SAMPLING AND ANALYSIS PLAN ADDENDUM FOR THE INTERIM REMOVAL ACTION AT LOAD LINE 11 (AOC 44)

RAVENNA ARMY AMMUNITION PLANT
RAVENNA, OHIO 44266

Prepared for

OPERATIONS COMMAND
AMSIO - ACE- D
Procurement Directorate
Rock Island, IL 61299-6000

Prepared by

MKM ENGINEERS, INC
4153 BLUEBONNET DRIVE
STAFFORD, TEXAS 77477

JANUARY 2001

FINAL
SAMPLING AND ANALYSIS PLAN ADDENDUM

FOR THE

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January 2001

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Part I

Final
Field Sampling Plan Addendum for the Interim Removal Action at Load Line 11 (AOC44) at the Ravenna Army Ammunition Plant, Ravenna, Ohio

January 2001

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DEFINITIONS

Action Plan (AP)	An annual plan submitted by U.S. Army installations showing the status of current and future planned environmental activities at the installations.
Ammatol	A mixture of ammonium nitrate and trinitrotoluene (TNT).
Area of Concern (AOC)	Under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), a site where contamination is known or suspected to exist.
Defense Environmental Restoration Program (DERP)	A program established by Congress in 1984 to evaluate and clean up contamination from past U.S. Department of Defense (DoD) activities (Title 10 U.S. Code 2701-2707 and 2810).
Facility	All contiguous land and structures, other appurtenances, and improvements within the boundaries of a property or parcels.
Facility-Wide	A term used to reference all land and structures comprising a facility.
Facility-Wide Sampling and Analysis Plan (SAP)	A submittal document comprised of the Field Sampling Plan (FSP) and Quality Assurance Project Plan (QAPP); used to define all aspects of sampling and analytical work expected to be common to an installation. Not implementable without an investigation-specific SAP Addendum.
Feasibility Study (FS)	Based on data collected during the remedial investigation, options for final cleanup actions are developed and evaluated in the FS. The FS is divided into two phases: (1) an initial screening of alternatives, followed by (2) the detailed analysis of alternatives. The detailed analysis considers, among other things, cost-effectiveness, short- and long-term effectiveness, and the overall protection of human health and the environment.
Installation	A military facility or base.
Interim Removal Action (IRA)	An early response action that is identified and implemented at any time during the study or design phase. IRAs are limited in scope, and they address only areas or media for which a final remedy will be developed by the remedial investigation (RI)/FS process. An IRA should be consistent with the final remedy for a site.
Investigation-Specific Sampling and Analysis Plan (SAP) Addendum	A submittal document comprised of the FSP and QAPP; used to define specific aspects of sampling and analytical work during the investigation of one or more AOCs. Tiered under the Facility-Wide SAP and not implementable without the Facility-Wide SAP.

Site	An area(s) of known or suspected release or source of contamination including all potentially affected media (soil, groundwater, surface water, sediment, air).
Strategic and Critical Materials	A government phrase referring to substances/ materials essential to the effective conduct of war.

ABBREVIATIONS

A&E	Architect and engineer
AOC	Area of concern
ASTM	American Society for Testing and Materials
BGS	Below ground surface
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COPC	Chemical of potential concern
CRREL	Cold Regions Research and Engineering Laboratory
D&D	Decontamination and decommissioning
DNT	Dinitrotoluene
DQO	Data quality objective
FW SAP	Facility Wide Sample and Analysis Plan
FID	Flame ionization detector
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
ID	Inside diameter
IDW	Investigation-derived waste
IOC	Industrial Operations Command
IR	Industrial Readiness (Command)
MCL	Maximum contaminant level
OE	Ordnance and explosives
OEPA	Ohio Environmental Protection Agency
OVA	Organic vapor analyzer
PAH	Polyaromatic hydrocarbon
PCB	Polychlorinated biphenyl
PID	Photoionization detector
PRG	Preliminary remediation goal
PVC	Polyvinyl chloride
QA	Quality assurance
OHARNG	Ohio Army National Guard
QAPP	Quality Assurance Project Plan
QC	Quality control
RDX	Hexahydro-1,2,5-trinitro-1,3,5-triazine
RI	Remedial investigation
RI/FS	Remedial investigation/feasibility study
RVAAP	Ravenna Army Ammunition Plant
SAIC	Science applications International Corporation
SAP	Sampling and Analysis Plan
SVOC	Semivolatile organic compound

TAL	Target Analyte List
TCLP	Toxicity Characteristic Leaching Procedure
TNB	Trinitrobenzene
TNT	Trinitrotoluene
USACE	U.S. Army Corps of Engineers
USACHPPM	U.S. Army Center for Health Promotion and Preventative Medicine
USEPA	U.S. Environmental Protection Agency
USCS	Unified Soil Classification System
UXO	Unexploded ordnance
VOC	Volatile organic compound

1.0 PROJECT DESCRIPTION

1.1 INTRODUCTION

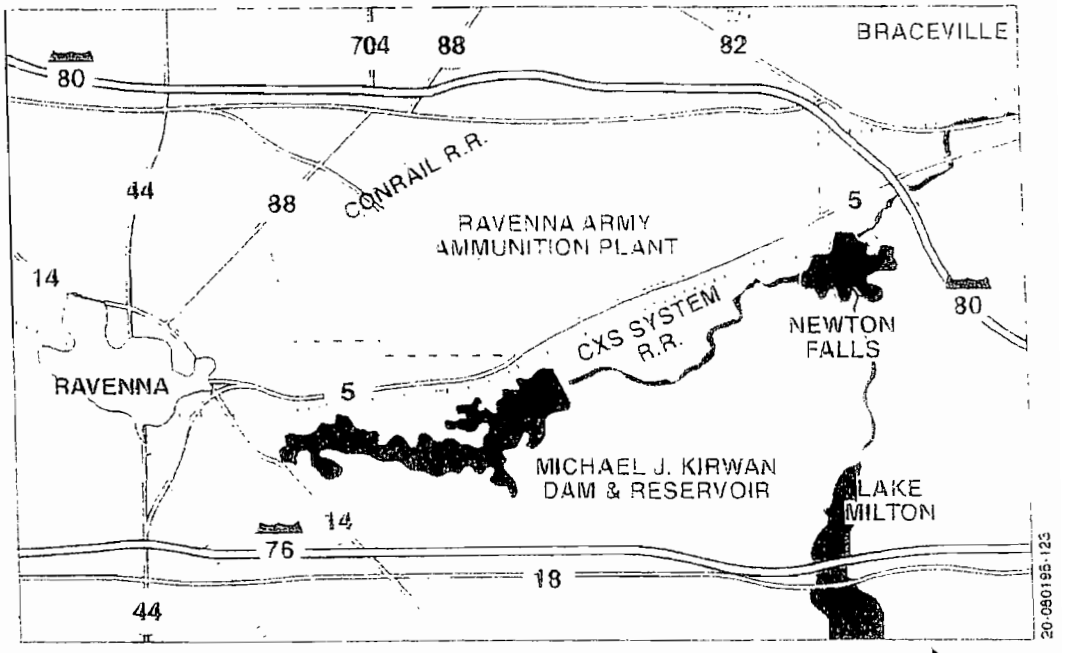
This Sampling and Analysis Plan (SAP) Addendum has been developed under contract number DAAA 09-98-G-0001 with the US Army Operations Support Command (OSC). A scoping meeting, attended by representatives from the OSC, Ravenna Army Ammunition Plant (RVAAP), Ohio Army National Guard (OHANG) and MKM Engineers, Inc. was held at RVAAP during the week of January 10, 2000 to establish the requirements of the Remedial Investigation. Comments were received from the participants during the scoping meeting and have been incorporated into the work plans. This plan is developed to tier under and supplement the Facility-Wide Sampling and Analysis Plan (FWSAP) for the Ravenna Army Ammunition Plant, Ravenna, Ohio (USACE 1996a). The purpose is to perform the Interim Removal Action (IRA), at Load Line 11 (LL-11) (AOC 44). The FWSAP provides the base documentation (i.e., technical and investigative protocols) for conducting investigation under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) at RVAAP, whereas this SAP Addendum includes all of the investigation-specific sampling and analysis objectives, rationale, planned activities, and criteria. Consequently, both documents are necessary in order to perform this remedial investigation. Where appropriate, this SAP Addendum contains references to the FWSAP for base procedures and protocols.

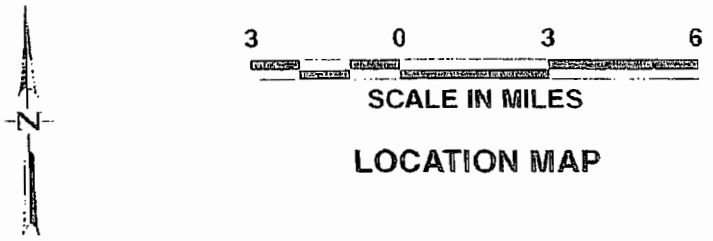
The FW SAP and this SAP Addendum have been developed following the USACE guidance document, Requirements for the Preparation of Sampling and Analysis Plans, EM 200-1-3, September 1994 (USACE 1994a), to collectively meet the requirements established by the Ohio Environmental Protection Agency (Ohio EPA), Northeast District, and the U.S. Environmental Protection Agency (EPA).

1.2 FACILITY BACKGROUND

Past Department of Defense (DoD) activities at the Ravenna Army Ammunition Plant (RVAAP) dates back to 1940 and include storage, handling, and packing of military ammunition and explosives. The site is located in northeastern Ohio in Portage and Trumbull Counties. RVAAP lies 23 miles east-northeast of Akron, Ohio and 30 miles west-northwest of Youngstown, Ohio (Figure 1-1). The installation includes 21,419 acres in a tract approximately 3.5 miles wide by 11 miles long. The RVAAP is a government-owned, contractor-operated (GOCO) military industrial installation.

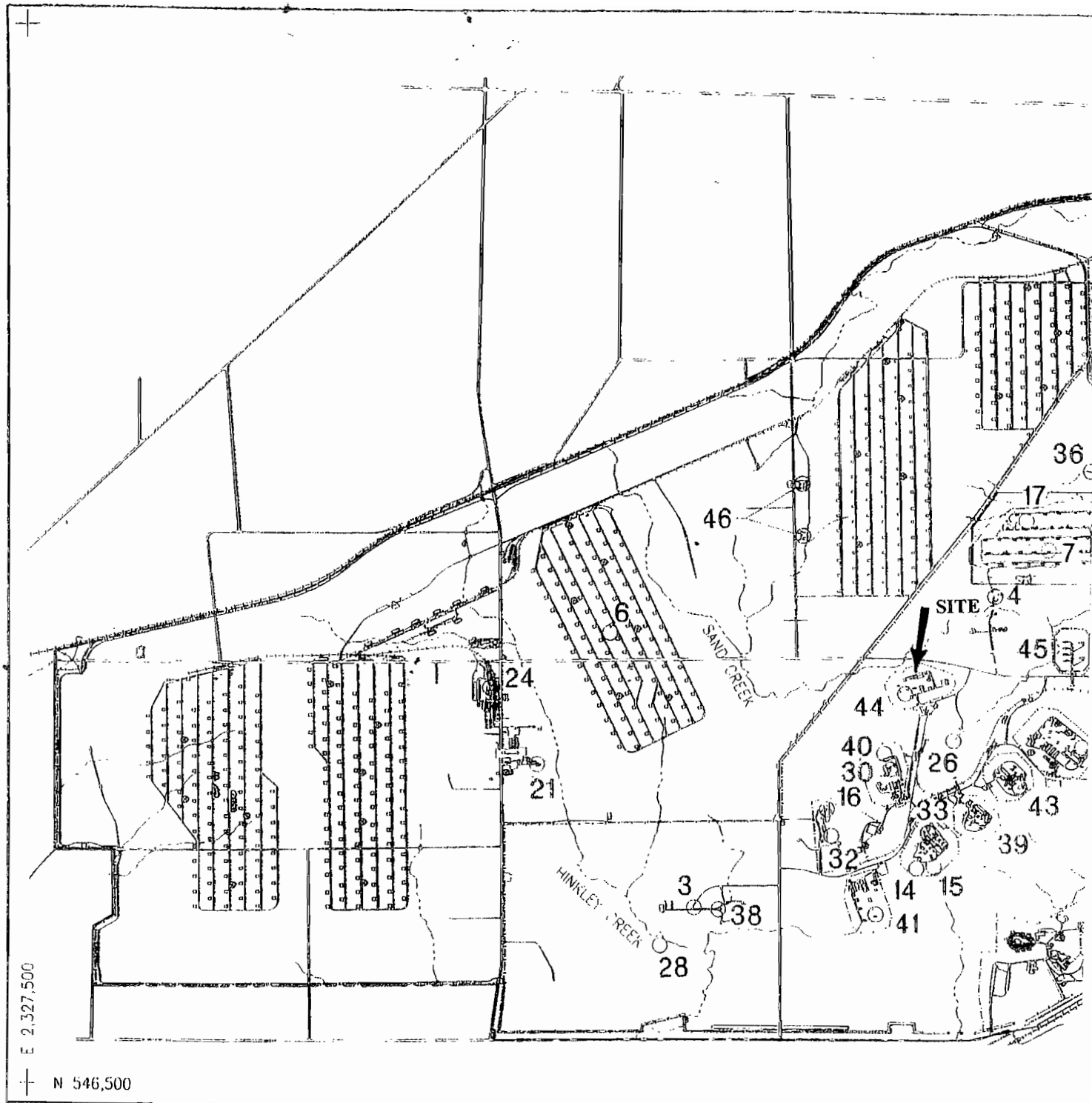
The facility is under the control of the Operations Support Command (OSC) of the U.S. Army, and the current Modified Caretaker contractor on-site is Toltest, Inc. The land use surrounding the installation is primarily farmland, woodland, and low density housing. The industrial operations at RVAAP consisted of 12 munitions assembly facilities referred to as "load lines". In addition, RVAAP also had several areas used for burning, demolition and testing of munitions and buildings/areas designated for clean up and decontamination activities for the production equipment (Figure 1-2). In May 1999, the National Guard Bureau assumed operational control of 16,164 acres of RVAAP and licensed Ohio Army National Guard (OHARNG) to use the





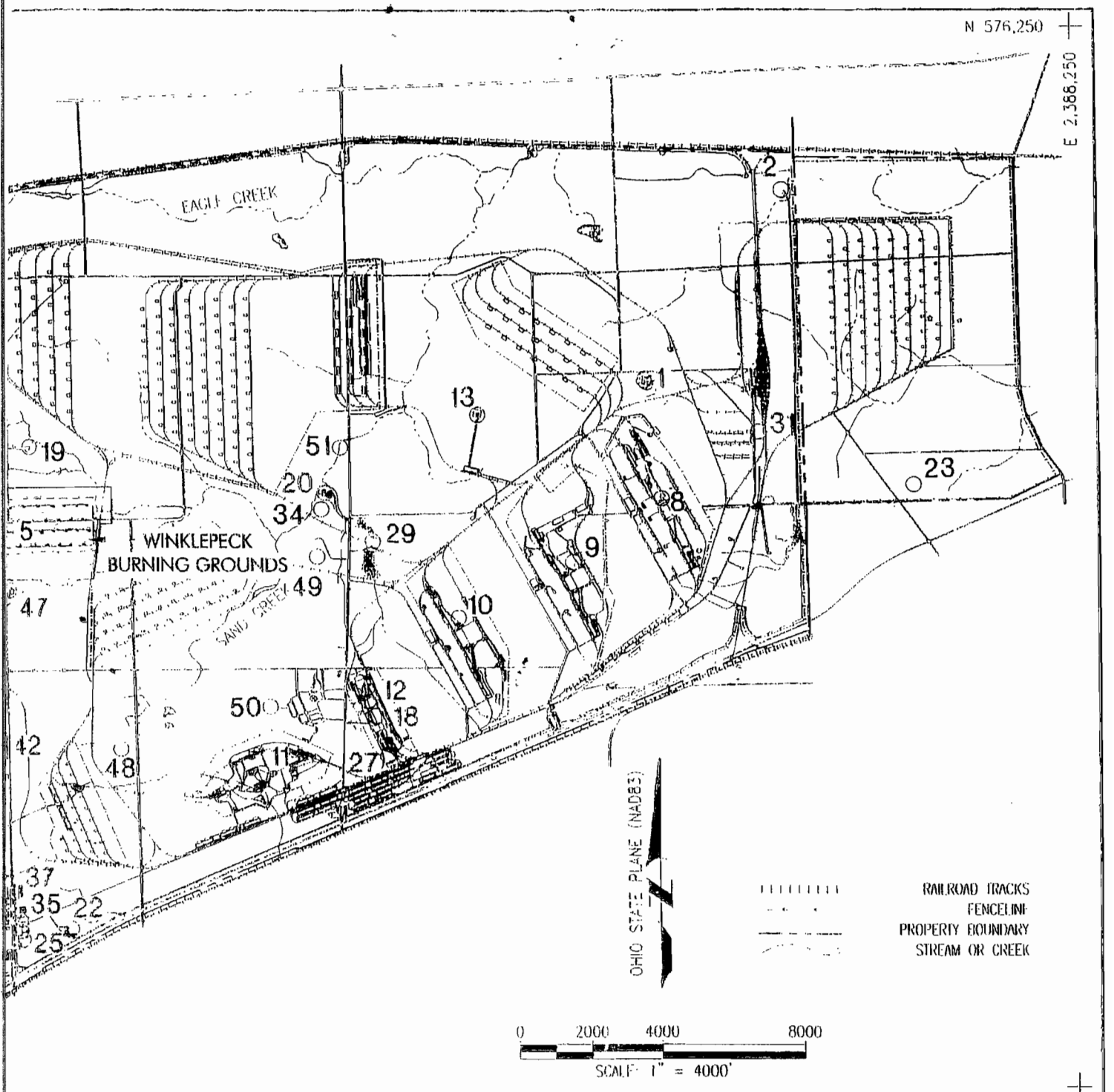
LOCATION MAP

Figure 1-1 General Location and Orientation of RVAAP



LEGEND OF SITES.

