United States
Environmental Protection
Agency

Office of Research and
Development
Washington, D.C. 20460

EPA/600/R-01/065
August 2001

Environmental Technology Verification Report

Explosives Detection Technology

SRI Instruments
Model 8610C, Gas Chromatograph/ Thermionic Ionization Detection

Environmental Security
Technology Certification
Program

Oak Ridge National Laboratory

ETV ETV ETV

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

ETV

EPA
U.S. Environmental Protection Agency

ESTCP
Environmental Security Technology Certification Program

ornl
Oak Ridge National Laboratory

Joint Verification Statement

TECHNOLOGY TYPE:	**GAS CHROMATOGRAPHY**		
APPLICATION:	**MEASUREMENT OF EXPLOSIVES IN CONTAMINATED SOIL**		
TECHNOLOGY NAME:	**Model 8610C Gas Chromatograph/Thermionic Ionization Detection**		
COMPANY:	**SRI Instruments**		
ADDRESS:	**20720 Earl Street** **Torrance, CA 90503**	**PHONE:** **FAX:**	**(310) 214-5092** **(310) 214-5097**
WEB SITE:	**www.srigc.com**		
EMAIL:	**hagoldsmith@earthlink.net**		

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

ETV works in partnership with recognized standards and testing organizations, stakeholder groups 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 test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

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 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 field tested and commercialized more rapidly.

The Oak Ridge National Laboratory (ORNL) is one of the verification organizations operating under the Site Characterization and Monitoring Technologies (SCMT) program. SCMT, which is administered by EPA's National Exposure Research Laboratory, is one of 12 technology areas under ETV. In this verification test, ORNL evaluated the performance of explosives detection technologies. This verification statement provides a summary of the test results for SRI Instruments' Model 8610C gas chromatograph with thermionic ionization detection (GC/TID). This verification was conducted jointly with DoD's ESTCP.

VERIFICATION TEST DESCRIPTION

This verification test was designed to evaluate technologies that detect and measure explosives in soil. The test was conducted at ORNL in Oak Ridge, Tennessee, from August 21 through 30, 2000. Spiked samples of known concentration were used to assess the accuracy of the technology. Environmentally contaminated soil samples, collected from DoD sites in California, Louisiana, Iowa, and Tennessee and ranging in concentration from 0 to approximately 90,000 mg/kg, were used to assess several performance characteristics. The primary constituents in the samples were 2,4,6-trinitrotoluene (TNT); isomeric dinitrotoluene (DNT), including both 2,4-dinitrotoluene and 2,6-dinitrotoluene; hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). The results of the soil analyses conducted under field conditions by the GC/TID were compared with results from reference laboratory analyses of homogenous replicate samples analyzed using EPA SW-846 Method 8330. Details of the verification, including a data summary and discussion of results, may be found in the report entitled *Environmental Technology Verification Report: Explosives Detection Technology—SRI Instruments, GC/TID*, EPA/600/R-01/065.

TECHNOLOGY DESCRIPTION

The SRI Model 8610C gas chromatograph (GC) is a transportable instrument that can provide on-site analysis of soils for explosives. Coupling this transportable gas chromatograph with a thermionic ionization detector (TID) allows for the determination of explosives in soil matrices following simple sample preparation procedures. Samples are extracted in acetone, diluted, and 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. 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. 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. In this verification test, the instrument was verified for its ability to detect and quantify 2,4-dinitrotoluene (2,4-DNT), RDX, and TNT. Analytical run times were typically less than 7 min and reporting limits were typically 0.5 mg/kg.

VERIFICATION OF PERFORMANCE

The following performance characteristics of SRI's GC/TID were observed.

Precision: The mean relative standard deviations (RSDs) for 2,4-DNT, RDX, and TNT were 15%, 14% and 23%, respectively, indicating that the determinations of all analytes were precise.

Accuracy: Accuracy was assessed using the performance evaluation (PE) soil samples, which were spiked to nominal TNT and RDX concentrations of 0, 10, 50, 100, 250, and 500 mg/kg each by an independent laboratory. The mean percent recoveries for RDX and TNT were 91% and 97%, respectively, indicating that the analyses were unbiased.

False positive/false negative results: Of the 20 blank soils, SRI reported TNT in five samples (25% false positives). No false positives were reported for 2,4-DNT and RDX. False positive and false negative results were also estimated by comparing the GC/TID result to the reference laboratory result for the environmental and spiked samples (e.g., whether SRI reported a result as a nondetect that the reference laboratory reported as a detection, and vice versa). For these soils, 3% of the 2,4-DNT results and 7% of the TNT results were reported as false positives relative to the reference laboratory results, but none of the RDX results were reported as false positives. Similarly, a small percentage of the results were reported as nondetects by SRI (i.e., false negatives) when the laboratory reported a detection (2% for RDX , 4% for TNT, none for 2,4-DNT).

Completeness: The GC/TID generated results for all 108 soil samples for a completeness of 100%.

Comparability: A one-to-one sample comparison of the GC/TID results and the reference laboratory results was performed for all samples (spiked and environmental) that were reported as detects. The correlation coefficient (r) for the comparison of the entire soil data set for TNT (excluding one suspect measurement for the reference laboratory) was 0.95 (slope (m) = 1.32). When comparability was assessed for specific concentration ranges, the r value did not change dramatically for TNT, ranging from 0.89 to 0.93 depending on the concentrations selected. RDX correlation coefficient with the reference laboratory for all soil results was slightly lower than TNT (r = 0.85, m = 0.91). The GC/TID's results for RDX correlated better with the reference laboratory for concentrations <500 mg/kg (r = 0.96, m = 0.83) than for samples where concentrations were >500 mg/kg (r = 0.49, m = 0.56). For the limited number of data points where both the reference laboratory and SRI reported results for 2,4-DNT (n = 14), the correlation was 0.44 (m = 0.33).

Sample Throughput: Throughput was approximately three samples per hour. This rate was accomplished by two operators and included sample preparation and analysis.

Ease of Use: No particular level of educational training is required for the operator, but knowledge of chromatographic techniques and experience in field instrument deployments would be advantageous.

Overall Evaluation: The overall performance of the GC/TID for the analysis of 2,4-DNT, RDX, and TNT was characterized as precise and unbiased. As with any technology selection, the user must determine if this technology is appropriate for the application and the project's data quality objectives. For more information on this and other verified technologies, visit the ETV web site at http://www.epa.gov/etv.

Gary J. Foley, Ph.D.
Director
National Exposure Research Laboratory
Office of Research and Development

W. Frank Harris, Ph.D.
Associate Laboratory Director
Biological and Environmental Sciences
Oak Ridge National Laboratory

Jeffrey Marqusee, Ph.D.
Director
Environmental Security Technology Certification Program
Department of Defense

EPA/600/R-01/065
August 2001

Environmental Technology Verification Report

Explosives Detection Technology

SRI Instruments
Gas Chromatograph/Thermionic Ionization Detection

By

Amy B. Dindal
Charles K. Bayne, Ph.D.
Roger A. Jenkins, Ph.D.
Oak Ridge National Laboratory
Oak Ridge Tennessee 37831-6120

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

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

Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), and the U.S. Department of Defense's Environmental Security Technology Certification Program (ESTCP) Program, funded and managed, through Interagency Agreement No. DW89937854 with Oak Ridge National Laboratory, the verification effort described herein. This report has been peer and administratively reviewed and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use of a specific product.

Table of Contents

List of Figures

List of Tables

Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. In particular, we recognize Dr. Thomas Jenkins (U.S. Army, Cold Regions Research and Engineering Laboratory) and Dr. Michael Maskarinec (Oak Ridge National Laboratory) who served as the technical experts for this project. We thank the people who helped us to obtain the samples from the various sites, including Dr. Jenkins, Danny Harrelson (Waterways Experiment Station), Kira Lynch (U.S. Army Corp of Engineers, Seattle District), Larry Stewart (Milan Army Ammunition Plant), Dick Twitchell and Bob Elmore (Volunteer Army Ammunition Plant). For external peer review, we thank Dr. C. L. Grant (Professor Emeritus, University of New Hampshire) and Harry Craig (US EPA, Region 10) for EPA peer review. The authors also acknowledge the participation of Hugh Goldsmith of SRI Instruments and Alan Hewitt and Tom Ranney of U.S. Army Cold Regions Research and Engineering Laboratory, who performed the analyses during verification testing.

For more information on the Explosives Detection Technology Verification contact

Eric N. Koglin
Project Technical Leader
Environmental Protection Agency
Environmental Sciences Division
National Exposure Research Laboratory
P. O. Box 93478
Las Vegas, Nevada 89193-3478
(702) 798-2432
koglin.eric@epa.gov

Roger A. Jenkins
Program Manager
Oak Ridge National Laboratory
Chemical and Analytical Sciences Division
P.O. Box 2008
Building 4500S, MS-6120
Oak Ridge, TN 37831- 6120
(865) 574-4871
jenkinsra@ornl.gov

For more information on SRI Instruments' Model 8610C GC contact

Hugh Goldsmith
President
SRI Instruments
20720 Earl Street
Torrance, CA 90503
(310) 214-5092
hagoldsmith@earthlink.net
www.srigc.com.

Abbreviations and Acronyms

%D	percent difference
2-Am-DNT	2-amino-4,6-dinitrotoluene
4-Am-DNT	4-amino-2,6-dinitrotoluene
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
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
ESTCP	Environmental Security Technology Certification Program (DoD)
ETV	Environmental Technology Verification Program
FA	false-acceptance error rate
fn	false negative result
fp	false positive result
FR	false-rejection error rate
GC	gas chromatograph
GC/TID	gas chromatograph with thermionic ionization detection
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine
HPLC	high-performance liquid chromatograph
LAAAP	Louisiana Army Ammunition Plant
MLAAP	Milan Army Ammunition Plant
NERL	National Exposure Research Laboratory (EPA)
NO_2	nitro
OB/OD	open burning and open detonation
ORNL	Oak Ridge National Laboratory
PE	performance evaluation
QA	quality assurance
QC	quality control
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RSD	relative standard deviation
SAI	Specialized Assays, Inc.
SCMT	Site Characterization and Monitoring Technologies Center
SD	standard deviation
TBAOH	5 millimolar (mM) tetrabutyl-ammonium hydroxide
TID	thermionic ionization detector
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene

Section 1 — Introduction

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 centers covering a broad range of environmental areas. ETV began with a 5-year pilot phase (1995–2000) to test a wide range of partner and procedural alternatives in various technology areas, as well as the true market demand for and response to such a program. In these centers, 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) Center, 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.) The SCMT Center is administered by EPA's National Exposure Research Laboratory (NERL), Environmental Sciences Division, in Las Vegas, Nevada.

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 field tested and commercialized more rapidly. (To learn more about ESTCP, visit ESTCP's web site at www.estcp.org.)

