EXECUTIVE SUMMARY

Development and Optimization of Analytical Methods for Simultaneous Determination of IM and Legacy Explosive Compounds

SERDP Project ER-2722

APRIL 2019

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FINAL REPORT

Project: ER-2722

TABLE OF CONTENTS

Page

1.0 INTRODUCTION 1

2.0 OBJECTIVES 3

3.0 TECHNICAL APPROACH 5

4.0 RESULTS AND DISCUSSION 7

4.1 ANALYTICAL METHODS 7

4.1.1 Primary HPLC-UV Method 7

4.1.2 Secondary HPLC-UV Method 8

4.1.3 HPLC-MS Method 8

4.1.4 MEKC Method 12

4.2 EXTRACTION METHODS FOR SAMPLES ANALYZED BY HPLC-UV AND HPLC-MS 13

4.2.1 Method for Preparation of Waters for Direct-Injection Analysis 13

4.2.2 SPE Method for Waters 13

4.2.3 SE Method for Soils 14

4.2.4 SE Method for Tissues and Interference Reduction Method for Tissue Extracts 15

4.3 STABILITY STUDIES & INTER-LABORATORY BATCH ANALYSIS STUDIES 17

4.4 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS 17

LIST OF FIGURES

Page

Figure 1. HPLC Chromatograms of a Mixed Standard Containing 5 mg/L of 24 Compounds of Interest and Two Surrogates Analyzed by the Developed Primary HPLC-UV Method.7
Figure 2. HPLC Chromatograms of a Mixed Standard Containing 10 mg/L of 24 IM Compounds of Interest and Two Surrogates Analyzed by the Developed Secondary HPLC-UV Method..... 10
Figure 3. TIC for a Mixed Standard Containing 10 mg/L of 24 Compounds of Interest and Two Surrogates Analyzed by the Developed Confirmatory HPLC-MS Scan Mode Method. 10
Figure 4. Representative Separation of a Standard Solution of the 24 Target Compounds of Interest and Two Surrogates Using the MEKC Method. 12

LIST OF TABLES

Page

Table 1. Retention Times (min), MDLs and LDRs for the 24 Compounds of Interest and Two Surrogates, Determined in Direct-injection Water Samples ("Estimated"), Reagent Water Samples That Underwent SPE Pre-concentration, and Ottawa Sand Samples That Underwent SE, Analyzed by the Primary HPLC-UV Method. 9

Table 2. Retention Times (min), Ion Masses (m/z) and Identities Obtained for Mixed Standard Containing 24 Compounds of Interest and Two Surrogates Using the Developed HPLC-MS Scan Mode Method. 11

Table 3. Compound Recoveries (%) from Laboratory-spiked Reagent Water Samples Using Stacked SPE Cartridges for Extraction and Pre-concentration of the 24 Compounds of Interest and 1,2-DNB Surrogate. 14

Table 4. Recoveries (%) from Two Laboratory-spiked Soils Using Four Different 2-/3-Stage Ultrasonication Sequences. *24 Compounds of Interest and 1,2-DNB Surrogate.*..... 15

Table 5. Recoveries (%) from Pre-extraction Spiked Tissue MeOH Extracts, Following Chromatographic Treatment with Silica Gel for Matrix-related Analytical Interference Reduction. *24 Compounds of Interest, Two Surrogates, and Three Additional Ions.*16

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1.0 INTRODUCTION

No standard method currently exists for analyzing insensitive munitions (IM) compounds in environmental matrices (with or without concurrent legacy compounds). Lacking established methods, contract and research laboratories either do not measure IM compounds at all; quantify some but not all, using US Environmental Protection Agency (USEPA) Method 8330B developed for legacy compounds (leading to inaccuracies for certain IM compounds and degradation products (Felt et al., 2016)); or, use methods originally developed for neat materials with no proven performance metrics.

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2.0 OBJECTIVES

The objective of this project was to fulfill the requirements of SON ERSON-17-02 by developing new methods of extraction, pre-concentration, and analytical separation/quantitation of 17 legacy munition compounds included in USEPA Method 8330B and seven IM compounds, daughter products of IM, and other munition compounds absent from USEPA Method 8330B (nitroguanidine [NQ], 3-nitro-1,2,4-triazol-5-one [NTO], picric acid [PA], 2,4-dinitroanisole [DNAN], 2,4-dinitrophenol [2,4-DNP], 2-nitrophenol [2-NP], and 4-nitrophenol [4-NP]). The final product is a single standardized method for simultaneous analysis in environmental matrices, leading to cost savings with minimal increase in environmental monitoring and no change to existing sample collection procedures.