1	RAMSDELL QUARRY LANDFILL	13	BLDG 1200 AND DILUTION/SETTLING POND	25	BLDG 1034 MOTOR POOL WASTE OIL TANK	3
2	ERIE BURNING GROUNDS	14	LOAD LINE 6, EVAPORATION UNIT	26	FUZE BOOSTER AREA SETTLING TANKS	3
3	DEMOLITIONS AREA #1	15	LOAD LINE 6, TREATMENT PLANT	27	BLDG 854 PCB STORAGE	3
4	DEMOLITIONS AREA #2	16	QUARRY LANDFILL/FORMER FUZE & BOOSTER BURNING PITS	28	MUSTARD AGENT BURIAL SITE	4
5	**WINKLEPECK BURNING GROUNDS**	17	DEACTIVATION FURNACE	29	UPPER AND LOWER COBBS POND COMPLEX	4
6	C BLOCK QUARRY	18	LOAD LINE 12 PINK WASTE WATER TREATMENT	30	LOAD LINE 7 PINK WASTEWATER TREATMENT PLANT	4
7	BLDG 1601 HAZARDOUS WASTE STORAGE	19	LANDFILL NORTH OF WINKLEPECK BURNING GROUND	31	ORE PILL RETENTION POND	4
8	LOAD LINE 1 AND DILUTION/SETTLING POND	20	SAND CREEK SEWAGE TREATMENT PLANT	32	40 AND 60 MM FIRING RANGE	4
9	LOAD LINE 2 AND DILUTION/SETTLING POND	21	DEPOT SEWAGE TREATMENT PLANT	33	FIRESTONE TEST FACILITY	4
10	LOAD LINE 3 AND DILUTION/SETTLING POND	22	GEORGE ROAD SEWAGE TREATMENT PLANT	34	SAND CREEK DISPOSAL ROAD LANDFILL	4
11	LOAD LINE 4 AND DILUTION/SETTLING POND	23	UNIT TRAINING SITE WASTE OIL TANK	35	1037 BUILDING-LAUNDRY WASTEWATER SUMP	4
12	LOAD LINE 12 AND DILUTION/SETTLING POND	24	RESERVE UNIT MAINTENANCE AREA WASTE OIL TANK	36	PISTOL RANGE	4



49 PESTICIDE STORAGE BUILDING T-4452
50 NACA TEST AREA
51 LOAD LINE 5 / FUZE LINE 1
LOAD LINE 7 / BOOSTER LINE 1 ○ XX
LOAD LINE 8 / BOOSTER LINE 2 ○ XX
LOAD LINE 9 / DETONATOR LINE ○ XX
LOAD LINE 10 / PERCUSSION ELEMENT ○ XX
LOAD LINE 11 / ARTILLERY PRIMER
WET STORAGE AREA
BUILDING'S F-15 AND F-16
BUILDING T-5301 DECONTAMINATION
ANCHOR TEST AREA

CENTRAL BURN PITS
ATLAS SCRAP YARD
DUMP ALONG PARIS-WINDHAM ROAD
CERCLA
RCRA
OTHER REGULATORY

US Army Corps of Engineers Louisville District

U.S. ARMY ENGINEER DISTRICT
CORPS OF ENGINEERS
LOUISVILLE, KENTUCKY

RAVENNA ARMY AMMUNITION PLANT
RAVENNA, OHIO
INSTALLATION MAP

DRAWN BY:	REV. NO./DATE:	CAD FILE:
P. HOLM	REV. 1/ 07-13-99	/98026/DWGS/D23SITE

Figure 1-2

facility for training and other activities. The facility is jointly operated by the Army Operations Support Command (OSC) and the Ohio Army National Guard Bureau. The OSC controls environmental areas of concern (AOCs) and bulk explosives storage areas. A detailed history of process operations and waste processes for each AOC at RVAAP is presented in the Preliminary Assessment for the Ravenna Army Ammunition Plant, Ravenna, Ohio (USACE 1996b).

1.3 LL-11 BACKGROUND:

The U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) conducted a Relative Risk Site Evaluation for Newly Added Sites at the RVAAP in 1998 (Hazardous and Medical Waste Study No. 37-EF-5360-99, 19-23 October 1998). From the 13 sites that were evaluated, five were classified as high-priority areas of concern and the others were classified as medium. The five high-priority areas of concern listed in this report including LL-11are:

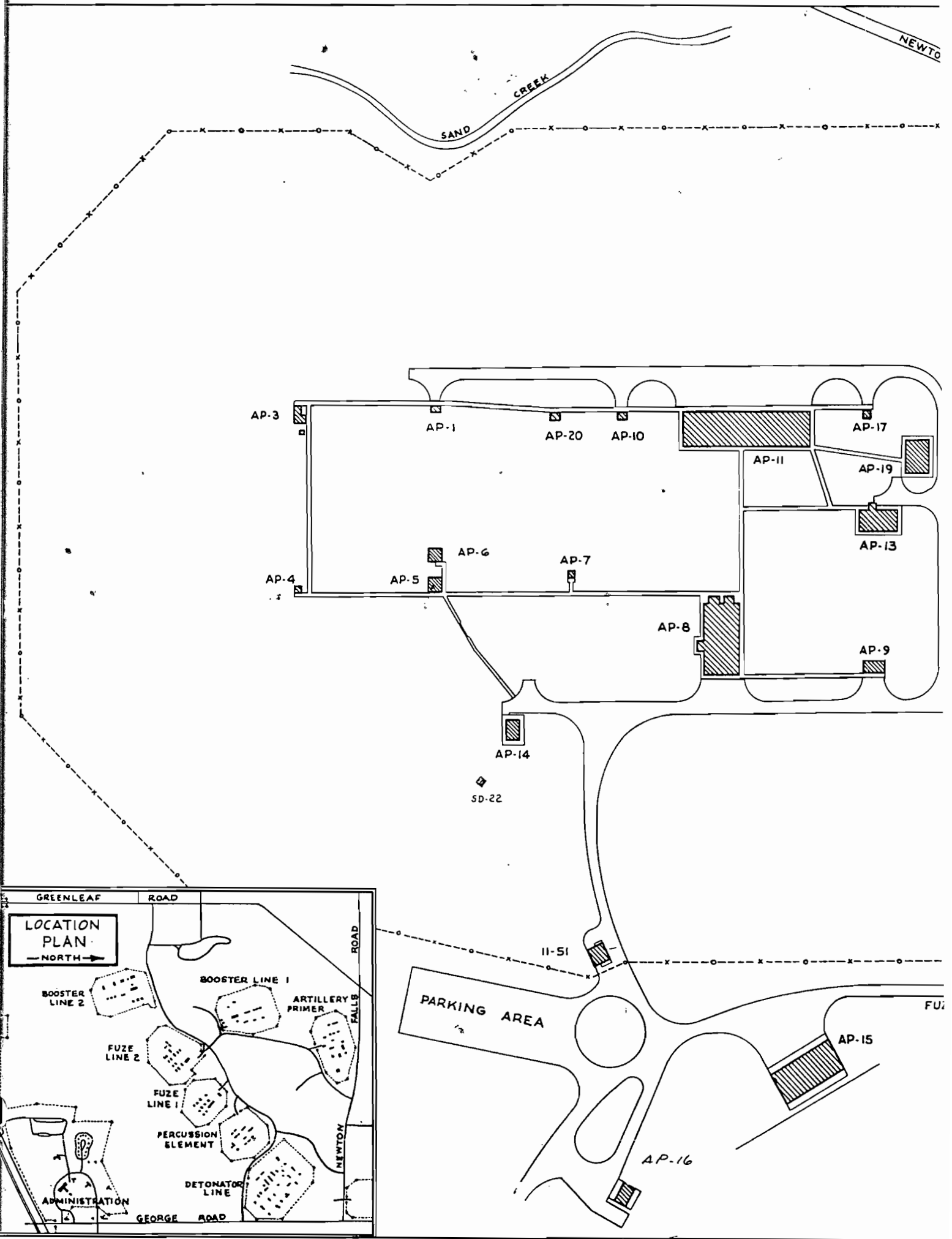
- **RVAAP 44 (LL-11)** (Figure 1-3),
- RVAAP 46 (Building F-15, F-16),
- RVAAP 47 (Building T-5301)
- RVAAP 49 (Central Burns Pits), and
- RVAAP 51 (Dump along Paris-Windham Road).

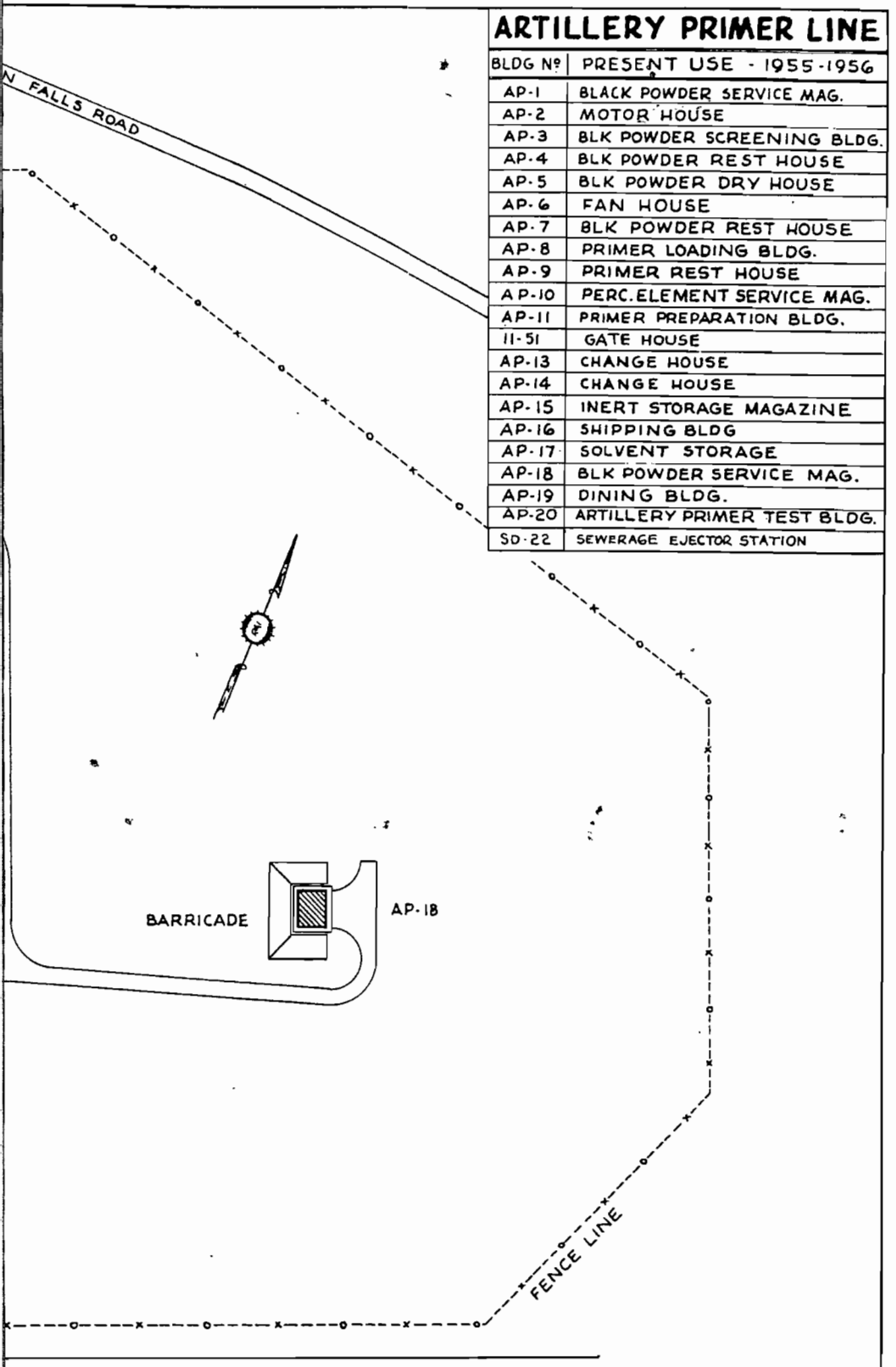
The remaining eight areas that were ranked medium priority were:

- RVAAP 39 (LL-5)
- RVAAP 40 (LL-7)
- RVAAP 41 (LL-8)
- RVAAP 42 (LL-9)
- RVAAP 43 (LL-10)
- RVAAP 45 (Wet Storage Area)
- RVAAP 48 (Anchor Test Area)
- RVAAP 50 (Atlas Scrap Yard)

LL-11 is located in the south central area of the facility on Fuze and Booster Spur Road (Figure 1-2). LL-11 was utilized primarily for the production of artillery primers and fuzes. During the period from 1941 to 1945 Load Line 11 operated at full capacity to produce primers for artillery projectiles. After being placed on standby in 1945 the Load Line was reactivated twice, once during the during the 1951 to 1957 time frame to produce primers, and then again from 1969 to 1971 to produce fuzes in support of the Southeast Asia Conflict.

The proposed interim removal action addresses these issues and will support the Remedial Investigation.


NEWTO
SAND CREEK
AP-3
AP-1
AP-20
AP-10
AP-17
AP-11
AP-19
AP-13
AP-6
AP-7
AP-4
AP-5
AP-8
AP-9
AP-14
SD-22
11-51
PARKING AREA
AP-15
AP-16
GREENLEAF ROAD
LOCATION PLAN
NORTH
BOOSTER LINE 2
BOOSTER LINE 1
ARTILLERY PRIMER
FUZE LINE 2
FUZE LINE 1
PERCUSSION ELEMENT
DETONATOR LINE
ADMINISTRATION
GEORGE ROAD
NEWTON ROAD
FALLS



ARTILLERY PRIMER LINE

BLDG Nº	PRESENT USE - 1955-1956
AP-1	BLACK POWDER SERVICE MAG.
AP-2	MOTOR HOUSE
AP-3	BLK POWDER SCREENING BLDG.
AP-4	BLK POWDER REST HOUSE
AP-5	BLK POWDER DRY HOUSE
AP-6	FAN HOUSE
AP-7	BLK POWDER REST HOUSE
AP-8	PRIMER LOADING BLDG.
AP-9	PRIMER REST HOUSE
AP-10	PERC. ELEMENT SERVICE MAG.
AP-11	PRIMER PREPARATION BLDG.
11-51	GATE HOUSE
AP-13	CHANGE HOUSE
AP-14	CHANGE HOUSE
AP-15	INERT STORAGE MAGAZINE
AP-16	SHIPPING BLDG
AP-17	SOLVENT STORAGE
AP-18	BLK POWDER SERVICE MAG.
AP-19	DINING BLDG.
AP-20	ARTILLERY PRIMER TEST BLDG.
SD-22	SEWERAGE EJECTOR STATION

MKM

FIGURE 1-3

RAVENNA ARMY AMMUNITION PLANT

SITE MAP - LOAD LINE # 11

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DATE: 09 Aug 00

CHECKED BY: RC

NOT TO SCALE

The planned activities within the scope of this SAP Addendum include:

- Field screening (Jenkins, XRF, and Nitrates).
- Confirmation soil sampling.
- Data validation.

1.4 SUMMARY OF EXISTING DATA

Only one previous investigation has been conducted at this site: Relative Risk Site Evaluation (RRSE) (USACHPPM, 1996). The USCHPPM Report identifies surface soils and sediments as the primary media for contaminant migration with potential impact to a state endangered species. The CHPPM report identifies surface soil and sediments to be potential media for contaminant migration due to lack of any physical barriers/fence around the site. Samples were collected and analyzed for metals and explosives. The report indicates hunters and scrappers to be potential receptors of the soil contamination. Appendix A presents a summary of the USACHPPM evaluation performed at LL-11.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The organization chart shown in Figure 2-1 outlines the management structure that will be used to implement the IRA at LL-11. The functional responsibilities of key personnel are also described in brief.

2.1 PROGRAM MANAGER

The Program Manager ensures the overall management and quality of all projects performed at RVAAP under the general contract. This individual will ensure that all project goals and objectives are met in a high-quality and timely manner. This individual, in coordination with the Project Manager, will address quality assurance and non-conformance issues for corrective action.

2.2 PROJECT MANAGER

The Project Manager has direct responsibility for implementing a specific project, including all phases of work plan development, field activities, data management, and report preparation. This individual will also provide the overall management of the project, and serve as the technical lead and principal point of contact with the RVAAP Environmental Coordinator. These activities will involve coordinating all personnel working on the project, interfacing with RVAAP personnel, and tracking project budgets and schedules. The Project Manager will also develop, monitor, and fill project staffing needs, delegate specific responsibilities to project team members, and coordinate with administrative staff to maintain a coordinated and timely flow of all project activities. The Project Manager will also serve in the capacity of Laboratory Coordinator for this project and will coordinate sample collection and subsequent laboratory analysis. The Project Manager reports directly to the Program Manager.

2.3 TECHNICAL MANAGER

The Technical Manager is responsible for the project QA/QC in accordance with the requirements of the Facility-wide Quality Assurance Project Plan (QAPP), the project-specific QAPP addendum, and appropriate management guidance. This individual, in coordination with the Field Operations Manager, will be responsible for the technical aspects of all field operations; all field sampling activities; adherence to required sample custody and other related QA/QC field procedures; coordination of field subcontractor personnel activities; and management of project investigation-derived wastes (IDW). The Technical Manager is also responsible for coordinating the sampling activities with the Sampling Manager.

2.4 CORPORATE HEALTH AND SAFETY MANAGER

The Corporate Health and Safety Manager will ensure that health and safety procedures designed to protect personnel are maintained throughout all field activities conducted at RVAAP. This will be accomplished by strict adherence to the Facility-wide FSHP, which has been prepared as a companion document to this FW SAP,

and the project-specific Site Safety and Health Plan (SSHP), which has been prepared as an addendum to the FW FSHP for each investigation. This individual will have the authority to halt field work if health and/or safety issues arise that are not immediately resolvable in accordance with the FW FSHP and the project-specific SSHP addendum. This individual will report to the Program and Project Managers.

