ETV

ESTCP
Environmental Security
Technology Certification
Program

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Technology Demonstration Plan

Evaluation of Explosives Field Analytical Techniques

Sponsored by:

U. S. Environmental Protection Agency
National Exposure Research Laboratory
Las Vegas, NV 89193-3478

and

U.S. Department of Defense
Office of the Deputy under Secretary of Defense for Environmental Security
Environmental Security Technology Certification Program
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ornl

APPROVAL SIGNATURES

This document is intended to ensure that all aspects of the demonstration are documented, scientifically sound, and that operational procedures are conducted within quality assurance/quality control specifications and health and safety regulations.

The signatures of the individuals below indicate concurrence with, and agreement to operate compliance with, procedures specified in this document.

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FOREWORD

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's natural resources. The National Exposure Research Laboratory (NERL) is EPA's center for the investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. NERL's research goals are to (1) develop and evaluate technologies for the characterization and monitoring of air, soil, and water; (2) support regulatory and policy decisions; and (3) provide the science support needed to ensure effective implementation of environmental regulations and strategies.

EPA created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies. This program is administered by NERL's Environmental Sciences Division in Las Vegas, Nevada.

The Department of Defense (DoD) Environmental Security Technology Certification Program's (ESTCP) goal is to demonstrate and validate promising, innovative technologies that target DoD's most urgent environmental needs. The ETV and ESTCP can meet their common goal by working with technology developers in planning and conducting demonstrations, evaluating the data generated, and promoting acceptance of the technology. In addition to a detailed technical report, ETV provides the developers with a verification statement, which summarizes the performance of the technology under the conditions of the demonstration. ESTCP provides a cost and summary report and aids in the dissemination of the results across the DoD.

Candidate technologies for these programs originate from the private sector and must be commercially ready. Through the ETV Program, developers are given the opportunity to conduct rigorous demonstrations of their technologies under realistic field conditions. By completing the evaluation and distributing the results, EPA establishes a baseline for acceptance and use of these technologies.

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EXECUTIVE SUMMARY

EPA created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies. This program is administered by the EPA's National Exposure Research Laboratory in Las Vegas, Nevada. For the verification of explosives field analytical technologies, ETV is working in partnership with the Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP). ESTCP's goal is to demonstrate and validate promising, innovative technologies that target DoD's most urgent environmental needs. ETV and ESTCP can meet their common goal by working with technology developers in planning and conducting demonstrations, evaluating the data generated, and promoting acceptance of the technology.

This technology demonstration plan has been developed to describe the verification of field analytical technologies for the determination of explosives compounds in contaminated soil and groundwater. Technologies from Barringer Instruments (GC-IONSCAN) and Research International Inc. (FAST 2000) will be evaluated. The Oak Ridge National Laboratory (ORNL) will serve as the verification organization for the demonstration, with the U.S. Army Cold Regions Research and Engineering Laboratory providing technical guidance and support. ORNL's role is to provide technical and administrative leadership in conducting the demonstration.

The purpose of this demonstration is to obtain performance information regarding the technologies, to compare the results to conventional fixed-laboratory results, and to provide supplemental information (e.g., cost, sample throughput, and training requirements) regarding the operation of the technology. Multiple soil types, collected from sites in California, Louisiana, Iowa, and Tennessee, will be used in this study. In addition, explosives-contaminated water samples from Tennessee, Oregon, and Louisiana will also be evaluated. The concentrations will range from 0 to approximately 90,000 mg/kg . Water samples will range in concentration from 0 to 25,000 µg/L. The primary constituents in the samples are expected to be 1,3,5-trinitrotoluene (TNT), isomeric dinitrotoluene (DNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX).

ABBREVIATIONS AND ACRONYMS

AAP	Army Ammunition Plant
2-Am-DNT	2-amino-4,6-dinitrotoluene, CAS # 35572-78-2
4-Am-DNT	4-amino-2,6-dinitrotoluene, CAS # 1946-51-0
ANOVA	Analysis of Variance
Cy5	cyano-based fluorescent dye
CASD	Chemical and Analytical Sciences Division
CFI	Continuous Flow Immunosensor
CRREL	U. S. Army Cold Regions Research and Engineering Laboratory
DL	detection limits
2,4-DNT	2,4-dinitrotoluene, CAS # 121-14-2
2,6-DNT	2,6-dinitrotoluene, CAS # 606-20-2
DNT	isomeric dinitrotoluene (includes both 2,4-DNT and 2,6-DNT)
DoD	U. S. Department of Defense
ELISA	enzyme linked immunosorbent assay
EPA	U. S. Environmental Protection Agency
ERA	Environmental Resource Associates
ESD-LV	Environmental Science Division-Las Vegas
ESH&Q	Environmental Safety, Health, and Quality
ESTCP	Environmental Security Technology Certification Program
ETV	Environmental Technology Verification Program
ETVR	Environmental Technology Verification Report
fn	false negative result
fp	false positive result
GC	gas chromatography
HASP	Health and Safety Plan
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, CAS # 2691-41-0
HPLC	High performance liquid chromatography

IMS	ion mobility spectrometry
LAAAP	Louisiana Army Ammunition Plant
LCS	Laboratory Control Sample
LMER	Lockheed Martin Energy Research
MLAAP	Milan Army Ammunition Plant
MS/MSD	matrix spike/matrix spike duplicate
MSDS	Material Safety Data Sheets
NRL	Naval Research Laboratory
ORNL	Oak Ridge National Laboratory
PARCC	precision, accuracy, representativeness, completeness, comparability
PE	performance evaluation
PPE	personal protective equipment
ppm	parts per million, mg/kg for soil
ppb	parts per billion, µg/L for water
QA	quality assurance
QAPP	Quality Assurance Project Plan
QAS	Quality Assurance Specialist
QC	quality control
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine, CAS # 121-82-4
RPD	relative percent difference
RSD	percent relative standard deviation
SAI	Specialized Assays Inc.
SCMT	Site Characterization and Monitoring Technologies Pilot of ETV
SD	standard deviation
SITE	Superfund Innovative Technology Evaluation program
SVOCs	semivolatile organic compounds
TNB	1,3,5-trinitrobenzene, CAS # 99-35-4
TNT	2,4,6-trinitrotoluene, CAS # 118-96-7

USACE	U.S. Army Corp of Engineers
VOCs	volatile organic compounds

1.0 INTRODUCTION

This chapter discusses the purpose of the demonstration and the demonstration plan, describes the elements of the demonstration plan, and provides an overview of the Environmental Technology Verification (ETV) Program and the technology verification process.

1.1 Demonstration Objectives

The purpose of this demonstration is to evaluate the performance of commercially available field analytical technologies for performing explosives analyses in water and/or soil samples. Specifically, this plan defines the following elements of the demonstration:

- Roles and responsibilities of demonstration participants;
- Procedures governing demonstration activities such as sample collection, preparation, analysis, data collection, and interpretation;
- Experimental design of the demonstration;
- Quality assurance (QA) and quality control (QC) procedures for conducting the demonstration and for assessing the quality of the data generated from the demonstration; and,
- Health and safety requirements for performing work at hazardous waste sites.

1.2 What is the Environmental Technology Verification Program?

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high quality, peer reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations, stakeholder groups which consist of regulators, buyers, and vendor organizations, and with the full participation of individual technology developers. The Program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

ETV is a voluntary program that seeks to make objective performance information available to all of the actors in the environmental marketplace for their consideration and to assist them in making informed technology decisions. ETV does not rank technologies nor compare their performance, label or list technologies as acceptable or unacceptable, nor seek to determine “best available technology”, nor approve or disapprove technologies. The program does not evaluate technologies at the bench- or pilot-scale and does not conduct or support research.

The program now operates twelve pilots covering a broad range of environmental areas. ETV has begun with a 5-year pilot phase (1995-2000) to test a wide range of partner and procedural alternatives in various pilot areas, as well as the true market demand for and response to such a program. In these pilots, EPA utilizes the expertise of partner "verification organizations" to design efficient processes for conducting performance tests of innovative technologies. EPA has selected its partners from both the public and private sectors including Federal laboratories, states, industry consortia, and private sector facilities. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from all major stakeholder/customer groups associated with the technology area.. This demonstration will be administered by the Site Characterization and Monitoring Technology (SCMT) Pilot [Note: To learn more about ETV, go to ETV's Internet Web site at the following address: http://www.epa.gov/etv].

1.3 Technology Verification Process

The technology verification process is intended to serve as a template for conducting technology demonstrations that will generate high quality data which can be used to verify technology performance. Four key steps are inherent in the process:

- Needs identification and technology selection
- Demonstration planning and implementation
- Report preparation
- Information distribution

1.3.1 Needs Identification and Technology Selection

The first step in the technology verification process is to determine technology needs of the user-community (typically state and Federal regulators and the regulated community). Each Pilot utilizes stakeholder groups. Members of the stakeholder groups come from EPA, the Departments of Energy and Defense, industry, and state regulatory agencies. The stakeholders are invited to identify technology needs and to assist in finding technology developers with commercially available technologies that meet the needs. Once a technology need is established, a search is conducted to identify suitable technologies. The technology search and identification process consists of reviewing responses to *Commerce Business Daily* announcements, searches of industry and trade publications, attendance at related conferences, and leads from technology developers. The following criteria are used to determine whether a technology is a good candidate for the verification:

- Meets user needs
- May be used in the field or in a mobile laboratory
- Applicable to a variety of environmentally impacted sites
- High potential for resolving problems for which current methods are unsatisfactory
- Costs are competitive with current methods
- Performance is better than current methods in areas such as data quality, sample preparation, or analytical turnaround
- Uses techniques that are easier and safer than current methods
- Is commercially available and field-ready.

1.3.2 Demonstration Planning and Implementation

After a developer agrees to participate, EPA, the Verification Organization, and the developer meet to discuss each participants responsibilities in the demonstration process. In addition, the following issues are addressed:

- Site selection. Identifying sites that will provide the appropriate physical or chemical environment, including contaminated media
- Determining logistical and support requirements (for example, field equipment, power and water sources, mobile laboratory, communications network)
- Arranging analytical and sampling support
- Preparing and implementing a demonstration plan that addresses the experimental design, sampling design, QA/QC, health and safety considerations, scheduling of field and laboratory operations, data analysis procedures, and reporting requirements

1.3.3 Report Preparation

Innovative technologies are evaluated independently and, when possible, against conventional technologies. The technologies being verified are operated by the developers in the presence of independent observers. The observers are EPA staff , state staff or from a independent third-party organization. The data generated during the demonstration are used to evaluate the capabilities, limitations, and field applications of each technology. A data summary and detailed evaluation of each technology are published in an Environmental Technology Verification Report (ETVR). The original complete data set is available upon request.

An important component of the ETVR is the Verification Statement. Verification Statements of three to five pages, using the performance data contained in the report, are issued by EPA and appear on the ETV Internet Web page. The Verification Statement is signed by representatives of EPA and the Verification Organization.

1.3.4 Information Distribution

Producing the ETVR and the Verification Statement represents a first step in the ETV outreach efforts. ETV gets involved in many activities to showcase the technologies that have gone through the verification process. The Program is represented at many environmentally-related technical conferences and exhibitions. ETV representatives also participate in panel sessions at major technical conferences. ETV maintains a traveling exhibit that describes the program, displays the names of the companies that have had technologies verified, and provides literature and reports.

We have been taking advantage of the Web by making the ETVRs available for downloading to anyone interested. The ETVRs and the Verification Statements are available in Portable Document Format (.pdf) on the ETV Web site (http://www.epa.gov/etv).