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3.0 TECHNICAL APPROACH

Currently accepted methods of analysis (high-performance liquid chromatography [HPLC], capillary electrophoresis [MEKC], and capillary electrophoresis [CE]) and extraction (solid phase extraction and solvent extraction) were modified for applicability to the proposed compounds of interest. New methods of extraction, pre-concentration, and analytical separation/quantitation of the proposed list were developed for simultaneous analysis of legacy and IM compounds in environmental matrices. The methods were verified in laboratory-spiked water, soil, and tissue samples. Stability studies were performed to investigate applicability of current extraction and analysis hold times. Inter-laboratory studies were performed using batch-spiked water and soil samples to investigate extraction and analytical method transfer from the originating laboratory.

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4.0 RESULTS AND DISCUSSION

4.1 ANALYTICAL METHODS

The HPLC-ultraviolet (UV) and -mass spectrometry (MS) methods developed under SERDP ER-2722 were modified from existing methods and established laboratory techniques, including previously developed (Russell et al., 2014) and currently used explosives analysis methods (USEPA 8330B, in-house IM methods). MEKC methods were developed as an alternative for analysis of samples with high concentrations of munitions compounds.

4.1.1 Primary HPLC-UV Method

The primary HPLC-UV method for simultaneous separation and quantitation of legacy and IM compounds was developed by adapting Method 8330B and previously developed ERDC methods. Method development was carried out using Phenomenex Synergi 4µm Hydro-RP, 80Å, 250 x 4.6 mm HPLC columns. An optional Phenomenex SecurityGuard AQ C18 pre-column guard cartridge was included, which could extend column lifetime, especially when analyzing samples containing complex environmental matrices. An example chromatogram is shown in Figure 1. Chromatographic peaks were identified (using individual reference standards) for all 24 legacy and IM compounds and two surrogates (1,2-dinitrobenzene [1,2-DNB] and ortho-nitrobenzoic acid [o-NBA]). Typical retention times (min), estimated method detection limits (MDLs), verified MDLs (reagent water, Ottawa sand), and linear dynamic range (LDRs) are listed in Table 1.

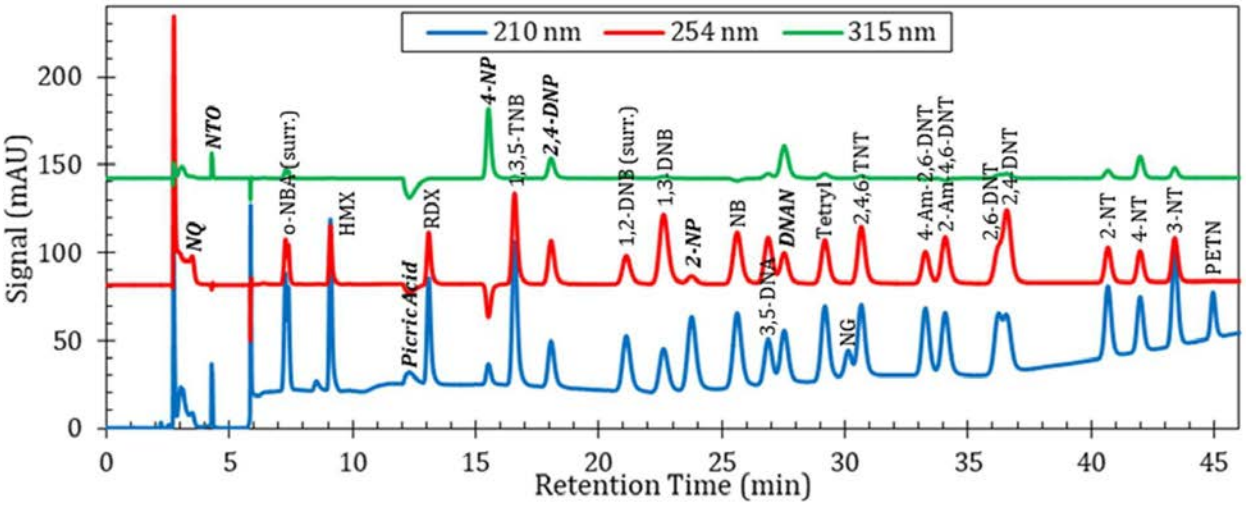


Figure 1. HPLC Chromatograms of a Mixed Standard Containing 5 mg/L of 24 Compounds of Interest and Two Surrogates Analyzed by the Developed Primary HPLC-UV Method.

IM compound and degradation product names are in bold italics.

4.1.2 Secondary HPLC-UV Method

A secondary HPLC-UV method was developed for confirmatory analysis, which was carried out using Restek Pinnacle II Biphenyl, 5 µm, 150 X 4.6 mm columns. Again, an optional Phenomenex SecurityGuard AQ C18 pre-column guard cartridge was included to protect the analytical column from concomitant sample matrix components. An example chromatogram is shown in Figure 2. Peaks were identified (using individual reference standards) for all 24 legacy and IM compounds and two surrogates.

