Environmental Security Technology Certification Program

Field Demonstration Report
Applied Innovative Technologies for Characterization of Nitrocellulose- and Nitroglycerine Contaminated Buildings and Soils

Badger Army Ammunition Plant
Baraboo, Wisconsin

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Revision 1

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LIST OF ACRONYMS

BAAAP	Badger Army Ammunition Plant
°C	degrees Celsius
cm	centimeter
CRREL	Cold Regions Research and Engineering Laboratory
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
EJM	Expansion Joint Material
F	Fahrenheit
g	gram
GC	gas chromatograph(y)
GC/TID	gas chromatograph(y) with thermionic ionization detection
HPLC	high-performance liquid chromatography
LCS	laboratory control sample
MCAWW	Methods for the Chemical Analysis of Wastewater
MS	matrix spike sample
MSD	matrix spike duplicate sample
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
µL	microliter
mL	milliliter
mm	millimeter
NC	nitrocellulose
NG	nitroglycerine
nm	nanometer
psi	pounds per square inch
RDX	Royal Demolition Explosive, cyclotrimethylenetrinitramine
SRI	SRI Instruments, Inc.
SS	stainless steel
STL	Severn Trent Laboratories, Inc.
TDL	Technology Development Laboratory
TID	thermionic ionization detector
UXO	unexploded ordinance
SUXOSO	Shaw UXO Safety Officer

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Abstract

A field demonstration was conducted to assess the performance of three field analytical methodologies for the presence and/or concentration of nitrocellulose (NC) and nitroglycerine (NG) in soils as well as wood and concrete building materials collected at Badger Army Ammunition Plant (BAAAP) in Baraboo, WI. Acetone extracts of soils, concrete material, and wood samples were analyzed by each of the on-site methods and results compared to off-site laboratory analysis using high performance liquid chromatography (HPLC) with EPA SW-846 Method 8330 for NG and MCWAA Method 353.2 for NC, an automated colorimetric method. The field methods evaluated included EXPRAY™ and DROPEX^{Plus} colorimetric test kits (total NC/NG), CRREL RDX colorimetric test (proposed EPA SW-846 8510) (total NC/NG) and GC/TID field gas chromatograph (NG only). Accuracy of the qualitative methods was evaluated based on percent false positive / false negatives. The quantitative on-site methods were evaluated using linear regression analysis and relative percent difference (RPD) comparison criteria. The primary use of these analytical methods would be for characterization of explosive–contaminated buildings. Adequate characterization could allow many buildings to be left in place resulting in substantial cost avoidance and expedited transfer of properties out of Department of Defense (DOD) control. Findings from the field demonstration are presented.

FIELD DEMONSTRATION REPORT
APPLIED INNOVATED TECHNOLOGY FOR CHARACTERIZATION OF NITROCELLULOSE- AND NITROGLYCERINE CONTAMINATED BUILDINGS AND SOILS
BADGER ARMY AMMUNITION PLANT
BARABOO, WISCONSIN

SHAW ENVIRONMENTAL & INFRASTRUCTURE, INC.

January 5, 2007

1.0 INTRODUCTION

1.1 Background

Badger Army Ammunition Plant (BAAAP) is one of many inactive Army ammunition plants currently under the control of the Department of Defense (DOD) with transitioning missions in place. These plants are in varying stages of transfer out of DOD control. In order to transfer these properties, DOD must characterize and decontaminate the properties to a level protective of human health and the environment. To accomplish this task, many buildings used in the production, loading, handling, and storage of explosives will have to be demolished or characterized and decontaminated. BAAAP alone has more than 1,400 buildings on the installation that have to be addressed. The contaminants of concern associated with the buildings at BAAAP include nitrocellulose (NC), nitroglycerine (NG), dinitrotoluene (DNT), and common environmental compounds such as asbestos-containing material (ACM), solvents, and metals.

1.2 Study Objectives

The objectives for the Environmental Security Technology Certification Program (ESTCP) demonstration are to evaluate and document the performance of three distinct candidate experimental fields analytical methods for detecting and quantifying NC and NG associated with structural concrete pads, underlying soils, and structural building materials such as framing timbers and wallboard. With adequate characterization, many buildings could be safely left in place or building materials salvaged resulting in substantial cost reduction and the ability to transfer the properties out of DoD control more quickly**.** A secondary purpose for some of the demonstration concrete and soil samples was to provide NG and NC data for specific locations awaiting demolition safety clearance. The technologies evaluated in the field demonstration included: DROPEX^{Plus}/EXPRAY™ colorimetric indicator, gas chromatography with thermionic ionization detection (GC-TID), and the Cold Regions Research and Engineering Laboratory (CRREL) Royal Demolition Explosive (RDX) colorimetric field screening method.

1.3 Regulatory Issues

There are no regulatory drivers per se governing this project. Nor are there state or federal environmental standards for NC and NG cleanup. There is a site-specific Wisconsin Department of Natural Resources (WDNR) cleanup criterion for NG in the area soils of 3.6 milligrams per kilogram (mg/kg) (EPA & WDNR, 1988). There is no DoD standard for NC and NG residual contamination; however, safety concerns related to the explosive nature of these materials provide the driver for this investigation.

The Department of Army Industrial Operations Command Pamphlet IOCP-385-1 (1997) defined building explosives contamination as follows:

- 1X – (X) level of contamination. This level applies to articles, equipment or buildings subjected to only routine, after-use cleaning. Substantial contamination (explosive residue) continues to exist.

- 3X - (XXX) level of contamination. This level applies where cleaning has removed surface contamination, but significant amounts (enough to present an explosive safety hazard) may remain in less obvious places. The article, equipment or building is safe for its intended purpose.

- 5X - (XXXXX) level of contamination. This level applies when no significant amounts (enough to present an explosive safety hazard) of contaminants remain. The article, equipment or building does not pose an explosive hazard and is safe for welding, drilling, sawing, etc., and sale to the general public.

- 0 – (zero) level of contamination. This level applies when the articles, equipment or buildings were never contaminated,

Figure 1-1 BAAAP Building with XXX (3X) Classification

The 1X level of contamination is not clearly defined, but it is interpreted to mean that the potential for substantial contamination exists and there is also the potential of an explosive safety hazard. At BAAAP alone, over 900 of the buildings have been classified as 3X. Pamphlet IOCP-385-1 further states that up through the early 1990s, each time production ceased at government-owned explosive production facilities, managers assumed that they would need facilities and equipment in the future and preserved them. The contamination status decisions on

buildings and equipment were simple. Classifiers marked almost everything as 3X (see Figure 1-1), even if uncontaminated. This was the simplest, most economical course when keeping everything for its original purpose. In the 1990s, the assumption changed (that the Army will always keep the production facilities), and Army began the process of transferring property and equipment. In 2004, Plexus Scientific surveyed over 800 buildings and either confirmed or reclassified these structures to 1X, 3X, or 5X.

The 1X, 3X, 5X and 0 system of building classification is still visible on markings at the site, but it is no longer used and the classification has been replaced with "Safe and "Hazardous" terminology as defined by Army documentation: TB 700-4 and DODI 4140.62.

1.4 Stakeholder/End-User Issues

By verifying these technologies, stakeholders will have additional tools that will aid in the decision-making process for transfer of property at BAAAP. The demonstration, if successful, will help streamline the property disposal process.

1.5 Previous Testing

A previous ESTCP demonstration was performed between April 28, 2002 and May 13, 2002. The 2002 demonstration of candidate field test methods included Raman spectroscopy, EXPRAY™ colorimetric indicator, and the CRREL RDX colorimetric field screening method were used to test for the presence and/or concentration of NC or NG in soil samples and concrete slabs. Attempts were made to compare the results from these field measurements to laboratory analyses of NC and NG in the same materials to evaluate the reliability of the field screening and analytical methods for identifying and quantifying NC and NG in buildings and soils. Raman spectroscopy was also used for identifying the presence of other organic compounds used in the manufacturing processes conducted in the study area.

The results of the previous demonstration and lessons learned were presented in the *Phase I Final Report, Rocket Paste Production Building Investigation, Badger Army Ammunition Plant, dated June 24, 2003, and published by Stone & Webster, Inc.* (Stone & Webster, 2003). Due to a number of factors, including the lack of energetic compounds in the buildings used for the demonstration, attempts at validation of the field methods for detection of these materials were inconclusive.

This Demonstration will apply lessons learned during the BAAAP 2002 demonstration to obtain results that would allow validation of the field analytical techniques. One of the major findings during the previous demonstration was that the building(s) selected for the demonstration must have sufficient residual energetic material in place to adequately apply the test methods. The buildings selected for this demonstration were used directly in the production or use of energetic materials and present a variety of potential contamination sites and locations that may likely serve as specific accumulators of contamination residue.

Prior to the field demonstration, a bench scale study of the experimental technologies was conducted by Shaw Environmental & Infrastructure, Inc. (Shaw) and results were described in a bench test report (Shaw, 2005). The technologies evaluated at the bench scale level included Raman spectroscopy, DROPEX^{Plus}/EXPRAY™ colorimetric indicator, GC-TID, and the CRREL RDX colorimetric field screening method. Uncontaminated soil and building materials (concrete, wood, and wallboard) from the BAAAP site were spiked with known amounts of NG,

NC and NC/NG combined at specified levels. Splits of these samples were submitted to Severn Trent Laboratories, Inc. (STL) in Sacramento, CA for analysis by reference methods for comparison. The results of the Bench Scale tests were presented in the *Draft BAAAP Bench-Scale Treatability Report for Applied Innovative Technologies for Characterization of Nitrocellulose and Nitroglycerine Contaminated Buildings and Soils, dated November 2005* (Shaw Bench Test, 2005). Results from the bench scale tests were used to optimize the testing and analysis processes for the subsequent field demonstration.

2.0 DEMONSTRATION APPROACH

2.1 Demonstration Site / Facility Description

Shaw Environmental & Infrastructure, Inc. (Shaw) as the prime contractor to the U.S. Army Corps of Engineers Omaha District (USACE) performed the field demonstration testing for the U.S. Department of Defense Environmental Security Technology Certification Program (ESTCP). The demonstration took place at BAAAP, located on 7,354 acres of land in Sauk County, Wisconsin. Laboratory personnel from the Shaw Technology Development Laboratory (TDL) located in Knoxville, Tennessee conducted the field analysis on soil, concrete and wood samples collected from and around production buildings as selected on site from December 1, 2005 to December 19, 2005. A description of the on-site analytical methods employed and a comparison of results and method performance considerations are presented in this report to compare qualitative and quantitative field analysis results with the laboratory reference methods results obtained for NG and NC and to determine if they can be used wholly or partially in lieu of conventional demolition, removal and clearance using the laboratory reference methods. All testing was conducted in general accordance with the ESTCP Demonstration Plan, April 28, 2005 Revision 2, Applied Innovative Technologies for Characterization of Nitrocellulose and Nitroglycerine Contaminated Buildings and Soils, Badger Army Ammunition Plant, Baraboo, Wisconsin (Shaw Work Plan, 2005). Exceptions to the work plan were as follows: no Asbestos Containing Material (ACM) was tested due to safety issues related to crushing of ACM and Raman spectroscopy was not used due to safety issues related to heat generation noted during the bench scale testing.

Figure 2-1 BAAAP Shaw Lab Trailer Location on Site

A Shaw 28 foot mini- mobile lab trailer was delivered to the BAAAP site on November 29, 2005 for the 2 week ESTCP demonstration. The trailer was located on site at the end of a short dead-

end road extending north from the main gate road off of Hwy 12 and was one mile east of Hwy 12. It was just east of a row of five production buildings and was bound by field to the north and further east. The trailer was powered by a Wagner diesel powered 100 (kilovolt-amp) KVA generator with a 240 Volt single phase output supplied by a local equipment rental company. The trailer came equipped with a fume hood and small refrigerator. The trailer set-up is shown in Figures 2-1, 2-2, and 2-3

Figure 2-2 Shaw Lab Trailer and Generator On-site

Figure 2-3 Testing Inside Lab Trailer

Additional instrumentation and testing equipment shipped to the site by Shaw Lab personnel included a drying oven, a bench top shaker table, an analytical balance, a SRI Instruments, Inc. (SRI) portable field GC/TID, and a HACH DR 2010 portable spectrophotometer. Miscellaneous lab and sampling supplies were either purchased locally or ordered and delivered from a laboratory supply company.

An onsite concrete bunker located 100 yards from the mobile lab was used for sample storage and breaking concrete cores. Samples were secured inside the bunker during the demonstration and prior to testing. Temperatures inside the bunker ranged from minus 10 to 20° F. Outside and inside the bunker is shown in the pictures below, Figures 2-4 and 2-5.

Figure 2-4 BAAAP Storage Bunker

Figure 2-5 Wood Samples Inside Bunker

2.2 Demonstration Objectives

The purpose of the demonstration is to evaluate the reliability of field technologies for NC and NG detection in building materials and soil. The technology verification will result in building characterization procedures that may benefit many U.S. Army ammunition plants with similar explosive materials. The implementation of these procedures may also result in substantial savings over conventional remedial investigation techniques of explosive-contaminated buildings. The objectives of the study are as follows:

- Compound Identification: Compare the accuracy, feasibility, strengths, and weaknesses of on-site field instrumental and analytical techniques for identifying and measuring NC and NG in or on building materials, foundations and soils.

- Compound Quantitation: Evaluate field data obtained for NC and NG using the quantitative CRREL RDX method and the reference laboratory Methods for the Chemical Analysis of Wastewater (MCAWW) 353.2 for NC and (EPA) SW-846 Method 8330 method for NG using samples of soil, concrete and wood collected at the BAAAP site.

- Compound Quantitation: Evaluate the repeatability of the quantitative analytical results between the ESTCP demonstration methods for NG detection (CRREL RDX method, EPA SW-846 Method 8330, and GC/TID).

- Evaluate the repeatability of qualitative NC detection results of the DROPEX^{Plus} and EXPRAY™ screening methods and quantitative testing using MCAWW 353.2 for NC (i.e., determine the likelihood of false positive or false negative results from the screening methods versus the laboratory quantitative analytical results).

- Evaluate the repeatability of qualitative NG detection results between the DROPEX^{Plus} and EXPRAY™ screening methods and quantitative testing using U.S. Environmental Protection Agency (EPA) SW-846 Method 8330 and gas chromatography (GC)/thermionic ionization detector (TID) for NG (i.e., determine the likelihood of false positive or false negative results from the screening methods versus the quantitative analytical results).

- Evaluate the repeatability of quantitative analytical results between the ESTCP demonstration methods for NC detection (CRREL RDX method and the MCAWW 353.2 method).

2.3 Testing Design and Description

A field demonstration of analytical procedures for NG and NC in soil and building materials was performed to verify the usability of the work flow in a technology demonstration for field characterization of buildings used in the production of NC and NG.

2.4 Sampling Plan

At the time of converting the BAAAP facility to standby status, buildings at BAAAP were classified by their assessed level of contamination. A recent survey of the buildings was conducted by the Army to verify these classifications. Some buildings have never been used for explosive material production and others were assigned designations based on the possible level of exposure to these materials. Many of the plant buildings were constructed of the same materials (Figures 2-6a and 2-6b).

2.4.1 Sample Locations

The primary objective of sampling at BAAAP was to obtain samples typically encountered in munitions remediation projects which would provide measurable levels of NG and NC for comparison of field analytical methods to established methodologies. However it was not a requirement that all samples contain both NC and NG. Three matrices of interest for the BAAAP ESTCP project were concrete, wood and soil. A secondary purpose for some of the concrete and soil samples was to provide some NG and NC data for specific locations awaiting demolition safety clearance.

Sample locations were chosen based upon input from the Shaw UXO Safety Officer (SUXOSO), field wipe tests using the DROPEX^{Plus} field analytical method, and areas of interest requested by Army personnel.

Figure 2-6a and Figure 2-6b Typical Structures Found at BAAAP

The SUXOSO, who had previously performed characterizations of buildings on BAAAP for energetic materials, supervised all activities during sampling. Some buildings listed in the initial

sampling list were not sampled because there was no indication of measurable contamination from field wipe tests performed by the SUXOSO.

The samples collected for the building investigation portion of the demonstration are summarized below in Table 2-1.

Demonstration Building Selection

The sampling process of the building investigation portion of this demonstration was designed to determine the presence or absence of NC or NG compounds within the concrete floors or foundations, in the soils under the concrete, or in the structural materials of the buildings that were selected for the study. Buildings were selected for the demonstration based on the likelihood that the compounds may have entered the concrete, soils or structural materials as a result of the physical processes conducted in them. Samples were selected based on the likelihood of NG, NC or NG and NC, but did not necessarily require the presence of both for the study. A total of 103 samples were collected: thirty three samples of wood, thirty three samples of soil, and thirty-seven concrete samples were collected during the demonstration.

Samples for the building investigation demonstration were taken from the following areas as summarized below in Table 2-1:

Table 2-1 Sample Summary

Building Name (Process Line)	Building ID No.	Wood Samples	Concrete Samples	Soil Samples	Duplicate Samples (A)[1]
Neutralizer House (NG)	6657-02N	2			
Nitrate House (NG)	6657-02I	2			1
Boiling Tub House (NC)	5024	7			
Pre Dry House (NC, NG)	6709-17	10			1
Powder Storage Pit (NC, NG)	9590	3	1		1
Box Wash House (NC, NG)	1890-01	9	9	3	3
Box Storage Houses (NC, NG)	1885-01, -02, 03		3, 14, 10	0, 25, 5	4
Total Samples Collected		**33**	**37**	**33**	**10**

[1] Duplicate samples were prepared from splits of the parent sample after collection and identified with an (A) added to the sample identification number.

Refer to Table 2-2 Sampling Log Summary Table below for sample details. See also Appendix B.1 for copies of sampling location maps of the selected building.

Table 2-2 Sampling Log Summary Table

Field Sample Identification #	Map ID Number	Sample Matrix	Sample Description	Comments
6657-02N-WD-001	1	Wood	upper room - wooden railing near floor	
6657-02N-WD-002	2	Wood	lower room - wooden railing near floor	
6657-02I-WD-003	3	Wood	liquid transfer trough wooden support	
6657-02I-WD-004	4	Wood	transfer trough cover - bottom (inner) side	
5024-000-WD-005	5	Wood	upper level - board - side 1	
5024-000-WD-006	6	Wood	upper level - board - side 2	
5024-000-WD-007	7	Wood	lower level support column for upper level near southwest entrance	
5024-000-WD-008	8	Wood	lower level near southwest entrance - board 1	
5024-000-WD-009	9	Wood	lower level near southwest entrance - board 2	
5024-000-WD-010	10	Wood	lower level near southwest entrance - board (rafter beam) - side 1	
5024-000-WD-011	11	Wood	lower level near southwest entrance - board (rafter beam) - side 2	
6709-17-WD-012	12	Wood	pre-drying rack room A	
6709-17-WD-013	13	Wood	pre-drying rack room A	
6709-17-WD-014	14	Wood	pre-drying rack room A	
6709-17-WD-015	15	Wood	pre-drying rack room B	
6709-17-WD-016	16	Wood	pre-drying rack room B	
6709-17-WD-017	17	Wood	pre-drying rack room B	
6709-17-WD-018	18	Wood	pre-drying rack room C	
6709-17-WD-019	19	Wood	pre-drying rack room C	
6709-17-WD-020	20	Wood	pre-drying rack room C	
6709-17-WD-021	21	Wood	was 1890-01-WD-021, pre-drying rack room C - surface covered with visible free propellant powder	
1890-01-WD-022	22	Wood	conveyor wooden support	see map
1890-01-WD-023	23	Wood	wall	see map
1890-01-WD-024	24	Wood	conveyor wooden support	see map
1890-01-WD-025	25	Wood	conveyor wooden support	see map
1890-01-WD-026	26	Wood	wall	see map
1890-01-WD-027	27	Wood	rack - top	see map
1890-01-WD-028	28	Wood	rack - bottom	see map
1890-01-WD-029	29	Wood	wall	see map
1890-01-WD-030	30	Wood	shelf	see map
9590-000-WD-031	31	Wood	east entrance tank support blocks (railroad tie - end)	
9590-000-WD-032	32	Wood	east entrance tank support blocks (railroad tie - side)	
5024-000-WD-033	33	Wood	composite of hot spots from upper level and one support beam lower level	

Table 2-2 Sampling Log Summary Table Continued				
Field Sample Identification #	**Map ID Number**	**Sample Matrix**	**Sample Description**	**Comments**
9590-000-CM-034	34	Concrete	Piece of loose concrete picked up from floor	
1885-01-CM-035	35	Concrete	concrete core sample	see map
1885-01-CM-036	36	Concrete	concrete core sample	see map
1885-01-CM-037	37	Concrete	concrete core sample	see map
1890-01B-CM-038	38	Concrete	concrete core sample	see map
1890-01B-CM-039	39	Concrete	concrete core sample	see map
1890-01B-CM-040	40	Concrete	concrete core sample	see map
1890-01B-CM-041	41	Concrete	concrete core sample	see map
1890-01B-CM-042	42	Concrete	concrete core sample	see map
1890-01B-CM-043	43	Concrete	concrete core sample	see map
1890-01B-CM-044	44	Concrete	concrete core sample	see map
1890-01B-CM-045	45	Concrete	concrete core sample	see map
1890-01B-CM-046	46	Concrete	concrete core sample	see map
1885-03S-CM-047	47	Concrete	concrete core sample	see map
1885-03S-CM-048	48	Concrete	concrete core sample	see map
1885-03S-CM-049	49	Concrete	concrete core sample	see map
1885-03S-CM-050	50	Concrete	concrete core sample	see map
1885-03-CM-051	51	Concrete	concrete core sample	see map
1885-03-CM-052	52	Concrete	concrete core sample	see map
1885-03-CM-053	53	Concrete	concrete core sample	see map
1885-03-CM-054	54	Concrete	concrete core sample	see map
1885-03-CM-055	55	Concrete	concrete core sample	see map
1885-03-CM-056	56	Concrete	concrete core sample	see map
1885-02-CM-057	57	Concrete	concrete core sample	see map
1885-02-CM-058	58	Concrete	concrete core sample	see map
1885-02-CM-059	59	Concrete	concrete core sample	see map
1885-02-CM-060	60	Concrete	concrete core sample	see map
1885-02-CM-061	61	Concrete	concrete core sample	see map
1885-02-CM-062	62	Concrete	concrete core sample	see map
1885-02-CM-063	63	Concrete	concrete core sample	see map
1885-02-CM-064	64	Concrete	concrete core sample	see map
1885-02-CM-065	65	Concrete	concrete core sample	see map
1885-02-CM-066	66	Concrete	concrete core sample	see map
1885-02-SS-067	67	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map
1885-02-SS-068	68	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map
1885-02-SS-069	69	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map

Table 2-2 Sampling Log Summary Table Continued				
Field Sample Identification #	**Map ID Number**	**Sample Matrix**	**Sample Description**	**Comments**
1885-02-SS-070	70	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map
1885-02-SS-071	71	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map
1885-02-SS-072	72	Soil	surface soil separate hole dug near stake	see map
1885-02-SS-073	73	Soil	soil and debris from drain pipe at east (rear of building)	see map
1885-03-SS-074	74	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-03-SS-075	75	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-03-SS-076	76	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-03-SS-077	77	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-03-SS-078	78	Soil	composite subsurface soil sample from core holes 048 and 049	see map
1890-01B-SS-079	79	Soil	subsurface soil sample from hole where core sample was removed	see map
1890-01B-SS-080	80	Soil	subsurface soil sample from hole where core sample was removed	see map
1890-01B-SS-081	81	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-082	82	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-083	83	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-084	84	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-085	85	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-086	86	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-087	87	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-088	88	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-089	89	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-090	90	Soil	subsurface soil sample from hole where core sample was removed	see map

Table 2-2 Sampling Log Summary Table Continued				
Field Sample Identification #	**Map ID Number**	**Sample Matrix**	**Sample Description**	**Comments**
1885-02-SS-091	91	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-092	92	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-093	93	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-094	94	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-095	95	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-096	96	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-097	97	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-098	98	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-099	99	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-CM-100	100	Concrete	concrete core sample	see map
1885-02-CM-101	101	Concrete	concrete core sample	see map
1885-02-CM-102	102	Concrete	concrete core sample	see map
1885-02-CM-103	103	Concrete	concrete core sample	see map
EQ-RINSE 12/2/05	NA	Water	composite of concrete core equipment decon rinses	
EQ-RINSE 12/6/06	NA	Water	composite of concrete core equipment decon rinses	
EQ-RINSE 12/7/06	NA	Water	composite of concrete core equipment decon rinses	

WD= wood, SS= soil, CM= concrete material, EQ = equipment

2.4.2 Sample Collection

Sample collection methods varied with each matrix. The wood, soil and concrete matrices are described separately below. Sample locations were examined and swipe tested by the SUXOSO prior to sample collection to ensure the safety of the sampling crew.

Wood

Wood samples were generated using a cordless drill with a ¾" fluted bit. Wood sampling involved drilling multiple (35-50) holes to a depth of approximately one-half inch. Holes were placed close to each other, collecting the shavings on an aluminum foil lined tray. Single-use paint brushes were used to sweep errant wood shavings onto the foil-lined tray as necessary. The shavings were then transferred to a heavy duty Ziploc bag and were weighed on-location with a portable top-loading balance to ensure a sample size of at least 100 grams (g).

Concrete

Concrete samples were obtained using a remotely operated hydraulic drill. A water cooled, three inch (3") diameter diamond tipped hollow coring bit was used to drill completely through 6-8" concrete floor slabs. This allowed sampling of underlying soil at selected locations. All coring operations were performed under the supervision of a qualified unexploded ordinance (UXO) technician. The drill operator and the UXO technician controlled the drill from behind a blast shield placed a minimum of 250 feet from the coring site, and watched the progress of the drill using a remote camera.

Figure 2-7 Concrete Core Sampling Team

Core samples were taken at expansion joints between slab sections when possible, since these joints were expected to be likely pathways of contamination to underlying soil. Where cores were taken at expansion joints (Figure 2-8), the core was taken such that it included a portion of the expansion joint material, if possible. Though this material was not included in the list of matrices of the demonstration, swipe testing by the SUXOSO indicated that the joint compound might produce positive results. Samples were staged on aluminum foil and transferred to heavy duty Ziploc double bags.

Figure 2-8 Core Taken at Expansion Joint

Between 1 and 2 gallons of water per minute was applied to the drill location just enough to ensure that the bit remained well wetted for safety purposes. Water was discontinued as soon as the concrete slab was cored. Displacement of NC and NG was recognized as a possibility; however, for this demonstration, the water would most likely affect the total amount of NC and NG that may have been present (i.e. washed some away), but was unlikely to affect the ability to detect its presence, due to the insolubility of NC and NG in water. Determination of total quantities of NC and NG was not a primary goal of the demonstration, only the ability to provide a sample matrix for analytical method comparison. The impact on analysis was judged to be minimal when considering alternatives for safely obtaining samples for method testing.

Soil

Surface soil samples were taken by first loosening the soil with a one inch soil coring tool, then collecting the soil with a stainless steel (SS) spoon. Samples were staged on aluminum foil and transferred to trace-clean, 500ml amber, wide mouth glass sample jars. Figure 2-9 shows an example of soil sample location and conditions at the time of sampling.

Figure 2-9 Surface Soil Sample 1885-02-SS-0-72–Tunnel location Beside Bldg. 1885-02 Box Storage House

Sub-surface soil samples were taken from bore holes after concrete core samples were removed. Many of the sub-surface samples required thawing of the frozen ground before soil could be loosened and excavated from the holes. For samples requiring thawing, warm air of no higher than 140 degrees Fahrenheit was blown into each bore hole, soil was loosened using a SS auger, and soil was excavated using 16” SS spoon tongs. Samples were staged on aluminum foil or in heavy duty Ziploc bags and transferred to trace-clean, 500ml amber, wide mouth jars.

Samples of the expansion joint material were transferred to Ziploc bags, stored, and returned to the Knoxville Shaw Lab for subsequent testing.

Figure 2-10 Sub-Surface Soil-Bore Hole

Collection Equipment Decontamination

Decontamination of sampling equipment included rinsing drill bits, core sampler tongs and spoons with acetone and distilled water. Equipment rinse water composite samples were taken at various points during the concrete sample collection process (as listed in the Sampling Log Summary) and submitted to STL Sacramento for NC and NG analysis. In addition, brushes, aluminum foil and nitrile gloves were disposed of after each sample taken.

Sample Storage

Concrete core, wood shaving and soil samples used in the study were stored in an underground, explosion-proof bunker prior to analysis. The bunker temperature ranged from -10 to 20 degrees F (for the duration of on-site field testing) and was located approximately 100 yards from the field laboratory trailer. Samples transferred to the Shaw Lab in Knoxville were stored under refrigeration at 4°C.

2.4.3 Test Sample Preparation

Sample preparation methods included drying, crushing, grinding or chopping, sieving, and homogenization as needed per each matrix. The wood, soil and concrete matrices are described separately below.

Wood

Wood samples, as received, varied in consistency from fine chips or shavings (less than 1/8" thick) to four-inch splinters (thicker than ¼ inch) as shown in Figure 2-11. Samples were chopped intermittently for several minutes using a kitchen blender with a large capacity glass reservoir and stainless steel (SS) blades. Size reduction was deemed complete when the whole sample could pass through a ¼ inch sieve (Figure 2-12). Samples were further homogenized as needed, before taking aliquots, by stirring with a SS laboratory spatula. Sample preparation was performed in the field laboratory trailer's fume hood.

Figure 2-11 Nitrate House Wood Shavings from Transfer Trough Cover

Figure 2-12 Blender Homogenized Wood Less Than ¼ inch

Decontamination of preparation equipment included rinsing with acetone and distilled water, and blotting dry. In addition, aluminum foil and nitrile gloves were disposed of after each sample preparation was completed.

Concrete

Concrete core samples were screened for surface contamination using DROPEX^{Plus} prior to size reduction. Then core samples were prepared in a manner which maximized recovery of expected areas of contamination. This was accomplished by chipping away the top 1-1½ inch cross section and in some cases the side ½ inch longitudinal section next to the seam, if a seam existed. Large chips of concrete were crushed on a steel plate covered with Tyvek material using a hammer as shown in Figure 2-13. Size reduction was deemed complete when all particles were ¼ inch or less. Crushed concrete samples were transferred to Ziploc bags. Samples were further homogenized as needed before taking aliquots, by stirring with a SS laboratory spatula.

Figure 2-13 Crushing Concrete

Figure 2-14 Removal of Expansion Joint Material (EJM)

The expansion joint material (EJM) was removed from the concrete portion of the core and crushed with a hammer in the same manner as the concrete until particles were less than ¼ inch. The crushed EJM was then transferred to a plastic Ziploc bag and labeled using the concrete core sample number with an "EJM" appended. The joint material was a dried, tarry, rubber-like compound (Figure 2-14).

Concrete and EJM preparation was performed in the same bunker used for sample storage noted above. Because temperatures within the bunker ranged from minus10 to 0 degrees F, during the time when concrete was crushed, decontamination procedures were limited to replacing Tyvek material and carefully sweeping away residual dust particles between samples.

Analysis of the expansion joint material (EJM) was not included in the scope of work for the field demonstration. This material was sampled from 6 of the concrete cores and returned to the Shaw Knoxville lab for investigative analysis on this matrix. Results for the CRREL analysis of the EJM extracts are included in the CRREL concrete results section of the report.

Soil

Soil samples were air dried or oven dried at 40 degrees C as needed prior to sieving. Drying times varied greatly due to the moisture content of the samples. Some of the samples contained considerable amounts of moisture and rocks. Samples were mixed or shaken to loosen soil from rocks, sieved through a four (4) inch diameter SS hand strainer with ¼ inch openings, and collected on aluminum foil (Figure 2-15). Materials larger than ¼ inch were primarily rocks and were wasted. Soil samples were then spread thinly on foil and inspected closely for propellant material. Prepared soils were transferred to trace-clean, 500 milliliter (ml) amber, wide mouth glass jars. Small amounts of recovered propellants (Figure 2-16 and Figure 2-17) were removed from the soil samples, weighed, retained separately in 20 ml glass vials and submitted to the BAAAP UXO Officer for proper disposal. The solid propellant found in soil samples was not included for detection. Since the soil was being subsampled for field and reference lab analyses, there was no way to ensure that a solid piece could be appropriately portioned for each sample aliquot (obtain a homogeneous sample). Samples were further homogenized as needed before taking aliquots, by stirring with a SS laboratory spatula until visually homogenous.

Figure 2-15 Sieving Soil Samples

Figure 2-16 Propellant Removed from Soil Sample 1885-02-SS-073

Figure 2-17 Propellant Recovered from Soil Sample 1885-02-SS-072

Decontamination of sample preparation equipment between samples included rinsing with acetone and distilled water, and blotting dry. The hand strainer was obtained in kitchen supplies and was chosen to simplify decontamination between samples. In addition, aluminum foil and nitrile gloves were disposed of after each sample preparation was completed.

2.5 Sample Analysis Scheme

Three technologies for identifying and quantifying NC and NG in the field were evaluated on acetone extracts of wood, soil, and concrete material for comparison against off-site laboratory analysis. The methods evaluated were the following:

- DROPEX^{Plus} and EXPRAY™ colorimetric indicator for NC and NG,
- CRREL RDX colorimetric field screening method for NC and NG, and
- GC/TID portable field gas chromatograph for NG

Sample aliquots were weighed out from each of the prepared wood, concrete and soil samples into amber 4-ounce wide-mouth jars and labeled. Wood samples were weighed into 8-ounce jars due to the bulk size of the wood and to allow for mixing. An additional 20-gram aliquot of a sample was prepared for every 10 samples and analyzed as a field duplicate. Field duplicates were identified with the addition of an (A) to the respective sample number.

Acetone extracts were prepared of each concrete and soil sample using a 1:1 (v:w) ratio of acetone to sample material. Wood samples were extracted using a 3:1 ratio of acetone to wood material due to absorbtion characteristics of the pulverized wood. Extraction time was 1.5 hours for all three material types using a bench top shaker table on low speed. After extraction, the sample was allowed to settle prior to filtering. The extract was transferred to a 10-mL syringe, filtered into vials as shown in Figure 2-18, and stored at 4°C pending analysis.

Figure 2-18 Acetone Extracts of Soil Samples

Calibration standards and QC) samples were prepared and extracted along with the test samples from the clean homogenized background materials (wood, soil and concrete) prepared during the Shaw 2005 bench test. With each matrix extraction batch, or at a minimum of one every 20 samples, an extraction blank, laboratory control sample (LCS) and a matrix spike/matrix spike duplicate (MS/MSD) were prepared and extracted along with the test samples. A 10 milligram per milliliter (mg/ml) Nitroglycerine in methanol stock solution obtained from AccuStandard® was used for spiking NG standards/QC samples. A 4.2 mg/ml stock solution of NC in acetone prepared at the Shaw Lab from reference material 71% NC flake material (Lot 9H-9027, Hercules, Inc.) was used for preparing NC spiked material. Aqueous suspensions using NC were also prepared as described in the bench test (Shaw Bench Test, 2005) and used in spiking material for CRREL method tests.

Data obtained using the three field methods to analyze the prepared extracts is compared in the following sections with results from the conventional fixed-laboratory analyses of homogenous replicate sample splits submitted to STL Sacramento, CA. A split of each of the sample materials collected was packed into a cooler at 4°C and submitted to the off-site lab for quantitative analysis by the reference methods MCAWW 353.2 for NC and EPA SW-846 8330/8332 for NG.

Due to the extremely cold weather encountered during the demonstration, analytical problems, and time restraints all analysis could not be completed during the two week field demonstration. Test samples were returned to the Shaw Knoxville Lab to allow for completion and method development. Details of analytical problems encountered with NC analysis by the CRREL RDX method are discussed in the following field method sections per matrix.

2.6 Reference Test Methods

The reference methods SW-846 8330/8332 and MCAWW 353.2 are generally accepted to be the standard laboratory methods of analyses for NC and NG in homogeneous soil, water and sludge samples, but they were not developed nor thoroughly validated for the analysis of NC and/or NG in the sample matrices being tested at BAAAP. Any method may be affected by non-homogeneous matrices or matrix interferences, which cause poor sample extraction or inaccurate and imprecise analysis results, so comparison to the field methods may not be entirely appropriate for validation of the field methods. Nevertheless, it was not within the scope of this project to validate the reference methods, but to compare the field method performance to the results obtained by the reference methods.