1.4 Purpose of this Demonstration Plan

The purpose of the demonstration plan is to describe the procedures that will be used to verify the performance goals of the technologies participating in this demonstration. This document incorporates the QA/QC elements needed to provide data of appropriate quality sufficient to reach a credible position regarding performance. This is not a method validation study, nor does it represent every environmental situation which may be appropriate for these technologies. But it will provide data of sufficient quality to make a judgement about the application of the technology under conditions similar to those encountered in the field under normal conditions.

2.0 DEMONSTRATION RESPONSIBILITIES AND COMMUNICATION

This section identifies the organizations involved in this demonstration and describes the primary responsibilities of each organization. It also describes the methods and frequency of communication that will be used in coordinating the demonstration activities.

2.1 Demonstration Organization and Participants

Participants in this demonstration are listed in Table 2-1. The specific responsibilities of each demonstration participant are discussed in Section 2.3 This demonstration is being coordinated by Oak Ridge National Laboratory (ORNL) under the direction of the U.S. Environmental Protection Agency's (EPA) Office of Research and Development, National Exposure Research Laboratory, Environmental Sciences Division - Las Vegas, Nevada (ESD-LV) and the U. S. Department of Defense’s Environmental Security Technology Certification Program (ESTCP), Washington, DC. The U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) is assisting ESTCP by providing technical guidance and support to ORNL. ESD-LV and ESTCP's roles are to administer the demonstration program. ORNL's role is to provide technical and administrative leadership and support in conducting the demonstration. Barringer Instruments and Research International Inc. are the technology developers participating in this demonstration. Note that the Naval Research Laboratory, which developed the FAST 2000 technology that was licensed to Research International, will be performing the on-site analysis.

2.2 Organization

In Figure 2-1 is presented an organizational chart depicting the lines of communication for the demonstration. Note that the double-arrow lines signify that each participant is encouraged to openly communicate with other members of the demonstration team.

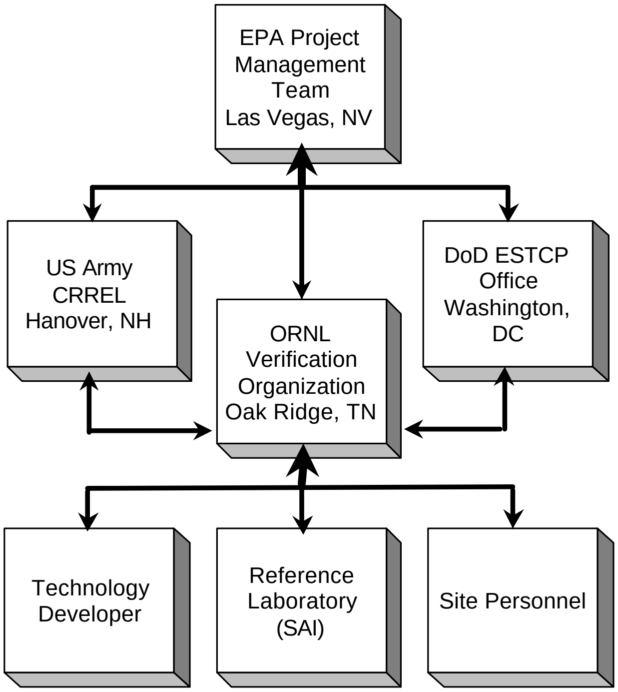

Figure 2-1. Organizational chart.

2.3 Responsibilities

The following is a delineation of each participant's responsibilities for the demonstration. Henceforward, the term "developer" applies to Barringer Instruments and Research International, Inc./Naval Research Laboratory.

The Developer, in consultation with ORNL, ESTCP, and EPA, is responsible for the following elements of this demonstration:

- Contribute to the design and preparation of the demonstration plan;
- Provide detailed procedures for using the technology;
- Prepare the technology for demonstration;
- Operating the technology during the demonstration;
- Documenting the methodology and operation of the technology during the demonstration;
- Furnishing data in a format that can be compared to reference values;
- Logistical and other support, as required.

Table 2-1. Participants in Explosives Detection Technology Demonstration

Organization	Point(s) of Contact	Role
Oak Ridge National Laboratory P.O. Box 2008 Bethel Valley Road Bldg. 4500S, MS-6120 Oak Ridge, TN 37831-6120	**Program Manager:** Roger Jenkins phone: (423) 576-8594 fax: (423) 576-7956 email: jenkinsra@ornl.gov	verification organization
U.S. Army Cold Regions Research and Engineering Laboratory 72 Lyme Road Hanover, NH 03755	**Technical Lead:** Tom Jenkins phone: (603) 646-4385 fax: (603) 646-4785 email: tjenkins@crrel.usace.army.mil	technical advisor
U. S. EPA National Exposure Research Laboratory Environmental Science Division P.O. Box 93478 Las Vegas, NV 89193-3478	**Program Manager:** Eric Koglin phone: (702) 798-2432 fax: (702) 798-2261 email: Koglin.Eric@epa.gov	EPA project management
U. S. DOE ORNL Site Office P.O. Box 2008 Bldg. 4500N, MS-6269 Oak Ridge, TN 37831-6269	**Program Manager:** Regina Chung phone: (423) 576-9902 fax: (423) 574-9275 email: chungr@ornl.gov	DOE/ORO project management
U.S. DoD Office of the Deputy under Secretary of Defense for Environmental Security Environmental Security Technology Certification Program Washington, DC 20301-3400	**Program Manager:** Cathy Vogel phone: (703) 696-2118 fax: (703) 696-2114 email: vogelc@acq.osd.mil	DoD project management
Barringer Instruments 30 Technology Drive Warren, NJ 07059 (see Section 3.1)	**Contact:** John Avolio phone: (908) 222-9100, ext 3003 fax: (908) 222-1557 email: javolio@bii.barringer.com	technology developer
Naval Research Laboratory 4555 Overlook Avenue, S. W. Washington, DC 20375	**Contact:** Anne Kusterbeck phone: (202) 404-6042 fax: (202) 404-8897 email:akusterbeck@cbmse.nrl.navy.mil	technology developer
Research International Inc. 18706 142nd Avenue, NE Woodinville, WA 98072-8523 (see Section 3.4)	**Contact:** Elric Saaski phone: (425) 486-7831 email: resrchintl@aol.com	technology developer
Specialized Assays Incorporated (SAI) 2960 Foster Creighton Drive Nashville, TN 37204 (see Section 4.0)	**Contact:** Mike Dunn phone: (615) 726-0177 fax: (615) 726-3404	reference laboratory

ORNL has responsibilities for:

- Preparing the demonstration plan;
- Developing a quality assurance project plan (QAPP) (Section 8 of the demonstration

plan);
- Preparing a health and safety plan (HASP) (Section 9 of the demonstration plan) for the demonstration activities;
- Acquiring the necessary reference analysis data;
- Performing sampling activities (including collecting, homogenizing, dividing into replicates, bottling, labeling, and distributing);
- Conducting the demonstration.

ORNL, ESTCP, and EPA have coordination and oversight responsibilities for:

- Providing needed logistical support, establishing a communication network, and scheduling and coordinating the activities of all demonstration participants;
- Auditing the on-site sampling activities;
- Managing, evaluating, interpreting, and reporting on data generated by the demonstration; and,
- Evaluating and reporting on the performance of the technologies.
- Site access;
- Characterization information for the site;
- Other logistical information and support needed to coordinate access to the site for the field portion of the demonstration, such as waste disposal.

3.0 TECHNOLOGY DESCRIPTION

This section provides a description of the technologies participating in the verification. The descriptions were provided by the technology developers, with minimal editing by ORNL. This section also describes the performance factors of the technology that will be assessed based on the data generated during the demonstration. Note that TNT is 2,4,6-trinitrotoluene, RDX is hexahydro-1,3,5-trinitro-1,3,5-triazine, HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, and DNT is isomeric dinitrotoluene, including both 2,4-dinitrotoluene and 2,6-dinitrotoluene.

3.1 Barringer Instruments' GC-IONSCAN

3.1.1 Technology Overview

The GC-IONSCAN® is a fully transportable field screening instrument combining the rapid analysis time of ion mobility spectrometry (IMS) with the separation ability of gas chromatography. The unit can be used to detect and quantify explosives based on their retention time, ion mobility, characteristic chemical ionization peaks, and amplitude of the response. The instrument can be operated in IONSCAN® mode or in GC-IONSCAN® mode. The user can switch between the two modes in less than 30 seconds.

In the IONSCAN® mode, samples are thermally desorbed from a substrate and the GC column is bypassed permitting the direct and fast analysis of residue or particulate material in 6 to 8 seconds. In GC-IONSCAN® mode liquid samples or extracts are directly injected onto the GC column and analysis occurs within 1 to 5 minutes, depending on the type of explosive. The operating conditions of the IONSCAN® mode permits rapid prescreening of samples, identifying the major constituents of the sample and semi-quantitative analysis, while the GC-IONSCAN® mode permits full characterization and quantitative analysis of the sample.

The GC-IONSCAN® is fully controlled by the front panel or through an external computer with the GC-IONSCAN® software. The injector port can be set in split or splitless modes, providing a means for quantitative analysis within the linear dynamic range of the detector. One to five microliter samples are directly injected onto the heated injector. For explosive analysis, a 15 m DB-1 column, (internal diameter of 0.53 mm and film thickness of 0.1 µm) is used. Other types of columns can be used, provided that the coil diameter of the column does not exceed 4". The oven temperature can be operated under isothermal conditions or multi-stage temperature ramping conditions. Maximum allowable oven temperature is 300EC and maximum temperature ramping rate is 40 EC/min. The transfer line from the column to the detector is heated at a control temperature (usually 150 EC , adjustable range from 30 to 300 EC) and consists of an extension of the column to the heated inlet of the IONSCAN®. Eluent from the GC column enters the IONSCAN® inlet combining with a makeup gas doped with reactant and proceeds into the ionization region. This occurs only during the analysis cycle. When the analysis is finished, the drift gas of the IONSCAN® is vented through the heated inlet acting like a purge gas and ensuring that the ionization region and inlet are free of any contaminants or carry over from the sample.

3.1.2 Sample Preparation and Analysis Procedure

In both solid and liquid matrices, minimal sample preparations are required. Soil sample preparation involves a one-step solvent extraction with acetone. Ten mL of acetone is added to a 2 g of soil sample in a 20 mL vial. The mixture is shaken and allowed to settle to extract the explosives into the acetone fraction. For rapid field screening protocol, up to 50 µl of the acetone solution can be deposited on the Teflon filter and, once the solvent has evaporated, analyzed by thermal desorption in the IONSCAN® mode. If explosives are detected, quantitative analysis and peak confirmation are performed by injecting 1 to 5 µL of the same acetone sample onto the heated injector after selecting the GC-IONSCAN® mode of operation. Serial dilution of the extracted solution may be performed for highly contaminated samples.

For the analysis of aqueous samples, 10µL of water sample are deposited onto the Teflon filter and analyzed as described previously. If explosives are detected, 1 to 4 µL is directly injected into the heated injector for GC separation and analysis.

Quantitative assessment of explosives in the sample is done by either integration of GC peaks or from peak maximum amplitude of target explosive signals. Barringer states that both methods are extremely reliable within standard laboratory practices. Amounts of explosives in the soil (mg explosive/kg soil) will be determined from the quantitative analysis of the GC peaks and knowing the ratio of solvent extraction to liquid injection volumes. Barringer indicates that, in the IONSCAN® mode, larger aliquots can be analyzed (up to 100 uL), permitting a 30 to 100 fold increase in sensitivity.

