

US EPA ARCHIVE DOCUMENT



Environmental Technology Verification Program

Verification Test Plan

Evaluation of Field Explosives Detection Technologies



Environmental Security
Technology Certification
Program

ornl

Oak Ridge National Laboratory

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Verification Test Plan

Evaluation of Field Explosives Detection Technologies

By

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Oak Ridge, Tennessee 37831-6120

and

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

This verification test was conducted in cooperation with the
U.S. Department of Defense
Environmental Security Technology Certification Program

APPROVAL SIGNATURES

This document is intended to ensure that all aspects of the verification 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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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 vendors in planning and conducting verifications, evaluating the data generated, and promoting acceptance of the technology.

This technology verification test plan has been developed to describe the verification of field analytical technologies for the determination of explosives compounds in contaminated soil. Technologies from SRI Instruments (GC-TID-1) and Texas Instruments (Spreeta Sensor) will be evaluated. The Oak Ridge National Laboratory (ORNL) will serve as the verification organization for the verification, 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 verification.

The purpose of this verification 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. The concentrations will range from 0 to approximately 90,000 mg/kg. 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
CASD	Chemical and Analytical Sciences Division
CRREL	U. S. Army Cold Regions Research and Engineering Laboratory
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
EPA	U. S. Environmental Protection Agency
ERA	Environmental Resource Associates
ESD-LV	Environmental Science Division-Las Vegas
ESH&Q	Environmental Safety, Health, and Quality
EST	Electronic Sensor Technology
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
LAAAP	Louisiana Army Ammunition Plant
LCS	Laboratory Control Sample
MLAAP	Milan Army Ammunition Plant
MS/MSD	matrix spike/matrix spike duplicate
MSDS	Material Safety Data Sheets
NERL	National Exposure Research Laboratory
ORNL	Oak Ridge National Laboratory

PE	performance evaluation
PPE	personal protective equipment
ppm	parts per million, mg/kg for soil
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
SCMT	Site Characterization and Monitoring Technologies Pilot of ETV
SD	standard deviation
SVOCs	semivolatile organic compounds
TID	thermionic ionization detector
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 INTRODUCTION

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

1.1 Verification Objectives

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

- Roles and responsibilities of verification participants;
- Procedures governing verification activities such as sample collection, preparation, analysis, data collection, and interpretation;
- Experimental design of the verification;
- Quality assurance (QA) and quality control (QC) procedures for conducting the verification and for assessing the quality of the data generated from the verification; 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) 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 and stakeholder groups consisting of regulators, buyers, and vendor organizations, with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing verification 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 (QA) 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 provide objective performance information to all of the participants in the environmental marketplace and to assist them in making informed technology decisions. ETV does not rank technologies or compare their performance, label or list technologies as acceptable or unacceptable, seek to determine “best available technology,” or approve or disapprove technologies. The program does not evaluate technologies at the bench or pilot scale and does not conduct or support research. Rather, it conducts and reports on testing designed to describe the performance of technologies under a range of environmental conditions and matrices.

The program now operates 12 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. These expert partners are both public and private organizations, including federal laboratories, states, industry consortia, and private sector entities. Verification organizations oversee and report verification activities based on testing and QA protocols developed with input from all major stakeholder/customer groups associated with the technology area. The verification described in this report was administered by the Site Characterization and Monitoring Technologies (SCMT) Pilot, with Oak Ridge National Laboratory (ORNL) serving as the verification organization. (To learn more about ETV, visit ETV’s Web site at www.epa.gov/etv and ORNL’s web site at www.ornl.gov/etv). The SCMT pilot is administered by EPA’s National Exposure Research Laboratory (NERL), Environmental Sciences Division, in Las Vegas, Nevada.

1.3 Joint Verification with DoD's ESTCP

The Department of Defense (DoD) has a similar verification program known as the Environmental Security Technology Certification Program (ESTCP). The purpose of ESTCP is to demonstrate and validate the most promising innovative technologies that target DoD's most urgent environmental needs and are projected to pay back the investment within 5 years through cost savings and improved efficiencies. ESTCP responds to (1) concern over the slow pace and cost of remediation of environmentally contaminated sites on military installations, (2) congressional direction to conduct demonstrations specifically focused on new technologies, (3) Executive Order 12856, which requires federal agencies to place high priority on obtaining funding and resources needed for the development of innovative pollution prevention programs and technologies for installations and in acquisitions, and (4) the need to improve defense readiness by reducing the drain on the Department's operation and maintenance dollars caused by real world commitments such as environmental restoration and waste management. ESTCP demonstrations are typically conducted under operational field conditions at DoD facilities. The demonstrations are intended to generate supporting cost and performance data for acceptance or validation of the technology. The goal is to transition mature environmental science and technology projects through the demonstration/ validation phase, enabling promising technologies to receive regulatory and end user acceptance in order to be fielded and commercialized more rapidly. (To learn more about ESTCP, visit ESTCP's web site at <http://www.estcp.org>.)