EPA's ETV program and DoD's ESTCP program established a memorandum of agreement in 1999 to work cooperatively 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 report was conducted jointly by ETV's SCMT Center and ESTCP. The verification was conducted at ORNL in Oak Ridge, Tennessee, from August 21 through 30, 2000. The performances of two field analytical techniques for explosives were determined under field conditions. Each technology was independently evaluated by comparing field analysis results with those obtained using an approved reference method, EPA SW-846 Method 8330. The verification was designed to evaluate the field technology's ability to detect and measure explosives in soil. The primary constituents in the samples were 2,4,6-trinitrotoluene (TNT); isomeric dinitrotoluene (DNT), including both 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT); hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Naturally contaminated environmental soil samples, ranging in concentration from 0 to about 90,000 mg/kg, were collected from DoD sites in California, Louisiana, Iowa, and Tennessee, and were used to assess several performance characteristics. This report discusses the performance of SRI Instruments' Model 8610C gas chromatograph equipped with a thermionic ionization detector (TID).

Section 2 — Technology Description

In this section, the vendor (with minimal editorial changes by ORNL) provides a description of the technology and the analytical procedure used during the verification testing activities.

Figure 1. SRI Model 8610C gas chromatograph.

Technology Overview

The SRI Model 8610C gas chromatograph (GC) is a transportable instrument that can provide on-site analysis for explosives (Figure 1). Coupling this field-portable gas chromatograph with a thermionic ionization detector allows for the determination of explosives in soil matrices following simple sample preparation procedures. The instrument has a TID that uses an electrically heated emission source composed of alkali metals impregnated into a ceramic bead. When compounds containing nitro (NO_2) 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.

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 <7 min long, and baseline resolution often is achieved between explosives that are frequently identified at munition manufacturing facilities, depots, training ranges, and military test centers.

Sample Preparation

Soil samples were prepared by extracting 20 to 40 g of soil with a 40 mL volume of acetone. Extraction was performed by intermittently shaking (manual) the soil:acetone slurry for several short time intervals (2 min) over a 30 min extraction period, then allowing the soil to settle. A clear aliquot of the extractant was filtering by passing it through a Millex SR (0.5-µm) filter using a disposable plastic syringe with a Luer-Lock type fitting. To screen sample extracts for high concentrations of nitroaromatic compounds (i.e., TNT), a 0.25 mL volume was transferred to a clear 2 mL vial and 0.01 mL of 5 mM tetrabutyl-ammonium hydroxide (TBAOH [Aldrich]) was added. The formation of a dark purple or red solution gives a visual indication that a high concentration of nitroaromatics are present. Depending on the color formed, extraction aliquots were diluted from 1:2000 to 1:10, or not diluted at all, prior to analysis.

Analytical Procedure

Manual injections of 1 µL volumes of the acetone extracts are made with a 10-µL glass syringe equipped with an extra long needle (6.0 to 7.0 cm), into the injection port of a field-portable SRI Model 8610C gas chromatograph equipped with a TID detector. The injection port is heated to 225°C and the oven holding the 15-m MXT-1 column (i.e., 0.53 mm; 1.5-µm crossbond 100% dimethyl polysiloxane film coating) is programmed to separate and elute the explosives of interest. The detector voltage and temperature are set at -3.4 V 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

requires only that electrical service and a source of nitrogen gas be available.

Instrument Calibration and Quantification of Sample Results

A five-point calibration ranging from 0.4 to 40 mg/L in acetone was established at the beginning of the field trial, and when instrumental response for an explosive of interest has changed by more than ±20%. Concentrations of explosives in sample extracts were calculated from curves generated from the calibration standards. Instrument performance was continuously monitored by reanalysis of standards after every fifth sample.

Section 3 — Verification Test Design

Objective

The purpose of this section is to describe the verification test design. It is a summary of the test plan (ORNL 2000).

Testing Location and Conditions

The verification of field analytical technologies for explosives was conducted on the grounds outside of ORNL's Building 5507, in Oak Ridge, Tennessee. The temperature and relative humidity were monitored during field testing. Over the five days of testing, the average temperature was 83°F, and ranged from 63 to 98°F. The average relative humidity was 58%, and ranged from 27 to 95%.

The samples used in this study were shipped to the testing location for evaluation by the vendors. Explosives-contaminated soils from Army ammunition plants in Iowa, Louisiana, Tennessee, and a former Army base in California (Fort Ord) were used in this verification. Because samples were obtained from multiple DoD sites, the samples represented a reasonable cross section of the population of explosives-contaminated matrices, such that the versatility of the field technology could be evaluated. More specific details about the samples are presented in the following sections

Soil Sample Descriptions

The primary contaminants in the soil samples were TNT, DNT, RDX, and HMX. The samples also contained trace amounts of 2-amino-4,6-dinitrotoluene (2-Am-DNT) and 4-amino-2,6-dinitrotoluene (4-Am-DNT), which are degradation products of TNT. The total concentration of explosives ranged from 0 to approximately 90,000 mg/kg. The following sections describe the sites from which the samples were collected.

Sources of Samples

Iowa Army Ammunition Plant

Currently 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. During the early years of operation, the installation used surface impoundments, landfills, and sumps for disposal of industrial wastes containing explosives. The major contaminants in these samples are TNT, RDX, and HMX.

Louisiana Army Ammunition Plant

The Louisiana Army Ammunition Plant (LAAAP), near Shreveport, Louisiana, is a government-owned facility that began production in 1942. The facility is currently an Army Reserve plant. Production items at LAAAP have included metal parts for artillery shells; the plant also loads, assembles, and packs artillery shells, mines, rockets, mortar rounds, and demolition blocks. As a result of these activities and the resulting soil and groundwater contamination, EPA placed LAAAP on the National Priorities List of contaminated sites (Superfund) in 1989. The major constituents in the samples from this site are TNT, RDX, and HMX, with trace levels of 1,3,5-trinitrobenzene (TNB), DNT, 2-Am-DNT, and 4-Am-DNT.

Milan Army Ammunition Plant

Currently active, the 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 loading, assembly, and packaging lines. Munitions-related wastes have resulted in soil contamination. The primary contaminants in these soils are RDX and TNT.

Volunteer Army Ammunition Plant

The Volunteer Army Ammunition Plant, in Chattanooga, Tennessee, was built in 1941 to manufacture TNT and DNT. All production ceased in 1977. Past production practices resulted in significant soil and groundwater contamination. In the samples from this site, concentrations of TNT and DNT ranged from 10 to 90,000 mg/kg, with significantly smaller concentrations of Am-DNT isomers.

Fort Ord Military Base

Fort Ord, located near Marina, California, was opened in 1917 as a training and staging facility for infantry troops and was closed as a military installation in 1993. Since then, several nonmilitary uses have been established on the site: California State University at Monterey Bay has opened its doors on former Fort Ord property, the University of California at Santa Cruz has established a new

research center there, the Monterey Institute of International Studies will take over the officer's club and several other buildings, and the post's airfield was turned over to the city of Marina. The Army still occupies several buildings.

An Army study conducted in 1994 revealed that the impact areas at the inland firing ranges of Fort Ord were contaminated with residues of high explosives (Jenkins, Walsh, and Thorne 1998). Fort Ord is on the National Priorities List of contaminated sites (Superfund), requiring 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) was HMX; much lower concentrations of RDX, TNT, 2-Am-DNT, and 4-Am-DNT are present.

Performance Evaluation Samples

Spiked soil samples were obtained from Environmental Resource Associates (ERA, Arvada, Colorado). The soil was prepared using ERA's semivolatile blank soil matrix. This matrix was a 40% clay topsoil that had been dried, sieved, and homogenized. Particle size was 60 mesh and smaller. The samples, also referred to as performance evaluation (PE) samples, contained known levels of TNT and RDX. The concentrations that were evaluated contained 10, 50, 100, 250, and 500 mg/kg of each analyte. Prior to the verification test, ORNL analyzed the spiked samples to confirm the concentrations were within the performance acceptance limits established by the preparation laboratory. The method used was a modified Method 8330, similar to the reference laboratory method described in Section 4. For the verification test, four replicates were prepared at each concentration level.

Blank soil samples were evaluated to determine the technology's ability to identify samples with no contamination (i.e., to ascertain the false positive error rate). The soil was collected in Monroe County, Tennessee, and was certified by ORNL to be free of contamination prior to verification testing. A reasonable number of blanks ($N = 20$) was chosen to balance the uncertainty for estimating the false positive error rate and the required number of blank samples to be measured.

Soil Sample Preparation

A few weeks prior to the verification test, all of the soil samples were shipped in plastic bags at ambient temperature to ORNL. The samples were stored frozen (<0°C) prior to preparation. To ensure that the vendors and the reference laboratory analyzed comparable samples, the soils were homogenized prior to sample splitting. The process was as follows. The sample was kneaded in the Ziplock plastic bag to break up large clumps. Approximately 1500 g of soil was poured into a Pyrex pan, and debris was removed. The sample was then air dried overnight. The sample was sieved using a 10-mesh (2-mm particle size) screen and placed in a 1-L widemouthed jar. After thorough mixing with a metal spatula, the sample was quartered. After mixing each quarter, approximately 250 g from each quarter was placed back in the 1-L widemouthed jar, for a total sample amount of approximately 1000 g. Analysis by the ORNL method confirmed sample homogeneity (variability of 20% relative standard deviation or less for replicate measurements). The sample was then split into subsamples for analysis during the verification test. Each 4-oz sample jar contained approximately 20 g of soil. Four replicate splits of each soil sample were prepared for each participant. The design included a one-to-one pairing of the replicates, such that the vendor and reference lab samples could be directly matched. Three replicate sets of samples were also prepared for archival storage. To ensure that degradation did not occur, the soil samples were frozen (<0°C) until analysis (Maskarinec et al. 1991).

Sample Randomization

The samples were randomized in two stages. First, the order in which the filled jars were distributed was randomized so that the same vendor did not always receive the first jar filled for a given sample set. Second, the order of analysis was randomized so that each participant analyzed the same set of samples, but in a different order. Each jar was labeled with a sample number. Replicate samples were assigned unique (but not sequential) sample numbers. Spiked materials and blanks were labeled in the same manner, such that these quality control samples were indistinguishable from other samples. All samples were analyzed blindly by both the developer and the reference laboratory.

Summary of Experimental Design

The distribution of samples from the various sites is described in Table 1. A total of 108 soil samples were analyzed, with approximately 60% of the samples being naturally contaminated environmental soils, and the remaining 40% being spikes and blanks. Four replicates were analyzed for each sample type. For example, 4 replicate splits of each of 3 Fort Ord soils were analyzed, for a total of 12 individual Fort Ord samples.