3.1.3 Instrument Calibration

Barringer states that the GC-IONSCAN® system is very stable and daily response variation is small. System calibration once prior to the field screening is sufficient to provide the required response factors for quantitative analysis of the sample. Four to five point calibration curves for each explosive analyte will be first established using pre-mixed standard solutions of explosive mixtures in acetone. Repeatability of the measurements will be established by performing 3 to 5 injections of the same standard solution. The concentration of the explosive of interest in the standard solution will cover the linear dynamic range of the detection system. Linear regression of calibration points, as well as standard deviation in each measurement, will be plotted.

3.2 Research International/Naval Research Laboratory's FAST 2000

3.2.1 General Technology Description

The Continuous Flow Immunosensor (CFI) is based on a displacement assay that utilizes antibodies as a means of detection. The key elements of the sensor are: 1) antibodies specific for the analyte, 2) signal molecules which are similar to the analyte but labeled with a fluorophore (usually a cyano-based fluorescent dye (Cy5)) so they are highly visible to a fluorescence detector, and 3) a fluorescence detector. For analysis, the antibodies which specifically recognize the contaminants are immobilized onto a solid support and the fluorescently labeled signal molecule is bound, creating an antibody/signal molecule complex. If the sample contains the target analyte, a proportional amount of the labeled signal molecule is displaced from the antibody and detected by the fluorimeter downstream.

The technology was originally developed by the Naval Research Laboratory. The manufacturable, field-portable version of the CFI, the FAST 2000, has been engineered by Research International. The optically-based signal gathering capabilities are combined with precise fluidics control in a computer application. The software provides a simple menu driven interactive user interface to lead users through the steps required to successfully determine if a trace amount of analyte is present in a given sample. The software also allows the more advanced user complete control of the operational parameters for running nonstandard procedures. Data analysis is made easy with the use of real time plotting of the data, data logging, and custom calibration. The Windows-based software allows for both ease of use and complex system manipulation, keeping all skill levels in mind.

The FAST 2000 unit can be easily carried into the field (2.8 lbs, dimensions: 6 cm x 15.5 cm x 16 cm)) and plugged directly into a portable PC for on-site data acquisition and analysis. The assay chemistry for TNT and RDX detection has been developed to be a functional and robust system that can be successfully used in the field without the need for excessive environmental controls. Analysis time for each sample is approximately 2 minutes. The coupon and membrane can be used for repeated assays. The life of the membrane is dependent upon the number and concentration of positive assays that were run.

3.2.2 Instrument Calibration

Calibration of the FAST 2000 immunosensor is performed with an initial injection (150 µL) of a prepared explosive standard (100 or 1000 µg/L). Subsequent injections of the explosive standard during sample analysis occur every 3rd sample injection. The explosive standards are prepared by drying down 20 µL from the stock explosive vial (1,000,000 µg/L stored in acetonitrile) with a nitrogen air stream. Using a micropipettor 2.0 mL of system flow buffer (10 mM sodium monophosphate, 2.5% ethanol and 0.01% Tween, pH 7.4) is added to the tube to dissolve the explosive residue, forming the 10 ppm explosive standard. Serial dilutions of the 10,000 µg/L standard are made in flow buffer to obtain the 10, 100 and 1000 µg/L standards. Signals from the samples (peak unit area) are compared to the peak unit area of the closest standard for quantitation.

3.2.3 Sample Analysis

The CFI is based on a displacement immunoassay in which the explosive molecules in the sample selectively "displace" a fluorescently labeled signal molecule from an immobilized antibody. The Naval Research Laboratory's 11B3 TNT and Strategic Diagnostics RDX monoclonal antibodies are immobilized onto porous membrane supports and saturated with the fluorescent analog using the detailed protocols outlined in draft U.S. EPA Method 4656. The membrane is inserted into a disposable coupon, placed in the FAST 2000, and the buffer flow is started by a computer command. Once the fluorescence background signal due to unbound Cy5 has stabilized (generally 15-20 minutes), the biosensor is ready for sample injection.

3.2.3.1 Groundwater Samples

For analysis of groundwater, 40 µL 0.5 M sodium phosphate/0.5% Tween 20 and 50 µL ethanol are added to 1.91 mL of a 20 mL test water sample. Test samples (150 µL) are injected using a 1 cc tuberculin syringe in the following order: standard (10-1000 µg/L), three test samples, standard. Additional standards can be assayed to optimize the quantitation.

For all samples, the computer calculates the Peak Area (integral) that are designated by the operator corresponding to the start of the peak and the end of the peak. From the standards that are co-injected with the samples, a sample value is calculated. Ideally, the concentrations of the standards give signals that are close to the signals that are obtained from the samples being analyzed. This value is then used to derive a concentration/unit signal value (ng/mL/Peak Area Unit). This averaged value is then applied to the peak area from each sample injection to acquire a concentration for that injection of the sample.

3.3 Performance Characteristics

For each of the technologies, the following performance characteristics will be evaluated during the demonstration. Specific calculations (where applicable) are described in Section 7.7

- Precision
- Accuracy
- Representativeness
- Completeness
- Comparability
- False positive/false negative results
- Detection limits
- Sample throughput
- Ease of use

4.0 CONFIRMATORY PROCESS

The verification process is based on the presence of a statistically validated data set against which the performance goals of the technology may be compared. The choice of an appropriate reference method and reference laboratory are critical to the success of the demonstration.

4.1 Method Selection

The reference analytical method will be EPA SW-846 Method 8330 [1].

4.2 Reference Laboratory Selection

To assess the performance of the explosives field analytical technologies, the data obtained will be compared to data obtained using conventional analytical methods. This decision is based on the experience of prospective laboratories with QA procedures, reporting requirements, and data quality parameters consistent with the goals of the Program.

In selecting a reference laboratory, Specialized Assays Inc. (SAI), Nashville, Tennessee, was chosen as the leading candidate to perform the analyses based on ORNL's experience with laboratories capable of performing explosives analyses. ORNL reviewed SAI's record of laboratory validation which was performed by the U.S. Army Corp of Engineers (USACE, Omaha, Nebraska). EPA and ORNL decided that, based on the credibility of USACE program and ORNL's prior experience with the laboratory, SAI would be selected to perform the reference analyses. Selection was finalized with the successful analyses of the predemonstration samples. In Appendix A is presented SAI's standard operating procedures for preparation and analysis.

A contingency laboratory has been selected, in case SAI is incapable of analyzing the samples, or if there is some question concerning the sample results. Severn Trent Laboratories (Colchester, Vermont) was selected as the contingency laboratory based on successful analysis of predemonstration samples.

4.3 Laboratory Audit

ORNL's technical expert and statistician conducted an audit of laboratory operations on May 4, 1999. This evaluation focused specifically on the procedures that will be used for the analysis of the demonstration samples. Results from this audit indicated that SAI was proficient in several areas, including quality management, document/record control, sample control, and information management. SAI was found to be compliant with Method 8330 analytical procedure implementation. SAI provided a copy of its QA plan, which details all of the QA/QC procedures for all laboratory operations [2]. Additionally, the audit team noted that SAI had excellent procedures in place for data back-up, retrievability, and long-term storage. The audit report was reviewed and approved by ORNL's Quality Assurance Specialist.

4.4 Validation and Evaluation of Reference Laboratory Data

The demonstration samples will be sent to the reference laboratory at the start of the demonstration activities (August 23). The full data package of results for a given analytical batch of 40 samples will be due to ORNL in 21 working days (per SAI project/quote # 120998A199) after the start of analysis.

4.4.1 Data Validation

ORNL will be responsible for validating the reference laboratory data. Validation determines the quality of the results relative to the end use of the data. (Note that the developer is responsible for validating its own data prior to final submission.) Several aspects of the data (listed below) will be reviewed. The findings of the review will be documented in the validation records. As appropriate, the ETVR will describe instances of failure to meet quality objectives and the potential impact on data quality.

4.4.1.1 Completeness of Laboratory Records

This qualitative review ensures that all of the samples that were sent to the laboratory were analyzed, and that all of the applicable records and relevant results are included in the data package.

4.4.1.2 Holding Times

For soil, the method requirement is that the samples be extracted within 14 days of receipt and analyzed within 40 days of extraction. For water, the analysis requirement is the same, but the samples must be prepared within 7 days of receipt. ORNL has requested that SAI analyze the water samples as soon after receipt as possible.

4.4.1.3 Correctness of Data

So as not to bias the assessment of the technology's performance, errors in the reference laboratory data will be corrected as necessary. Corrections may be made to data that has transcription errors, calculation errors, and interpretation errors. These changes will be made conservatively, and will be based on the guidelines provided in the method used. The changes will be justified and documented in the validation records.

4.4.1.4 Correlation Between Replicates

Normally, one would not know if a single sample result was "suspect" unless (a) the sample was a spiked sample, where the concentration is known or (b) a result was reported and flagged by the reference laboratory as suspect for some obvious reason (e.g., no quantitative result was determined). The experimental design implemented in this verification study will provide an additional indication of the abnormality of data through the inspection of the replicate results from homogenous sample sets. Criteria may be established to determine if data is suspect. For example, data sets could be considered suspect if the percent relative standard deviation for replicate samples was greater than 50%, because this criteria would indicate imprecision. These data would be flagged so as not to bias the assessment of the technology's performance. Precision and accuracy evaluations may be made with and without these suspect values to represent the best and worst case scenarios. If both the reference laboratory and the developer(s) report erratic results, the data may be discarded if it is suspected that the erratic results are due to a sampling error.

4.4.1.5 Evaluation of QC Results

QC samples will be analyzed by the reference laboratory with every batch of samples to indicate whether or not the samples were analyzed properly. Acceptable QC results are specified in the reference laboratory's procedure and in Section 8.4 of this demonstration plan. The QC samples will include, but are not limited to: initial calibration, continuing calibration verification, laboratory control samples, matrix spike and matrix spike duplicates, surrogate recoveries, and blank results. See Section 8.4 of the Quality Assurance Project Plan for a more detailed description of the QC results evaluation.

4.4.1.6 Evaluation of Spiked Sample Data

Spiked samples are homogenous samples containing known concentrations of analyte(s). The performance of the reference laboratory will be evaluated relative to the spiked samples. Results for these samples represent the best estimate of accuracy and precision for verification testing.

4.4.2 Data Analysis

Where possible, the reference laboratory data will be analyzed identically to the technologies that perform quantitative analyses (see Section 7.7 for specific calculations). For example, precision and accuracy will be evaluated.

5.0 DEMONSTRATION SITE AND SAMPLE DESCRIPTIONS

This section discusses the demonstration site, and the history and characteristics of the sites where the explosives-contaminated soil and water samples were collected. This information was gathered from the Internet [3, 4] and published reports [5].

5.1 Demonstration Testing Location and Conditions

The demonstration of explosives field analytical technologies will be conducted at the Oak Ridge National Laboratory, Freels Bend Cabin site, in Oak Ridge, Tennessee. A map of the site is presented in Figures 5-1a and 5-1b. The samples used in this study will be brought to the demonstration testing location for evaluation by the vendors. Explosives-contaminated soils from several Army Ammunition Plants (AAP) in Iowa, Louisiana, and Tennessee will be used in this demonstration. Soils from a former Army base in California (Fort Ord) will also be evaluated. Additionally, explosives-contaminated water samples from Oregon, Louisiana, and Tennessee will be evaluated.