EPA's ETV program and DoD's ESTCP program established a memorandum of agreement in 1999 to work cooperatively with ESTCP on the verification of technologies that are used to improve environmental cleanup and protection at both DOD and non-DOD sites. The verification of field analytical technologies for explosives detection described in this test plan will be conducted jointly by ETV's SCMT pilot and ESTCP.

1.4 Technology Verification Process

The technology verification process is intended to serve as a template for conducting technology verifications 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
- Verification planning and implementation
- Report preparation
- Information distribution

1.4.1 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 vendors 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 vendors. 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.

1.4.2 Verification Planning and Implementation

After a vendor agrees to participate, EPA, the Verification Organization, and the vendor meet to discuss each participants responsibilities in the verification 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 verification test 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

1.4.3 Report Preparation

Innovative technologies are evaluated independently and, when possible, against conventional technologies. The technologies being verified are operated by the vendors 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 verification 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, ESTCP, and the Verification Organization.

1.4.4 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>).

1.5 Purpose of this Verification test plan

The purpose of the verification test plan is to describe the procedures that will be used to verify the performance goals of the technologies participating in this verification. 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 VERIFICATION RESPONSIBILITIES AND COMMUNICATION

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

2.1 Verification Organization and Participants

Participants in this verification are listed in Table 2-1. The specific responsibilities of each verification participant are discussed in Section 2.3 This verification 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 verification program. ORNL's role is to provide technical and administrative leadership and support in conducting the verification. SRI Instruments and Texas Instruments are the technology vendors participating in this verification.

Table 2-1. Participants in Explosives Detection Technology Verification Test

Organization	Point(s) of Contact	Role
<p>Oak Ridge National Laboratory P.O. Box 2008 Bethel Valley Road Bldg. 4500S, MS-6120 Oak Ridge, TN 37831-6120</p>	<p>Program Manager: Roger Jenkins phone: (865) 576-8594 fax: (865) 576-7956 email: jenkinsra@ornl.gov</p> <p>Technical Lead: Amy Dindal phone: (865) 574-4863 fax: (865) 576-7956 email: dindalab@ornl.gov</p>	<p>verification organization</p>
<p>U.S. Army Cold Regions Research and Engineering Laboratory 72 Lyme Road Hanover, NH 03755</p>	<p>Technical Lead: Tom Jenkins phone: (603) 646-4385 fax: (603) 646-4785 email: tjenkins@crrel.usace.army.mil</p>	<p>technical advisor</p>
<p>U. S. EPA National Exposure Research Laboratory Environmental Science Division P.O. Box 93478 Las Vegas, NV 89193-3478</p>	<p>Program Manager: Eric Koglin phone: (702) 798-2432 fax: (702) 798-2261 email: koglin.eric@epa.gov</p>	<p>EPA project management</p>
<p>U. S. DOE ORNL Site Office P.O. Box 2008 Bldg. 4500N, MS-6269 Oak Ridge, TN 37831-6269</p>	<p>Program Manager: Regina Chung phone: (865) 576-9902 fax: (865) 574-9275 email: chungr@ornl.gov</p>	<p>DOE/ORO project management</p>
<p>U.S. DoD Office of the Deputy under Secretary of Defense for Environmental Security Environmental Security Technology Certification Program Washington, DC 20301-3400</p>	<p>Program Manager: Cathy Vogel phone: (703) 696-2118 fax: (703) 696-2114 email: vogelc@acq.osd.mil</p>	<p>DoD project management</p>
<p>SRI Instruments 20720 Earl Street Torrance, CA 90503</p>	<p>Contact: Hugh Goldsmith phone: (310) 214-5092 fax: (310) 214-5097 email: hagoldsmith@earthlink.net</p>	<p>technology vendor</p>
<p>Texas Instruments 13536 N. Central Expressway, MS 945 Dallas, TX 75243</p>	<p>Contact: Jerry Elkind phone: (972) 995-1214 fax: (972) 995-8787 email: elkind@ti.com</p>	<p>technology vendor</p>
<p>TestAmerica Inc. Specialized Assays of Nashville 2960 Foster Creighton Drive Nashville, TN 37204</p>	<p>Contact: John Mitchell phone: (615) 726-0177 fax: (615) 726-3404 email: jmitchell@testamericainc.com</p>	<p>reference laboratory</p>

2.2 Organization

In Figure 2-1 is presented an organizational chart depicting the lines of communication for the verification.