Table 1. Summary of Soil Samples

Sample source or type	No. of soil samples
Fort Ord	12
Iowa	4
LAAAP	16
MLAAP	20
Umatilla	0
Volunteer	12
Spiked	24
Blank	20
Total	108

Description of Performance Factors

In Section 5, technology performance is described in terms of precision, accuracy, completeness, and comparability, which are indicators of data quality (EPA 1996). False positive and negative results, sample throughput, and ease of use are also described. Each of these performance characteristics is defined in this section.

Precision

Precision is the reproducibility of measurements under a given set of conditions. Standard deviation (SD) and relative standard deviation (RSD) for replicate results are used to assess precision, using the following equation:

$$RSD = (SD/\text{average concentration}) \times 100\% \quad \text{(Eq. 1)}$$

The overall RSD is characterized by three summary values:

- mean (average);
- median (50th percentile value, at which 50% of all individual RSD values are below and 50% are above); and
- range (the highest and lowest RSD values that were reported).

The average RSD may not be the best representation of precision, but it is reported for convenient reference. RSDs greater than 100% should be viewed as indicators of large variability and possibly non-normal distributions.

Accuracy

Accuracy represents the closeness of the technology's measured concentrations to known (in this case, spiked/PE) values. Accuracy is assessed in terms of percent recovery, calculated by the following equation:

$$\%\ \text{recovery} = (\text{measured concentration}/\text{known concentration}) \times 100\% \quad \text{(Eq. 2)}$$

As with precision, the overall percent recovery is characterized by three summary values: mean, median, and range.

False Positive/Negative Results

A false positive (fp) result is one in which the technology detects explosives in the sample when there actually are none (Berger, McCarty, and Smith 1996). A false negative (fn) result is one in which the technology indicates that no explosives are present in the sample, when there actually are (Berger, McCarty, and Smith 1996). The evaluation of fp and fn results is influenced by the actual concentration in the sample and includes an assessment of the reporting limits of the technology. False positive results are assessed in two ways. First, the results are assessed relative to the blanks (i.e., the technology reports a detected value when the sample is a blank). Second, the results are assessed on environmental and spiked samples where the analyte was not detected by the reference laboratory (i.e., the reference laboratory reports a nondetect and the field technology reports a detection). False negative results, also assessed for environmental and spiked samples, indicate the frequency that the technology reported a nondetect (i.e., < reporting limits) and the reference laboratory reported a detection. Note that the reference laboratory results were validated by ORNL so that

fp/fn assessment would not be influenced by faulty laboratory data. The reporting limit is considered in the evaluation. For example, if the reference laboratory reported a result as 0.9 mg/kg, and the technology's paired result was reported as below reporting limits (<1 mg/kg), the technology's result was considered correct and not a false negative result.

Completeness

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

Comparability

Comparability refers to how well the field technology and reference laboratory data agree. The difference between accuracy and comparability is that accuracy is judged relative to a known value, and comparability is judged relative to the results of a standard or reference procedure, which may or may not report the results accurately. Note that the reference laboratory result is not assumed to be the "correct" result. This evaluation is performed for comparison of the field analytical technology result with what a typical fixed analytical laboratory might report for the same sample. A one-to-one sample comparison of the technology results and the reference laboratory results is performed in Section 5.

A correlation coefficient quantifies the linear relationship between two measurements (Draper and Smith 1981). The correlation coefficient is denoted by the letter *r;* its value ranges from –1 to +1, where 0 indicates the absence of any linear relationship. The value $r = -1$ indicates a perfect negative linear relation (one measurement decreases as the second measurement increases); the value $r = +1$ indicates a perfect positive linear relation (one measurement increases as the second measurement increases). The slope of the linear regression line, denoted by the letter *m*, is related to *r*. Whereas *r* represents the linear association between the vendor and reference laboratory concentrations, *m* quantifies the amount of change in the vendor's measurements relative to the reference laboratory's measurements. A value of +1 for the slope indicates perfect agreement. (It should be noted that the intercept of the line must be close to zero [i.e., not statistically different from zero], in order for the slope value of +1 to indicate perfect agreement.) Values greater than 1 indicate that the vendor results are generally higher than the reference laboratory's, while values less than 1 indicate that the vendor results are usually lower than the reference laboratory's.

In addition, a direct comparison between the field technology and reference laboratory data is performed by evaluating the percent difference (%D) between the measured concentrations, defined as:

$$\%D = ([\textit{field technology}] - [\textit{ref lab}])/(\textit{ref lab}) \times 100\% \quad \text{(Eq. 3)}$$

The range of %D values is summarized and reported in Section 5.

Sample Throughput

Sample throughput is a measure of the number of samples that can be processed and reported by a technology in a given period of time. This is reported in Section 5 as the number of samples per hour times the number of analysts.

Ease of Use

A significant factor in purchasing an instrument or a test kit is how easy the technology is to use. Several factors are evaluated and reported on in Section 5:

- What is the required operator skill level (e.g., technician or advanced degree)?
- 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?
- How much subjective decision-making is required?

Cost

An important factor in the consideration of whether to purchase a technology is cost. Costs involved with operating the technology and the standard reference analyses are estimated in Section 5. To account for the variability in cost data and assumptions, the economic analysis is 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 are addressed so that decision makers can independently complete a site-specific economic analysis to suit their needs.

Miscellaneous Factors

Any other information that might be useful to a person who is considering purchasing the technology is documented in Section 5. 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 that make it easy to use.

Section 4 — Reference Laboratory Analyses

Reference Laboratory Selection

The verification process is based on the presence of a statistically validated data set against which the performance of the technology may be compared. The choice of an appropriate reference method and reference laboratory are critical to the success of the verification test. To assess the performance of the explosives field analytical technologies, the data obtained from verification test participants were compared to data obtained using conventional analytical methods.

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 were used for comparison with the vendor results.

The following describes how SAI was chosen to perform the 1999 analyses. Specialized Assays, Inc. was selected to perform the analyses based on ORNL's experience with laboratories capable of performing explosives analyses using EPA SW-846 Method 8330. ORNL reviewed Specialized Assays' record of laboratory validation performed by the U.S. Army Corps of Engineers (Omaha, Nebraska). EPA and ORNL decided that, based on the credibility of the Army Corps program and ORNL's prior experience with the laboratory, Specialized Assays would be selected to perform the reference analyses.

ORNL conducted an audit of Specialized Assays' laboratory operations on May 4, 1999. This evaluation focused specifically on the procedures that would be used for the analysis of the verification test samples. Results from this audit indicated that Specialized Assays was proficient in several areas, including quality management, document/record control, sample control, and information management. Specialized Assays was found to be compliant with implementation of Method 8330 analytical procedures. The company provided a copy of its QA plan, which details all of the QA and quality control (QC) procedures for all laboratory operations (Specialized Assays 1999). The audit team noted that Specialized Assays had excellent procedures in place for data backup, retrievability, and long-term storage. ORNL conducted a second audit at Specialized Assays while the analyses were being performed. Since the initial qualification visit, management of this laboratory had changed because Specialized Assays became part of TestAmerica. 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 technology test plan (ORNL 1999).

Reference Laboratory Method

The reference laboratory's analytical method, presented in the technology test plan, followed the guidelines established in EPA SW-846 Method 8330 (EPA 1994). According to Specialized Assays' procedures, soil samples were prepared by extracting 2-g samples of soil in acetonitrile by sonication for approximately 16 h. An aliquot of the extract was then combined with a calcium chloride solution to precipitate out suspended particulates. After the solution was filtered, the filtrate was ready for analysis. The analytes were identified and quantified using a high-performance liquid chromatograph (HPLC) with a 254-nm UV detector. The primary analytical column was a C-18 reversed-phase column with confirmation by a secondary cyano column. The practical quantitation limit for soil was 0.5 mg/kg.

Reference Laboratory Performance

ORNL validated all of the reference laboratory data according to the procedure described in the test plan (ORNL 2000). During the validation, the following aspects of the data were reviewed: completeness of the data package, adherence to holding time requirements, correctness of the data, correlation between replicate sample results, evaluation of QC sample results, and evaluation of spiked sample results. Each of these categories is described in detail in the test plan. The reference laboratory reported valid results for all samples, so

completeness was 100%. Preanalytical holding time requirements (14 days to extract; 40 days to analyze) were met. A few errors were found in a small portion of the data (~4%). Those data were corrected for transcription and calculation errors that were identified during the validation. One data point, a replicate Iowa soil sample, was identified as suspect. The result for this sample was 0.8 mg/kg; the results from the other three replicates averaged 27,400 mg/kg. Inclusion or exclusion of this data point in the evaluation of comparability with the field technology (reported in Section 5) did not significantly change the *r* value, so it was included in the analysis. The reference laboratory results for QC samples were flagged when the results were outside the QC acceptance limits. The reference laboratory results were evaluated by a statistical analysis of the data. Due to the limited results reported for the other Method 8330 analytes, only the results for the major constituents in the samples (2,4-DNT, HMX, RDX, and TNT) are evaluated in this report.

The accuracy and precision of the reference laboratory results are summarized in Table 2. Accuracy was assessed using the spiked samples, while precision was assessed using the results from both spiked and environmental samples. The reference laboratory results were unbiased (accurate), as mean percentage recovery values were near 100%. The reference laboratory results were precise; all but one of the mean RSDs were less than 30%. The one mean RSD that was greater than 30% (soil, DNT, 56%) was for a limited data set of three, and the problem was caused by one replicate of one sample.

Table 3 presents the laboratory results for blank samples. A false positive result is identified as any detected result on a known blank. For the soil samples, one false positive detection appeared to be a preparation error because the concentration was near 70,000 mg/kg. Overall, it was concluded that the reference laboratory results were unbiased, precise, and acceptable for comparison with the field analytical technology.

Table 2. Summary of the Reference Laboratory Performance for Soil Samples

Statistic	Accuracy (% recovery)		Precision [a] (% RSD)			
	RDX N = 20	TNT N = 20	2,4-DNT N_R = 3 [b]	HMX N_R = 13	RDX N_R = 13	TNT N_R = 18
Mean	102	100	56	29	25	29
Median	99	96	25	30	21	25
Range	84–141	76–174	19–123	12–63	4–63	2–72

[a] Calculated from those samples where all four replicates were reported as a detect.
[b] N_R represents the number of replicate sets; N represents the number of individual samples.

Table 3. Summary of the Reference Laboratory Performance on Blank Samples

Statistic	Soil			
	DNT	HMX	RDX	TNT
Number of data points	20	20	20	20
Number of detects	0	0	0	2
% of fp results	0	0	0	10

Section 5 — Technology Evaluation

Objective and Approach

The purpose of this section is to present a statistical evaluation of the GC/TID data and determine the instrument's ability to measure explosives in contaminated soil samples. The technology's performance is presented for 2,4-DNT, RDX, and TNT, including an evaluation of comparability through a one-to-one comparison with the reference laboratory data. Other aspects of the technology (such as cost, sample throughput, hazardous waste generation, and logistical operation) are also evaluated in this section. Appendix A contains the raw data, provided by the vendor during the verification test, that were used to assess the performance of the GC/TID.