To test the capabilities of the technologies under actual field conditions, the demonstration activities will occur outdoors. While studies are being conducted, the temperature and relative humidity will be monitored regularly by ORNL so that the working conditions will be documented. Generally, the average August temperature for eastern Tennessee is 77EF.

5.2 Soil Sample Descriptions

Multiple soil types, collected from sites in California, Louisiana, Iowa, and Tennessee, will be used in this study. The primary constituents in the samples are expected to be 1,3,5-trinitrotoluene (TNT), isomeric dinitrotoluene (DNT) including both 2,4-dinitrotoluene and 2,6-dinitrotoluene, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2-amino-4,6-dinitrotoluene (2-Am-DNT), and 4-amino-2,6-dinitrotoluene (4-Am-DNT), with concentrations ranging from 0 to approximately 90,000 mg/kg.

5.2.1 Iowa Army Ammunition Plant

Currently still an active site, the Iowa Army Ammunition Plant was constructed to load, assemble, and pack various conventional ammunition and fusing systems. Current production includes 120 mm tank rounds, warheads for missiles, and mine systems. Disposal of industrial wastes containing explosives through the early years primarily consisted of disposing the wastes into surface impoundments, landfills, and sumps on the installation. These operations caused contamination of both the soil and groundwater. The major contaminants in these samples will be TNT, RDX, and HMX.

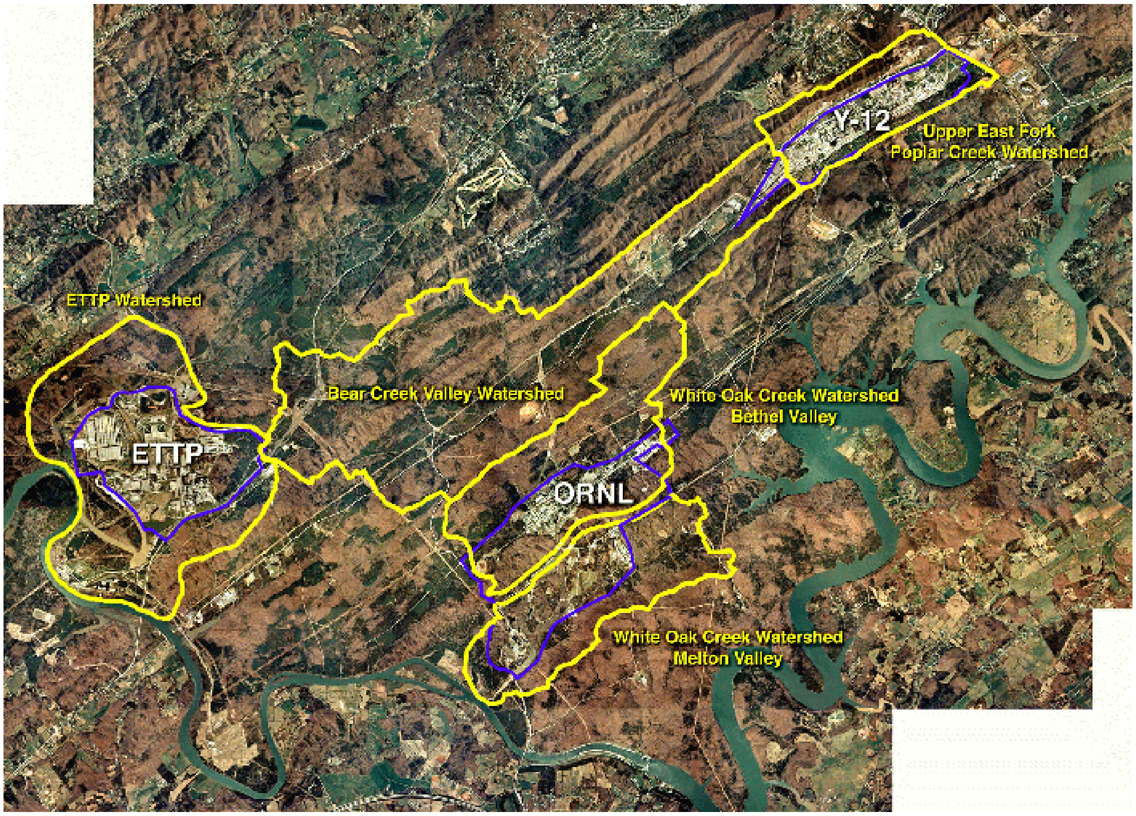

Figure 5-1a. Overview of Oak Ridge Reservation. Freels Bend area is in right center of photo.

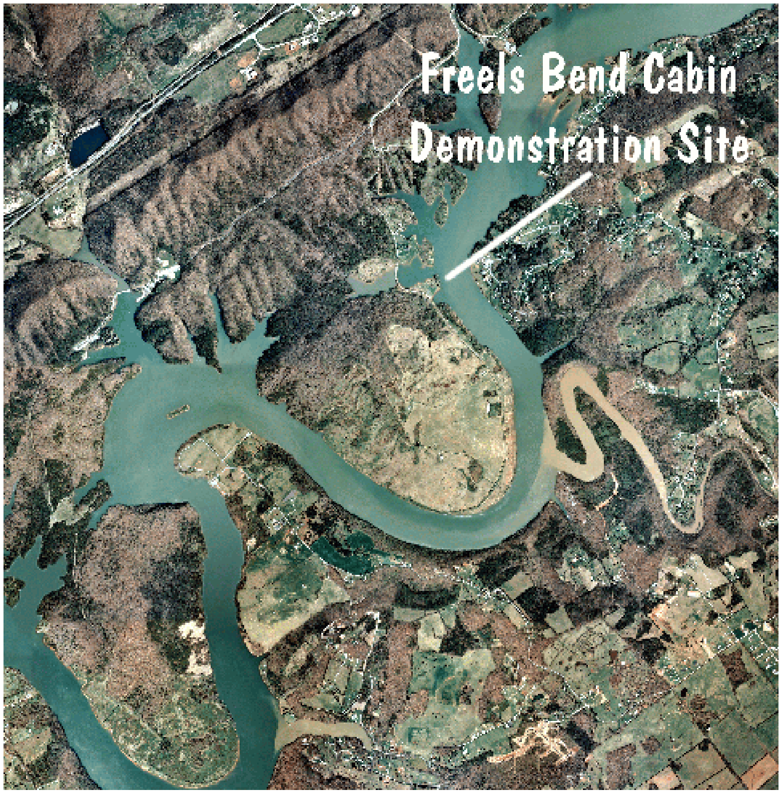

Figure 5-1b. Close up of Freels Bend area.

5.2.2 Louisiana Army Ammunition Plant

Louisiana Army Ammunition Plant (LAAAP), near Shreveport, Louisiana, is a government-owned facility where production began in 1942. The facility is currently an Army Reserve Plant. Production items at LAAAP have included artillery shell metal parts, and load, assemble, and pack of artillery shells, mines, rockets, mortar rounds, and demolition blocks. As a result of these activities and the resulting soil and groundwater contamination, the EPA placed LAAAP on the National Priorities List in 1989. The major constituents in the samples are expected to be TNT, RDX, and HMX, with trace levels of 1,3,5-trinitrobenzene (TNB), DNT, 2-Am-DNT, and 4-Am-DNT.

5.2.3 Milan Army Ammunition Plant

Currently still active, Milan Army Ammunition Plant (MLAAP) in Milan, Tennessee was established in late 1940 as part of the pre-World War II buildup. The facility still has ten ammunition load, assemble, and package lines. Munitions-related wastes have resulted in soil contamination. Primary contaminants in the soils are expected to be RDX and TNT.

5.2.4 Volunteer Army Ammunition Plant

Volunteer Army Ammunition Plant, in Chattanooga, Tennessee, was built beginning in 1941 to manufacture TNT and DNT. All production ceased in 1977. Past production practices resulted in significant soil and groundwater contamination. Concentrations of TNT and DNT are expected to range from 10 to 90,000 mg/kg in the samples from this site, with significantly less contributions from the Am-DNT isomers.

5.2.5 Fort Ord Military Base

Fort Ord, located near Marina, California, is a military base that was closed as a military installation in 1993. Currently, the California State University at Monterey Bay opened its doors on former Fort Ord property, the University of California at Santa Cruz has based a new research center there, and the Monterey Institute of International Studies will take over the officer's club and several other buildings. The post's airfield was turned over to the city of Marina. The Army still occupies several buildings. Since its opening in 1917, Fort Ord primarily served as a training and staging facility for infantry troops. A study conducted in 1994 by the Army revealed that the impact areas at the inland firing ranges of Fort Ord were contaminated with residues of high explosives [5]. Fort Ord is on the National Priorities List of contaminated sites (Superfund) that requires the installation to be characterized and remediated to a condition that does not pose unacceptable risks to public health or the environment. The contaminant present at the highest concentration (as much as 300 mg/kg) is expected to be HMX, with much lower concentrations of RDX, TNT, 2-Am-DNT, and 4-Am-DNT.

5.3 Water Sample Descriptions

Explosives-contaminated water samples from Tennessee, Oregon, and Louisiana will be evaluated. Primary contaminants are expected to be RDX, TNT, and DNT. Water samples will range in concentration from 0 to 25,000 µg/L.

5.3.1 Louisiana Army Ammunition Plant

See Section 5.2.2 for site description. Major contaminants in the water samples are expected to be RDX, TNT, TNB, and HMX.

5.3.2 Milan Army Ammunition Plant

See Section 5.2.3. MLAAP has two sewage treatment plants. In the past, wastewater from various production activities was discharged to open ditches that drained from sumps or surface impoundments into both intermittent and perennial steams and rivers. Currently, MLAAP treats all process water from the lines that generate explosives-contaminated wastewater. The EPA placed MLAAP on the National Priorities List in 1987. These water samples are expected to contain RDX, as well as TNT and DNT.

5.3.3 Umatilla Chemical Depot

Umatilla Chemical Depot is located in northeastern Oregon. The mission of the facility recently changed to static storage of chemical warfare ammunition. Once the chemicals are destroyed, the installation is scheduled to close. Several environmental sites have been identified for cleanup prior to base closure. One site has explosives-contaminated groundwater; the cleanup identified for this site is to pump and treat the water with granulated activated carbon. The major contaminants in these samples are expected to be TNT, RDX, HMX, and TNB. According to a remedial investigation conducted at the site, these groundwater samples will not be contaminated with any chemical warfare agents.

5.3.4 Volunteer Army Ammunition Plant

See Section 5.2.4. The major contaminants in the groundwater samples are expected to be TNT, 2,4-DNT, and 2,6-DNT, with lower levels of TNB and 1,3-dinitrobenzene.

5.4 Sample Preparation

5.4.1 Sample Collection Procedures

All of the soil samples will be shipped at ambient temperature to ORNL for use in the demonstration. This effort will be coordinated by CRREL. The soil samples will be from the various sites described in Section 5.2. The soil samples will be shipped in double-bagged plastic Ziplock™ bags and stored frozen (< 0 EC) prior to splitting.

The water samples will be shipped to ORNL for use in the demonstration. Again, these efforts will be coordinated by CRREL. The water samples will be collected approximately 7 days prior to the demonstration start date (August 23) and shipped immediately to ORNL. The samples will be collected in 2.5-gallon carboy containers and stored under refrigeration (~4 EC).