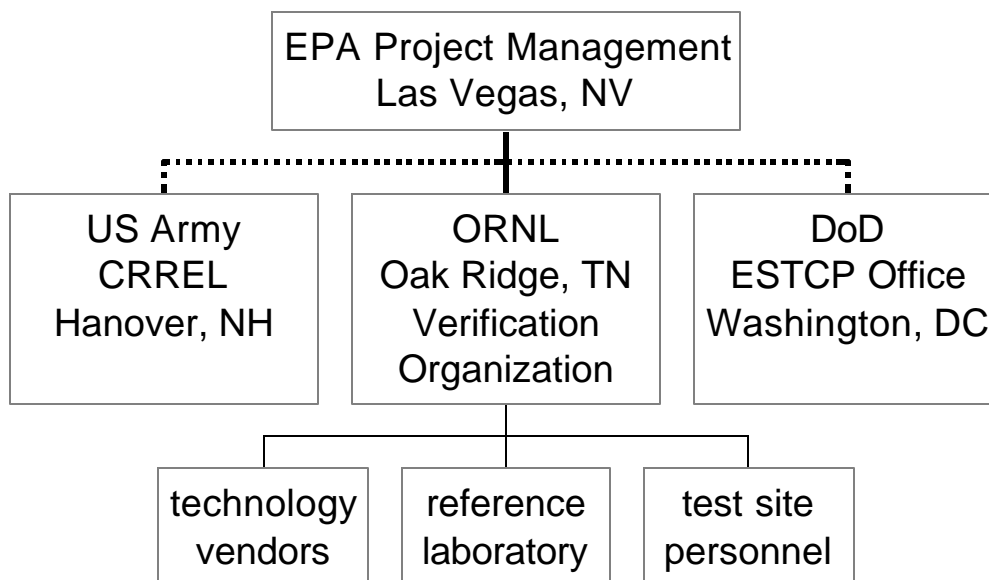


Figure 2-1. Organizational Chart.

2.3 Responsibilities

The following is a delineation of each participant's responsibilities for the verification. Henceforward, the term "vendor" applies to SRI Instruments and Texas Instruments.

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

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

ORNL has responsibilities for:

- Preparing the verification test plan;
- Developing a quality assurance project plan (QAPP) (Section 8 of the verification test plan);
- Preparing a health and safety plan (HASP) (Section 9 of the verification test plan) for the verification activities;
- Acquiring the necessary reference analysis data;
- Performing sampling activities (including collecting, homogenizing, dividing into replicates, bottling, labeling, and distributing);
- Conducting the verification.

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 verification participants;
- Auditing the on-site sampling activities;
- Managing, evaluating, interpreting, and reporting on data generated by the verification; 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 verification, such as waste disposal.

3 TECHNOLOGY DESCRIPTION

This section provides a description of the technologies participating in the verification. The descriptions were provided by the technology vendors, 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 verification. Note that TNT is 1,3,5-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 SRI Instruments' GC-TID (Model 8610C)

3.1.1 Technology Overview

The GC-TID-1, shown in Figure 3-1 is a on-site analysis of explosives (Table 3-1). Coupling this economical field-portable gas chromatograph with a thermionic ionization detector allows for the analysis of explosives in soil matrices following simple sample preparation procedures. The TID-1 is a thermionic ionization detector (TID) that uses an electrically heated emission source composed of alkali metals impregnated into a ceramic bead. When compounds containing nitro (NO₂) functional groups impinge on the bead's surface, they are selectively ionized and measured with a collector electrode. The stationary phase of the GC column and the programmable oven temperature separate the components present in sample extracts based on their relative affinities and vapor pressures.