Prior to the field demonstration as a part of the bench study samples of various substrates; soil, wallboard, wood and cement were spiked with various concentrations of NC, NG and a combination of NC and NG. The spiked samples were submitted to the STL outside laboratory for standard laboratory analysis using the reference methods. The resulting data was compared to the concentrations of the spike values added to the matrices for each analysis. The percent recovery for the reference methods are found along with the field method data in the Shaw Draft Bench Scale Report (Shaw, 2005). Percent recoveries varied between the different analyses and substrates, but in all cases with the exception of nitroglycerine in cement the analytes were detected, quantifiable and produced useable calibration curves for all of the sample matrices using the reference methods. The concentrations determined from the reference methods were plotted against the known spike concentrations to determine a calibration curve to compare verification/test samples using the reference and field methodologies.

Sample data obtained using the field methods on-site during the demonstration and subsequently at the Shaw Lab are compared in the following sections with results from the reference method analyses of homogenous replicate sample splits submitted to STL. Reference method data and data validation reports are included in Appendix B.2 and B.3, respectively, of this report.

2.6.1 Reference Method MCAWW 353.2 Methodology

MCAWW 353.2 method (EPA, 1983) is a colorimetric method that was used to determine nitrate, nitrite, each singularly, or a combination thereof. The method has been adapted for NC determination in the form of nitrate plus nitrite in waters, soils, and sediments. Solid samples are washed initially with methanol and water, agitated on a shaker, centrifuged, and then decanted. The residue is then extracted with acetone, agitated on a shaker, centrifuged, and decanted. The

acetone extracts are treated with sodium hydroxide and hydrolyzed. Once hydrolyzed, the extract is filtered, additional reagents are added for color development and analyzed colorimetrically on an automated colorimetric instrument.

The method is specific for the analysis of NC in a sample. The method pre-extraction steps with methanol and water remove inorganic forms of nitrate and nitrite as well as nitroglycerin from the sample. NC is insoluble in these solvents and is subsequently removed from the solid matrix in an acetone solvent extraction. The acetone extract is then hydrolyzed to remove NC compound nitro groups and produce inorganic nitrite and nitrate ions. The nitrate ions are then reduced to nitrite with a cadmium column and the total nitrite content is quantified colorimetrically after reaction with a reagent to produce a highly colored species that is a pink-red color.

2.6.2 Reference Method EPA SW-846 8330/8332 Methodology

EPA SW-846 Methods 8330/8332 (EPA, 1995/EPA, 1998) are high-performance liquid chromatography (HPLC) ultraviolet methods for the extraction and detection of explosive residues in waters, soils and sediments. Samples are analyzed on an HPLC with a reverse-phase column at an ultraviolet detection of 250 nanometers (nm). Solid samples are air-dried, ground, sieved through a 30-mesh screen, extracted with acetonitrile, treated with calcium chloride solution, filtered, and the extracts are analyzed by HPLC.

Results from the reference laboratory methods are incorporated into the appropriate sections below for comparison with the field method test results. Data validation reports are included in Appendix B.3.

3.0 FIELD TEST METHODS AND RESULTS

3.1 Qualitative Sample Screening Using DROPEX^{Plus} and EXPRAY™

3.1.1 Introduction/Narrative

DROPEX^{Plus} and EXPRAY™ colorimetric test kits were used to screen the prepared extracts of the collected site materials for the presence of NC and NG. Both test kits are designed to provide immediate detection of explosives (including NC and NG) by application of supplied reagents in a specified sequence. Qualitative screening using DROPEX^{Plus} was also performed by the field team at the time of sample collection to aid in the selection of the sample locations based on a positive indication of NC or NG contamination. Analyses were then performed at the field trailer on prepared sample extracts to give a qualitative indication of whether explosive compounds were present. Spiked reference materials prepared from the background soil, concrete and wood samples prepared during the bench testing were analyzed as control standards along with the test samples to obtain an indication of response for both NC and NG.

DROPEX^{Plus} wipe tests were also used to screen the surface of the concrete cores for explosive residue prior to crushing and pulverization. These results are included in the data table along with the extract results. DROPEX^{Plus}/EXPRAY™ was completed on 33 wood samples, 38 concrete samples, and 15 soil samples during the field demonstration. Due to time constraints, and frozen ground causing sampling problems 18 soil samples were returned to the Shaw Knoxville Lab for preparation and analysis.

3.1.2 Materials

DROPEX^{Plus} and EXPRAY™ colorimetric test kits were both purchased from Medimpex United, Inc. Both systems are based on the same reagents but are in different delivery form, i.e., spray can vs. dropper bottles. Each test kit is supplied with 2–inch-by-3-inch collection papers to perform the test. The kit wipes were used in the field during sample collection and to screen the concrete cores for surface contamination. For comparison purposes, the sample extracts were tested on Whatman No. 1 filter paper. An initial study was conducted during the bench scale testing to determine if a qualitative filter paper larger in size would provide the same reaction as the test kit paper and allow for testing multiple samples on the same test paper. A set of prepared NG standards were spotted on two different 15-cm Whatman filters, a Whatman No. 40 and a Whatman No. 1, and on the supplied DROPEX^{Plus}/EXPRAY™ paper. The test results showed that a Whatman No. 1 filter expressed the same sensitivity as the test kit and performing slightly better than the Whatman No. 40 paper. The larger test paper allows multiple samples from one test group to be tested side-by-side for ease of comparison and documentation of results. Figure 3-1 shows testing of sample extracts inside the field trailer.

Figure 3-1 Shaw Lab Trailer DROPEX^{Plus} and EXPRAY™ Testing on Sample Extracts

3.1.3 Method

Sample extracts were prepared using the procedure described in Section 2.5, Sample Analysis Scheme. Tests were performed using 10 micro liters (µLs) of extract placed onto the 15-cm filter paper using a 10-µL glass syringe and allowing it to air dry.

Using the EXPRAY™ kit the spray bottle labeled EXPRAY™ No. 1 was applied briefly at a distance of about 15 cm. The same area was then sprayed with the EXPRAY™ No. 2 can until slightly damp. In cases where NC or NG was detected, color change to pink or red was completed in seconds.

The DROPEX^{Plus} kit was tested identical to the EXPRAY™ using the same extracts. A couple of drops of Reagent No. 1 were spotted on the extract aliquot on the filter. Approximately 15 seconds later, a couple of drops of Reagent No. 2 were added.

If the test was positive for NC or NG, color change to red or pink was noted immediately as pictured in Figure 3-2.

Figure 3-2 Comparison of EXPRAY™ and DROPEX^{Plus} on BAAAP Wood Extracts

3.1.4 Data Assessment

For convenience, Table 3-2 provides a side by side comparison of the DROPEX^{Plus}/EXPRAY™ test kit results along with the off-site STL reference method results for each matrix tested. The DROPEX^{Plus}/EXPRAY™ results were recorded as either a positive (+) or negative (-) test response. In some cases, sample concentrations near the detectable limit for the method gave a positive result that was only faintly discernable, but in general, the test response was increasingly more intense as the test NC or NG concentration increased above the detectable limit. Detectable limits of spiked NC and NG material varied for each test matrix. Detection levels for each matrix were determined in the bench scale tests portion of this demonstration and are presented in Table 3-1 for reference. The qualitative response key used in the summary tables is as follows:

- = indistinguishable from blank
+- = possible detection
+ = detectable pink color
++ = darker pink-red color
+++ = red color
++++ = dark red

Table 3-1
Bench Test Detectable Limits DROPEX^{Plus}/EXPRAY™

Soil Extracts

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{Plus} Detectable Limit mg/kg
NC	250	100
NG	40	40
Combined NC/NG	250/25	250/25

Wood Extracts

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{Plus} Detectable Limit mg/kg
NC	2500	250
NG	250	80
Combined NC/NG	4000/400	250/400

Concrete Extracts

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{Plus} Detectable Limit mg/kg
NC	250	250
NG	ND	ND
Combined NC/NG	1000/100	250/25

NG – Nitroglycerine; NC – Nitrocellulose; mg/kg – milligrams per kilogram.

The performance of DROPEX^{Plus} and EXPRAY™ for identification of NC and/or NG compounds in acetone extracts of the wood, soil and concrete samples collected during the field demonstration was evaluated by comparison with the STL laboratory results. During the bench test both test kits seemed to work equally well and correlate well with the reference method, STL 8330/8332, with limitations based on detectable concentration limits for each matrix, which were matrix dependent. Findings from the bench test are included in the sections below for reference. Results obtained during the field demonstration by each test kit are evaluated for each of the three sample types tested in the sections below. Statistical analysis was applied to positive or

negative results from the field identification with the off-site STL lab results as reference. Test kit percent false negatives or false positives for each matrix are summarized in the tables below with the demonstration performance pass/fail criteria.

The demonstration field personnel preferred DROPEX^{Plus} during the sample collection screening due to the extremely cold temperatures (sub 0) at the BAAAP site in December. The Ex-pray spray cans did not perform as well in the extreme conditions encountered outdoors and were not used by the sample collection team. Results from the bench tests also indicated DROPEX^{Plus} test had lower detectable limits for NC spiked soil and wood, and for the combined NC and NG spiked samples of wood and concrete.

Wood

The DROPEX^{Plus} / EXPRAY™ ® detection levels described above were applied to the field demonstration samples. Table 3-2 shows the DROPEX^{Plus} / EXPRAY™ results for the 37 wood samples that were compared to the STL lab. The STL results indicate that all 37 wood samples had NC and/or NG present.

The false negative rate for the DROPEX^{Plus} analysis was 16.2 percent when compared with the laboratory reference methods. When looking at the false negative rate, it appears that DROPEX^{Plus} does not pass the performance metrics. However, when looking at the false positive rate of 5.4 percent, DROPEX^{Plus} passed the performance metrics. In certain situations DROPEX^{Plus} might still be used to indicate the presence of explosive compounds above the detectable level, given its low rate of false positives. Fifty percent, or 3 out of six of the false negative results showed possible detection but not conclusive (+-), these results were treated as non-detect for data comparison purposes.

The false negative rate for the EXPRAY™ analysis was 0 percent when compared with the laboratory reference methods and passes the performance metrics. However, when looking at the false positive rate of 13.5 percent, EXPRAY™ does not pass the performance metrics. In certain situations DROPEX^{Plus} might still be used to indicate the lack of explosive compounds above the detectable level, given its low rate of false negatives. The lack of false negatives and high percent of false positives for EXPRAY™ was most likely due to the higher detection level (2500 mg/kg) for this test kit. The detection limits for Drop-Ex and Expray were defined in the bench testing portion of the demonstration on spiked homogenized sample matrix. The concentrations used in the test were 0, 2.5, 10, 80, 250, 2500 mg/kg NC on wood and the detection limit was based on the first level with a clear positive indication, which was 2500 mg/kg; however, additional standards at levels between 250 mg/kg and 2500 mg/kg may have been able to better define the detection level. In the field demonstration, samples were chopped and mixed as much as possible to obtain homogeneous media; however, it is believed there was still a considerable amount of non-homogeneity. This was probably due to the inability to chop and blend contaminated surface pieces into the bulk sample to the level necessary. As a result NC was detected by Expray on a sample with a concentration of 138 mg/kg by the reference method, but also NC was not detected on a sample with an NC concentration of 1020 mg/kg. It is believed that the discrepancy was due primarily to sample non-homogeneity.

Table 3-2 DROPEX^{Plus} / EXPRAY™ Wood Results

Sample Identification	STL Reference Method Results (mg/kg)		Drop-Ex	Expray
	Method 8330 NG	Method 353.2 NC	Extract (10 uls)	Extract (10 uls)
6657-02N-WD-001	3.7	190	-	-
6657-02N-WD-002	18	851	-	-
6657-02I-WD-003	ND<0.5	39.9	-	-
6657-02I-WD-003A	ND<5	43.2	-	-
6657-02I-WD-004	ND<0.5	1020	-	-
5024-000-WD-005	ND<5	221	+	-
5024-000-WD-006	ND<5	174	+	-
5024-000-WD-007	ND<5	697	+	-
5024-000-WD-008	ND<5	40.5	-	-
5024-000-WD-009	ND<0.5	44.6	-	-
5024-000-WD-010	ND<5	332	++	++
5024-000-WD-011	ND<2.5	138	+	+
6709-17-WD-012	99	143	+-	-
6709-17-WD-013	88	115	+	-
6709-17-WD-014	230	198	+	+
6709-17-WD-015	240	198	+	++
6709-17-WD-016	180	156	+-	-
6709-17-WD-017	130	172	+-	-
6709-17-WD-018	84	122	+	-
6709-17-WD-019	120	149	+	-
6709-17-WD-020	110	96.2	+	-
6709-17-WD-020A	120	113	+	-
6709-17-WD-021	62	286	++	++
1890-01-WD-022	ND<0.5	35.3	+-	-
1890-01-WD-023	ND<0.5	19.1	-	-
1890-01-WD-024	ND<0.5	27.6	-	-
1890-01-WD-025	ND<0.5	61.8	+-	-
1890-01-WD-026	ND<0.5	19.8	-	-
1890-01-WD-027	ND<5	46.3	+	-
1890-01-WD-028	ND<5	29.1	-	-
1890-01-WD-028A	ND<5	42.4	-	-
1890-01-WD-029	ND<5	56.5	-	-
1890-01-WD-030	ND<5	46.6	+-	-
9590-000-WD-031	ND<0.5	42.9	+	-
9590-000-WD-032	ND<10	54.8	-	-
5024-000-WD-033	ND<0.5	2880	+++	+++
5024-000-WD-033A	ND<0.5	7080	+++	+++

ND = Not detected at the specified method detection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Soil

The DROPEX^{Plus}/ EXPRAY™ detection levels described above were applied to the field demonstration samples. Table 3-3 shows the DROPEX^{Plus} / EXPRAY™ results for the 37 soil samples that were compared to the offsite STL lab. These results indicate that all 37 soil samples had NC and/or NG present.

Of the 37 results for soil samples tested using DROPEX^{Plus} there were (6) or 16.2 percent false positives and 10.8 percent false negative results. Three of the 6 false positive results were very near the 100 mg/kg detectable level for NC on soil. The results from the reference method 8330 were very low for NG with values ranging from ND to 3.0 mg/kg. Since the lowest detectable level for NG by DROPEX^{Plus}/EXPRAY™ is 40 mg/kg only NC could be evaluated for false positives, however DROPEX^{Plus} does not meet the performance metrics for false positives or false negatives on soil extracts.

EXPRAY™ analysis gave a false negative rate of 2.7 percent with 8.1 percent false positives when compared with the laboratory reference methods. EXPRAY™ does not meet the performance metrics criteria for < 5 percent false positives.

Concrete Material

Concrete Core Sample Pre-analysis Screens (DROPEX^{Plus})

Concrete samples were screened for the presence of NC and NG prior to extraction and analysis of the extracts. Samples were screened using the DROPEX^{Plus} test kit on wipes of sample surfaces. Concrete cores were wiped on the top-end exposed surface and the bottom-end or ground side surface. If the core had exposed crack or expansion joint material surfaces, they were wiped and tested. One sample, sample 9590-000-CM-034, was composed of a number of surface chips each approximately three quarters of an inch or less in thickness. The upper surface of a number of the chips in the sample were wiped and tested using the DROPEX^{Plus} test. Sample 1885-03-CM-055 was stuck in the core drill bit and was overlooked during sample screening. After removal from the bit it was crushed for extraction without being screened, so screen results are not available for this sample. The results from the surface wipe tests are included with the sample extract results in summary Table 3-4 below.

The surface wipe test produced more positive results for the indication of NC/NG than either the DROPEX^{Plus} test or EXPRAY™ test on sample extracts. This suggests that contamination was more concentrated on the concrete surface rather than being predominantly incorporated into the bulk material. There were ten (10) samples with positive wipe indications for NC/NG as compared to only two (2) sample extracts with positive DROPEX^{Plus} indications as described below. Wipe tests on core crack surfaces or surfaces against expansion joint material typically gave similar NC/NG indication as that obtained for the top-end exposed surface. In most cases the wipes of core bottom-end surfaces gave similar NC/NG indication as that obtained for the top-end exposed surfaces.

Concrete Material Extracts

The DROPEX^{Plus}/ EXPRAY™ detection levels described above were applied to the field demonstration samples and evaluated. Table 3-4 shows the DROPEX^{Plus}/ EXPRAY™ results for the 41 concrete samples that were compared to the offsite lab. The reference method results indicate that all 41 concrete samples had NC present while only 1 sample contained NG above the reporting limit.

Table 3-3 DROPEX^{Plus} / EXPRAY™ Soil Results

Sample Identification	STL Reference Method Results (mg/kg)		Drop-Ex	Expray
	Method 8330 NG	Method 353.2 NC	Extract (10 uls)	Extract (10 uls)
1885-02-SS-067	ND<0.5	203	+	+
1885-02-SS-068	0.55	551	++	++
1885-02-SS-069	0.36	400	++	+
1885-02-SS-070	ND<0.5	57.6	++	+
1885-02-SS-071	ND<0.5	11.2	-	-
1885-02-SS-072	2.1	6200	+++	++
1885-02-SS-072A	1.4	6640	++++	+++
1885-02-SS-073	ND<0.5	11.8	+	-
1885-03-SS-074	ND<0.5	2.5	-	-
1885-03-SS-075	ND<0.5	39.6	-	-
1885-03-SS-076	ND<0.5	51.3	+-	-
1885-03-SS-077	ND<0.5	15.0	-	-
1885-03-SS-078	ND<0.5	31.4	-	-
1890-01B-SS-079	ND<0.5	3.2	-	-
1890-01B-SS-080	0.55	182	+	+
1890-01B-SS-081	ND<0.5	11.6	+	+-
1890-01B-SS-081A	ND<0.5	39.5	-	-
1890-01B-SS-081B	NA	NA	NA	NA
1890-01B-SS-081C	NA	NA	NA	NA
1885-02-SS-082	1.0	1970	+	++
1885-02-SS-083	3.0	275	+	++
1885-02-SS-083A	ND<0.5	431	+	+
1885-02-SS-084	ND<0.5	234	+	+
1885-02-SS-085	0.19	174	+	+
1885-02-SS-086	ND<0.5	21.4	+-	-
1885-02-SS-087	0.82	558	+	+
1885-02-SS-088	0.39	11.2	-	-
1885-02-SS-089	ND<0.5	24.4	-	-
1885-02-SS-090	ND<0.5	2.8	-	-
1885-02-SS-091	ND<0.5	266	+	+
1885-02-SS-092	ND<0.5	37.4	+	+-
1885-02-SS-093	0.18	340	-	-
1885-02-SS-093A	ND<0.5	92.2	-	-
1885-02-SS-094	ND<0.5	9.9	-	-
1885-02-SS-095	ND<0.5	66.8	+-	+
1885-02-SS-096	ND<0.5	2.3	-	-
1885-02-SS-097	ND<0.5	87.9	+-	-
1885-02-SS-098	ND<0.5	55.7	++	+
1885-02-SS-099	ND<0.5	62.5	+	+-

ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table 3-4 DROPEX^{Plus} / EXPRAY™ Concrete Material Results

	STL Reference Method Results (mg/kg)		Core Surface Wipes Drop-Ex Test			Drop-Ex	Expray
Sample Identification	Method 8330 NG	Method 353.2 NC	Top	Bottom	Crack	Extract (10 uls)	Extract (10 uls)
9590-000-CM-034	ND<0.5	201Q	++	-	-	-	-
9590-000-CM-034A	ND<0.5	63.0	++	NA	NA	-	-
1885-01-CM-035	ND<0.5	17.1	+	+	NA	+-	-
1885-01-CM-035B	NA	NA	NA	+	NA	+-	-
1885-01-CM-036	ND<0.5	20.3	+-	+-	NA	-	-
1885-01-CM-037	ND<0.5	17.9	+	+	NA	-	-
1890-01B-CM-038	ND<0.5	5.7	-	-	NA	-	-
1890-01B-CM-039	ND<0.5	30.1	+	+	NA	-	-
1890-01B-CM-040	ND<0.5	17.8	+	+	NA	-	-
1890-01B-CM-041	ND<0.5	9.9	+	+	NA	-	-
1890-01B-CM-042	ND<0.5	95.9Q	+	+	NA	-	-
1890-01B-CM-043	ND<0.5	71.9Q	++	+	++	-	-
1890-01B-CM-043A	ND<0.5	36.8	NA	NA	NA	-	-
1890-01B-CM-044	ND<0.5	10.2	-	-	NA	-	-
1890-01B-CM-045	0.23J	87.8Q	-	-	NA	-	-
1890-01B-CM-046	1.1	261Q	++	++	NA	+	-
1890-01B-CM-046A	0.46J	42.7	NA	NA	NA	+	-
1885-03S-CM-047	ND<0.5	3.1JB	-	-	-	-	-
1885-03S-CM-048	ND<0.5	3.0JM	-	-	NA	-	-
1885-03S-CM-049	ND<0.5	6.8JM	-	-	NA	-	-
1885-03S-CM-050	ND<0.5	3.4JM	-	-	NA	-	-
1885-03-CM-051	ND<0.5	3.2JM	-	-	NA	-	-
1885-03-CM-052	ND<0.5	5.3JM	-	-	NA	-	-
1885-03-CM-053	ND<0.5	8.8JM	-	-	NA	-	-
1885-03-CM-054	ND<0.5	5.0JM	-	-	NA	-	-
1885-03-CM-055	ND<0.5	4.0JM	NA	NA	NA	-	-
1885-03-CM-056	ND<0.5	9.8JM	+-	NA	+-	-	-
1885-02-CM-057	ND<0.5	36.1JM	-	-	NA	-	-
1885-02-CM-058	ND<0.5	3.1JM	-	NA	NA	-	-
1885-02-CM-059	ND<0.5	6.1JM	-	-	NA	-	-
1885-02-CM-060	ND<0.5	8.7JM	-	-	NA	-	-
1885-02-CM-061	ND<0.5	9.8JM	-	NA	+-	-	-
1885-02-CM-062	ND<0.5	7.3JM	-	-	NA	-	-
1885-02-CM-063	ND<0.5	11.5JM	-	-	NA	-	-
1885-02-CM-064	ND<0.5	4.2JM	+-	+-	NA	-	-
1885-02-CM-065	ND<0.5	6.9JM	-	-	NA	-	-
1885-02-CM-066	ND<0.5	7.6JM	-	-	NA	-	-
1885-02-CM-100	ND<0.5	3.5JB,JM	+	-	NA	-	-
1885-02-CM-100A	ND<0.5	4.4JB,JM	NA	NA	NA	-	-
1885-02-CM-100B	NA	NA	NA	NA	NA	-	-
1885-02-CM-101	ND<0.5	2.2JB,JM	-	-	NA	-	-
1885-02-CM-102	ND<0.5	3.4JM,JB	-	-	NA	-	-
1885-02-CM-103	ND<0.5	3.5JM,JB	-	NA	+-	-	-

Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JM = Estimated result. MS/MSD recovery is outside stated control limits.
JB = Estimated result. Method blank contains contamination.
ND = Not detected at the specified method detection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

For the 41 results for concrete samples tested DROPEX^{Plus} had 2.4 percent false positives and 2.4 percent false negative results. DROPEX^{Plus} does meet the performance metrics for false positives and false negatives on concrete extracts.

EXPRAY™ ® analysis gave a false positive rate of 0 percent with 4.9 percent false negatives when compared with the laboratory reference methods. EXPRAY™ meets the performance metrics criteria of less than 5 percent (<5%) percent false positives and less than 10 percent (<10%) false negatives.

3.1.5 Data Assessment Summary

Performance metrics for each sample group are summarized in Table 3-5 below. EXPRAY™ on wood and concrete and DROPEX^{Plus} on concrete extracts all pass performance criteria within matrix dependent detection limitations. Values meeting the specified demonstration performance metrics are bolded in the table.

Table 3-5 DROPEX^{Plus} / EXPRAY™ Summary of Performance Measures

Sample Type		Wood		Soil		Concrete	
Performance Measure	Pass/Fail Criteria	DROPEX	EXPRAY	DROPEX	EXPRAY	DROPEX	EXPRAY
% False Positives	NMT 5%	**5.4**	13.5	16.2	8.1	**2.4**	**0.0**
%False Negatives	NMT 10%	16.2	**0.0**	10.8	**2.7**	**2.4**	**4.9**
%Combined False Positive/Negative	NMT 15%	21.6	**13.5**	27.0	**10.8**	**4.8**	**4.9**
Total# Samples Evaluated		37	37	37	37	41	41

NMT= not more than

3.1.6 Conclusion

- DROPEX^{Plus} analysis of concrete core samples by surface wipes yielded more positive results (10 positives) than the sample extract analyses (2 positives) and suggested

increased sensitivity was observed because contamination was concentrated on the sample surface.

- EXPRAY™ was effective in detecting NC and NG in the matrices with results consistent with the STL 8330/8332 reference method as long as concentrations were above detectable limits.

- DROPEX^{Plus} did not meet the performance metrics for wood or soil and this was likely due to lower detection limits, which involved more samples with concentrations near the detection limit where variability in method performance is the highest and has the greatest impact.

- NG was detected on three samples in the cement matrix at very low levels (45, 46, 46A) This is believed to be due to hydrolysis degradation caused by the alkaline nature of the matrix. After applying the bench scale response curve to the STL data (see discussion in Section 3.2.4), NC was detected above the 250 mg/kg detection level for DROPEX^{Plus}/EXPRAY™ on two samples (34, 46) by the reference method. The low value for percent false positive/false negative is largely influenced by the lack of significant quantities of energetic materials in this matrix.

- Detectable limits were affected by the ratio of solvent to sample that was necessary to get complete matrix wetting for extraction. Wood matrix required a 3:1 ratio of acetone volume to sample weight. For soil and cement, a ratio of 1:1 was used.

- During Bench scale tests three false negatives were obtained (one EXPRAY™ and two DROPEX^{Plus}) out of a possible 91 tests that had concentrations above the detectable limits. The detectable limits were defined as the lowest concentration detected for each matrix. The three false negatives were for tests with concentrations just above the lowest detectable concentration observed for the matrix, and the test responses were faint near the detectable limit.

- EXPRAY™ tests, while slightly less sensitive, was easier to evaluate as either detect or non-detect. This can be seen in figure 3-2 above. DROPEX^{Plus} when applied seemed to spread out more and had more prevalent yellow discoloration. With both applications only an immediate and distinct color change should be considered to be a positive result. If the collection paper is left exposed, once reagents have been applied, it is possible for a color change to occur after a given amount of time due to pollutants or contaminants present in the ambient air.

- Both the EXPRAY™ and DROPEX^{Plus} field kits are easy to use with little specialized training and equipment. Each kit contains reagents for 200 tests. Cost of each EXPRAY™ kit is $240 and contains reagents for 100 tests. Cost of each DROPEX^{Plus} kit is $190 and contains reagents for 50 tests.

- Overall EXPRAY™ / DROPEX^{Plus} is thought to be a useful tool for screening the presence of significant concentrations of NC and or NG in the field or on sample extracts. Given its relatively low rate of false negative results, in combination with other field methods it could be a beneficial screening tool for identifying areas that do not contain explosive contamination in buildings within specified limits. Detectable levels are matrix dependent, with low confidence in results at or near the detection

limit. The field method should only be used as a screening tool in combination with other supportive methods of analysis.

3.2 Quantitative Analysis Using CRREL RDX Method

3.2.1 Introduction/Narrative

Samples were analyzed for NC and NG based on CRREL RDX Method (SW-846 Method) 8510 "Colorimetric Screening Procedure for RDX and HMX in Soil" (EPA, 2000). The CRREL RDX method is a non specific method for analysis of RDX and HMX, but it also provides response for chemically related organonitrate esters such as NC and NG. It has been used for these analytes in previous testing (Stone & Webster, 2003 and Shaw, Bench Scale Test, 2005). The method is a colorimetric procedure for the determination of nitrite released from the NC and NG propellant compounds. Matrix specific calibration on wood, soil and concrete was performed for each analyte using clean matrix material from the site, which was used in the previous bench test (Shaw, Bench Scale Test, 2005). Results were obtained for the total of NC and NG in terms of either NC or NG depending upon whether the calibration for NC or NG was used, respectively. Generating a calibration curve using both NC and NG combined was not practicable, due to the infinite number of ratios between NC relative to NG or NG relative to NC that may be encountered during analysis.

3.2.2 Instrumentation and Materials

Colorimetric analyses were performed using a HACH DR/2010 spectrophotometer set in the absorbance mode at 507 nanometers (nm). Sample extracts were filtered and treated using method procedures and then transferred into 25-mL glass cuvettes for absorbance measurement. Other critical materials used in the analysis are listed below.

Zn dust:	Zinc, 325-mesh (Aldrich catalog # 20,998-8)
Ion exchange resin:	Alumin-A, 3-mL (Supelclean, Supelco 5-7082)
Filters:	0.45 µm syringe filters (Acrodisc, 25 mm)
Nitrite color development reagent:	NitriVer 3 powder pillow, 25-mL (Hach Company)
Acetic acid	Glacial acetic acid, J.T. Baker, Baker Instra-Analyzed Reagent, 99.9%.
Sodium hydroxide	Aqueous sodium hydroxide solution, Ricca Chemical Company, 50% (w/w) aqueous solution, Lot# 2112341

3.2.3 CRREL Methodology

Aliquots of sample extracts for analysis were obtained as described in Section 2.5, Sample Analysis. This extraction method was somewhat different than that used in the bench tests for the CRREL method, but was used so that a single sample extraction would provide extract for analysis by all procedures rather than having to do separate extractions for each procedure. In the bench tests the acetone extractant volume to solid sample ratio was 5:1 (v/w). In these tests the ratio was decreased to 1:1 for soil and concrete matrices and 3:1 for wood samples. The decrease in extractant volume offered the potential for an increase in method sensitivity/decrease in detection limits.

The CRREL method steps for analysis of NC and NG in the sample matrices comprise the following:

1. Extraction of NC and NG from the solid matrix into acetone solvent
2. Filtering of the acetone extract to remove particulate and passing the extract through an alumina ion exchange resin to remove free nitrate and nitrite (inorganic forms)
3. Hydrolysis of NC and NG to remove nitro groups from the analytes and produce free nitrite and nitrate ions
4. Reduction of the free nitrate to nitrite ions
5. Reaction of the free nitrite ions with a coloring agent to produce a characteristic colored solution for quantitative determination.

The ion exchange resin used to remove inorganic nitrites/nitrates was a Supelco Alumin-A disposable resin column. Sample extracts were pushed through the resin column using a syringe at a rate of approximately one milliliter per minute. The CRREL RDX method hydrolysis step was performed under acid conditions using acetic acid and nitrate reduction to nitrite was performed with zinc dust. The color for absorbance measurement was developed by adding the contents of a HACH NitriVer 3 powder pillow dissolved in deionized water to the zinc reacted solution. After a minimum of 90 minutes, the color was developed, the sample was transferred to a 30cc syringe and filtered into a 25-mL cuvette and absorbance read at 507 nanometers (nm). A pink to rose color was indicative of NC/NG. See Figure 3-3.

Figure 3-3. CRREL Method Color Development

3.2.4 Data Assessment

Method Quantification and Data Treatment

Sample concentrations were quantified using the method by comparing sample color responses to those for matrix specific standards. Matrix standards were prepared separately for NC and NG by spiking blank matrix from the bench tests with standard NC or NG solutions as described in Section 2.5, Sample Analysis. Calibration curves were developed for each matrix to correct for matrix influences on the analysis method. New curves from those used in the bench tests were prepared primarily due to changes in extraction procedures as previously described. The calibration curve was checked at a minimum before and after sample analyses by reading control standard test samples to verify instrument response within 25 percent of the expected value.

During the field demonstration matrix effects prevented the ability to obtain a usable calibration curve for NC in wood. Due to time constraints the wood extracts were returned to the Shaw Lab for further method development and optimization. As a result of this, a Shaw Modified CRREL Method for NC and NG detection was developed which improved the NC response for all matrices tested. Details of these developments and method results are described in the following sections.

For the STL reference methods, MCAWW 353.2 and SW-846 8330, the results for the analysis of samples were reported by STL as absolute concentrations that were determined from the analysis of standard calibration solutions. The results from STL analyses have been corrected for matrix effects based on results obtained in the bench test for spiked matrix calibration

samples. Except for the concrete matrix the STL results for NG by Method 8330 were within 10 percent and results were not corrected. The NG results on concrete from the bench test were significantly affected by the matrix, which is believed to be due to decomposition because of the alkaline nature of concrete. Because the nature of this effect is dynamic, and the NG results were typically low in comparison to NC, the STL results for NG on concrete samples were also not corrected. The STL MCAWW 353.2 results for NC on wood, soil and concrete have been corrected for comparison to CRREL method results and the corrections were similar for the three matrices resulting in an increase in value by a factor of 1.5 to 2. Also, since the CRREL method is a total analysis method for NC and NG, for comparison with STL results the STL NG specific result by Method 8330 and the corrected NC specific result by MCAWW 353.2 were totaled for each sample.

Method Detection and Comparison

The detection limit for the CRREL field methods was set as the value for the lowest standard used in the matrix calibration curve. Detection of NC/NG by the CRREL method was indicated as a "1" for values above the NC detection limit and a "0" for non-detect (ND) results. The NC detection limit was used as a conservative measurement because it was less sensitive than NG. In addition, there were no samples analyzed containing detectable levels of NG that did not contain detectable amounts of NC and they were typically substantially higher than the NG amounts.

Total NC/NG analyte detection for the STL reference methods was indicated for NC values above the MCAWW 353.2 method detection limit for the same reasons described above for the CRREL methods. In fact, there were no STL "non-detects" for NC/NG because NC was detected in all samples by the MCAWW 353.2 method. However, for comparison of the CRREL field methods with the STL reference methods the total of the STL Method 8330 NG result and the corrected STL MCAWW 353.2 result was also screened against the appropriate CRREL method detection limit. STL total values above the CRREL method detection limit were indicated as "detects" and each was given a value of "1" and values below were designated as "non-detects" and given values of "0." The sum of detects for analysis of samples by a method was the total of positive results by the method. The difference in detection between the STL methods and the CRREL methods was quantified by subtracting the detect value for the CRREL method from the STL methods detect value (using the CRREL detection limit screened detect value). Zero difference values indicated method agreement, -1 value was designated as "false positives" and +1 values were designated as "false negatives." The percentage of false positives and false negatives were calculated from these numbers.

Quantitative Method Comparison

To quantitatively compare CRREL method results to the STL totaled NG and corrected NC results the relative percent difference (RPD) between the two results for each sample was calculated. The result difference was taken as the total STL value minus the CRREL result, so a positive difference indicated a lower value was obtained for the CRREL method relative to the STL total result and a negative difference indicated the CRREL method gave a higher value. Non-detect (ND) results were set at the detection limit for this comparison except when non-detects were obtained for both methods and the non-detect levels were not similar. In this case the sample results were not included in the comparison analysis. If a positive result by one method was significantly lower than a non-detect level in the other method, these results were also excluded from the comparison analysis. The average RPD for the qualified data set was calculated and this metric indicated the bias of the CRREL results relative to the STL total

results as described. The standard deviation of the sample RPD data set was also calculated and this indicated the degree of scatter in the method agreement. The average RPD for the data set was also used to calculate the average ratio of CRREL result value to STL result value and this was expressed as a percentage.

In addition, a correlation plot of field method (CRREL) results to STL reference method results was prepared and the ideal 1:1 data line was shown. This helped to visualize result bias and scatter in method agreement. A linear regression of the results was also performed as a further metric of agreement between method results. A linear regression R^2 value of 0.95 or greater was defined as one criterion for method agreement. In some cases where results were obtained over several orders of magnitude logarithmic scales were used on the plots and linear regression results were not linear on the plots. In these cases it was found that plotting the line represented by the average RPD obtained between the CRREL and STL results provided a usable visual indicator for the central tendency of the CRREL data.

3.2.5 Wood

Calibration and Method Development

Analysis of NG spiked wood samples in the field by the CRREL RDX method did produce a response consistent with the bench test results that would allow calibration and sample analysis. However, initial attempts at analysis of NC spiked wood standards in the field with the CRREL RDX method did not yield a response even at a high concentration of 6,000 mg/kg. Sample analyses were delayed until method development at the Shaw Lab in Knoxville, TN was able to modify the procedure to obtain usable results for both NC and NG. Sample extracts that were returned from the field were analyzed at the Shaw Lab by the Shaw Modified CRREL procedure for NC/NG.