5.4.2 Sample Preparation for Demonstration

5.4.2.1 Soil Samples

In order to ensure that the developers and the reference laboratory analyze comparable samples, the soils will be homogenized prior to sample splitting. The process is as follows. The sample will be kneaded in the Ziplock™ bag to break up large clumps. Approximately 1500 g of soil will be poured into a Pyrex™ pan. Debris will be removed. The sample will be air-dried overnight (or longer, as necessary). The sample will be sieved using a 9 mesh (2 mm particle size) screen and placed in a 1-L wide-mouth jar. After thorough mixing with a metal spatula, the sample will be quartered. After mixing each quarter, approximately 250 g from each quarter will be placed in the 1-L wide-mouth jar, for a total sample amount of approximately 1000 g.

After analysis by an in-house method (modified Method 8330) to confirm homogeneity, the sample will be split into jars for distribution. Each 4-oz sample jar will contain approximately 20 g of soil. The sample will be remixed after every five 20-g subsamples have been removed. Four replicate splits of each soil sample will be prepared for each participant. The samples will be randomized in two stages. First, the order in which the filled jars will be distributed will be randomized so that the same developer does not always receive the first jar filled for a given sample set. Second, the order of analysis will be randomized so that each developer analyzes the same set of samples, but in a different order.

5.4.2.2 Water Samples

To prepare the water sample, the 2.5-gallon carboy will be gently shaken to stir the contents. A spout will be attached to the carboy. The water sample will be split by filling 250-mL amber glass bottles. Due to holding time issues, sample splitting will be performed at the last possible moment. The water samples will be sent immediately to the reference laboratory for analysis and will also be analyzed in-house.

5.4.3 Sample Labeling

Each jar will be labeled with a sample number. Replicate samples will be assigned unique (but not sequential) sample numbers. Spike materials and blanks will be labeled in the same manner, such that these QC samples are indistinguishable from other samples. The order of analysis will be randomized and set for each developer. A separate label will be used to identify the developer analysis order.

5.4.4 Sample Storage

To ensure that degradation will not occur, the soil samples will be frozen (< 0 EC)prior to analysis. The water samples will be kept refrigerated (~4 EC). Additionally, the samples will be shipped to the reference laboratory under these conditions. These precautions will be taken per the guidance outlined in, “Stability of Explosives in Environmental Water and Soil Samples [6].”

6.0 PREDEMONSTRATION STUDY

A predemonstration study is required by this demonstration program to allow the technology developers to refine their technologies and revise their operating instructions, if necessary. This analysis also allows an evaluation of matrix effects or interferences that may affect performance. A failure to meet the performance goals at this point could indicate a lack of maturity of the technology and the demonstration would be canceled for that developer.

This requirement has the following objectives:

- To allow the developers to analyze samples that will be included in the demonstration and, if necessary, refine and calibrate their technologies and revise their operating instructions;
- To allow an evaluation of any unanticipated matrix effects or interferences that may occur during the demonstration

For the predemonstration study, the developers analyzed six explosives-contaminated soils (including one spiked sample) from LAAAP (see site information in Section 5.2.2) and/or six explosives-contaminated water samples (including two spiked samples) from Volunteer (see site information in Section 5.3.4). The spiked soil sample was obtained from Environmental Resource Associates (ERA, Arvada, CO). The soil was prepared using ERA's semivolatile blank soil matrix. This matrix was a top soil that had been dried, sieved, and homogenized. Particle size was approximately 60 mesh. The soil was approximately 40% clay. Some of the groundwater samples were fortified with RDX and TNT to represent the type of sample that may be obtained from other AAPs, such as a load, assemble, and pack facility. The spiked water samples were prepared by CRREL.

6.1 Predemonstration Sample Distribution

The predemonstration samples were sent to the developers and the reference laboratory on June 9, 1999. The developer results for the predemonstration sample analyses were provided to ORNL two weeks after the receipt of the samples.

6.2 Predemonstration Results

The developers’ predemonstration results were compared to the reference laboratory results. Additionally, the results were compared to performance acceptance ranges generated from analytical verification data. The acceptance ranges were guidelines established by ORNL’s statistician to gauge acceptable analytical results. The results indicated the technologies described in this demonstration plan are mature and ready for field testing.

7.0 EXPERIMENTAL DESIGN

This section discusses the objectives of the demonstration, factors that must be considered to meet the performance objectives, and the information that ORNL, ESTCP, and EPA will use to evaluate the results of the demonstration.

7.1 Objectives

The primary objectives of this demonstration are to evaluate the explosives field analytical technologies in the following areas: (1) comparability relative to Method 8330, (2) variability of replicate samples, (3) the effect of different soil and/or water matrices, (4) accuracy for spiked samples, and (5) the logistical and economic resources necessary to operate the technology. Secondary objectives for this demonstration are to evaluate the technologies in terms of portability, cost, sample throughput, and ease of operation. Where possible, the performance will be compared to the performance of the conventional analytical method that would be used in similar site characterization activities. The verification process will also evaluate the performance of the technology against the performance goals as stated in Section 3.3.

7.2 Experimental Performance Measures

This section discusses performance measures that will be considered in the design and implementation of the demonstration. These performance measures include accuracy, precision, portability, ease of operation, health and safety issues, sample throughput, and sample matrix effects.

7.2.1 Qualitative Performance measures

Some performance measures, while important, are difficult or impossible to quantify. These are considered qualitative performance measures: ease of operation, operator training requirements, portability, and special requirements.

7.2.2 Quantitative Performance measures

Many performance measures in this demonstration can be quantified by various means, including the following: accuracy, precision, detection limits, number of false positive (fp) results, number of false negative (fn) results, waste generation, sample throughput, and operating costs. These quantitative performance measures will be used to assess the technology performance by comparison to reference laboratory data, where possible.

7.3 Summary of Demonstration Design

The demonstration will be held at ORNL's Freels Bend Cabin site from August 23 through September 5, 1999. The samples to be evaluated during the demonstration consist of (1) naturally-contaminated samples from DoD sites, (2) spiked samples, and (3) blank samples. The demonstration samples will be homogenized and split such that the developer and the reference laboratory will be supplied with comparable samples. Some features of the approach are presented in Table 7-1. The developer will analyze a total of 108 soil samples and/or 176 water samples. Note that Barringer will analyze both soil and water samples, and RI/NRL will analyze only water samples.

The concentrations of the samples will range from 0 to 90,000 mg/kg for soil, and 0 to 25,000 µg/L for water. This large dynamic range is necessary to thoroughly evaluate the capability of the technology. Additionally, a significant issue when evaluating field technologies for explosives is whether the technology is capable of indicating if the concentrations are above levels that will sustain a detonation. This level has been established for soil by the U.S. Army Environmental Center to be 10% by weight (100,000 mg/kg) [7]. Equally as important is evaluating if the technology can accurately determine if a sample meets a specified cleanup level, such as 0.5 mg/kg for RDX [6], or if it exceeds the EPA's health advisory limit of 2 µg/L for TNT [8].

In order to provide site characterization information that would normally be supplied during site remediation activities, the developer will be provided with a list which designates which samples came from which sites (Sections 5.2 and 5.3). This will allow the developer to consider possible interferents or cross-reactive compounds, and which samples are suspected to contain extremely high levels of a particular contaminant.

Table 7-1. Experimental Design Features

Properties: 23 unique samples for soil and 41 unique samples for water; acquire more data on fewer samples; statistically rich approach

Replicates: equal number (quadruplicate) for all sample types and concentration levels

Accuracy: equal number of comparisons with certified and spike concentrations for the PE soils and extract samples, respectively, at all concentration levels

Precision: estimated for all sample types and concentration levels

Data Analysis: simplified statistics due to consistency with number of replicates

7.4 Field Data

The technology will be operated by the developer, who will provide the results to ORNL. The developer will be responsible for reducing the raw data into a presentation format consistent with the evaluation requirements. ORNL will provide a sample results form to the developers. Before leaving the demonstration site, the developers will submit all final results and raw data to ORNL.

7.5 Demonstration Schedule

Demonstration activities will occur from August 23 through September 5, 1999**.** Visitors will be scheduled to talk with the vendors and view technology demonstrations as necessary.

7.6 Field Operations

This demonstration requires close communication between the developer, ORNL, and EPA. Preliminary site training (on August 23) will be required before initiation of the field study. Successful field operations require detailed planning and extensive communication. The implementation of the demonstration must be consistent with the requirements of the study and routine operation of the technology.

7.6.1 Communication and Documentation

ORNL will communicate regularly with the demonstration participants to coordinate all field activities associated with this demonstration and to resolve any logistical, technical, or QA issues that may arise as the demonstration progresses. The successful implementation of the demonstration will require detailed coordination and constant communication between all demonstration participants. All developer/ORNL field activities will be thoroughly documented. Field documentation will include field logbooks, photographs, field data sheets, and chain-of-custody forms.

The ORNL technical lead will be responsible for maintaining all field documentation. Field notes will be kept in a bound logbook. Each page will be sequentially numbered. Completed pages will be signed and dated by the individual responsible for the entries. Errors will have one line drawn through them, and this line will be initialed and dated. Any deviations from the approved final demonstration plan will be thoroughly documented in the field logbook and provided to ORNL**.** Photographs will be taken with a digital camera.

The developers will obtain all equipment needed for field work associated with this demonstration. Prior to the demonstration, the developers will work with ORNL to secure any equipment requirements (such as tables, chairs, etc.) that the developers will need for the demonstration.

7.6.2 Sample Distribution

ORNL will be responsible for sample distribution. Soil samples will be packaged in 4 ounce (120 mL) jars. Water samples will be packaged in 250-mL amber bottles. All samples will be prepared for distribution at the start of the demonstration. The developers will go to a sample distribution table to pick-up the samples. The samples will be distributed in batches of 12. Completion of chains-of-custody will document sample transfer.

7.6.3 Archive Samples

Archive samples which are replicates of the developer samples will be retained by ORNL. An archive sample will be used during the demonstration if the integrity of a developer's sample has been compromised. Additional unhomogenized material and unused archive samples will also be retained at ORNL at the completion of the demonstration, in case any questions arise where reanalysis is necessary.

7.7 Evaluation of Performance Factors

This section describes the performance factors that will be evaluated from the data generated during the demonstration. It also discusses the characteristics of the technologies which will be reported in the ETVR and verification statement.

Technology performance will be evaluated in terms of precision, accuracy, representativeness, completeness, and comparability (PARCC) parameters [9], which are indicators of data quality. Additionally, false positive and negative results, sample throughput, and ease of use will also be evaluated. Results will be evaluated from the analysis of naturally-contaminated, spiked, and blank samples.

During any experiment, unusual measurements may occur either as random events or from determinable causes. It is important that the developer note and record any problems with each measurement. Identification of unusual measurements does not mean that they will be automatically set aside. The statistical analysis can be performed with or without the suspected measurements to see if there are any changes in the conclusions of the demonstration experiment.

7.7.1 Precision

Precision is the reproducibility of measurements under a given set of conditions. For those technologies which report quantitative (i.e., continuous) data, standard deviation (SD) and relative standard deviation (RSD) for replicate results will be used to assess precision. The following equation will be used:

$$RSD = \frac{standard\ deviation}{average\ concentration} \times 100\% \qquad (7\text{-}1)$$

The overall RSD will be characterized by three summary values:

- mean—i.e., average;
- median—i.e., 50th percentile value, at which 50% of all individual RSD values are below and 50% are above; and
- 95th percentile—i.e., the value at which 95% of all individual RSD values are below and 5% are above.