4.1.3 HPLC-MS Method

An HPLC-MS scan mode method was developed using an Agilent 6120B single quadropole (SQ) system equipped with an atmospheric-pressure chemical ionization (APCI) source for confirmatory analysis of the 24 compounds of interest and two surrogates. Chromatographic separation was effected by the primary HPLC-UV method. An example MS total ion chromatogram (TIC) is shown in Figure 3. Several ion masses were observed for each of the 26 compounds analyzed (shown in Table 2), with the exception of nitroglycerine (NG) and 2-/3-/4-nitrotoluene (2-/3-/4-NT), which did not produce any detectable MS signal under the developed spray chamber and detector conditions, and 1,3-dinitrobenzene (1,3-DNB), for which just a single ion was observed. Ions were identified where possible. Observed ions are listed in order of abundance for each compound.

Table 1. Retention Times (min), MDLs and LDRs for the 24 Compounds of Interest and Two Surrogates, Determined in Direct-injection Water Samples ("Estimated"), Reagent Water Samples That Underwent SPE Pre-concentration, and Ottawa Sand Samples That Underwent SE, Analyzed by the Primary HPLC-UV Method.

Peak #	Compound	Retention Time (min)	Estimated MDL (n=10 at 40 µg/L)	MDL in Reagent Water (n=10 at 40 µg/L)	MDL in Ottawa Sand (n=10 at 4 mg/kg)	LDR (mg/L)
1	NQ	3.51	16	12	132	≥80
2	NTO (210nm)	4.29	6	20	63	≥50
2	NTO (315nm)	4.29	9	15	41	≥60
3	o-NBA (surrogate)	7.45	12	49	16	≥80
4	HMX	8.96	6	11	59	≥70
5	RDX	12.81	6	9	33	≥70†
6	PA (210nm)	14.64	10	23	194	≥70†
6	PA (315nm)	14.58	12	11	72	≥80‡
7	4-NP	15.31	10	7	47	≥80
8	1,3,5-TNB	16.17	11	13	57	≥80
9	2,4-DNP	17.86	9	22	221	≥80
10	1,2-DNB (surrogate)	20.35	15	16	119	≥70
11	1,3-DNB	21.80	7	12	47	≥80
12	2-NP	22.91	12	14	63	≥80
13	NB	25.42	9	10	87	≥80
14	3,5-DNA (210nm)	26.16	13	16	151	≥70
14	3,5-DNA (254nm)	25.93	13	13	19	≥70
15	DNAN	26.89	11	16	79	≥70
16	Tetryl	28.43	12	8	104	≥70
17	NG	29.30	17	27	253	≥70
18	2,4,6-TNT	30.06	15	11	107	≥70
19	4-Am-2,6-DNT	32.60	11	17	128	≥80
20	2-Am-4,6-DNT	33.43	11	22	125	≥80
21	2,6-DNT	35.25	14	37	141	≥70
22	2,4-DNT	35.57	7	12	35	≥80
23	2-NT	40.18	13	14	54	≥80
24	4-NT	41.42	12	16	100	≥80
25	3-NT	42.84	14	21	42	≥80
26	PETN	44.38	16	22	173	≥80