2.5 FIELD OPERATIONS MANAGER

The Field Operations Manager is responsible for implementing all field activities in accordance with the FW FSP and QAPP. This individual will be responsible for ensuring technical performance of all field activities; coordination of field subcontractor personnel activities; and preparation of Field Change Orders (FCOs), if required. This individual reports directly to the Project Manager.

2.6 SAMPLING MANAGER

The Sampling Manager is responsible for planning and executing all sampling activities on site and coordinating the field laboratory activities for analysis of explosives, metals, nitrate, sulfide, sulfate, cyanide and associated QC parameters. This individual will be responsible for obtaining required sample containers from the laboratory for use during field sample collection, resolving questions the laboratory may have regarding QAPP requirements and deliverables, and preparing a quality assessment report for sample data package deliverables received from the laboratory. This individual reports directly to the Project Manager.

2.7 UXO TEAM

The UXO Team will comprise of a Senior UXO Superintendent and a UXO Supervisor. These individuals will be responsible for conducting initial field screening of structures using EXPRAY wipe test, if necessary, and assist during the entire project with ordnance and explosives related issues (if any). The UXO Superintendent will report directly to the Project Manager.

2.8 FIELD PERSONNEL

Other field personnel participating in the implementation of field activities will, in coordination with field subcontractor personnel, be responsible for performing all field activities in accordance with the FW SAP and FSHP and their project-specific addenda. These individuals report directly to the Field Operations Manager.

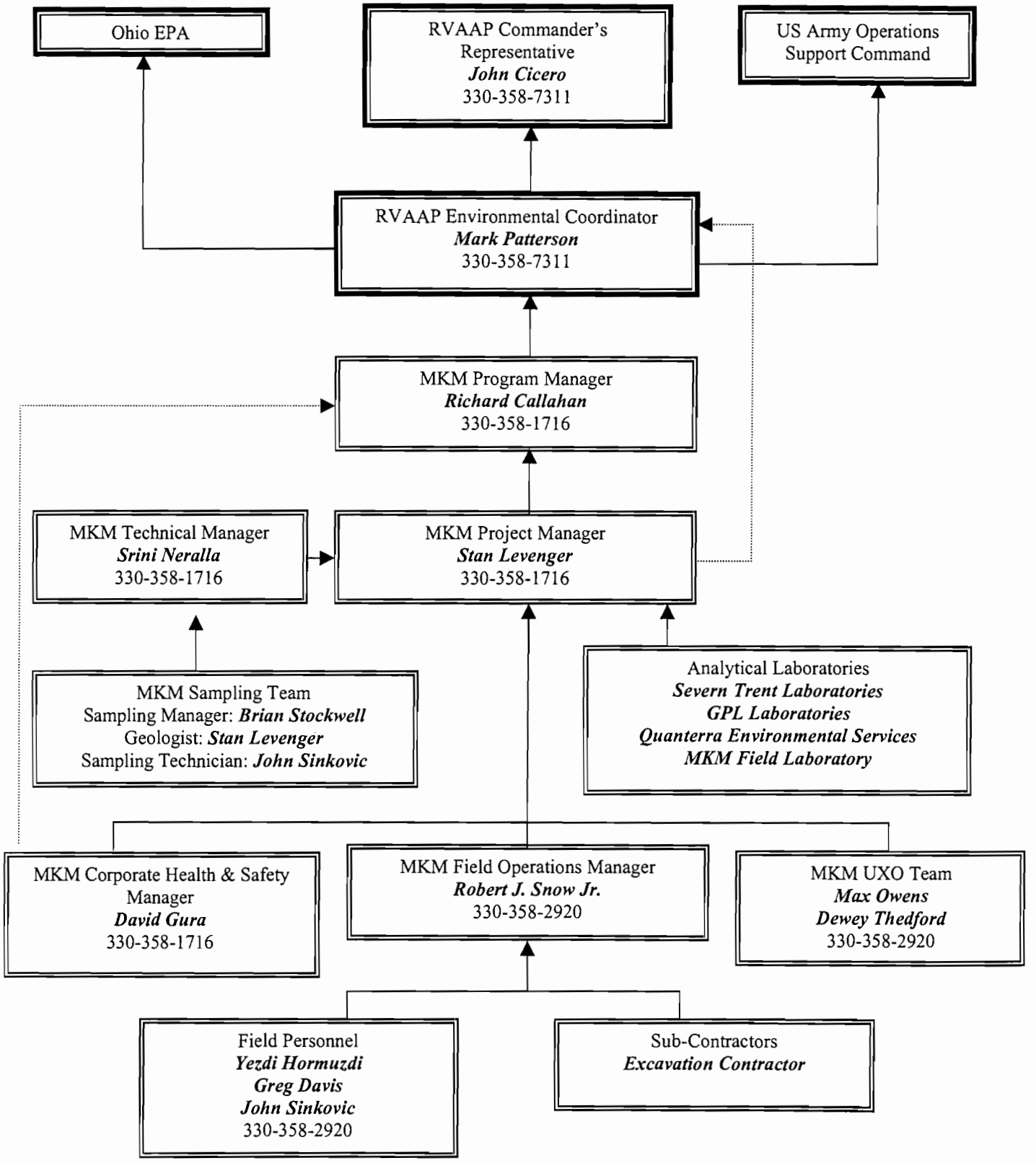


Figure 2-1. Project Organization Chart for the LL-11 IRA

3.0 SCOPE AND OBJECTIVES

Previous studies conducted by the U.S Army Center for Health Promotion and Preventative Medicine (USCHPPM, October 1988) have indicated that the surface soil, groundwater and sediment pathways are complete at LL-11 and as a result the Relative Risk Site Evaluation for this AOC was scored High. A remedial investigation of the load line is to be completed concurrently with the IRA, and will expand on the USCHPPM effort to evaluate the shallow and deep soils, groundwater, surface water and sediment media associated with the AOC.

3.1 PROJECT OBJECTIVES

The primary objective of this project is to remove primary pathways of migration for contamination originating from the load line. This includes sedimentation sumps and portions of the sanitary sewer system and open ditch systems, which drains the site. The data from this IRA will be folded into Remedial Investigation evaluation of risk for the site followed by recommendations for remedial efforts, as necessary. This involves the following field activities:

- Field screening for explosives, lead and nitrates.
- Sewer/sump water removal/treatment
- Excavation
- Confirmation sampling and analysis
- Backfilling and site restoration
- Waste characterization sampling and analysis

3.1.1 Field Screening

Field screening techniques will be used to direct IRA excavation operations around the load line sumps/sewer systems and surface drainage ditches. Pre-excavation field screening samples, if necessary, will be collected using Geoprobe® direct push technology. Post excavation field screening samples will be collected with the excavator bucket to avoid personnel entering excavations greater than four feet deep. If finished excavations are less than four feet in depth, samples will be collected using a stainless steel hand auger, bowls, and trowel. Field screening for the pre-excavation and post excavation samples will include analysis for explosives by modified Jenkins method, lead using XRF technology and nitrates using the HACH N-Trak® soil test kit. Specific details for collecting samples via direct push and hand auger methodologies are provided in Section 4.0. The field screening methods to be utilized for this IRA are summarized in Section 4.0.

3.1.2 Sewer/Sump Water Removal/Treatment

The site sumps and sewers are presently full of water. The quantity of water contained in the sumps and sewers that are to be removed will be analyzed as described in Section 4.2 of this document. Prior to initiating the excavation operations, the sewer system will be strategically blocked and the water will be pumped from sections that will be removed. All sewer water will be pumped into holding tanks for subsequent disposal. Additionally, any water that enters the excavation will be containerized and disposed of in a similar manner.

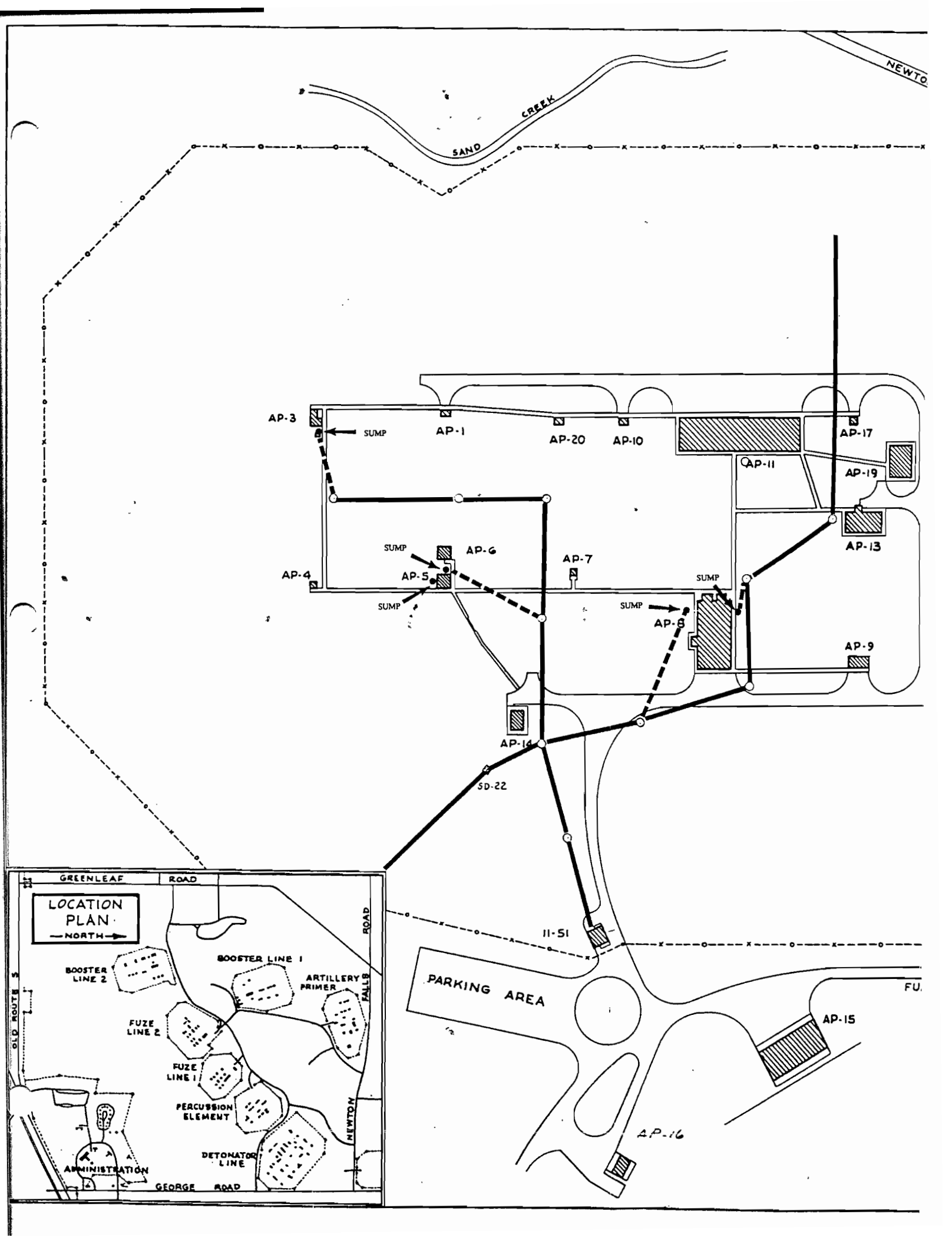
3.1.3 Excavation

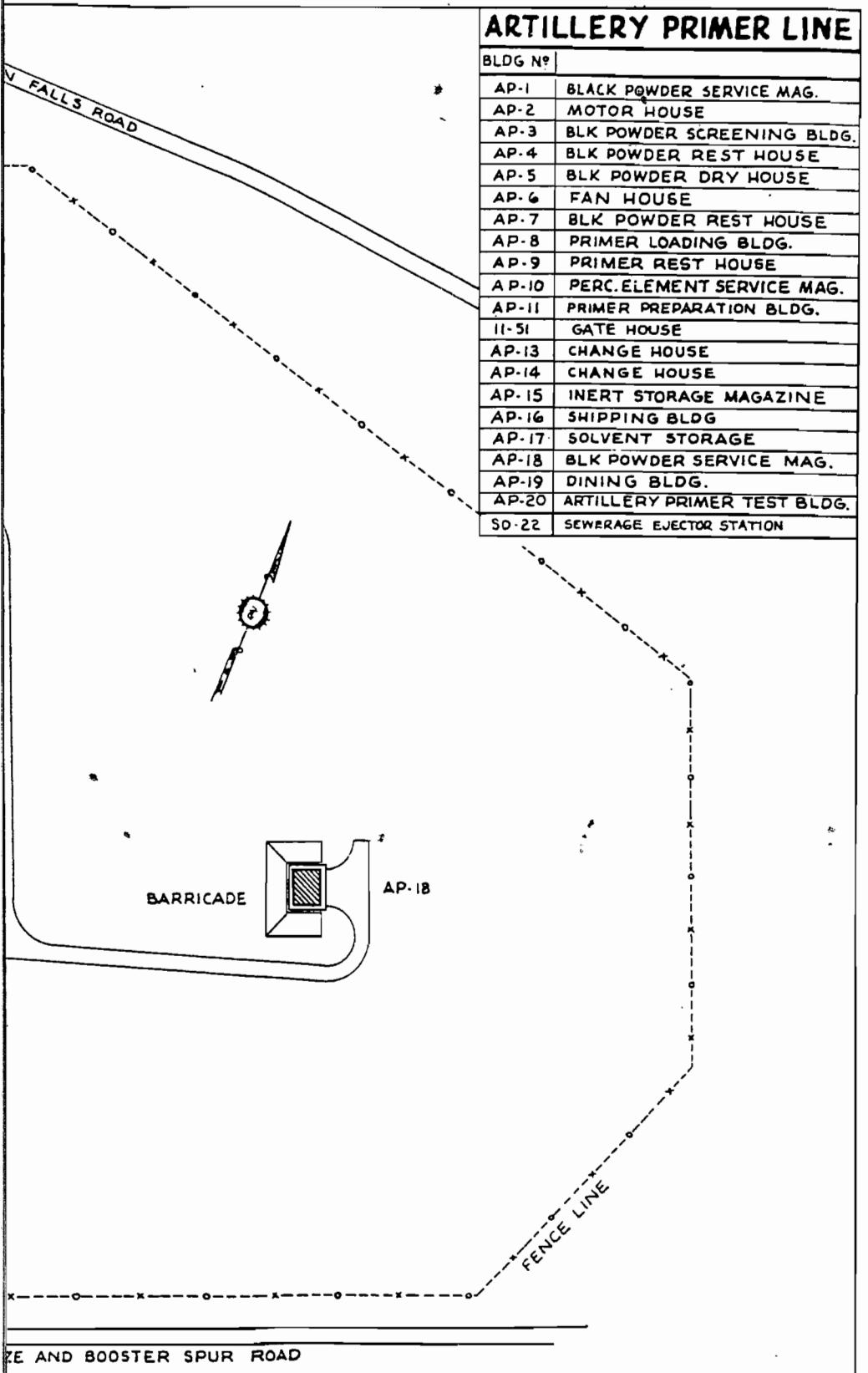
This task involves the excavation and removal of 5 sedimentation sumps and associated eight-inch sewer line (up to the first manhole) and surface drainage ditches at LL-11. The potential limits of the sewer line and drainage ditch excavations are depicted in Figure 3-1 and Figure 3-2 respectively. Based on the RI sample data and pre-excavation field screening samples, excavation of the sumps and sewer lines will proceed to the invert depth or groundwater whichever is encountered first. Upon conclusion of the excavation activities, confirmation samples will be submitted for laboratory analysis.

Both the sewer line and drainage ditches will be excavated using a track-mounted excavator. All soil will be stockpiled adjacent to the excavations (at least 4 feet from the edge). Based on the pre-excavation field screening samples, soils will be placed in two separate stockpiles. One stockpile will be for "clean" soils for which field tests indicate no residual contamination. The other stockpile will be for the remaining soils which the field tests indicate residual contamination to be present. Immediately following excavation to final depth, the excavation bottom will be field screened for TNT/RDX, lead and nitrates. If the post excavation field screening indicates residual contamination exists, additional excavation and field screening will be conducted (1-foot lifts). Only those portions of the excavation which field screening indicate residual contamination exists will be excavated to the next one-foot increment. When the field screening indicates no residual contamination within the excavation, confirmation samples will be collected for laboratory analysis and the excavation will be backfilled.