The mean RSD of the developer's technology will be compared with the mean RSD of the reference laboratory.

For those technologies which report interval data, precision will be quantified by the frequency with which the same interval is reported for sample replicates. Reporting a higher number of replicates in the same interval will indicate higher precision. The highest possible precision is reporting all four replicate results as the same interval.

7.7.2 *Accuracy*

Accuracy represents the closeness of the technology’s measured concentrations to known values. For those technologies which report quantitative data, accuracy will be assessed in terms of percent recovery, which is

$$\text{percent recovery} = \frac{\text{measured concentration}}{\text{known concentration}} \times 100\% \qquad (7\text{-}2)$$

As with precision, the overall percent recovery will be characterized by three summary values: mean, median, and 95th percentile. The mean percent recovery of the developer's technology will be compared with the mean percent recovery of the reference laboratory.

For those technologies which produce interval results, accuracy will be evaluated in terms of the percentage of samples which agree with, are above (i.e., biased high), and are below the known value (i.e., biased low). For example, if a technology reports a result as 10 to 50 mg/kg, and the known amount is 40 mg/kg, the results would agree because 40 mg/kg falls into the interval from 10 to 50 mg/kg. If the known amount is 100 mg/kg and the technology reported 10 to 50 mg/kg, the technology would be biased low. If the known amount was 5 mg/kg and the technology reported 10 to 50 mg/kg, the technology would be biased high.

7.7.3 *Representativeness*

Representativeness expresses the degree to which the sample data accurately and precisely represent the capability of the technology. Representative samples, in general, are samples that contain a reasonable cross-section of the “population” over which they are to be used to make inferences. The population for demonstrations analyzed as part of this project includes a variety of media and contaminants that the innovative technologies are developed to accommodate. The performance data will be accepted as representative of the technology if the technology is capable of analyzing diverse samples types (i.e., performance is not affected based on the matrix).

7.7.4 *Completeness*

Completeness is defined as the percentage of measurements that are judged to be useable (i.e., the result is not rejected). The optimum completeness is 95% or greater.

7.7.5 *Comparability*

Comparability refers to the confidence with which one data set can be compared to another. A one-to-one sample comparison of the technology results and the reference laboratory results will be performed for all samples. For the quantitative technologies, coefficients of determination (R^2) [10] will computed for the plot of the field technology’s concentrations versus the reference laboratory concentrations. Perfect correlation between the reference laboratory and field technology will be indicated by an R^2 value of 1.0.

Additional examinations of the data using multiple comparison tests will indicate the similarities and differences between the field technology and the reference laboratory measurements. Statistical tests (such as Analysis of Variance (ANOVA) [11, 12] and the Wilcoxon signed rank test [13]) may be performed to assess if there is a significant difference between the technology and the reference laboratory results. Nonparametric statistical methods will be used if the approximating data distributional assumptions are not supported. The nonparametric Wilcoxon signed rank test is particularly useful because of the pairing of developer’s and reference laboratory's samples. The Wilcoxon test is designed to test whether the developer’s and reference laboratory's measurements have the same median.

Additionally, a direct comparison between the field technologies and reference laboratory data will be performed by evaluating the percent difference (%D) between the measured concentrations, defined as

$$\% D = \frac{[Field\ Technology] - [Ref\ Lab]}{[Ref\ Lab]}\ x\ 100\% \qquad (7\text{-}3)$$

The range of %D values will be summarized and reported.

The ANOVA and Wilcoxon statistical tests are useful for analyzing continuous (i.e., quantitative) measurements, but several of the technologies will give interval or qualitative measurements. Similar to accuracy, the technologies which report interval results will be evaluated in terms of the percentage of samples which agree with, are above (i.e., biased high), and are below (i.e., biased low) relative to the results generated by the reference laboratory.

7.7.6 False Positive/Negative Results

A false positive (fp) result [14] is one in which the technology detects explosives in the sample when there actually are none. A false negative (fn) result [14] is one in which the technology indicates that there are no explosives present in the sample, when there actually are. Both fp and fn results are influenced by the method detection limit of the technology. False positive and false negative results will be assessed using all of the samples, based on the reference laboratory results, and will be reported as a percentage. Those technologies reporting interval data will be given the benefit of the doubt when reporting the lowest reporting interval. For example, if the reference laboratory indicates that no explosives were detected in a sample, and the technology reports the result as 0 to 1 mg/kg, the technology's result will be considered correct, and not a false positive result. Similarly, if the reference laboratory reports a result as 0.9 mg/kg, and the technology's paired result is 0 to 1 mg/kg, the technology's result will be considered correct, and not a false negative result.

7.7.7 Detection Limits

Detection limits (DLs) are often defined as the minimum concentration of a substance that can be measured and reported. DLs are determined from repeated analyses of a sample in a given matrix containing the analyte. The DL for quantitative technologies will be calculated, most likely from the results for spiked samples, using regression methods to calculate DL [15]. Where possible, the DL calculated from the demonstration analyses will be compared to that which is reported in the developer's literature.

7.7.8 Sample Throughput

Sample throughput is a measure of the number of samples that can be processed and reported by a technology in an hour. ORNL will record the total number of hours required to analyze the total sample suite and report an estimated sample throughput rate. In addition, each sample will be logged in and out using chain-of-custody documentation. A sample will be considered completed when the final result is submitted to ORNL. This data will be considered when calculating the sample throughput rate. Sample throughput will be affected by the number of analysts operating the technology and the skill of those operators.

7.7.9 Ease of Use

A significant factor in purchasing an instrument or a test kit is how easy the technology is to use. Several factors will be considered when assessing this parameter:

- What is the operator skill level (e.g., technician, BS, MS, or Ph.D.)?
- How many operators were used during the demonstration? Could the technology be run by a single person?
- How much training would be required in order to run this technology?
- Is the technology portable and easy to set-up?

7.7.10 Miscellaneous Factors

Any information that might be useful to a person who is considering purchasing the technology will be documented in the ETVR. ORNL will be looking for this type of information during field activities. Examples of information that might be useful to a prospective purchaser are: the amount of hazardous waste generated during the analyses, the ruggedness of the technology, the amount of electrical or battery power necessary to operate the technology, and aspects of the technology or method which makes it easy to use (for example, “Reagent handling was minimized by the use of premeasured, breakable glass ampules.”).

An important factor in the consideration of whether to purchase a technology is cost. ORNL will estimate the cost involved with operating the technology and the standard reference analyses. To account for the variability in cost data and assumptions, the economic analysis will be presented as a list of cost elements and a range of costs for sample analysis. Several factors affect the cost of analysis. Where possible, these factors will be addressed so that decision-makers can independently complete a site-specific economic analysis to suit their needs.

8.0 QUALITY ASSURANCE PROJECT PLAN (QAPP)

The QAPP for this demonstration specifies procedures that will be used to ensure data quality and integrity. Careful adherence to these procedures will ensure that data generated from the demonstration will meet the desired performance objectives and will provide sound analytical results. EPA considers the demonstration to be classified as a Category II project. This section of the demonstration plan addresses the key elements that are required for Category II projects prepared according to guidelines in EPA guidance documents [16, 17].

8.1 Quality Assurance Responsibilities

Each developer is responsible for adhering to this QAPP and ensuring the quality of data submitted to ORNL for evaluation. ORNL will be responsible for evaluating the reference laboratory's performance on the various QA/QC factors outlined in this QAPP.

8.2 Data Validation

The developer is responsible for supplying final results that have been validated. ORNL is responsible for validating the reference laboratory's results (see Section 4.4).

8.3 Data Quality Indicators

The data obtained during the demonstration must be of sufficient quality for conclusions to be drawn on the explosives field analytical technology. For all measurement and monitoring activities conducted for EPA, the Agency requires that data quality parameters be established based on the proposed end uses of the data. Data quality parameters include five indicators of data quality: representativeness, completeness, comparability, accuracy, and precision. These are discussed in detail in Section 7.7.

8.4 Calibration Procedures and Quality Control Checks

This section describes the calibration procedures and method-specific QC requirements that apply to the reference analyses. Some may also apply to the field technology. It also contains a discussion of the corrective action to be taken if the QC parameters fall outside of the evaluation criteria. Note that a batch includes no more than 20 samples. SAI’s analytical procedures and QC acceptance criteria are described in Appendix A of this document and in their QA plan [2].

8.4.1 Initial Calibration Procedures

The reference laboratory's initial calibration procedure includes analysis of five standards at 100, 250, 500, 1000, and 2000 µg/L. A successful calibration using response factors must have RSD less than 20% or a linear fit greater than 0.99. The initial calibration must also be verified with a mid-point standard prepared from a different source or lot of stock standard. The RSD must be less than 15% or the instrument must be recalibrated.

8.4.2 Continuing Calibration Procedures

The initial calibration is verified daily with a mid-level standard. It must be within 15% of the initial calibration or the initial calibration procedure must be repeated. Additionally, mid-level check standards must be run with every 10 samples and at the end of a batch. The same acceptance criteria applies.

8.4.3 Method Blanks

A method blank is an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing, and is carried through the complete sample preparation and analytical procedures. One method blank will be included with each batch. To be acceptable, no analytes must be detected above the practical quantitation limits (0.5 µg/L for water and 0.5 mg/kg for soil).

8.4.4 Matrix Spike Samples

Matrix spikes are prepared by fortifying a sample chosen from the sample batch with known amounts of the method analytes (5 µg/L for water and 5 mg/kg for soil). The sample is analyzed with and without spiking. The percent relative difference between the known concentration (spike + original sample concentration) and the analyzed value is termed the percent recovery. SAI will prepare and analyze a matrix spike and a matrix spike duplicate (MS/MSD) with every batch. The relative percent difference (RPD) between the MS and MSD results will be evaluated. The equation for determining RPD is:

$$RPD = \frac{|MS - MSD|}{1/2 \times (MS + MSD)} \; x \; 100\% \qquad (8\text{-}1)$$

SAI's acceptance criteria for MS/MSD accuracy and precision, which are documented in their QA plan [2], are presented in Table 8-1. If the acceptance criteria for the MS/MSD are not met, the acceptance of the analytical batch is determined by the validity of the Laboratory Control Sample (Section 8.4.5). A MS analyte may not be reported in the QC report if the level of contamination in the sample is exceedingly high.

8.4.5 Laboratory Control Samples

Laboratory control samples (LCS) are samples of known composition that are analyzed periodically to assure that the analytical system is in control. One LCS will be analyzed per batch. The concentration level for the LCS will be 5 µg/L in water and 5 mg/kg in soil. SAI's acceptance criteria will be 60 -140% recovery for both soil and water. The LCS criteria must be met in order for the batch results to be acceptable.

8.4.6 Surrogate Recovery

Compounds having similar chemical characteristics to those being analyzed but which are not generally found in environmental samples are used as surrogate compounds. SAI will use 3,4-dinitrotoluene as the surrogate compound for these analyses. Known concentrations of this compound will be added to all samples in the batch prior to sample preparation. The performance acceptance ranges for surrogate recovery will be 65-153% for soil and 35-125% for water. If the surrogate is out of limits, the individual sample must be repeated.

8.4.7 Spiked Samples

Soil and water samples will be spiked with known concentrations of explosives and included in the suite of samples for evaluation. These will be blind to the developer and the reference laboratory. The matrix will be interference-free, so that accuracy can be assessed on relatively “clean” samples. The samples will be obtained from Environmental Resource Associates or prepared by ORNL.