†co-elute at concentrations >30 mg/L; ‡RDX not detected appreciably at 315 nm

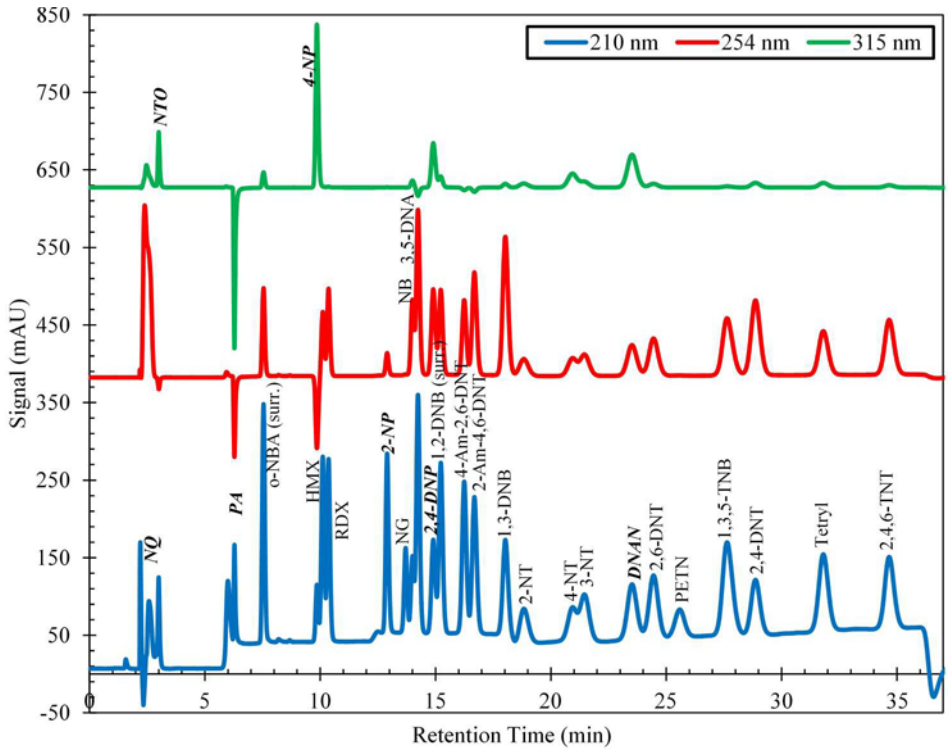


Figure 2. HPLC Chromatograms of a Mixed Standard Containing 10 mg/L of 24 IM Compounds of Interest and Two Surrogates Analyzed by the Developed Secondary HPLC-UV Method.

IM compound and degradation product names are in bold italics.

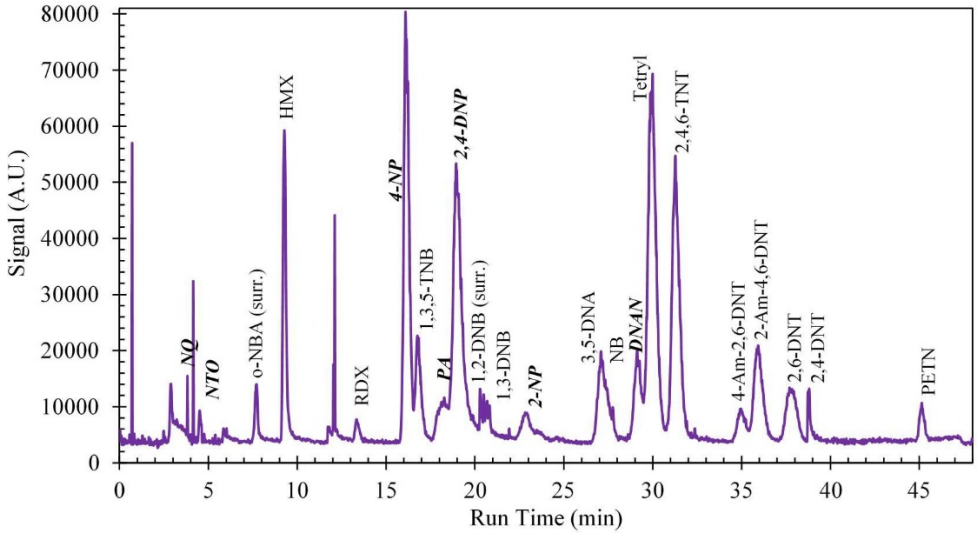


Figure 3. TIC for a Mixed Standard Containing 10 mg/L of 24 Compounds of Interest and Two Surrogates Analyzed by the Developed Confirmatory HPLC-MS Scan Mode Method.

IM compound and degradation product names are in bold italics.

Table 2. Retention Times (min), Ion Masses (m/z) and Identities Obtained for Mixed Standard Containing 24 Compounds of Interest and Two Surrogates Using the Developed HPLC-MS Scan Mode Method.