Method development at the Shaw Lab focused on determining which step or steps in the CRREL procedure was or were being interfered with by the wood matrix during NC analysis. Dilutions of wood matrix standards failed to produce a usable response for NC, so the matrix effect could not be diluted out even to obtain results with an elevated detection limit. Analyses of extracts of clean wood matrix spiked with NC also did not give an NC response, which suggested that the interference was likely due to something other than the failure to extract NC from the wood matrix. Subsequent analyses of clean wood extracts spiked with nitrite ion and nitrate ion produced very strong responses and these results indicated that the nitrate ion reduction step and the reagent color development steps were not being interfered with by the matrix. The cumulative results pointed to the acid hydrolysis step as the one being interfered with by the wood matrix. An increase in the amount of acetic acid and extension of the hydrolysis reaction time was tested for improvement but neither provided a significant impact, so alkaline hydrolysis using sodium hydroxide was investigated. Alkaline hydrolysis of NC and NG is used in the STL reference method (MCAWW 353.2). To modify the CRREL RDX method for alkaline hydrolysis the amount of sodium hydroxide had to be small so that addition of a minimum amount of acetic acid could re-establish an acidic pH for the Zn reduction and color development steps. This was accomplished in the test by using 0.1 mL (100 microliters) of 50 percent sodium hydroxide for hydrolysis of 5 mL of sample extract followed by addition of 0.5 mL of acetic acid. The hydrolysis step included mixing the sample extract with the sodium hydroxide for two minutes before adding the acetic acid. Tests were also performed to optimize the Zn reduction reaction time for NC and NG by this procedure and this was determined to be 15 to 30 seconds. Alkaline hydrolysis by this procedure provided a much better response for NC in wood extract than what was previously obtained for NC using the CRREL RDX method for any matrix. The

wood matrix did not interfere significantly with the NC response when the acetone extract volume to matrix ratio of 9:1 (v/w) was tested. At a lower solvent to wood ratio of 3:1 the more concentrated wood matrix extract did interfere by suppressing the NC response. Based on these results a Modified CRREL method was used to analyze the wood samples. This method used a 3:1 dilution of the wood sample extract with acetone. The wood sample extractions were performed at a solvent to wood ratio of 3:1, so a further 3:1 dilution provided an extract at a concentration equivalent to a 9:1 extraction ratio. The extract was then treated with alkaline hydrolysis and acidified by addition of acetic acid as described. The Zn reduction and color development steps were then performed per the CRREL method.

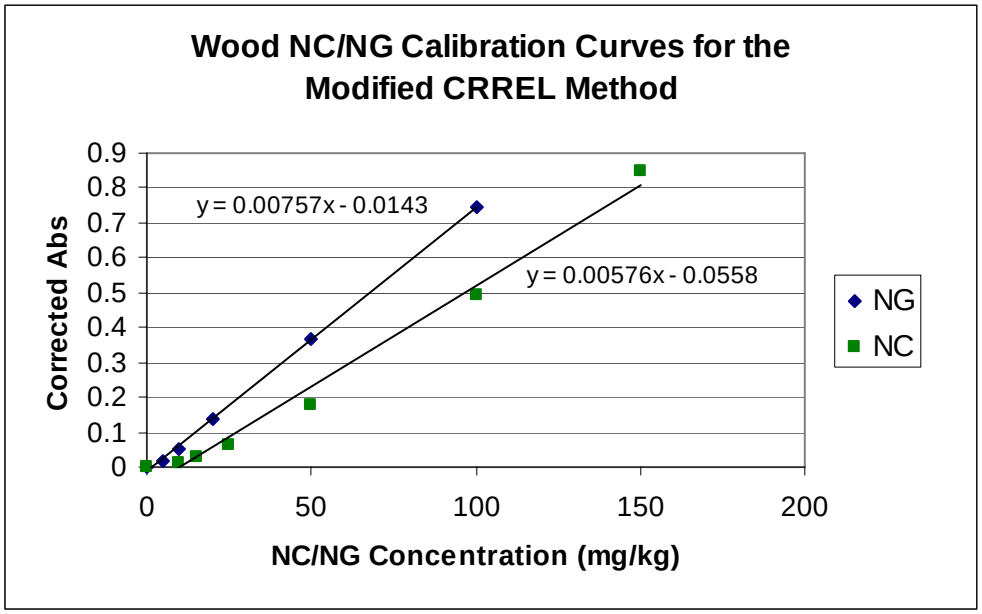
A calibration curve for NC in wood using the CRREL RDX procedure was obtained in the bench tests, but only at high concentrations and Table 3-6 shows a comparison of the standard concentrations and method responses with those from the Modified CRREL procedure. The data show that the response for NC by the modified method is on the order of a hundred times greater than the CRREL RDX method and suggests that the CRREL RDX procedure on wood extracts converts less than one or two percent of the NC nitrogen (N) to nitrite for analysis. The increase in response for NC is seen on other matrices as well and suggests the degree of N conversion to nitrite from NC is incomplete for the CRREL RDX procedure or is easily interfered with by sample matrices.

Table 3-6 Comparison of CRREL Method Calibration Results for Wood

CRREL RDX Method Bench Scale Wood Calibration Sample Analyses		**Shaw Modified CRREL NC/NG Method Field Demonstration Wood Calibration Sample Analyses**	
mg/kg NC	Absorbance	mg/kg NC	Absorbance
20	0.001	10	0.017
50	0.003	15	0.029
100	0.001	25	0.068
400	0.000	50	0.183
4000	0.080	100	0.498
40000	0.209	150	0.850

For NG a separate calibration curve was generated using the background materials prepared during the bench scale test. Five NG-spiked wood samples (calibration samples) were prepared and analyzed by the CRREL RDX method. Absorbance responses for NG were found to be linear and similar to those obtained for NC as shown in Figure 3-4. The calibration response for NG was 1.31 times that of NC, which is exactly the expected theoretical ratio based on the ratio of N content of NG (molecular fraction of N, $f_N = 0.185$) to the N content of completely nitrated NC ($f_N = 0.141$). The f_N ratio of NG to NC is 0.185/0.141 = 1.31. The similarity of NC and NG responses was not observed with the CRREL RDX method in the bench test where the NC response for wood samples was much lower and the ratio of NG response to NC response was two orders of magnitude higher. However, the NG response by the Modified CRREL method was similar to that observed in the bench test (correcting for extraction volumes and dilution) and suggests that conversion of N to nitrite for NG is substantially complete or at least similar in completeness for both methods.

Figure 3-4



Wood Sample Analysis

The results of wood sample extract analyses by the Modified CRREL method are tabulated in Table 3-7. This table also shows STL results for MCAWW 353.2 for NC and Method 8330 for NG and the corrected total for STL NC and NG results. DROPEX^{Plus} / EXPRAY™ and GC/TID results for the sample extracts are also shown for comparison. Concentrations of both NG and NC were detected in many of the samples, so calculation of CRREL results were performed as NC and as NG and both results are included in the Table 3-7. Since NC was detected in more samples than NG and typically at substantially higher concentrations, the CRREL results calculated as NC were used in the comparison to STL reference method results. Results for NG QC sample analyses for NG spike laboratory control samples (LCS); NG matrix spike (MS) and matrix spike duplicate (MSD) samples were calculated as NG.

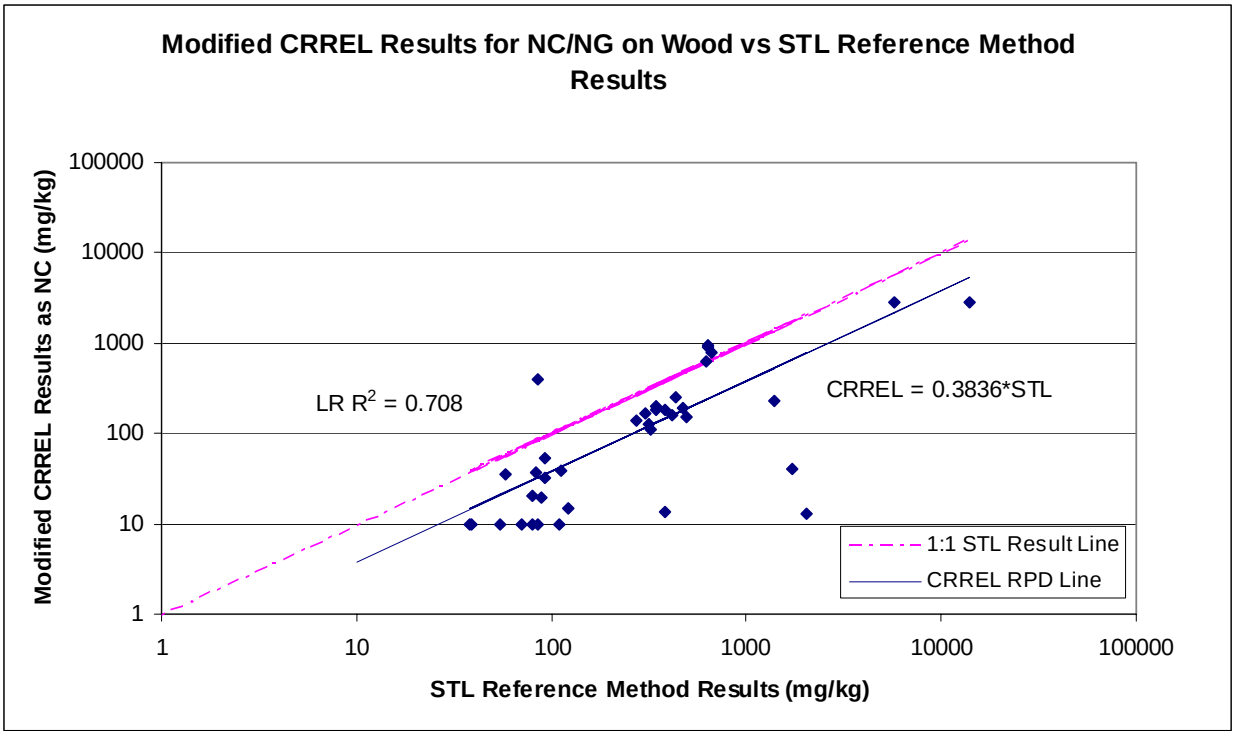
The detection limit using the Modified CRREL method for the wood samples was 10 mg/kg for NC and 5 mg/kg for NG in undiluted samples. There were 33 wood samples analyzed, four (4) of them were analyzed in duplicate. NC was detected in all 33 (including duplicates) by the STL MCAWW 353.2 method at concentrations ranging from 38 mg/kg to 14,000 mg/kg. NG was detected in twelve (12) of these samples by the STL Method 8330 method at concentrations ranging from 3.7 mg/kg to 240 mg/kg. The Modified CRREL method detected NC/NG in 27 of the samples at NC concentrations ranging from 13 mg/kg to 2,820 mg/kg.

There were zero false positive results for the Modified CRREL method and 7 out of 37 analyses or 18.9 percent that gave false negative results. The false negatives were for the samples that were non-detect by the CRREL method, and STL reported values in the range of 38 mg/kg to 109 mg/kg. The STL MCAWW 353.2 analysis results were qualified because of contamination in the method blanks that ranged from 5.8 mg/kg to 9.4 mg/kg, and after applying the wood matrix correction, resulted in blank values equal to 12-19 mg/kg on a sample basis. The positive STL blank values indicate the possibility of false positives in the STL data and high bias in results, especially at the lower concentrations. This should be taken into consideration before placing too much significance on the accuracy of the STL wood sample results, especially the lower concentration results. The bench test results also showed that the STL MCAWW 353.2

results were consistently biased high, especially at lower NC concentrations and NC was detected in unspiked clean background samples.

The average CRREL/STL RPD for the results data set was 89.1 percent and the standard deviation of the RPD data set was 69.9 percent indicating that the results have considerable scatter in agreement and the CRREL results are clearly biased low compared to the STL results. Figure 3-5 shows a correlation plot of quantitative results for wood sample analyses for the Modified CRREL method versus the total STL reference method results. The upper line shows the ideal 1:1 correlation line and the lower line shows the values for the average CRREL RPD with respect to the STL results. The average CRREL RPD line is at 38.4 percent of the STL reference method values, and this is equal to the average ratio for the Modified CRREL result obtained relative to the STL result.

Figure 3-5



There are no clear explanations for the high RPD in results between the methods. The first consideration, however, is the potential high bias in the STL MCAWW 353.2 results, especially at lower concentrations, that was indicated by positive results in method blanks and demonstrated in the bench test. A high bias may be due to matrix interference with the method and this effect could be systemic to the wood results. In the bench test, uncorrected MCAWW 353.2 results for two analyses of unspiked clean background wood were both 14.2 mg/kg NC. With the matrix correction applied these results would both be 28.2 mg/kg. A second consideration is the matrix correction applied to the STL MCAWW 353.2 results. The results were corrected using bench test data that increased the reported values by a factor of 1.98 or a 98% increase. This factor may have changed since the bench test because of method modifications, difference in wood matrix, etc., but even if the results were not corrected, there would still be a detectable negative bias. Finally, the high degree of scatter in results agreement may be due to the small aliquot size used in the wood analysis by the STL MCAWW 353.2 reference method. Typically 10 grams are used, but for the wood samples 2 grams were used because of the sample bulk, and this increases the probability of sample non-homogeneity

effects. The smaller a sample aliquot is that is used in an analysis the more likely it is to obtain aliquots that differ in composition. For the CRREL method, 20 grams were used, the same size aliquot that was used for soil and concrete matrices, but larger solvent volume and sample bottles were used for extraction. The results for duplicate sample pair analyses gave results within 40 percent RPD for three out of four of the pairs for the STL reference method and 4 out of 4 for the Modified CRREL method; however, and this does not indicate a significant problem with precision for either method.

There is difficulty in validating the Modified CRREL method by comparing sample analysis results to those from the STL MCAWW 353.2, since there is no validation data that asserts the validity of either of the methods. These analyses are showing that there is some degree of bias with either one or both the methods. Analysis of NC is affected by a lack of standard material, potential for incomplete extraction from the matrix and analysis chemistry that seems to be impacted by adverse sample matrices. The task may be manageable by validating NC extraction using spiked matrices as was done in the bench tests but using the Modified CRREL rather than the CRREL RDX method that was used. In the bench test the reference method demonstrated a positive bias below about 50 mg/kg, so concentrations at or below this level will not be accurately quantified by this method unless modifications are made. Using spiked matrices the method results can be compared to prepared concentrations for absolute bias assessment. Matrix samples along with matrix spike samples can be used to assess method performance on actual samples and again have prepared spike concentrations for comparison to assess performance. Also, it would be useful to compare results for analysis of sample extract splits by both the field and reference methods to assess method differences when analyzing the same extract. This would eliminate sample non-homogeneity issues. Finally, prepared NC spike/standard solutions from both labs should be analyzed by both labs to incorporate potential differences in standard concentrations into the data assessment.

Table 3-7 Modified CRREL Results for Wood Samples

Sample Identification	STL Reference Method Results (mg/kg)				Shaw Modified CRREL NG+NC		NG GC/TID	Drop-Ex	Expray
	Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	Analyzed conc as NG	Analyzed conc as NC	Conc mg/Kg	Extract (10 uls)	Extract (10 uls)
6657-02N-WD-001	3.7J	190JB	377	381	5	13	ND<5.0	-	-
6657-02N-WD-002	18	851Q,JB	1690	1710	25	40	3.22 J	-	-
6657-02I-WD-003	ND<0.5	39.9JB	79	79	ND<5	ND<10	ND<5.0	-	-
6657-02I-WD-003A	ND<5	43.2JB	86	86	ND<5	ND<10	ND<5.0	-	-
6657-02I-WD-004	ND<0.5	1020Q,JB	2020	2020	4	13	ND<5.0	-	-
5024-000-WD-005	ND<5	221JB	438	438	172	250	7.67	+	-
5024-000-WD-006	ND<5	174JB	345	345	122	184	ND<5.0	+	-
5024-000-WD-007	ND<5	697Q,JB	1380	1380	158	231	ND<5.0	+	-
5024-000-WD-008	ND<5	40.5JB	80	80	10	20	ND<5.0	-	-
5024-000-WD-009	ND<0.5	44.6JB	88	88	9	19	ND<5.0	-	-
5024-000-WD-010	ND<5	332JB	659	659	579	806	ND<5.0	++	++
5024-000-WD-011	ND<2.5	138JB	274	274	95	137	ND<5.0	+	+
6709-17-WD-012	99	143JB	284	383	101	180	31.6	+-	-
6709-17-WD-013	88	115JB	228	316	62	129	19.2	+	-
6709-17-WD-014	230	198JB	393	623	442	627	98.3	+	+
6709-17-WD-015	240	198JB	393	633	661	914	104	+	++
6709-17-WD-016	180	156JB	310	490	79	152	47.3	+-	-
6709-17-WD-017	130	172JB	341	471	106	187	44.5	+-	-
6709-17-WD-018	84	122JB	242	326	49	111	22.9	+	-
6709-17-WD-019	120	149JB	296	416	84	157	44.5	+	-
6709-17-WD-020	110	96.2JB	191	301	90	165	25.4	+	-
6709-17-WD-020A	120	113JB	224	344	120	204	25.9	+	-
6709-17-WD-021	62	286JB	567	629	682	965	58.5	++	++
1890-01-WD-022	ND<0.5	35.3JB	70	70	ND<5	ND<10	ND<5.0	+-	-
1890-01-WD-023	ND<0.5	19.1JB	38	38	ND<5	ND<10	ND<5.0	-	-
1890-01-WD-024	ND<0.5	27.6JB	55	55	ND<5	ND<10	ND<5.0	-	-
1890-01-WD-025	ND<0.5	61.8JB	123	123	6	15	ND<5.0	+-	-
1890-01-WD-026	ND<0.5	19.8JB	39	39	ND<5	ND<10	ND<5.0	-	-
1890-01-WD-027	ND<5	46.3JB	92	92	20	33	ND<50	+	-
1890-01-WD-028	ND<5	29.1JB	58	58	21	35	ND<5.0	-	-
1890-01-WD-028A	ND<5	42.4JB	84	84	23	37	ND<5.0	-	-
1890-01-WD-029	ND<5	56.5JB	112	112	24	39	ND<5.0	-	-
1890-01-WD-030	ND<5	46.6JB	92	92	35	53	ND<5.0	+-	-
9590-000-WD-031	ND<0.5	42.9JB	85	85	285	397	ND<5.0	+	-
9590-000-WD-032	ND<10	54.8JB	109	109	ND<5	ND<10	ND<50	-	-
5024-000-WD-033	ND<0.5	2880Q,JB	5710	5710	1830	2870	ND<20	+++	+++

Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JB = Estimated result. Method blank contains contamination.
PG = The percent difference between the original and confirmation analysis is greater than 40%.
ND = Not detected at the specified method detection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

3.2.6 Soil

Calibration

An initial set of soil samples collected in the first week of the field demonstration were analyzed on-site by the CRREL RDX method. Subsequently, a second set of soil samples were submitted near the end of the on-site testing and these samples were returned to the Shaw Lab in Knoxville, TN for analysis by the CRREL RDX method. In addition, after the development of the Shaw Modified CRREL method at the Shaw Lab, sample extracts with sufficient volume for re-analysis were analyzed by this method to assess performance on the soil matrix. Separate calibration curves were prepared for the Shaw Modified CRREL and the CRREL RDX methods using NC and NG spiked onto background soil material prepared for the bench test.

Calibration curves for NC and NG in soil extracts using the CRREL RDX procedure were obtained during the field tests and used for the analysis of both the first set and the second set (at the Shaw Lab) of soil sample extracts. Table 3-8 shows a comparison of the standard concentrations for NC and method responses obtained for both CRREL methods. The data show that the response for NC by the modified method is on the order of 50-100 times greater than the CRREL RDX method and suggests that the CRREL RDX procedure on soil extracts converts less than about ten percent of the NC nitrogen (N) to nitrite for analysis. The results are consistent with those obtained for the wood samples, but the NC response by the CRREL RDX method was not as affected by the soil matrix and allowed calibration and sample analysis on undiluted extracts, although at elevated detection limits due to the lower response.

Table 3-8. Comparison of CRREL Method Calibration Results for Soil

CRREL RDX Method Field Demonstration Soil Calibration Sample Analyses		Shaw Modified CRREL NC/NG Method Field Demonstration Soil Calibration Sample Analyses	
mg/kg NC	Absorbance	mg/kg NC	Absorbance
0	0.025	0	0.000
25	0.036	1.5	0.067
50	0.071	5	0.239
100	0.308	10	0.411
200	0.447	15	0.742
500	0.529	NA	NA

Figures 3-6a and 3-6b show the NC and NG calibration curves for both CRREL methods. The plots show that NG response was not significantly different for the methods and suggests the N conversion from NG to nitrite is substantially complete for both methods with soil samples. The calibration response for NG was 71.4 times that of NC by the CRREL RDX method and 1.22 by the Modified CRREL method. The NC/NG response ratio for the Modified CRREL method is similar to that obtained for wood samples and is close to the expected theoretical ratio (1.31) based on the ratio of N content of NG to the N content of NC as discussed for the wood matrix samples. The increase in NC response provided by the Modified CRREL procedure is a big advantage for this method not only because of the increase in NC sensitivity, but also because of the similarity in responses that result for NC and NG. As a total method for NC and NG with similar responses for both analytes, calibration can be performed with only one of these and results for samples containing both NC and NG should be within acceptable accuracy for the total concentration. With a response ratio of NG to NC at the theoretical ratio of 1.31 the

relative percent difference (RPD) for a result calculated as NG compared to a result calculated as NC would be 27 percent. This is still within the acceptable performance range for accuracy of the CRREL screening method of 40 percent.

Figure 3-6a

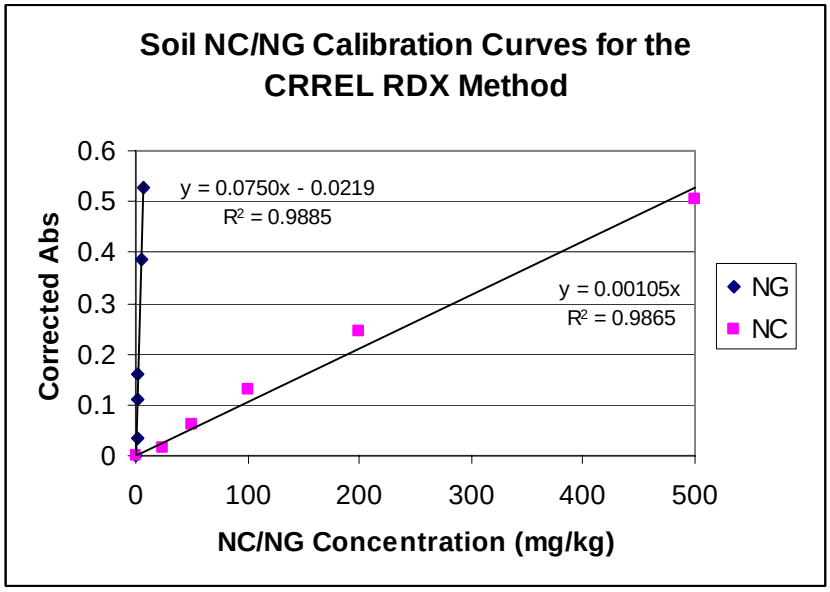
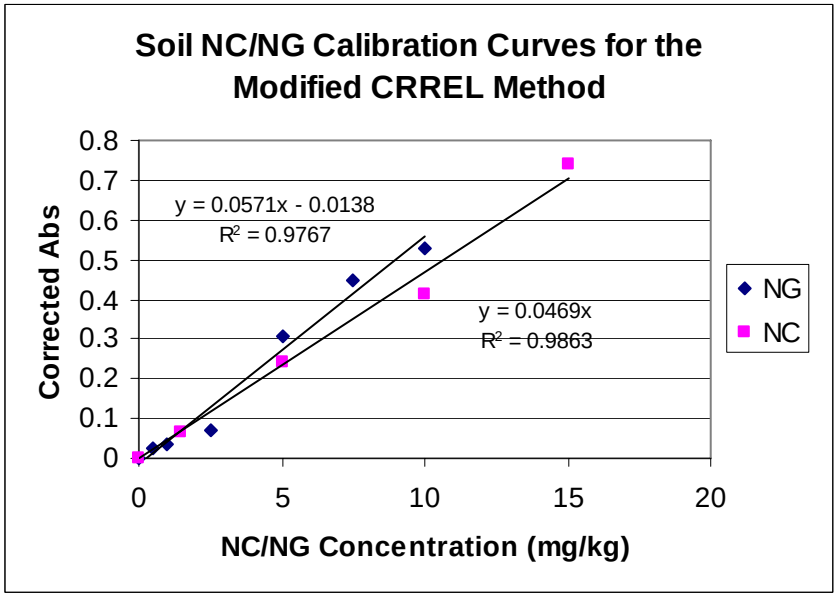


Figure 3-6b



Soil Sample Analysis

The results of soil sample extract analyses by the CRREL RDX method and the Modified CRREL method for NC/NG are tabulated in Table 3-9. This table also shows STL results for MCAWW 353.2 for NC and Method 8330 for NG and the corrected total for STL NC and NG results. DROPEX^{Plus} / EXPRAY™ and GC/TID results for the sample extracts are also shown for comparison. Concentrations of NG were detected in only a few of the samples and the levels were substantially below those for NC, so only results quantified as NC are shown in the Table 3-9. Results for NG QC sample analyses for NG spike laboratory control samples (LCS); NG matrix spike (MS) and matrix spike duplicate (MSD) samples were calculated as NG.

Two samples, 1885-02-SS-072 and 1885-02-SS-073, had pieces of propellant material physically removed during visual inspection at the time of sample preparation. Sample -072 had 0.023 grams removed from 695 grams of soil or 33.1 mg/kg. Sample -073 had 0.56 grams removed from 445 grams of soil or 1,260 mg/kg.

The detection limit using the CRREL RDX method for the soil samples was 25 mg/kg for NC and 1.0 mg/kg for NG in undiluted samples. The detection limit using the Modified CRREL method for the soil samples was 1.5 mg/kg for NC and 0.5 mg/kg for NG in undiluted samples. There were 33 soil samples analyzed, four (4) of them were analyzed in duplicate. There were only 27 of the samples that were analyzed by the Modified CRREL method due to limitations in the amount of sample extract available for re-analysis of six (6) of the samples. NC was detected in all 33 samples (including duplicates) by the STL MCAWW 353.2 method at concentrations ranging from 4 mg/kg to 10,300 mg/kg. NG was detected in ten (10) of these samples by the STL Method 8330 method at concentrations ranging from 0.18 mg/kg to 3.0 mg/kg. The CRREL RDX method detected NC/NG in 12 of the samples at NC concentrations ranging from 30.5 mg/kg to 7,500 mg/kg. The Modified CRREL method detected NC/NG in 20 out of 30 samples analyzed at NC concentrations ranging from 7 mg/kg to 8,610 mg/kg.

There was one (1) false positive result (2.7%) for the CRREL RDX method and 14 out of 37 analyses or 37.8 percent that were false negatives. For the Modified CRREL method there were zero false positive results and 10 out of 31 analyses or 32.3 percent that were false negatives. However, six (6) of the STL results for the false negatives were relatively low concentrations (4 mg/kg to 18 mg/kg) near the detection limit where there is greater variability and probability for false indication. Some of the STL MCAWW 353.2 analysis results were qualified because of contamination in the method blank. Two of the three STL method blanks contained detectable amounts of NC at values of 1.3 mg/kg and 2.9 mg/kg, and after applying the soil matrix correction, the blank values were equal to 2 mg/kg and 4 mg/kg on a sample basis. The positive STL blank values indicate the possibility of false positives in the STL data and high bias in results, especially at the lower concentrations. This should be taken into consideration before placing too much significance on the accuracy of the STL soil sample results, especially the lower concentration results. The bench test results also showed that the STL MCAWW 353.2 results were consistently biased high, especially at lower NC concentrations and NC was detected in unspiked clean background samples. Nevertheless, omitting the questionable six (6) STL detections would still leave 4 out of 31 analyses or 12.9 percent false negatives

The average CRREL/STL RPD for the CRREL RDX method data set was 82.7 percent and the standard deviation was 81.8 percent. For the Modified CRREL results data set the average CRREL/STL RPD was 82.7 percent and the standard deviation was 72.0 percent. This data is similar to what was obtained for wood samples and similarly indicates considerable scatter in results agreement and a low bias for the CRREL results compared to the STL results. The STL

comparison results for the two CRREL methods were similar and indicate agreement between the two CRREL methods. The average RPD between the results for the CRREL RDX method and the Modified CRREL method was 36.5 percent, which is within the 40 percent accuracy expectation for the CRREL RDX method. Figure 3-7 and Figure 3-8 show correlation plots of quantitative results for wood sample analyses for the CRREL methods versus the total STL reference method results. The upper line in both plots shows the ideal 1:1 correlation line and the lower line shows the values for the average CRREL RPD with respect to the STL results. It can be seen that the data for the CRREL RDX method are influenced by the higher detection limit. The average CRREL RPD line is at 41.5 percent of the STL reference method values for both CRREL methods and this value is equal to the average ratio for the CRREL result obtained by either method relative to the STL result. The biggest difference between the two CRREL methods is the correlation of results to the STL results. The CRREL RDX method has a linear regression (LR) correlation coefficient (R^2) value of 0.8979 while the Modified CRREL method has a correlation coefficient of 0.9548, which meets the method comparison performance criterion of greater than 0.95

Figure 3-7

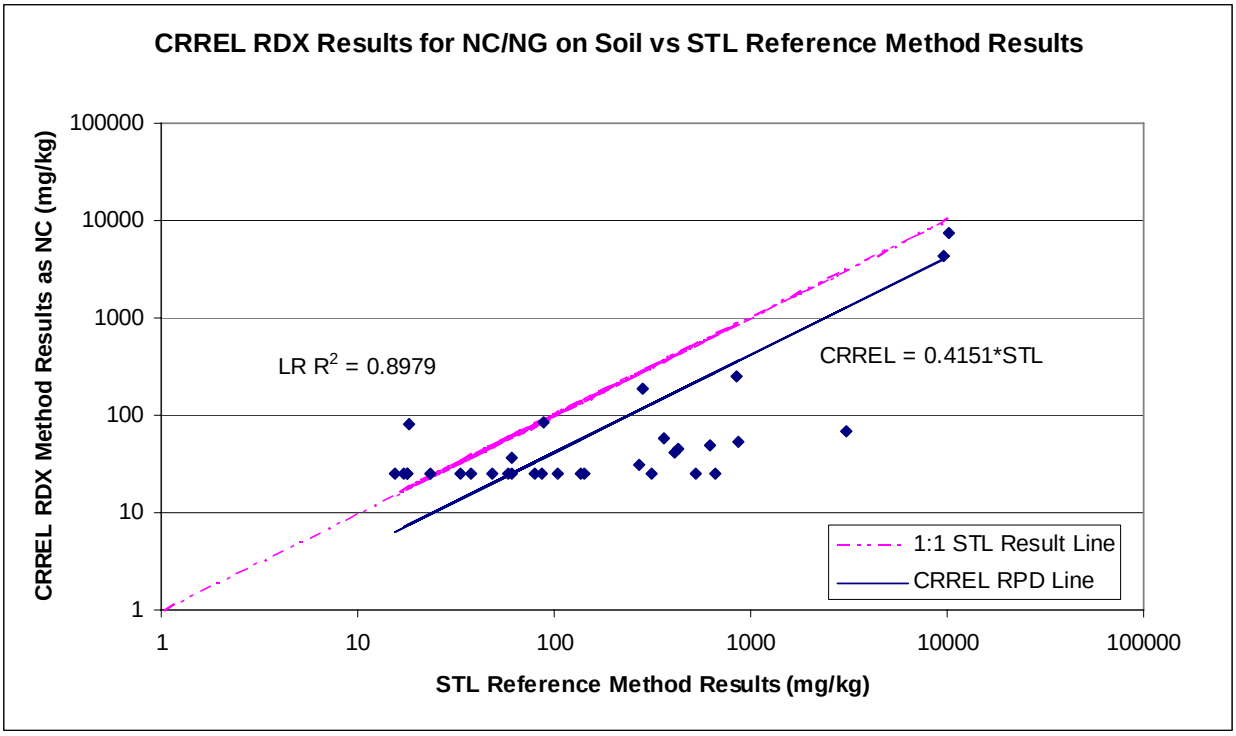
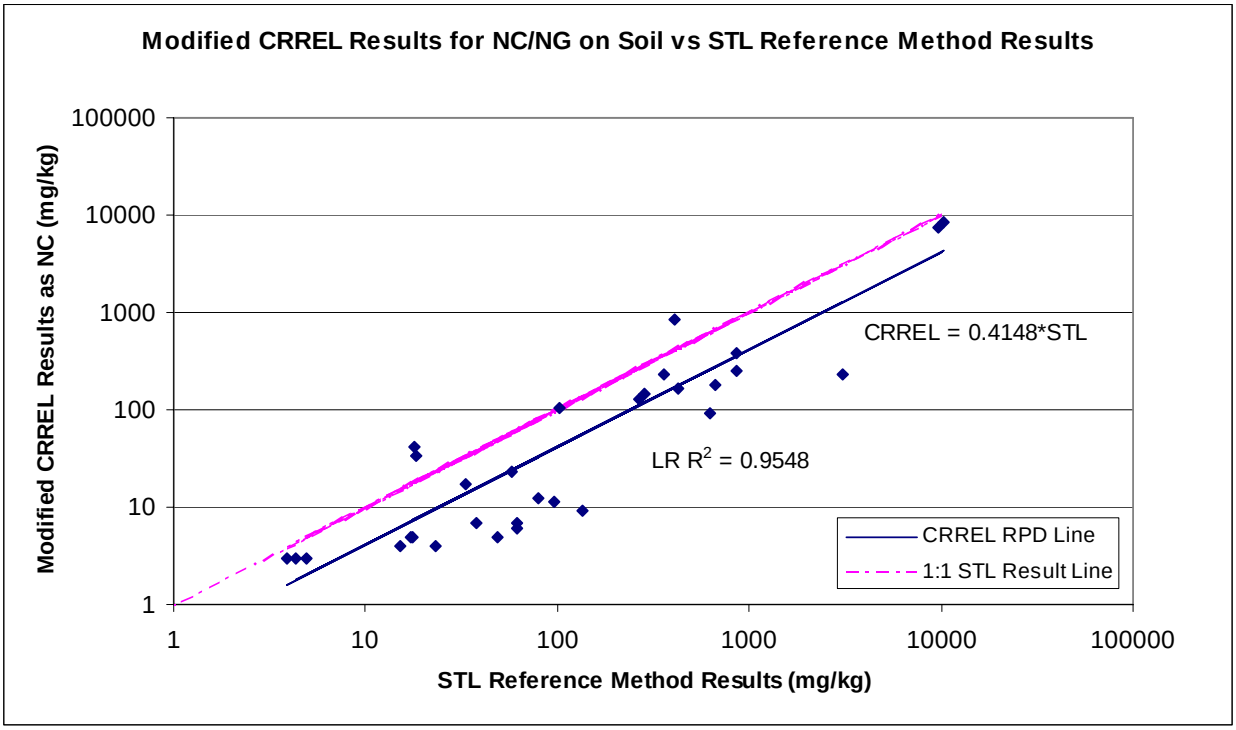


Figure 3-8



There are no clear explanations for the high RPD in results between the methods. The first consideration, however, is the potential high bias in the STL MCAWW 353.2 results, especially at lower concentrations, that was indicated by positive results in method blanks and also demonstrated by a positive result for unspiked clean background soil in the bench test (test verification sample). A high bias may be due to matrix interference with the method and this effect could be systemic to the soil results. A second consideration is the matrix correction applied to the STL MCAWW 353.2 results. The STL results for MCAWW 353.2 were corrected for the soil matrix using bench test data that increased the reported values by a factor of 1.55 or a 55% increase. This factor may have changed since the bench test because of method modifications, difference in soil matrix, etc., but even if the results were not corrected, there would still be a significant negative bias. Finally, the high degree of scatter in results agreement is believed to be due to sample non-homogeneity and this is highly probable because of pieces of NC/NG propellant material, such as those picked out of the two samples described above, that may be grabbed in a sample aliquot The results for duplicate sample pair analyses gave results within 40 percent RPD for only one out of four of the pairs for the STL reference method and 2 out of 3 (one pair was a pair of non-detect results) for the Modified CRREL method, which supports the explanation.

