

Automated μ SPE for rapid detection of aqueous nitro aromatic explosives

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Overview

- Easy fully automated sample preparation from calibration to analysis.
- Rapid automated high efficiency micro SPE analysis for aqueous explosives samples.
- The explosive samples were loaded onto Eprep μ SPEd Cartridges (Figure 1) packed with PS/DVB-3 μ m/300Å or C18RPS-3 μ m/120Å. PS/DVB performed better than C18 in trapping HMX and RDX.
- Analyses were by high performance liquid chromatography (HPLC) with dual wavelength analysis at 210 and 254 nm.
- All explosives had recoveries within the 70 – 130% levels specified by EPA method 3535A which outlines SPE methods for semi volatiles.

Introduction

Sample preparation is both vital and the most time consuming aspect of laboratory analysis. The ability to automate extractions and preconcentration streamlines workflows and reduces common sources of error. Micro solid-phase extraction (μ SPE) is an effective sample preparation technique that utilises smaller bed volumes and particle size (<3 μ m) which provides a number of advantages over traditional SPE including reduced sample volumes, increased speed, efficacy, and reduced solvent use. Here we demonstrate the extraction of explosives in water samples using a new automated μ SPE workstation. Validation of SPE extractions of explosives are required to meet the guidelines including obtaining spiked recoveries of the 70 – 130%.

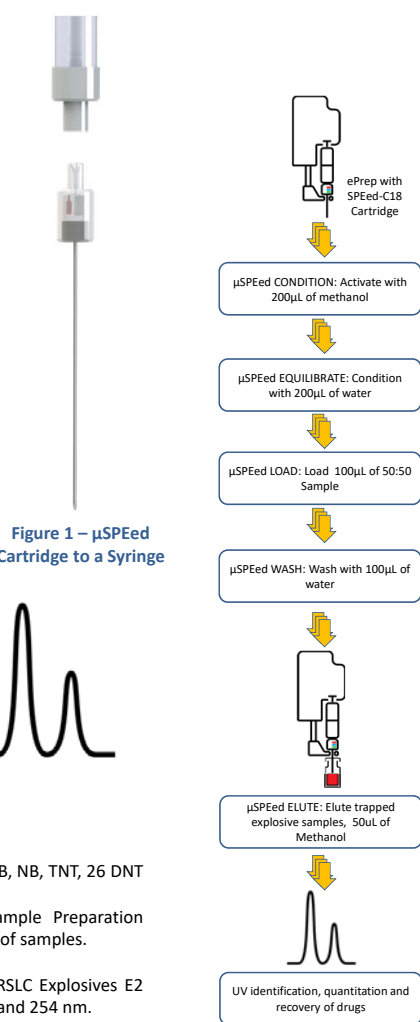


Figure 1 – μ SPEd Cartridge to a Syringe

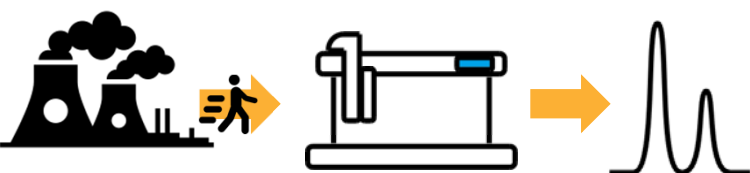


Figure 2 – ePrep Workstation workflow

Methods

- Explosives targeted for preconcentration included HMX, RDX, 135 TNB, 13 DNB, NB, TNT, 26 DNT and 3 NT (Table 1).
- All samples and standards were prepared by the ePrep Automated Sample Preparation Workstation (Figure 2) which automates the dilution of standards and the SPE of samples.
- μ SPEd cartridges included PS/DVB-3 μ m/300Å and C18RPS-3 μ m/120Å.
- Thermo Fisher Scientific Vanquish UHPLC system equipped with a Acclaim RSLC Explosives E2 column (150 mm x 2.1 mm, 2.2 μ m) was utilised with detection via UV @ 210 and 254 nm.

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Automated μ SPE Sequence – The aqueous samples were loaded onto the μ SPEd cartridges (PS/DVB-3 μ m/300Å and C18RPS-3 μ m/120Å), washed with ultrapure water and then eluted with 200 μ L of methanol. Conditioning and equilibration steps were carried out at 200 μ L/min flow rate, all other steps at 10 μ L/min. Procedures as shown in Figure 3.

Results

A Thermo Fisher HPLC-UV system was used to confirm adsorption of compounds to a C18 or PS/DVB packing cartridge. Liquid handling reproducibility was excellent with an average %RSD less than 0.01% and r^2 greater than 0.999 (see Table 1). Filtered environmental aqueous samples were spiked and used to test the effectiveness of the trapping and clean up procedures as shown in figure 4.