3.1.4 Confirmation Sampling and Analysis

Upon completion of the sewer system and surface drainage ditch excavation operations, confirmation samples will be collected to quantify the effectiveness of the IRA on the explosive and lead contaminated soils. A maximum of 30 sewer system confirmation samples and 25 surface drainage ditch (sediment) confirmation samples will be collected during this IRA. The confirmation samples will be collected at the RI sample points that exhibited elevated concentrations of site contaminants. Field screening (described earlier) will precede confirmation sampling to help evaluate the success of the IRA. Confirmation samples will be collected with the excavator bucket to avoid personnel entering excavations greater than four feet deep. If finished excavations are less than four feet in depth, samples will be collected using a stainless steel hand auger from the surface of the excavated areas to a depth of 0 to 6-inches below ground surface. All confirmation samples will be analyzed for


SAND CREEK
AP-3
SUMP
AP-1
AP-20
AP-10
AP-17
AP-11
AP-19
AP-13
SUMP
AP-6
AP-7
AP-4
AP-5
SUMP
SUMP
SUMP
AP-8
AP-9
AP-14
SD-22
11-51
PARKING AREA
AP-15
AP-16
LOCATION PLAN
NORTH
GREENLEAF ROAD
BOOSTER LINE 2
BOOSTER LINE 1
ARTILLERY PRIMER
FUZE LINE 2
FUZE LINE 1
PERCUSSION ELEMENT
DETONATOR LINE
ADMINISTRATION
GEORGE ROAD
OLD ROUTE 5
NEWTON FALLS ROAD



ARTILLERY PRIMER LINE	
BLDG Nº	
AP-1	BLACK POWDER SERVICE MAG.
AP-2	MOTOR HOUSE
AP-3	BLK POWDER SCREENING BLDG.
AP-4	BLK POWDER REST HOUSE
AP-5	BLK POWDER DRY HOUSE
AP-6	FAN HOUSE
AP-7	BLK POWDER REST HOUSE
AP-8	PRIMER LOADING BLDG.
AP-9	PRIMER REST HOUSE
AP-10	PERC. ELEMENT SERVICE MAG.
AP-11	PRIMER PREPARATION BLDG.
11-51	GATE HOUSE
AP-13	CHANGE HOUSE
AP-14	CHANGE HOUSE
AP-15	INERT STORAGE MAGAZINE
AP-16	SHIPPING BLDG
AP-17	SOLVENT STORAGE
AP-18	BLK POWDER SERVICE MAG.
AP-19	DINING BLDG.
AP-20	ARTILLERY PRIMER TEST BLDG.
SD-22	SEWERAGE EJECTOR STATION

SANITARY SEWER SYSTEM

SANITARY SEWER SYSTEM TO BE REMOVED UNDER IRA

SUMP LOCATION

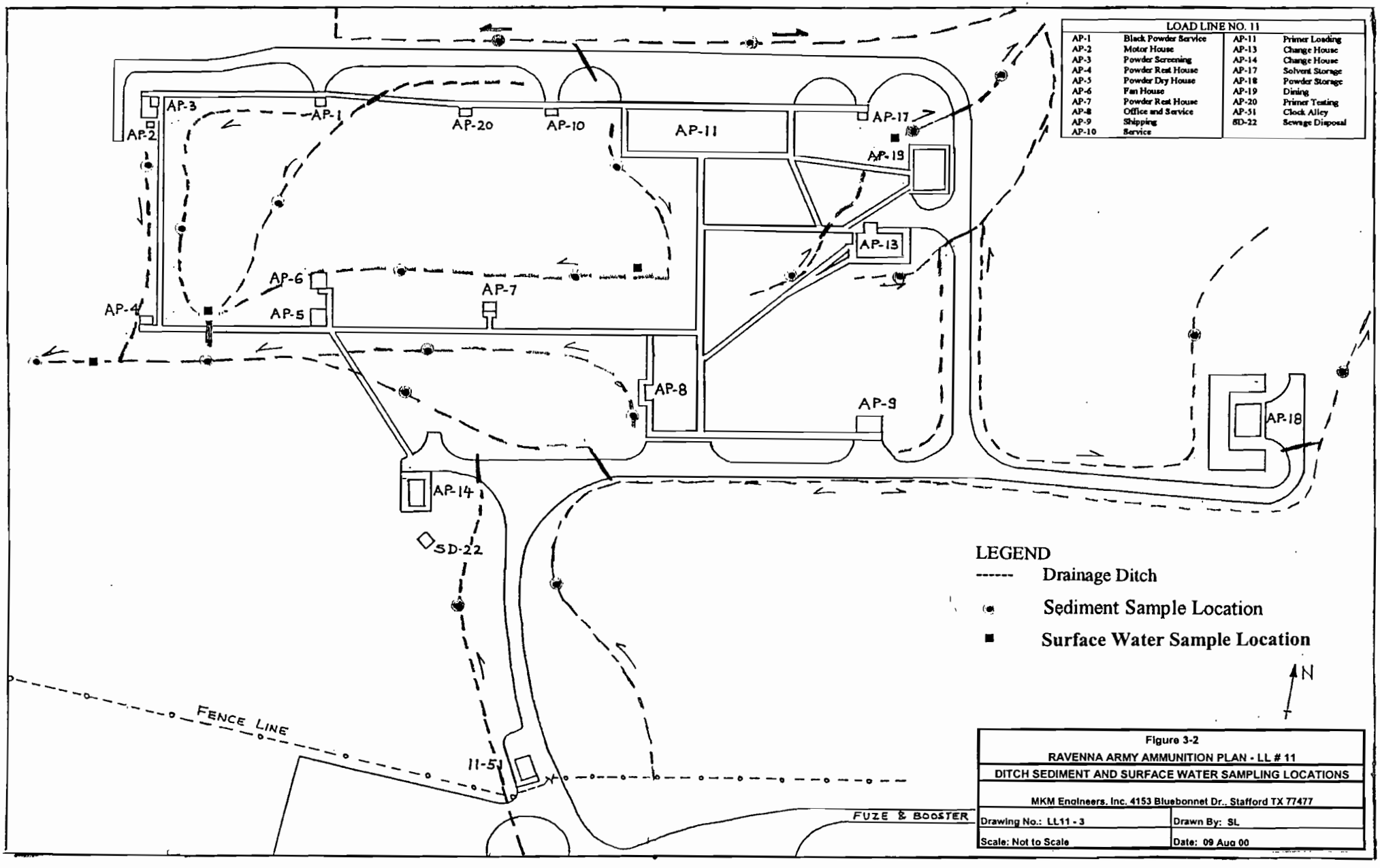
FIGURE 3-1

RAVENNA ARMY AMMUNITION PLANT

IRA Sewer-Sump Excavation Map - LL # 11

DRAWN BY: SL DATE: 09 Aug 00

CHECKED BY: RC NOT TO SCALE


LOAD LINE NO. 11
AP-1 Black Powder Service
AP-2 Motor House
AP-3 Powder Screening
AP-4 Powder Rest House
AP-5 Powder Dry House
AP-6 Fan House
AP-7 Powder Rest House
AP-8 Office and Service
AP-9 Shipping
AP-10 Service
AP-11 Primer Loading
AP-13 Change House
AP-14 Change House
AP-17 Solvent Storage
AP-18 Powder Storage
AP-19 Dining
AP-20 Primer Testing
AP-51 Clock Alley
SD-22 Sewage Disposal
AP-1
AP-2
AP-3
AP-4
AP-5
AP-6
AP-7
AP-8
AP-9
AP-10
AP-11
AP-13
AP-14
AP-17
AP-18
AP-19
AP-20
SD-22
FENCE LINE
11-51
FUZE & BOOSTER
LEGEND
Drainage Ditch
Sediment Sample Location
Surface Water Sample Location
N
Figure 3-2
RAVENNA ARMY AMMUNITION PLAN - LL # 11
DITCH SEDIMENT AND SURFACE WATER SAMPLING LOCATIONS
MKM Engineers, Inc. 4153 Bluebonnet Dr., Stafford TX 77477
Drawing No.: LL11 - 3
Drawn By: SL
Scale: Not to Scale
Date: 09 Aug 00

Explosives, TAL Metals, Cyanide, Sulfide/Sulfate and Nitrates. Additionally, ten percent of the samples will be analyzed for Propellants, VOCs, SVOCs, and Pest/PCB.

The explosive aliquots will be composited and homogenized from three subsamples collected about 0.9 M (3 feet) from one another in a roughly equilateral triangle pattern. The sample aliquots for all other analyses will be will be collected as discrete samples from the midpoint of the three samples. The location of all confirmation samples will be verified with OEPA prior to sampling and field checked based on visual survey of the area conditions. All sampling procedures will be consistent with the RVAAP Facility-Wide Sampling and Analysis Plan (1996). Detailed procedures for collecting soil samples via the hand auger methodology are presented in Section 4.0.

3.1.5 Backfilling and Site Restoration

Upon completion of the excavation, and collection of the confirmation samples, the excavations will be lined with poly and backfilled with stockpiled soils which field screening indicated no residual contamination. The poly liner will provide the demarcation where excavation ceased and will keep the backfill from being re-contaminated should any residual contamination remain. The remaining stockpiled soil not used for backfill (due to detects with the field test kits) will be seeded and secured with silt fence. Additional backfill material will be obtained from an off-site source as needed. The backfill will be obtained from a local vendor with access to material from a virgin point of origin source or from RVAAP backfill areas as approved by OEPA. The backfill material will be analyzed for VOCs, SVOCs, Explosives, Propellants, TAL Metals, Pesticides/PCBs, Cyanide, Sulfide/Sulfate and Nitrate to satisfy the OEPA's requirement for analytical data on any source of backfill used at RVAAP. A composite sample will be collected from the source material using a stainless steel hand auger to a depth of 0 to 1-foot below ground surface. All sampling procedures will be consistent with the RVAAP Facility-Wide Sampling and Analysis Plan (1996). Detailed procedures for collecting soil samples via the hand auger methodology are presented in Section 4.0 of this document.

3.1.6 Waste Characterization Sampling and Analysis

Representative composite samples from each waste stream including sewer water and excavated soils will be collected and analyzed per requirements of the disposal facility. The sewer water sample will be collected using a disposable Teflon® bailer. The water samples will be placed directly into the sample jars from the bailer with the volatile jars being filled first. Representatives samples of excavated soil stock piles will be collected using a stainless steel hand auger, trowels and bowls. All sampling procedures will be consistent with the RVAAP Facility-Wide Sampling and Analysis Plan (1996). Detailed procedures for collecting water samples via the Teflon® bailer and soil samples via the hand auger methodology are presented in Section 4.0.

3.2 DATA QUALITY OBJECTIVES

The project DQO is to provide sufficient high-quality data to address the primary project objectives identified in Section 3.1. Specific DQOs for the LL-11 IRA are designed to address the following data needs:

- Implement the Site-Specific Plans for LL-11 IRA by developing data of sufficient quality to assure Remedial Investigation requirements have been met;
- Achieve data of sufficient quality to complete 100% USEPA Tier II Data Verification;
- Achieve data of sufficient quality to complete 10% USEPA Tier I CLP Data Validation; and
- Achieve data of sufficient quality to incorporate into the Human Health and Ecological Risk Assessments necessary to evaluate LL # 11and complete the IRA.

3.3 CONCEPTUAL SITE MODEL

Based on current data, the conceptual site model presented in the FW SAP is applicable to this element of the IRA. The samples collected during the LL-11 IRA will serve to update the site-specific conceptual model.

Confirmation Soils. During the IRA, a total of 30 soil samples will be collected from the sewer system excavation and one composite soil sample form the excavated soil stockpile. These soil samples will be will be collected using a combination of the excavator bucket and stainless steel hand augers, bowls and trowels.

Confirmation Sediment. Samples will be collected from 25 locations (1 per location) within excavated drainage ways using stainless steel hand augers, trowels and bowls.

3.4 PROBLEM DEFINITION

Industrial operations at LL-11 took place during the 1941 to 1945, 1951 to 1957 and 1969 to 1971 time frames for production of artillery primers and fuzes. According to the Installation Assessment Of Ravenna Army Ammunition Plant, Report No. 132 dated November 1978 from 1941 to1945 load lines 5 through 11 combined, produced 19,257,297 Misc Fuzes, 44,297,485 Misc Boosters, 50,660,725 Misc Primers, 79,580,576 Detonators and 226,387,306 Percussion Elements. From 1951 to 1957 LL-11 alone produced 9,927,118 MK2A4 Percussion Primers, some 24,482,465 MK2A4 Primers and 1,504,935 Repack Primers. No definitive information is available for LL-11 regarding production during the 1969 to 1971 time frame. A total of nineteen (19) Artillery Primer (AP) Buildings were used at the load line to carry out the specific industrial operations. A brief description of each AP Building is provided below:

- Building AP-18 was designated as a bunkered storage area for percussion element. Inside the building there are no drains or troughs. Exterior drainage follows the contour of the land in the immediate proximity of the building.
- Building AP-9 was used as a percussion element storage and staging area for operations conducted from 1969 through 1971. Prior to product manufactured in the later 60's to early 70's, AP-9 was used for palletization and shipping of the finished products. The building contains no drains, troughs, or sumps. Exterior drainage follows the contour of the land in the immediate proximity of the building.
- Building AP-7 has been used throughout operation of Load Line 11 as a Black Powder staging (Rest House) area for primer charging conducted in building AP-8. The interior walls are covered with lead base paint and

the floors are covered with a non-conductive material for the prevention of electrostatic charge. There are no drains, troughs or sumps associated with the building. Exterior drainage follows the contour of the land in the immediate proximity of the building.

- Building AP-1, AP-4 and AP-10 utilization, condition and characteristics are the same as Building AP-7.
- Buildings AP-5 and AP-6 were used exclusively as a Black Powder processing area. Building AP-5 contained forced air blowers for the drying ovens in AP-6. Building AP-6 has troughs and drains that lead to exterior sumps. Two sets of sumps are associated with these buildings. One set is locate outside the SW wall of AP-6 and one set is located between the AP-5 and AP-6. Schematics indicate the sumps are connected with lead piping, which in turn connect with the sewer mains of the facility
- Building AP-20 was the Quality Assurance Primer Sensitivity Testing facility. Standard Operating Procedures permitted a maximum of only 3 pounds of finished product in the building at any one time. There are no troughs or drains in this building. Exterior drainage follows the contour of the land in the immediate proximity of the building.
- Building AP-11 was the major assembly building for the MK2A4 product during the 1969 to 1971 time frame. Bay A of AP-11 was used for the insertion of the Percussion Element via Pennsylvania Heading Machines in to the main primer head. (All machines have been removed from the building). Bay B was used for the charging of the primer assemblies with the Black Powder. Bay C was used to apply lacquer sealing materials and pack out the finish product. The difference in the manufacturing process used during the periods 1941 to 1945, 1951 to 1957, and 1969 to 1971 is the black powder charging operations were shifted from Building AP-8 to AP-11 in later years. There are no troughs or drains along the walls of AP-11. There are several utility sinks with drains and piping that most likely connect to the sewer mains. Exterior drainage follows the contour of the land in the immediate proximity of the building.
- Building AP-8 was used as a primer loading and administrative building. Two sets of sumps (east side and west side) are associated with this building. The schematics indicate that the sumps are lead lined and are connected to the sewer mains of the facility. There are several drains located in the building.
- Building AP-17 was used as a solvent storage facility. The building contains no sumps, troughs, or drains.
- Building AP-2 was used as a motor house to support the black powder screening operation in AP-3.
- AP-3 was used as a black powder screening facility. The floor of AP-3 is covered with a conductive lead liner. There is a trough are associated drain on the south wall of the building connects to a sump located outside of the building. The facility drawing indicates that the trough and sump are connected with lead piping. The sump is connected to the facility sewer main.
- Support type buildings at Load Line 11 included AP-13 and AP-14 which functioned as locker rooms (Change Houses), AP15 which was used for Inert Storage, AP-16 the shipping building and AP-19 the dining building.

3.5 REMEDIAL ACTION OBJECTIVES

Section 3.2.3 of the FW SAP identifies the remedial action objectives.

3.6 IDENTIFY DECISIONS

The key decisions for all investigations at RVAAP have been identified in the FW SAP Section 3.2.4.

3.7 DEFINE THE STUDY BOUNDARIES

The investigation area boundary for LL-11 is that presented in Figure 1-3. The boundary was established to encompass all known or reported historical activities and potential surface water exit pathways.

3.8 IDENTIFY DECISION RULES

Decision rules used to guide remediation decisions are provided in Section 3.2.6 of the FW SAP. As stated therein, the data obtained by USACHPPM were sufficient to define the potential environmental hazards associated with the LL-11 and promote the implementation of this IRA.

3.9 SPECIFY LIMITS ON DECISION ERROR

Limits on decision errors are addressed in Section 3.2.8 of the FW SAP.

3.10 OPTIMIZE SAMPLE DESIGN

The sample design for the IRA at LL-11 is described in detail in Section 4.0 of this SAP Addendum.

3.11 DATA EVALUATION METHODS

Data reduction and validation will be performed in accordance with the QAPP. Data will be held in a database pending completion of field activities. Upon completion of the IRA, data screening and evaluation processes will be implemented for the entire data set as part of the report preparation. All field data will be documented on field forms by the field sampling team, which will be reviewed on a daily basis by the Project Manager. Analytical data (both field and laboratory) will undergo a 100% verification process. Confirmation sample results will undergo 100% USEPA Tier II verification. Ten percent of this data will receive USEPA Tier I (CLP) data validation. If the 10% validation process indicates that there are concerns with the data, additional validation (in accordance with the procedures specified in the site-wide plans) will be conducted. Field screening data will be compared to the laboratory data to provide information as to the effectiveness of the field methods. The data will then be reduced and summarized for presentations in the IRA report.

4.0 FIELD SAMPLING METHODS AND PROCEDURES

The Interim Removal Action field activities must be performed in a well-defined and consistent manner to ensure that the resulting data are comparable between sampling locations and can be validated against all applicable QA/QC requirements. This section defines field methods and/or procedures applicable to the following field activities.

- Sub-surface soil pre-characterization sampling;
- Confirmation soil sampling; (sewer and sump excavations) and
- Confirmation sediment sampling (drainage ditch sediment excavation areas).

The methods and procedures are written with the intent of providing specific details so as to ensure consistent data quality, while providing sufficient flexibility to allow for unexpected or changing geologic, environmental, or sampling conditions. Occasionally, modifications to the field procedures are required for reasons of safety or practicality. Any modifications will be reviewed and approved by the MKM Program Manager and Ohio EPA. All variances to the procedures presented in this Field Sampling Plan will be documented.

All field activities will be under the overall supervision of the Project Manager or his designees. Specific sampling activities will be performed or controlled by the Sampling Manager. Subcontractors performing specific activities (e.g. drilling) will be required to comply with all project procedures and requirements.

The following sections discuss the field protocols and procedures to be used for each of the activities to be conducted for this IRA.

4.1 SUBSURFACE SOIL SAMPLING

Subsurface soil sampling will be conducted to provide additional data as necessary prior to excavation. All subsurface soil sampling operations will be screened for ordinance and explosives as described in section 4.6. Subsurface soil samples will be collected using direct push and hand auger methods. The actual soil sampling method used will be sample depth dependent. Each sampling method is further discussed is the following subsections.