Precision

Precision is the reproducibility of measurements under a given set of conditions. Precision was determined by examining the results of blind analyses for four replicates of each sample. Data were evaluated for only those samples where all four replicates were reported as a detect. For example, for RDX, N_R = 13 (13 sets of four replicates) represents a total of 52 individual sample analyses. A summary of the overall precision of the GC/TID for the soil sample results is presented in Table 4. For the soil samples, the mean RSDs for 2,4-DNT, RDX, and TNT were 15%, 14%, and 23%, respectively, indicating that the analyses were precise.

Accuracy

Accuracy represents the closeness of the GC/TID's measured concentrations to the known content of spiked samples. A summary of the GC/TID's overall accuracy for the soil results is presented in Table 5. Note that the PE samples were spiked with only TNT and RDX, so accuracy for 2,4-DNT could not be evaluated. For the soil samples, the recoveries for both RDX and TNT were similar, ranging from 74 to 112% overall. The mean recovery values for RDX = 91% and TNT = 97% suggested that the results were unbiased. Based on the performance acceptance ranges shown in Table 6, which are the guidelines established by the provider of the spiked materials to gauge acceptable analytical results, 90% of the results (18 of 20) met the acceptance criteria for RDX, while 100% (20 of 20) met the criteria for TNT.

False Positive/False Negative Results

Table 7 shows the GC/TID performance for false positive (fp) results for blank samples. Of the 20 blank soils, SRI did not report 2,4-DNT or RDX in any samples, but reported TNT in 5 samples (25% fp). Table 8 summarizes the GC/TID's fp and fn results relative to the reference laboratory results. (See Section 3 for a more detailed discussion of this evaluation.) For the environmental and spiked soils, 3% of the 2,4-DNT results, 0% of the RDX results, and 7% of the TNT results were reported as false positives relative to the reference laboratory results (i.e., the laboratory reported the analyte as a nondetect when SRI reported it as a detect). In the case where the laboratory reported a detection and SRI reported a nondetect (i.e., false negatives), 0%

Table 4. Summary of the GC/TID Precision

Statistic	Soil RSD [a] (%)		
	2,4-DNT N_R = 4 [b]	**RDX N_R = 13**	**TNT N_R = 17**
Mean	15	14	23
Median	9.0	10	13
Range	8.9–31	5–44	2–107

[a] Calculated from only those samples where all four replicates were reported as a detect.
[b] N_R represents the number of replicate sets.

Table 5. Summary of the GC/TID Accuracy

Statistic	Soil recovery (%)	
	RDX N = 20	**TNT N = 20**
Mean	91	97
Median	90	96
Range	74–112	87–110

Table 6. Number of GC/TID Results within Acceptance Ranges for Spiked Soils

Spike concentration (mg/kg)	RDX		TNT	
	Acceptance range (mg/kg)	No. of results within range	Acceptance range (mg/kg)	No. of results within range
10	8–11	3 out of 4	7–13	4 out of 4
50	38–57	4 out of 4	35–63	4 out of 4
100	76–113	3 out of 4	70–126	4 out of 4
250	190–283	4 out of 4	174–315	4 out of 4
500	379–566	4 out of 4	348–630	4 out of 4

Table 7. Summary of GC/TID False Positive Performance on Blank Samples

Statistic	2,4-DNT	RDX	TNT
Number of data points	20	20	20
Number of fp results	0	0	5
% of total results which were fp	0%	0%	25%

Table 8. Summary of the GC/TID Detect/Nondetect Performance Relative to the Reference Laboratory Results

Statistic	2,4-DNT	RDX	TNT
Number of data points lab reported as non-detect	74	33	14
Number of fp results by GC/TID	2	0	1
% of total results which were fp	3%	0%	7%
Number of data points lab reported as detection	14	55	74
Number of fn results by GC/TID	0	1	3
% of total results which were fn	0%	2%	4%

of the 2,4-DNT, 2% of the RDX, and 4% of the TNT results were false negatives.

Completeness

Completeness is defined as the percentage of measurements that are judged to be usable (i.e., the result was not rejected). Valid results were obtained by the technology for all 108 soil samples. Therefore, completeness was 100%.

Comparability

Comparability refers to how well the GC/TID and reference laboratory data agreed. In this evaluation, the laboratory results are not presumed to be the "correct" answers. Rather, these results represent what a typical fixed laboratory would report for these types of samples. A one-to-one sample comparison of the GC/TID results and the reference laboratory results was performed for all

environmental and spiked samples that were reported as a detect. (Please refer to Appendix A to review the raw data. See Section 4 for a complete evaluation of the reference laboratory results.) In Table 9, the comparability of the results are presented in terms of correlation coefficients (r) and slopes (m) of the linear regression analysis.

A limited number of comparable data points (N = 14) was available for 2,4-DNT. All of these values were less than 50 mg/kg. The correlation coefficient for the comparison was 0.44 (m = 0.33) for the entire soil data set of 2,4-DNT results. Figure 2 is a plot of the GC/TID RDX results versus those for the reference laboratory for all results (N = 52). One unusual SRI result at approximately 8,000 mg/kg is highlighted by a box surrounding the point. This data point greatly influenced the correlation coefficient value. The GC/TID correlation coefficient with the reference laboratory for all

Table 9. GC/TID Correlation with Reference Data for Various Vendor Soil Concentration Ranges

Vendor concentration range	2,4-DNT		RDX		TNT [a]	
	Correlation coefficient (*r*)	Slope (*m*)	Correlation coefficient (*r*)	Slope (*m*)	Correlation coefficient (*r*)	Slope (*m*)
All values [b]	0.44	0.33	0.85/0.96 [c]	0.91/0.86	0.95	1.32
≤500 mg/kg [d]	0.44	0.33	0.96	0.83	0.89	0.72
>500 mg/kg	n/a [e]	n/a	0.49/0.84	0.56/0.64	0.93	1.46
>10,000 mg/kg	n/a	n/a	n/a	n/a	0.89	1.46

[a] Excluding the one reference laboratory TNT unusual value.
[b] Excluding those values reported as "< reporting limits."
[c] Including/excluding the one SRI unusual value.
[d] Based on SRI's reported values.
[e] No values above were reported at this concentration level.

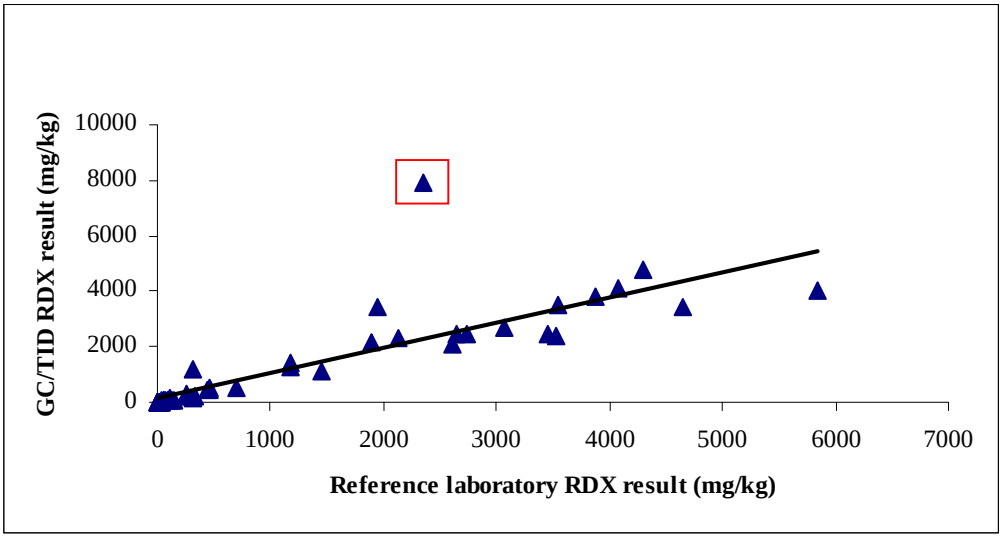

Figure 2. Comparison of reference laboratory results with GC/TID results for all RDX soil concentrations. The data point highlighted by a box is considered an unusual value for SRI. Please refer to Table 9 for regression constants calculated with and without this unusual value.

samples was 0.85 (m = 0.91) including the unusual value and 0.96 (m = 0.86) excluding it. The effect is even more pronounced when the results are evaluated exclusively for samples where concentrations were >500 mg/kg [r = 0.49 (m = 0.56) including the unusual value, while r = 0.84 (m = 0.64) excluding it]. The GC/TID's correlation coefficient with the reference laboratory for RDX concentrations <500 mg/kg was r = 0.96 (m = 0.83). The correlation coefficient for the comparison of the entire soil data set for TNT (excluding one suspect measurement for the reference laboratory) was 0.95 (m = 1.32). When comparability was assessed for specific concentration ranges, the r value did not change dramatically for TNT, ranging from 0.89 to 0.93 depending on the concentrations selected. Figure 3 presents a plot of the GC/TID TNT results versus those for the reference laboratory for concentrations <500 mg/kg. As this figure indicates, the GC/TID TNT soil measurements generally agreed with but were slightly lower than the reference laboratory results.

Another metric of comparability is the %D between the reference laboratory and the GC/TID results. The ranges of %D values for 2,4-DNT, RDX, and TNT are presented in Figure 4. Acceptable %D values would be between –25% and 25% or near the middle of the x-axis of the plots. For 2,4-DNT, the values were mostly negative, indicating that the GC/TID result was usually less than the reference laboratory result. For RDX, 65% of the %D values were between –25% and 25%, supporting the conclusions that the RDX results generally agreed with the reference laboratory results. For TNT, most of the %D values are near the middle of the x-axis, with 45% of the results were between –25% and 25%. The median absolute %D values for 2,4-DNT, RDX, and TNT were 66%, 19%, and 28%, respectively.

Sample Throughput

Sample throughput is representative of the estimated amount of time required to prepare and analyze the sample and perform the data analysis. Operating in the field, the two-person SRI team accomplished a sample throughput rate of approximately three samples per hour for the 108 soil analysis. The instrument run time for each analysis was approximately 7 min.

Ease of Use

Two operators were used for the test because of the number of samples and working conditions, but the technology can be operated by a single person. SRI Instruments provides a free one-half day of training at their Torrance, California facility with an instrument purchase. Users unfamiliar with gas chromatography may need one or two days of additional training to operate the instrument. No particular level of educational training is required for the operator.

