

Introduction

Nitroaromatic and nitroamine explosives are highly toxic substances that can persist in the environment. Through natural leaching processes, these toxic substances can accumulate and concentrate in both surface and ground water supplies and jeopardize potable water. Of concern are areas near military bases and munitions sites where contaminated soil can leach into public water systems. It is for this reason that there are strict guidelines that address proper handling procedures for clean-up and maintenance of these areas.

A reliable liquid-liquid extraction procedure has been developed for the determination of explosive residues in environmental samples (EPA method 8330A, Sept. 1994). Unfortunately, this salting-out extraction procedure requires a high degree of cumbersome sample manipulation, which may not be suitable for high-throughput applications. The draft revision of method 8330A (Jan. 1998) uses solid phase extraction (SPE). The convenience of this analytical method is more suitable for high-throughput analysis.

This poster introduces an improved SPE protocol for a simple, efficient and reproducible LC-UV determination of nitroaromatic and nitroamine explosive residues in surface and ground water. Compared to EPA method 8330A, this new protocol uses a smaller and more efficient SPE cartridge to process 500 mL samples. This results in greater sample enrichment and lowers the quantitation limit. Also, the effectiveness of the sample clean-up guarantees that the lowered quantitation limit can be achieved for water samples containing high amounts of humic material.

The lowest possible elution volume and the cleanest extract are critical for this analysis. In many SPE methods for non-reactive compounds, using a relatively large volume of eluent is common. The eluent is then evaporated and the sample is reconstituted in a much smaller volume of solvent to further increase the enrichment factor. However, in this case, evaporation of the eluent could be potentially dangerous. Because of the inherent reactive nature of many explosive compounds, a highly concentrated sample is not desirable. Therefore, it is important to choose an eluent that is appropriate for the LC-UV analysis and to use the minimum volume of that eluent to achieve good recovery of the analytes.

Experimental

Sample Preparation

SPE cartridge: Oasis® HLB, 6cc, 200 mg of sorbent
Sample size: 500 mL, 1000 mL (< 1 µg/L)
Source water was obtained from the Sudbury River

at

Hopkington, MA. (Contains approximately10 mg/L of natural organic matter.)