4.1.1 Direct Push Technology

A maximum of 20 direct push soil borings will be advanced adjacent to the sanitary sewer system between the manhole locations during the IRA for pre-excavation field screening analysis. The maximum anticipated depth for this subsurface sampling technology is 18 feet bgs (or less depending on groundwater elevation). Samples will be collected continuously from ground surface to total depth. A 2 inch Macro-Core® sampler will

be used where possible with the Geoprobe® rig. A JMC sampler will also be utilized for shallow (less than three feet) sample locations. All direct push spoon samplers will be internally fitted with a disposable butyrate

acetate liner, into which the soil will be collected. Each sample will be collected in a new liner. The spoon samples will also be used for lithologic descriptions. In the event that the ground surface is covered by asphalt or concrete, the first sample will begin at the base of the surface cover. All decontamination and sampling procedures presented in Section 4 of the FW SAP will be followed.

4.1.2 Bucket Hand Auger

The bucket hand auger method will be the second method for subsurface soil sampling. This sampling method will be used for the collection of confirmation samples within sewer system and drainage ditch excavations (< 4-feet deep) and waste characterization samples from the excavated soil stockpiles. The depth interval over which soils will be collected using this method will be limited to a depth of 5.0 feet bgs. This method will be implemented in the same method as those described in Section 4.5.2.1.1 of the FW SAP. Excavations greater than 4-feet deep will be sampled remotely (i.e., excavator bucket) to avoid exposing personnel to potential hazards. All confirmation samples will be analyzed for Explosives, TAL Metals, Cyanide, Sulfates and Nitrates. Additionally, ten percent of the samples will be analyzed for Propellants, VOCs, SVOCs, and Pest/PCB. The soil waste characterization sample will be analyzed for parameters both representative of the site and in accordance with the disposal facility requirements.

4.2 SEWER WATER SAMPLING

The sewer water sample will be collected for waste characterization purposes prior to initiating any pumping or excavation operations. This composite sample will be collected from six separate manhole locations using a disposable Teflon® bailer. The manholes included for the composite sewer water sample include: the manhole at Building AP-3, the manhole down gradient to Buildings AP-5 and AP-6, the manhole at Building AP-14, the manhole southwest of Building AP-8, Building AP-8 manhole and the manhole southeast of Building AP-8 (Figure 3-1). The water samples will be placed directly into the sample jars from the bailer with the volatile jars being filled first. The sample will be submitted to the laboratory for waste profile/characterization analysis of the following parameters:

4.3 DECONTAMINATION PROCEDURES

Decontamination of equipment associated with groundwater sampling will be in accordance with the procedure presented in Section 4.3.8 of the FW SAP.

4.4 FIELD SCREENING

Site soils will be field screened prior to and following the excavation activities to help direct the removal efforts to ensure success of the IRA. Field screening at LL-11 will include analysis for explosives (TNT/RDX), metals and nitrates as described below.

All field tests of TNT/RDX will be conducted in an on-site field laboratory under constantly controlled temperatures in accordance with the procedures of the method. After samples are extracted and processed in the field, samples are analyzed using a field-portable spectrophotometer capable of absorbance measurements at 507 and 540 nanometers. The instrument is calibrated on a daily basis using the following:

- a TNT calibration standard and a TNT spiking standard to establish calibration response factors;
- an RDX calibration standard and an RDX spiking standard to establish calibration response factors;
- a field reagent blank; and
- a field soil blank;

The method detection limit for TNT is 0.7 mg/Kg. The method detection limit for RDX is 1.4 mg/Kg. Complete instructions for conducting the TNT/RDX field analysis tests are described in the *Determination of TNT/RDX in Soils using Colorimetry* prepared by Jenkins and Walsh and presented in Appendix B of this document.

The X-Ray Fluorescence (XRF) technology uses energy dispersive X-Ray fluorescence spectroscopy to determine the concentration of metals in soil. Additional information on XRF technology is provided in Appendix C. Previous research indicates that XRF-determined metals values will correlate with laboratory-analyzed metals values.

Field screening for nitrates in soil will be accomplished through the use of the N-Trak® soil test kit. Technical information and instructions for conducting the nitrate field analysis tests are included in Appendix D of this document.

4.5 FIELD MEASUREMENT PROCEDURES AND CRITERIA

All field measurement procedures and criteria will follow Section 4.3.3 of the FW SAP.

4.6 ORDANACE AND EXPLOSIVES SCREENING

UXO staff will conduct a field survey of the entire area prior to the start-up of the project. Previous investigations and site operational history indicate that OE concerns include black powder, lead styphenate, lead azide, and other potential bulk high explosives. The UXO team will screen the soil in work zones with a magnetometer for potential UXO items prior to and during the excavation and sampling operattions. All work zones will be screened prior to entry by sample team members. The Geoprobe® boreholes will be screened with a down hole magnetometer (Schonstedt GeoMag) to a total depth of 20 feet or less.

Immediately following excavation to final depth, the excavation bottom will be field screened for TNT/RDX, lead and nitrates using the field test kits described earlier. If the field screening indicates residual contamination exists, additional excavation and field screening will be conducted (1 foot lifts). Only those portions of the excavation which the field test screening indicate residual contamination exists will be excavated

to the next one foot increment. When the field tests indicate no residual contamination within the excavation, confirmation samples will be collected for laboratory analysis.

Refer to the LL-11 IRA Ordinance Avoidance Plan in Appendix E for details on all the ordinance and explosive screening operations for this project.

5.0 SAMPLE CHAIN OF CUSTODY/DOCUMENTATION

5.1 FIELD LOGBOOK

All field logbook information will follow structures identified in Section 5.1 of the FW SAP where appropriate, field forms will be used to record specific sampling or investigational data to ensure consistency across sampling locations.

5.2 PHOTOGRAPHS

Photographic documentation of field efforts will be performed in accordance with Section 4.3.2.4.3 of the FW SAP. Representative photographs of field activities and any significant observations will be taken during IRA field operations. Photographs will be suitable for presentation in a public forum, as well as for documenting scientific information.

5.3 SAMPLE NUMBERING SYSTEM

The sample numbering system that will be used to identify samples collected during IRA is explained in Section 5.3 of the FW SAP.

5.4 SAMPLE DOCUMENTATION

All sample label, logbook, field records, chain of custody forms and field form information will follow procedures identified in Section 5.4 of the FW SAP.

5.5 DOCUMENTATION PROCEDURES

Documentation involves the tracking of samples through the receipt of final laboratory data package for the IRA. Documentation procedures will be performed in accordance with Section 5.5 of the FW SAP.

5.6 CORRECTIONS TO DOCUMENTATION

This procedure is required to ensure that all field/sampling records are correct and legally defensible. Corrections to documentation will follow the protocol established in Section 5.6 of the FW SAP.

5.7 REPORTS

Reports will be submitted during the field and analytical investigation tasks for the IRA on a regular basis and will meet the requirements as presented in Section 5.7 of the FW SAP.

5.8 FIELD QUALITY CONTROL

The Project Manager will monitor the quality control of the data collection activities on a daily basis. This process will ensure that data is collected in a manner, which is consistent with the LL-11 IRA Site-Specific and FW SAPs. Field quality control will be maintained as follows:

- Review of all Project Plans by project personnel;
- Training of project personnel on the sampling documentation and field procedures;
- Daily safety and technical briefings of project staff;
- Daily review of all field data collection forms by the Project Manager;
- Enter the Environmental and Quality Control into the sample tracking spreadsheet daily;
- Confirm laboratory receipt, integrity and login with the laboratory Project Manager;
- Daily monitoring and management of IRA subcontractors;
- Conduct ongoing field audits of the data collection procedures and implement corrective measures;
- Complete daily reports summarizing the work completed and decision points.

6.0 SAMPLE PACKAGING AND SHIPPING REQUIREMENTS

Sample packaging and shipping will generally follow the protocols in Section 6.0 of the FW SAP. Exceptions to the FW SAP procedures include:

- No tape of any kind will be placed on the volatile sample containers;
- All VOC sample containers will be placed in either foam bubble wrap or paper towels to reduce the potential for breakage during shipping; and
- The field laboratory will comply with the procedural requirements presented in the forms in Figures 6-2 and 6-3 of the FW SAP.

7.0 INVESTIGATION-DERIVED WASTE

All IDW, including auger cuttings, personal protective equipment, disposable sampling equipment, and decontamination fluids, will be properly segregated handled, labeled, characterized, managed and disposed in accordance with the state and federal rules, regulations and laws. At the conclusion of the field activities for the IRA, all IDW will be documented as to characterization, classification and disposition. All shipments of IDW off site will be coordinated through the RVAAP Environmental Coordinator. The following specific protocols will be followed during the IRA at LL-11:

General: The following types of IDW are anticipated. The different types of IDW will be contained separately:

- Solid auger cuttings – consolidate with excavation stockpile;
- Personal protective equipment and disposable sampling equipment – up to two 55-gallon drums;
- IDW water (liquid effluents, sewer water and decontamination fluids) and poly storage tank.

Should environmental sample data indicate that the contents of drums are potentially hazardous, then Toxicity Characteristic Leaching Procedure (TCLP) samples will be collected for additional characterization purposes.

Water generated during purging and sampling will be placed in a poly storage tank. Management of this type of IDW will be based on analytical results for environmental groundwater samples. Decontamination fluids disposition will be based on collection and analysis of a liquid sample as required by the disposal facility.

All analytical reporting limits and quantitation levels will be consistent with Section 7.1 of the FW SAP.

Labeling of all IDW containers will be in accordance with Section 7.2 of the FW SAP. All field staging, characterization, classification, sampling, transportation and disposal will comply with state and federal rules, regulation and laws, as well as the permit requirements for the receiving facility as applicable.

8.0 REFERENCES

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Part II

Final
Quality Assurance Project Plan Addendum for the Load Line 11 (AOC44) Interim Removal Action at the Ravenna Army Ammunition Plant, Ravenna, Ohio

January 2001

Prepared for

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PART II – QUALITY ASSURANCE PROJECT PLAN ADDENDUM

LIST OF TABLES

ABBREVIATIONS

COC	Chain of Custody
CX	Center of Excellence
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
HTRW	Hazardous, Toxic, and Radioactive Waste
LCS	laboratory control sample
MS	matrix spike
MSD	matrix spike duplicate
PCB	polychlorinated biphenyl
QA	quality assurance
QC	quality control
QAMP	Quality Assurance Management Plan
QAPP	Quality Assurance Project Plan
RI	remedial investigation
RVAAP	Ravenna Army Ammunition Plant
SAP	Sampling and Analysis Plan
SOP	standard operating procedure
TAL	Target Analyte List
TCL	Target Compound List
USACE	U.S. Army Corps of Engineers.

INTRODUCTION

This Quality Assurance Project Plan (QAPP) addendum addresses supplemental project-specific information in relation to the FW QAPP for the Ravenna Army Ammunition Plant (RVAAP), Ravenna, Ohio (April 1996). Each QAPP section is presented documenting adherence to the FW QAPP or stipulating project-specific addendum requirements.

1.0 PROJECT DESCRIPTION

1.1 SITE HISTORY/BACKGROUND INFORMATION

This information is presented in Section 1.1 of the Field Sampling Plan (FSP) Addendum for the Load Line 11 (AOC 44) Interim Removal Action (IRA).

1.2 PAST DATA COLLECTION ACTIVITY/CURRENT STATUS

This information is presented in Section 1.3 of the Field Sampling Plan (FSP) Addendum for the Load Line 11 (AOC 44) Interim Removal Action.

1.3 PROJECT OBJECTIVES AND SCOPE

This information is presented in Section 3.0 of the Field Sampling Plan (FSP) Addendum for the Load Line 11 (AOC 44) Interim Removal Action.

1.4 SAMPLE NETWORK DESIGN AND RATIONALE

This information is presented in Section 4.0 of the Field Sampling Plan (FSP) Addendum for the Load Line 11 (AOC 44) Interim Removal Action.

1.5 PARAMETERS TO BE TESTED AND FREQUENCY

Sample matrix types, analytical parameters, and analytical methods are discussed in Section 4.0 of the Field Sampling Plan (FSP) Addendum for the Load Line 11 (AOC 44) Interim Removal Action. These analyses are summarized in Table 1-1 of this QAPP addendum, in conjunction with anticipated sample numbers, quality assurance (QA) sample frequencies, and field quality control (QC) sample frequencies.

1.6 PROJECT SCHEDULE

The project schedule for this IRA is discussed in Section 2.0 of the Field Sampling Plan (FSP) Addendum for the Load Line 11 (AOC 44) Interim Removal Action.

TABLE 1-1
LOAD LINE 11 - RVAAP
SAMPLING AND ANALYTICAL REQUIREMENTS
NOVEMBER 2000 INTERIM REMOVAL ACTION

Parameter	Methods	Field Samples	Field Duplicates	MS/MSD	Site Source Water	Sampler Rinsates	Trip Blanks	Total A-E Samples	USACE QA Split Samples	USACE Trip Blanks
Soils (sewer and drainage ditch confirmation samples)										
Volatile Organics, TCL	SW-846, 5030/8260B	--	3	2	--	3	3	11	3	3
Semivolatile Organics, TCL	SW-846, 8270C	--	3	2	--	3	--	8	3	--
PCBs, TCL	SW-846, 8082	--	3	2	--	3	--	8	3	--
Pesticides, TCL	SW-846, 8081	--	3	2	--	3	--	8	3	--
Explosives	SW-846, 8330	30	3	2	--	3	--	38	3	--
Propellants	SW-846, 8330 Mod/353.2	--	3	2	--	3	--	38	3	--
TAL Metals	SW-846, 6010B/7471A	30	3	2	--	3	--	38	3	--
Cyanide	SW-846, 9012A	30	3	2	--	3	--	38	3	--
Sulfide/Sulfate	SW846, 9034-EPA 375.4	30	3	2	--	3	--	38	3	--
Nitrate	EPA 353.2	30	3	2	--	3	--	38	3	--
Surface Water (sewer water waste characterization sample)										
Volatile Organics, TCL	SW-846, 5030/8260B	1	--	--	--	--	--	--	--	--
Semivolatile Organics, TCL	SW-846, 8270C	1	--	--	--	--	--	--	--	--
PCBs, TCL	SW-846, 8082	1	--	--	--	--	--	--	--	--
Pesticides, TCL	SW-846, 8081	1	--	--	--	--	--	--	--	--
Explosives	SW-846, 8330	1	--	--	--	--	--	--	--	--
Propellants	SW-846, 8330 Mod/353.2	1	--	--	--	--	--	--	--	--
TAL Metals	SW-846, 6010B/7471A	1	--	--	--	--	--	--	--	--
Cyanide	SW-846, 9012A	1	--	--	--	--	--	--	--	--
Sulfide/Sulfate	SW846, 9034-EPA 375.4	1	--	--	--	--	--	--	--	--
Nitrate	EPA 353.2	1	--	--	--	--	--	--	--	--
Sediment (drainage ditches)										
Volatile Organics, TCL	SW-846, 5030/8260B	--	3	2	--	3	3	11	3	3
Semivolatile Organics, TCL	SW-846, 8270C	--	3	2	--	3	--	8	3	--
PCBs, TCL	SW-846, 8082	--	3	2	--	3	--	8	3	--
Pesticides, TCL	SW-846, 8081	--	3	2	--	3	--	8	3	--
Explosives	SW-846, 8330	25	3	2	--	3	--	33	3	--
Propellants	SW-846, 8330 Mod/353.2	--	3	2	--	3	--	8	3	--
TAL Metals	SW-846, 6010B/7471A	25	3	2	--	3	--	33	3	--
Cyanide	SW-846, 9012A	25	3	2	--	3	--	33	3	--
Sulfide/Sulfate	SW846, 9034-EPA 375.4	25	3	2	--	3	--	33	3	--
Nitrate	EPA 353.2	25	3	2	--	3	--	33	3	--
Grain Size	ASTM D-422	25	3	2	--	3	--	33	3	--

A-E = Architect Engineer
PCB = Polychlorinated Biphenyl
TAL = Target Analyte List
TCL = Target Compund List
USACE = Army Corps of Engineers

2.0 PROJECT ORGANIZATION AND RESPONSIBILITY

The functional project organization and responsibilities are described in Section 2.0 of the FW SAP and the Load Line 11 Remedial Investigation FSP. Analytical support for this work has been assigned to Severn Trent Laboratories, Inc. All of the analysis will be performed by Severn Trent's Chicago, Illinois laboratory with the exception of the explosive and propellant analysis (nitrocelluose/nitroguanidine). The propellants will be analyzed by Quanterra Environmental Services, Inc. at their West Sacramento California facility. The QA lab which will receive splits of 10% of the environmental samples is GPL Laboratories in Gaithersburg, Maryland. These laboratories have been validated by the U.S. Army Corp of Engineers (USACE) Hazardous, Toxic, and Radioactive Waste (HTRW) Center of Excellence (CX), Omaha, Nebraska. Severn Trent's and Quanterra Environmental Services' Quality Assurance Management Plans (QAMP), are available for review upon request. The laboratory's organizational structure, roles, and responsibilities are identified in their QAMP and facility-specific appendices. Addresses and telephone numbers for the laboratories facilities are as follows:

Analytical Facilities
Severn Trent Laboratories, Inc. – general analytical and explosive analytical services:
2417 Bond Street, University Park
Chicago, IL 60466
Tel: (708) 534-5200
Fax: (708) 534-5211

Quanterra Environmental Services, Inc. – Propellants (nitrocellulose/nitroguanidine) and explosives analyses:
Sacramento, CA
880 Riverside Parkway
West Sacramento, CA 95605
Tel: (916) 373-5600
Fax: (916) 372-1059.

GPL Laboratories - general analytical and explosive analytical services
202 Perry parkway
Gaithersburg, MD 20877
Tel: (301) 926-6802
Fax: (301) 840-1209

3.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT

3.1 DATA QUALITY OBJECTIVES

Analytical Data Quality Objectives (DQO) summaries for this investigation will follow Tables 3-1 and 3-2 in the FW QAPP. All QC parameters stated in the specific U.S. Environmental Protection Agency (EPA) SW-846 methods will be adhered to for each chemical listed. SW-846 Method references found in the FW QAPP have been revised to the Update III Methods (i.e., 8260A is now 8260B, 8270B is now 8270C, etc.). Laboratories are required to comply with all methods as written; recommendations are considered requirements.

