

Automated μ SPE for Rapid Detection of Aqueous Nitro Aromatic Explosives

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Introduction: Sample preparation is both vital and the most time consuming aspect of laboratory analysis. The ability to automate extractions and pre-concentration streamlines workflows and reduces common sources of error. Micro solid-phase extraction (μ SPE) is an effective sample preparation technique that utilizes smaller bed volumes and particle size ($<3\mu\text{m}$) 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 70 – 130%.

Experimental: Explosives targeted for pre-concentration 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 1) which automates the dilution of standards and the SPE of samples. Extractions were performed on PS/DVB- $3\mu\text{m}/300\text{\AA}$ and C18 RPS- $3\mu\text{m}/120\text{\AA}$ μ SPEed cartridges. The aqueous samples were loaded onto the μ SPEed cartridges, washed with ultrapure water, and then eluted with $200\mu\text{L}$ of methanol. Conditioning and equilibration steps were carried out at $200\mu\text{L}/\text{min}$ flow rate, all other steps at $10\mu\text{L}/\text{min}$. A Thermo Fisher Scientific Vanquish UHPLC system equipped with a Acclaim RSLC Explosives E2 column ($150\text{ mm} \times 2.1\text{ mm}$, $2.2\mu\text{m}$) was utilised with UV @ 210 and 254 nm.

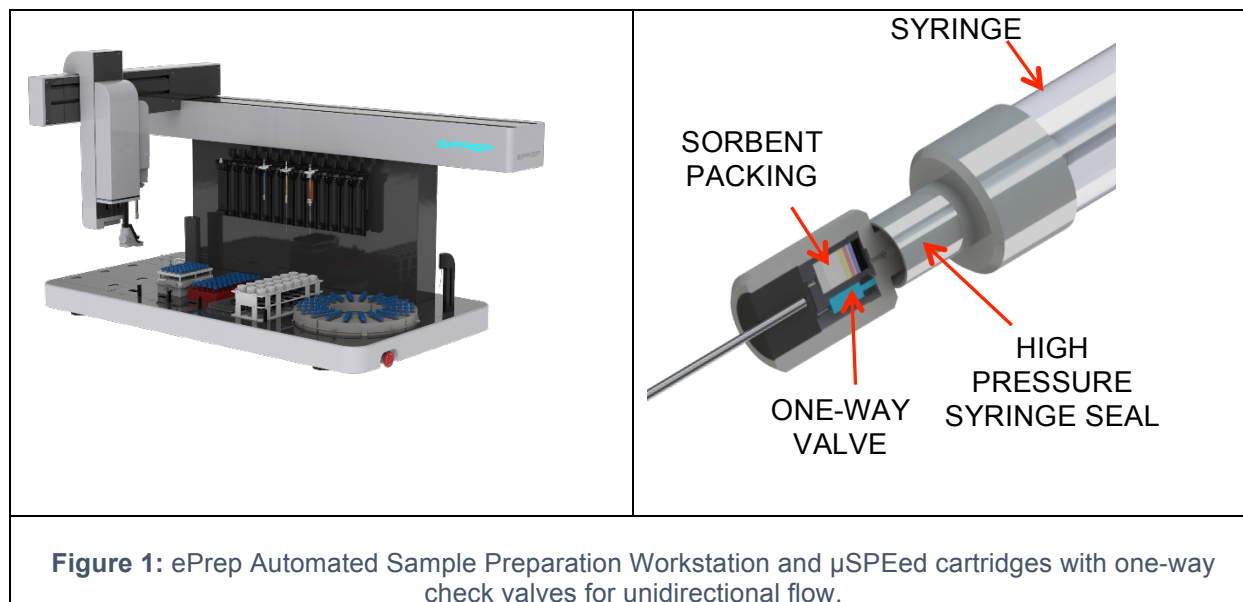


Figure 1: ePrep Automated Sample Preparation Workstation and μ SPEed cartridges with one-way check valves for unidirectional flow.

Results and Discussion: A Thermo Fisher HPLC-UV system was used to confirm adsorption of compounds to a C18 or PS/DVB packing cartridge. Liquid handling reproducibility of ePrep Workstation 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 2.

