

Blowing Analytical Precision and Accuracy out of the Water – microSPE of Explosives

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Introduction

Automated sample preparation is an essential part of any modern laboratory workflow. Manual sample handling and preparation often introduces systematic or analysts' errors into any laboratory process. Adoption of automation for standard methods provides faster, more accurate and more repeatable sample preparation. The ePrep Workstation allows fully automated standard and sample preparation for highly accurate and repeatable analyses that may be applied to almost any analytical workflow.

In this poster we demonstrate the accuracy, precision and repeatability of automated standard and sample preparation for organic explosives in natural waters. River water samples spiked with 14 explosive compounds were prepared by the ePrep Workstation using a novel micro solid phase extraction technique (μ SPEed) prior to analysis by UHPLC.



Figure 1 – μ SPEed cartridges with one-way check valves and ePrep sample preparation Workstation

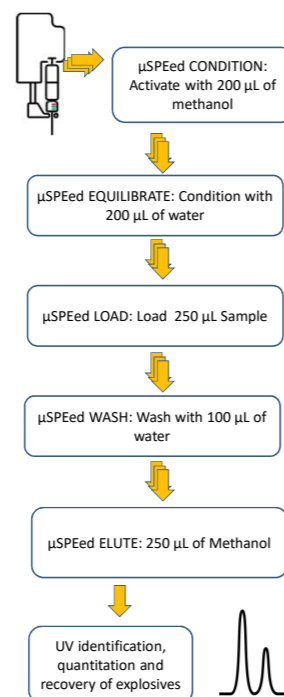


Figure 2 – μ SPE Workflow

Methods

Using a mixture of 14 explosives (cited in EPA Method 8330 and 3535A), an automated sample handling workflow was developed for processing highly turbid water samples. The samples were loaded onto the μ SPEed cartridge, (PS/DVB, 3 μ m/120Å), washed with ultrapure water and then eluted with 250 μ L of MeOH. All standards and samples were prepared using the ePrep Workstation prior to analysis by Thermo Scientific's Vanquish UHPLC system using a C18+ 100 mm x 2.1 mm 1.5 μ m column (Figure 2).

Experimental

1) **HPLC separation for nitroaromatic standards:** Figure 3 shows a typical HPLC chromatogram for a standard mix containing 8 target compounds at 5ppm. An isocratic mobile phase (Water:MeOH 52:48 v/v) was used at a flow of 0.38 mL/min with an injection volume of 1 μ L. Chromatograms were extracted at the wavelengths of 210 and 254 nm. Chromatographic separation was carried out in less than 14 min

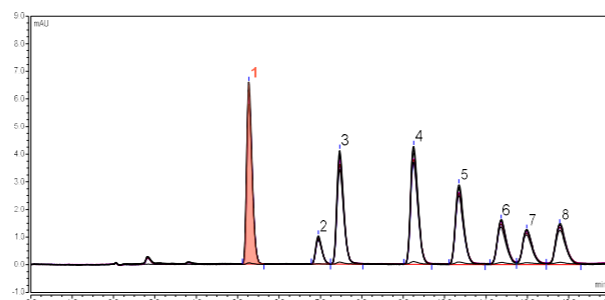


Figure 3 Representative chromatographic separation of standard Mix using a C18 column (Peak 1 = RDX, 2 = 13 DNB, 3 = NB, 4 = TNT, 5 = 26 DNT, 6 = 4NT, 7 = 2NT, 8 = 3NT)

Compound	R-Square
RDX	0.9999
13 DNB	0.9997
NB	0.9998
TNT	0.9998
26 DNT	0.9993
2NT	0.9998
4NT	0.9995
3NT	0.9991
HMX	0.9919
TNB	0.9977
Tetryl	0.9949
24DNT	0.9914
4a26 DNT	0.9935
2a46 DNT	0.9903

Table 1 Automated calibration curve linearity of the 14 explosives

2) **μ SPEed DVB/PS SPE Reproducibility:** Method reproducibility was tested by loading a single 5 ppm sample onto 10 cartridges and then eluted using the procedure described before. Table 2 shows highly reproducible recoveries with average recovery of explosives by area with a %RSD of 5.59% indicating that the SPE mechanism provides very repeatable extraction.