3.2 LEVEL OF QUALITY CONTROL EFFORT

QC efforts will follow Section 3.2 of the FW QAPP. Field QC measurements will include field source water blanks, trip blanks, field duplicates, and equipment rinsate blanks. Laboratory QC measurements will include method blanks, laboratory control samples (LCSs), laboratory duplicates, and matrix spike/matrix spike duplicate (MS/MSD) samples, as dictated by the individual methods.

3.3 ACCURACY, PRECISION, AND SENSITIVITY OF ANALYSIS

Accuracy, precision, and sensitivity goals identified in Section 3.3 and Tables 3-1 and 3-2 of the FW QAPP and 3-1 of this document will be utilized for this IRA.

3.4 COMPLETENESS, REPRESENTATIVENESS, AND COMPARABILITY

Completeness, representativeness, and comparability goals identified in Section 3.4 and Tables 3-1 and 3-2 of the FW QAPP will be utilized for this investigation.

Table 3-1
Load Line 11 - RVAAP
Analytical Methods, Parameters, and Project Quantitation Levels
August 2000 Interim Removal Action

Parameters	Analytical Methods		Project Quantitation	
	Water	Soil/Sediment	Water	Soil/Sediment
Propellant Compounds	SW-846-8330 Modified	SW-846-8330 Modified	(µg/L)	(µg.kg)[d]
Nitroglycerin			10	2.5
Nitroquanidine			10	1
Nitrocellulose	EPA 353.2 Modified	EPA 353.2 Modified	10	1
Metals (Target Analyte List)	SW-846-3010A/6010B, 6020, or 7000 Series[c]	SW-846-3010A/6010B, 6020, or 7000 Series[c]	(µg/L)	(µg.kg)[df]
Aluminum			200	20
Antimony			3	0.5
Arsenic			5	0.5
Barium			200	20
Beryllium			4	0.5
Cadmium			2	0.5
Calcium			5,000	500
Chromium			10	1
Cobalt			50	15
Copper			25	2.5
Iron			100	10
lead			3	0.3
Magnesium			5,000	500
Manganese			15	1.5
mercury (CVAA)	SW-846-7470A	SW-846-7471A	0.2	0.1
Nickel			40	4
Potassium			5,000	500
Selenium			5	0.5
Silver			10	1
Sodium			5,000	500
Thallium			2	0.5
Vanadium			50	5
Zinc			20	2
Cyanide	SW-846-9010B	SW-846-9014	10	1
Anions				
Sulfate	EPA 300.00[d]	--	5.0	--
Nitrate/Nitrite	EPA 352.2 or 352.3	--	0.2	--

[a] These are expected quantitation limits based on reagent-grade water or a purified solid matrix. Actual quantitation limits may be higher depending upon the nature of the sample matrix. The limit reported on final laboratory reports will take into account the actual sample volume or weight, percent solids (where applicable), and the dilution factor, if any. The quantitation limits for additional analytes to this list may vary, depending upon the results of laboratory studies.

[b] Values determined between the laboratory method detection levels and the project quantitation levels will be reported as estimated ('J').

[d] Soils and sediment analysis will be reported on a dry-weight basis.

[e] Modification of the SW-846 preparation and analysis procedures may be required to achieve these quantitation levels.

[f] Estimated detection limits for metals in soil are based on a 2-gram sample diluted to 200 milliliters.

CVAA = Cold vapor atomic absorption.

RI = remedial Investigation

Table 3-1
Load Line 11 - RVAAP
Analytical Methods, Parameters, and Project Quantitation Levels
August 2000 Interim Removal Action

Parameters	Analytical Methods		Project Quantitation	
	Water	Soil/Sediment	Water	Soil/Sediment
Semivolatile Organic Compounds (continued)	SW-846-3520/8270C[c]	SW-846-3550/8270C[c]	(µg/L)	(µg.kg)[d]
Indenol(*1,2,3-cd*)pyrene			10	330
Dibenzo(*a,h*)anthracene			10	330
Benzo(*g,h,I*)perylene			10	330
Pesticides/PCBs	SW-846-8081[b]/8082[c]	SW-846-8081[b]/8082[c]	(µg/L)	(µg.kg)[d]
alpha-BHC			0.05	1.7
beta-BHC			0.05	1.7
delta-BHC			0.05	1.7
gamma-BHC (Lindane)			0.05	1.7
Heptachlor			0.05	1.7
Aldrin			0.05	1.7
Heptachlor epoxide			0.05	1.7
Endosulfan I			0.05	1.7
Dieldrin			0.1	3.3
4,4-DDE			0.1	3.3
Endrin			0.1	3.3
Endosulfan II			0.1	3.3
4,4-DDD			0.1	3.3
Endosulfan sulfate			0.1	3.3
4,4-DDT			0.1	3.3
Methoxychlor			0.5	17
Endrin ketone			0.1	3.3
Endrin aldehyde			0.1	3.3
alpha-Chlorodane			0.05	1.7
gamma-Chlorodane			0.05	1.7
Toxaphene			3.0	170
Arochlor-1016			1.0	33
Arochlor-1221			2.0	67
Arochlor-1232			1.0	33
Arochlor-1242			1.0	33
Arochlor-1248			1.0	33
Arochlor-1254			1.0	33
Arochlor-1260			1.0	33
Explosive Compounds	SW-846-8330[c]	SW-846-8330[c]	(µg/L)	(µg.kg)[d]
HMX [Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocinel]			20	2
RDX (cyclonite) [Hexahydro-1,3,5-trinitro-1,3,5-triazine]			20	2
1,3,5,-Trinitrobenzine			2e	1
1,3-Dinitrobenzene			3e	1
Tetryl			50	5
Nitrobenzene			10	1
2,4,6-Trinitroltoluene			3e	1
2,4-Dinitrotoluene			0.13e	1
2,6-Dinitrotoluene			0.13e	1
o-Nitrotoluene			10	1
m-Nitrotoluene			10	1
p-Nitrotoluene			10	1

Table 3-1
Load Line 11 - RVAAP
Analytical Methods, Parameters, and Project Quantitation Levels
August 2000 Interim Removal Action

Parameters	Analytical Methods		Project Quantitation	
	Water	Soil/Sediment	Water	Soil/Sediment
Semivolatile Organic Compounds (continued)	SW-846-3520/8270C[c]	SW-846-3550/8270C[c]	(µg/L)	(µg.kg)[d]
Nitrobenzene			10	330
Isophorone			10	330
2-Nitrophenol			10	330
2,4-Dimethylphenol			10	330
bis (2-Chloroethoxy) methane			10	330
2,4-Dichlorophenol			10	330
1,2,4-Trichlorobenzene			10	330
Naphthalene			10	330
4-Chloroaniline			10	330
Hexachlorobutadiene			10	330
4-Chloro-3-methylphenol			10	330
2-Methylnaphthalene			10	330
Hexachlorocyclopentadiene			10	330
2,4,6-Trichlorophenol			10	330
2,4,5-Trichlorophenol			25	800
2-Chloronaphthalene			10	330
2-Nirtoaniline			25	800
Dimethylphthalate			10	330
Acenaphthylene			10	330
2,6 Dinitrotoluene			10	330
3-Nitroaniline			25	800
Acenaphthene			10	330
2,4-Dinitrophenol			25	800
4-Nitrophenol			25	800
Dibenzofuran			10	330
2,4-Dinitrotoluene			10	330
Diethylphthalate			10	330
4-Chlorophenyl-phenyl ether			10	330
Fluorene			10	330
4-Nitroaniline			25	800
4,6-Dinitro-2-methylphenol			25	800
N-nitrosodiphenylamine			10	330
4-Bromophenyl-phenylether			10	330
Hexachlorobenzene			10	330
Pentachlorophenol			25	800
Phenanthrene			10	330
Anthracene			10	330
Carbazole			10	330
di-N-butylphthalate			10	330
Fluoranthene			10	330
Pyrene			10	330
Butylbenzylphthalate			10	330
3,3'-Dichlorobenzidine			10	330
Benzo(a)anthracene			10	330
Chrysene			10	330
bis(2-Ethylhexyl)phthalate			10	330
di-N-octylphthalate			10	330
Benzo(*b*)fluoranthene			10	330
Benzo(*k*)fluoranthene			10	330
Benzo(*a*)pyrene			10	330

Table 3-1
Load Line 11 - RVAAP
Analytical Methods, Parameters, and Project Quantitation Levels
August 2000 Interim Removal Action

Parameters	Analytical Methods		Project Quantitation	
	Water	Soil/Sediment	Water	Soil/Sediment
Volatile Organic Compounds	SW-846-5030/8260B[c]	SW-846-5030/8260B[c]	(µg/L)	(µg/kg)[d]
Chloromethane			10	10
Bromomethane			10	10
Vinyl chloride			10	10
choroethane			10	10
Methylene chloride			5	5
Acetone			10	10
Carbon disulfide			5	5
1,1-Dichloroethene			5	5
1,1-Dichloroethane			5	5
1,2-Dichloroethene (total)			5	5
Chloroform			5	5
1,2-Dibromomethane			5	5
1,2-Dichloroethane			5	5
2-Butanone			10	10
1,1,1-Trichloroethane			5	5
Carbon tetrachloride			5	5
Bromodichloromethane			5	5
1,2-Dichloropropane			5	5
1,3-*cis*-Dichloropropene			5	5
Trichloroethene			5	5
Dibromochloromethane			5	5
1,1,2-Trichloroethane			5	5
Benzene			5	5
1,3-*trans*-Dichloropropene			5	5
Tribromomethane			5	5
4-Methyl-2-pentanone			10	10
2-Hexanone			10	10
Tetrachloroethane			5	5
Toluene			5	5
1,1,2,2-Tetrachloroethane			5	5
Chlorobenzene			5	5
Ethylbenzene			5	5
Styrene			5	5
Xylenes (total)			5	5
Semivolatile Organic Compounds	SW-846-3520/8270C[c]	SW-846-3550/8270C[c]	(µg/L)	(µg.kg)[d]
Phenol			10	330
bis(2-Chloroethyl) ether			10	330
2-Chlorophenol			10	330
1,3-Dichlorobenzene			10	330
1,4-Dichlorobenzene			10	330
1,2-Dichlorobenzene			10	330
2-Methylphenol			10	330
2,2'-Oxybis (1-chloropropane)			10	330
4-Methylphenol			10	330
N-nitroso-di-n-dipropylamine			10	330
Hexachloroethane			10	330

4.0 SAMPLING PROCEDURES

Sampling procedures are discussed in Section 4.0 of the FW SAP and SAP Addendum for the Load Line 11 (AOC 44) Interim Removal Action. Tables 4-1 and 4-2 summarize sample container, preservation, and holding time requirements for the groundwater and soil matrices for this investigation. The number of containers required is estimated in these tables.

Table 4-1
Load Line 11 - RVAAP
Container Requirements for Soil and Sediment Samples
November 2000 Interim Removal Action

Analyte Group	Approx. No. of Bottles incl. Field QC	Container	Minimum Sample Size	Preservative	Holding Time
Volatile Organic Compounds	10	One 2-ounce glass jar with Teflon® - lined cap (no headspace)	20 grams	Cool, 4° C	14 days
Semivolatile Organic Compounds	10	One 4-ounce glass jar with Teflon® - lined cap (no headspace)	100 grams	Cool, 4° C	14 days (extraction) 40 days (analysis)
Persticides/PCBs	10	One 4-ounce glass jar with Teflon® - lined cap (no headspace)	100 grams	Cool, 4° C	14 days (extraction) 40 days (analysis)
Explosive Compounds	65	One 4-ounce glass jar with Teflon® - lined cap (no headspace)	100 grams	Cool, 4° C	14 days (extraction) 40 days (analysis)
Propellant Compounds	65	One 4-ounce glass jar with Teflon® - lined cap (no headspace)	100 grams	Cool, 4° C	14 days (extraction) 40 days (analysis)
Metals	65	One 4-ounce wide mouth polybottle	50 grams	Cool, 4° C	180 days
Cyanide	65	Use same container as metals	25 grams	Cool, 4° C	14 days
Sulfide/Sufate	65	One 4-ounce glass jar with Teflon® - lined cap (no headspace)		Cool, 4° C	7 days/28 days
Nitrate/Nitrite	65	One 4-ounce glass jar with Teflon® - lined cap (no headspace)		Cool, 4° C	none
Total Organic Carbon	0	One 4-ounce glass jar with Teflon® - lined cap (no headspace)	10 grams	Cool, 4° C	28 days
Grain Size	30	One 8-ounce wide mouth container	100 grams	None	None

QC = Quality Control

Table 4-2
Load Line 11 - RVAAP
Container Requirements for Groundwater And All RI Rinsate Samples
November 2000 Interim Removal Action

Analyte Group	Approx. No. of Bottles incl. Field QC	Container	Minimum Sample Size	Preservative	Holding Time
Volatile Organic Compounds	15	Three 40-mililiter glass vials with Teflon® - lined septum (no headspace)	80 Milliliters	Cool, 4° C HCL to pH < 2	14 days
Semivolatile Organic Compounds	8	Two 1-liter amber glass bottles with Teflon® - lined lid	1000 Milliliters	Cool, 4° C	14 days (extraction) 40 days (analysis)
Pesticides/PCBs	8	Two 1-liter amber glass bottles with Teflon® - lined lid	1000 Milliliters	Cool, 4° C	7 days
Explosive Compounds	8	Two 1-liter amber glass bottles with Teflon® - lined lid	1000 Milliliters	Cool, 4° C	14 days (extraction) 40 days (analysis)
Propellant Compounds	8	Four 1-liter amber glass bottles with Teflon® - lined lid	1000 Milliliters	Cool, 4° C	14 days (extraction) 40 days (analysis)
Metals	4	One 1-liter polybottle	500 Milliliters	Cool, 4° C HNO_3 to pH < 2	180 days
Cyanide	4	One 1-liter polybottle	500 Milliliters	Cool, 4° C	14 days
Sulfide	4	One 300 ml plastic wide mouth	300 Milliliters	Zn acetate, NaOH to pH >9, Cool to 4° C	7 days
Sulfate	4	One 300 ml plastic wide mouth	25 Milliliters	Cool, 4° C	28 days
Nitrate	4	One 300 ml plastic wide mouth	25 Milliliters	Cool, 4° C	48 hrs
Nitrite	4	One 300 ml plastic wide mouth	50 Milliliters	Cool, 4° C	48 hrs

[a] Additional sample volume will be collected for one sample in order for the laboratory to perform appropriate laboratory quality control (QC) analysis

5.0 SAMPLE CUSTODY

5.1 FIELD CHAIN-OF-CUSTODY PROCEDURES

Sample handling, packaging, and shipment procedures will follow those identified in Section 5.1 of the FW FSP and as amended in the Load Line 11 IRA FSP Addendum.

5.2 LABORATORY CHAIN-OF-CUSTODY PROCEDURES

Laboratory chain of custody (COC) will follow handling and custody procedures identified in the laboratories QAMPs.

5.3 FINAL EVIDENCE FILES CUSTODY PROCEDURES

Custody of evidence files will follow those criteria defined in Section 5.3 of the FW QAPP.

6.0 CALIBRATION PROCEDURES AND FREQUENCY

6.1 FIELD INSTRUMENTS/EQUIPMENT

Field instruments and equipment calibrations will follow those set forth in Section 6.1 of the FW QAPP. This will be amended only as specified by the manufacturer's operating instructions.

6.2 LABORATORY INSTRUMENTS

Calibration of laboratory equipment will follow procedures identified in the laboratories QAMPs, corporate, and facility-specific operating procedures.

7.0 ANALYTICAL PROCEDURES

7.1 LABORATORY ANALYSIS

Analytical methods, parameters and quantitation or reporting limits are those listed in Table 3-1 of this document and applicable amendments. The laboratories QAMPs will be followed during the analysis of these samples. The following laboratory Standard Operating Procedures (SOPs) will implement the defined EPA methods.

- GC/MS Volatile Organics Analysis Based on Method 8260B, SW-846, UMV-SOP-8260, 03/10/99.
- GC/MS Semivolatile Analysis Based on Methods 8270B and 8270C, SW-846, UMB-SOP-8270, 07/23/99.
- Gas Chromatographic Analysis Based on Method 8000A, 8010B, 8020A, 8021A, 8080A, 8081, 8082, 8150B, and 8051, SW-846, UGE-SOP-8081A, 03/01/99 and UGE-SOP-8082, 03/01/99.
- Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW-846 3500 Series, 3600 Series, 8150, 8151, and 600 Series Methods, CORP-OP-0001, Rev. 3.4, 4/15/99.
- Analysis of Nitroaromatic and Nitramine Explosives in water and soil by HPLC/UV and Liquid Chromatography/Thermospray/Mass Spectrometry, SAC-LC-0001.
- Total Organic Carbon and Total Inorganic Carbon, UWC-SOP-415.1, 06/25/99.
- Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis, Methods 6010B, UME-SOP-6010B-1T, 02/05/99.
- Graphite Furnace Atomic Absorption Spectroscopy, SW-846 Methods 7000A, UME-SOP-ILM GF, 04/19/99.
- Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1, UME-SOP-245.1, 04/19/99.
- Preparation and analysis of Nitrocellulose in Aqueous, Soil, and Sediments by Colorimetric Autoanalyzer, SAC-WC-0050, Rev. 0.
- Determination of nitroaromatics, nitramines, and specialty explosives in water and soil by high performance liquid chromatography/ultraviolet detector (HPLC/UV) and liquid chromatography/thermospray/mass spectrometry (LC/TSP/MS), SAC-LC-0001, Rev. 5.0.

The laboratories will at all times maintain a safe and contaminant free environment for the analysis of samples. The laboratories will demonstrate, through instrument blanks, holding blanks, and analytical method blanks, that the laboratory environment and procedures will not and do not impact analytical results.

The laboratories will also implement all reasonable procedures to maintain project reporting levels for all sample analyses. Where contaminant and sample matrix analytical interferences impact the laboratories ability

to obtain project reporting levels, the laboratory will institute sample clean-up processes, minimize dilutions, adjust instrument operational parameters, or propose alternative analytical methods or procedures. Elevated reporting levels will be kept to a minimum throughout the execution of this work.