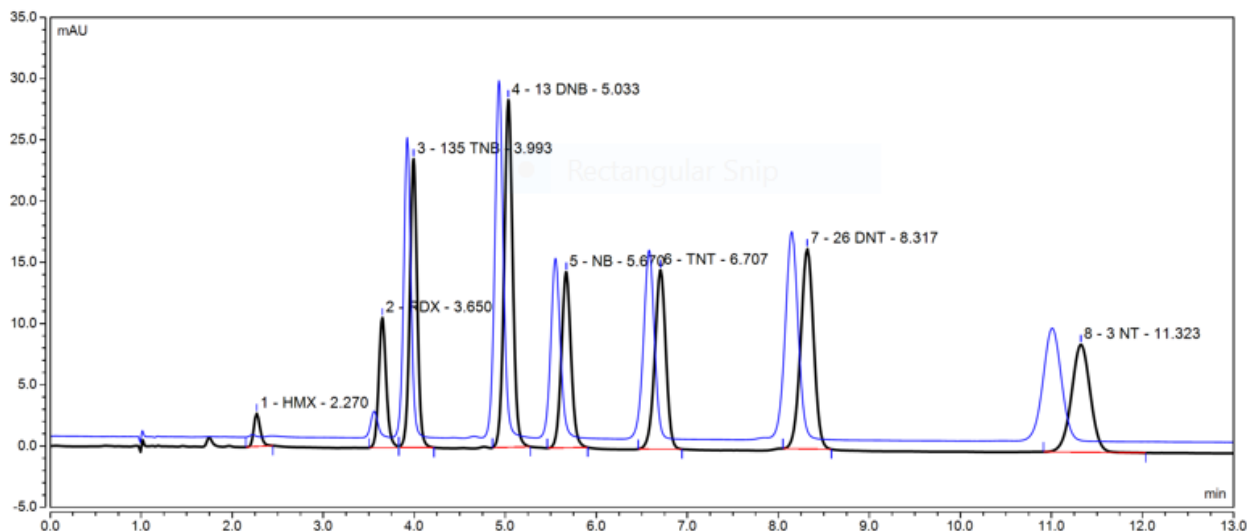


Figure 2: HPLC Chromatograms of 10ppm spiked water sample at 254nm after SPE clean up. PS/DVB (Black), C18 (Blue)

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.

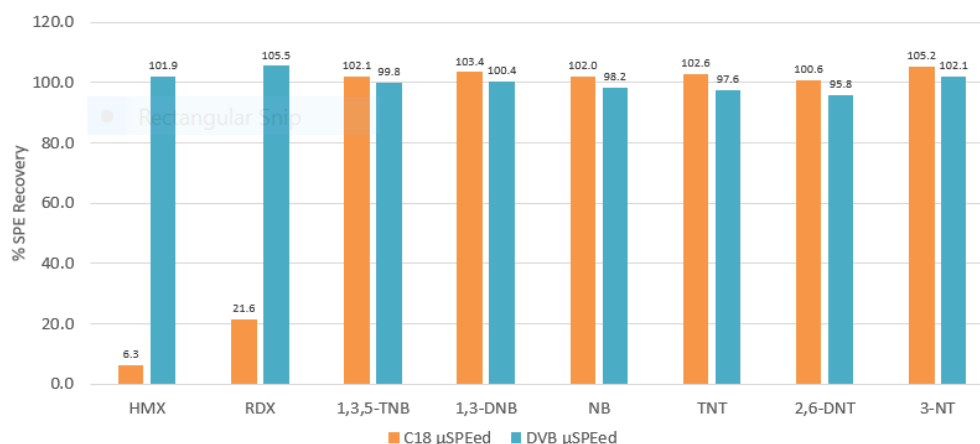


Figure 3: Recoveries of μ SPE determined by UV

Analysis of Aqueous Samples: Water samples were spiked with explosives at 10 ppm. These samples were mixed and loaded on to μ SPEed cartridges for clean-up and trapping/concentrating of the explosive 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 3, 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 3). However, the remaining explosives showed excellent recoveries ranging from 97 to 101%.

Conclusion: 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 SPEed cartridges performed superior than C18, and were highly effective in the SPE concentration and clean-up of explosives samples. C18 μ SPEed 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.

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References:

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