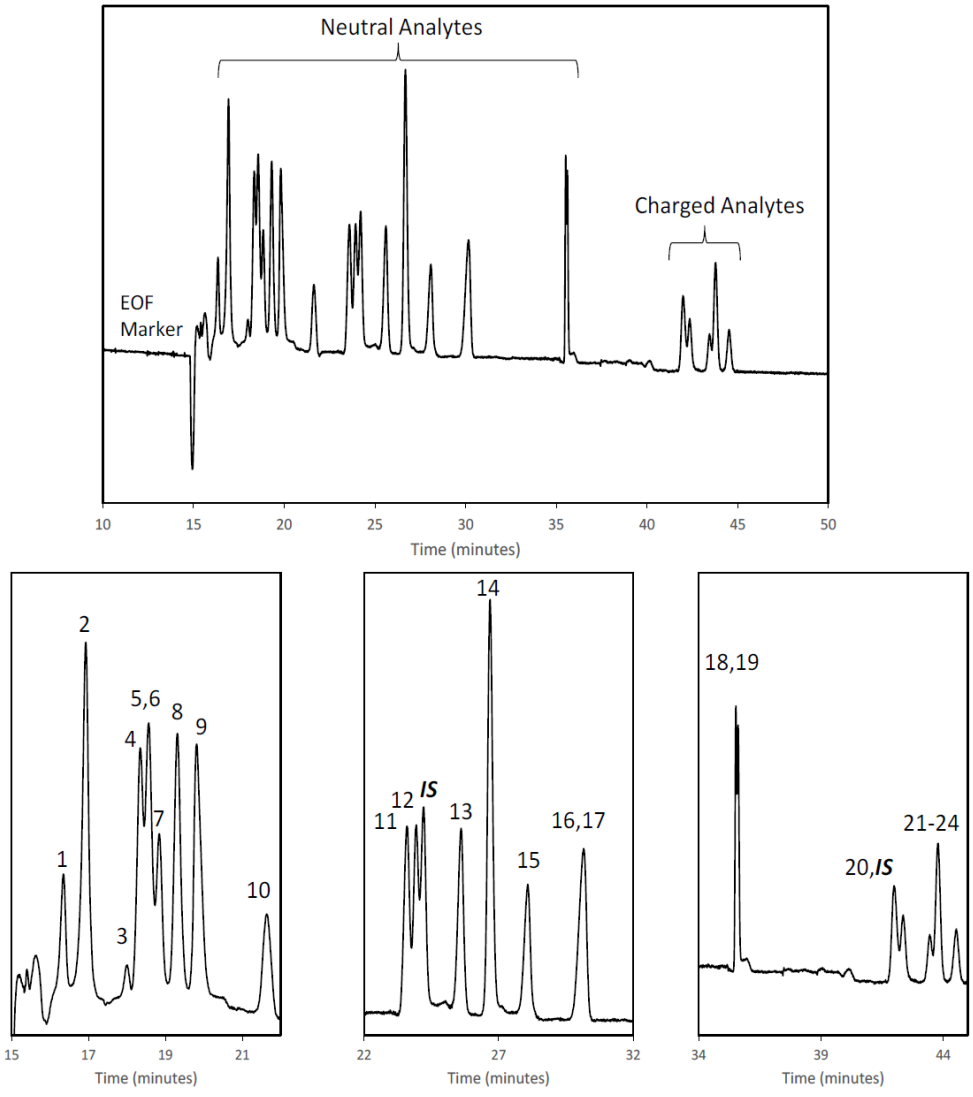
Retention Time (min)	Compound	Ion Mass (m/z)	Ion Identity
3.78	NQ	203.6	
		103.0	[M]-H
4.50	NTO	129.0	[M]-H
		55.0	
7.64	o-NBA (surrogate)	122.0	
		167.0	[M]-H
9.21	HMX	341.0	[M]-H+FA
		147.0	[M]/2-H
13.40	RDX	267.0	[M]-H+FA
		335.0	[M]-H+TFA
16.00	4-NP	108.0	
		138.0	[M]-H
16.80	1,3,5-TNB	213.0	[M]-H
		183.0	
18.20	PA	228.0	[M]-H
		211.9	
18.80	2,4-DNP	183.0	[M]-H
		153.0	
22.70	1,2-DNB (surrogate)	138.0	
		168.0	[M]-H
23.55	1,3-DNB	168.0	[M]-H
24.60	2-NP	138.0	[M]-H
		122.0	[M]-H_2O-H
27.10	3,5-DNA	182.0	[M]-H
		138.0	
27.80	NB	182.0	[M]-H+HOAc
		153.0	
29.00	DNAN	183.0	[M]-CH_3
		152.9	
30.00	Tetryl	241.0	[M]-H+NO^-*2
		288.0	[M]-H
	NG	226.1	[M]-H (not obsv.)
31.30	2,4,6-TNT	226.0	[M]-H
		210.0	[M]-H_2O-H
35.10	4-Am-2,6-DNT	196.9	[M]-H
		167.0	
35.95	2-Am-4,6-DNT	196.0	[M]-H
		179.9	[M]-H_2O-H
37.54	2,6-DNT	152.0	[M]-30*
		122.1	
37.87	2,4-DNT	165.0	[M]-H_2O-H
		181.0	[M]-H
42.00 - 44.50	2-NT/3-NT/4-NT	136.1	[M]-H (not obsv.)
45.10	PETN	62.0	NO^-*3
		270.9	

HOAc: acetic acid.