7.2 FIELD SCREENING ANALYTICAL PROTOCOLS

Procedures for field analysis are identified in Section 7.2 of the FW QAPP and in Section 4.0 of the SAP Addendum for the Interim Removal Action at Load Line 11 (AOC 44).

8.0 INTERNAL QUALITY CONTROL CHECKS

8.1 FIELD SAMPLE COLLECTION

Field QC sample types, numbers, and frequencies are identified in Section 4.0 of the SAP Addendum for the Interim Removal Action at Load Line 11 (AOC 44). In general, field duplicates will be collected at a frequency of 10 percent, field equipment rinsates and blanks will be collected at a frequency of 10 percent for samples collected with non-dedicated equipment, and volatile organic trip blanks will accompany all shipments containing volatile organic water samples.

8.2 FIELD MEASUREMENT

Refer to Section 4.0 of the LL-11 (AOC 44) Interim Removal Action SAP Addendum for details regarding these measurements.

8.3 LABORATORY ANALYSIS

Analytical QC procedures will follow those identified in the referenced EPA methodologies. These will include method blanks, LCS, MS, MSD, laboratory duplicate analysis, calibration standards, internal standards, surrogate standards, and calibration check standards as required by specific methods. The laboratories facilities will conform to their QAMP, facility-specific appendices, and implement their established SOPs to perform the various analytical methods required by the project. QC frequencies will follow those identified in Section 8.3 of the FW QAPP.

9.0 DATA REDUCTION, VALIDATION, AND REPORTING

9.1 DATA REDUCTION

Sample collection and field measurements will follow the established protocols defined in the FW QAPP, FW SAP, and the Load Line 11 (AOC 44) Remedial Investigation SAP Addendum. Laboratory data reduction will follow the laboratories' QAMPs guidance and conform to general direction provided by the FW QAPP.

9.2 DATA VALIDATION

An independent third party will provide laboratory data verification and validation as follows:

- 100% verification equivalent to USEPA Tier II
- 10% validation equivalent to USEPA Tier I CLP validation

The data validation report will be provided for incorporation into the IRA final report.

The addresses and telephone number for the third party contractor providing LL 11 IRA data validation services is as follows:

Purves Environmental
7484 Woodspring Ln.
Hudson, OH 44236
Contact: William Purves
Tel: (330) 650-2918
Fax: (330) 650-0463

9.3 DATA REPORTING

Analytical data reports will follow the direction provided in the FW QAPP.

10.0 PERFORMANCE AND SYSTEM AUDITS

10.1 FIELD AUDITS

Informal field audits will be conducted on an on-going basis to ensure the consistency of implementation. This includes field training, daily review of field forms and observing field procedures. The MKM QA Officer and/or the MKM Field Team Leader will perform a minimum of one formal field audit for the media being sampled during the investigation. This audit will encompass the sampling of groundwater from the wells, surface water, soils and sediment. USACE, EPA Region V, or Ohio EPA audits may be conducted at the discretion of the respective agency.

10.2 LABORATORY AUDITS

Routine Missouri River Division HTRW CX on-site laboratory audits will be conducted at the discretion of the USACE. EPA Region V or Ohio EPA audits may be conducted at the discretion of the respective agency. Internal performance and systems audits will be conducted by the laboratories QA staff as defined in the laboratories QAMPs.

11.0 PREVENTIVE MAINTENANCE PROCEDURES

11.1 FIELD INSTRUMENTS AND EQUIPMENT

Maintenance of all field analytical and sampling equipment will follow direction provided in Section 11.1 of the FW QAPP.

11.2 LABORATORY INSTRUMENTS

Routine and preventive maintenance for all laboratory instruments and equipment will follow the direction of the laboratories QAMPs.

12.0 SPECIFIC ROUTINE PROCEDURES TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

12.1 FIELD MEASUREMENTS DATA

Field data will be assessed as outlined in Section 12.1 of the FW QAPP.

12.2 LABORATORY DATA

Laboratory data will be assessed as outlined in Section 12.2 of the FW QAPP.

13.0 CORRECTIVE ACTIONS

13.1 SAMPLE COLLECTION/FIELD MEASUREMENTS

Field activity corrective action protocol will follow directions provided in Section 13.1 of the FW QAPP.

13.2 LABORATORY ANALYSES

Laboratory activity corrective action protocol will follow directions provided in Section 13.2 of the FW QAPP and the laboratories QAMPs.

14.0 QA REPORTS TO MANAGEMENT

Procedures and reports will follow the protocol identified in Section 14 of the FW QAPP and those directed by the laboratories QAMPs.

15.0 REFERENCES

Additional references to the FW QAPP are:

Quanterra Environmental Services, Inc. 1998. *Quality Assurance Management Plan* (QAMP), and Severn Trent Laboratories Laboratory Standard Operating Procedures/QAMP.

GPL Laboratories. *Quality SOP's and Assurance Management Plan* (QAMP),

APPENDIX A

US Army CHPPM Report – Relevant Sections Only

U.S. Army Center for Health Promotion and Preventive Medicine

USCHPPM

HAZARDOUS AND MEDICAL WASTE STUDY NO. 37-EF-5360-99
RELATIVE RISK SITE EVALUATION FOR
NEWLY ADDED SITES AT THE
RAVENNA ARMY AMMUNITION PLANT
RAVENNA, OHIO
19-23 OCTOBER 1998

VOLUME I

Readiness Thru Health

1. Site Name: RVAAP-44, LL-11/Artillery Primer.

2. Site Summary: This AOC operated from 1941 to 1945 to produce primers for artillery projectiles. Load Line 11 was placed on standby in 1945. From 1951 to 1957, LL-11 was used to produce primers and from 1969 to 1971, LL-11 was used to produce fuzes. The surface soil, ground-water, and sediments pathways are considered complete at this site. Five surface samples were collected from outside of the production buildings and analyzed for explosives and metals. The buildings were selected based on the production use. Emphasis was placed on those buildings that were used to produce and store explosives. One sediment sample was collected and analyzed for the same parameters. The sediment sample was collected from a drainage ditch running north from the Load Line to the north. Data collected for RVAAP-26, Fuze and Booster Area Settling Tanks during the first RRSE (reference 11), was used to score the ground-water pathway at the AOC. The subsurface soil used to estimate the ground-water pathway was collected adjacent to the settling tank immediately to the east of Building AP-3$_5$.

3. Pathway Evaluation:

a. Ground Water: *Medium*. Ground-water concentrations were estimated from subsurface soil data from a soil sample collected from 10 to 12 feet (soil at 12 feet was saturated, an attempt was made to recover water from 12 to 16 feet failed) using a standard linear equilibrium soil/water partition equation developed by the USEPA (to estimate contaminant release as a soil leachate) and a dilution factor (to account for dilution of the leachate as it enters the aquifer). This method is consistent with the derivation of soil screening levels and the investigation and modeling efforts conducted at Superfund sites to develop soil cleanup goals and ground-water protection goals (references 6, 7, and 8). A sample equation is shown for RVAAP-41 on page D-11.

(1) Contaminant Hazard Factor: *2.79 = Moderate*

Contaminant	Max Soil Concentration (mg/kg)	pH	K_d	q_s/r_s	Max Ground-Water Concentration (µg/L)	Standard (µg/L)	Ratio
arsenic	20.2	7.5	30	0.2	33.4	4.5	2.39
barium	55.3	7.5	46	0.2	59.8	2600	0.005
chromium	20.3	7.5	16	0.2	62.7	180	0.37
copper	17.9	7.5	unkn	0.2		1400	
zinc	62.3	7.5	160	0.2	19.4	11000	0.00

unkn – K_d value for copper is not provided in references 6 or 8, so ground-water concentration could not be calculated.

(2) **Migration Pathway Factor:** *Potential.* There is no evidence that site contaminants are migrating. However, there are no physical barriers in place to prevent migration.

(3) **Receptor Pathway Factor:** *Potential.* It is unknown if any wells are directly down gradient from this AOC; however, groundwater from near this AOC may be used for irrigation or drinking water.

b. **Surface Water/Human Endpoint:** *Not Evaluated.* While surface water may be intermittently present at this AOC, none was identified during the RRSE at this AOC.

c. **Sediment/Human Endpoint:** *Medium.*

(1) **Contaminant Hazard Factor:** *3.45 = Moderate.*

Contaminant	Max Concentration (mg/kg)	Standard (mg/kg)	Ratio
Aluminum	12000	77000	0.16
Arsenic	15	22	0.68
Barium	63	5500	0.01
Chromium	17	3000	0.01
Copper	14	2800	0.01
Iron	24000	23000	1.04
Manganese	570	380	1.50
Vanadium	23	540	0.04
Zinc	89	23000	0.00

(2) **Migration Pathway Factor:** *Potential.* There is no evidence that site contaminants are migrating. However, there are no physical barriers in place to prevent migration.

(3) **Receptor Pathway Factor:** *Potential.* While this area is surrounded by a fence with locked gates, hunters, scrappers, and fire wood cutters may have access to the site.

d. **Surface Water/Ecological Endpoint.** *Not Evaluated.* There is no surface water at this AOC.

e. **Sediment/Ecological Endpoint:** *High*

(1) Contaminant Hazard Factor: *7.21 = Moderate.*

Contaminant	Max Concentration (mg/kg)	Standard (mg/kg)	Ratio
aluminum	12000	nit	
arsenic	15	6	2.5
barium	63	nit	
chromium	17	26	0.66
copper	14	16	0.88
iron	24000	20000	1.20
manganese	570	460	1.24
vanadium	23	nit	
zinc	89	120	0.74

nit - compound is not in RRSE Appendix B-3 Relative Risk Comparison Values Marine and Aquatic Sediments.

(2) Migration Pathway Factor: *Potential.* There is no evidence that site contaminants are migrating. However, there are no physical barriers in place to prevent migration.

(3) Receptor Pathway Factor: *Identified.* Sediment running off of this site enters into Sand Creek, which is a known habitat for State Endangered Species.

f. Surface Soil: *Medium.*

(1) Contaminant Hazard Factor: *39.5 = Moderate.*

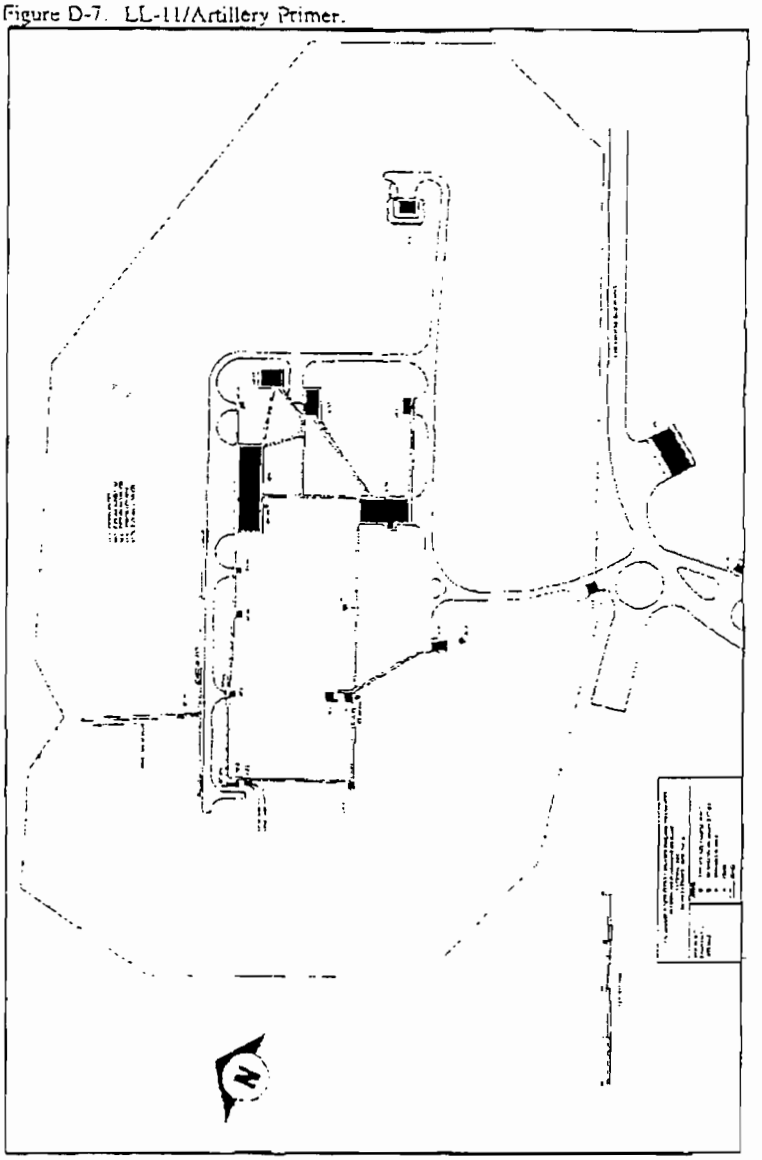
Contaminant	Max Concentration (mg/kg)	Standard (mg/kg)	Ratio
aluminum	23000	77000	0.30
antimony	41.9	31	1.35
arsenic	17.2	22	0.78
barium	2100	5300	0.40
beryllium	4.8	14	0.34
cadmium	41	38	1.08
chromium	170	3000	0.06
copper	3300	2800	1.18
iron	40000	23000	1.74
lead	11000	400	27.5
manganese	1700	380	4.47
mercury	1.8	23	0.08
nickel	34	1500	0.02
silver	2.7	380	0.01
vanadium	33	540	0.04
zinc	3900	23000	0.17
HMX	0.38	3300	0.00

(2) Migration Pathway Factor: *Potential.* There is no evidence that site contaminants are migrating. However, there are no physical barriers in place to prevent migration.

(3) Receptor Pathway Factor: *Potential.* While this area is surrounded by a fence with locked gates, hunters, scrappers, and fire wood cutters may have access to the site.

4. Final Score. High (1), four Media of Concern

Figure D-7. LL-11/Artillery Primer.



APPENDIX B

Jenkins Method

I. DETERMINATION OF TNT/RDX IN SOILS USING COLORIMETRY

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II. INTRODUCTION

Simple colorimetric tests have been developed for on-site determination of TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) in soil (Jenkins and Walsh, 1992). Soils are extracted by shaking samples with acetone. The acetone extracts are subjected to two simple reaction sequences that result in the production of colored reaction products. For TNT determination, the acetone extracts are reacted with potassium hydroxide and sodium sulfite (or EnSys reagent) to form their reddish-colored Janowsky complexes. For RDX determination, the filtered acetone extracts are passed through a disposable anion exchange resin to remove nitrate, and then acidified with acetic acid; the RDX is reduced with zinc to form nitrous acid. The nitrous acid is determined by the Griess Reaction using a Hach NitriVer3 powder pillow, which produces a highly colored (reddish) azo dye. These analytes can be detected visually, and their concentrations are estimated from absorbance measurements at 540 nm for TNT and at 507 nm for RDX. Concentrations of TNT and RDX are linearly related to absorbance up to 1.0 absorbance unit (AU). Detection limits are about 1 µg/g. Concentration estimates from on-site analysis have been found to correlate well with laboratory analyses.

This protocol describes the step-by-step procedures to use these methods for on-site analysis of TNT and RDX in soil. A 20-g sample of field-moist soil is extracted by shaking with 100 mL of commercial-grade acetone for a minimum of three minutes. The actual shaking time that is appropriate for various soils should be determined by conducting a short kinetic study at the beginning of each new field activity. After shaking, soil particles are allowed to settle and the extract is filtered

with a 0.5-μm disposable syringe filter. For TNT determination, the initial absorbance of the filtered extract at 540 nm is obtained using a field-portable spectrophotometer. Then a 25-mL extract aliquot is reacted with either a pellet of solid potassium hydroxide and approximately 0.2 g of sodium sulfite, or with one drop of EnSys reagent, in a glass vial with a Teflon-lined cap. The vial is shaken for three minutes to allow the reaction to take place and the extract is filtered into a cuvette. If a visually detectable pink-red color is present, a final absorbance measurement is made, and the TNT concentration obtained by subtracting twice the initial absorbance from the final absorbance and dividing by the response factor obtained from the analysis of a standard TNT solution. The concentration of TNT is proportional to absorbance for absorbance values below 1.0 AU. If the absorbance is above 1.0 AU, the extract must be diluted and reanalyzed. This colorimetric reaction will also produce reddish Janowsky complexes for TNB (1,3,5-trinitrobenzene), tetryl (2,4,6-trinitrophenyl-N-methylnitramine), and a bluish Janowsky complex for 2,4-DNT (2,4-dinitrotoluene). The presence of these compounds at similar or greater concentrations will interfere with TNT quantification. On the other hand, if TNT is absent or in low concentration, this test can be used to provide quantitative estimates of TNB, tetryl, or 2,4-DNT concentrations in soils. Often, information on the history of site contamination will indicate which of these compounds is present. Walsh et al. (1993) have shown that by far the two most commonly encountered explosives are TNT and RDX.

For RDX determination, a 10-mL extract aliquot is passed through an Alumina-A strong anion exchange cartridge at approximately 5 mL/min to remove any

nitrate ion present in the extract. A 5-mL aliquot of this treated extract is acidified with 0.5 mL of glacial acetic acid and reacted with 0.3 g of zinc dust in the barrel of a plastic disposable syringe fitted with a disposable filter unit. The solution is rapidly filtered (contact between the extract and the zinc should be approximately 15 seconds and not exceed 30 seconds) into a glass vial containing 20 mL of deionized (or distilled) water. The contents of a Hach NitriVer3 powder pillow are added and the vial shaken briefly and allowed to stand for 15 minutes while the reaction takes place. Once the reaction is complete, the presence of a pink-to-red color is indicative of the presence of RDX and the absorbance is measured at 507 nm. To obtain an estimate of the RDX concentration, the absorbance is divided by the response factor obtained from the analysis of a standard RDX solution. The concentration of RDX is proportional to absorbance for absorbance values below 1.0 AU. If the absorbance is above 1.0 AU, the extract must be diluted and reanalyzed. This reaction sequence will also produce the same reddish-colored products if HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), NG (nitroglycerine), nitrocellulose, PETN (pentaerythritol tetranitrate), or NQ (nitroguanidine) are present in the soil. For cases where RDX is absent or in low concentration relative to one of these other compounds, this test can be used to estimate its concentration.