Table 3-9 CRREL Results for Soil Samples

Sample Identification	STL Reference Method Results (mg/kg)				CRREL NG+NC	Modified CRREL	GC/TID NG	Drop-Ex	Expray
	Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	Conc as NC mg/kg	Conc as NC mg/kg	Conc mg/Kg	Extract (10 uls)	Extract (10 uls)
1885-02-SS-067	ND<0.5	203Q	314	314	ND<25	ND<57	ND<2.0	+	+
1885-02-SS-068	0.55	551Q	852	853	256	382	ND<2.0	++	++
1885-02-SS-069	0.36J,JS	400Q	619	619	ND<50	91	ND<2.0	++	+
1885-02-SS-070	ND<0.5	57.6	89	89	82.9	NS	ND<2.0	++	+
1885-02-SS-071	ND<0.5	11.2	17	17	ND<25	ND<5	ND<2.0	-	-
1885-02-SS-072	2.1JS	6200Q	9590	9590	4290	7570	22.0	+++	++
1885-02-SS-072A*	1.4PG,JS	6640Q	10300	10300	7500	8610	44.5	++++	+++
1885-02-SS-073*	ND<0.5	11.8	18	18	80.0	34	ND<2.0	+	-
1885-03-SS-074	ND<0.5	2.5	4	4	ND<25	ND<3	ND<2.0	-	-
1885-03-SS-075	ND<0.5	39.6	61	61	37.1	ND<7	ND<2.0	-	-
1885-03-SS-076	ND<0.5	51.3	79	79	ND<25	12	ND<2.0	+-	-
1885-03-SS-077	ND<0.5	15.0	23	23	ND<25	ND<4	ND<2.0	-	-
1885-03-SS-078	ND<0.5	31.4	49	49	ND<25	ND<5	ND<2.0	-	-
1890-01B-SS-079	ND<0.5	3.2	5	5	ND<25	ND<3	ND<2.0	-	-
1890-01B-SS-080	0.55JS	182Q	282	282	185	147	3.0	+	+
1890-01B-SS-081	ND<0.5	11.6	18	18	ND<25	42	ND<2.0	+	+-
1890-01B-SS-081A	ND<0.5	39.5	61	61	ND<25	ND<6	ND<2.0	-	-
1890-01B-SS-081(B)	NA	NA	NA	NA	NA	ND<5	NA	NA	NA
1890-01B-SS-081(C)	NA	NA	NA	NA	NA	ND<5	NA	NA	NA
1885-02-SS-082	1.0	1970Q, JB	3050	3050	68.6	235	ND<2.0	+	++
1885-02-SS-083	3.0JS	275Q,JB	425	428	44.8	163	ND<2.0	+	++
1885-02-SS-083A	ND<0.5JS	431Q,JB	667	667	ND<25	183	ND<2.0	+	+
1885-02-SS-084	ND<0.5	234Q,JB	362	362	57.1	233	ND<2.0	+	+
1885-02-SS-085	0.19J	174Q,JB	269	269	30.5	127	ND<2.0	+	+
1885-02-SS-086	ND<0.5	21.4JB	33	33	ND<25	17	ND<2.0	-+	-
1885-02-SS-087	0.82	558Q,JB	863	864	53.3	251	ND<2.0	+	+
1885-02-SS-088	0.39J	11.2JB	17	18	ND<25	ND<5	ND<2.0	-	-
1885-02-SS-089	ND<0.5	24.4JB	38	38	ND<25	7	ND<2.0	-	-
1885-02-SS-090	ND<0.5	2.8J, JB	4	4	ND<25	ND<3	ND<2.0	-	-
1885-02-SS-091	ND<0.5	266Q,JB	412	412	41.9	838	ND<2.0	+	+
1885-02-SS-092	ND<0.5	37.4JB	58	58	ND<25	23	ND<2.0	+	-+
1885-02-SS-093	0.18J	340Q,JB	526	526	ND<25	ND<45	ND<2.0	-	-
1885-02-SS-093A	ND<0.5	92.2Q,JB	143	143	ND<25	ND<15	ND<2.0	-	-
1885-02-SS-094	ND<0.5	9.9JB	15	15	ND<25	ND<4	ND<2.0	-	-
1885-02-SS-095	ND<0.5	66.8JB	103	103	ND<25	104	ND<2.0	-+	+
1885-02-SS-096	ND<0.5	2.3J,JB	4	4	ND<25	NS	ND<2.0	-	-
1885-02-SS-097	ND<0.5	87.9Q,JB	136	136	ND<25	9	ND<2.0	+-	-
1885-02-SS-098	ND<0.5	55.7JB	86	86	ND<25	NS	ND<2.0	++	+
1885-02-SS-099	ND<0.5	62.5JB	97	97	NA	11	ND<2.0	+	+-

* = Propellant pieces removed from samples 72A and 73

(B) (C) = triplicate analysis

Q= Elevated reporting Limit

J = Estimated result. Result is less than reporting limits.

JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.

JB = Estimated result. Method blank contains contamination.

PG = The percent difference between the original and confirmation analysis is greater than 40%.

ND = Not detected at the specified method detrection limit

NA = Not analyzed or not applicable

+ = Detected

- = Not detected

+- = Possible detection; slight coloration, but difference from blank color was inconclusive

3.2.7 Concrete

Calibration and Matrix Testing

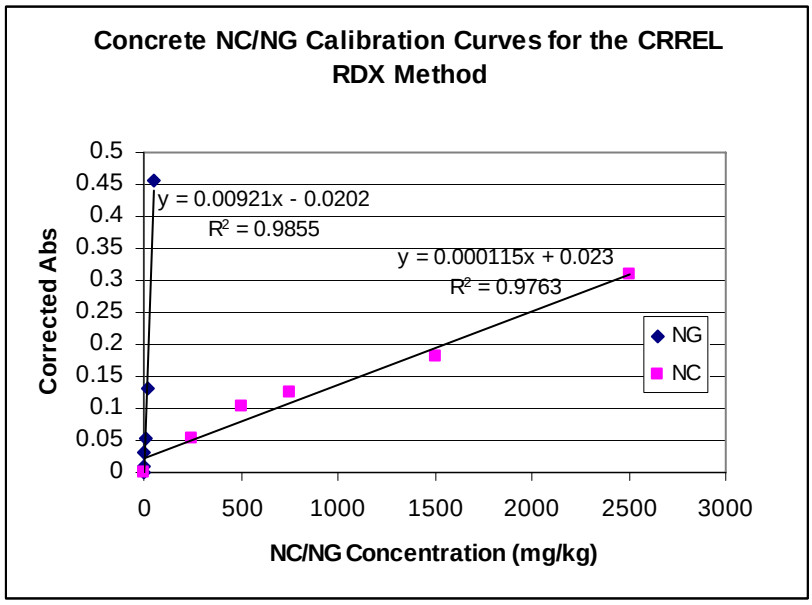
Extracts of the top one to one and one-half inch of concrete core samples and two concrete core bottom samples (one to one and one-half inch of concrete core bottom) were analyzed on-site by the CRREL RDX method. In addition, after the development of the Shaw Modified CRREL method, concrete NC standard samples were analyzed at the Shaw Lab in Knoxville by the modified method to assess performance on the concrete matrix. Only two concrete core samples had positive results for NC by the CRREL RDX method and these samples were re-analyzed by the Modified CRREL method as well at the Shaw Lab. Concrete standard samples prepared using suspended NC fibers in water were also analyzed at the Shaw Lab by the CRREL RDX and Modified CRREL methods to evaluate the response compared to standards prepared using spike solutions of NC dissolved in acetone.

Separate calibration curves were prepared for the Shaw Modified CRREL and the CRREL RDX methods using NC spiked onto background concrete material prepared for the bench test. The calibration for NG on concrete was only performed on-site during the field demonstration using the CRREL RDX method for analysis.

Extracts of expanded joint material (EJM), a somewhat hard, dry, rubbery material that was used between concrete slabs to allow expansion of the slabs were also analyzed at the Shaw Lab. Since there was no background material to make matrix specific standards for calibration, background concrete matrix extracts were spiked with NC after matrix extraction and separation to prepare a calibration curve. NC was used for calibration because it was found at substantially higher concentrations than NG in concrete samples where NG was detected.

<u>CRREL RDX Method Calibration in the Field</u>
During the bench test NG calibration with the CRREL RDX method could not be performed and this was attributed to decomposition of NG by hydrolysis due to the alkalinity of the concrete matrix. In the field demonstration, concrete standards were extracted immediately after being spiked with NG or NC in acetone to minimize time on the matrix and maximize analyte recovery. This was different than what was done in the bench test. In the bench test the NC spike solutions were composed of fine fibrous NC suspended in aqueous solution. After matrix material was spiked, overnight drying of the material was required to remove water added from the spike solution before it could be extracted with acetone. For NG in the bench test, spiked materials were also allowed to dry overnight for more complete incorporation of NG into the matrix as a better representation of actual sample material containing NG. This was done before analyte recovery problems were discovered and suspicions of decomposition on the matrix were formulated. As a result of the procedure changes for the field demonstration, a standard calibration was achieved for both NG and NC with the CRREL RDX method. The curves obtained are shown in Figure 3-9. The NC/NG response ratio (80.1) was similar to what was obtained with the CRREL RDX method on the soil matrix (71.4); however, the absolute responses for both analytes were a factor of eight to nine times lower for the concrete matrix. This indicated that either decomposition was still affecting analyte recovery or the matrix was interfering with either the extraction efficiency or the method chemistry.

Figure 3-9



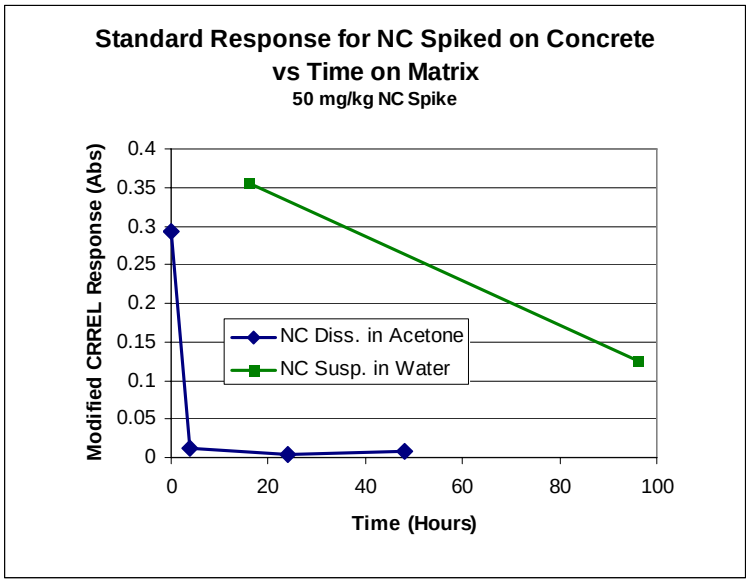
Compared to the results obtained in the bench test, the response for NG was greatly improved, but the response for NC was only marginally better. It was noted however in the bench test that NC was not as affected by the concrete matrix as was NG and this suggested NC was more stable with respect to decomposition by the matrix. However, what was not considered in the bench test was the difference in spiking procedure. It is now reasoned that the use of analyte dissolved in acetone for matrix spiking provides more intimate contact with the matrix (molecular level) than does the use of fibrous particulate and that this may be the reason NC was not as affected by the matrix as NG in the bench test. NC was also used at much higher concentrations, so there was a higher level of loading and greater chance of recovering some NC to obtain a response during analysis. Nevertheless, the use of NC dissolved in acetone for the field demonstration may have altered the extraction efficiency or increased decomposition effects.

NC Stability on Concrete Tests

When the Modified CRREL method was used at the Shaw Lab to analyze prepared NC concrete standards the response for the standards was lower than that obtained for wood and soil, which must be due to matrix interference. To investigate the matrix interference, background concrete material was extracted with acetone and the extract was removed from the matrix and spiked with NC. This provided a matrix extract with a known amount of NC added for analysis by the Modified CRREL procedure. The response obtained for NC in this test was greater and was consistent with results obtained with wood and soil matrix standards. The results showed that the concrete matrix was not interfering with the method chemistry. By elimination it was concluded that the matrix was either interfering with NC extraction or was decomposing NC even on the time frame involved for standard preparation by the new procedure, which was on the order of minutes.

To investigate analyte stability on concrete matrix several tests were performed where NC was spiked onto background concrete matrix and the tests were extracted at different times after being spiked with NC. In addition, tests were performed with NC spiked onto concrete using a sheared fibrous NC suspension in aqueous solution as was done during the bench test. The data from these tests are summarized in Figure 3-10.

Figure 3-10

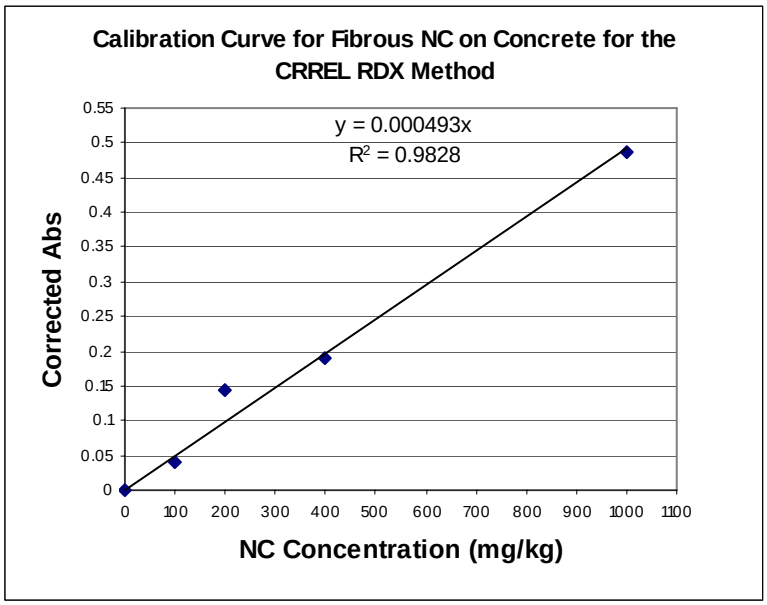


The results from these tests show two things. First, that recovery of NC from concrete decreases with time and this is most likely due to decomposition of NC by hydrolysis in the matrix. Secondly, the manner in which NC is deposited on the matrix affects its ability to be recovered, again, most likely due to decomposition. Particulate NC is more completely recovered from the matrix. The test using a 50 mg/kg NC spike dissolved in acetone was nearly below detection (less than 10% recovered) after only four (4) hours on the matrix, while about one third of the particulate NC was recovered after 96 hours. These results suggested that the ability to recover NC from the matrix would also be affected by the amount of NC deposited and the NC particle size, i.e., a higher NC loading and larger NC particle size would be more efficiently recovered, but these variables were not tested.

<u>CRREL RDX Method Calibration with Particulate NC</u>

The analyte stability tests on concrete demonstrated the difficulty in analyzing NC/NG in the concrete matrix. The ability to obtain a response for these analytes is dynamic, which more than likely depends on numerous factors as discussed above. Because of this, it is hard to imagine being able to prepare and analyze concrete matrix standards that can accurately reflect the nature of the analytes in actual samples. It may be best to use background concrete material to prepare extracts and then spike the extracts with NC/NG for analysis, but this may significantly bias results low, because it assumes no NC/NG loss to effects during the extraction process. For example, analytes that may be positioned in or on the sample matrix such that they are stable and extractable will be exposed to the matrix differently during the extraction process and may not be recovered efficiently. Because of these considerations, it was decided that the best alternative for NC analysis would be to assess how NC may be deposited in the matrix being analyzed and use standards prepared in a similar manner. For the field demonstration this may be to use standards prepared with the fibrous NC suspension and extract them as soon as possible. For NG there was no better alternative than to do what was done in the field and that was to spike matrix samples with the only NG spike source available and extract immediately. A standard curve for NC on concrete using a fibrous NC suspension by the CRREL RDX method was prepared at the Shaw Lab and the curve is shown in Figure 3-11. The curve obtained shows a response for NC that is about four (4) times greater than that obtained in the field using the NC in acetone spike solution for standard preparation.

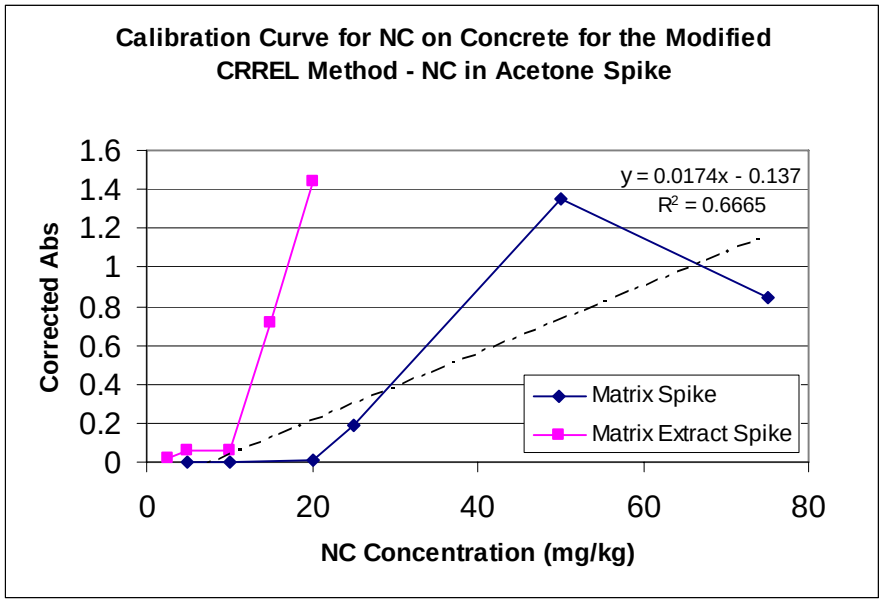
Figure 3-11



Modified CRREL Method Calibration

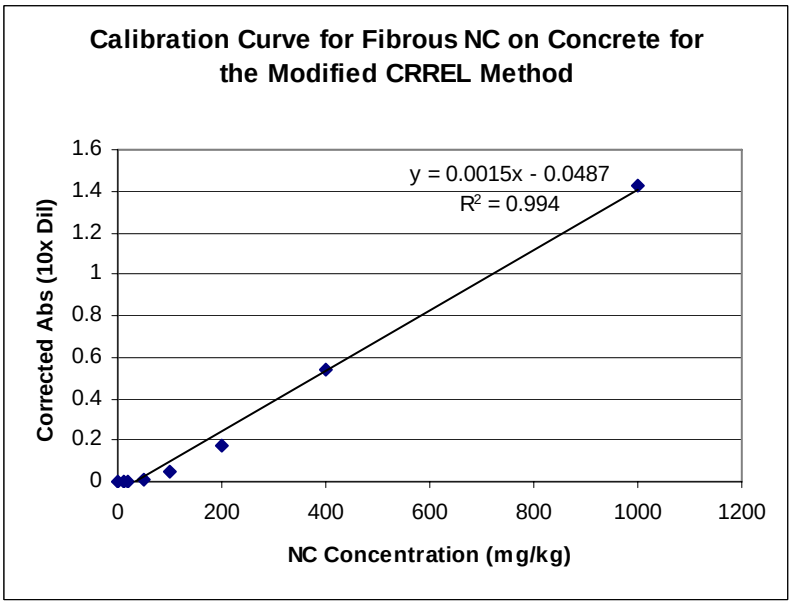
Calibration using the Modified CRREL method for NC on concrete was also performed to assess the performance of this method. A curve was prepared initially using concrete standards prepared with acetone spike solutions of NC and extracted immediately. Figure 3-12 shows the curve obtained. The figure shows a somewhat inconsistent trend for the response as a function of concentration and this was attributed to concrete matrix effects on the relatively low concentrations used with the Modified CRREL method. The standard concentrations for the Modified CRREL method ranged from 5 mg/kg to 75 mg/kg and those used for the CRREL RDX method (NC in acetone) ranged from 250 mg/kg to 2,500 mg/kg. The NC response by the Modified CRREL method for concrete standards was about one hundred times greater than the response with the CRREL RDX method. However, the response for the concrete standards by the Modified CRREL method was only about one third of that for either the wood or soil standards and indicates the relative degree of matrix interference. Also shown in this figure is a curve showing responses for standards prepared using NC spikes into background concrete matrix extract after extraction and separation from the matrix. These standards should not have had any matrix interference effects involving extraction problems or decomposition. The responses were much higher and the curve difference illustrates the degree of matrix interference obtained at the concentration levels for the Modified CRREL method. The curves also indicate loss of analyte at concentrations of 10 mg/kg and below to other effects not definitely identified, but may be related to loss during resin column treatment per the method. This is discussed in more detail below. Calibration curves for NG using the Modified CRREL method were not performed.

Figure 3-12



A calibration curve with concrete matrix standards prepared using fibrous NC spikes was also generated with the Modified CRREL method to assess the performance of the method with these standards. The standards were prepared at higher concentrations than what was anticipated for the method response range to minimize matrix effects. Prepared extracts were then diluted by a factor of ten for analysis by the method. The curve is shown in Figure 3-13. The response obtained was similar to that obtained for NC in acetone spiked standards when corrected for dilution. The curve was more consistent, but the standard concentrations were higher and that apparently had the desired effect of minimizing the impact of matrix effects.

Figure 3-13

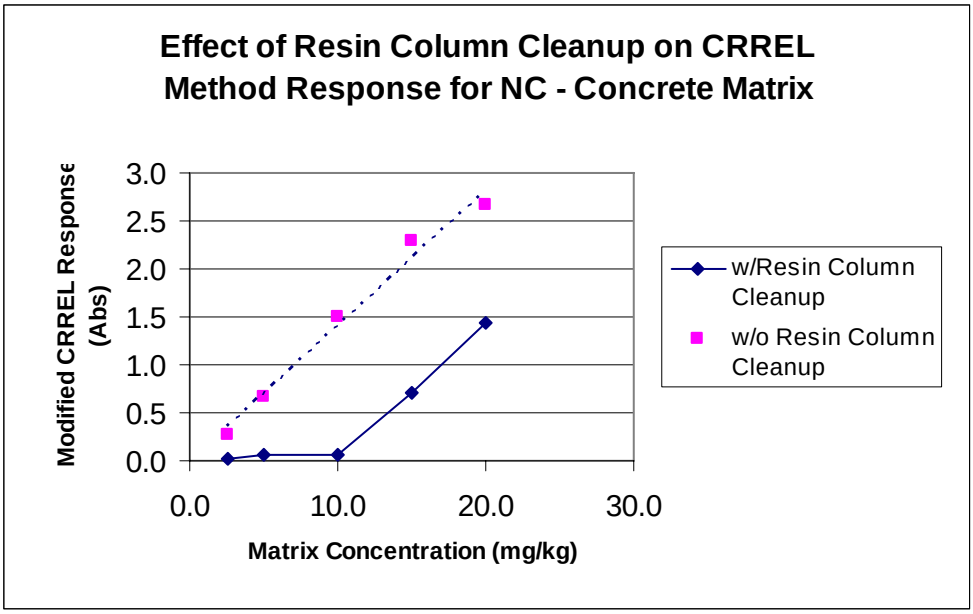


CRREL Method Resin Column Tests – Effect on NC Recovery

One other area of the CRREL methodology that was investigated during tests on concrete was the performance of the alumina ion exchange resin column used in the procedure. The recovery of analyte at relatively low concentrations from the column was investigated as part of the tests

performed to identify sources of interference with the concrete matrix. The resin column removes interferences including free nitrate and free nitrite ions prior to hydrolysis of the sample extract and subsequent color development. Tests were performed using background concrete extract spiked with NC to remove matrix contact effects but still have concrete extract as the analysis medium. Data from the bench test showed that the background concrete material contained less than 1 mg/kg of free nitrate or free nitrite, so column treatment to remove these ions was not necessary for this material. Extracts were spiked at five concentrations in the range of 2.5 to 20 mg/kg. The extracts were then analyzed by the Modified CRREL method using the method resin column cleanup and not using the resin column cleanup. Figure 3-14 shows the curves obtained. The data indicate that the resin column may hold onto about the first 10 mg/kg (concrete concentration basis) of NC, which is 10 mg/L extract concentration or 0.05 milligrams of NC (5 mL test). This loss was not noted in either the wood or soil sample testing and may be related to the concrete extract matrix or the batch of alumina columns that were used, since a new batch of columns was used for the concrete tests conducted at the Shaw Lab. This effect was not investigated further, since this level of interference was small with respect to the state of the methodology, i.e., a detection limit of 100 mg/kg. However, the effect illustrates the potential for this kind of interference and need for possible consideration during future testing and evaluation of the CRREL method.

Figure 3-14



Concrete Material Sample Analysis

Sample concentrations from CRREL RDX method analysis were quantified using calibration curves generated standards prepared with aqueous suspensions of NC spiked onto concrete. It was reasoned that contamination on concrete samples would be of a nature that is relatively stable because of the length of time involved for the history of the samples, and that this would be best represented by calibration with the NC particulate standards. Only two samples (-046 and -046A) had positive results for NC by the CRREL RDX method and they were also analyzed by the Modified CRREL method at the Shaw Lab. The results of concrete sample extract analyses are tabulated in Table 3-10. This table also shows STL results for MCAWW 353.2 for NC and Method 8330 for NG and the corrected total for STL NC and NG results. DROPEX^{Plus}/ EXPRAY™ and GC/TID results for the sample extracts are also shown for comparison.

Concentrations of NG were detected in only a few of the samples and the levels were substantially below those for NC, so only results quantified as NC are shown in the Table 3-10. Results for NG QC sample analyses for NG spike laboratory control samples (LCS); NG matrix spike (MS) and matrix spike duplicate (MSD) samples were calculated as NG.

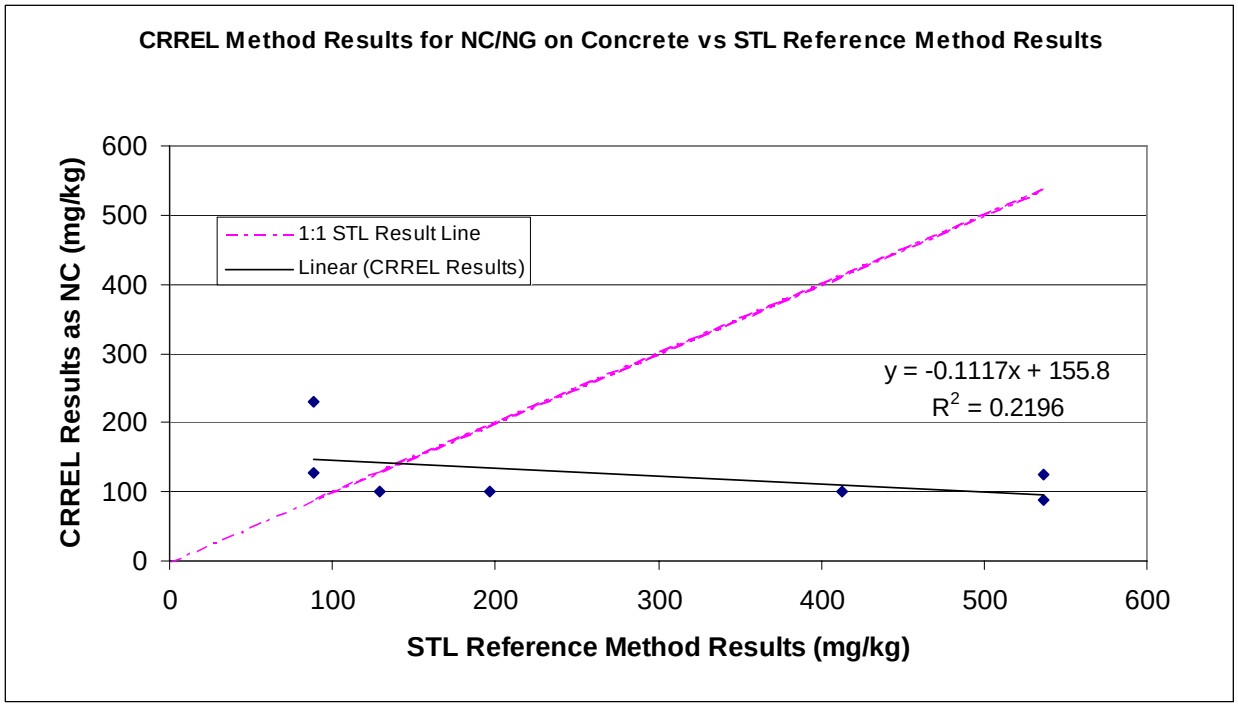
The detection limit using the CRREL RDX method for the concrete samples was 100 mg/kg for NC and 5.0 mg/kg for NG in undiluted samples. There were 37 concrete core top samples analyzed, four (4) of them were analyzed in duplicate and there were two (2) concrete core bottom samples (not submitted to STL). NC was detected in all 41 samples (including duplicates) by the STL MCAWW 353.2 method at concentrations ranging from 5 mg/kg to 536 mg/kg. NG was detected in three (3) of these samples by the STL Method 8330 method at concentrations ranging from 0.23 mg/kg to 1.1 mg/kg. The CRREL RDX method detected NC/NG in only two (2) of the samples, one sample (1890-01B-CM-046) and its duplicate (1890-01B-CM-046A), at NC concentrations of 124 mg/kg and 128 mg/kg (ND level was 100 mg/kg as NC). The Modified CRREL method detected NC/NG in the -046 sample as well at NC concentrations of 87 mg/kg and 230 mg/kg. Sample analyses for this sample by the modified method in duplicate are designated as samples 1890-01B-CM-046(B) and -046(C).

NC/NG was not detected in the two core bottom samples 1885-01-CM-035B and 1885-02-CM-100B neither analyzed by the CRREL RDX method nor was it detected in the corresponding core top samples. The DROPEX^{Plus} top surface wipe screens on both these cores indicated the presence of NC/NG. The bottom surface wipe screen on the -035 core also indicated the presence of NC/NG although it was not detected on the bottom of the -100 core.

There was one (1) false positive result (2.4%) for the CRREL RDX method at 128 mg/kg, but there was good agreement with the STL result (88 mg/kg) even though it was below the CRREL detection limit of 100 mg/kg, which classified this as a false positive. There were 5 out of 41 analyses or 12.2 percent that were false negatives. However, four (4) of the STL results for the false negatives were near the detection limit for the CRREL method where there is greater analytical variability and probability for false indication. . The bench test results also showed that the STL MCAWW 353.2 results were consistently biased high, especially at lower NC concentrations and NC was detected in unspiked clean background samples.

The average CRREL/STL RPD for the qualifying results data set was 42.2 percent and the standard deviation of the RPD data set was 40.0 percent. The data set was limited due to the number of non-detect results obtained for the CRREL method, but indicates a low or negative bias for the CRREL results compared to the STL results with the average CRREL result being 65.1 percent of the STL result. Figure 3-15 shows the correlation plot of quantitative results for concrete sample analyses for the CRREL methods versus the total STL reference method results. The axes are not logarithmic as they are for the wood and soil plots because the range of values was limited. The upper line in the plot shows the ideal 1:1 correlation line and the lower line shows the results of linear regression analysis of the qualifying CRREL data versus the STL results. The linear regression line shows there is little correlation between the CRREL results and the STL results and this is primarily attributed to the concrete matrix effect on the analytical process, which is likely method dependent. It is likely that non-homogeneity of NC/NG in the concrete sample also contributed to the non-agreement of results. Surface wipe screens indicated contamination of the core surface so sample results were likely affected by how many surface pieces or particles were included in the analysis aliquot grab. Finally, the data set was limited and only included two STL reference method analysis results that were significantly above the CRREL method detection limit of 100 mg/kg.

Figure 3-15



Expansion Joint Material Sample (EJM) Analysis

There were six concrete core samples that had expansion joint material (EJM) attached. EJM is a somewhat hard, dry, rubbery material approximately one-half to three-quarters of an inch in thickness that was placed in between concrete slabs to allow expansion. Because it is an organic matrix that may retain NC/NG contamination upon exposure and in a potential pathway for contamination to the underlying soil, there was interest in analyzing the material to assess levels of contamination. The EJM was scraped off the concrete core sample and was analyzed separately. The sample was labeled using an "EJM" identifier appended to the core sample designation to identify both the sample and its core source. The EJM was prepared for analysis in the same manner as the concrete, i.e., the material was crushed with a hammer to pieces of approximately one-quarter of an inch and collected in a Ziploc bag. The material was extracted for analysis by placing 5.0 grams of crushed material into a clean sample bottle, adding 50.0 milliliters of reagent acetone and agitating for an hour and a half. The extract was then removed from residual solids, filtered and analyzed by the Modified CRREL method for NC/NG. Sample responses were quantified by comparing to responses of standards prepared from NC spikes into background concrete material extract. A summary of the results obtained is shown in Table 3-11 along with the CRREL analyzed NC/NG concentration for the associated concrete core sample.

Table 3-10 CRREL Results for Concrete Material Samples

Sample Identification	STL Reference Method Results (mg/kg)				CRREL NG+NC	NG GC/TID	Drop-Ex	Expray
	Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	Analyzed conc as NC	Conc mg/Kg	Extract (10 uls)	Extract (10 uls)
9590-000-CM-034	ND<0.5	201Q	413	413	ND<100	ND<2.0	-	-
9590-000-CM-034A	ND<0.5	63.0	129	129	ND<100	ND<2.0	-	-
1885-01-CM-035	ND<0.5	17.1	35	35	ND<100	ND<2.0	+-	-
1885-01-CM-035B	NA	NA	NA	NA	ND<100	ND<2.0	+-	-
1885-01-CM-036	ND<0.5	20.3	42	42	ND<100	ND<2.0	-	-
1885-01-CM-037	ND<0.5	17.9	37	37	ND<100	ND<2.0	-	-
1890-01B-CM-038	ND<0.5	5.7	12	12	ND<100	ND<2.0	-	-
1890-01B-CM-039	ND<0.5	30.1	62	62	ND<100	ND<2.0	-	-
1890-01B-CM-040	ND<0.5	17.8	37	37	ND<100	ND<2.0	-	-
1890-01B-CM-041	ND<0.5	9.9	20	20	ND<100	ND<2.0	-	-
1890-01B-CM-042	ND<0.5	95.9Q	197	197	ND<100	ND<2.0	-	-
1890-01B-CM-043	ND<0.5	71.9Q	148	148	ND<100	ND<2.0	-	-
1890-01B-CM-043A	ND<0.5	36.8	76	76	ND<100	ND<2.0	-	-
1890-01B-CM-044	ND<0.5	10.2	21	21	ND<100	ND<2.0	-	-
1890-01B-CM-045	0.23J	87.8Q	180	180	ND<100	ND<2.0	-	-
1890-01B-CM-046	1.1	261Q	536	537	124	2.52	+	-
1890-01B-CM-046A	0.46J	42.7	88	88	128	1.44	+	-
1890-01B-CM-046(B)	NA	NA	NA	NA	87 [1]	NA	NA	NA
1890-01B-CM-046(C)	NA	NA	NA	NA	230 [1]	NA	NA	NA
1885-03S-CM-047	ND<0.5	3.1JB	6	6	ND<100	ND<2.0	-	-
1885-03S-CM-048	ND<0.5	3.0JM	6	6	ND<100	ND<2.0	-	-
1885-03S-CM-049	ND<0.5	6.8JM	14	14	ND<100	ND<2.0	-	-
1885-03S-CM-050	ND<0.5	3.4JM	7	7	ND<100	ND<2.0	-	-
1885-03-CM-051	ND<0.5	3.2JM	7	7	ND<100	ND<2.0	-	-
1885-03-CM-052	ND<0.5	5.3JM	11	11	ND<100	ND<2.0	-	-
1885-03-CM-053	ND<0.5	8.8JM	18	18	ND<100	ND<2.0	-	-
1885-03-CM-054	ND<0.5	5.0JM	10	10	ND<100	ND<2.0	-	-
1885-03-CM-055	ND<0.5	4.0JM	8	8	ND<100	ND<2.0	-	-
1885-03-CM-056	ND<0.5	9.8JM	20	20	ND<100	ND<2.0	-	-
1885-02-CM-057	ND<0.5	36.1JM	74	74	ND<100	ND<2.0	-	-
1885-02-CM-058	ND<0.5	3.1JM	6	6	ND<100	ND<2.0	-	-
1885-02-CM-059	ND<0.5	6.1JM	13	13	ND<100	ND<2.0	-	-
1885-02-CM-060	ND<0.5	8.7JM	18	18	ND<100	ND<2.0	-	-
1885-02-CM-061	ND<0.5	9.8JM	20	20	ND<100	ND<2.0	-	-
1885-02-CM-062	ND<0.5	7.3JM	15	15	ND<100	ND<2.0	-	-
1885-02-CM-063	ND<0.5	11.5JM	24	24	ND<100	ND<2.0	-	-
1885-02-CM-064	ND<0.5	4.2JM	9	9	ND<100	ND<2.0	-	-
1885-02-CM-065	ND<0.5	6.9JM	14	14	ND<100	ND<2.0	-	-
1885-02-CM-066	ND<0.5	7.6JM	16	16	ND<100	ND<2.0	-	-
1885-02-CM-100	ND<0.5	3.5JB,JM	7	7	ND<100	ND<2.0	-	-
1885-02-CM-100A	ND<0.5	4.4JB,JM	9	9	ND<100	ND<2.0	-	-
1885-02-CM-100B	NA	NA	NA	NA	ND<100	ND<2.0	-	-
1885-02-CM-101	ND<0.5	2.2JB,JM	5	5	ND<100	ND<2.0	-	-
1885-02-CM-102	ND<0.5	3.4JM,JB	7	7	81	ND<2.0	-	-
1885-02-CM-103	ND<0.5	3.5JM,JB	7	7	ND<100	ND<2.0	-	-

[1] Shaw modified CRRELanalysis
A= sample duplicate (B)=triplicate (C)=quadruplicate
B= Core Bottom
Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JM = Estimated result. MS/MSD recovery is outside stated control limits.
JB = Estimated result. Method blank contains contamination.
ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table 3-11. NC/NG Results for Concrete Expansion Joint Material

Sample Identification	Matrix	CRREL RDX Method Analyzed NC/NG Concentration of Associated Concrete as NC (mg/kg)	Modified CRREL Method Estimated NC/NG Concentration of EJM as NC[a] (mg/kg)
1885-01-CM-036-EJM	EJM	ND<100	ND<50
1890-01B-CM-042-EJM	EJM	ND<100	132
1890-01B-CM-046-EJM	EJM	124, 128	128
1885-03S-CM-049-EJM	EJM	ND<100	90
1885-03-CM-053-EJM	EJM	ND<100	ND<50
1885-02-CM-064-EJM	EJM	ND<100	ND<50

[a]Values are estimates because calibration was performed with background concrete extract matrix.
ND = Not detected at the specified estimated detection limit.

