartridge with 5.0 mL of MeOH into solvent waste	Condition
2	Condition cartridge with 10.0 mL of water into aqueous waste	Condition
3	Dry cartridge with gas for 5 min	Dry
4	Load 100.0 mL of sample onto cartridge at 10 mL/min	Load
5	Rinse cartridge with 5.0 mL of water into aqueous waste	Wash
6	Collect 5.0 mL fraction into sample tube using acetonitrile	Elute

FIGURE 2. Separation of 14 explosives in tap water using the Acclaim Explosives E2 column and Dionex SolEx SPE HRPHS cartridge for sample preparation with the Dionex AutoTrace 280 Solid-Phase Extraction instrument for automated SPE.

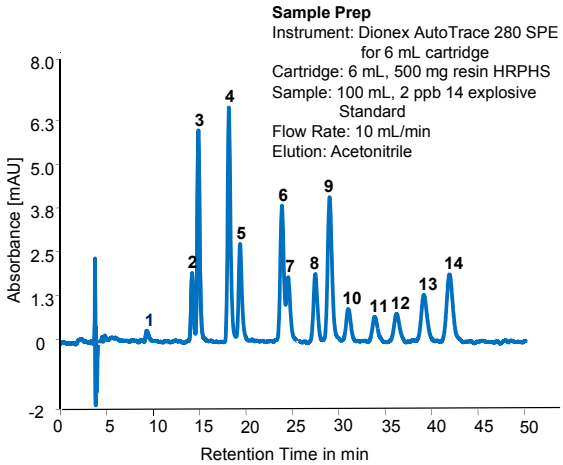


TABLE 5. Recoveries of 14 explosives in Sunnyvale tap water by automated SPE.

Peaks	Recovery%	RSD%
HMX	108.61%	5.61%
RDX	95.19%	4.01%
1,3,5-Trinitrobenzene	100.31%	3.98%
1,3-Dinitrobenzene	106.39%	5.15%
Nitrobenzene	108.38%	4.98%
2,4,6-Trinitrotoluene	101.68%	5.20%
Tetryl	111.58%	1.76%
2,6-Dinitrotoluene	103.01%	6.04%
2,4-Dinitrotoluene	104.98%	3.86%
2-Nitrotoluene	119.98%	4.27%
4-Nitrotoluene	119.63%	2.67%
3-Nitrotoluene	117.96%	4.00%
4-Amino-2,6-Dinitrotoluene	107.60%	3.11%
2-Amino-2,4-Dinitrotoluene	103.00%	5.23%

Good recoveries of all 14 explosives were achieved ranging from 95% for RDX to 120% for 2-nitrotoluene, indicating that the method is robust.

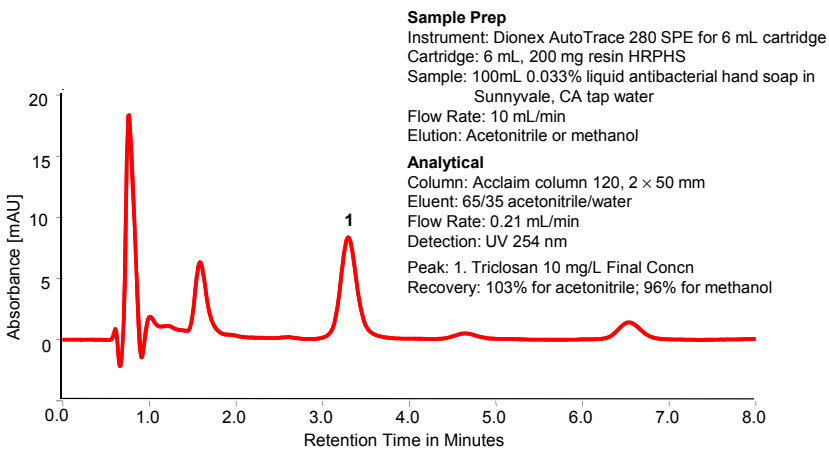
Method B: Automated solid-phase extraction of triclosan in tap water using hydrophilic reversed-phase cartridges and HPLC with UV detection

Triclosan is a powerful antibacterial and antifungal agent that is an ingredient added to many consumer products to reduce or prevent bacterial contamination. Its safety is currently under review by the U.S. FDA based on recent studies that indicate it may cause endocrine disruption in the body and possibly lead to the emergence of drug-resistant “super” bacteria. Triclosan-contaminated samples of tap water were simulated by adding known amounts of triclosan-containing liquid hand soap to Sunnyvale tap water. The Dionex AutoTrace 280 Solid-Phase Extraction instrument along with the Dionex SolEx SPE HRPHS cartridge were used to concentrate triclosan.

TABLE 6. Automated SPE conditions for triclosan in soap water using the Dionex SolEx SPE HRPHS cartridge and Dionex AutoTrace 280 Solid-Phase Extraction instrument.

Step No.	Step Description	Step Function
1	Condition cartridge with 5.0 mL of MeOH into solvent waste	Condition
2	Condition cartridge with 10.0 mL of water into aqueous waste	Condition
3	Dry cartridge with gas for 5 min	Dry
4	Load 100.0 mL of sample onto cartridge at 10 mL/min	Load
5	Rinse cartridge with 5.0 mL of water into aqueous waste	Wash
6	Collect 5.0 mL fraction into sample tube using methanol	Elute

FIGURE 3. Chromatogram showing the separation of triclosan using the Dionex Acclaim 120 column and the Dionex SolEx HRPHS cartridge for sample preparation with the Dionex AutoTrace 280 Solid-Phase Extraction instrument for automated SPE.



Recovery of triclosan from soap water is 96% using methanol as elution solvent and 103% using acetonitrile with RSDs less than 3% in both cases.

Conclusion

Five polymer-based stationary phases are developed for large-volume SPE.

- 14 explosives regulated in U.S. EPA Method 8330 in tap water was successfully analyzed by automated SPE using the Dionex AutoTrace 280 Solid-Phase Extraction instrument and Dionex SolEx SPE HRPHS cartridge.
- Triclosan in tap water was recovered by automated SPE using the Dionex SolEx SPE HRPHS cartridge in two different elution solvents without laborious sample preparation.

References

1. Thermo Scientific Application Note 1081: Automated Solid Phase Extraction of Triclosan in Tap water Using Hydrophilic-Reversed Phase Cartridges and HPLC with UV Detection, Sunnyvale, CA. [Online] http://www.dionex.com/en-us/webdocs/115038-AN1081-SPE-HPLC-Triclosan-Tap-Water-AN70884_E.pdf (accessed April 17, 2014).
2. Thermo Scientific Application Note 1086: Automated Solid Phase Extraction of 14 Explosives in Tap Water Based on U.S. EPA Method 8330 Using Hydrophilic Reversed-Phase Cartridge Followed by HPLC with UV Detection, Sunnyvale, CA. [Online] http://www.dionex.com/en-us/webdocs/115039-AN1086-SPE-HPLC-Explosives-Tap-Water-AN70897_E.pdf (accessed April 17, 2014).

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