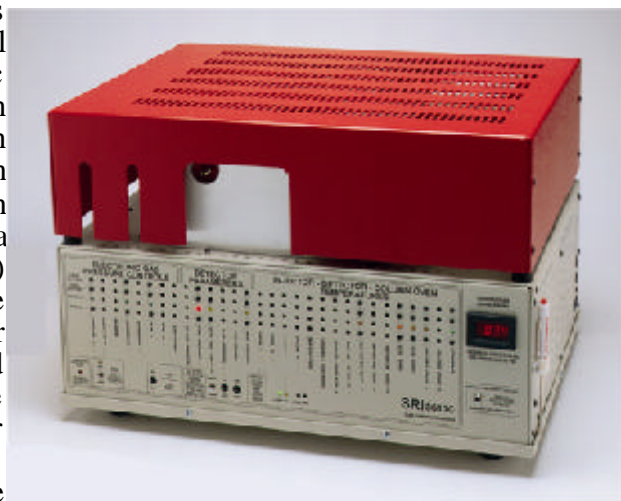


Figure 3-1. GC-TID-1

For instrumental analysis, sample extracts are injected directly onto the GC column within a heated injection port. The high temperature of the injection port instantaneously vaporizes the solvent extract and explosives, allowing them to travel as a vapor through the GC-column in the presence of the nitrogen carrier gas. Upon elution from the column's end, compounds containing nitro groups are ionized on the surface of the thermionic bead, and the increased conductivity of atmosphere within the heated detector is measured with a collector electrode. Analytical run times are typically less than 7 minutes long and baseline resolution often is achieved between explosives that are frequently identified at munition manufacturing facilities, depots, training ranges, and military test centers.

The SRI 8610C Gas Chromatograph equipped with TID detector, heated injector, built-in air compressor, PeakSimple serial data system and, 15-m MXT-1 capillary column has a list price of US\$ 8230.00 and comes with a reusable plastic shipping container that allows the GC to ship via FedEx or UPS, and even meets the size and weight limits for airline baggage.

3.1.2 Sample Preparation

Soil samples are prepared by extracting 2 to 20 g of sample with an equal or a five fold greater volume of acetone (i.e., 1:1 to 1:5), depending on the soil moisture and the data quality objectives. Extraction is performed by first manually shaking a soil acetone slurry for 3 to 5 minutes prior to allowing the soil to settle,

and second filtering an aliquot of the extract by passing it through a Millex SR (0.5- μ m) filter using a disposable plastic syringe with a Luer-Lock type fitting.

3.1.3 Analytical Procedure

Manual injections of 1 μ L volumes of the acetone extracts are made with a 10- μ L glass syringe equipped with an extra long needle (6.0 to 7.0 cm), into the injection port of a field-transportable SRI Model 8610C gas chromatograph equipped with a TID-1 detector. The injection port is heated to 225°C and the oven holding the 15-m MXT-1 column (i.d. 0.53 mm; 1.5- μ m crossbond 100% dimethyl polysiloxane film coating) is programmed to separate and elute the explosives of interest. The detector voltage and temperature are set at 340 mV and 250°C, respectively. The nitrogen carrier gas is supplied at a pressure of 10 psi or greater and an on-board air compressor set at 5 psi supplies make up gas to the detector. Operation under these conditions only requires that an electrical service and a source of nitrogen gas be available.

3.1.4 Instrument Calibration and Quantification of Sample Results

For typical field work, a five-point calibration ranging from 50 to 0.1 of mg/L in acetone, is established at the beginning of each day, and when instrumental response for an explosive of interest has changed by more than $\pm 20\%$. Concentrations of explosives in sample extracts are calculated from response factors generated from the calibration standards. Instrument performance is continuously monitored by reanalysis of standards after every fifth sample. Daily through-put is on the order of 40 \pm 10 samples. When necessary, the instrument can be optimized for the analysis of selected nitro-aromatic's (e.g., 2,4-DNT, TNT, and 2-Am-DNT) at concentrations less than 0.005 mg/L in acetone extracts. Hardware store grade acetone can be used for extraction without causing any adverse effects to the analytical system or its capabilities.

Table 3-1. Explosive analytes detected by GC-TID-1.

Analyte	GC-TID-1
1,3-DNB	x
2,6-DNT	x
2,4-DNT	x
TNB	x
TNT	x
RDX	x
4-Am-DNT	x
2-Am-DNT	x
Tetryl	x
HMX	x
PETN	x
nitrobenzene	x
nitroglycerine	x

3.2 Texas Instruments' Spreeta™ Sensor

3.2.1 General Overview and Description

Spreeta is an integrated, miniaturized sensor platform which employs Surface Plasmon Resonance (SPR) to detect changes in refractive index within a few thousand Angstroms of the active gold surface. Specificity is provided by placing a thin biofilm on the sensor surface. For example, by placing an antibody to Fluorescein on the sensor surface, the binding of fluoresceinated proteins, seen as a local increase in refractive index, is simply performed. SPR has been used in this way to study biomolecular binding events for more than a decade, but Spreeta is the first miniaturized SPR platform. TNT detection is most efficiently performed by

methods other than direct binding. This is because on a molecule-for-molecule basis, small molecules are much less effective than large molecules at changing refractive index, and, so, any direct SPR assay can detect large molecules at a lower concentration than for small molecules. For this reason, Texas Instruments (TI) has developed a robust inhibition assay in which the presence of two TNT molecule (228 daltons) effectively inhibits the binding of one antibody molecule (150,000 daltons). TI reports that detection of TNT in water at less than 10 $\mu\text{g/L}$ has been demonstrated.