3.2.8 Data Assessment Summary

The data provided in Table 3-12 should be used to define the method performance capabilities for the CRREL RDX method for analysis of NC/NG on samples of the matrices tested.

Table 3-12

CRREL RDX Method Performance Metrics for NC/NG Analysis

Matrix (Test Group)	NG STL 8330 Detection Limit (mg/kg)	NC STL 353.2 Detection Limit (mg/kg)	CRREL RDX Detection Limit (NC) (mg/kg)	Test Sample Analysis Performance Indicators				
				%RPD Mean	%RPD STD	%False Positive	%False Negative	LR R Value
Wood	0.5 - 10	10-200	NA	NA	NA	NA	NA	NA
Soil	0.5	2.0-400	25	82.7	81.8	**2.7**	37.8	0.8979
Concrete	0.5	2.0-20	100	42.2	40.0	**2.4**	12.2	0.2196
Performance Criteria	3.6	NA	NA	NMT 20%	NA	NMT 10%	NMT 5%	≥0.95

NMT = not more than
RPD = relative percent difference
STD = standard deviation
NC = not calculated due to insufficient data points for correlation
NA = not applicable, wood only analyzed by Modified CRREL method

These data provided in Table 3-13 should be used to define the method performance capabilities for the Modified CRREL method for analysis of NC/NG on samples of the matrices tested.

Table 3-13

Modified CRREL Method Performance Metrics for NC/NG Analysis

Matrix (Test Group)	NG STL 8330 Detection Limit (mg/kg)	NC STL 353.2 Detection Limit (mg/kg)	Modified CRREL Detection Limit (NC) (mg/kg)	Test Sample Analysis Performance Indicators				
				%RPD Mean	%RPD STD	%False Positive	%False Negative	LR R Value
Wood	0.5 - 10	10-200	10-15	89.1	69.9	**0**	18.9	0.708
Soil	0.5	2.0-400	1.5	82.7	72.0	**0**	32.3	**0.9548**
Concrete	0.5	2.0-20	100	NA	NA	NA	NA	NA
Performance Criteria	3.6	NA	NA	NMT 20%	NA	NMT 10%	NMT 5%	≥0.95

NMT = not more than
RPD = relative percent difference
STD = standard deviation
NC = not calculated due to insufficient data points for correlation
NA = not applicable, wood only analyzed by Modified CRREL method

3.2.9 CRREL Method Conclusions

Findings from the field demonstration are as follows:

- The CRREL RDX method of analysis gives a relatively low response for NC compared to NG that is easily impacted by matrix interferences. Modifications to the CRREL RDX procedure to replace the acidic hydrolysis step with an alkaline hydrolysis greatly increased the method response for NC and retained the response for NG. The increase in response made the method more robust for NC analysis and allowed analysis of NC on the three sample matrices. The NC/NG response ratio obtained with the Shaw Modified CRREL method for NC/NG was close to the desired theoretical value of 1.31 based on the N content of each compound. It is Shaw's opinion that the CRREL RDX method is not appropriate for analysis of NC, especially in the matrix samples used in this study, and the Modified CRREL method is more suitable. With the limited amount of experience Shaw has with use of the Modified CRREL method since its development it appears to perform well for NC analysis providing low detection limits and predictable response.

- Tests conducted with NC on concrete showed that recovery of NC from the matrix was a function of both time and the manner in which NC was deposited on the matrix. Acetone solutions containing dissolved NC provided intimate contact of NC with the matrix when spiked onto concrete and only 10% of the initially recoverable NC was recovered after four hours by CRREL analysis. When NC was spiked onto concrete in the form of particulate material in an aqueous suspension approximately one-third was recovered after 96 hours. These results were attributed to decomposition of NC by the concrete matrix due to its alkaline nature in a similar manner as to what was concluded for NG in the bench test. The instability of NC/NG compounds on concrete matrix makes analysis difficult not only due to the potential impact on samples during handling and preparation, but also due to the effect on matrix standards.

- Compound detection performance metrics for NC/NG using the CRREL methods were not met for the three matrices (wood, soil, and concrete) tested during the field demonstration. False positives with both the CRREL RDX and the Modified CRREL method were less than 5 percent. False negatives, however, were greater than 10 percent for both CRREL methods and all three matrices, ranging from 12.2 percent to 37.8 percent. Performance metrics for concrete samples were limited by the number of positive results obtained by the CRREL methods.

  It is possible that the number of false negatives was elevated because NC was biased high by the STL Method 353.2 at low concentrations. An indication of this was provided by positive responses for NC in a number of the method blanks (false positives) for wood and soil, which had the highest percentages of CRREL false negatives. The bench test results also showed that the STL MCAWW 353.2 results were consistently biased high, especially at lower NC concentrations and NC was detected in unspiked clean background samples.

- Compound concentration metrics with respect to RPD values were not met by either CRREL method with any of the three matrices sampled during the building investigation. CRREL results were consistently biased low in comparison to the STL reference method results. The RPD between CRREL and STL results ranged from 42.2 to 89.1 percent. However, the results for the Modified CRREL method on soil showed a linear regression correlation to the STL results with a coefficient (R^2) of 0.9548, which is above the 0.95 performance metric. Performance metrics for concrete samples were limited by the number of positive results obtained by the CRREL methods.

There was no clear indication of why the CRREL results were biased low compared to the STL results. Most likely reasons include the following:

- STL Method 353.2 results were biased high due to matrix interference or contamination phenomenon similar to what affected method blanks and results from the bench test.
- Additional matrix interference in samples over that in background material used for standard preparation that caused low response for the CRREL methods.
- A change in STL analysis conditions such that the applied matrix sample correction from the bench test produced values that were too high. The applied correction increased the STL Method 353.2 result by a factor of 1.5 to 2.0.

- There was considerable scatter in the RPD values for the method result comparisons and this was attributed to non-homogeneous sample material and sources of contamination. Contamination of building materials (concrete and wood) was likely concentrated on exposed surfaces of the material. It is probable that the sample particle size of about a quarter of an inch was not small enough to provide sufficient distribution of contaminated pieces for uniform sampling. Soil samples contained pieces of propellant material that made preparing a homogeneous sample difficult.
- Analysis of six (6) samples of concrete expansion joint material associated with concrete samples were analyzed separately for NC/NG by the Modified CRREL method and concentrations detected were consistent with concentrations for the associated concrete sample.
- One field chemist with experience wet chemistry techniques is required for onsite analysis by the CRREL methods. Instrument (visible spectrophotometer) costs are about $2,000. Sample analysis rate during the demonstration was about 3-5 samples per hour.
- No routine maintenance is required. There was no downtime during the demonstration. Check standards are analyzed every day before and after sample analyses and after every 10 samples. Percent down time is estimated at less than one (1) percent.
- Field colorimetric analysis requires electrical power (110v) and a stable environment during operation, but is portable and can be used under a wide variety of site conditions.
- Some hazardous materials are generated by the method primarily acetone solvent and aqueous acetone solutions. Due to time constraints samples and standards were returned to the Shaw Lab in Knoxville. The left-over acetone extracts (~4 liters) will be disposed of as hazardous waste.
- Minimal investigative-derived waste was generated during the project.

3.3 Quantitative Analysis for NG by GC/TID

3.3.1 Introduction

A field-capable gas chromatography (GC) instrument equipped with a thermionic ionization detector (TID) was used to analyze the prepared sample extracts for NG. This method is selective for NG and does not produce a response for NC. The configuration is the same as the unit that was used in the bench study. Following a simple extraction procedure, sample extracts are injected directly onto the GC column within a heated injection port. Analytical times varied by matrix and ranged from less than 6 minutes to 11 minutes.

This method is not applicable to the analysis of NC because NC is nonvolatile. In order for a compound to be analyzed by GC it needs to be volatilized into the gas phase. It is in the gas phase that the compound can be mobilized, transferred and separated in the column and subsequently transferred to the detector for analysis. In addition NC decomposes at temperatures below the detector temperature and therefore is not detectable.

Background sample material of each test matrix (remaining from the bench test) was spiked at concentrations of NG ranging from 2.0 mg/kg to 400 mg/kg and used as calibration standards. A calibration curve was developed using the calibration samples for each test group. Results were calculated based on these curves. Instrument performance was continuously monitored by reanalysis of standards before and after each test group or every 10 samples. A blank, LCS, and MS/MSD were extracted and analyzed for each 20 samples of each matrix evaluated.

Figure 3-16. SRI GC/TID

3.3.2 Instrumentation

The GC used was the SRI Instruments, Inc (SRI) Model 8610C equipped with a heated TID, a heated on column injection port, and an internal air compressor. Separations were performed on a metal Crossbond 100 percent dimethyl polysiloxane column (DB-1), 15 m x 0.53 mm inside diameter, 0.5 micrometer film thickness.

The SRI Model 8610C as shown in Figure 3-16 is a transportable unit designed for field use Manual injections were made directly on the column using a 10 µL glass syringe with an extra long (6.0-7.0 cm) syringe needle that was supplied by SRI. GC data were collected on a Dell Latitude laptop computer using Peak Simple data collection software. The software was provided with the instrument from SRI.

3.3.3 Method

Sample extractions were prepared for each sample using acetone. This was the same extraction used for the colorimetric testing of EXPRAY™ / DROPEX^{Plus} and the CRREL method. The extraction is described above in Section 2.5. Manual injections of 1 µL volumes of the acetone extracts were directly injected onto the GC using the following GC conditions which were optimized as part of the bench study.

Injection port temperature:	180°C
Detector temperature:	250°C
TID bead voltage:	-320 millivolts
Internal air compressor pressure:	7 pounds per square inch (psi) for carrier gas 1 psi for make-up gas
GC oven temperature program:	95°C for 0.5 minutes 20°C/min to 160°C 160°C for 2 minutes 40°C/min to 210°C-240°C 210°C-240°C for up to 3.25 minutes

Using the internal air compressor for both carrier and make-up gas eliminated the need for a high pressure gas cylinder, which is beneficial for field applications.

The GC oven temperature program listed above was modified for the different sample matrices based on the level of non-target analytes detected. In concrete samples the presence of non-target analytes was minimal allowing the maximum oven temperature to be lowered to 210°C decreasing the overall analytical time to 5.75 minutes per sample. By contrast, wood samples contained high levels of non-target analytes necessitating the oven temperature be held at 240°C for 3.25 minutes yielding a total analytical time of 11.0 minutes per sample. In addition to longer analytical times, samples containing high levels of non-target compounds resulted in a more rapid reduction of sensitivity caused by loading of the injection end of the column. Therefore, when wood extracts were analyzed, instrument performance was tested more frequently by analyzing standards as often as every 5 sample injections. When the recovery of a standard fell to less than 80 percent of the expected concentration approximately 6 inches were removed from the injection end of the column to regain sensitivity.

Evaluation of clean-up procedures on the sample extracts prior to injection may result in an effective way to minimize the effects of non-target compounds leading to less instrument downtime and therefore increased efficiency. For example, the alumina column cleanup used in the CRREL method described above may provide a benefit.

A calibration curve for each sample matrix was generated in the field by spiking the background wood, soil and concrete samples obtained during the bench scale testing with NG. The concentration for NG in the test samples was calculated based on this curve.

3.3.4 Data Assessment

For comparison purposes, the results for the GC-TID analyses of the samples are summarized in Table 3-6 (Wood), Table 3-7 (Soil) and Table 3-8 (Concrete Material) along with results for the lab reference method, STL (SW-846) Method 8330. Results for sample analyses for each matrix were obtained using the corresponding method calibration curve as described above and are reported in the tables.

The relative percent difference (RPD) between the reference method values (sample results) and the field method concentration have been calculated and tabulated in the summary along with the mean and standard deviation of the RPD. Non-detect (ND) results were set at the detection limit for this comparison except when non-detects were obtained for both methods and the non-detect levels were not similar. In this case the sample results were not included in the comparison analysis. If a positive result by one method was significantly lower than a non-detect level in the other method, these results were also excluded from the comparison analysis. The RPD data

provide a measure of the agreement between reference method results and the field method results to aid in method comparison. The RPD measures the analytical bias of the GC/TID results compared to the STL method results for the data set, and the standard deviation is a measure of scatter in the agreement between the method results for the data set.

In addition, for each matrix a linear regression plot was generated of the GC/TID sample results versus the reference Method 8330 results. The linear regression coefficient (R^2) values for each data set are also tabulated in the tables below. This provides another measure of the agreement of field method sample results with Method 8330 values.

Results for each sample matrix are discussed separately below. All samples were analyzed on site with the exception of the last soil samples collected, (sample numbers 82 through 99) which were returned to the Shaw Lab in Knoxville for analysis due to time constraints for the field demonstration.

Wood

Analysis results for NG on the wood samples by GC-TID are shown in Table 3-14 along with STL reference (SW-846 Method 8330) results for sample splits.

The detection limit for the GC/TID analysis of wood samples was 5 mg/kg NG. Twenty-four of the 37 samples evaluated had no detectable levels above the Method 8330 or GC/TID reporting limits. Detection limits for SW-846 Method 8330 results ranged from 0.5 to 10 mg/kg due to dilutions required because of matrix interference. Field method values for the samples with detectable concentrations (above 5 mg/kg NG) were an average of 62 percent lower than results from the STL 8330 reference method. For this set of data the average relative percent difference (RPD) was 89.9 percent and the standard deviation was 52.4 percent. For the entire data set, which includes non-detect results, the mean of the method percent differences was 48.7 percent and the standard deviation of the method percent differences was 53.0 percent. The data indicates there was a detectable negative bias to the GC/TID results. A correspondence plot of the GC/TID values and the STL 8330 value is shown on Figure 3-17 for the 13 wood samples with detectable values for NG.

The reason for the negative or high bias indicated by the field demonstration results is not known. Bench scale test results (as shown below) for NG spiked wood for STL Method 8330 and GC/TID correlated very well (R^2 = 0.985) with the NG spike concentration with no detectable bias. An average RPD of -2.3 percent and standard deviation of 14.9 percent were within performance metrics. A plot of the bench scale test NG spiked wood sample data is shown below in Figure 3-18 for comparison purposes.

Figure 3-17

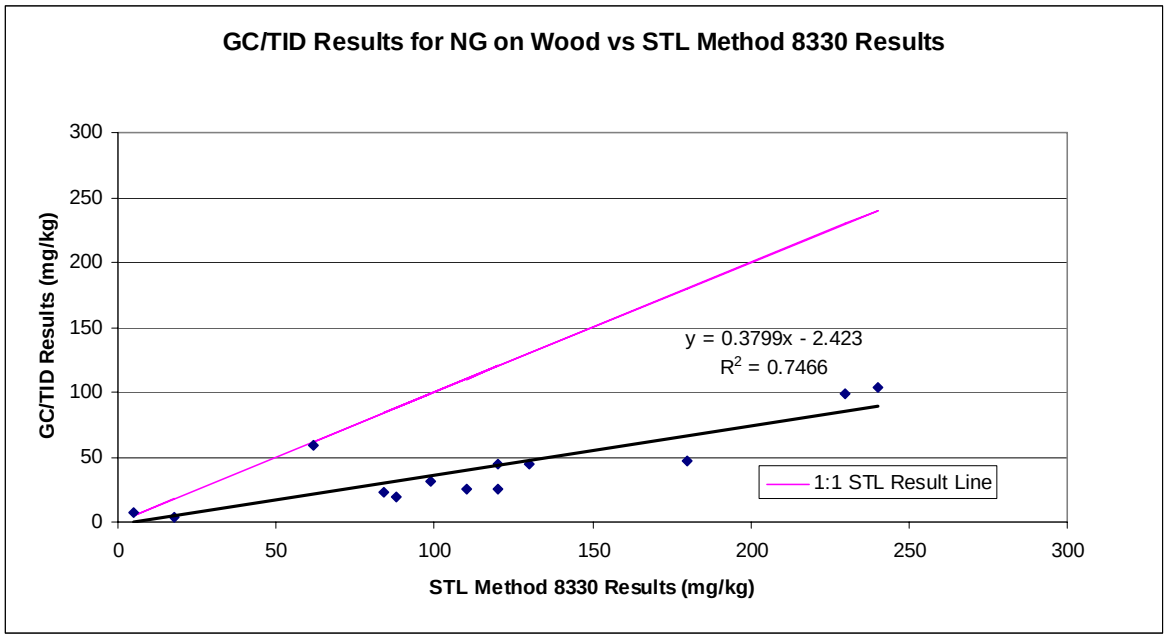
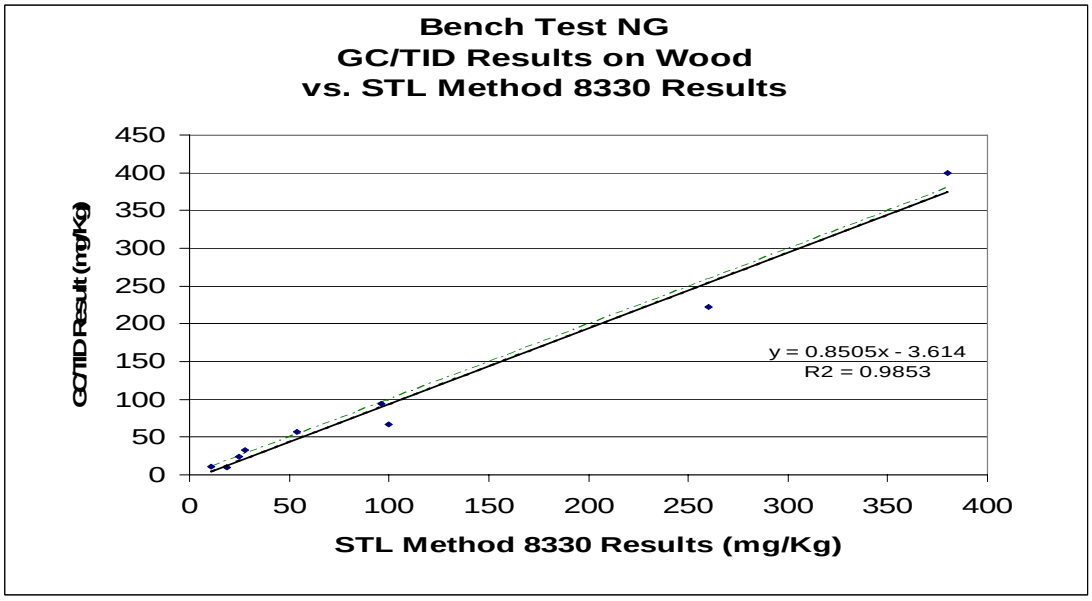


Figure 3-18



The bias in the field demonstration samples is thought to be matrix related. Ten (10) of the 13 samples with detectable concentrations were from the same building: 6709-17 pre-drying house. GC/TID field analysis included NG spiked MS/MSD samples for 6709-17-WD-019 and 1890-01-WD-022. Percent recovery for the MS/MD samples at 86%, 97% and 101%, 85%, respectively was within the method control limits (75%-125%. Method 8330 MS/MSD percent recovery for sample 6709-17-WD-012 was 38% and 137%, outside of method control limits (74%-112%). Sample 1890-01-WD-023 MS/MSD percent recovery was within limits at 87%, 89% respectively.

The percent of false negatives and false positives at 0 and 2.7, respectively, indicate general agreement between methods with regard to detection and non-detection; however, both the linear regression (LR) correlation coefficient (R^2 value) and RPD do not meet performance metrics of greater than 0.95 and not more than (NMT) 20 percent for the field demonstration samples.

Table 3-14. GC/TID Results for Wood Samples

Sample Identification	STL Reference Method Method 8330 Results	NG GC/TID Results
	NG Concentration mg/Kg	NG Concentration mg/Kg
6657-02N-WD-001	3.7	ND<5.0
6657-02N-WD-002	18	3.2
6657-02I-WD-003	ND<0.5	ND<5.0
6657-02I-WD-003A	ND<5	ND<5.0
6657-02I-WD-004	ND<0.5	ND<5.0
5024-000-WD-005	ND<5	7.7
5024-000-WD-006	ND<5	ND<5.0
5024-000-WD-007	ND<5	ND<5.0
5024-000-WD-008	ND<5	ND<5.0
5024-000-WD-009	ND<0.5	ND<5.0
5024-000-WD-010	ND<5	ND<5.0
5024-000-WD-011	ND<2.5	ND<5.0
6709-17-WD-012	99	31.6
6709-17-WD-013	88	19.2
6709-17-WD-014	230	98.3
6709-17-WD-015	240	104
6709-17-WD-016	180	47.3
6709-17-WD-017	130	44.5
6709-17-WD-018	84	22.9
6709-17-WD-019	120	44.5
6709-17-WD-020	110	25.4
6709-17-WD-020A	120	25.9
6709-17-WD-021	62	58.5
1890-01-WD-022	ND<0.5	ND<5.0
1890-01-WD-023	ND<0.5	ND<5.0
1890-01-WD-024	ND<0.5	ND<5.0
1890-01-WD-025	ND<0.5	ND<5.0
1890-01-WD-026	ND<0.5	ND<5.0
1890-01-WD-027	ND<5	ND<50
1890-01-WD-028	ND<5	ND<5.0
1890-01-WD-028A	ND<5	ND<5.0
1890-01-WD-029	ND<5	ND<5.0
1890-01-WD-030	ND<5	ND<5.0
9590-000-WD-031	ND<0.5	ND<5.0
9590-000-WD-032	ND<10	ND<50
5024-000-WD-033	ND<0.5	ND<20
5024-000-WD-033A	ND<0.5	ND<20

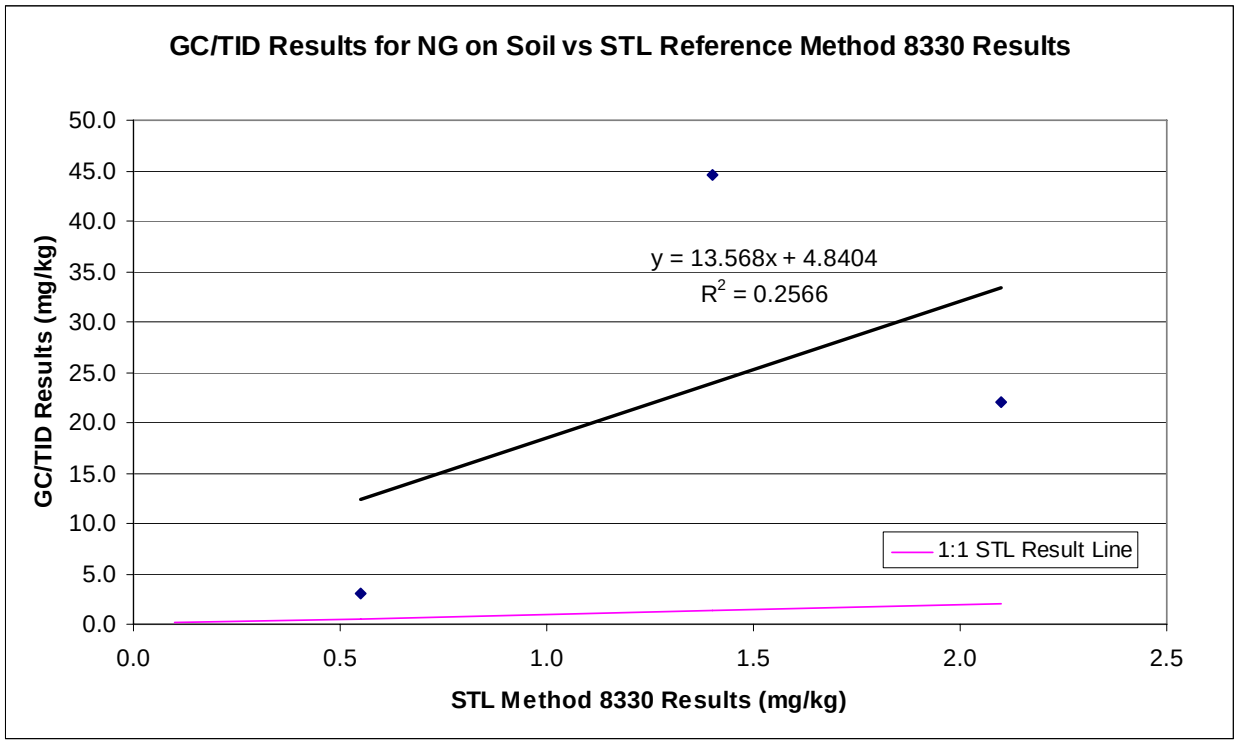
ND = Not detected at the specified method detection limit
NA = Not analyzed or not applicable

Soil

Analysis results for NG on the soil samples by GC-TID are shown in Table 3 15 along with STL reference (SW-846 Method 8330) results for sample splits.

The detection limit for the GC/TID analysis of soil samples was 2.0 mg/kg NG. Detection limit for SW-846 Method 8330 was 0.5 mg/kg. The RPD for the entire data set including non-detects was -12.9 percent with a standard deviation of 45.4 percent. A plot of the GC/TID values and the STL 8330 value is shown in Figure 3-19 for the three soil samples with detectable values of NG. The average RPD for these three results was -163 percent and the standard deviation was 25.2 percent. This data indicates a positive bias for the GC/TID results above the detection limit compared to the STL results with the GC/TID result being on the average ten times the value obtained by the STL reference method.

Figure 3-19



Data from the bench scale test for GC/TID and STL Method 8330 correlated very well with the spike concentration with no detectable bias to the results. Samples collected for the field demonstration did not have significant NG contamination and did not provide enough data to obtain a good evaluation of data correlation.

The percent of false negatives and false positives at 2.7 and 5.4, respectively, as well as the average RPD for the entire data set of -12.9 percent indicate general agreement between methods with regard to detection and non-detection. However, the linear regression correlation coefficient (R^2) and average RPD (-163%) for the results above of the detection limit do not meet performance metrics of greater than 0.95 and not more than 20 percent for the field demonstration samples. These metrics are based on three results, which are not significantly above the detection limit, however, and it is felt they do not provide sufficient data and data of high enough quality to base a meaningful evaluation.

Table 3-15. GC/TID Results for Soil Samples

Sample Identification	STL Reference Method Method 8330 Results NG Concentration mg/Kg	NG GC/TID Results NG Concentration mg/Kg
1885-02-SS-067	ND<0.5	ND<2.0
1885-02-SS-068	0.55	ND<2.0
1885-02-SS-069	0.36	ND<2.0
1885-02-SS-070	ND<0.5	ND<2.0
1885-02-SS-071	ND<0.5	ND<2.0
1885-02-SS-072	2.1	22.0
1885-02-SS-072A	1.4	44.5
1885-02-SS-073	ND<0.5	ND<2.0
1885-03-SS-074	ND<0.5	ND<2.0
1885-03-SS-075	ND<0.5	ND<2.0
1885-03-SS-076	ND<0.5	ND<2.0
1885-03-SS-077	ND<0.5	ND<2.0
1885-03-SS-078	ND<0.5	ND<2.0
1890-01B-SS-079	ND<0.5	ND<2.0
1890-01B-SS-080	0.55	3.0
1890-01B-SS-081	ND<0.5	ND<2.0
1890-01B-SS-081A	ND<0.5	ND<2.0
1890-01B-SS-081B	NA	NA
1890-01B-SS-081C	NA	NA
1885-02-SS-082	1.0	ND<2.0
1885-02-SS-083	3.0	ND<2.0
1885-02-SS-083A	ND<0.5	ND<2.0
1885-02-SS-084	ND<0.5	ND<2.0
1885-02-SS-085	0.19	ND<2.0
1885-02-SS-086	ND<0.5	ND<2.0
1885-02-SS-087	0.82	ND<2.0
1885-02-SS-088	0.39	ND<2.0
1885-02-SS-089	ND<0.5	ND<2.0
1885-02-SS-090	ND<0.5	ND<2.0
1885-02-SS-091	ND<0.5	ND<2.0
1885-02-SS-092	ND<0.5	ND<2.0
1885-02-SS-093	0.18	ND<2.0
1885-02-SS-093A	ND<0.5	ND<2.0
1885-02-SS-094	ND<0.5	ND<2.0
1885-02-SS-095	ND<0.5	ND<2.0
1885-02-SS-096	ND<0.5	ND<2.0
1885-02-SS-097	ND<0.5	ND<2.0
1885-02-SS-098	ND<0.5	ND<2.0
1885-02-SS-099	ND<0.5	ND<2.0

ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable

Concrete Material

In the bench test, calibration could not be performed with NG on concrete material and this was attributed to decomposition of NG by the concrete due its alkaline nature (See the discussion in the CRREL concrete results section 3.2.7). In the field demonstration concrete standards were spiked and analyzed immediately to minimize the time NG spent on the matrix and this procedure was successful in allowing a calibration for NG on concrete to be obtained. The GC/TID calibration response for NG on concrete was similar to that for NG on soil, so there was little adverse effect due to the matrix.

Analysis results for NG on the concrete samples by GC-TID are shown in Table 3-16 along with STL reference (SW-846 Method 8330) results for sample splits. There were only three samples with detectable amounts of NG by the STL reference method and they were; 1890-01B-CM-045, 1890-01B-CM-046 and its duplicate, 1890-01B-CM-046A. Two of these were the only samples that had detectable levels of NG by the GC/TID method and they were 1890-01B-CM-046 and its duplicate, 1890-01B-CM-046A. None of these results exceeded the NG cleanup criterion of 3.6 mg/kg. The values were near the method detection limits for both methods. The detection limit for the GC/TID analysis of concrete samples was 2.0 mg/kg NG. Detection limits for SW-846 Method 8330 was 0.5 mg/kg.

The RPD for the entire data set including non-detects was -4.4 percent with a standard deviation of 19.5 percent. The RPDs for the two samples with positive results by both methods were -78 percent and -103 percent. The GC/TID results were high compared to the STL results, but due to the low levels near the detection limits, and the increased analytical variability at these levels, the results are not considered to be of high enough quality to base a comparison.

The percent of false negatives and false positives at 0.0 and 4.9, respectively, as well as the average RPD for the entire data set of -4.4 percent indicate general agreement between methods with regard to detection and non-detection.

Table 3-16. GC/TID Results for Concrete Material Sample

Sample Identification	STL Reference Method Method 8330 Results NG Concentration mg/Kg	NG GC/TID Results NG Concentration mg/Kg
9590-000-CM-034	ND<0.5	ND<2.0
9590-000-CM-034A	ND<0.5	ND<2.0
1885-01-CM-035	ND<0.5	ND<2.0
1885-01-CM-035B	NA	ND<2.0
1885-01-CM-036	ND<0.5	ND<2.0
1885-01-CM-037	ND<0.5	ND<2.0
1890-01B-CM-038	ND<0.5	ND<2.0
1890-01B-CM-039	ND<0.5	ND<2.0
1890-01B-CM-040	ND<0.5	ND<2.0
1890-01B-CM-041	ND<0.5	ND<2.0
1890-01B-CM-042	ND<0.5	ND<2.0
1890-01B-CM-043	ND<0.5	ND<2.0
1890-01B-CM-043A	ND<0.5	ND<2.0
1890-01B-CM-044	ND<0.5	ND<2.0
1890-01B-CM-045	0.23J	ND<2.0
1890-01B-CM-046	1.1	2.52
1890-01B-CM-046A	0.46J	1.44
1885-03S-CM-047	ND<0.5	ND<2.0
1885-03S-CM-048	ND<0.5	ND<2.0
1885-03S-CM-049	ND<0.5	ND<2.0
1885-03S-CM-050	ND<0.5	ND<2.0
1885-03-CM-051	ND<0.5	ND<2.0
1885-03-CM-052	ND<0.5	ND<2.0
1885-03-CM-053	ND<0.5	ND<2.0
1885-03-CM-054	ND<0.5	ND<2.0
1885-03-CM-055	ND<0.5	ND<2.0
1885-03-CM-056	ND<0.5	ND<2.0
1885-02-CM-057	ND<0.5	ND<2.0
1885-02-CM-058	ND<0.5	ND<2.0
1885-02-CM-059	ND<0.5	ND<2.0
1885-02-CM-060	ND<0.5	ND<2.0
1885-02-CM-061	ND<0.5	ND<2.0
1885-02-CM-062	ND<0.5	ND<2.0
1885-02-CM-063	ND<0.5	ND<2.0
1885-02-CM-064	ND<0.5	ND<2.0
1885-02-CM-065	ND<0.5	ND<2.0
1885-02-CM-066	ND<0.5	ND<2.0
1885-02-CM-100	ND<0.5	ND<2.0
1885-02-CM-100A	ND<0.5	ND<2.0
1885-02-CM-100B	NA	ND<2.0
1885-02-CM-101	ND<0.5	ND<2.0
1885-02-CM-102	ND<0.5	ND<2.0
1885-02-CM-103	ND<0.5	ND<2.0

Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JM = Estimated result. MS/MSD recovery is outside stated control limits.
JB = Estimated result. Method blank contains contamination.
ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable

3.3.5 Summary of GC/TID Performance Metrics

The GC/TID field demonstration analysis performance parameters are summarized below in Table 3-17 for the matrix test groups.

Table 3-17. GC-TID Performance Metrics for NG Analysis

Matrix (Test Group)	STL 8330 Detection Limit (mg/kg)	GC/TID Detection Limit (mg/kg)	Test Sample Analysis Performance Indicators				
			%RPD Mean	%RPD STD	%False Positive	%False Negative	LR R Value
Wood	0.5 - 10	5	48.7	53.0	**2.7**	**0**	0.7466
Soil	0.5	2.0	**-12.9**	45.3	**5.4**	**2.7**	0.257
Concrete	0.5	2.0	**-4.43**	19.5	**4.9**	**0**	NC[1]
Performance Criteria	3.6	3.6	NMT 20%	NA	NMT 10%	NMT 5%	≥0.95

NMT = not more than
RPD = relative percent difference
STD = standard deviation
[1] NC = not calculated due to insufficient data points for correlation

3.3.6 GC/TID Method Conclusions

Findings from the field demonstration are as follows:

- Analyte detection performance metrics for NG were met for all three matrices (wood, soil, and concrete) tested during the field demonstration with <5 percent false negatives and <10 percent positives.
- Analyte concentration performance metrics for NG by GC/TID were not met with any of the three matrices sampled during the building investigation. The linear regression correlation coefficient (R^2) and average RPD for the results above of the detection limit do not meet performance metrics of greater than 0.95 and not more than 20 percent for the field demonstration samples.
- GC/TID analysis of NG on soil, and concrete samples was sensitive; a detection limit of 2 mg/kg, which was comparable to the reference method, was observed. Wood had a slightly higher detection limit of 5 mg/kg.