8.4.8 Replicate Samples

As part of the experimental design, all of the samples (naturally-contaminated, spike, and blank) will be analyzed in quadruplicate (i.e., four separate subsamples), so that precision can be determined for every sample type.

8.5 Data Reduction, Review, and Reporting

To maintain good data quality, specific procedures will be followed during data reduction, review, and reporting. These procedures are detailed below.

8.5.1 Data Reduction

Data reduction refers to the process of converting the raw results from the technology into a concentration or other data format which will be used in the comparison. The reference laboratory and the developer will be responsible for reducing the data to final results. The procedures to be used will be technology dependent. The following is required for data reduction:

8.5.1.1 Quantitative (Continuous) Data

For quantitative technologies (including the reference laboratory), the reported concentrations will be in mg/kg for soil samples and µg/L for water samples.

8.5.1.2 Semi-quantitative (Interval) Data

For technologies reporting interval data, the data will be reported using a “[” and “)” notation. The brackets indicate that the end-points are included, while the parentheses indicate that the end-points of the concentration range are excluded. Additionally, the range of intervals used will be inclusive for all possible results. Each developer will provide a list of all possible interval reporting ranges to ORNL at the start of the demonstration activities. Table 8-2 is an example of how the intervals would be reported.

8.5.1.3 Nondetect Concentrations for Quantitative Data

If no explosives are detected in a sample, the concentration should be reported as less than the reporting limit. For example, the reference laboratory should report a blank soil as “< 0.5 mg/kg” for each analyte.

8.5.2 Data Review

The developer will verify the completeness and correctness of data acquisition and reduction. The ORNL technical lead may review calculations and inspect laboratory logbooks and data sheets to verify accuracy, completeness, and adherence to the specific analytical method protocols. Calibration and QC data may also be examined by ORNL. The developer will verify that all instrument systems are in control and that QA objectives for accuracy, completeness, and method detection limits have been met.

The reference laboratory will be responsible for providing a complete data package to ORNL per their QA procedures [2]. In addition, ORNL will validate the reference laboratory data as described in Section 4.4.

8.5.3 Data Reporting

This section contains a list of the data to be reported by both the technology and the reference method. At a minimum, the data tabulation will list the results for each sample and include reporting units, sample numbers, results, and data qualifiers. (A sample results form will be provided for completion by the developers.) Where applicable, all QC information such as calibrations, blanks and reference samples will also be included with the raw analytical data. All data should be reported in hardcopy.

Developer results will be due to ORNL at the conclusion of the field activities. For sample throughput

Table 8-1. Specialized Assays Inc. Acceptance Criteria for MS/MSD

Analyte	Matrix Precision (percent RPD)		Matrix Accuracy (percent recovery)	
	soil	water	soil	water
HMX	30	29	55-147	40-128
RDX	27	9	66-142	49-112
1,3,5-trinitrobenzene	31	16	55-149	42-127
1,3-dinitrobenzene	23	6	67-140	29-120
Tetryl	48	32	24-146	47-129
Nitrobenzene	30	21	64-145	12-117
2,4,6-Trinitrotoluene	41	27	51-129	34-121
4-Amino-2,6-dinitrotoluene	23	15	43-156	51-105
2-Amino-4,6-dinitrotoluene	28	13	60-142	60-122
2,6-Dinitrotoluene	29	12	62-147	59-117
2,4-Dinitrotoluene	30	13	60-143	24-110
2-Nitrotoluene	25	26	63-138	39-109
4-Nitrotoluene	24	41	68-132	38-107
3-Nitrotoluene	26	46	58-143	35-111

Table 8-2. Example of reporting intervals

Interval	Soil concentration range for TNT
[0, 1)	0# TNT mg/kg < 1
[1, 10)	1# TNT mg/kg < 10
[10, 50)	10 #TNT mg/kg < 50
[50, 4)	TNT mg/kg $ 50

calculations, a sample will not be considered completed until the final result is submitted to ORNL. The developer's final report will be due to ORNL one week after the conclusion of the demonstration. Any discrepancies between the originally reported result and the final result must be described.

For the reference laboratory, the full data package of results for a given analytical batch of 40 samples will be due to ORNL in 21 working days (per SAI project/quote # 120998A199) after the start of analysis.

8.6 Audits

The following audits will be performed during this demonstration. These audits will determine if this demonstration plan is being implemented as intended.

8.6.1 Technical Systems Audit

ORNL's Quality Assurance Specialist (QAS) will perform a surveillance during the field demonstration activities to assess compliance with the demonstration plan. After the surveillance, the QAS will prepare a report which will be signed by the ORNL program manager. Corrective actions for noncompliance will be taken either on-the-spot, or a plan will be devised.

8.6.2 Performance Audit

Both the field technology and the reference laboratory will evaluate spiked samples, which will be of known concentration. The results will be compared to the range of acceptable results for the spiked samples, as determined by the provider of the spiked material and verified by the statistician. This evaluation will serve as a measure of accuracy and precision, and will be reported in the ETVR. During the field activities, ORNL may choose to inform a developer if their results on spiked samples are significantly different from the expected concentrations. Spiked samples will be obtained from Environmental Resource Associates or prepared by ORNL.

8.6.3 On-Site System Audits

During the field demonstration activities, ORNL will observe the operation of the field technology, such as observing the vendor operations, photo-documenting the demonstration activities, surveying calibration procedures, and reviewing sample data. The observations will be documented in a laboratory notebook or by completing a field audit form. The reference laboratory was audited by ORNL on May 4.

8.7 Quality Assurance Reports

QA reports provide the necessary information to monitor data quality effectively. It is anticipated that the following types of QA reports will be prepared as part of this demonstration.

8.7.1 Status Reports

When problems occur, the developer will discuss them with ORNL, estimate the type and degree of impact, and describe the corrective actions taken to mitigate the impact and to prevent a recurrence of the problems. ORNL will regularly inform the EPA project manager of the status of the project. ORNL should discuss project progress, problems and associated corrective actions, and future scheduled activities associated with the demonstration.

8.7.2 Audit Reports

A copy of the technical systems audit report will be provided to the EPA project manager. Informal reporting of audit results will be reported immediately to EPA.

8.8 Corrective Actions

Routine corrective action may result from common monitoring activities, such as:

- Performance evaluation audits

- Technical systems audits
- Calibration procedures

If the problem identified is technical in nature, the individual developers will be responsible for seeing that the problem is resolved. If the issue is one that is identified by ORNL or EPA, the identifying party will be responsible for seeing that the issue is properly resolved. All corrective actions will be documented. Any event that causes discrepancies from the demonstration plan will be noted in the technology verification report. Section 8.4 describes the reference laboratory's corrective action plan for not meeting minimum QC requirements.

9.0 HEALTH AND SAFETY PLAN

9.1 Introduction

This chapter describes the specific health and safety procedures that will be used during the field work at the Oak Ridge National Laboratory's Freels Bend Cabin site.

9.2 Contact Information

The ORNL program manager is Roger Jenkins, (423) 576-8594.
The ORNL technical lead is Amy Dindal, (423) 574-4863.
The environmental, safety, and health officer is Fred Smith, (423) 574-4945.
The environmental protection officer is Kim Jeskie, (423) 574-4947.
The laboratory shift superintendent phone number is (423) 574-6606.

9.3 Health and Safety Plan Enforcement

ORNL program manager and technical lead will be responsible for enforcing the health and safety plan. ORNL program manager will ultimately be responsible for ensuring that all demonstration participants abide by the requirements of this HASP. ORNL technical lead will oversee and direct field activities compliant with this HASP.

9.4 Site Location

The demonstration of explosives field analytical techniques will be conducted at the Oak Ridge National Laboratory, which is managed by Lockheed Martin Energy Research Corporation, Oak Ridge, Tennessee. The demonstration will be held at the Freels Bend Cabin site, which is located on the Oak Ridge Reservation, a short distance (5-6 miles) from ORNL. The site consists of a cabin that is primarily used as an educational facility. The cabin has electrical power, but no running water.

9.5 Site Access

Developers and any other visitors will be escorted at all times by ORNL personnel. Visitors will follow standard ORNL safety and health policies and practices. Visitors will not be allowed to physically operate the developers' equipment.

9.6 Training Requirements

Site-specific training will be provided by the ORNL program manager or designated representative on the first day of testing to ensure that the developers are familiar with the requirements of the HASP.

9.7 Technology-Specific Hazards

The hazards associated with this demonstration include the specific physical and chemical hazards associated with operating the technology. Potentially, each developer will be exposed to different hazards. Each developer is responsible for identifying these hazards and taking the appropriate precautions. In addition, all participants should be aware of the demonstration site hazards listed in Section 9.8.

9.8 Demonstration Site Hazards

Because the developers will be operating their technologies in the field for several consecutive days, there are a number of site hazards that the participants should be aware of.

9.8.1 Chemical Hazards

Prior to the start of the demonstration activities, all developers will evaluate the potential chemical hazards associated with the technology and report it to ORNL. ORNL will have Material Safety Data Sheets (MSDS) available at the site for all chemicals. If hazardous chemicals are used, a portable eye wash station will be located at the site. The developers will label all chemicals.

ORNL will provide all compressed gas cylinders. After hours, each cylinder will be strapped to a cylinder cart and stored in the cabin or on the cabin porch.

9.8.2 Physical Hazards

Physical hazards associated with field activities present a potential threat to on-site personnel. Dangers are posed by unseen obstacles, noise, heat, and poor illumination. Injuries may results from the following:

- Accidents due to slipping, tripping, or falling
- Improper lifting techniques
- Moving or rotating equipment
- Improperly maintained equipment

Injuries resulting from physical hazards can be avoided by adopting safe work practices and by using caution when working with machinery.

9.8.3 Mechanical, Electrical, Noise Hazards

Some technology-specific hazards may be identified once the developers set-up their equipment. Proper hazards controls (i.e., guarding or markings) or personal protective equipment (PPE) (i.e., ear plugs for noise hazards) will be implemented as necessary.

Electrical cables represent a potential tripping hazards. When practical, cables will be placed in areas of low pedestrian travel. If necessary, in high pedestrian travel areas, covers and/or markings will be installed over cables.

9.8.4 Inclement Weather

The demonstration will occur the latter part of August. The possibility of inclement weather (particularly rain and thundershowers) exists. The developers should be prepared to deal with a possible inclement weather situation. No work shall be performed if there is an electrical storm.

9.8.5 Heat Stress

Since the demonstration will occur in August, the possibility of a heat-related injury during field work is possible. All demonstration participants are encouraged to be attentive and responsive to signs of heat-induced illness. Heat stress symptoms include heat cramps, heat exhaustion, and heat stroke. Heat stroke is the most serious condition and can be life-threatening. Some symptoms of heat-related injuries are pale clammy skin, sweating, headache, weakness, dizziness, and nausea. Signs of heat stroke include dry, hot, red skin, chills, and confusion. In the case of a suspected heat-related injury, try to cool the person down and contact medical help. ORNL will provide drinking water to the participants to help avoid heat stress. Also, the participants will be encouraged to take several breaks during the day.

9.8.6 Insect and Other Animal Stings and Bites

A potential for insect (e.g., honey bees, wasps, yellow jackets), snake (e.g., rattlesnake, copperhead), arachnid (e.g., black widow, brown recluse, scorpions), and other animal (such as reptiles) stings or bites exists during the technology demonstration. Insect repellent may be used to minimize insect bite hazards. In the event of snake or other large animal bite, the injury should be immobilized and immediately reported to medical personnel. The number for medical personnel will be posted at the demonstration site.