The assay starts with a conjugate of trinitrobenzene (TNB) and Bovine Serum Albumin on the gold sensing surface. Assays are then performed by exposing that sensing surface to an anti-TNT antibody solution which may or may not contain free TNT. When free TNT is present, it binds to anti-TNT antibodies in solution and thereby keeps them from binding to the surface-bound TNT analog. This inhibited binding is compared to a reference run where the antibody solution did not contain free TNT.

3.2.2 Sample Preparation

Soil extracts are prepared using a simple protocol. 100 mg of soil is suspended in approximately 1.15 mL of Phosphate Buffered Saline and 0.1% Triton X-100 (a non-ionic detergent) in a centrifuge tube. The soil is gently shaken in the solution for 5 minutes. The mixture is then allowed to settle for approximately 45 minutes. One mL of the supernatant is removed by pipette and is incubated with 5 μL of antibody solution. This is then analyzed for TNT content as described above.

3.2.3 Calibration and Data Analysis

Reference runs (with no TNT present) are made periodically to verify assay fidelity and bio-film integrity. The antibody used in this assay has a 10% cross-reactivity with dinitrotoluene (DNT) and smaller cross reactivities with other nitro-aromatic compounds. Therefore, we report an “effective” TNT concentration, which includes contributions from TNT, DNT and other interferents. It is known that RDX and HMX do not react with this antibody and are not a factor in this assay.

A negative result with an undiluted sample indicates an effective TNT concentration of less than 0.1 ppm (mg/kg) in soil. A positive result with an undiluted sample calls for a dilution and retest of the diluted sample until a dilution bracket is achieved. For the purposes of this Verification series, answers will be reported such that the central point of the bracket is approximately 50% above the lower limit and approximately 50% below the upper limit. For example, if the test is positive for a 100X dilution and negative for a 300X dilution, the reported result will be approximately [10-30] mg/kg.

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

4 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

The first evaluation of explosives-detection technologies under the ETV program occurred in 1999. Specialized Assays Inc. (SAI), now known as TestAmerica Inc., of Nashville, Tennessee, was selected as the

reference laboratory for that study. A sample holding time study performed by ORNL in May 2000 indicated that the concentration of explosives in the samples had not changed significantly. Therefore, archived soil samples and the reference laboratory data generated in 1999 will be used for comparison with the vendor results.

The following describes how SAI was chosen to perform the 1999 analyses. SAI 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.

4.3 Laboratory Audits

ORNL's technical expert and statistician conducted an audit of laboratory operations on May 4, 1999. This evaluation focused specifically on the procedures that would be used for the analysis of the verification 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.

ORNL conducted a second audit at Specialized Assays while the 1999 analyses were being performed. Since the initial qualification visit, management of this laboratory had changed because Specialized Assays became part of Test America. The visit included tours of the laboratory, interviews with key personnel, and review of data packages. Overall, no major deviations from procedures were observed and laboratory practices appeared to meet the QA requirements of the test plan.

4.4 Validation and Evaluation of Reference Laboratory Data

The soil verification samples were sent to the reference laboratory at the start of the verification activities (August 23, 1999). Results were received in batches of 20 samples. All data packages were received by mid-October.

4.4.1 Data Validation

ORNL was 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 vendor is responsible for validating its own data prior to final submission.) ORNL's procedure for data validation includes several aspects, that are listed below.

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.

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 are corrected as necessary. Corrections may be made to data that has transcription errors, calculation errors, and interpretation errors. These changes are made conservatively, and are based on the guidelines provided in the method used. The changes are 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 provides an additional indication of the abnormality of data through

the inspection of the replicate results from homogenous sample sets. These data are 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 vendor(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 are 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 test plan. The QC samples include: 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.

4.4.1.7 Summary of 1999 Soil Data Validation

Two of the original SAI results were corrected due to calculation and transcription errors that were identified during the validation. One blank sample was reported as 70,900 mg/kg of TNT and was assumed to be a sample preparation error, but was counted as a false positive result for the reference laboratory. One Iowa sample, again presumed a preparation error, was reported as 0.8 mg/kg TNT, where the remaining three replicates were consistently reported near 25,000 mg/kg. Comparative data analyses with the vendor results was performed with and without this data point.