- Thirteen (13) of the 37 wood samples evaluated had positive values for NG by the 8330 reference method for comparison. The GC/TID results were low in comparison with values that averaged 38.0 percent of the STL values. This bias was not observed during the bench scale testing. Matrix interference with the STL Method 8330 results is a possible explanation but is unconfirmed. The analysis report by STL indicated that many samples required dilution due to matrix interferences and surrogates were diluted out preventing evaluation. Evaluation of matrix related QC samples was also inconclusive

- Soil sample results by GC/TID were possibly biased high; however, there was insufficient NG contamination in the field demonstration samples collected to effectively evaluate performance. The thirteen samples containing detectable amounts of NG by STL Method 8330 had concentrations ranging from 0.18 to 3.0 mg/k and these are right around the method detection limit of 0.5 mg/kg where analytical variability is the greatest (four values were estimates below the detection limit).

- Concrete sample results by GC/TID were possibly biased high; however, there was insufficient NG contamination in the samples collected in the field demonstration to effectively evaluate performance. Only one sample contained NG above the 8330 method detection limit of 0.5 mg/kg. The GC/TID method also gave only one result above the detection limit of 2 mg/kg. It is believed that NG is not stable in the alkaline concrete matrix.

- In general, reliability of the GC/TID ability to detect NG on the building materials was consistent with the reference Method 8330. Both methods may be subject to matrix interference effects and QC samples should be included to help assess data quality.

- One field chemist with experience in gas chromatography is required for onsite analysis by GC/TID. Instrument costs are about $10,000 and do not require the use of compressed gases. Sample analysis rate during the demonstration was about 3-5 samples per hour

- Minimal routine GC maintenance (septa replacement, cutting column) is required. There was relatively little downtime during the demonstration. Maintaining sensitivity required frequent cutting of the injection end of the column. The frequency is matrix dependent and thought to be due to loading or degradation of the column material by non-target constituents in the sample. This problem was most prevalent with the wood samples. Check standards are analyzed frequently; every 10 samples for soil and concrete, every 5 samples for wood, to monitor loss of sensitivity. Percent down time was estimated at 5-7 percent.

- Field GC/TID analysis requires electrical power (110v) and a stable environment during operation, but is portable and can be used under a wide variety of site conditions.

- Minimal hazardous materials were generated by the method. Due to time constraints samples and standards were returned to the Shaw Lab in Knoxville. The left-over acetone extracts (~2 liters) will be disposed of as hazardous waste.

- Minimal investigative-derived waste was generated during the project.

4.0 SUMMARY OF METHOD CONCLUSIONS

During the field demonstration three field analytical methodologies were evaluated for identifying and/or quantifying nitrocellulose (NC) and nitroglycerine (NG) in soils as well as wood and concrete building materials collected at Badger Army Ammunition Plant (BAAAP) in Baraboo, WI. This was accomplished by analysis of acetone extracts of soils, concrete material, and wood samples by each of the on-site methods and results compared to off-site laboratory analysis of sample splits using high performance liquid chromatography (HPLC) with EPA SW-846 Method 8330 for NG and MCAWW Method 353.2 for NC, a chemical treatment and adapted automated colorimetric method. The field methods evaluated included EXPRAY™ and DROPEX^{Plus} colorimetric test kits (qualitative for total NC/NG), and the following quantitative methods: CRREL RDX colorimetric test (proposed EPA SW-846 8510) for total NC/NG and GC/TID field gas chromatograph for NG only. EXPRAY™ and DROPEX^{Plus} analyses that were evaluated were performed on sample extracts. Surface wipe analyses with DROPEX^{Plus} only were performed on concrete core samples prior to extraction. Accuracy of the qualitative methods was evaluated based on percent false positive / false negatives. The quantitative on-site methods were evaluated using linear regression analysis and relative percent difference (RPD) comparison criteria. General comments as well as major findings from the field demonstration are summarized below for each of the three technologies evaluated; more detailed discussions are included in the respective technology sections.

General Comments

The field methods can be implemented as quantitative detection tools depending on the method performance requirements for use. The data quality objectives including the required method detection/quantitation limits and precision and accuracy for the intended use need to be established before use can be assessed. If NC concentrations need to be quantitated below about 50 mg/kg then the STL MCAWW reference method is not usable for the matrices studied whereas the modified CRREL field method may be usable. For concentrations above about 50 mg/kg either method should be usable providing the requirements for precision and accuracy can be demonstrated. Further development may be needed on sample preparation of these sample matrices to obtain an aliquot for analysis that is representative and produces consistent results before precision and accuracy can be assessed.

The concrete matrix presents an issue for validation and use of the methods. Since the analytes are not stable on the matrix, the analysis needs to use standards and spikes prepared in matrix extract solutions rather than spiked matrix samples. This will be an issue regardless of the analytical method used.

DROPEX^{Plus}/EXPRAY™

- DROPEX^{Plus} analysis of concrete core samples by surface wipes yielded more positive results (10 positives) than the sample extract analyses (2 positives) and suggested increased sensitivity was observed because contamination was concentrated on the sample surface.

- EXPRAY™ was effective in detecting NC and NG in the matrices with results consistent with the STL 8330/8332 reference method as long as concentrations were above detectable limits.

- DROPEX^{Plus} did not meet the performance metrics for wood or soil. This was likely due to lower detection limits, which involved more samples with concentrations near the detection limit where variability in method performance is the highest and has the greatest impact.

- EXPRAY™ tests, while slightly less sensitive, was easier to evaluate as either detect or non-detect. DROPEX^{Plus} when applied seemed to spread out more and had more prevalent yellow discoloration. With both applications only an immediate and distinct color change should be considered to be a positive result. If the collection paper is left exposed, once reagents have been applied, it is possible for a color change to occur after a given amount of time due to pollutants or contaminants present in the ambient air.

- Both the EXPRAY™ and DROPEX^{Plus} field kits are easy to use with little specialized training and equipment. Each kit contains reagents for 200 tests. Cost of each EXPRAY™ kit is $240 and contains reagents for 100 tests. Cost of each DROPEX^{Plus} kit is $190 and contains reagents for 50 tests.

- Overall EXPRAY™ / DROPEX^{Plus} is thought to be a useful tool for screening the presence of significant concentrations of NC and or NG (0.1 to 1 percent and above) in the field or on sample extracts. Given its relatively low rate of false negative results, in combination with other field methods it could be a beneficial screening tool for identifying areas that do not contain explosive contamination in buildings within specified limits. Detectable levels are matrix dependent, with low confidence in results at or near the detection limit. The field method should only be used as a screening tool in combination with other supportive methods of analysis. During the bench test portion of testing the performance of both of these field kit technologies was not affected by the cold temperature when used at 4°C.

CRREL Method for NC/NG

- The CRREL RDX method of analysis gives a relatively low response for NC compared to NG that is easily impacted by matrix interferences. Modifications to the CRREL RDX procedure greatly increased the method response for NC and retained the response for NG. The increase in response made the method more robust for NC analysis and allowed analysis of NC on the three sample matrices. It is Shaw's opinion that the CRREL RDX method is not appropriate for analysis of NC, especially in the matrix samples used in this study, and the Modified CRREL method is more suitable. With the limited amount of experience Shaw has with use of the Modified CRREL method since its development it appears to perform well for NC analysis providing low detection limits and predictable response.

- Tests conducted with NC on concrete showed that recovery of NC from the matrix was a function of both time and the manner in which NC was deposited on the matrix. Acetone solutions containing dissolved NC provided intimate contact of NC with the matrix when spiked onto concrete and only 10% of the initially recoverable NC was recovered after four hours by CRREL analysis. When NC was spiked onto concrete in the form of particulate material in an aqueous suspension approximately one-third was recovered after 96 hours. These results were attributed to decomposition of NC by the concrete matrix due to its alkaline nature in a similar manner as to what was concluded for NG in the bench test. The instability of NC/NG compounds on concrete matrix makes analysis

difficult not only due to the potential impact on samples during handling and preparation, but also due to the effect on matrix standards.

- Compound detection performance metrics for NC/NG using the CRREL methods were not met for the three matrices (wood, soil, and concrete) tested during the field demonstration. False positives with both the CRREL RDX and the Modified CRREL method were less than 5 percent. False negatives, however, were greater than 10 percent for both CRREL methods and all three matrices, ranging from 12.2 percent to 37.8 percent. Performance metrics for concrete samples were limited by the number of positive results obtained by the CRREL methods.

  It is speculated that the number of false negatives was elevated because NC was biased high by the STL Method 353.2 at low concentrations. An indication of this was provided by positive responses for NC in a number of the method blanks (false positives) for wood and soil, which had the highest percentages of CRREL false negatives. False positives at low concentrations were also obtained in the bench test results.

- Compound concentration metrics with respect to RPD values were not met by either CRREL method with any of the three matrices sampled during the building investigation. CRREL results were consistently biased low in comparison to the STL reference method results. The RPD between CRREL and STL results ranged from 42.2 to 89.1 percent. However, the results for the Modified CRREL method on soil showed a linear regression correlation to the STL results with a coefficient (R^2) of 0.9548, which is above the 0.95 performance metric. Performance metrics for concrete samples were limited by the number of positive results obtained by the CRREL methods.

  Most likely reasons why the CRREL results were biased low compared to the STL results include the following:

  - STL Method 353.2 results were biased high due to matrix interference or contamination phenomenon similar to what affected method blanks and clean background matrix analyses in the bench test.

  - Additional matrix interference in samples over that in background material used for standard preparation that caused low response for the CRREL methods.

  - A change in STL analysis conditions such that the applied matrix sample correction from the bench test produced values that were too high.

- There was considerable scatter in the RPD values for the method result comparisons and this was attributed to non-homogeneous sample material and sources of contamination. Soil samples in particular contained pieces of propellant material that made preparing a homogeneous sample difficult.

- Analysis of six (6) samples of concrete expansion joint material associated with concrete samples were analyzed separately for NC/NG by the Modified CRREL method and concentrations detected were consistent with concentrations for the associated concrete sample.

- One field chemist with experience wet chemistry techniques is required for onsite analysis by the CRREL methods. Instrument (visible spectrophotometer) costs are about $2,000. Sample analysis rate during the demonstration was about 3-5 samples per hour.

GC/TID Method for NG Conclusions

- Analyte detection performance metrics for NG were met for all three matrices (wood, soil, and concrete) tested during the field demonstration with <5 percent false negatives and <10 percent positives.

- Analyte concentration performance metrics for NG by GC/TID were not met with any of the three matrices sampled during the building investigation. The linear regression correlation coefficient (R^2) and average RPD for the results above of the detection limit do not meet performance metrics of greater than 0.95 and not more than 20 percent for the field demonstration samples.

- GC/TID analysis of NG on soil, and concrete samples was sensitive; a detection limit of 2 mg/kg, which was comparable to the reference method, was observed. Wood had a slightly higher detection limit of 5 mg/kg.

- Thirteen (13) of the 37 wood samples evaluated had positive values for NG by the 8330 reference method for comparison. The GC/TID results were low in comparison with values that averaged 38.0 percent of the STL values. This bias was not observed during the bench scale testing. Matrix interference with the STL Method 8330 results is a possible explanation but is unconfirmed.

- Soil sample results by GC/TID were possibly biased high; however, there was insufficient NG contamination in the field demonstration samples collected to effectively evaluate performance. The thirteen samples containing detectable amounts of NG by STL Method 8330 had concentrations ranging from 0.18 to 3.0 mg/k and these are right around the method detection limit of 0.5 mg/kg where analytical variability is the greatest (four values were estimates below the detection limit).

- Concrete sample results by GC/TID were possibly biased high; however, there was insufficient NG contamination in the samples collected in the field demonstration to effectively evaluate performance.

- In general, reliability of the GC/TID ability to detect NG on the building materials was consistent with the reference Method 8330. NG methods seem to perform well, but validation was hampered primarily by limited number of samples and sample non-homogeneity. Both methods may be subject to matrix interference effects and QC samples should be included to help assess data quality.

- One field chemist with experience in gas chromatography is required for onsite analysis by GC/TID. Instrument costs are about $10,000 and do not require the use of compressed gases. Sample analysis rate during the demonstration was about 3-5 samples per hour

- Maintaining sensitivity required frequent cutting of the injection end of the column. The frequency is matrix dependent and thought to be due to loading or degradation of the

column material by non-target constituents in the sample. This problem was most prevalent with the wood samples.

Method Performance Evaluations

A summary of accomplishment for each of each of the field methods investigated in the field demonstration is tabulated below for each of the building materials tested in Tables 4-1, 4-2 and 4-3.

Table 4-1 Wood Samples
Performance Evaluation against Primary and Secondary Criteria

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Primary Criteria			
Compound Identification	NMT 5% False Negatives NMT 10% False Positives (Applies to DROPEX^{Plus} / EXPRAY™)	Confirm by laboratory analysis. Data will be evaluated on agreement of detection.	• DROPEX^{Plus} Field Method False negatives=16.2% • EXPRAY™ Field Method False negatives= 0% • DROPEX^{Plus} Field Method False Positives= 5.4% • EXPRAY™ Field Method False Positives= 13.5% Field Method does not meet specified criteria
Compound Concentration	RPD NMT 20% and/or Correlation Coefficient ≥ 0.95 (Applies to CRREL and GC/TID)	Confirm by laboratory analysis. Data are evaluated on agreement of detection and concentration	• Mod. CRREL Field Method RPD=89.1 • GC/TID Field Method RPD= 48.7 • Mod. CRREL Field Method LR R value=0.7080 • GC/TID Field Method LR R value= 0.7466 Field Methods do not meet specified criteria
Reliability	Achieve identification and quantitation requirements in multiple locations and conditions	Confirm by laboratory analysis	• GC/TID- wood does not pass RPD criteria • CRREL/Mod. CRREL does not meet specified criteria

Ease of Use	Reduced or constant crew size. Level of technical training required. Need for special assistance or training during project. Calibration and maintenance can be performed by operating crew.	Experience from demonstration	• EXPRAY™/ DROPEX^{Plus} ® is easy to use with little specialized training and equipment. • CRREL requires a moderate level of training in regards to matrix • GC/TID requires specialized training

Wood Samples Table 4-1 (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Maintenance	Percent downtime when operations are scheduled. Routine maintenance required. Specialized personnel or equipment for maintenance activities.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ does not use equipment that requires maintenance or repair. CRREL does not use equipment that requires maintenance or repair. GC/TID maintenance and repair can be performed by trained GC analyst with 5-10% downtime
Secondary Criteria			
Versatility	Use conditions and ease of use under a variety of site conditions.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ can be used under a wide variety of site conditions CRREL can be used under a wide variety of site conditions GC/TID requires a relatively stable environment with temperatures within 70 ±20 degrees F All equipment is portable, light and easily transported

Wood Samples Table 4-1 (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Hazardous Materials	Volume of hazardous materials generated by project operations. Number of waste streams requiring characterization and disposal	Experience from demonstration	• Minimal hazardous materials were generated during project. • Remaining acetone extracts were returned to Shaw Knoxville Lab for disposal as hazardous waste
Process Waste	Amount of investigative-derived waste generated by project operations.	Experience from demonstration	Minimal investigation-derived waste was generated during the project

Notes:
NMT = not more than
RPD = Relative Percent Difference

Table 4-2 Soil Samples
Performance Evaluation against Primary and Secondary Criteria

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Primary Criteria			
Compound Identification	NMT 5% False Negatives NMT 10% False Positives (Applies to DROPEX^{Plus} / EXPRAY™)	Confirm by laboratory analysis. Data will be evaluated on agreement of detection.	• DROPEX^{Plus} Field method false negatives=10.8% • EXPRAY™ Field method false negatives= 2.7% • DROPEX^{Plus} Field Method False Positives= 16.2% • EXPRAY™ Field Method False Positives= 8.1% DROPEX^{Plus} does not meet criteria. EXPRAY™ does meet criteria.
Compound Concentration	RPD NMT 20% and/or Correlation Coefficient ≥ 0.95 (Applies to CRREL and GC/TID)	Confirm by laboratory analysis. Data are evaluated on agreement of detection and concentration	• Mod. CRREL Field Method RPD=82.7 • GC/TID Field Method RPD= -12.9 • Mod. CRREL Field Method R value=0.9548 • GC/TID Field Method LR R value= 0.2566
Reliability	Achieve identification and quantitation requirements in multiple locations and conditions	Confirm by laboratory analysis	• GC/TID- soil and concrete quantitation not confirmed because of absence of NG compound. • CRREL/Mod. CRREL does not meet specified criteria
Ease of Use	Reduced or constant crew size. Level of technical training required. Need for special assistance or training during project. Calibration and maintenance can be performed by operating crew.	Experience from demonstration	• EXPRAY™/ DROPEX^{Plus} ® is easy to use with little specialized training and equipment. • CRREL requires a moderate level of training in regards to matrix • GC/TID requires specialized training

Soil Samples Table 4-2 (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Maintenance	Percent downtime when operations are scheduled. Routine maintenance required. Specialized personnel or equipment for maintenance activities.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ does not use equipment that requires maintenance or repair. CRREL does not use equipment that requires maintenance or repair. GC/TID maintenance and repair can be performed by trained GC analyst with 5-10% downtime
Secondary Criteria			
Versatility	Use conditions and ease of use under a variety of site conditions.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ can be used under a wide variety of site conditions CRREL can be used under a wide variety of site conditions GC/TID requires a relatively stable environment with temperatures within 70 ±20 degrees F All equipment is portable, light and easily transported

Soil Samples Table 4-2 (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Hazardous Materials	Volume of hazardous materials generated by project operations. Number of waste streams requiring characterization and disposal	Experience from demonstration	• Minimal hazardous materials were generated during project. • Remaining acetone extracts were returned to Shaw Knoxville Lab for disposal as hazardous waste
Process Waste	Amount of investigative-derived waste generated by project operations.	Experience from demonstration	Minimal investigation-derived waste was generated during the project

Notes:
NMT = not more than
RPD = Relative Percent Difference

Table 4-3 Concrete Material
Performance Evaluation against Primary and Secondary Criteria

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Primary Criteria			
Compound Identification	NMT 5% False Negatives NMT 10% False Positives (Applies to DROPEX^{Plus} / EXPRAY™)	Confirm by laboratory analysis. Data will be evaluated on agreement of detection.	• DROPEX^{Plus} Field method false negatives=2.4% • EXPRAY™ Field method false negatives= 4.9% • DROPEX^{Plus} Field Method False Positives= 2.4% • EXPRAY™ Field Method False Positives= 0% DROPEX^{Plus} and EXPRAY™ meet performance criteria.
Compound Concentration	RPD NMT 20% and/or Correlation Coefficient ≥ 0.95 (Applies to CRREL and GC/TID)	Confirm by laboratory analysis. Data are evaluated on agreement of detection and concentration	• CRREL Field Method RPD=45.9 • GC/TID Field Method RPD= -4.43 • CRREL Field Method R value=0.0894 • GC/TID Field Method LR R value= NC insufficient data points. • CRREL and GC/TID fail to meet specified criteria
Reliability	Achieve identification and quantitation requirements in multiple locations and conditions	Confirm by laboratory analysis	• GC/TID- soil and concrete quantitation not confirmed because of absence of NG compound. • CRREL performance not confirmed

Ease of Use	Reduced or constant crew size. Level of technical training required. Need for special assistance or training during project. Calibration and maintenance can be performed by operating crew.	Experience from demonstration	• EXPRAY™/ DROPEX^{Plus} ® is easy to use with little specialized training and equipment. • CRREL requires a moderate level of training in regards to matrix • GC/TID requires specialized training

Table 4-3. Concrete Material (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Maintenance	Percent downtime when operations are scheduled. Routine maintenance required. Specialized personnel or equipment for maintenance activities.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ does not use equipment that requires maintenance or repair. CRREL does not use equipment that requires maintenance or repair. GC/TID maintenance and repair can be performed by trained GC analyst with 5-10% downtime
Secondary Criteria			

Versatility	Use conditions and ease of use under a variety of site conditions.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ can be used under a wide variety of site conditions CRREL can be used under a wide variety of site conditions GC/TID requires a relatively stable environment with temperatures within 70 ±20 degrees F All equipment is portable, light and easily transported

Table 4-3. Concrete Material (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Hazardous Materials	Volume of hazardous materials generated by project operations. Number of waste streams requiring characterization and disposal	Experience from demonstration	• Minimal hazardous materials were generated during project. • Remaining acetone extracts were returned to Shaw Knoxville Lab for disposal as hazardous waste
Process Waste	Amount of investigative-derived waste generated by project operations.	Experience from demonstration	Minimal investigation-derived waste was generated during the project

Notes:
NMT = not more than
RPD = Relative Percent Difference

5.0 COST ASSESSMENT

5.1 Cost Reporting

Project costs were tracked and the costs associated with the field demonstration are summarized in Table 5-1. These costs include those for planning, concrete drill fabrication/modification, lab trailer and generator rental, fuel for the lab trailer generator and on-site operations, personnel travel, on-site materials and supplies, shipping, off-site analytical and other subcontractor charges and labor for on-site sampling and analytical work as well as off-site (Knoxville) analytical method development work.

5.2 Cost Analysis

5.2.1 Cost Basis

The project costs from November 2005 through March of 2006 are directly related to the field demonstration and associated administrative activities and can be divided into five (5) cost categories:

1. On-site sampling
2. On-site sample analysis
3. Off-site sample analysis and data validation
4. Off-site method development/sample reanalysis, and
5. Administration and reporting

Administrative and reporting costs totaled $53,035 and are not included in Table 5-1. The costs for the field demonstration activities that are included in Table 5-1 totaled $176,264. The total project cost for the field demonstration including administrative and reporting activities was $229,299.

Sampling costs of $37,229 included sample design and planning, equipment fabrication (remote operated concrete drill, and sample crusher), materials and supplies related to sampling activities, equipment rental, personnel travel costs and labor for sampling activities. These costs can be used for estimating sampling costs, but they were affected by the sub-freezing temperatures, which necessitated special efforts to thaw soil for sampling beneath the concrete slab at concrete core sampling sites. A water-cooled, diamond tipped, hollow coring bit was used to drill through concrete floor slabs. This was chosen as a method to provide safe access to sub-slab samples. This method was expensive and likely caused some disturbance to the sample due to the water used to cool the drill bit. Alternative methods of obtaining these samples should continue to be investigated. Costs related to concrete cutting will also be affected by the thickness and strength of the concrete slab.

On-site sample analysis costs of $61,808 included those for planning, materials and supplies related to analyses, lab trailer and generator rental as well as associated delivery charges, generator fuel costs, personnel travel costs, shipping charges for equipment and supplies during mobilization and demobilization and labor for sample preparation and analysis. The costs are subdivided into the three analytical method technologies, i.e., EXPRAY™ / DROPEX^{Plus}, GC/TID and CRREL. The estimated cost breakdown for each method technology is $10,493 for EXPRAY™ / DROPEX^{Plus}, $24,078 for GC/TID and $27,237 for CRREL. These costs are for the analysis of the 115 samples; 103 field samples and 12 field sample duplicates.

Off-site sample analysis costs of $22,830 included those for sample shipping, unit price charges for samples analyzed by STL and costs for data validation. What are not included are labor costs for sample shipment and administrative activities as well as for sample preparation activities, which are included in on-site analytical charges. Sample preparation that was necessary for both on-site and off-site analyses was performed on-site during the analysis efforts and the costs are difficult to separate out accurately; however, they are estimated to be fifteen (15) percent of the estimated on-site analytical labor costs of $33,081or approximately $4,960. The off-site analysis costs plus the estimated sample preparation cost gives a total cost of $27,790 for the off-site analysis of the 115 field and field duplicate samples.

There was a significant effort expended after the on-site field demonstration at the TDL in Knoxville, TN for CRREL RDX method development/modification and sample re-analysis that would not be needed for routine use of the developed method. It was felt that the labor expended on site is a good estimate of the labor needed to complete the analysis of the samples collected for the field demonstration using the EXPRAY™ /DROPEX^{PLUS}, GC/TID and the developed Modified CRREL field methods. Therefore the off-site method development costs were not included with the costs for on-site analytical work. An estimate of the labor and materials cost for off-site CRREL method development has been separated from the on-site work and shown in a separate column in Table 5-1.

5.2.2 Cost Comparison

The off-site analytical laboratory (STL) costs for the demonstration samples of $27,790 (includes $4,960 cost for sample preparation) can be compared to the on-site analytical costs to assess cost effectiveness for on-site analyses. This comparison does not include administrative costs previously mentioned or the cost for expedited turnaround of results from the off-site lab that would be incurred to get a more direct comparison to the on-site field analysis. On-site analysis typically generates results the same day or within 24-48 hours. The off-site analyses were performed by STL with a three week turnaround time for results. STL typically charges a fifty (50) to one hundred (100) percent surcharge for results within a 24-48 hour turn around time. However, there is typically a 24 hour delay due to overnight shipping, so it is difficult for an off-site lab to duplicate the turn around time for results that an on-site lab can provide.

Another factor affecting the cost that should be considered for cost comparison is the experience level of the analysts used for field method analysis. Since this was a method evaluation and included analytical method development, the experience level and associated pay rate for analysts were higher than what would typically be used for field work using established analytical procedures.

It is difficult to get a clear cost comparison for the EXPRAY™ / DROPEX^{Plus} and CRREL methods to the off-site reference method analyses because the results for the methods are not equivalent. The CRREL method provides a total for NC and NG while EXPRAY™ and DROPEX^{Plus} are not quantitative and the MCAWW 353.2 reference method only quantifies NC. The estimated total cost for the GC/TID and CRREL analyses, which provide separate results for NG and NC (by difference between the CRREL total NC and NG result and the GC/TID NG result), was $51,315. This is approximately twice the cost for the off-site STL reference method analyses of $27,790 that provides separate results for NC and NG; however, the costs would be more comparable if expedited surcharges and less experienced field analysts impacts discussed above were considered. The GC/TID method and the STL 8330/8332 method both provide quantitative results for NG only and the estimated costs for these analyses were $24,078 and approximately $13,000, respectively. The on-site GC/TID cost was approximately twice that for

the off-site lab analysis and is consistent with the former comparison, but again lacks the considerations for a more valid comparison.

Table 5-1 Demonstration Costs

Cost Category	Sub Category	Details	Field Sampling	On-Site DROPEX^{Plus} / EXPRAY™ Analysis	On-Site GC/TID Analysis	On-Site Modified CRREL Analysis	Off-Site CRREL Method Development	Off-Site STL Reference Method Analyses	Total Actual Demonstration Costs (Includes Shaw Costs)
Start-Up Costs	Site Characterization	N/A	$	$	$	$	$	$	$
	Mobilization	Project planning	$5,000	$2,500	$2,500	$2,500	$	$	$12,500
		Project coordination	$	$	$	$	$	$	$
		Personnel travel to site	$5,845	$3,333	$3,333	$3,334	$	$	$15,845
		Equipment travel to site	$	$	$	$	$	$	$
		Shipping costs	$483	$	$400	$400	$	$	$1,283
Capital Costs	Capital Equipment Purchase	N/A	$	$	$	$	$	$	$
	Ancillary Equipment Purchase	N/A	$	$	$	$	$	$	$
	Modifications	N/A	$940	$	$	$	$	$	$940
	Structures Installation	N/A	$	$	$	$	$	$	$
	Engineering	N/A	$	$	$	$	$	$	$
Operating Costs	Capital Equipment Rental	Shaw Rental	$	$402	$403	$403	$	$	$1,208
		N/A	$	$	$	$	$	$	$
		N/A	$	$	$	$	$	$	$
	Ancillary Equipment Rental	Generator/fuel	$	$380	$380	$381	$	$	$1,141
		Phone Services	$450	$96	$200	$200	$	$	$946
	Supervision	Salary	$	$	$	$	$	$	$
		Travel	$	$	$	$	$	$	$
		Per diem	$	$	$	$	$	$	$
	Operator Labor	Salary	$24,511	$2,200	$14,362	$16,519	$49,631	$	$107,223
		Travel	$	$	$	$	$	$	$
		Per diem	$	$	$	$	$	$	$
	Training	OSHA	$	$	$	$	$	$	$
		Procedures	$	$	$	$	$	$	$
	Maintenance	Concrete drill	$	$	$	$	$	$	$
	Consumables	Drop-Ex & Expray kits	$	$832	$	$	$	$	$832
		Personal protective equipment	$	$	$	$	$	$	$
		Laboratory supplies	$	$750	$2,500	$3,500	$4,766	$	$11,516
		Fuel	$	$	$	$	$	$	$
		Tools	$	$	$	$	$	$	$
		Other (Specified):	$	$	$	$	$	$	$
	Residual Waste Handling	N/A	$	$	$	$	$	$	$
	Off-site Disposal	Hazardous waste	$	$	$	$	$	$	$
	Analytical Laboratory Costs	NG – Method 8330/8332	$	$	$	$	$	$12,000	$12,000
		NC – MCAWW 353.2	$	$	$	$	$	$8,160	$8,160
		Shipping Costs	$	$	$	$	$	$300	$300
		Data validation	$	$	$	$	$	$2,370	$2,370
	Long Term Monitoring	N/A	$	$	$	$	$	$	$
Indirect Costs	Equipment Repair	Other (specified)	$	$	$	$	$	$	$
Demobilization	Housekeeping	Site cleanup/maintenance	$	$	$	$	$	$	$
		Personnel travel from site	$	$	$	$	$	$	$
		Equipment travel from site	$	$	$	$	$	$	$
		Shipping costs	$	$	$	$	$	$	$
		Total	$37,229	$10,493	$24,078	$27,237	$54,397	$22,830	$176,264

6.0 IMPLEMENTATION ISSUES

6.1 Environmental Checklist

There are no regulations envisioned that apply to the application of the field analytical methods for NC and NG determination.

6.2 Other Regulatory Issues

The primary regulatory/guidance issues that need to be resolved for the use of the field method technologies are the detection and quantitation limits as well as the data quality objectives, i.e., accuracy and precision requirements for the methods. The requirements need to be compared to the method capabilities to determine suitability.

6.3 End-User Issues

6.3.1 EXPRAY™ / DROPEX^{Plus} Test Kits for NC and NG

Overall EXPRAY™ and DROPEX^{Plus} are thought to be useful tools for screening the presence of significant concentrations of NC and or NG (0.1 to 1 percent and above) in the field or on sample extracts. Given its relatively low rate of false negative results, in combination with other field methods it could be a beneficial screening tool for identifying areas that contain explosive contamination in buildings above specified limits. Detectable levels are matrix dependent, with low confidence in results at or near the detection limit. The field method should only be used as a screening tool in combination with other supportive methods of analysis.

The EXPRAY™ / DROPEX^{Plus} tests (test kits) are inexpensive and easy to use. The EXPRAY™ test kit for 100 samples was $230 or $2.30 per sample and the DROPEX^{Plus} test kit for 50 samples was $186 or $3.72 per sample.

The EXPRAY™ test, while slightly less sensitive, was easier to evaluate as either detect or non-detect. DROPEX^{Plus} reagents seemed to spread out more on the test paper and had more prevalent yellow discoloration, which may interfere with detecting the positive pink color for the test.

Both of the field kits are easy to use with little specialized training and equipment except for analysis of sample extracts. Kits are designed for wipe tests of matrices using the supplied wipe papers, which can be completed in a matter of a few minutes. As tested however for analysis of the bulk matrices, the samples required crushing, homogenization and extraction prior to analysis, which complicates sample analysis and turns it into a lab procedure requiring more equipment and chemicals, analyst experience and significantly more time. Analysis times for extracted matrices will be about two hours due to the 1.5 hour solvent extraction time, as compared to a few minutes for the matrix surface wipe test.

6.3.2 CRREL Methodology for NC/NG

The CRREL RDX method of analysis gives a relatively low response for NC compared to NG that is easily impacted by matrix interferences. The wood matrix interfered with the method such that calibration with wood matrix standards could not be performed due to extremely low and non-reproducible response. The Modified CRREL method that was developed appears to

perform well for NC and NG analysis providing low detection limits in the range of 2 mg/kg to 10 mg/kg and predictable response for the matrices used in this test.

The analysis of NC and NG on concrete is hampered by decomposition of the explosive compounds by the concrete matrix due to its alkaline nature, which causes alkaline hydrolysis of the nitro groups. The instability of NC/NG compounds on concrete matrix makes analysis difficult not only due to the potential impact on samples during handling and preparation, but also due to the effect on matrix standards.

CRREL results are biased low in comparison to the STL reference method results. STL Method 353.2 results are believed to be biased high due to matrix interference or contamination phenomenon that was observed on method blanks and clean background matrix analyses.

Non-homogeneous sample material and sources of contamination, such as pieces of propellant material, make preparing a homogeneous sample difficult for reproducible results or split sample result comparison.

The CRREL method requires a small spectrophotometer in the $1,000 to $2,000 price range and assorted expendable supplies such as; reagents, syringes, sorbent tube cartridges and syringe filters. One field chemist with experience in wet chemistry techniques is required for onsite analysis by the modified CRREL method. Approximately 10 to 20 samples may be analyzed in a day depending on the amount of sample preparation required.

6.3.3 GC/TID Method for NG

GC/TID analysis of NG is selective and sensitive with detection limits in the range of 2 mg/kg to 5 mg/kg, which is comparable to the reference method. In general, reliability of the GC/TID ability to detect NG on the building materials is consistent with the reference Method 8330. Both methods may be subject to matrix interference effects and QC samples should be included to help assess data quality.

The GC/TID method requires a portable field GC with a TID, which is the most costly piece of equipment for use with these methods. The price for a portable GC/TID instrument is approximately $10,000. One field chemist with experience in gas chromatography is required for onsite analysis by GC/TID and it is estimated that 10 to 20 samples may be analyzed in a day depending on the sample matrix and the amount of sample preparation required.

Maintaining instrument sensitivity requires frequent cutting of the injection end of the column. The frequency is matrix dependent and thought to be due to loading or degradation of the column material by non-target constituents in the sample. This problem was most prevalent with the wood samples.

