Solventless Extraction Techniques for Long Term Monitoring of Military Unique Compounds

DAVID E. SPLICHAL[1], Douglas B. Taggart[1], Denise K. MacMillan[1], John P. Shannon[2], and Bradley Varhol[3]

[1] U.S. ARMY CORPS OF ENGINEERS, ENGINEER RESEARCH and DEVELOPMENT CENTER (ERDC), OMAHA, NE

[2]Analytical Services, Inc., 689 Discovery Road, Vicksburg, MS

[3]EON Products, Inc., P.O. Box 390246, Snellville, GA

OVERVIEW

The costs of solvents, used solvent disposal, and labor involved in extraction of contaminants from groundwater can approach 25% of the total amount charged by environmental laboratories for many organic analyses including EPA SW -846 procedures. High costs are also associated with transporting at least two one-liter amber bottles per sample from each sampling point under proper storage conditions and before sample expiration to the laboratory. The ERDC is exploring alternative technologies to reduce costs associated with long term monitoring of military unique compounds (MUCs). Three techniques are being investigated to determine their applicability with explosives. The first technique utilizes a new field sampling extraction procedure (InSTED) developed in-house. The other two techniques use commercially available technologies: SPME and Twister™.

THEORY of the HYDRASLEEVE™

The HydraSleeve™ discrete interval sampler consists of three basic components: a reusable weight, a long, flexible, lay-flat sample sleeve, and a reed valve. To use, the closed sampler is lowered into the screened well interval, and the well is allowed to return to equilibrium. To collect a sample, the device is pulled upward the reed valve opens, and water is "pumped" downward into the sleeve. Once withdrawn from the well, the water can be transferred from the sample tube to holding vials for analysis.

THEORY of the InSTED

The InSTED (*In Situ* Tubular Extraction Device) takes the HydraSleeve™ process one step further than collection by also performing extraction/concentration in the field. The InSTED takes a HydraSleeve that has been specially modified and couples it to a solid phase extraction (SPE) large volume sampling cartridge (Porpak RDx, WAT047220, Waters Corporation, Milford, MA) and a submersible pump assembly (pump MG204XPS17, motor MGC412VDC from Clark Solutions, Hudson, MA). Once the water of known volume is collected into the bag, the pump is started and analyte concentration onto the SPE cartridge commences. Once the bag is void of water, the pump stops.

The InSTED EXPERIMENTAL DESIGN

For the first set of experiments, nine (9) 500 mL DI water samples were spiked with explosives analytes (SW -846 method 8330A list) at 10 ug/L (ppb). Three samples were extracted using SPE described in method 8330A. The remaining six (6) samples were poured into the modified HydraSleeve, and pumped through the SPE cartridge. The cartridge was detached from the sleeve and analytes were eluted with 5 mL acetonitrile. A second experiment was conducted using composited real-world aqueous samples (3 method 8330A; 7 InSTED). Two additional real-world samples were collected using the InSTED, wrapped in foil, stored at room temperature, and then eluted with acetonitrile nine days after sample collection. Extracts, plus method blanks, were analyzed by HPLC according to SW -846 method 8330A.

RESULTS

Compound	8330 DI*	InSTED DI*	8330 RW#	InSTED RW#	InSTED RW++
HMX	90	82	22	21	19
RDX	99	93	158	153	137
TNB	85	88	ND	ND	ND
DNB	88	90	ND	ND	ND
Tetryl	89	106	ND	ND	ND
NB	83	88	ND	ND	ND
TNT	89	93	ND	ND	ND
4-A-DNT	89	100	1.5	1.5	1
2-A-DNT	86	92	0.1	0.1	0.06
2,6-DNT	89	94	ND	ND	ND
2,4-DNT	83	88	ND	ND	ND
2-NT	81	90	ND	ND	ND
3-NT	79	90	ND	ND	ND
4-NT	80	90	ND	ND	ND

DI: Laboratory De- ionized water; *: Percent Recovery from 10 ug/L
RW: Real world composited sample; #: Units = ug/L (ppb)
++: Eluted 9 days after collection on SPE, ug/L

FUTURE WORK WITH THE InSTED

1. Monitor extraction efficiency with a pre-spiked surrogate.
2. Simulated well studies with laboratory stand-pipes.
3. LCS/MS/MSD considerations.
4. Field evaluation at DoD site(s).
5. Laboratory evaluations for other compounds.

EXPLOSIVES WITH SPME

The SPME, (US patent number 5,691,206 licensed to SUPELCO, Bellefonte, PA), is a fiber coated with a liquid polymer, or solid sorbent, or both that concentrates analytes from soil or water samples. Either GC or LC detection can be used. Preliminary results using various fiber coatings (Carbowax, PDMS/divinylbenzene, and Carboxen/DVB/PDMS) to adsorb explosives and a HP 5890 Series II GC (Restek RTx-TNT, 15 m x 0.25 mm ID x 0.25 µm column)/Agilent 5972 MSD for detection, gave adequate responses for most explosive analytes spiked into DI water, except for RDX, HMX and Tetryl where responses approached zero even when spiked at 100 ug/L.

EXPLOSIVES WITH TWISTER™

The Twister™ (Gerstel, Baltimore, MD) is a magnetic stir bar coated with PDMS. While it is stirring, Twister™ efficiently extracts most non-polar organic compounds from aqueous samples. Analytes are thermally desorbed or back-extracted with a small volume of solvent for GC or LC analysis. Preliminary results using the solvent back-extraction technique followed by LC analysis indicate poor sensitivity for many of the explosive analytes.

The InSTED – CONCLUSIONS

Explosive recoveries using the InSTED compare favorably with results from the traditional SPE technique referenced in SW -846 method 8330. Cost savings of approximately 90% may be observed in shipping charges alone, with up to 50% reduction in overall extraction costs. Projected cost savings do not include the one time initial fee for the pumping mechanisms.