**Avci, et al., 2017; Gapeev, et al., 2003; Jiang, 2010; Kinghorn, et al., 2005; Thurman, et al., 2012; Xu, et al., 2004.*

4.1.4 MEKC Method

A CE based separation method was developed to as an alternative analysis of munition compounds in environmental matrices. MEKC separation of the 24 compounds of interest and two surrogates in a standard solution was achieved through careful development of two background electrolyte solutions and sample loading procedure. Example electropherograms are shown in Figure 4. Peaks were identified using individual reference standards. Before extracts from water, soil, and tissue could be analyzed, extracts were diluted with water to reduce analytical interference due to Methanol (MeOH). However, large dilutions resulted in poor detection of compounds at lower concentrations due to relatively high MDLs. Therefore, it was concluded that analysis of munition compounds using this method would only be recommended in samples containing high concentrations of legacy and/or IM compounds.



	Analyte
1	NQ
2	1,3,5-TNB
3	HMX
4	NG
5	2,4,6-TNT
6	PETN
7	RDX
8	1,3-DNB
9	Tetryl
10	NB
11	2,4-DNT
12	2,4-DNAN
IS	***1,2-DNB***
13	2,6-DNT
14	3,5-DNA
15	4-NT
16	2-NT
17	3-NT
18	2AM46DNT
19	4AM26DNT
20	PA
IS	***o-NBA***
21	2,4-DNP
22	4NP
23	2NP
24	NTO

Figure 4. Representative Separation of a Standard Solution of the 24 Target Compounds of Interest and Two Surrogates Using the MEKC Method.

Sample concentration was 20 mg/L.

4.2 EXTRACTION METHODS FOR SAMPLES ANALYZED BY HPLC-UV AND HPLC-MS

4.2.1 Method for Preparation of Waters for Direct-Injection Analysis

Water samples known or suspected to contain the compounds of interest at levels detectable without extraction/pre-concentration can be analyzed by direct injection using the developed analytical HPLC-UV/- MS methods. In order to ensure the accurate analysis of ionic species (including NTO), an acidification step was added for direct-injection water samples, for final acid concentration of 0.5% (v/v) and final solvent ratio of 50/50 MeOH/Water.

4.2.2 SPE Method for Waters

The solid phase extraction (SPE) method developed under SERDP ER-2722 involved the sequential stacking of three different commercially-available SPE cartridges: 1) Strata X (polymeric reverse phase, 500 mg/6 mL, Phenomenex), 2) Strata X-A (polymeric strong anion exchange, 500 mg/6 mL, Phenomenex), and 3) Supelclean™ ENVI-Carb™ (granular activated carbon, GAC, 500 mg/6 mL, Supelco). Recoveries for water samples that underwent extraction/pre-concentration using this SPE option (B) or different double-/triple-stacked options are shown in Table 3.

Table 3. Compound Recoveries (%) from Laboratory-spiked Reagent Water Samples Using Stacked SPE Cartridges for Extraction and Pre-concentration of the 24 Compounds of Interest and 1,2-DNB Surrogate.

Compound	Recoveries (%)					
	A PRP500 | PSA500 | GAC250	B PRP500 | PSA500 | GAC500	C C181G | PSA500 | GAC250	D C181G | PSA500 | GAC500	E PSA500 | C181G | GAC250	F PSA500 | GAC250
NQ	2	19	48	4	43	38
NTO (210nm)	107	98	109	103	107	111
HMX	97	95	117	102	113	110
RDX	91	92	114	99	107	109
PA (210nm)	94	86	96	67	102	101
4-NP	87	90	110	97	103	104
1,3,5-TNB	93	91	113	100	106	109
2,4-DNP	93	94	110	93	112	115
1,2-DNB (surrogate)	90	88	101	97	95	98
1,3-DNB	90	87	113	97	106	109
2-NP	76	76	95	85	91	91
NB	92	90	114	100	107	109
3,5-DNA (254nm)	79	84	111	80	105	107
DNAN	77	84	106	93	102	105
Tetryl	94	88	109	96	71	81
NG	94	103	114	101	184	108
2,4,6-TNT	93	89	113	100	96	99
4-Am-2,6-DNT	93	92	112	100	105	108
2-Am-4,6-DNT	95	92	113	99	106	108
2,6-DNT	85	86	115	99	109	113
2,4-DNT	97	89	105	96	99	95
2-NT	74	75	108	71	101	105
4-NT	78	77	109	77	102	104
3-NT	77	76	112	74	101	105
PETN	89	89	110	98	101	105

Bold, italicized are IM compounds and degradation products.
Green: 75-125%; Light Green: 57-74% or 126-135%; Red: <57% or >135% (DoD QSM Ver5.2 for Waters – Lowest LCL: MNX, 57%; Highest UCL: HMX, 135%)

4.2.3 SE Method for Soils

The solvent extraction (SE) method developed under SERDP ER-2722 for soils was a two-stage extraction procedure, modified from the current USEPA Method 8330B. Sample collection, storage, drying, and grinding procedures were not modified. Samples were extracted using a two-stage ultrasonication procedure, including a 6 h MeOH extraction followed by a 14 h MeOH/Water extraction. Recoveries for water samples that under- went extraction using this SE method or using different two-/three-stage options are shown in Table 4.