Cost Assessment

The purpose of this economic analysis is to estimate

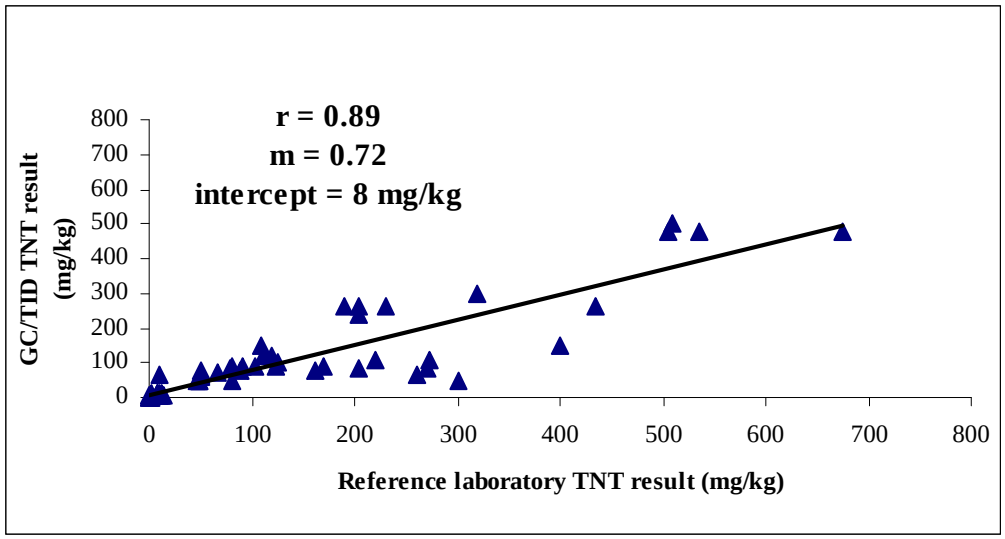

Figure 3. Comparison of reference laboratory results with GC/TID results for SRI TNT soil concentrations <500 mg/kg.

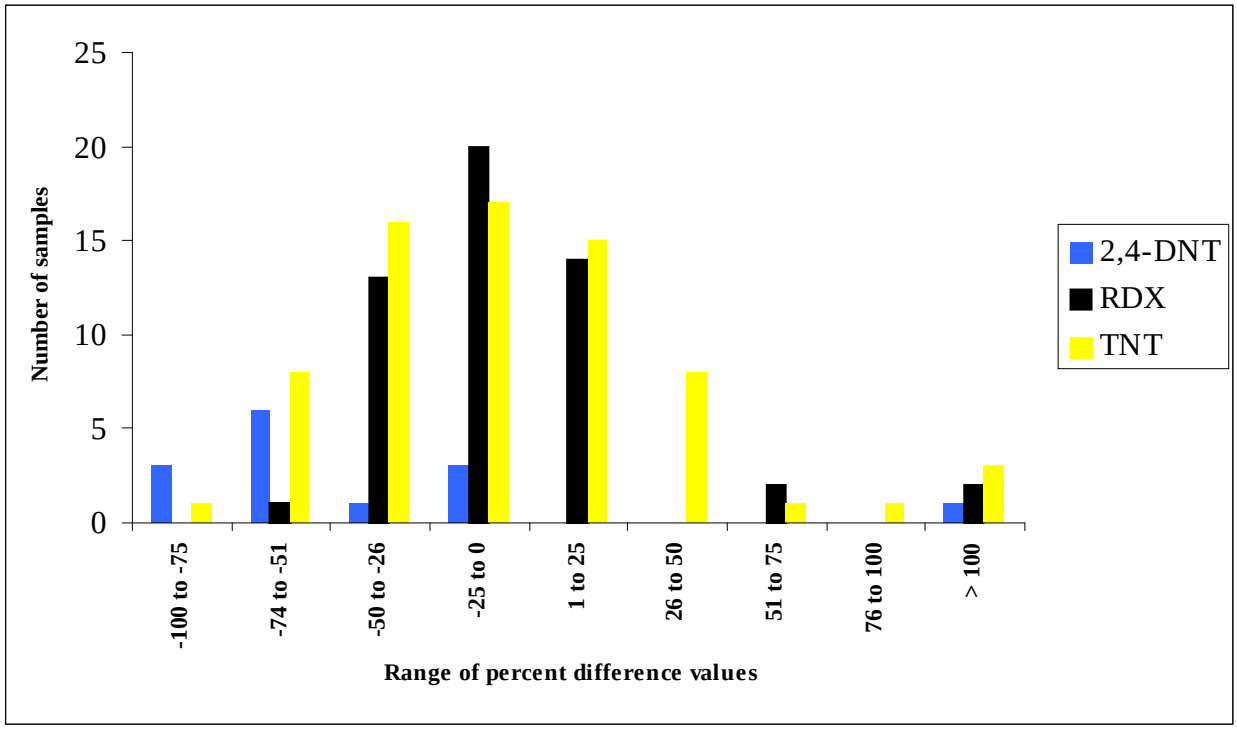

Figure 4. Range of percent difference values for 2,4-DNT, RDX, and TNT.

the range of costs for analysis of explosives-contaminated soil samples using the GC/TID and a conventional analytical reference laboratory method. The analysis was based on the results and experience gained from this verification test, costs are provided by SRI, and representative costs provided by the reference analytical laboratories that offered to analyze these samples. To account for the variability in cost data and assumptions, the economic analysis is presented as a list of cost elements and a range of costs for sample analysis by the GC/TID instrument and by the reference laboratory.

Several factors affected the cost of analysis. Where possible, these factors were addressed so that decision makers can complete a site-specific economic analysis to suit their needs. The following categories are considered in the estimate:

- sample shipment costs,
- labor costs, and
- equipment costs.

Each of these cost factors is defined and discussed and serves as the basis for the estimated cost ranges presented in Table 10. This analysis assumed that the individuals performing the analyses are fully trained to operate the technology. Costs for sample acquisition and preanalytical sample preparation, which are tasks common to both methods, were not included in this assessment.

GC/TID Costs

The costs associated with using the GC/TID instrument included labor, equipment, and waste disposal costs. No sample shipment charges were associated with the cost of operating the instrument because the samples were analyzed on-site.

Labor

Labor costs included mobilization/demobilization, travel, per diem expenses and on-site labor.

- *Mobilization/demobilization*. This cost element included the time for one person to prepare for and travel to each site. This estimate ranged from 0 (if the analyst was on-site) to 5 h, at a rate of $50/h.
- *Travel*. This element was the cost for the analyst(s) to travel to the site. If the analyst is located at the site, the cost of commuting to the site would be zero. The estimated cost of an analyst traveling to the site for this verification test ($1000) included the cost of airline travel and rental car fees.
- *Per diem expenses*. This cost element included food, lodging, and incidental expenses. The estimate ranged from zero (for a local site) to

Table 10. Estimated Analytical Costs for Explosives-Contaminated Samples

Analysis method: GC/TID **Analyst/manufacturer:** SRI Instruments **Sample throughput:** 3 samples/h		**Analysis method:** EPA SW-486 Method 8330 **Analyst/manufacturer:** Reference laboratory **Typical turnaround:** 21 working days	
Cost category	**Cost ($)**	**Cost category**	**Cost ($)**
Sample shipment	0	**Sample shipment**	
		Labor	100–200
		Overnight shipping	50–150
Labor		**Labor**	
Mobilization/demobilization	0–250	Mobilization/demobilization	Included [a]
Travel	0–1,000 per analyst	Travel	Included
Per diem expenses	0–150/day per analyst	Per diem expenses	Included
Rate	30–75/h per analyst	Rate	150–188 per sample
Equipment		**Equipment**	Included
Mobilization/demobilization	0–150		
Instrument purchase price	8,995		
Reagents/supplies	variable		

[a] "Included" indicates that the cost is included in the labor rate.

$150/day for each analyst.

- *Rate*. The cost of the on-site labor was estimated at a rate of $30–75/h, depending on the required expertise level of the analyst. This cost element included the labor involved with the entire analytical process, comprising sample preparation, sample management, analysis, and reporting.

Equipment

Equipment costs included mobilization/demobilization, rental fees or purchase of equipment, and the reagents and other consumable supplies necessary to complete the analysis.

- *Mobilization/demobilization*. This included the cost of shipping the equipment to the test site. If the site is local, the cost would be zero. For this verification test, the cost of shipping equipment and supplies was estimated at $150.
- *Instrument purchase*. At the time of the verification test, the SRI Model 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 $8,995. It comes with a reusable plastic shipping container that allows the GC to ship via overnight express services, and even meets the size and weight limits for airline baggage. As with any instrument, the cost on a per-sample basis would decrease as the number of analyses performed increases. The instrument can also be rented from SRI for $67.46 per day (12-day minimum) or $1799 per month. With the purchase of an instrument, SRI offers one-half day training at their Torrance, California facility on the functional aspects of the instrument. If the operator requires additional training in basic gas chromatography, SRI has a list of recommendations of qualified people in their manual.
- *Reagents/supplies*. These items are consumable and are purchased on a per sample basis.

Reference Laboratory Costs

Sample Shipment

Sample shipment costs to the reference laboratory included the overnight shipping charges, as well as labor charges associated with the various organizations involved in the shipping process.

- *Labor*. This cost element included all of the tasks associated with the shipment of the samples to the reference laboratory. Tasks included packing the shipping coolers,

completing the chain-of-custody documentation, and completing the shipping forms. The estimate to complete this task ranged from 2 to 4 h at $50/h.

- *Overnight shipping*. The overnight express shipping service cost was estimated to be $50 for one 50-lb cooler of samples.

Labor and Equipment

The labor bids from commercial analytical reference laboratories that offered to perform the reference analysis for this verification test ranged from $150 to $188 per sample. The bid was dependent on many factors, including the perceived difficulty of the sample matrix, the current workload of the laboratory, and the competitiveness of the market. This rate was a fully loaded analytical cost that included equipment, labor, waste disposal, and report preparation.

Cost Assessment Summary

An overall cost estimate for use of the GC/TID instrument versus use of the reference laboratory was not made because of the extent of variation in the different cost factors, as outlined in Table 10. The overall costs for the application of any technology would be based on the number of samples requiring analysis, the sample type, and the site location and characteristics. Decision-making factors, such as turnaround time for results, must also be weighed against the cost estimate to determine the value of the field technology's providing immediate answers versus the reference laboratory's provision of reporting data within 30 days of receipt of samples.