5 TEST SITE AND SAMPLE DESCRIPTIONS

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

5.1 Testing Location and Conditions

This verification of explosives field analytical technologies will be conducted at the Oak Ridge National Laboratory, in Oak Ridge, Tennessee, near Building 5507. A map of the site is presented in Figure 5-1. The samples used in this study will be brought to the 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.

To test the capabilities of the technologies under actual field conditions, the verification test 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 daily temperatures for eastern Tennessee in August will range from 66 °F to 88 °F with a range of relative humidities from 60% to 90%

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.

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 Sample Preparation

5.3.1 Sample Collection

The soil samples from the various sites described in Section 5.2 were shipped at ambient temperature to ORNL for use in the verification test. This effort was coordinated by CRREL. The soil samples were shipped in double-bagged plastic Ziplock™ bags and stored frozen (< 0 °C) prior to splitting.

5.3.2 Sample Preparation

In order to ensure that the vendors and the reference laboratory analyze comparable samples, the soils were homogenized prior to sample splitting. The process was as follows. The sample was kneaded in the Ziplock™ bag to break up large clumps. Approximately 1500 g of soil was poured into a Pyrex™ pan. Debris was removed. The sample were air-dried overnight (or longer, as necessary). The sample was sieved using a 10 mesh (2 mm particle size) screen and placed in a 1-L wide-mouth jar. After thorough mixing with a metal spatula, the sample was quartered. After mixing each quarter, approximately 250 g from each quarter was 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 was split into jars for distribution. Each 4-oz sample jar contains approximately 20 g of soil. Four replicate splits of each soil sample was prepared for each participant. The samples were randomized in two stages. First, the order in which the filled jars will be distributed was randomized so that the same vendor does not always receive the first jar filled for a given sample set. Second, the order of analysis were randomized so that each

vendor analyzes the same set of samples, but in a different order. Note that the samples used in this verification are archives from the 1999 test.

5.3.3 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 vendor. A separate label will be used to identify the vendor analysis order.

5.3.4 Sample Storage

To ensure that degradation will not occur, the soil samples will be frozen ($< 0\text{ }^{\circ}\text{C}$) prior to analysis. These precautions will be taken per the guidance outlined in, "Stability of Explosives in Environmental Water and Soil Samples [6]."

6 PREDEMONSTRATION STUDY

A predemonstration study is required by the SCMT program to allow the vendors 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. Poor performance at this point could indicate a lack of maturity of the technology.

This requirement has the following objectives:

- To allow the vendors to analyze samples that will be included in the verification test 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 verification.

For the predemonstration study, the vendors analyzed six explosives-contaminated soils (including one spiked sample) from LAAAP (see site information in Section 5.2.2). These samples were identical to those used in the 1999 predemonstration study. The spiked soil sample was obtained from Environmental Resource Associates (ERA, Arvada, CO). The soil was prepared using ERA's semivolatle 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.

6.1 Predemonstration Sample Distribution

The predemonstration samples were sent to the vendors on May 31, 2000. The vendor results for the predemonstration sample analyses were provided to ORNL two weeks after the receipt of the samples.

6.2 Predemonstration Results

ORNL analyzed the predemonstration samples, and confirmed that the reference laboratory results did not change significantly for these samples. The vendor results were compared to performance acceptance ranges generated from analytical verification data generated by ORNL and the reference laboratory. The acceptance ranges were guidelines established by ORNL's statistician to gauge acceptable analytical results. The results indicated the technologies described test plan are mature and ready for field testing.

7 EXPERIMENTAL DESIGN

This section discusses the objectives of the verification test, 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 verification.

7.1 Objectives

The primary objectives of this verification 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 matrices, (4) accuracy for spiked samples, and (5) the logistical and economic resources necessary to operate the technology. Secondary objectives for this verification are to evaluate the technologies in terms of portability, cost, sample throughput, and ease of operation. 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 verification can be quantified by various means, including the following: accuracy, precision, 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 Test Design

The verification will be held at ORNL from August 21 through September 1, 2000. The samples to be evaluated during the demonstration consist of (1) naturally-contaminated samples from DoD sites, (2) spiked samples, and (3) blank samples. Some features of the approach are presented in Table 7-1. The vendor will analyze a total of 108 soil samples. The concentrations of the samples will range from 0 to 90,000 mg/kg. 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].

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 interferences or cross-reactive compounds, and which samples are suspected to contain extremely high levels of a particular contaminant.