Several multi-stage options were shown to be effective for the majority of compounds.

Table 4. Recoveries (%) from Two Laboratory-spiked Soils Using Four Different 2-/3-Stage Ultrasonication Sequences. *24 Compounds of Interest and 1,2-DNB Surrogate.*

Compound	Recoveries (%)															
	Yuma								ASTM Fat Clay							
	A		B		C		D		A		B		C		D	
	Average (n=3)	Std Dev	Average (n=3)	Std Dev	Average (n=3)	Std Dev	Average (n=3)	Std Dev	Average (n=3)	Std Dev	Average (n=3)	Std Dev	Average (n=3)	Std Dev	Average (n=3)	Std Dev
NQ	109	7	106	2	122	4	115	4	101	7	100	5	116	3	113	5
NTO (210nm)	103	3	88	2	111	5	98	1	90	1	92	2	118	1	101	3
HMX	86	4	84	3	105	2	93	2	66	1	65	1	92	2	75	2
RDX	92	3	89	2	111	2	98	<1	72	1	72	1	101	1	82	2
PA (210nm)	117	6	107	4	127	6	123	3	106	5	103	7	119	5	120	2
4-NP	119	5	110	3	132	10	125	2	115	6	112	3	124	1	125	1
1,3,5-TNB	120	5	111	1	130	7	127	2	114	4	103	1	110	1	124	4
2,4-DNP	102	4	98	1	117	3	105	1	92	2	91	3	110	1	100	3
1,2-DNB (surrogate)	122	7	116	7	134	16	124	5	121	10	115	7	125	3	125	1
1,3-DNB	121	4	114	1	134	9	127	2	119	4	115	2	125	1	129	5
2-NP	85	5	81	4	99	6	93	1	89	2	88	2	102	3	93	5
NB	122	4	116	1	135	9	128	2	118	5	113	2	122	<0	127	5
3,5-DNA (254nm)	75	3	72	4	84	9	79	2	96	5	93	1	101	1	103	3
DNAN	120	4	114	2	133	7	129	1	117	4	110	2	119	2	127	4
Tetryl	93	11	93	5	118	6	113	6	99	4	98	2	111	3	111	1
NG	114	11	106	8	125	17	118	13	106	7	108	9	116	10	114	5
2,4,6-TNT	128	5	119	2	138	12	130	5	116	2	112	4	119	2	124	3
4-Am-2,6-DNT	126	4	118	1	137	9	130	2	121	4	117	4	126	1	127	2
2-Am-4,6-DNT	123	4	117	1	136	9	129	2	119	4	113	2	122	1	126	2
2,6-DNT	116	11	109	6	132	4	121	3	118	4	109	6	123	5	124	4
2,4-DNT	123	2	115	2	135	8	127	1	114	4	112	3	122	2	125	3
2-NT	88	5	83	3	98	9	92	2	105	4	101	1	110	4	111	3
4-NT	97	2	93	3	110	10	104	1	110	6	105	3	114	2	117	5
3-NT	94	4	88	4	101	10	97	1	103	6	101	2	108	<1	111	1
PETN	120	7	113	1	130	11	123	2	117	5	115	3	123	1	126	3

A: 6-h MeOH – 14-h MeOH/Water; B: 1) 6-h MeOH – 14-h Water; C: 3-h MeOH – 3-h Water – 14-h Water; D: 3-h MeOH – 3-h MeOH – 14-h Water.

Green: 75-125%; Light Green: 64-74% or 126-135%; Red: <64% or >135%
(DoD QSM Ver5.2 for Solids – Lowest LCL: 4-Am-2,6-DNT, 64%; Highest UCL: Tetryl, 135%)

4.2.4 SE Method for Tissues and Interference Reduction Method for Tissue Extracts

The SE method developed under SERDP ER-2722 for tissues was a single 18-h ultrasonic extraction procedure, modified from the current USEPA Method 8330B. Without lyophilization, homogenized samples were extracted using a single 18-h ultrasonication with MeOH. The tissue interference reduction method developed under SERDP ER-2722 was a modified chromatographic method (Larson, et al, 1999). Other common organic laboratory procedures were tested, including storage at low temperature or acidification to induce complete precipitation (observed for some tissue types, especially earthworm), followed by filtration. However, these methods were not as effective as chromatographic methods. Initial tests were performed using either neutral alumina or

florisil, and later tests included combinations of these, basic alumina, or silica. Several of the treatment options were effective at reducing the analytical interferences observed for the tissues. However, the silica gel option proved most effective for the majority of compounds in the majority of tissue types (Table 5).