Sample	Average	SD	%RSD
HMX	3.44	0.14	3.96%
135 TNB	2.53	0.15	5.77%
24DNT	2.00	0.09	4.33%
TNT	1.15	0.06	5.51%
4a26DNT	1.98	0.11	5.49%
2a46DNT	1.95	0.13	6.66%
RDX	1.98	0.07	3.38%
13 DNB	0.11	0.01	5.32%
NB	0.78	0.02	3.15%
Tetryl	1.16	0.07	5.81%
26 DNT	1.11	0.03	3.10%
4NT	0.76	0.05	6.52%
2NT	0.60	0.07	11.95%
3NT	0.83	0.06	7.28%

Table 2 Repeatability and reproducibility of explosives extraction procedure quantified by area.

3) **Quantification of Explosive compounds in water by μ SPEed-HPLC analysis:** The validated methodology was used for the identification and quantification of explosives in spiked natural and sedimentary river water samples. Figure 4 shows an overlay of 2 chromatograms, one from an SPE procedure performed with pure water and the other from a spiked river water. The samples show a very high level of similarity thanks to the effectiveness of the clean-up technique.

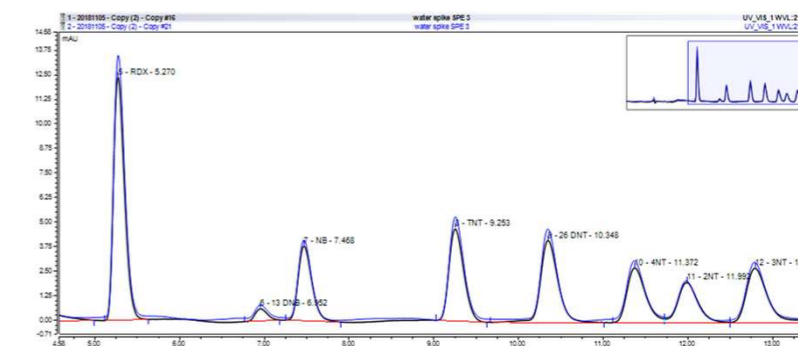


Figure 4 Overlay of SPE extraction. Blue = 5ppm pure water sample, Black = 5ppm spiked sedimentary river water sample

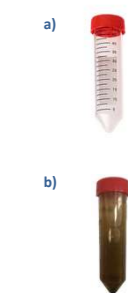


Figure 5 Natural (a) and sedimentary river water samples (b)

Conclusions

This work describes a simple automated, fast and effective method for the analysis of explosives in aqueous samples. The method requires no complex solvent preparation, no sample pre-treatment and minimal waste. Automated sample preparation and liquid handling allows for rapid and simple processing of aqueous samples, as well as the creation of calibration curves with a high degree of accuracy and repeatability.

Linearity for all components dispensed using the Eprep system were over 0.99. Eprep PS/DVB μ SPEed cartridges showed recoveries ranging from 87% to 121% (Table 3) well in excess of the 70 - 130% suggested by EPA method 3535A making it ideal of the analysis of aqueous samples containing explosives even when faced with difficult sample matrices.

Compound	Pure water Spike % (5 ug/mL)	Sedimentary river water spike % (5 ug/mL)
HMX	141 ± 4.2	123 ± 10.23
135 TNB	108 ± 5.71	106 ± 11.15
24DNT	114 ± 4.33	108 ± 10.29
Tetryl	86 ± 5.7	85 ± 17.69
4a26DNT	108 ± 5.48	103 ± 12.48
2a46DNT	108 ± 6.55	104 ± 4.96
RDX	102 ± 2.18	102 ± 5.91
13 DNB	107 ± 4.32	105 ± 9.25
NB	94 ± 4.1	93 ± 8.33
TNT	110 ± 3.85	109 ± 7.16
26 DNT	112 ± 3.29	112 ± 7.3
2NT	89 ± 5.07	87 ± 8.91
4NT	90 ± 4.34	88 ± 8.21
3NT	119 ± 4.02	121 ± 8.31

Table 3: Recovery from spiked water samples