Miscellaneous Factors

The following are general observations regarding the field operation and performance of the GC/TID instrument:

- The system, which weighs approximately 75 lb, was transportable by one person. The instrument comes with a plastic carrying case that can be used to ship the instrument or be checked as baggage on an airplane.
- The instrument appeared to be rugged, as the analysts were able to run the instrument during a late afternoon storm that had strong winds.
- The SRI team completely disassembled their work station at the close of each day. It took the team less than an hour each morning to prepare for sample analyses.
- The instrument required 110 V of electrical power for operation.
- The SRI team employed a colorimetric method to screen samples for high concentration of TNT and related nitroaromatic compounds. This undoubtedly prevented unnecessary overloading of the instrument and potential downtime.
- Sample preparation, including extraction, colorimetric screening, and dilutions was completed for all 108 samples in 18 h of labor by one analyst (approximately 10 min per sample).
- Other SW-846 Method 8330 analytes (e.g., trinitrobenzene, tetryl, HMX) could potentially be determined by this method, but this was not verified in this study.
- Hazardous waste generated during the test included the following, which was classified as RCRA waste: 0.2 L of vials with acetone and trace explosives; 0.5 L of syringe filters with spent acetone and trace explosives; 0.3 L of acetone used for rinsing; and 4.3 L of acetone and soil mixtures.

Summary of Performance

A summary of performance is presented in Table 11. Precision, defined as the mean RSD, was 15%, 14%, and 23% for 2,4-DNT, RDX, and TNT soil sample results, respectively. Accuracy, defined as the mean percent recovery relative to the spiked concentration, was 91% and 97% for RDX and TNT soil sample results, respectively, indicating that the soil results were unbiased. Of the 20 blank soil samples, SRI reported TNT in five samples (25% false positives); no false positives were reported for 2,4-DNT or RDX . Additionally, false positive and false negative results were determined by comparing the GC/TID result to the reference laboratory result for the environmental and spiked samples. None of the RDX results were reported as false positives, but 3% of the 2,4-DNT and 7% of the TNT results were, relative to the reference laboratory results. A low percentage of results were also found to be false negatives (0% for 2,4-DNT, 2% for RDX, and 4% for TNT). The SRI results were comparable to the reference laboratory results, with r values of 0.85 and 0.95 for RDX and TNT, respectively.

The verification test found that the GC/TID instrument was relatively simple for a trained analyst to operate in the field, requiring less than an hour for initial setup. The sample throughput of the GC/TID was three samples per hour. Two operators analyzed samples during the verification test, but the technology can be run by a single trained operator. The overall performance of the GC/TID for the analysis of 2,4-DNT, RDX, and TNT was characterized as unbiased and precise for soil analyses.

Table 11. Performance Summary for the GC/TID

Feature/Parameter	Performance summary				
Precision	**Mean RSD**				
	2,4-DNT:	15%			
	RDX:	14%			
	TNT:	23%			
Accuracy	**Mean recovery**				
	RDX:	91%			
	TNT:	97%			
False positive results on blank samples	2,4-DNT:	none			
	RDX:	none			
	TNT:	25%			
False positive results relative to reference laboratory results	2,4-DNT:	3%			
	RDX:	none			
	TNT:	7%			
False negative results relative to reference laboratory results	2,4-DNT:	none			
	RDX:	2%			
	TNT:	4%			
Comparison with reference laboratory results (all data, excluding suspect values)		**Correlation coefficient**	**Slope**	**Absolute median percent difference**	**Range of percent difference**
	2,4-DNT:	0.44	0.33	66%	–83% to 216%
	RDX:	0.96	0.86	19%	–51% to 275%
	TNT:	0.95	1.32	28%	–85% to 475%
Completeness	100% of 108 soil samples				
Weight	75 lb				
Sample throughput (2 operators)	3 samples per hour				
Power requirements	110 V				
Training requirements	One-half day instrument-specific training				
Cost	Instrument: $8,995				

Section 6 — Representative Applications

In this section, the vendor (with minimal editorial changes by ORNL) provides a list of representative applications in which its technology has been used.

The SRI Model 8610C GC/TID has been used on-site for the analysis of soil samples contaminated with explosives that have been obtained from locations used for the open burning and open detonation (OB/OD) of obsolete munitions and from a land mine test facility. The GC/TID analysis of soil samples taken from the OB/OD sites established the presence of nitroaromatic, nitramine, and nitrate ester explosive compounds. Reanalysis of the soil sample extracts from the OB/OD sites by EPA SW-846 Method 8095 (EPA 1999) confirmed the on-site GC/TID concentrations established for TNB, TNT, and RDX, and qualitatively confirmed the presence of nitroglycerin (NG) and pentaerythritol tetranitrate (PETN); these two compounds were not present in the field calibration standards.

To detect explosive residues around buried land mines the GC/TID was optimized for the analysis of 2,4-DNT, TNT, 2-Am-DNT at concentrations between 0.005 and 0.1 mg/kg, and for 4-Am-DNT at concentrations between 0.05 and 0.5 mg/kg. Most of the land mines at this test facility contained TNT as the main charge. This on-site capability made it possible to establish whether these four explosives were present in surface soil samples taken above the land mines. For a couple of mines where mg/kg levels of explosive residues were detected, an extensive, iterative sampling protocol was performed to delineate the surface boundaries of the explosive-related chemical signature. The reanalysis of soil sample extracts from this mine-field site by Method 8095 confirmed the on-site GC/TID results for these explosive compounds.

Additional applications using the GC/TID instrument have been (1) to analyze explosive vapors collected on solid phase microextraction fibers after thermal desorption in the heated inlet, and (2) to characterize explosive residues on range scrap following wipe sampling or solvent immersion.

Section 7 — References

ASTM (American Society for Testing and Materials). 1997a. *Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Quality Assurance and Quality Control Planning and Implementation,* D5283-92.

ASTM (American Society for Testing and Materials). 1997b. *Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives,* D5792-95.

Berger, W., H. McCarty, and R-K. Smith. 1996. *Environmental Laboratory Data Evaluation.* Genium Publishing Corp., Schenectady, N.Y.

Draper, N. R., and H. Smith. 1981. *Applied Regression Analysis.* 2nd ed. John Wiley & Sons, N.Y.

EPA (U.S. Environmental Protection Agency). 1994. "Method 8330: Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)." In *Test Methods for Evaluating Solid Waste: Physical/ Chemical Methods, Update II.* SW-846. U.S. Environmental Protection Agency, Washington, D.C., September.

EPA (U.S. Environmental Protection Agency). 1996. *Guidance for Data Quality Assessment,* EPA QA/G-9; EPA/600/R-96/084, EPA, Washington, D.C., July.

EPA (U.S. Environmental Protection Agency). 1999. "Method 8095: Nitroaromatics and Nitramines by GC-ECD." In *Test Methods for Evaluating Solid Waste: Physical/ Chemical Methods, Update II.* SW-846. U.S. Environmental Protection Agency, Washington, D.C..

Jenkins, T. F., M. E. Walsh, and P. G. Thorne. 1998. *Site Characterization for Explosives Contamination at a Military Firing Range Impact Area.* Special Report 98-9. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H. Available at http://www.crrel.usace.army.mil/.

Maskarinec, M. P., C. K. Bayne, L. H. Johnson, S. K. Holladay, R. A. Jenkins, and B. A. Tomkins. 1991. *Stability of Explosives in Environmental Water and Soil Samples.* ORNL/TM-11770. Oak Ridge National Laboratory, Oak Ridge, Tenn., January.

ORNL (Oak Ridge National Laboratory). 1999. *Technology Demonstration Plan: Evaluation of Explosives Field Analytical Techniques.* Oak Ridge National Laboratory, Oak Ridge, Tenn., August.

ORNL (Oak Ridge National Laboratory). 2000. *Technology Verification Test Plan: Evaluation of Explosives Field Analytical Techniques.* Oak Ridge National Laboratory, Oak Ridge, Tenn., August.

Specialized Assays, Inc. 1999. *Comprehensive Quality Assurance Plan.* SAL-QC-Rec 5.0. January 6.

Appendix A

GC/TID Sample Results Compared with Reference Laboratory Results

Sample site or type	Sample no.	Sample replicate	2,4-DNT (mg/kg)		RDX (mg/kg)		TNT (mg/kg)		SRI Analysis Order [a]
			SRI	Ref Lab	SRI	Ref Lab	SRI	Ref Lab	
Blank	1	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1079
Blank	1	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1076
Blank	1	3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1062
Blank	1	4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1078
Blank	2	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1070
Blank	2	2	<0.5	<51	<0.5	<51	<0.5	70900.0	1108
Blank	2	3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1038
Blank	2	4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1054
Blank	3	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1043
Blank	3	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1052
Blank	3	3	<0.5	<0.5	<0.5	<0.5	1.1	<0.5	1008
Blank	3	4	<0.5	<0.5	<0.5	<0.5	0.5	<0.5	1102
Blank	4	1	<0.5	<0.5	<0.5	<0.5	<0.5	0.9	1024
Blank	4	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1018
Blank	4	3	<0.5	<0.5	<0.5	<0.5	0.7	<0.5	1101
Blank	4	4	<0.5	<0.5	<0.5	<0.5	0.5	<0.5	1022
Blank	5	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1088
Blank	5	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1046
Blank	5	3	<0.5	<0.5	<0.5	<0.5	6.3	<0.5	1006
Blank	5	4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1053
Fort Ord	1	1	<0.5	<0.5	<0.5	0.6	<0.5	<0.5	1050
Fort Ord	1	2	<0.5	<0.5	<0.5	<0.5	<0.5	0.8	1073
Fort Ord	1	3	<0.5	<0.5	<0.5	<0.5	<0.5	0.8	1092
Fort Ord	1	4	<0.5	<0.5	<0.5	0.5	<0.5	<0.5	1013
Fort Ord	2	1	<0.5	<0.5	<0.5	<0.5	0.6	0.8	1034
Fort Ord	2	2	<0.5	<0.5	<0.5	<0.5	<0.5	2.1	1031
Fort Ord	2	3	<0.5	<0.5	<0.5	<0.5	3.0	0.8	1098
Fort Ord	2	4	<0.5	<0.5	<0.5	<0.5	0.5	0.8	1067
Fort Ord	3	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1026
Fort Ord	3	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1084
Fort Ord	3	3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1066
Fort Ord	3	4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1030
Iowa	1	1	11.0	<51	<50	<51	21000.0	20400.0	1077
Iowa	1	2	<500	<0.5	<500	<0.5	31000.0	0.8	1003
Iowa	1	3	18.0	<532	<50	<532	23000.0	33400.0	1021
Iowa	1	4	10.0	<50.5	<50	<50.5	22000.0	28300.0	1023