Table 5. Recoveries (%) from Pre-extraction Spiked Tissue MeOH Extracts, Following Chromatographic Treatment with Silica Gel for Matrix-related Analytical Interference Reduction. *24 Compounds of Interest, Two Surrogates, and Three Additional Ions.*

Compound	Recoveries (%)			
	Fathead Minnow	Polychaete Worm	Earthworm	Ryegrass
NQ	113	73	86	68
NTO (210)	8477	5318	4503	149
NTO (315)	87	113	98	133
o-NBA (surrogate)	101	82	111	67
HMX	81	66	79	99
RDX	86	66	93	85
PA (210)	79	73	37	79
PA (315)	66	66	68	71
4-NP	83	71	72	84
1,3,5-TNB	84	52	3670	83
2,4-DNP	110	72	81	93
1,2-DNB (surrogate)	93	72	82	73
1,3-DNB	76	65	65	86
2-NP	105	81	74	94
NB	84	94	83	90
3,5-DNA (210)	183	139	73	90
3,5-DNA (254)	69	75	80	73
DNAN	123	72	86	76
Tetryl	16	6	4	62
NG	116	132	87	125
2,4,6-TNT	119	100	80	80
4-Am-2,6-DNT	78	57	74	88
2-Am-4,6-DNT	102	67	88	85
2,6-DNT	110	71	79	85
2,4-DNT	108	67	69	88
2-NT	129	101	68	89
4-NT	95	73	69	80
3-NT	64	64	68	86
PETN	109	74	67	91

Green: 75-125%; Light Green: 64-74% or 126-135%; Red: <64% or >135%
(DoD QSM Ver5.2 for Solids – Lowest LCL: 4-Am-2,6-DNT, 64%; Highest UCL: Tetryl, 135%)

4.3 STABILITY STUDIES & INTER-LABORATORY BATCH ANALYSIS STUDIES

Photo-/thermal stability was investigated for each of the 24 compounds of interest and two surrogates by testing the current pre-/post-extraction hold times for water and soils, which are 7 and 14 days for extraction, respectively, and 40 days for analysis for munition compound determinations performed using USEPA Method 8330B. Extraction/analysis hold times were not previously reported for tissues in Method 8330B. Overall, the majority of compounds were stable during the pre-extraction and post-extraction hold times. For both water and soil, however, hold times might need to be investigated further for the IM compounds NQ and NTO; furthermore, some legacy compounds were observed to have possible stability issues, including HMX, RDX, and the three NTs. These may also warrant further investigation.

An inter-laboratory batch study was carried out at the US Army Corps of Engineers, Engineer Research and Development Center-Environmental Laboratory and the US Army Corps of Engineers-Cold Regions Research and Engineering Laboratory on five water sources (reagent, tap, river, sea, and ground) and six soil sources (Aberdeen, Jefferson, Memphis, Riley, Yuma, and American Society for Testing and Materials fat clay). High-level direct-injection water samples and low-level water samples for SPE extraction/pre-concentration were prepared, along with high-level soils. Each laboratory received identical protocols for sample extraction, analytical sample preparation, and analysis. Overall, the majority of compounds were recovered at levels similar to those observed during SPE and SE method development. Some differences were observed at each laboratory, but results were in general agreement for the majority of compounds in the majority of water and soil matrices.

In addition, during cross-laboratory studies using the direct injection method for waters, much lower recoveries for NTO, and in some cases o-NBA surrogate, were observed for field water samples than for reagent water. Therefore, further experiments were carried out in which the pH of samples to be analyzed by direct injection was adjusted so that the final acid concentration was the same as in SPE extracted/pre-concentrated samples. Acidification of the direct-injection water samples was effective to bring NTO recoveries within current DoD quality systems manual (QSM) limits for water samples analyzed by USEPA Method 8330B (57- 135%).

4.4 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

The development of methods to simultaneously analyze legacy and IM compounds is necessary to enable monitoring of each component at firing ranges, demilitarization and manufacturing facilities, and environmental sites, where munition compounds are tested, produced, and detected (Felt et al., 2013; Walsh et al., 2014). New methods for extraction and analysis of the legacy and IM compounds of interest were developed. The new primary HPLC method reduces total analytical run time by approximately 25% (48 min) versus the use of separate legacy and IM methods (62 min). Simultaneous extraction and preparation of one rather than two sets of analytical samples could reduce labor and supply costs by 50%. Products of this work will assist in conducting fate and transport studies for IM compounds by providing a standardized method for quantitation of concurrent IM and legacy materials. This is needed to determine long-term environmental impacts.