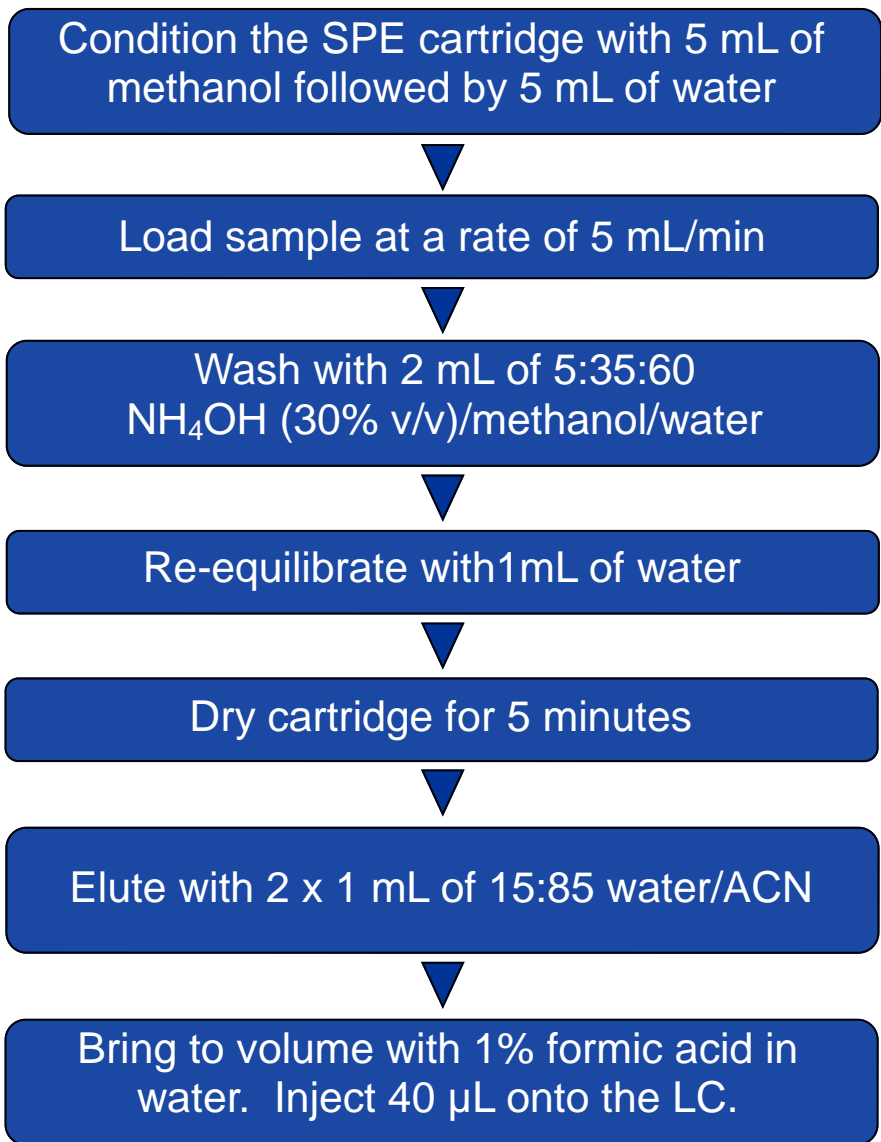
Instrumentation

Waters Alliance® 2690 Separations Module
Sample temperature: 4°C
Column Temperature: 45°C
Waters 2487® Dual Wavelength Detector
Monitored wavelengths: 240 nm, 270 nm

Chromatography

XTerra® Phenyl, 4.6 x 150 mm, 5µm particle size
Isocratic mobile phase
71% water
13% 100 mM ammonium format (pH 3.0)
16% 2-propanol
Flow: 0.85 mL/min

SPE Procedure



Results

Figure 1. A 5 µg/L spiked river water sample. The inset shows a 5 µg/L sample without SPE clean-up.