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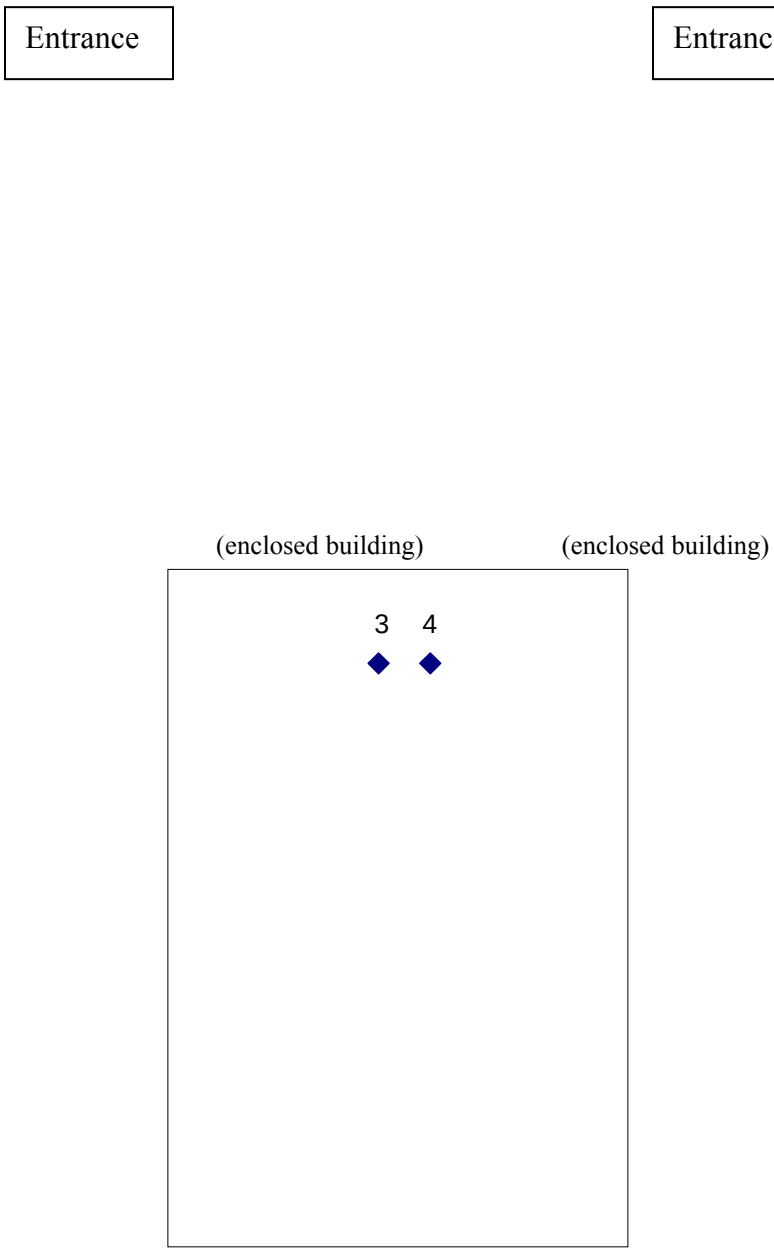
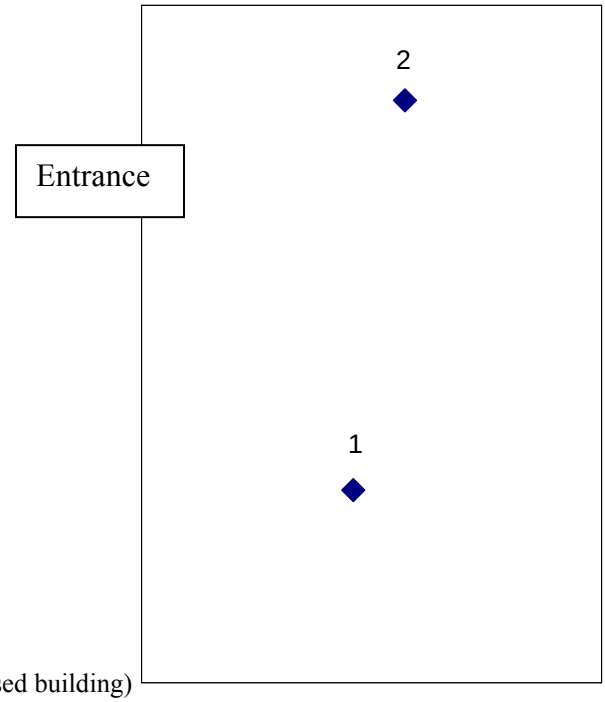
APPENDIX B.1
Sampling Building Maps

6657-02 Neutralizer House

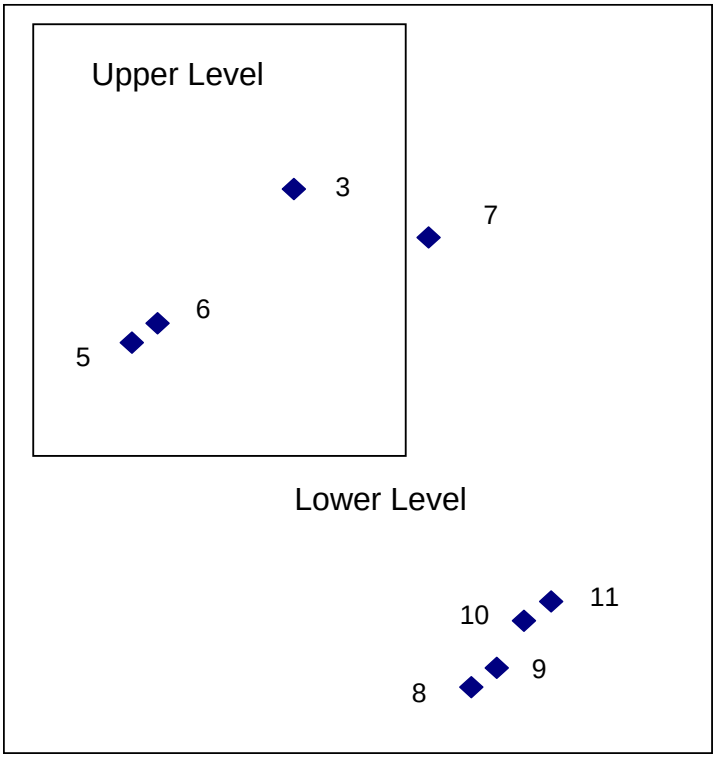


6657-02 Nitrate House

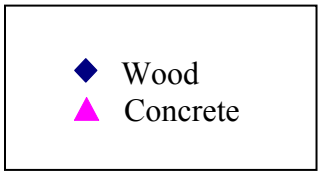


Bldg. 5024 Boiling Tub House

(enclosed building - large 2-story warehouse)

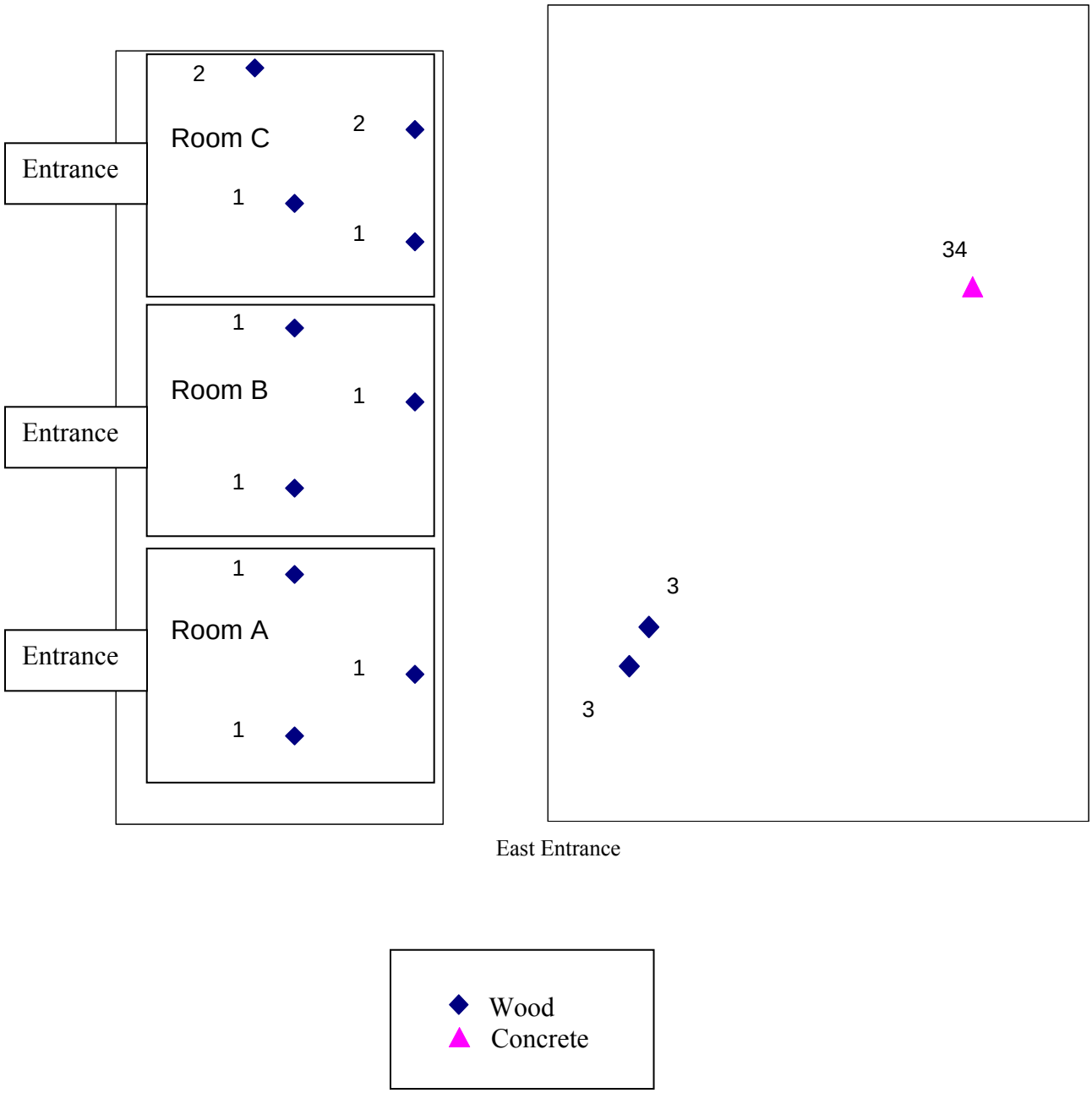


Southwest Entrance



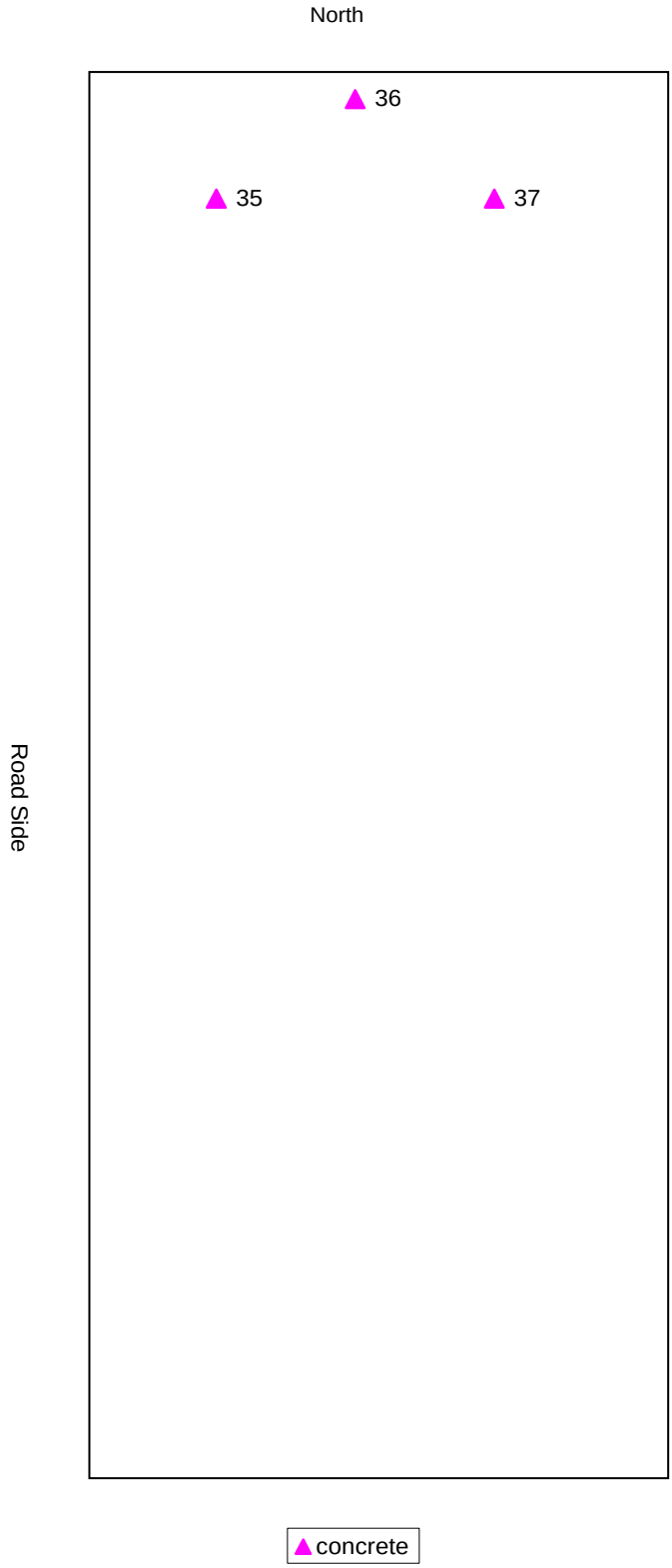
Bldg. 6709-17 Pre-Drying House
(enclosed building)

Bldg. 9590 Powder Storage Pit
(enclosed building – large pit warehouse)

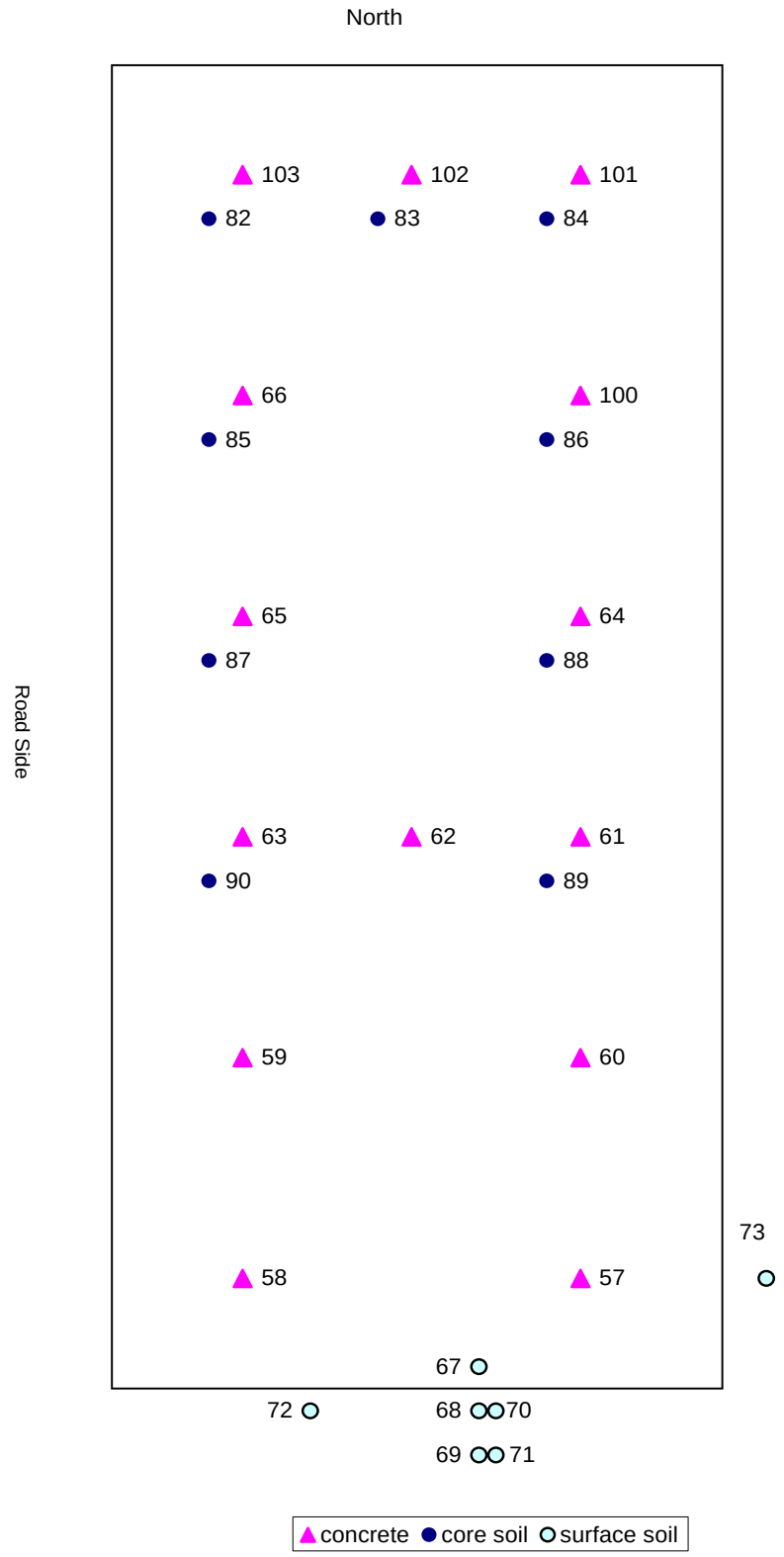


Bldg. 1885-01 Box Storage House

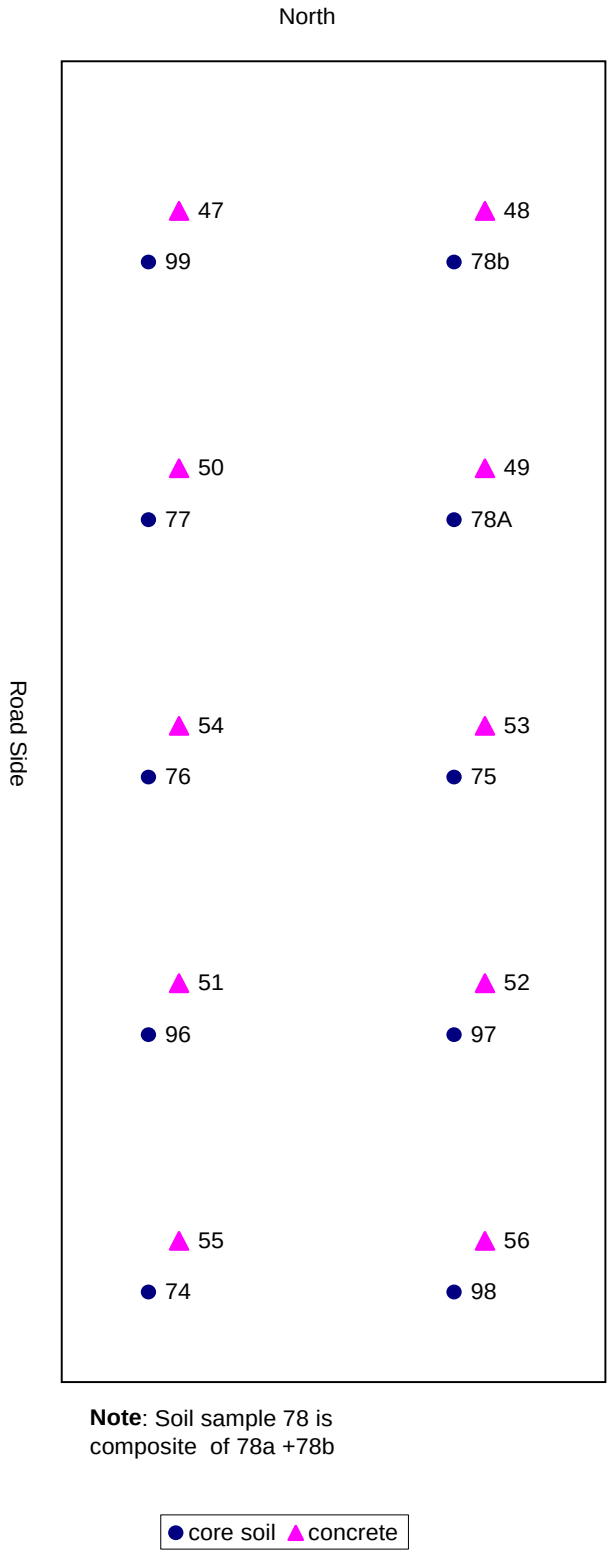
(enclosed building – large empty warehouse)



Bldg. 1885-02 Box Storage House (open concrete slab)

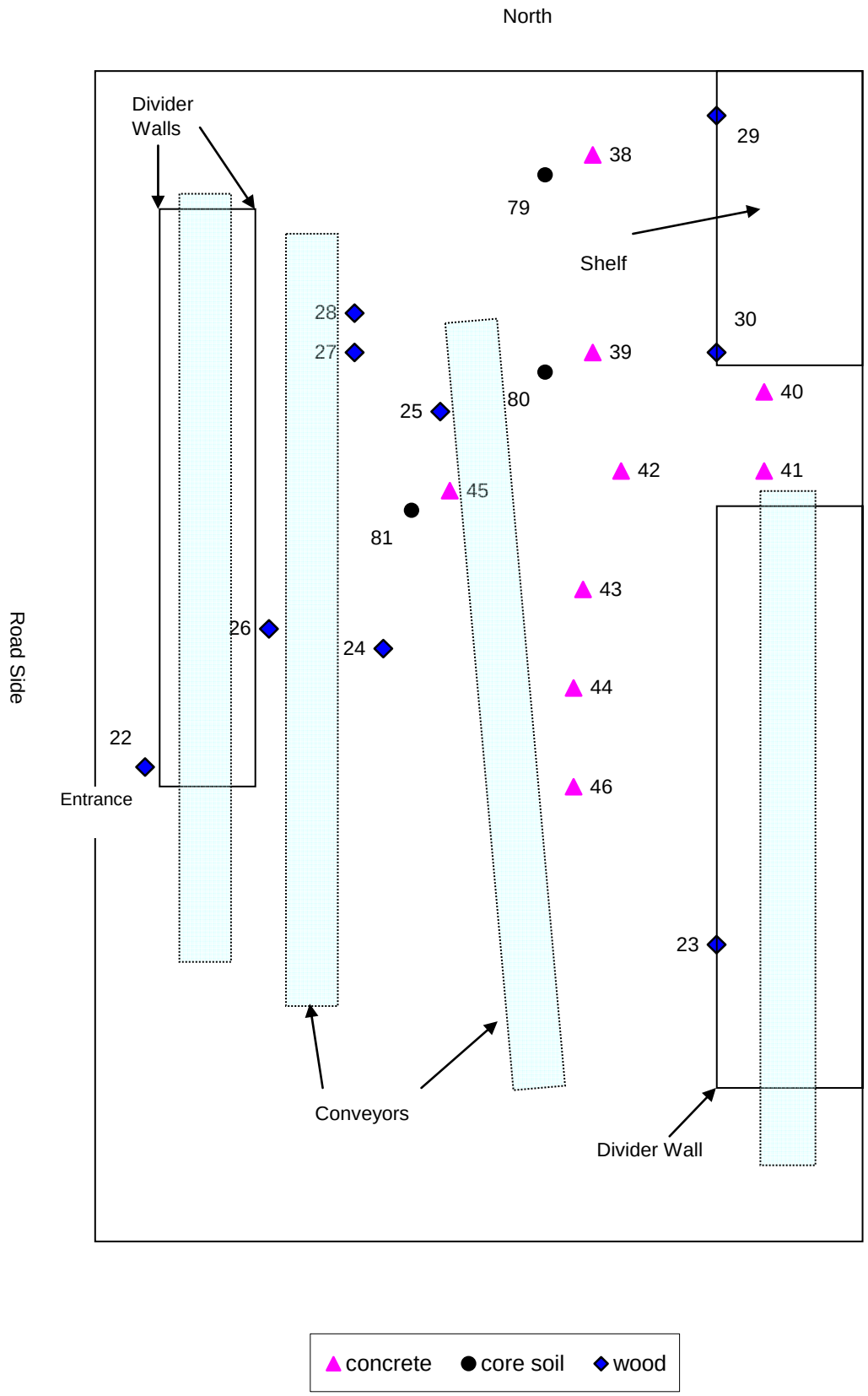


Bldg. 1885-03 Box Storage House (open concrete slab)



Note: Soil sample 78 is composite of 78a +78b

Bldg. 1890-01 Box Wash House (enclosed building)



APPENDIX B.2
Lab Data Summary Tables

Table B.2-1 BAAAP/ESTCP Field Demonstration Wood Analytical Summary

Sample Identification	Matrix	QC Spike Description mg/K	Sampl wt (g)	Aceton ml	STL Reference Method Results (mg/kg) Metho 8330 NG	Metho 353.2 NC	Corr. Metho 353.2 NC	Corr. Total NG+NC	Drop-Ex Extrac (10 uls)	Expray Extrac (10 uls)	NG GC/TID NG Conc mg/K	Shaw Modified NG+NC Abs 507n Reading 1	Analysis Dilution Factor	Analyzed conc as NG	Analyzed conc as NC	Comments/ Notes
BI-BLK-001-WD-NG	Wood	N	20	60	N	N	N	N	-	-	ND<5.0	0.003	1	ND<5	ND<10	
BI-LCS-001-WD-NG	Wood	100	20	60	N	N	N	N	+	-	102	0.824	1	110	N	
BI-LCS-001-WD-NC	Wood	211	N	N	N	N	N	N	+	+	N	1.286	1	N	231	
6657-02N-WD-001	Wood	N	20	60	3.7J	190J	377	381	-	-	ND<5.0	0.025	1	5	13	
6657-02N-WD-002	Wood	N	20	60	18	851Q,J	1690	1710	-	-	3.22 J	0.180	1	25	40	
6657-02I-WD-003	Wood	N	20	60	ND<0.5	39.9J	79	79	-	-	ND<5.0	0.008	1	ND<5	ND<10	
6657-02I-WD-003A	Wood	N	20	60	ND<5	43.2J	86	86	-	-	ND<5.0	0.005	1	ND<5	ND<10	
6657-02I-WD-004	Wood	N	20	60	ND<0.5	1020Q,J	2020	2020	-	-	ND<5.0	0.021	1	4	13	
5024-000-WD-005	Wood	N	20	60	ND<5	221J	438	438	+	-	7.67	0.382	3.33	172	250	
5024-000-WD-006	Wood	N	20	60	ND<5	174J	345	345	+	-	ND<5.0	0.267	3.33	122	184	
5024-000-WD-007	Wood	N	20	60	ND<5	697Q,J	1380	1380	+	-	ND<5.0	0.350	3.33	158	231	
5024-000-WD-008	Wood	N	20	60	ND<5	40.5J	80	80	-	-	ND<5.0	0.065	1	10	20	
5024-000-WD-009	Wood	N	20	60	ND<0.5	44.6J	88	88	-	-	ND<5.0	0.058	1	9	19	
5024-000-WD-010	Wood	N	20	60	ND<5	332J	659	659	++	++	ND<5.0	0.648	6.67	579	806	
5024-000-WD-011	Wood	N	20	60	ND<2.5	138J	274	274	+	+	ND<5.0	0.422	1.67	95	137	
6709-17-WD-012	Wood	N	20	60	99	143J	284	383	+	-	31.6	0.104	6.67	101	180	
6709-17-WD-013	Wood	N	20	60	88	115J	228	316	+	-	19.2	0.059	6.67	62	129	
6709-17-WD-014	Wood	N	20	60	230	198J	393	623	+	+	98.3	0.492	6.67	442	627	
6709-17-WD-015	Wood	N	20	60	240	198J	393	633	+	++	104	0.742	6.67	661	914	
6709-17-WD-016	Wood	N	20	60	180	156J	310	490	+	-	47.3	0.079	6.67	79	152	
6709-17-WD-017	Wood	N	20	60	130	172J	341	471	+	-	44.5	0.110	6.67	106	187	
6709-17-WD-018	Wood	N	20	60	84	122J	242	326	+	-	22.9	0.044	6.67	49	111	
6709-17-WD-019	Wood	N	20	60	120	149J	296	416	+	-	44.5	0.084	6.67	84	157	
6709-17-WD-019MS-NG	Wood	200	10	30	N	N	N	N	+	+	217	0.608	6.67	544	N	
6709-17-WD-019MSD-NG	Wood	200	10	30	N	N	N	N	+	+	238	0.701	6.67	625	N	
6709-17-WD-019MS-NC	Wood	421	10	30	N	N	N	N	+	+	N	0.617	6.67	N	770	
6709-17-WD-019MSD-NC	Wood	421	10	30	N	N	N	N	+	+	N	0.625	6.67	N	779	
6709-17-WD-020	Wood	N	20	60	110	96.2J	191	301	+	-	25.4	0.091	6.67	90	165	
6709-17-WD-020A	Wood	N	20	60	120	113J	224	344	+	-	25.9	0.125	6.67	120	204	
BI-BLK-002-WD-NG	Wood	N	20	60	N	N	N	N	-	-	ND<5.0	0.001	1	ND<5	ND<10	
BI-LCS-002-WD-NG	Wood	50	20	60	N	N	N	N	+	-	46.1	0.158	2	45	N	
BI-LCS-002-WD-NC	Wood	211	20	60	N	N	N	N	+	+	ND<5.0	0.428	3.33	N	187	
BI-BLK-003-WD-NG	Wood	N	20	60	N	N	N	N	-	-	ND<5.0	0.000	1	ND<5	ND<10	
BI-LCS-003-WD-NG	Wood	200	20	60	N	N	N	N	+	-	161	0.511	4	276	391	
BI-LCS-003-WD-NC	Wood	211	20	60	N	N	N	N	+	+	N	0.241	3.33	112	170	

Table B.2-1 BAAAP/ESTCP Field Demonstration WoodAnalytical Summary Cont.

Sample Identification	Matrix	QC Sample Spike Description mg/Kg	Sample wt (g)	Acetone mls	STL Reference Method Results (mg/kg)				Drop-Ex	Expray	NG GC/TID	Shaw Modified CRREL NG+NC				Comments/ Notes
					Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	Extract (10 uls)	Extract (10 uls)	NG Conc mg/Kg	Abs at 507nm Reading 1	Analysis Dilution Factor	Analyzed conc as NG	Analyzed conc as NC	
6709-17-WD-021	Wood	NA	20	60	62	286JB	567	629	++	++	58.5	0.504	10	682	965	
1890-01-WD-022	Wood	NA	20	60	ND<0.5	35.3JB	70	70	+-	-	ND<5.0	0.006	1	ND<5	ND<10	
1890-01-WD-022MS-NG	Wood	100	10	30	NA	NA	NA	NA	+	+-	101	0.064	10	103	NA	
1890-01-WD-022MSD-NG	Wood	100	10	30	NA	NA	NA	NA	+	+-	84.8	0.063	10	102	NA	
1890-01-WD-022MS-NC	Wood	211	10	30	NA	NA	NA	NA	+	+	NA	0.329	3.33	NA	221	
1890-01-WD-022MSD-NC	Wood	211	10	30	NA	NA	NA	NA	+	+	NA	0.358	3.33	NA	238	
1890-01-WD-023	Wood	NA	20	60	ND<0.5	19.1JB	38	38	-	-	ND<5.0	0.000	1	ND<5	ND<10	
1890-01-WD-024	Wood	NA	20	60	ND<0.5	27.6JB	55	55	-	-	ND<5.0	0.000	1	ND<5	ND<10	
1890-01-WD-025	Wood	NA	20	60	ND<0.5	61.8JB	123	123	+-	-	ND<5.0	0.032	1	6	15	
1890-01-WD-026	Wood	NA	20	60	ND<0.5	19.8JB	39	39	-	-	ND<5.0	0.000	1	ND<5	ND<10	
1890-01-WD-027	Wood	NA	20	60	ND<5	46.3JB	92	92	+	-	ND<50	0.135	1	20	33	
1890-01-WD-028	Wood	NA	20	60	ND<5	29.1JB	58	58	-	-	ND<5.0	0.147	1	21	35	
1890-01-WD-028A	Wood	NA	20	60	ND<5	42.4JB	84	84	-	-	ND<5.0	0.158	1	23	37	
1890-01-WD-029	Wood	NA	20	60	ND<5	56.5JB	112	112	-	-	ND<5.0	0.170	1	24	39	
1890-01-WD-030	Wood	NA	20	60	ND<5	46.6JB	92	92	+-	-	ND<5.0	0.252	1	35	53	
9590-000-WD-031	Wood	NA	20	60	ND<0.5	42.9JB	85	85	+	-	ND<5.0	0.636	3.33	285	397	
9590-000-WD-032	Wood	NA	20	60	ND<10	54.8JB	109	109	-	-	ND<50	0.000	1	ND<5	ND<10	
5024-000-WD-033	Wood	NA	20	60	ND<0.5	2880Q,JB	5710	5710	+++	+++	ND<20	0.194	66.6	1830	2870	
5024-000-WD-033A	Wood	NA	20	60	ND<0.5	7080Q,JB	14000	14000	+++	+++	ND<20	0.190	66.6	1790	2820	

Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JB = Estimated result. Method blank contains contamination.
PG = The percent difference between the original and confirmation analysis is greater than 40%.
ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table B.2-2 BAAAP/ESTCP Field Demonstration Soil Analytical Summary

					STL Reference Method Results				Drop-Ex	Expra	GC/TID NG	CRRE NG+N			Shaw Modified CRREL NG+N			
Sample Identification	Matri	QC Sample Spik Descriptio mg/K	Sample (g)	Acetone mls	Method 8330 NG	Method 353.2 N	Corr. Method 353.2 N	Corr. Total NG+N	Extract (10	Extract (10	NG Conc mg/K	Abs 507nm	Analysis Dilution Factor	Conc N mg/k	Abs 507nm	Analysis Dilution Factor	Conc as mg/k	Comments/
BI-BLK-001-SS-NG	Soi	N	20	20	N	N	N	N	-	-	ND<2.0	0.007	1	ND<25	0.000	2.3	ND<4	
BI-LCS-001-SS-NG	Soi	50	20	20	N	N	N	N	+	+	45.6	0.406	10	56.1	0.294	10	54	*calculated as
BI-LCS-001-SS-NC	Soi	200	20	20	N	N	N	N	+	+	N	0.275	1	255	0.306	25	163	
1885-02-SS-067	Soi	N	20	20	ND<0.5	203Q	314	314	+	+	ND<2.0	0.021	1	ND<25	0.041	38	ND<57	no more sample
1885-02-SS-068	Soi	N	20	20	0.55	551Q	852	853	++	++	ND<2.0	0.276	1	256	0.236	76	382	
1885-02-SS-069	Soi	N	20	20	0.36J,J	400Q	619	619	++	+	ND<2.0	0.015	2	ND<50	0.117	36.4	91	
1885-02-SS-070	Soi	N	20	20	ND<0.5	57.6	89	89	++	+	ND<2.0	0.094	1	82.9	NS	NS	NS	no more sample
1885-02-SS-071	Soi	N	20	20	ND<0.5	11.2	17	17	-	-	ND<2.0	0.000	1	ND<25	0.031	2.9	ND<5	
1885-02-SS-071MS NG	Soi	37.5	20	20	N	N	N	N	+	-	39.1	0.292	10	40.9	0.367	10	67	*calculated as
1885-02-SS-071MSD NG	Soi	37.5	20	20	N	N	N	N	+	-	39.5	0.256	10	36.1	0.413	10	75	*calculated as
1885-02-SS-071MS NC	Soi	37.5	20	20	N	N	N	N	+	-	N	0.00	1	ND<25	0.020	25	ND<38	no more sample
1885-02-SS-071MSD NC	Soi	37.5	20	20	N	N	N	N	+	-	N	0.00	1	ND<25	0.016	25	ND<38	no more sample
1885-02-SS-072[a]	Soi	N	20	20	2.1J	6200Q	9590	9590	+++	++	22.0	0.457	10	4290	0.710	500	7570	GC/TID extract, no resin
1885-02-SS-072A[a]	Soi	N	20	20	1.4PG,JS	6640Q	10300	10300	++++	+++	44.5	0.795	10	7500	0.808	500	8610	GC/TID extract, no resin
1885-02-SS-073[b]	Soi	N	20	20	ND<0.5	11.8	18	18	+	-	ND<2.0	0.091	1	80.0	0.495	3.2	34	
1885-03-SS-074	Soi	N	20	20	ND<0.5	2.5	4	4	-	-	ND<2.0	0.005	1	ND<25	0.000	1.8	ND<3	
1885-03-SS-075	Soi	N	20	20	ND<0.5	39.6	61	61	-	-	ND<2.0	0.046	1	37.1	0.002	4.4	ND<7	
1885-03-SS-076	Soi	N	20	20	ND<0.5	51.3	79	79	+	-	ND<2.0	0.019	1	ND<25	0.116	5	12	
1885-03-SS-077	Soi	N	20	20	ND<0.5	15.0	23	23	-	-	ND<2.0	0.000	1	ND<25	0.007	2.4	ND<4	
1885-03-SS-078	Soi	N	20	20	ND<0.5	31.4	49	49	-	-	ND<2.0	0.000	1	ND<25	0.063	3.2	ND<5	
1890-01B-SS-079	Soi	N	20	20	ND<0.5	3.2	5	5	-	-	ND<2.0	0.000	1	ND<25	0.000	1.7	ND<3	
1890-01B-SS-080	Soi	N	20	20	0.55J	182Q	282	282	+	+	3.0	0.201	1	185	0.461	15	147	
1890-01B-SS-081	Soi	N	20	20	ND<0.5	11.6	18	18	+	+	ND<2.0	0.005	1	ND<25	0.984	2	42	
1890-01B-SS-081A	Soi	N	20	20	ND<0.5	39.5	61	61	-	-	ND<2.0	0.001	1	ND<25	0.004	4.0	ND<6	
1890-01B-SS-081B	Soi	N	20	20	N	N	N	N	N	N	N	N	N	N	0.000	3	ND<5	
1890-01B-SS-081C	Soi	N	20	20	N	N	N	N	N	N	N	N	N	N	0.000	3	ND<5	
BI-BLK-002-SS-NC/NG	Soi	N	20	20	N	N	N	N	-	-	ND<2.0	0.000	1	ND<25	0.000	1	ND<2	
BI-LCS-002-SS-NG	Soi	50	20	20	N	N	N	N	-	-	55.0	0.359	10	50.8	0.275	15.4	78	*calculated as
BI-LCS-002-SS-NC	Soi	200	20	20	N	N	N	N	+	+	N	0.177	1	169	NS	NS	NS	no more sample
1885-02-SS-082	Soi	N	20	20	1.0	1970Q, JB	3050	3050	+	++	ND<2.0	0.072	1	68.6	0.550	20	235	GC/TID extract, SPICE column

Table B.2-2 BAAAP/ESTCP Field Demonstration Soil Analytical Summary Cont.