Sample site or type	Sample no.	Sample replicate	2,4-DNT (mg/kg)		RDX (mg/kg)		TNT (mg/kg)		SRI Analysis Order [a]
			SRI	Ref Lab	SRI	Ref Lab	SRI	Ref Lab	
Louisiana	1	1	<0.5	<0.5	2500.0	3460.0	150.0	109.0	1107
Louisiana	1	2	<50.0	<0.5	2400.0	3520.0	120.0	120.0	1090
Louisiana	1	3	<50.0	<0.5	2300.0	2140.0	120.0	111.0	1100
Louisiana	1	4	<5.0	<25.0	2200.0	1900.0	99.0	125.0	1025
Louisiana	2	1	<5	<0.5	1400.0	1180.0	66.0	50.0	1010
Louisiana	2	2	<5	<0.5	1100.0	1450.0	76.0	51.0	1027
Louisiana	2	3	<5	<0.5	1300.0	1170.0	61.0	51.0	1029
Louisiana	2	4	<5	<0.5	1200.0	320.0	63.0	10.6	1012
Louisiana	3	1	<50	<0.5	4800.0	4300.0	81.0	205.0	1082
Louisiana	3	2	<50	<50	3500.0	3550.0	89.0	170.0	1041
Louisiana	3	3	5.5	<50	3400.0	4650.0	45.0	300.0	1055
Louisiana	3	4	<5	<0.5	4000.0	5850.0	150.0	400.0	1037
Louisiana	4	1	14.0	80.0	6.1	12.0	80.0	89.0	1081
Louisiana	4	2	8.8	11.4	7.1	10.7	84.0	78.0	1007
Louisiana	4	3	8.5	11.9	6.9	10.8	82.0	81.5	1056
Louisiana	4	4	7.2	9.5	4.6	7.7	73.0	67.5	1087
Milan	1	1	<0.5	<0.5	110.0	149.0	3.3	2.7	1097
Milan	1	2	<0.5	<0.5	130.0	118.0	9.3	1.1	1019
Milan	1	3	<0.5	<0.5	110.0	72.2	0.9	1.4	1083
Milan	1	4	<0.5	<0.5	150.0	308.0	1.1	1.7	1039
Milan	2	1	<0.5	<0.5	22.0	34.8	<0.5	<0.5	1014
Milan	2	2	<0.5	<0.5	20.0	16.4	<0.5	<0.5	1074
Milan	2	3	<0.5	<0.5	26.0	28.0	<0.5	<0.5	1064
Milan	2	4	<0.5	<0.5	18.0	22.9	<0.5	<0.5	1072
Milan	3	1	<50	<0.5	7900.0	2350.0	260.0	190.0	1069
Milan	3	2	<50	<50	3400.0	1950.0	82.0	270.0	1065
Milan	3	3	<50	<200	4100.0	4080.0	300.0	320.0	1016
Milan	3	4	<50	<0.5	3800.0	3880.0	110.0	273.0	1033
Milan	4	1	<5	<50	2500.0	2740.0	110.0	220.0	1086
Milan	4	2	<50	<0.5	2500.0	2640.0	68.0	260.0	1028
Milan	4	3	<50	<0.5	2100.0	2600.0	45.0	80.0	1036
Milan	4	4	<50	<0.5	2700.0	3070.0	80.0	162.0	1005
Milan	5	1	0.7	2.1	<0.5	<0.5	7.7	11.5	1048
Milan	5	2	0.6	2.7	<0.5	<0.5	7.3	10.2	1047
Milan	5	3	0.7	1.7	<0.5	<0.5	7.1	11.3	1060
Milan	5	4	0.6	1.6	<0.5	<0.5	6.8	10.6	1059
Spike/PE	1	1	<0.5	<0.5	<0.5	<0.5	87.0	81.8	1103
Spike/PE	1	2	<0.5	<0.5	<0.5	<0.5	87.0	104.0	1044
Spike/PE	1	3	<0.5	<0.5	<0.5	<0.5	92.0	90.0	1095
Spike/PE	1	4	<0.5	<0.5	<0.5	<0.5	92.0	124.0	1094

Sample site or type	Sample no.	Sample replicate	2,4-DNT (mg/kg)		RDX (mg/kg)		TNT (mg/kg)		SRI Analysis Order [a]
			SRI	Ref Lab	SRI	Ref Lab	SRI	Ref Lab	
Spike/PE	2	1	<0.5	<0.5	84.0	111.0	<0.5	<0.5	1105
Spike/PE	2	2	<0.5	<0.5	76.0	90.5	<0.5	<0.5	1057
Spike/PE	2	3	<0.5	<0.5	88.0	98.0	2.4	<0.5	1020
Spike/PE	2	4	<0.5	<0.5	74.0	127.0	<0.5	<0.5	1063
Spike/PE	3	1	<0.5	<0.5	49.0	49.5	11.0	8.4	1049
Spike/PE	3	2	<0.5	<0.5	56.0	45.0	10.0	7.6	1001
Spike/PE	3	3	<0.5	<0.5	47.0	63.5	9.9	10.0	1058
Spike/PE	3	4	<0.5	<0.5	46.0	51.0	10.0	8.5	1061
Spike/PE	4	1	<0.5	<0.5	7.6	9.1	45.0	47.5	1104
Spike/PE	4	2	<0.5	<0.5	9.7	8.4	50.0	48.5	1096
Spike/PE	4	3	<0.5	<0.5	8.9	8.6	45.0	48.5	1071
Spike/PE	4	4	<0.5	<0.5	8.7	9.1	48.0	47.0	1106
Spike/PE	5	1	<0.5	<0.5	440.0	460.0	260.0	230.0	1068
Spike/PE	5	2	<5	<0.5	490.0	455.0	240.0	205.0	1004
Spike/PE	5	3	<5	<0.5	490.0	705.0	260.0	435.0	1075
Spike/PE	5	4	<0.5	<0.5	450.0	445.0	260.0	205.0	1045
Spike/PE	6	1	<5	<0.5	210.0	260.0	480.0	535.0	1099
Spike/PE	6	2	<5	<25	220.0	255.0	480.0	505.0	1042
Spike/PE	6	3	<5	<0.5	230.0	335.0	480.0	675.0	1093
Spike/PE	6	4	<0.5	<0.5	270.0	250.0	500.0	510.0	1017
Volunteer	1	1	<500	<50	<500	<50	190000.0	108000.0	1002
Volunteer	1	2	59.0	<25	<50	<25	110000.0	75500.0	1091
Volunteer	1	3	60.0	19.0	<50	<5	110000.0	117000.0	1089
Volunteer	1	4	67.0	<250	<50	<250	94000.0	61000.0	1015
Volunteer	2	1	30.0	<53.2	<50	<53.2	9000.0	11300.0	1085
Volunteer	2	2	29.0	<538	<50	<538	6200.0	12600.0	1051
Volunteer	2	3	35.0	<5.4	<50	6.5	8300.0	26200.0	1011
Volunteer	2	4	34.0	45.2	<50	<5.4	9400.0	8920.0	1009
Volunteer	3	1	0.7	2.0	<0.5	<0.5	9.9	12.0	1035
Volunteer	3	2	0.7	3.0	<0.5	<0.5	8.0	10.3	1032
Volunteer	3	3	0.6	2.2	<0.5	<0.5	7.7	13.8	1040
Volunteer	3	4	0.6	2.2	<0.5	<0.5	7.7	10.4	1080

[a]Indicates order of analysis by SRI; for example, 1001 was analyzed first, then 1002, etc.

Appendix B

Data Quality Objective (DQO) Example

Disclaimer

The following hypothetical example serves to demonstrate how the information provided in this report may be used in the data quality objectives (DQO) process. This example serves to illustrate the application of quantitative DQOs to a decision process, but it cannot attempt to provide a thorough education in this topic (EPA 1996, ASTM 1997a, ASTM 1997b). Please refer to other educational or technical resources for further details. Additionally, because the focus of this report is on the analytical technology, this example makes simplifying assumptions (such as the sample is homogeneous and the reference laboratory results represent the true concentration) in the example that may not be valid in the real world.

Background and Problem Statement

An Army Ammunition Plant that produced TNT was recently decommissioned. Past practices had resulted in contamination of four areas around the plant. Soils at each site were mixtures of clay, silt, and organic matter with initial concentrations of about 1500 mg/kg of TNT. Forty cubic yards of TNT-contaminated soil were loaded into a bioreactor. After three months of processing, the soil mixture was dewatered and put into drums. The simplifying assumption was made that the soil in each drum was homogeneous based on process knowledge. In agreement with regulators, the treatment goal established for the site was to reduce the soil concentration to <15 mg/kg of TNT. Soil with <15 mg/kg of TNT would be returned to the four areas around the plant. Those drums containing soil with TNT concentrations ≥15 mg/kg would be stored for additional processing (i.e., incineration).

The company's DQO team considered using SRI Instruments' Model 8610C gas chromatograph (GC) to measure the TNT concentration in each drum, based on the data generated in the ETV verification study. The SRI Model 8610C GC is an on-site gas chromatograph equipped with a thermionic ionization detector that allows for the determination of explosives in a soil matrix. The plan was to randomly select soil samples from each drum and determine the TNT concentration with the SRI Model 8610C GC. The DQO team decided that drums will be disposed by incineration if the TNT concentration is ≥15 mg/kg ("hot"). Those drums with TNT concentrations <15 mg/kg will be put into a landfill because incineration of TNT-contaminated soil is very expensive. With regulator agreement, the DQO Team determined that a decision rule for disposal would be based on the average concentration of TNT in each drum.

General Decision Rule

If the average TNT concentration is less than the action level, then the TNT drums are sent to the landfill.

If the average TNT concentration is greater than or equal to the action level, then the TNT drum is sent to the incinerator.

DQO Goals

The DQO team's primary goal was to calculate how many samples would need to be analyzed by the SRI Model 8610C GC in order to confidently make a decision about remediating the processed soil, given the uncertainties of the technology's results. Because the team decided that inadvertently sending soil to a landfill that exceeded 15 mg/kg of TNT was the worst possible mistake, the number of samples measured is primarily related to this false-rejection decision error rate. A secondary decision error would be to

unnecessarily incinerate soil with TNT concentrations <15 mg/kg. This decision would be a false-acceptance decision error. Consideration of both the false-rejection decision error and the false-acceptance decision error was used to determine the final sampling plan.

EPA required that a sufficient number of samples be measured from each drum so that the false-rejection error rate (FR) for the decision rule was 0.05 or less if the true soil concentration in a drum was 15 mg/kg or greater. This DQO goal represents a 5% chance of returning a drum with soil containing 15 mg/kg or more of TNT to a landfill.

The DQO team did not want to incinerate an excessive number of drums if a drum's TNT soil concentration was <5 mg/kg because of the expense. Therefore, the DQO team recommended that the false-acceptance error rate (FA) for the decision rule be 0.10 if the true drum concentration was less than 5 mg/kg. That is, there would be a 10% chance of incinerating a drum if the true TNT concentration for a drum was <5 mg/kg.