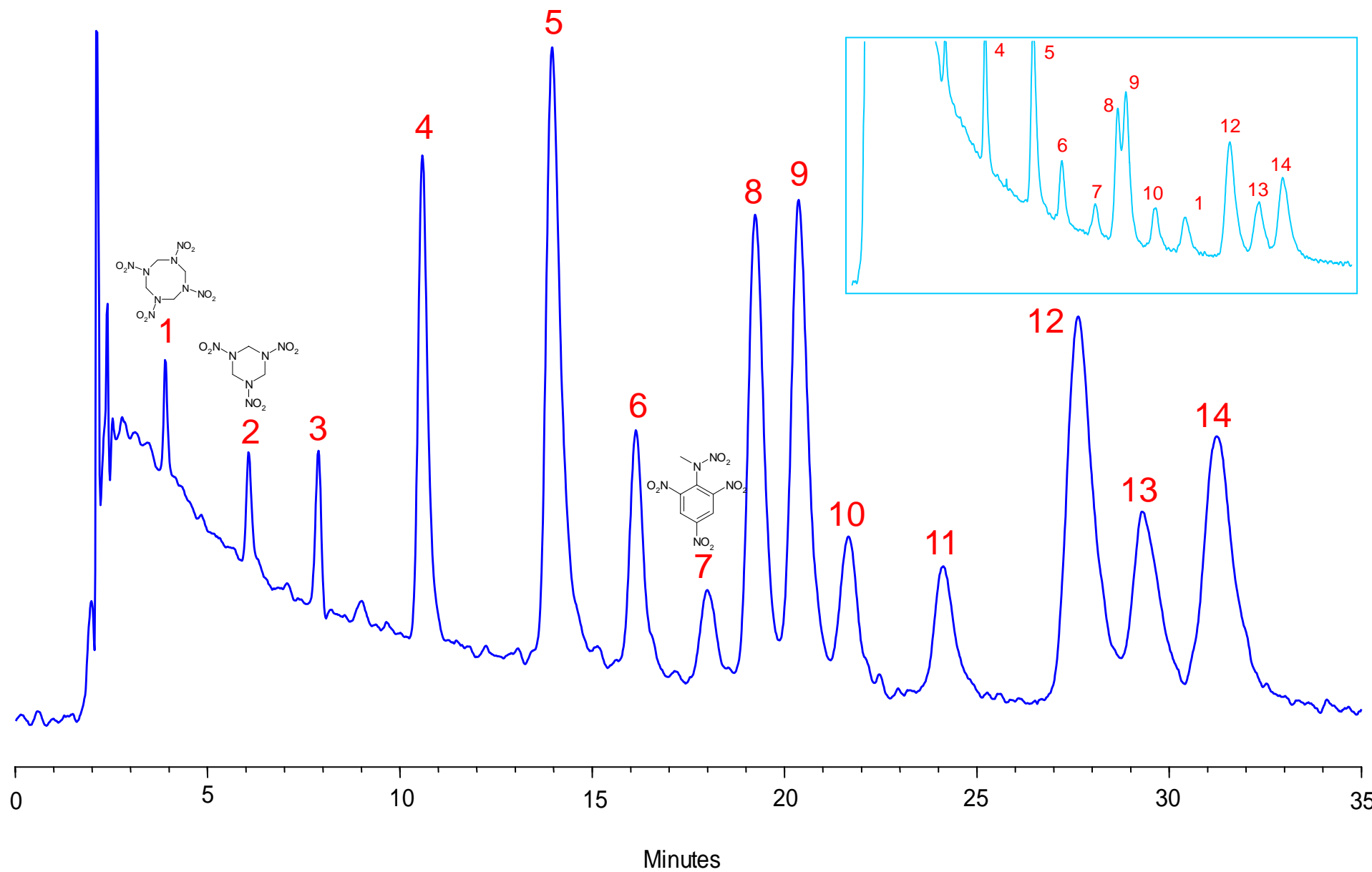


Table 1. Results for spiked river water samples (n=6). Bracketed descriptions indicate the wavelength used for quantification.

	% Recovery (± RSD)				% Recovery (± RSD)		
	0.25 µg/L	2.0 µg/L	10.0 µg/L		0.25 µg/L	2.0 µg/L	10.0 µg/L
1 HMX (240 nm)	102.4 (5.3)	93.8 (6.0)	95.8 (1.7)	8 2-Am-4,6-DNT (270 nm)	105.6 (4.2)	99.0 (1.7)	95.8 (1.1)
2 RDX (240 nm)	101.4 (7.5)	90.6 (3.9)	96.9 (1.7)	9 2,4-DNT (270 nm)	99.9 (5.5)	99.8 (3.9)	95.4 (1.0)
3 1,3,5-TNB (240 nm)	88.3 (5.4)	92.2 (2.6)	96.2 (1.6)	10 4-Am-2,6-DNT (240 nm)	83.1 (9.5)	115.5(10.6)	95.2(6.5)
4 1,3-DNB (270 nm)	93.9 (2.6)	97.5 (1.7)	96.1 (1.1)	11 2,6-DNT (270 nm)	122.7 (4.9)	107.7 (4.3)	94.9 (1.4)
5 NB (270 nm)	100.7 (3.6)	94.3 (2.2)	90.1 (1.5)	12 4-NT (270 nm)	81.5 (5.9)	93.9 (5.1)	88.5 (2.0)
6 2,4,6-TNT (270 nm)	79.6 (15.2)	101.8 (2.8)	95.0 (2.3)	13 3-NT (270 nm)	106.0 (13.9)	92.1(10.0)	84.1 (2.4)
7 Tetryl (240 nm)	88.0 (19.2)	71.2 (8.9)	68.1 (5.5)	14 2-NT (270 nm)	137.1 (10.4)	97.1 (10.5)	85.2 (2.6)

Discussion

The surface water that was chosen for this study contained a high amount of natural organic material (NOM). For such matrices, obtaining quantitation limits well below 1 µg/L can be challenging if careful optimization and sample clean-up are neglected. The high pH wash step that was employed in this SPE protocol is highly effective in removing the humic material found in typical surface waters and in ground waters.

Caution is required when using the high pH wash for this analysis because one of the analytes, Tetryl, is unstable at elevated pH. By using a minimum amount of wash solution and quickly re-equilibrating the SPE cartridge with deionized water, the exposure to the elevated pH was minimized. A compromise was achieved between the sample cleanliness and the minimization of analyte degradation. Indeed, if the determination of Tetryl is not required, an even stronger wash step can be utilized to further reduce the matrix interferences. This would allow for greater sensitivity for the early eluting compounds such as HMX and RDX.

Conclusions

In summary, improvements in SPE technology have allowed for the development of an improved SPE protocol for the LC-UV analysis of explosive residues in aqueous samples. Compared with current procedures, lower quantification limits have been achieved with high recovery; even for the most polar analytes such as HMX and RDX

References

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- Levsen, K., Mußmann, P., Berger-Preiß, E., Preiß, A., Volmer, D., Wünsch, G. *Acta Hydrochim. Hydrobiol.* **1993** 21, 153-166.
- EPA Method 8330A, *Nitroaromatics and Nitroamines by High Performance Liquid Chromatography (HPLC)* **1994**.
- EPA Method 3535A, *Solid Phase Extraction (SPE)* **2000**.