7.4 Field Data

The technology will be operated by the vendor, who will provide the results to ORNL. The vendor 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 vendors. Before leaving the demonstration site, the vendors will submit all final results and raw data to ORNL.

Table 7-1. Experimental Design Features

<p>Properties: 23 unique soil samples; acquire more data on fewer samples; statistically rich approach</p> <p>Replicates: equal number (quadruplicate) for all sample types and concentration levels</p> <p>Accuracy: equal number of comparisons with certified and spike concentrations for the PE soils and extract samples, respectively, at all concentration levels</p> <p>Precision: estimated for all sample types and concentration levels</p> <p>Data Analysis: simplified statistics due to consistency with number of replicates</p>

7.5 Verification Test Schedule

Verification activities will occur from August 21 through September 1, 2000. Visitors will be scheduled to talk with the vendors and view technology demonstrations as necessary.

7.6 Field Operations

This verification requires close communication between the vendor, ORNL, and EPA. Preliminary site training (on August 21) will be required before initiation of the field study. Successful field operations require detailed planning and extensive communication. The implementation of the verification must be consistent with the requirements of the study and routine operation of the technology.

7.6.1 Communication and Documentation

The successful implementation of the verification test plan will require detailed coordination and constant communication between all participants. ORNL will communicate regularly with the participants to coordinate all field activities associated with this verification test and to resolve any logistical, technical, or QA issues that may arise as the verification progresses. All vendor/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 verification test plan will be thoroughly documented in the field logbook and provided to ORNL. Photographs will be taken with a digital camera.

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

7.6.2 Sample Distribution

ORNL will be responsible for sample distribution. Soil samples will be packaged in 4 ounce (120 mL) jars. All samples will be prepared for distribution at the start of the verification test. The vendors 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 vendor samples will be retained by ORNL. An archive sample will be used during the verification test if the integrity of a vendor's sample has been compromised. Additional unhomogenized material and unused archive samples will also be retained at ORNL at the completion of the verification test, 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 verification test. 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, completeness, and comparability 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 vendor 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 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:

$$RSD = (\text{standard deviation} / \text{average concentration}) \times 100\%$$

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 vendor'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

$$\text{percent recovery} = (\text{measured amount} / \text{spiked amount}) \times 100\%$$

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 vendor'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 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.

7.7.4 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 be 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 vendor's and reference laboratory's samples. The Wilcoxon test is designed to test whether the vendor'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

$$\%D = ([\text{field technology}] - [\text{ref lab}]) / (\text{ref lab}) \times 100\%$$

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

Similar to accuracy, 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.

7.7.5 *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.

7.7.6 *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.

7.7.7 *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 verification test? 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?

7.7.8 *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 **QUALITY ASSURANCE PROJECT PLAN (QAPP)**

The QAPP for this verification test specifies procedures that will be used to ensure data quality and integrity. Careful adherence to these procedures will ensure that data generated from the verification test will meet the desired performance objectives and will provide sound analytical results. EPA considers the verification test to be classified as a Category II project. This section of the verification test 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 vendor 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 vendor 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 verification test 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 four indicators of data quality: 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 every with 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 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 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:

$$RPD = \left\{ \frac{MS - MSD}{\frac{1}{2}(MS + MSD)} \right\} \times 100\%$$

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 mg/kg in soil. SAI's acceptance criteria will be 60 -140% recovery for soil. 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. If the surrogate is out of limits, the individual sample must be repeated.

8.4.7 Spiked Samples

Soil samples are spiked with known concentrations of explosives and included in the suite of samples for evaluation. These will be blind to the vendor and the reference laboratory. The matrix will be interference-free, so that accuracy can be assessed on relatively "clean" samples. The samples were obtained from Environmental Resource Associates.

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 vendor 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.

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 vendor will provide a list of all possible interval reporting ranges to ORNL at the start of the verification test 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 would report a blank soil as "< 0.5 mg/kg" for each analyte.

8.5.2 Data Review

The vendor 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 vendor will verify that all instrument systems are in control and that QA objectives for accuracy, completeness, and method detection limits have been met.