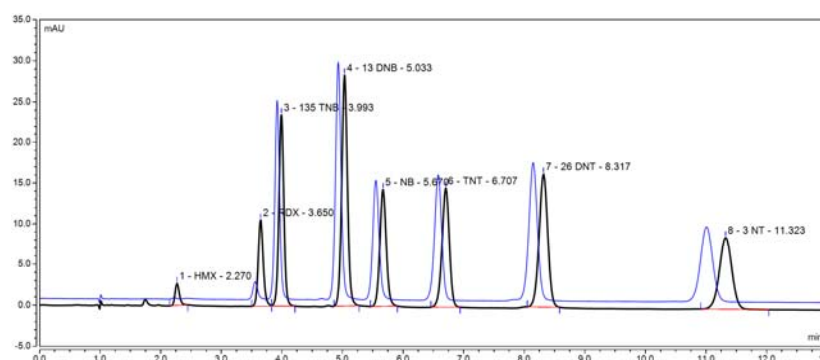


Figure 4 – HPLC Chromatograms of 10ppm spiked water sample at 254nm after SPE clean up. PS/DVB (Black), C18 (Blue)

Compound	Retention time (min)	R ²	RSD
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	2.3	0.99978	< 0.01%
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	3.6	0.99984	< 0.01%
1,3,5-Trinitrobenzene (1,3,5-TNB)	3.9	0.99936	< 0.01%
1,3-Dinitrobenzene (1,3-DNB)	4.9	0.99991	< 0.01%
Nitrobenzene (NB)	5.6	0.99986	< 0.01%
2,4,6-Trinitrotoluene (TNT)	6.6	0.99997	< 0.01%
2,6-Dinitrotoluene (2,6-DNT)	8.2	0.99992	< 0.01%
3-Nitrotoluene (3-NT)	11.3	0.99992	< 0.01%

Table 1 – Aqueous Explosive Standards linearity and repeatability for liquid handling by ePrep Automated Sample Preparation Workstation.

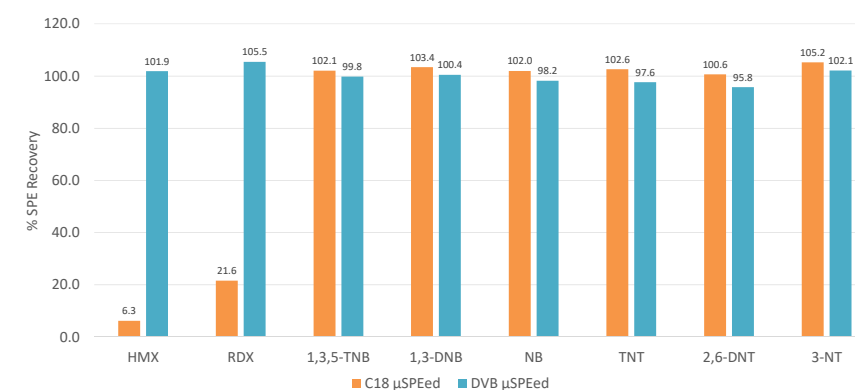


Figure 5 – Recoveries of SPE determined by UV

Analysis of Aqueous Samples – Water samples were spiked with explosives at 10 ppm. These samples were mixed and loaded on to μ SPEd cartridges for clean-up and trapping/concentrating of explosives compounds. Unwanted compounds were removed in the filtering and trapping process in a simple and effective manner. The clean up process was highly effective with good recoveries as shown in Figure 4, and little to no interference from other compounds was detected. The recoveries for early eluting compounds (e.g. HMX and RDX) with the C18 cartridges were low, in the range of 6 to 21% when compared to DVB (Figure 5). However, the remaining explosives showed excellent recoveries ranging from 97% to 101%.

Conclusions

Automated sample preparation allows for the rapid and simple processing of aqueous samples. Automated liquid handling of ePrep Sample Preparation Workstation creates calibration curves with a high degree of accuracy and repeatability. All components dispensed with the ePrep Workstation showed good linearity with r^2 values greater than 0.999. Eprep PS/DVB μ SPEd cartridges performed superior than C18, and are highly effective in the SPE concentration and clean up of explosives samples. C18 μ SPEd cartridges showed poor recovery for early eluting compounds such as HMX and RDX, while PS/DVB showed recoveries ranging from 97% to 101%, well in excess of the 70 – 130% suggested by EPA method 3535A, making it ideal for the analysis of aqueous samples containing explosives. Future work will couple the HPLC with mass spectrometry analyses.

References

1. EPA Method 3535A (SW-846): Solid-Phase Extraction (SPE). [cited 2016 20/09/2016]; Available from: <https://www.epa.gov/sites/production/files/2015-07/documents/epa-8270d.pdf>.
2. METHOD 8330B NITROAROMATICS, NITRAMINES, AND NITRATE ESTERS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC). [cited 2016 30/09/2016]; Available from: <https://www.epa.gov/sites/production/files/2015-07/documents/epa-8330b.pdf>.