9.8.7 Fire

The following specific actions will be taken to reduce the potential for fire during site activities:

- No smoking within 100 feet of any operating technology or the staging area.
- Fire extinguishers will be maintained on-site.
- All personnel will be trained on the location of the portable fire extinguishers.
- The number for the fire department will be posted.

9.8.8 Radiological Hazards

The proposed demonstration activities have been evaluated by ORNL radiation protection personnel. No radiation protection hazards have been identified.

9.9 Personal Protection

Based on the specific hazards associated with their technology, the technology developers will determine and provide the appropriate PPE. Appropriate work clothes (no shorts or open-toed shoes) shall be worn at all times. ORNL will provide visitors with PPE if necessary. If site conditions indicate that additional hazards are present, PPE levels will be reconsidered.

9.10 Emergency Support

In case of a medical or fire, emergency phone numbers will be posted at the demonstration site. A cellular phone will be available for use at all times.

9.11 Environmental Surveillance

The environmental protection officer will be responsible for surveying the site before, during, and after the demonstration. Appropriate personnel will be on-hand to assist all demonstration participants to deal with any health or safety concerns. All concerns will be reported to the environmental, safety, and health officer.

9.12 Hazardous Waste Disposal

All hazardous waste generated by the technology developers will be properly disposed of by the environmental protection officer. The technology developers will assist with this process by providing accurate records of the waste contents and approximate concentrations.

9.13 Site Control

Access to the demonstration site will be controlled. Any visitors to the site must be accompanied by ORNL personnel. The technology developers should be aware that there is unlimited access to the site from Melton Lake. As a result, vandalism can occur after hours. The developers should be prepared to secure their equipment while they are not at the site.

9.14 Safe Work Practices

Each company shall provide the required training and equipment for their personnel to meet safe operating practice and procedures. The individual technology developer and their company are ultimately responsible for the safety of their workers. The following safe work practices will be implemented at the site for worker safety:

- Eating, drinking, chewing tobacco, and smoking will be permitted only in designated areas;
- PPE requirements (See Section 9.9) will be followed.

9.15 Complaints

All complaints should be filed with the ORNL technical lead. All complaints will be treated on an individual basis and be dealt with accordingly.

REFERENCES

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APPENDIX A

Reference Laboratory Standard Operating Procedures

EXTRACTION, EXPLOSIVES

1.0 SCOPE

1.1 Method 8330 is intended for the trace level extraction of nitroaromatics from water, soil and sediment. Method 8332 is intended for the extraction of nitroglycerine.

2.0 SUMMARY

2.1 For nitroaromatics, method 8330, samples are prepared by salting-out and extracting for water and solvent extracting with acetonitrile for soils and sediments. For NG water samples are diluted, for soils samples are extracted with acetonitrile.

3.0 INTERFERENCES

3.1 Use reagent grade chemicals and cleaned glassware to minimize interferences.
3.2 Organics may interfere with subsequent analysis.

4.0 INSTRUMENTATION

4.1 Ultrasonic Bath
4.2 Refrigeration system, hold temperature to 4 C.
4.3 Balance, analytical, 0.0001 g accuracy.

5.0 REAGENTS

5.1 Acetonitrile (MeCN) and Methanol (MeOH), HPLC grade, commercial.
5.22.2 Sodium Chloride (NaCl) and Calcium Chloride (CaC12), reagent grade, commercial. Prepare a 5 % CaCl2 solution by adding 5 g to 1 L DI water.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples and extracts must be stored in the dark at 4 C.
6.2 Extraction must be within 14 days from date of collection.

7.0 PROCEDURE

7.1 Water

7.1.1 For nitroaromatics transfer 400 ml of sample into a 500 ml separatory funnel, add 130 g NaCl, shake until all salt is dissolved. Add 1.0 ml explosives spike standard, if needed.

7.1.2 Add 100 ml of MeCN, shake well for 5 minutes, allow phases to separate for at least 30 minutes. Discard lower water layer, collect top organic layer, rinse funnel with 10 ml MeCN and add to organic extract.

7.1.3 Reduce MeCN volume to 2.0 ml using warm-water bath not to exceed 40 C and nitrogen blowdown. Dilute with 2.0 ml DI water for a final volume of 4.0 ml. Sample is ready for HPLC analysis.

7.1.4 For nitroglycerine, dilute 5.0 ml of sample with 5.0 ml MeCN containing the surrogate at 1.0 ug/ml. Filter through a 0.45 um teflon filter. Store in dark at 4 +/- 2 C.

7.2 Soil/Sediment

7.2.1 Homogenize in a mortar and air dry about 5 g of sample. Place 2.0 g in a 15 ml glass vial and add 10 ml MeCN, cap and shake or 8.0 ml if spike is to be added. For spike add 2.0 ml of spike standard. For nitroaromatics, place in chilled ultrasonic bath and sonicate for 18 +/- 1 hour. For NG sonicate for 1 hour +/- 15 minutes. The bath must not exceed 4 C.

7.2.2 Allow sonicated sample to settle for 30 minutes. Take 5.0ml aliquot and add 5.0 ml of a 5 g/L CaC12 solution. Shake and let stand 15 minutes. Filter through a 0.45 um Teflon filter into a 15 ml vial. This filtrate is ready for HPLC analysis.

8.0 QA/QC

8.1 Every batch or every 20 sample must have a blank, spike and spike duplicate. Spike recovery should be 70-130%. %RPD < 20.

9.0 REFERENCES

9.1 SW-846, Third Ed., Method 8330, Rev. 0 1994

10.0 SAFETY

10.1 Grinding of soils could result in detonation, prescreen by grinding a small sample of about 0.2 g.

10.2 A distinct grey color may suggest high levels of explosives. Contact Safety Officer prior to initial grinding operation.

EXPLOSIVES BY HPLC

1.0 SCOPE:

1.1 Method 8330 is used to determine the concentration of nitroaromatic explosives in soil and water. The following compounds may be determined: 1,3 - Dinitrobenzene, 2,4 - Dinitrotoluene, 2,6 Dinitrotoluene, HMX, RDX, Nitrobenzene, 2 - Nitrotoluene, 3- Nitrotoluene, 4 - Nitrotoluene, Tetryl, TNT, 1,3,5 - Trinitrobenzene, 2 - Amino - 4,6 - Dinitrotoluene, and 4 - Amino - 2,6 - Dinitrotoluene. Practical quantitation limit for water is 0.0005 mg/L and 0.5 mg/kg for soils. This method with modifications is suitable for nitroglycerine. PQL/RL = 1.0 mg/l or 5 mg/kg.

2.0 SUMMARY:

2.1 Method 8330 provides liquid chromatographic conditions for the analysis of nitroaromatics. Samples are introduced by liquid injection and detected by U.V. Primary analytical column is a C- 18 reverse-phase with confirmation by a cyano column.

3.0 INTERFERENCES:

3.1 Tetryl decomposes in MeOH/H_2O and when exposed to heat. Degradation appears as a shoulder on TNT, use peak height for quantitation if both are present. Nitroglycerine is detected at 214 nm which is prone to interference from other non-target organics.

4.0 INSTRUMENTATION

4.1 HPLC (Shimadzu) with pulse-free pump (LC-600) and U.V detector set to 254 nm for nitroaromatics and 214 nm for NG. Data system is by Ezchrome.

4.2 Primary analytical column is a 25 cm x 4.6 mm RP-C18 (Phenomenex Ultracarb 5- ODS). Flow rate of 0.8 ml/min. is used.

4.3 Confirmation column is a 25 cm x 4.6 mn CN column. Mobile phase is 70 % MeOH/30 % Water at a flow rate of 1.5 ml/minute.

4.4 Optional: 10 cm x 4.6 mm RP-C18 ODS Hypersil, 3 um (Keystone Scientific); modify mobile phase as follows:
38 % MeOH/62 % Water with 2 % Tetrahydrofuran added to the water phase.
Flow rate of 1.0 ml/minute.

5.0 REAGENTS

5.1 Acetonitrile (MeCN) and Methanol (MeOH), HPLC grade, commercial source.

5.2 Calcium Chloride and Sodium Chloride, Reagent Grade, commmercial. Calcium Chloride solution: Add 5.0 g to 1 L DI water.

5.3 Stock standards: Accustandard or Ultra, 1000 µg/ml ea., certified, commercial..

5.4 Intermediate standards: dilute 0.1 ml stock to 10.0 ml in MeCN for a 10.0 ug/ml solution. Refrigerate. Usable for 30 days.

5.5 Prepare five calibration standards immediately before use by diluting the intermediate standard as follows:

µl added	final vol. (ml)	conc. std. (final)
10	1.0	0.1 µg/ml
25	1.0	0.25µg/ml
50	1.0	0.5 µg/ml
100	1.0	1.0 µg.ml
200	1.0	2.0 µg/ml

All Calibration standards should be prepared in a 50:50 solution of MeCN: 5% $CaCl_2$. For NG the low standard is 0.5 ug/ml up to 10 ug/ml.

5.6 Prepare matrix spike solution by adding 0.1 ml of stock solution (1000 µg/ml) to 9.9 ml MeCN. Add 1.0 ml of the 10 µg/ml spike solution to 1 L water sample for a 0.010 mg/L solution and 2.0 ml to 2 g soil for a 10 mg/kg standard.
NOTE: air dry soil to remove solvent prior to extraction.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Collection / preservation - N.A.

6.2 Sample and extracts must be stored in dark at 4° C. Holding times are 14 days for extraction and 40 days for analysis.

7.0 PROCEDURE

7.1 For extraction see SOP #26.

7.2 Install primary LC column, prepare mobile phase by adding 560 ml MeOH to 440 ml DI water . Load File 2 in system controller. Set flow to 0.8 ml/min., turn on UV and set wavelength to 254 nm. Allow to stabilize for at least 15 minutes. Injection volume is 25 µl.

7.3 Initially calibrate by loading the five calibration standards, highest to lowest, in the autosampler. Load "Explosiv" method. Start autosampler and calibrate using area. Successful calibration using RF must have a % RSD of less than 20 or a linear fit greater than 0.99. Verify calibration with a mid-point standard prepared from a different source or lot of stock standard. % RSD must be less than 15 or recalibrate.

7.4 Verify calibration daily using a mid-level standard. It must be within 15%

of initial calibration or repeat initial calibration porcedure.

7.5 Run samples using same procedure as standards. Include a mid-level check standard every 10 samples and at end of batch. % RSD should be less than 15 or rerun samples. All positive results must be confirmed using the CN column.

7.6 Concentrations are calculated using integrated results or manually as follows:

$$\text{conc. (mg/L or mg/kg)} = \frac{\text{(area or ht. sample)}}{\text{(area or ht. std.)}} \text{ x conc.std. x dilution x } \frac{\text{(vol. of extract)}}{\text{(vol. or wt. extracted)}}$$

7.7 Calculate spike recovery as follows: (conc.in extract)/1.0 x 100

8.0 QA/QC

8.1 Every batch or every 20 samples must have a blank, spike and spike duplicate. Acceptable spike recovery for water is 70-130% and soils 50-150%. If not, re-extract, if still outside range flag results.

8.2 No nitroaromatic target compounds in blank shall be greater than 0.05 µg/ml. For NG the blank must be less than 0.5 ug/ml.

9.0 REFERENCES

9.1 SW - 846, Third Ed., Method 8330 Rev. 0, 1994

9.2 SW – 846, Third Ed. Method 8332 Rev 0, 1996

10.0 SAFETY - Solvents are flammable. Avoid breathing.