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

Analyte	Matrix Precision (percent RPD)	Matrix Accuracy (percent recovery)
HMX	30	55-147
RDX	27	66-142
1,3,5-trinitrobenzene	31	55-149
1,3-dinitrobenzene	23	67-140
Tetryl	48	24-146
Nitrobenzene	30	64-145
2,4,6-Trinitrotoluene	41	51-129
4-Amino-2,6-dinitrotoluene	23	43-156
2-Amino-4,6-dinitrotoluene	28	60-142
2,6-Dinitrotoluene	29	62-147
2,4-Dinitrotoluene	30	60-143
2-Nitrotoluene	25	63-138
4-Nitrotoluene	24	68-132
3-Nitrotoluene	26	58-143

Table 8-2. Example of reporting intervals

Interval	Soil concentration range for TNT
[0, 1)	$0 \leq \text{TNT mg/kg} < 1$
[1, 10)	$1 \leq \text{TNT mg/kg} < 10$
[10, 50)	$10 \leq \text{TNT mg/kg} < 50$
[50, ¥)	$\text{TNT mg/kg} \geq 50$

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 vendors.) 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.

Vendor results will be due to ORNL at the conclusion of the field activities. For sample throughput calculations, a sample will not be considered completed until the final result is submitted to ORNL. The vendor’s final report will be due to ORNL one week after the conclusion of the verification test. Any discrepancies between the originally reported result and the final result must be described.

8.6 Audits

The following audits will be performed during this verification test. These audits will determine if this verification test 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 verification test activities to assess compliance with the verification test 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. Spiked samples will be obtained from Environmental Resource.

8.6.3 *On-Site System Audits*

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

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 verification test.

8.7.1 *Status Reports*

When problems occur, the vendor 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 verification test.

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 vendors 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 verification test 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 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.

9.2 Contact Information

The ORNL program manager is Roger Jenkins, (865) 576-8594.

The ORNL technical lead is Amy Dindal, (865) 574-4863.

The environmental, safety, and health officer is Fred Smith, (865) 574-4945.

The environmental protection officer is Kim Jeskie, (865) 574-4947.

The laboratory shift superintendent phone number is (865) 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 verification test 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 verification test of explosives field analytical techniques will be conducted at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, on the lawn outside Building 5507. The building has electrical power and running water.

9.5 Site Access

Vendors 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 vendors' 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 vendors are familiar with the requirements of the HASP.

9.7 Technology-Specific Hazards

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

9.8 Site Hazards

Because the vendors 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 verification test activities, all vendors 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 vendors will label all chemicals.

ORNL will provide all compressed gas cylinders. After hours, each cylinder will be secured.

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 result 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 vendors 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 verification test will occur the latter part of August. The possibility of inclement weather (particularly rain and thundershowers) exists. The vendors 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 verification test will occur in August, the possibility of a heat-related injury during field work is possible. All 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 verification test. 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 verification test 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 verification test 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 vendors will determine and provide the appropriate PPE. At a minimum, safety glasses shall be worn. 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, ORNL safety personnel may recommend different or additional PPE be used by the vendors.

9.10 Emergency Support

In case of a medical or fire, emergency phone numbers will be posted at the verification test site. A phone will be available for use at all times. (Note that cellular phones will not work on most of the Oak Ridge Reservation.)

9.11 Environmental Surveillance

The environmental protection officer will be responsible for surveying the site before, during, and after the verification test. Appropriate personnel will be on-hand to assist all verification test 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 vendors will be properly disposed of by the environmental protection officer. The technology vendors will assist with this process by providing accurate records of the waste contents and approximate concentrations.

9.13 Site Control

Access to the verification test site will be controlled. Any visitors to the site must be accompanied by ORNL personnel.

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 vendor 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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- [16] U. S. Environmental Protection Agency. "Preparation Aids for the Development of Category II Quality Assurance Project Plans." EPA/600/8-91/004, February 1991.
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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.
 - 5.2.2 Sodium Chloride (NaCl) and Calcium Chloride (CaCl₂), 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 CaCl₂ 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/H₂O 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 (I.C-600) and U.V detector set to 254 nm for nitroaromatics and 214 nm for NG. Data system is by Eschmole.
- 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 mm 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, commercial.
Calcium Chloride solution: Add 5.0 g to 1 L DI water.
- 5.3 Stock standards: Accustandard or Ultra, 1000 µg/ml ca., certified, commercial.
- 5.4 Intermediate standards: dilute 0.1 ml stock to 10.0 ml in MeCN for a 10.0 µg/ml solution. Refrigerate. Usable for 30 days.
- 5.5 Prepare five calibration standards immediately before use by diluting the intermediate standard as follows:

<u>µl added</u>	<u>final vol. (ml)</u>	<u>conc. std. (final)</u>
10	1.0	0.1 µg/ml
25	1.0	0.25 µg/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% CaCl₂. For NG the low standard is 0.5 µg/ml up to 10 µg/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 procedure.
- 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:

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

- 7.7 Calculate spike recovery as follows: $(\text{conc. in extract})/1.0 \times 100$
- 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 µg/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.