Permissible FR and FA Error Rates and Critical Decision Points

FR: Pr[take drum to landfill] $\leq$ 0.05 when true TNT concentration = 15 mg/kg

FA: Pr[take drum to incinerator] $\leq$ 0.10 when true TNT concentration = 5 mg/kg

Use of Technology Performance Information to Implement the Decision Rule

Technology performance information is used to evaluate whether a particular analytical technology can produce data of sufficient quality to support the site decision. Because the DQO team is considering the use of the SRI Model 8610C GC, the performance of this technology (as reported in this ETV report) was used to assess its applicability to this project. Two questions arise.

1. How many samples are needed from a single drum to permit a valid estimate of the true average concentration of TNT in the drum to the specified certainty? Recall that the simplifying assumption was made that the TNT distribution throughout the soil within a single drum is homogeneous; thus, matrix heterogeneity will not contribute to overall variability. The only variability, then, to be considered in this example is the variability in the SRI Model 8610C GC's analytical method, which is determined by precision studies.

2. What is the appropriate action level (AL) for using the SRI Model 8610C GC to make decisions in the field? After the required number of samples have been collected from a drum and analyzed, the results are averaged together to get an estimate of the "true" TNT concentration of the drum. When using the SRI Model 8610C GC, what is the value (here called "the action level for the decision rule") to which that average is compared to decide if the drum is "hot" or not? This method-specific or site-specific action level is derived from evaluations of the method's accuracy using an appropriate quality control regimen.

Determining the Number of Samples

With the critical decision points selected, the DQO team could then determine the number of samples needed from each drum to calculate the drum's "true" average TNT concentration. For a homogeneous matrix, the number of samples required depends on the precision of the analytical method.

Figure B-1 shows that the standard deviations for the SRI Model 8610C GC versus the average TNT concentration for the reference laboratory. Although the fitted line increases with average TNT

concentration, the linear model is not significantly different than a constant standard deviation over the 0 to 50 mg/kg concentration range. Therefore, the precision of the SRI Model 8610C GC can be represented by a pooled standard deviation of 3.1 mg/kg within the concentration range of 0 to 60 mg/kg (see Figure B-1). Note that the pooled standard deviation is calculated by first calculating the average variance then taking the square root. This estimate of analytical variability (precision) is used to calculate the number of soil samples required to be analyzed from each drum to achieve the DQOs as determined in the DQO Goals. The following formula is provided in EPA's *Guidance for Data Quality Assessment* (EPA 1996) that can be adapted to this example for calculating the number of samples required to meet the FR and FA requirements:

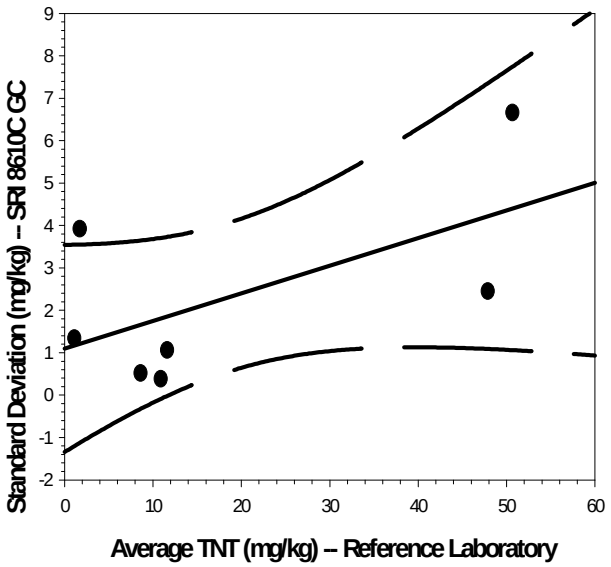

Figure B-1. Linear model for the standard deviation for SRI Model 8610C GC versus average TNT (mg/kg) result for the reference laboratory with 95% confidence intervals (dashed lines).

$$n = \frac{S^2 \left(Z_{1-FR} + Z_{1-FA} \right)^2}{\left(RT - C_{FA} \right)^2} + (0.5) Z_{1-FR}^2 \qquad \text{(Eq. B-1)}$$

where

- n = number of samples from a drum to be measured,
- S^2 = variance for the measurement [e.g., $S^2 = (3.1)^2$],
- RT = regulatory threshold (e.g., RT = 15 mg/kg),
- C_{FA} = concentration at which the FA is specified (e.g., C_{FA} = 5 mg/kg),
- FR = false-rejection decision error rate (e.g., FR = 0.05),
- FA = false-acceptance decision error rate (e.g., FA = 0.10),
- Z_{1-p} = $(1\text{-p})^{th}$ percentile of the standard normal distribution (see EPA 1996, Table A-1 of Appendix A). Example: $Z(1\text{-}_{FR}) = Z_{0.95} = 1.645$ and $Z_{(1-FA)} = Z_{0.90} = 1.282$.

$$n = \frac{(3.1)^2 \left(1.645 + 1.282 \right)^2}{(15 - 5)^2} + (0.5)(1.645)^2 = 2.18 \approx 3 \quad .$$

Therefore, three soil samples from each drum would be analyzed by SRI Model 8610C GC to meet the criteria established by the DQO process. To be conservative, the number of samples was rounded up to the next integer. The TNT results from the three samples are averaged (by taking the arithmetic mean) to produce an SRI Model 8610C GC value for a drum's TNT concentration.

Determining the Action Level

Now that the number of samples that need to be analyzed from each drum to meet the DQO goals has been determined, the action level can be calculated. The action level is the decision criterion (or "cut-off" value) that will be compared to the unbiased average TNT concentration determined for each drum. The AL for the

decision rule is calculated based on controlling the FR established in the DQO process. Recall that the DQO team set the permissible FR error rate at 5%.

The formula (EPA 1996) to compute the action level is

$$AL = RT - Z_{1-FR} \times \frac{S}{\sqrt{n}} \qquad \text{(Eq. B-2)}$$

$$AL = 15\,ppm - (1.645) \times \frac{3.1}{\sqrt{3}} = 12.1\,mg/kg \quad .$$

To summarize, three random samples from each drum are analyzed.. The three results are averaged to produce the average TNT concentration for the drum, which is then compared to the action level (i.e., AL = 12.1 mg/kg) for the decision rule. Therefore, the decision rule using the SRI Model 8610C GC to satisfy a 5% FR and a 10% FA is as follows:

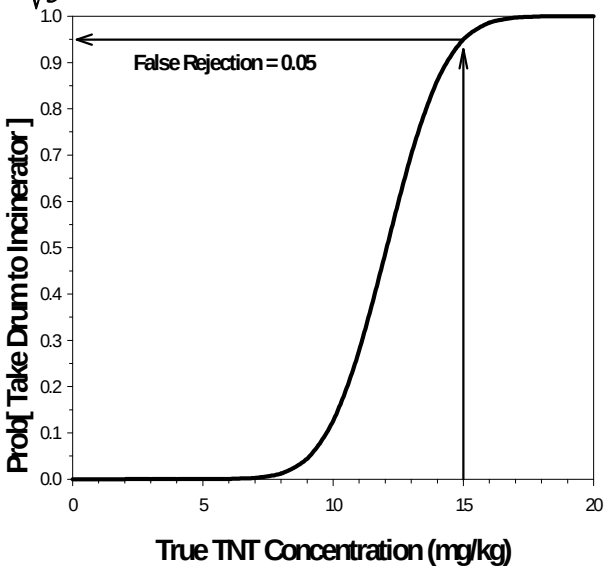

Figure B-2. Decision performance curve to TNT drum example.

Decision Rule for FR = 5% and FA = 10%

If the average TNT concentration of three random soil samples on a drum is <12.1 mg/kg, then send the drum to the landfill.

If the average TNT concentration of three random soil samples on a drum is ≥12.1 mg/kg, then send the drum to the incinerator.

The decision performance curve (for more information, see EPA 1996, pp. 34–36) calculates the probability of sending a drum to the incinerator for different values of true TNT soil concentration in a drum. Figure B-2 shows that the decision performance curve has the value of Pr[take drum to incinerator] = 0.95 for true = 15 mg/kg. This indicates that the decision rule meets the DQO team's FR of 5%. The actual Pr[take drum to incinerator] = 0.00004 for a true TNT concentration = 5 mg/kg, which is better than the FA of 10% that the DQO team had originally specified. This improved performance is due to rounding up the number of samples to the next integer in the calculation of number of samples required.

Alternative FR Parameter

Because of random sampling and analysis error, some chance always exists that analytical results will not accurately reflect the true nature of a decision unit (such as a drum, in this example). Often, 95% certainty (a 5% FR) is customary and sufficient to meet stakeholder comfort. But suppose that the DQO team wanted to be even more cautious about limiting the possibility that a drum might be sent to a landfill when its true value is 15 mg/kg. If the DQO team wanted to be 99% certain that a drum was correctly sent to a landfill, the

following describes how changing the FR requirement from 5% to 1% would affect the decision rule. Using FR = 0.01, the sample size is calculated to be four and the action level is calculated as 11.4 mg/kg. The decision performance curve has the value of Pr[take drum to incinerator] = 0.99 for true = 15 mg/kg. This indicates that the decision rule meets the DQO team's FR of 1%. The Pr[take drum to incinerator] = 0.00002 for true = 5 mg/kg is better than the FA of 10% that the DQO team had specified. This improved performance is due to rounding up the number of samples to the next integer in the calculation of number of samples required. The decision rule for the lower FR would be as follows:

Decision Rule for FR = 1% and FA = 10%

If the average TNT concentration of four random soil samples on a drum is <11.4 mg/kg, then send the drum to the landfill.

If the average TNT concentration of four random soil samples on a drum is ≥11.4 mg/kg, then send the drum to the incinerator.

Comparison to Sending the Samples Off-Site for Analysis

The DQO team wanted to compare the sampling plan using the SRI Model 8610C GC field measurements with a sampling plan using an off-site reference laboratory. For the off-site reference laboratory, the DQO team assumed a precision of SD = 0.9 mg/kg based on the ETV reference laboratory values. They also specified that the FA percentage would be at a TNT concentration of 10 mg/kg because the reference laboratory measurements are more precise. This specification means that there is only a 10% chance of sending a drum to the incinerator if the true TNT concentration in the drum is 10 mg/kg. A formula provided in EPA's *Guidance for Data Quality Assessment* (EPA 1996) shows that the number would be $n = 2$ for the 5% FR percentage and 10% FA percentage. The decision rule would be to take two randomly selected samples and send them to the reference laboratory for analysis. If the average TNT concentration is less than an action level of 14.0 mg/kg, restore the soil to the plant site; otherwise, send the soil drum to storage. In this example, the off-site laboratory appears to require fewer samples to be analyzed (two for the off-site laboratory versus three for the SRI Model 8610C GC). Other factors (such as a cost-benefit analysis, ability to detect other analytes) would need to be considered before choosing a method for this application.