					STL Reference Method Results (mg/kg)				Drop-Ex	Expray	GC/TID NG	CRREL NG+NC			Shaw Modified CRREL NG+NC			
1885-02-SS-083	Soil	NA	20	20	3.0JS	275Q,JB	425	428	+	++	ND<2.0	0.047	1	44.8	0.509	15	163	GC/TID extract, SPICE column
1885-02-SS-083A	Soil	NA	20	20	ND<0.5JS	431Q,JB	667	667	+	+	ND<2.0	0.021	1	ND<25	0.214	40	183	
1885-02-SS-084	Soil	NA	20	20	ND<0.5	234Q,JB	362	362	+	+	ND<2.0	0.060	1	57.1	0.520	21	233	
1885-02-SS-085	Soil	NA	20	20	0.19J	174Q,JB	269	269	+	+	ND<2.0	0.032	1	30.5	0.398	15	127	
1885-02-SS-086	Soil	NA	20	20	ND<0.5	21.4JB	33	33	-+	-	ND<2.0	0.016	1	ND<25	0.533	1.5	17	GC/TID extract, SPICE column
1885-02-SS-087	Soil	NA	20	20	0.82	558Q,JB	863	864	+	+	ND<2.0	0.056	1	53.3	0.210	56	251	
1885-02-SS-087MS NG	Soil	50	20	20	NA	NA	NA	NA	+	+	55.5	0.226	10	33.1	0.864	10	184	
1885-02-SS-087MSD NG	Soil	50	20	20	NA	NA	NA	NA	+	+	54.8	0.235	10	34.3	0.542	50	578	
1885-02-SS-087MS NC	Soil	316	20	20	NA	NA	NA	NA	+	+	NA	0.067	1	63.8	0.527	25	281	
1885-02-SS-087MSD NC	Soil	316	20	20	NA	NA	NA	NA	+	+	NA	0.090	1	85.7	0.365	25	195	
1885-02-SS-088	Soil	NA	20	20	0.39J	11.2JB	17	18	-	-	ND<2.0	0.000	1	ND<25	0.000	3	ND<5	
1885-02-SS-089	Soil	NA	20	20	ND<0.5	24.4JB	38	38	-	-	ND<2.0	0.000	1	ND<25	0.109	3	7	
1885-02-SS-090	Soil	NA	20	20	ND<0.5	2.8J, JB	4	4	-	-	ND<2.0	0.001	1	ND<25	0.000	2	ND<3	
1885-02-SS-091	Soil	NA	20	20	ND<0.5	266Q,JB	412	412	+	+	ND<2.0	0.044	1	41.9	0.393	100	838	
1885-02-SS-092	Soil	NA	20	20	ND<0.5	37.4JB	58	58	+	-+	ND<2.0	0.006	1	ND<25	0.273	4	23	
1885-02-SS-093	Soil	NA	20	20	0.18J	340Q,JB	526	526	-	-	ND<2.0	0.005	1	ND<25	0.010	30	ND<45	
1885-02-SS-093A	Soil	NA	20	20	ND<0.5	92.2Q,JB	143	143	-	-	ND<2.0	0.003	1	ND<25	0.001	9	ND<15	no more sample
1885-02-SS-094	Soil	NA	20	20	ND<0.5	9.9JB	15	15	-	-	ND<2.0	0.006	1	ND<25	0.000	2.3	ND<4	
1885-02-SS-095	Soil	NA	20	20	ND<0.5	66.8JB	103	103	-+	+	ND<2.0	0.016	1	ND<25	0.700	7	104	
1885-02-SS-096	Soil	NA	20	20	ND<0.5	2.3J,JB	4	4	-	-	ND<2.0	0.001	1	ND<25	NS	NS	NS	no more sample
1885-02-SS-097	Soil	NA	20	20	ND<0.5	87.9Q,JB	136	136	+-	-	ND<2.0	0.003	1	ND<25	0.053	8	9	
1885-02-SS-098	Soil	NA	20	20	ND<0.5	55.7JB	86	86	++	+	ND<2.0	0.011	1	ND<25	NS	NS	NS	no more sample
1885-02-SS-099	Soil	NA	20	20	ND<0.5	62.5JB	97	97	+	+-	ND<2.0	IF	1	NA	0.105	5	11	

[a]Solid propellant pieces (0.023 g) were physically removed from 695 g of soil during sample preparation (33.1 mg/kg).

[b]Solid propellant pieces (0.56 g) were physically removed from 445 g of soil during sample preparation (1,260 mg/kg).

Q= Elevated reporting Limit

J = Estimated result. Result is less than reporting limits.

JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.

JB = Estimated result. Method blank contains contamination.

PG = The percent difference between the original and confirmation analysis is greater than 40%.

ND = Not detected at the specified method detection limit

NA = Not analyzed or not applicable

+ = Detected

- = Not detected

+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table B.2-3 BAAAP/ESTCP Field Demonstration Concrete Material Analytical Summary

					STL Reference Method Results				Core Surface Drop-Ex Test			Drop-Ex	Expra	NG GC/TID	CRREL NG+N				
Sample Identification	Matrix	QC Spike Description mg/K	Sampl wt (g)	Aceton ml	Method 8330 NG	Method 353.2 N	Corr. Method 353.2 N	Corr. Total NG+N	Top	Bottom	Crack	Extract (10	Extract (10	NG Conc mg/K	Abs 507nm Reading	Analysis Dilution Factor	Analyzed conc as NG	Analyzed conc as NC	Comments/
BI-BLK-001-CM-NG	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
BI-LCS-001-CM-NG	Concrete	50	20.0	20.0	N	N	N	N	N	N	N	+	-	41	0.474	1	53.7	N	
BI-BLK-001-CM-NC	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	-	-	N	0.000	1	ND<5.0	ND<100	
BI-LCS-001-CM-NC	Concrete	211	20.0	20.0	N	N	N	N	N	N	N	-	-	N	0.020	1	ND<5.0	ND<100	
9590-000-CM-034	Concrete	N	20.0	20.0	ND<0.5	201Q	413	413	++	-	-	-	-	ND<2.0	0.017	1	ND<5.0	ND<100	
9590-000-CM-034A	Concrete	N	20.0	20.0	ND<0.5	63.0	129	129	++	N	N	-	-	ND<2.0	0.007	1	ND<5.0	ND<100	
1885-01-CM-035	Concrete	N	20.0	20.0	ND<0.5	17.1	35	35	+	+	N	+-	-	ND<2.0	0.007	1	ND<5.0	ND<100	
1885-01-CM-035	Concrete	N	20.0	20.0	N	N	N	N	N	+	N	+-	-	ND<2.0	0.001	1	ND<5.0	ND<100	
1885-01-CM-036	Concrete	N	20.0	20.0	ND<0.5	20.3	42	42	+-	+-	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	Wipe of EJM -
1885-01-CM-037	Concrete	N	20.0	20.0	ND<0.5	17.9	37	37	+	+	N	-	-	ND<2.0	0.006	1	ND<5.0	ND<100	
1890-01B-CM-038	Concrete	N	20.0	20.0	ND<0.5	5.7	12	12	-	-	N	-	-	ND<2.0	0.004	1	ND<5.0	ND<100	
1890-01B-CM-038MS-NC	Concrete	211	20.0	20.0	N	N	N	N	N	N	N	+	+-	ND<2.0	0.018	1	N	ND<100	
1890-01B-CM-038MSD-NC	Concrete	211	20.0	20.0	N	N	N	N	N	N	N	+	+-	ND<2.0	0.056	1	N	114	
1890-01B-CM-038MS-NG	Concrete	100	20.0	20.0	N	N	N	N	N	N	N	+	+	172	O	1	O	N	
1890-01B-CM-038MSD-NG	Concrete	100	20.0	20.0	N	N	N	N	N	N	N	+	+	156	O	1	O	N	
1890-01B-CM-039	Concrete	N	20.0	20.0	ND<0.5	30.1	62	62	+	+	N	-	-	ND<2.0	-0.002	1	ND<5.0	ND<100	
1890-01B-CM-040	Concrete	N	20.0	20.0	ND<0.5	17.8	37	37	+	+	N	-	-	ND<2.0	-0.005	1	ND<5.0	ND<100	
1890-01B-CM-041	Concrete	N	20.0	20.0	ND<0.5	9.9	20	20	+	+	N	-	-	ND<2.0	0.018	1	ND<5.0	ND<100	
1890-01B-CM-042	Concrete	N	20.0	20.0	ND<0.5	95.9Q	197	197	+	+	N	-	-	ND<2.0	0.008	1	ND<5.0	ND<100	
1890-01B-CM-043	Concrete	N	20.0	20.0	ND<0.5	71.9Q	148	148	++	+	++	-	-	ND<2.0	0.002	1	ND<5.0	ND<100	
1890-01B-CM-043A	Concrete	N	20.0	20.0	ND<0.5	36.8	76	76	N	N	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1890-01B-CM-044	Concrete	N	20.0	20.0	ND<0.5	10.2	21	21	-	-	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1890-01B-CM-045	Concrete	N	20.0	20.0	0.23	87.8Q	180	180	-	-	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1890-01B-CM-046	Concrete	N	20.0	20.0	1.1	261Q	536	537	++	++	N	+	-	2.52	0.061	1	8.8	124	Wipe of EJM ++
1890-01B-CM-046A	Concrete	N	20.0	20.0	0.46	42.7	88	88	N	N	N	+	-	1.44	0.063	1	9.0	128	
1890-01B-CM-046(B)	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	N	N	N	0.081	10	N	87	Shaw Modified CRREL
1890-01B-CM-046(C)	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	N	N	N	0.297	10	N	230	Shaw Modified CRREL
1885-03S-CM-047	Concrete	N	20.0	20.0	ND<0.5	3.1J	6	6	-	-	-	-	-	ND<2.0	0.007	1	ND<5.0	ND<100	
1885-03S-CM-048	Concrete	N	20.0	20.0	ND<0.5	3.0J	6	6	-	-	N	-	-	ND<2.0	-0.003	1	ND<5.0	ND<100	
1885-03S-CM-049	Concrete	N	20.0	20.0	ND<0.5	6.8J	14	14	-	-	N	-	-	ND<2.0	0.006	1	ND<5.0	ND<100	Wipe of EJM -
1885-03S-CM-050	Concrete	N	20.0	20.0	ND<0.5	3.4J	7	7	-	-	N	-	-	ND<2.0	0.001	1	ND<5.0	ND<100	Wipe of EJM -
BI-BLK-002-CM-NG	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	-	-	ND<2.0	-0.001	1	ND<5.0	ND<100	
BI-LCS-002-CM-NG	Concrete	50	20.0	20.0	N	N	N	N	N	N	N	-	-	48.2	0.396	1	45.2	N	
BI-BLK-002-CM-NC	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	-	-	N	0.003	1	ND<5.0	ND<100	
BI-LCS-002-CM-NC	Concrete	211	20.0	20.0	N	N	N	N	N	N	N	-	-	N	0.018	1	ND<5.0	ND<100	
1885-03-CM-051	Concrete	N	20.0	20.0	ND<0.5	3.2J	7	7	-	-	N	-	-	ND<2.0	0.025	1	ND<5.0	ND<100	
1885-03-CM-052	Concrete	N	20.0	20.0	ND<0.5	5.3J	11	11	-	-	N	-	-	ND<2.0	0.003	1	ND<5.0	ND<100	
1885-03-CM-053	Concrete	N	20.0	20.0	ND<0.5	8.8J	18	18	-	-	N	-	-	ND<2.0	0.005	1	ND<5.0	ND<100	

Table B.2-3 BAAAP/ESTCP Field Demonstration Concrete Material Analytical Summary Cont.

Sample Identification	Matrix	QC Sample Spike Description mg/Kg	Sample wt (g)	Acetone mls	STL Reference Method Results (mg/kg)				Core Surface Wipes Drop-Ex Test			Drop-Ex	Expray	NG GC/TID	CRREL NG+NC				
					Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	To	Botto	Crack	Extract (10 uls)	Extract (10 uls)	NG Conc mg/Kg	Abs at 507nm Reading 1	Analysis Dilution Factor	Analyzed conc as NG	Analyzed conc as NC	Comments/ Notes
1885-03-CM-054	Concrete	NA	20.0	20.0	ND<0.5	5.0JM	10	10	-	-	N	-	-	ND<2.0	0.006	1	ND<5.0	ND<100	
1885-03-CM-055	Concrete	NA	20.0	20.0	ND<0.5	4.0JM	8	8	N	N	N	-	-	ND<2.0	0.022	1	ND<5.0	ND<100	
1885-03-CM-056	Concrete	NA	20.0	20.0	ND<0.5	9.8JM	20	20	+-	N	+-	-	-	ND<2.0	0.007	1	ND<5.0	ND<100	Fractured vertical
1885-02-CM-057	Concrete	NA	20.0	20.0	ND<0.5	36.1JM	74	74	-	-	N	-	-	ND<2.0	0.002	1	ND<5.0	ND<100	
1885-02-CM-058	Concrete	NA	20.0	20.0	ND<0.5	3.1JM	6	6	-	N	N	-	-	ND<2.0	0.002	1	ND<5.0	ND<100	
1885-02-CM-059	Concrete	NA	20.0	20.0	ND<0.5	6.1JM	13	13	-	-	N	-	-	ND<2.0	0.001	1	ND<5.0	ND<100	
1885-02-CM-060	Concrete	NA	20.0	20.0	ND<0.5	8.7JM	18	18	-	-	N	-	-	ND<2.0	0.003	1	ND<5.0	ND<100	
1885-02-CM-061	Concrete	NA	20.0	20.0	ND<0.5	9.8JM	20	20	-	N	+-	-	-	ND<2.0	-0.001	1	ND<5.0	ND<100	
1885-02-CM-061MS-NC	Concrete	211	20.0	20.0	NA	NA	NA	NA	N	N	N	+-	-	NA	0.020	1	ND<5.0	ND<100	
1885-02-CM-061MSD-NC	Concrete	211	20.0	20.0	NA	NA	NA	NA	N	N	N	+	+-	NA	0.113	1	NC	229	
1885-02-CM-061MS-NG	Concrete	100	20.0	20.0	NA	NA	NA	NA	N	N	N	+	+	152	O	1	NC	NC	
1885-02-CM-061MSD-NG	Concrete	100	20.0	20.0	NA	NA	NA	NA	N	N	N	+	+	159	O	1	NC	NC	
1885-02-CM-062	Concrete	NA	20.0	20.0	ND<0.5	7.3JM	15	15	-	-	N	-	-	ND<2.0	0.001	1	ND<5.0	ND<100	
1885-02-CM-063	Concrete	NA	20.0	20.0	ND<0.5	11.5JM	24	24	-	-	N	-	-	ND<2.0	0.003	1	ND<5.0	ND<100	
1885-02-CM-064	Concrete	NA	20.0	20.0	ND<0.5	4.2JM	9	9	+-	+-	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1885-02-CM-065	Concrete	NA	20.0	20.0	ND<0.5	6.9JM	14	14	-	-	N	-	-	ND<2.0	0.003	1	ND<5.0	ND<100	
1885-02-CM-066	Concrete	NA	20.0	20.0	ND<0.5	7.6JM	16	16	-	-	N	-	-	ND<2.0	0.002	1	ND<5.0	ND<100	
1885-02-CM-100	Concrete	NA	20.0	20.0	ND<0.5	3.5JB,J	7	7	+	-	N	-	-	ND<2.0	-0.001	1	ND<5.0	ND<100	
1885-02-CM-100A	Concrete	NA	20.0	20.0	ND<0.5	4.4JB,J	9	9	N	N	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1885-02-CM-100 Bottom	Concrete	NA	20.0	20.0	NA	NA	NA	NA	N	N	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1885-02-CM-101	Concrete	NA	20.0	20.0	ND<0.5	2.2JB,J	5	5	-	-	N	-	-	ND<2.0	0.001	1	ND<5.0	ND<100	
1885-02-CM-102	Concrete	NA	20.0	20.0	ND<0.5	3.4JM,J	7	7	-	-	N	-	-	ND<2.0	0.040	1	6.5	81	*Interference- Yellow Color
1885-02-CM-103	Concrete	NA	20.0	20.0	ND<0.5	3.5JM,J	7	7	-	N	+-	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1885-01-CM-036-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND<25	
1890-01B-CM-042-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	130JC	
1890-01B-CM-046-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	126JC	
1885-03S-CM-049-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	92JC	
1885-03-CM-053-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND<25	
1885-02-CM-064-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND<25	
EQ-RINSE 12/2/05	Water	NA	NA	NA	ND<0.65	0.25J,J	0.57	0.57	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
EQ-RINSE 12/6/06	Water	NA	NA	NA	ND<0.65	0.28J,J	0.63	0.63	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
EQ-RINSE 12/7/06	Water	NA	NA	NA	ND<0.65	0.29J,J	0.65	0.65	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	

(B) = Sample re-analysis by Modified CRREL method
(C) = Sample duplicate re-analysis by Modified CRREL method
Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JM = Estimated result. MS/MSD recovery is outside stated control limits.
JB = Estimated result. Method blank contains contamination.
JC = Results are estimates. Values are based on a calibration using NC spiked into blank CM matrix extract.
ND = Not detected at the specified method detection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table B.2-4 BAAAP/ESTCP Field Demonstration Wood Analysis- QC Sample Summary					
			NG GC/TID	Shaw Modified CRREL NG+NC	
Sample Identification	Matrix	QC Sample Spike Description mg/Kg	Conc mg/Kg	Analyzed conc as NG	Analyzed conc as NC
BI-BLK-001-WD-NG	Wood	NA	ND<5.0	ND<5.0	ND<10.0
BI-LCS-001-WD-NG	Wood	100	102	110	NA
BI-LCS-001-WD-NC	Wood	211	NA	NA	231
6657-02I-WD-003	Wood	NA	ND<5.0	ND<5.0	ND<10.0
6657-02I-WD-003A	Wood	NA	ND<5.0	ND<5.0	ND<10.0
6709-17-WD-019	Wood	NA	44.5	83.6	157
6709-17-WD-019MS-NG	Wood	200	217	544	NA
6709-17-WD-019MSD-NG	Wood	200	238	625	NA
6709-17-WD-019MS-NC	Wood	421	NA	NA	770
6709-17-WD-019MSD-NC	Wood	421	NA	NA	779
6709-17-WD-020	Wood	NA	25.4	89.8	165
6709-17-WD-020A	Wood	NA	25.9	120	204
BI-BLK-002-WD-NG	Wood	NA	ND<5.0	ND<5.0	ND<10.0
BI-LCS-002-WD-NG	Wood	50	46.1	44.6	NA
BI-LCS-002-WD-NC	Wood	211	ND<5.0	NA	276
BI-BLK-003-WD-NG	Wood	NA	ND<5.0	ND<5.0	ND<10.0
BI-LCS-003-WD-NG	Wood	200	161	275	389
BI-LCS-003-WD-NC	Wood	211	NA	111	169
1890-01-WD-022	Wood	NA	ND<5.0	ND<5.0	ND<10.0
1890-01-WD-022MS-NG	Wood	100	101	102	NA
1890-01-WD-022MSD-NG	Wood	100	84.8	100	NA
1890-01-WD-022MS-NC	Wood	211	NA	NA	220
1890-01-WD-022MSD-NC	Wood	211	NA	NA	237
1890-01-WD-028	Wood	NA	ND<5.0	21.1	34.8
1890-01-WD-028A	Wood	NA	ND<5.0	22.5	36.7
5024-000-WD-033	Wood	NA	ND<20	1817	2857
5024-000-WD-033A	Wood	NA	ND<20	1782	2811
ND = Not detected at the specified method detection limit					
NA = Not analyzed or not applicable					
MS = Matrix Spike	MSD= Matrix Spike Duplicate				
A = Duplicate Sample, B = Triplicate Sample, C = Quadruplicate Sample					
NC = nitrocellulose	NG = nitroglycerine				

Table B.2-5 BAAAP/ESTCP Field Demonstration Soil Analysis- QC Sample Summary

Sample Identification	Matrix	QC Sample Spike Description mg/Kg	GC/TID NG Conc mg/Kg	CRREL NG+NC Conc as NC mg/kg	Shaw Modified CRREL NG+NC Conc as NC mg/kg
BI-BLK-001-SS-NG	Soil	NA	ND<2.0	ND<25	ND<4
BI-LCS-001-SS-NG	Soil	50	45.6	56.1	54
BI-LCS-001-SS-NC	Soil	200	NA	255	163
1885-02-SS-071	Soil	NA	ND<2.0	ND<25	ND<5
1885-02-SS-071MS NG	Soil	37.5	39.1	40.9	67
1885-02-SS-071MSD NG	Soil	37.5	39.5	36.1	75
1885-02-SS-071MS NC	Soil	37.5	NA	ND<25	ND<38
1885-02-SS-071MSD NC	Soil	37.5	NA	ND<25	ND<38
1885-02-SS-072	Soil	NA	22.0	4290	7570
1885-02-SS-072A	Soil	NA	44.5	7500	8610
1890-01B-SS-081	Soil	NA	ND<2.0	ND<25	42
1890-01B-SS-081A	Soil	NA	ND<2.0	ND<25	ND<6
1890-01B-SS-081B	Soil	NA	NA	NA	ND<5
1890-01B-SS-081C	Soil	NA	NA	NA	ND<5
BI-BLK-002-SS-NC/NG	Soil	NA	ND<2.0	ND<25	ND<2
BI-LCS-002-SS-NG	Soil	50	55.0	50.8	78
BI-LCS-002-SS-NC	Soil	200	NA	169	NS
1885-02-SS-083	Soil	NA	ND<2.0	44.8	163
1885-02-SS-083A	Soil	NA	ND<2.0	ND<25	183
1885-02-SS-087	Soil	NA	ND<2.0	53.3	251
1885-02-SS-087MS NG	Soil	50	55.5	33.1	184
1885-02-SS-087MSD NG	Soil	50	54.8	34.3	578
1885-02-SS-087MS NC	Soil	316	NA	63.8	281
1885-02-SS-087MSD NC	Soil	316	NA	85.7	195
1885-02-SS-093	Soil	NA	ND<2.0	ND<25	ND<45
1885-02-SS-093A	Soil	NA	ND<2.0	ND<25	ND<15

ND = Not detected at the specified method detection limit
NA = Not analyzed or not applicable
MS = Matrix Spike
MSD= Matrix Spike Duplicate
A = Duplicate Sample, B = Triplicate Sample, C = Quadruplicate Sample
NC = nitrocellulose NG = nitroglycerine

Table B.2-6 BAAAP/ESTCP Field Demonstration Concrete Analysis- QC Sample Summary

Sample	Matri	QC Sample Description	N GC/TI Conc mg/Kg	NG+NC Analyzed as NG	NG+NC Analyzed conc as NC
BI-BLK-001-CM-NG	Concret	N	ND<2.0	ND<5.0	ND<100
BI-LCS-001-CM-NG	Concret	50	41	53.7	NC
BI-BLK-001-CM-NC	Concret	N	N	ND<5.0	ND<100
BI-LCS-001-CM-NC	Concret	211	N	ND<5.0	ND<100
9590-000-CM-034	Concret	N	ND<2.0	ND<5.0	ND<100
9590-000-CM-034A	Concret	N	ND<2.0	ND<5.0	ND<100
1885-01-CM-035	Concret	N	ND<2.0	ND<5.0	ND<100
1885-01-CM-035B	Concret	N	ND<2.0	ND<5.0	ND<100
1890-01B-CM-038	Concret	N	ND<2.0	ND<5.0	ND<100
1890-01B-CM-038MS-NC	Concret	211	ND<2.0	NC	ND<100
1890-01B-CM-038MSD-NC	Concret	211	ND<2.0	NC	114
1890-01B-CM-038MS-NG	Concret	100	172	OR	NC
1890-01B-CM-038MSD-NG	Concret	100	156	OR	NC
1890-01B-CM-043	Concret	N	ND<2.0	ND<5.0	ND<100
1890-01B-CM-043A	Concret	N	ND<2.0	ND<5.0	ND<100
1890-01B-CM-046	Concret	N	2.52	8.8	124
1890-01B-CM-046A	Concret	N	1.44	9.0	128
BI-BLK-002-CM-NG	Concret	N	ND<2.0	ND<5.0	ND<100
BI-LCS-002-CM-NG	Concret	50	48.2	45.2	NC
BI-BLK-002-CM-NC	Concret	N	N	ND<5.0	ND<100
BI-LCS-002-CM-NC	Concret	211	N	ND<5.0	ND<100
1885-02-CM-061	Concret	N	ND<2.0	ND<5.0	ND<100
1885-02-CM-061MS-NC	Concret	211	N	ND<5.0	ND<100
1885-02-CM-061MSD-NC	Concret	211	N	NC	229
1885-02-CM-061MS-NG	Concret	100	152	NC	NC
1885-02-CM-061MSD-NG	Concret	100	159	NC	NC
1885-02-CM-100	Concret	N	ND<2.0	ND<5.0	ND<100
1885-02-CM-100A	Concret	N	ND<2.0	ND<5.0	ND<100

ND = Not detected at the specified method detection limit
NA = Not analyzed or not applicable
MS = Matrix Spike
MSD= Matrix Spike
A = Duplicate Sample, B = Triplicate Sample, C = Quadruplicate Sample
NC = nitrocellulose NG = nitroglycerine

Appendix B.3
STL Data Validation Reports

Data Validation Summary Report
ESTCP Demonstration Plan
Wisconsin

1.0 Introduction

Level III data validation was performed on 100 percent of the environmental samples collected for the December 2005 sampling event. The analytical data consisted of sample delivery groups (SDG's) G5L090406, G5L090407, G5L130251, G5L130268, G5L130276, G5L130291, and G5L280254, which were analyzed by STL. The chemical parameters for which the samples were analyzed and validated are identified below:

Parameter (Method)
Nitroglycerin by SW846 8332
Nitrocellulose by MCAWW 353.2

2.0 Procedures

The sample data were validated following the logic identified in the 1999 *EPA Contract Laboratory Program National Functional Guidelines for Organic Review* for all areas. Specific quality control (QC) criteria as identified in analytical methods, and laboratory standard operating procedures (SOP) were applied to all sample results. In light of applying CLP guidelines to SW846 methods and evaluating the usability of the data during the validation process, specific QC criteria were determined to address all target compounds and are identified in this report for each parameter, as well as in the validation checklists, which function as worksheets. All completed validation checklists are included in Attachment A. For those analytical methods not addressed by the CLP guidelines, the validation was based on the method requirements (i.e., SW846, Code of Federal Regulations, SOPs) and technical judgement, following the logic of the CLP validation guidelines.

3.0 Summary of Data Validation Findings

The overall quality of the data was determined to be acceptable with minimal qualification. The only rejected data ("R" qualified) were samples that were reanalyzed and have more than one set of results reported. The "R" qualifier was assigned to the samples with more than one set of results to indicate that a given result should not be used to characterize a particular constituent or an analysis for a given sample.

Individual validation reports have been prepared for each parameter, and the overall results of the validation findings are summarized in this report. A listing of the validation qualifiers and the reason codes, along with their definitions, can be found in Attachment A. The following section highlights the key findings of the data validation for each analysis.

4.0 Analysis-Specific Data Validation Summaries

4.1 Nitroglycerine by HPLC SW846 8332

Overall, the data are of good quality and are usable as reported by the laboratory with the exceptions noted below. Data were reviewed for the following:

Holding Times

Technical holding time criteria were met for all samples with the following exception(s):

SDG	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	*1885-02-SS-072, -072A	Nitroglycerine	J
G5L280254	*1885-02-SS-083	Nitroglycerine	J

*Note that the highest results were chosen for reporting between samples with low surrogates and re-analysis (due to low surrogate recoveries) outside of hold time.

Initial and Continuing Calibration

The initial calibration (ICAL) and continuing calibrations (CCAL) associated with the project samples met QC criteria.

Blanks

The 5X rule for contaminants found in the associated method and equipment rinse blanks were applied to all sample results. All were found to be acceptable.

SURROGATE RECOVERIES

Surrogate recovery QC criteria were met with the following exception(s):

SDG	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	*1885-02-SS-069, -080	Nitroglycerine	J
G5L280254	*1885-02-SS-083A, -084, -099, -072A	Nitroglycerine	J/UJ

*Note that the highest results were chosen for reporting between samples with low surrogates and re-analysis (due to low surrogate recoveries) outside of hold time.

Note for SDG G5L090407 non-detect sample 5024-000-WD-011 had low surrogate recoveries but was diluted (1-5), and non-detect sample 1890-01-WD-022 had high surrogate recoveries. No qualifiers were applied.

Matrix Spike / Matrix Spike Duplicate

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis was performed for the project

samples, and all QC criteria were met with the following exception(s):

SDG	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	*1885-02-SS-072	Nitroglycerine	J
G5L280254	*1885-02-SS-083	Nitroglycerine	J

***Original batch (includes all SDG samples) MS/MSDs were within QC limits. Re-extracted samples (outside of hold time) used for reporting were also used as MS/MSDs; therefore, only the re-analyzed samples were qualified due to MS/MSD %recovery.**

Note that MS/MSD %recoveries were not calculated for SDG G5L090407 because the original sample was diluted beyond the ability to quantitate a recovery.

Laboratory Control Sample

Laboratory Control Sample (LCS) analysis was performed for the project samples, and all QC criteria were met.

Field Duplicates

Original and field duplicate results were evaluated and no problems were identified.

2nd Column Confirmation

Percent difference between columns was within QC limits with the following exception(s):

SDG Number	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	1885-02-SS-072A	Nitroglycerine	J

Note SDG G5L0130251 original sample 1885-02-SS-072 results with %D between columns above the QC limits was rejected in favor of higher re-analysis results outside of hold time.

Quantitation

Results quantitated between the method detection limit (MDL) and the reporting limit (RL), which the lab qualified as “J”, were qualified as estimated “J“ unless blank contamination was present or the results were rejected. Results rejected in favor of a preferred result (e.g., due to dilution or reanalysis) were qualified as rejected “R.”

4.2 Nitrocellulose MCAWW 353.2

Overall, the data are of good quality and are usable as reported by the laboratory with the exceptions noted below. Data were reviewed for the following:

Holding Times

Technical holding time criteria were met for all samples.

Initial and Continuing Calibration

The initial calibration (ICAL) and continuing calibrations (CCAL) associated with the project

samples met QC criteria.

Blanks

The 5X rule for contaminants found in the associated method blanks and equipment rinse was applied to all sample results. All were found to be acceptable with the following exception(s):

SDG Number	Samples Affected	Compound(s)	Blank Contaminate	Validation Qualifier
G5L090406	1890-01-WD-023, -024, -026, -027, -028, -028A, -030, -031	Nitrocellulose	Method	U
G5L130268	1885-03S-CM-047	Nitrocellulose	Method	U
G5L130291	1885-02-CM-100, -101, -102, -103, -100A	Nitrocellulose	Method	*UJ
G5L280254	**1885-02-SS-088, -090, -094, -096	Nitrocellulose	Method	U

*** Results were "UJ" qualified due to low MS/MDS % recoveries.**
****Original sample results less than 10X the method blank contamination were re-analyzed to confirm their results. Original results were chosen over re-analysis and blank qualified ("U").**

Matrix Spike / Matrix Spike Duplicate

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis was performed for the project samples, and all QC criteria were met with the following exception(s):

SDG Number	Samples Affected	Compound(s)	Validation Qualifier
G5L090407	6709-17-WD-012, -013, -014, -015, -016, -017, -018, -019, -020, -020A, -021, -022	Nitrocellulose	J
G5L130276	1885-03S-CM-048, -48, -050 1885-03-CM-051, -052 -053, -054, -055, -056 1885-02-CM-057, -058, -059, -060, -061, -062, -063, -064, -065, -066	Nitrocellulose	J
G5L130291	1885-02-CM-100, -100A, -101, -102, -103 9590-000-CM-034A 1890-01B-CM-043A, -046A 1885-02-CM-100A	Nitrocellulose	J/UJ*

*** Results were "UJ" qualified due to method blank contamination.**

Note that MS/MSD %recoveries were not calculated because sample amounts were greater than 4X spike amounts for SDG's G5L130251 and G5L130268.

Laboratory Control Sample

Laboratory Control Sample (LCS) analysis was performed for the project samples, and all QC criteria were met.

Field Duplicates

Original and field duplicate results were evaluated and no problems were identified with the following exception(s):

SDG Number	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	1885-02-SS-081 (original), 1885-02-SS-081A (FD),	Nitrocellulose	J

Quantitation

No results were reported below the reporting limit (RL). Results rejected in favor of a preferred result (e.g., due to dilution or reanalysis) were qualified as rejected “R.”

Attachment A

Data Validation Qualifier Entry Verification Report

Validation Qualifiers

U Not detected. The compound/analyte was analyzed for, but not detected above the associated reporting limit.

J The compound/analyte was positively identified; the reported value is the estimated concentration of the constituent detected in the sample analyzed.

UB The concentration reported was detected significantly above the levels reported in the associated equipment rinse samples and/or laboratory method and trip blanks. (5X/10X Rule was applied).

R/UR The reported sample results are rejected due to the following:

1. Severe deficiencies in the supporting quality control data.
2. Anomalies noted in the sampling and/or analysis process which could affect the validity of the reported data.
3. The presence or absence of the constituent cannot be verified based on the data provided.
4. To indicate not to use a particular result in the event of a reanalysis.

UJ The compound/analyte was analyzed for, but not detected above the established reporting limit. However, review and evaluation of supporting QC data and/or sampling and analysis process have indicated that the “nondetect” may be inaccurate or imprecise. The nondetect result should be estimated.

Validation Reason Code Definitions

Reason Code	Definition
01	Sample received outside of 4+/-2 degrees Celsius
01A	Improper sample preservation
02	Holding time exceeded
02A	Extraction
02B	Analysis
03	Instrument performance – outside criteria
03A	BFB
03B	DFTPP
03C	DDT and/or Endrin % breakdown exceeds criteria
03D	Retention time windows
03E	Resolution
04	Initial calibration results outside specified criteria
04A	Compound mean RRF QC criteria not met
04B	Individual % RSD criteria not met
04C	Correlation coefficient >0.995
05	Continuing calibration results outside specified criteria
05A	Compound mean RRF QC criteria not met
05B	Compound % D QC criteria not met
06	Result qualified as a result of the 5x/10x blank correction
06A	Method or preparation blank
06B	ICB or CCB
06C	ER
06D	TB
06E	FB
07	Surrogate recoveries outside control limits
07A	Sample
07B	Associated method blank or LCS
08	MS/MSD/Duplicate results outside criteria
08A	MS and/or MSD recovery not within control limits (accuracy)
08B	% RPD outside acceptance criteria (precision)
09	Post digestion spike outside criteria (GFAA)
10	Internal standards outside specified control limits
10A	Recovery
10B	Retention time
11	Laboratory control sample recoveries outside specified limits
11A	Recovery
11B	% RPD (if run in duplicate)
12	Interference check standard
13	Serial dilution
14	Tentatively identified compounds
15	Quantitation
16	Multiple results available; alternate analysis preferred
17	Field duplicate RPD criteria is exceeded
18	Percent difference between original and second column exceeds QC criteria
19	Professional judgement was used to qualify the data
20	Pesticide clean-up checks
21	Target compound identification
22	Radiological calibration
23	Radiological quantitation
24	Reported result and/or lab qualifier revised to reflect validation findings