

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

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Key Words

Nitro Compounds, Dionex SolEx SPE HRPHS Cartridges, Dionex AutoTrace 280, Automated Off-Line SPE

Goal

Concentration of 14 Explosives in fortified tap water by automated SPE using the Dionex AutoTrace 280 and a new polymeric sorbent SolEx SPE HRPHS cartridge

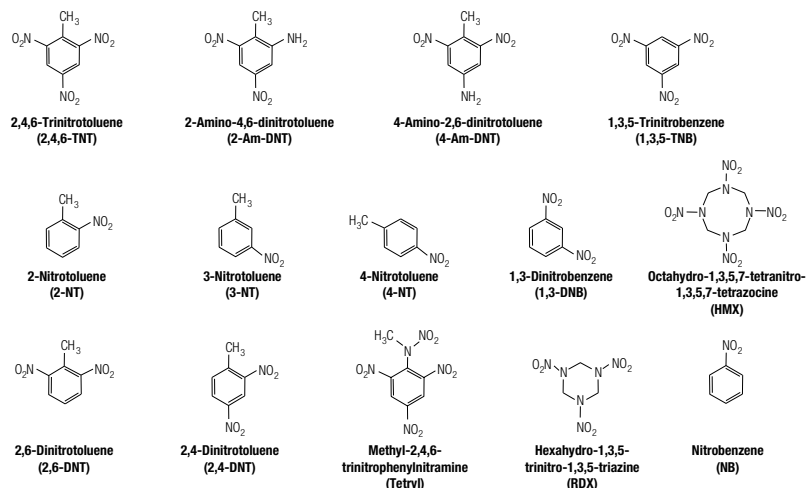


Figure 1. Structure of the 14 explosives listed in EPA Method 8330.

Introduction

Military installations and armament manufacturers have experienced closures for the last several years due to the nonproliferation treaties and disarmament agreements. These closures have resulted in munitions being disposed through combustion, thus causing major environmental problems in the soil and groundwater quality. Surrounding land and groundwater have been found to be laden with explosive residues such as 2, 4, 6-trinitrotoluene (TNT) and associated nitroamine impurities (Figure 1). Target compounds include nitroaromatics, nitramines, and nitrate esters, which present health concerns due to their carcinogenic, mutagenic, and toxic effects.

Gas chromatography is often used to determine these substances. However, for the separation of thermally unstable and nonvolatile compounds, high-performance liquid chromatography (HPLC) with ultraviolet detection is ideally suited and offers adequate detection limits for nitroaromatics.

The U.S. EPA Method 8330, first introduced in November 1990, is the most common method for the analysis of explosives. Analytes can be detected down to 2.5 ppb in water, soil, or sediment. Used here are the Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction (SPE) instrument and the Thermo Scientific™ Dionex™ SolEx™ SPE HRPHS cartridge to concentrate the pesticides, followed by HPLC.

Experimental

- Dionex AutoTrace 280 Automated Large Volume SPE for Cartridges 6 mL
- 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
 - DAD-3000 Diode Array Detector
 - Semi-Micro Flow Cell for DAD-3000 and MWD-3000 Series, SST, 2.5 µL Volume, 7 mm Path Length
 - 15 mL Conical Tubes (pack of 12)
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System, 6.80 SP4 and higher

SPE Conditions

Cartridge:	Dionex SolEx SPE HRPHS Polymer-Based Solid-Phase Extraction Cartridge, 6 mL, 500 mg, Package of 36
Flow Rate:	5mL/min
Elution Solvent:	Acetonitrile

Table 1. Dionex AutoTrace 280 instrument method: process one sample using the following steps.

No.	Method	SPE Steps
1	Condition cartridge with 5.0 mL of methanol into solvent waste	Condition
2	Condition cartridge with 10.0 mL of water into aqueous waste	Condition
3	Dry cartridge with gas for 5.0 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

Analytical Conditions

Column:	Thermo Scientific™ Acclaim™ Explosives E2 column, 3 μm
Dimensions:	3.0 × 250 mm
Mobile Phase:	48/52 v/v Methanol/H ₂ O
Flow Rate:	0.3 mL/min
Injection Volume:	5 μL
Temperature:	25 °C
Detection:	UV at 254 nm

Results and Discussion

The HRPHS SPE phase was packed into a 6mL barrel with a bed weight of 500 mg. In the Dionex AutoTrace 280 SPE method, 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 cyclotetramethylenetetraamitramine (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.

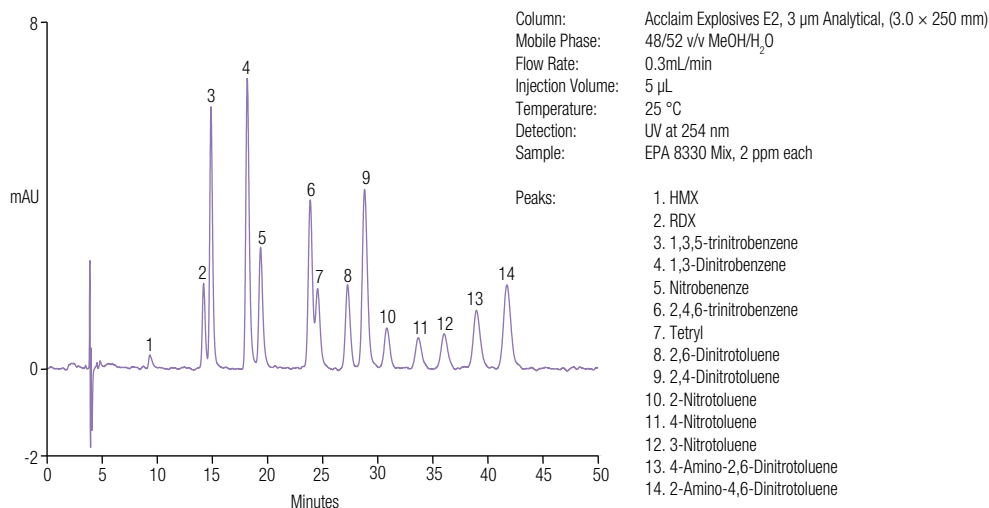


Figure 2. Separation of 14 explosives in tap water using the Acclaim Explosives E2 column and the Dionex SolEx SPE HRPHS cartridge for sample preparation using the Dionex AutoTrace 280 for automated SPE.

To verify that the matrix components do not interfere with the separation and quantification of 14 explosives, known amounts of each of the analytes were spiked into tap water. As seen in Table 2, the recoveries ranged from 95% for RDX to 109% for HMX.

Conclusion

Shown here is the successful recovery of 14 explosives in tap water by automated SPE using the Dionex AutoTrace 280 instrument and SolEx SPE HRPHS cartridge without laborious sample preparation, followed by HPLC analysis.

Table 2. Recovery of 14 explosives spiked into tap water and concentrated onto the Dionex SolEx SPE HRPHS cartridge using the AT280 followed by HPLC with UV Detection.

Peaks	Recovery %	RSD
HMX	109%	5.6%
RDX	95%	4.0%
1,3,5-Trinitrobenzene	100%	4.0%
1,3-Dinitrobenzene	106%	5.2%
Nitrobenzene	108%	5.0%
2,4,6-Trinitrotoluene	102%	5.2%
Tetryl	112%	1.8%
2,6-Dinitrotoluene	103%	6.0%
2,4-Dinitrotoluene	105%	3.9%
2-Nitrotoluene	120%	4.3%
4-Nitrotoluene	120%	2.7%
3-Nitrotoluene	118%	4.0%
4-Amino-2,6-Dinitrotoluene	108%	3.1%
2-Amino-2,4-Dinitrotoluene	103%	5.2%

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

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