III. STRATEGIC PLANNING

In addition to these colorimetric methods, several immunoassay-based on-site methods have been developed for TNT and RDX. The question often arises as to the advantages and disadvantages of the two types of approaches under various

circumstances. A detailed discussion of this issue is beyond the scope of this protocol, but has been addressed in detail elsewhere (Crockett et al 1996). A major difference, though, is the level of specificity offered by the two types of procedures. The colorimetric-based methods described here are class-specific methods. For instance, the TNT method will detect the presence of polynitroaromatic compounds and can be used to estimate concentrations of 2,4-DNT for sites where TNT is not present at similar or higher concentrations. This can be important if this propellant ingredient has been used on the site of interest. Likewise, the colorimetric RDX method will detect the presence of other nitramines such as HMX, and organonitrate esters such as nitroglycerine (NG) and pentaerythritol tetranitrate (PETN). In fact, the RDX method was successfully used to provide on-site measurements for HMX at an impact area in Quebec (Jenkins et al. 1997).

The immunoassay based tests are more specific to TNT and RDX and will not provide the broad range screening capability for structurally similar compounds. They do have crossreactivities to similar compounds, though. For example, the immunoassay RDX test has about a 15% level of crossreactivity to HMX at the detection limit. It is important to understand the level of crossreactivities for the various chemcials that one might reasonably encounter and these data are available from the manufacturers of the immunoassay-based tests.

IV. QUALITY CONTROL

Minimum quality control (QC) requirements include initial demonstration of the on-site methods using standards in acetone, blank soils, and fortified field blank

soils. Calibration, analysis of a reagent blank, analysis of a field blank soil, and analysis of a fortified soil should be run each day as a part of the routine quality assessment. Once experience is gained with these methods, daily response factors for calibration should be repeatable to ± 10%.

Initial demonstration of capabilities

Prior to the analysis of field samples, the analyst should demonstrate the following: the ability to reproduce response factors from the analysis of duplicate calibrations standards, and the ability to prepare and analyze blank and fortified soil samples.

Field reagent blank

A field reagent blank sample is analyzed each day using steps 4 to 9 (or 4a to 9a) for TNT and steps 10 to 15 for RDX. The reagent blank should be run using the same acetone (containing 3% water) that is used for sample extraction and sample dilution.

Field soil blank

A blank soil sample is analyzed each day according to the method steps outlined in steps 1 to 3 for sample extraction, steps 4 to 9 (or 4a to 9a) for TNT determination, and steps 10 to 15 for RDX determination.

Field fortified blank soil

An air-dried soil, previously determined to be free of TNT and RDX contamination, is used for running the daily fortified soil test. Two separate portions of soil are used for conducting the TNT and RDX spike/recovery tests. A 1.0-mL aliquot of the appropriate spiking standard (400 mg/L) is added to a 20-g portion of the soil in a 125-mL extraction bottle. The sample is allowed to stand for 15 minutes and then it is processed as described in steps 1 to 3 for extraction, and either steps 4 to 9 (or 4a to 9a) for TNT determination, or steps 10 to 15 for RDX determination. Analytical results for these samples should be 20 mg/kg ± 10%. Initially it will be easier to achieve this level of precision with the TNT test than with the RDX test. To achieve this level of precision for the RDX test, it is essential to reproduce the solution contact time with zinc as closely as possible.

V. Basic Protocol

A. Title: Determination of TNT/RDX in Soils Using Colorimetry

B. Introduction

The following are simple chemical methods for on-site determination of TNT and RDX in soil. The methods are based on classical chemical reactions developed in the nineteenth century; the Janowsky Reaction for TNT and the Greiss and Franchimont Reactions for RDX. In both cases, the development of a visual reddish color indicates the presence of the target analytes and the concentrations are estimated using absorbance measurements at 540 nm for TNT and 507 nm for RDX. The major interferences for both methods are chemicals with similar functionality such as 2,4-DNT for the TNT method and HMX for the RDX method.

C. Materials and Equipment

Reagents and standards

Acetone, commercial grade (available in local hardware stores)

Distilled or deionized water, commercial grade (available in local grocery stores)

Potassium hydroxide pellets (reagent grade) or EnSys liquid reagent

Sodium sulfite (reagent-grade crystals) or EnSys liquid reagent

Alumina-A strong anion exchange cartridge, 3 mL (Supelclean ion exchange, #5-7092 with adapter #5-7020M)

Glacial acetic acid, reagent grade

Zinc dust, reagent grade

TNT calibration standard in acetone containing 3% water (4 mg-TNT/L), prepared from 1000 mg/L standard from Supelco

RDX calibration standard in acetone containing 3% water (4 mg-RDX/L), prepared from 1000 mg/L standard from Supelco

TNT spiking standard in acetone (400 mg-TNT/L), prepared from 1000 mg/L standard from Supelco

RDX spiking standard in acetone (400 mg-RDX/L), prepared from 1000 mg/L standard from Supelco

Hach NitriVer 3 powder pillows

Equipment and other supplies

Analytical balance capable of weighing to the nearest 0.1 g

Field-portable spectrophotometer capable of absorbance measurements at 507 nm and 540 nm

Glass cuvettes for spectrophotometer, 25-mm path length

Extraction bottles, 125-mL wide-mouth plastic

Glass vials, 40 mL, Teflon-lined caps

Scintillation vials, 22 mL, plastic-lined caps

Disposable syringes, 50 mL, 25 mL, 10 mL

Membrane filters, 0.45 µm or 0.5 µm

Graduated cylinders, 100 mL, 25 mL, 10 mL

Gas-tight liquid syringes, 10 µL, 100 µL

Measuring dropper squeezers, graduated in increments of 0.5 mL (Hach 21247-10) for acetic acid measurement

Mixing cylinders, glass, 25 mL (graduated cylinders with ground glass stoppers)

Measuring spoons, #511-00 (for zinc dust) and #638-00 (for sodium sulfite) (Hach)

Nail clippers or scissors

Spatula or spoon

Stopwatch

D. Procedure

Calibration, determining response factors for TNT and RDX

Calibration of these protocols is accomplished by determining the absorbance of standard solutions of TNT and RDX in acetone subjected to the procedures detailed below in steps 4 to 9 (or 4a to 9a) for TNT, and in steps 10 to 15 for RDX. For both TNT and RDX, the acetone used to prepare the standards must contain approximately 3% water. The recommended concentration for these calibration solutions is 4 mg/L for both TNT and RDX. The TNT and RDX should be in separate solutions and not combined into one. The response factors for these solutions (using the 25-mm path-length cuvette), after they have been subjected to the procedures below, should be about 0.16 AU/(mg/L) for both RF_{TNT} and RF_{RDX}.

Sample extraction

1. Thoroughly homogenize the field-moist soil sample. Weigh out a representative 20.0-g subsample and place it into a 125-mL extraction bottle.

2. Measure 100 mL of acetone (containing 3% water) with a graduated cylinder and add the contents to the extraction bottle containing the soil sample. Shake the soil/acetone slurry vigorously for a minimum of three minutes (the appropriate shaking time for a given soil is determined by a short kinetic study described in detail in the Commentary section). Allow the soil to settle for at least 10 minutes; the appropriate settling time will vary for each soil.

3. Remove a 40-mL aliquot of the extract with a plastic disposable syringe, being careful not to disturb the settled material, and filter the extract through a disposable syringe filter into a 40-mL glass vial.

Steps for TNT determination (using solid reagents)

4. Place approximately 22 mL of acetone containing about 3% water into a spectrophotometer cuvette and zero the spectrophotometer with the wavelength set to 540 nm.

5. Pour approximately 22 mL of the filtered sample extract into a spectrophotometer cuvette and obtain the absorbance at 540 nm. This is called the initial absorbance (A_I).

6. Pour the extract from the cuvette into a 40-mL glass vial and add one pellet of potassium hydroxide and approximately 0.2 g of sodium sulfite with a measuring spoon. Cap the vial and shake the contents for three minutes. Attach a disposable filter unit to the tip of a 25-mL disposable syringe and place the outlet of the filter in the mouth of a clean cuvette. Pour the contents of the vial into the syringe, being careful to exclude any remaining solid and any viscous liquid from the bottom of the vial, and filter the contents into the cuvette.

7. If the filtered extract has a pink-red color, TNT is present. Measure the absorbance at 540 nm; this reading is called the final absorbance (A_F).

8. The TNT absorbance (A_{TNT}) is calculated by subtracting twice the initial absorbance (A_I) from the final absorbance (A_F).

$$A_{TNT} = A_F - 2A_I$$

Twice the initial absorbance is subtracted from the final absorbance in this calculation because of the increased background absorbance that occurs when yellowish-colored humic substances in the acetone extract react with base. This increases the

background absorbance by about a factor of two even in the absence of TNT or other nitroaromatics (Jenkins 1990).

9. The TNT concentration (C_{TNT}) is obtained by dividing the TNT absorbance by the TNT response factor (RF_{TNT}) and multiplying by 5 (L/kg), the factor which converts concentration in solution (mg/L) to concentration in soil (mg/kg) (based on a 20-g soil sample and a 100-mL volume of acetone used for extraction), and finally multiplying by the dilution factor (DF) used to get the final absorbance in the linear range (<1.0 AU).

$$C_{TNT}\ (mg/kg) = (A_{TNT} / RF_{TNT}) * 5 * DF$$

Steps for TNT determination (using liquid EnSys reagent)

4a. Place approximately 22 mL of acetone containing about 3% water into a spectrophotometer cuvette and zero the spectrophotometer with the wavelength set to 540 nm.

5a. Pour approximately 22 mL of the filtered sample extract into a spectrophotometer cuvette and obtain the absorbance at 540 nm. This is called the initial absorbance (A_i).

6a. Remove the cuvette from the spectrophotometer and add one drop of EnSys reagent to the cuvette. Swirl to thoroughly mix. Wait 30 seconds to allow the chemical reaction to be completed.

7a. If the extract has a pink-to-red color, TNT is present. Place the cuvette in the spectrophotometer and measure the absorbance at 540 nm; this reading is called the final absorbance (A_f).

8a. The TNT absorbance (A_{TNT}) is calculated by subtracting twice the initial absorbance (A_I) from the final absorbance (A_F).

$$A_{TNT} = A_F - 2A_I$$

Twice the initial absorbance is subtracted from the final absorbance in this calculation because of the increased background absorbance that occurs when yellowish-colored humic substances in the acetone extract react with base. This increases the background absorbance by about a factor of two even in the absence of TNT or other nitroaromatics (Jenkins 1990).

9a. The TNT concentration (C_{TNT}) is obtained by dividing the TNT absorbance by the TNT response factor (RF_{TNT}) and multiplying by 5, the factor which converts concentration in solution (mg/L) to concentration in soil (mg/kg) (based on a 20-g soil sample and a 100-mL volume of acetone used for extraction), and finally multiplying by the dilution factor (DF) used to get the final absorbance in the linear range (<1.0 AU).

$$C_{TNT}\,(mg/kg) = (A_{TNT} / RF_{TNT}) * 5 * DF$$

Steps for RDX determination

10. Draw approximately 10 mL of filtered acetone sample extract into a 10-mL disposable syringe, and attach a disposable membrane filter unit to the tip of the syringe. Attach the filter unit to an ion exchange cartridge using the adapter and slowly force the extract through the cartridge at a flow rate no greater than 5 mL/minute. Use the first two milliliters to rinse the cartridge and then collect 5.0

mL in a 10-mL graduated cylinder. Add 0.5 mL of glacial acetic acid to the graduated cylinder using a measuring dropper.

11. Remove the tip and plunger from a 10-mL disposable syringe and attach a disposable filter unit. Place about 0.3 g of zinc dust in the barrel of the syringe. Pour the contents of the graduated cylinder into the syringe, insert the plunger and mix briefly. As rapidly as possible, filter the extract into a vial containing 20 mL of deionized water. Contact between the solution and the zinc should be about 15 seconds but not exceed 30 seconds. An attempt should be made to keep the reaction time for the standard and samples as consistent as possible.

12. Open a NitriVer3 powder pillow and pour the contents into the vial. Shake the vial briefly and allow to stand for 15 minutes.

13. Place approximately 25 mL of acetone containing about 3% water into a spectrophotometer cuvette and zero the spectrophotometer with the wavelength set to 507 nm.

14. If, after standing for 15 minutes, the solution develops a visual pink-to-red color, RDX is present. Pour the contents of the vial into a cuvette and insert the cuvette into the spectrophotometer. Obtain the RDX absorbance (A_{RDX}) at 507 nm. You will note that unlike the TNT method, there is no requirement to obtain and subtract an initial absorbance from the final absorbance after color development. The reason is that any background yellow color due to the presence of humic substances in the acetone extract is removed when the extract is acidified with acetic acid and filtered in steps 10 and 11 (Jenkins and Walsh 1992).

15. Calculate the RDX concentration (C_{RDX}) by dividing the RDX absorbance (A_{RDX}) by the RDX response factor (RF_{RDX}) and multiplying by 5, the factor which converts concentration in solution (mg/L) to concentration in soil (mg/kg) (based on a 20-g soil sample and a 100-mL volume of acetone used for extraction), and finally multiplying by the dilution factor (DF) used to get the final absorbance in the linear range (<1.0 AU).

$$C_{RDX}\,(mg/kg) = (A_{RDX} / RF_{RDX}) * 5 * DF$$

VII. REAGENTS AND STANDARDS

Acetone

No special grade of acetone is required for use in these methods; the commercial grade available in local hardware stores is adequate. The chemistry of both the TNT and RDX tests requires that a minimum amount of water be present. For soil samples from humid regions this poses no problem because there is always sufficient moisture in the soil and this moisture is efficiently extracted by the acetone. For arid soils, and especially for the calibration standard, however, it is important to add about 3% water to the acetone to ensure that sufficient water is present for the reaction to proceed properly.

VIII. COMMENTARY

A. Background information

1. Potential interferences. The on-site chemical methods described here were developed to detect TNT (Jenkins, 1990) and RDX (Walsh and Jenkins, 1991). These

methods, however, are not specific for these two explosives, but will also detect other chemicals with similar structural features. The TNT test will also detect other polynitroaromatic compounds, including TNB, tetryl, and 2,4-DNT. The RDX test will also detect other nitramines and organonitrate esters, including HMX, NG, PETN, NC, and NQ. The class-specific (rather than compound-specific) nature of these tests can be a potential source of interference for the method, or enable the detection of other explosives not detectable using more compound-specific methods, such as ELISA. When these tests are used to estimate concentrations of other detectable compounds, a standard for that compound should be used for calibration. For example, the RDX method was used successfully to estimate HMX concentrations in soil at an active firing range, where the munition being tested was composed of HMX and TNT (Jenkins et al., in press). In this case, calibration was achieved using an HMX standard solution.

2. Dilutions. When final absorbance values for the TNT and RDX tests (A_{TNT} or A_{RDX}) are above 1.0, extracts need to be diluted and reanalyzed to obtain a reliable estimate of TNT or RDX concentration. For both the TNT and RDX tests, the dilution must use acetone containing 3% water to ensure that sufficient water is present for the reactions to proceed properly.

Because concentrations of TNT and RDX in soil can vary from low mg/kg to percent levels, required dilutions can vary over many orders of magnitude. An efficient method of obtaining high dilution ratios for extracts from highly contaminated soils has been to use either 10-µL or 100-µL glass liquid syringes and 25-mL

glass mixing cylinders. Using this technique, dilutions as great as 1:10,000 (2.0 µL to 20 mL) can be made accurately and efficiently under field conditions.

3. Kinetic extraction study. The rate of extraction of TNT and RDX from soil can vary substantially from soil to soil. In general, extraction rates are slower for clayey soils than for sandy soils, and for soils with low concentrations (low mg/kg) of TNT and RDX compared with those containing high concentrations (% levels). At the beginning of each new field activity, the following kinetic study should be conducted with the first field sample that gives a positive response. Do not conduct a kinetic study with a spiked soil, as it does not behave like a field-contaminated soil with respect to extraction kinetics.

When the first sample that gives a positive response is identified, a separate 20-g subsample is extracted to assess the extraction time required to achieve an acceptable extraction. The sample is placed in a 125-mL extraction bottle and 100 mL of acetone added. The sample is shaken for three minutes, the soil allowed to settle, and a 25-mL aliquot of extract removed. This extract is processed as described for TNT or RDX analysis, depending on which analyte had tested positive. If both tested positive, use the TNT test for this assessment. The 125-mL bottle containing the soil and the remaining 75 mL of extract is shaken periodically for 30 minutes, the soil allowed to settle, and an additional 25-mL sample withdrawn and processed as above. The 125-mL bottle is then shaken periodically for an additional 30 minutes, the soil allowed to settle, and a final 25-mL aliquot removed and processed as above. From these analytical results, a decision is made on whether the three-minute ex-

traction time is adequate or whether the 30-minute or one-hour extraction time is necessary to obtain an adequate extraction. It should be kept in mind when making this assessment that the major source of analytical uncertainty will be sampling error due to the heterogeneity of distribution of TNT and RDX in the soil (Jenkins et al., 1996). Requiring a 30-minute or one-hour extraction to improve recovery by only a few percent is unnecessary. In conducting the study described above, a single subsample must be used throughout; if separate subsamples were used, heterogeneity could distort the results.

B. Definitions

TNT - 2,4,6-trinitrotoluene

RDX - 1,3,5-hexahydro-1,3,5-trinitrotriazine

HMX - 1,3,5,7-octahydro-1,3,5,7-tetranitrotetrazocine

2,4-DNT - 2,4-dinitrotoluene

C. Safety

The most significant potential safety hazard associated with these protocols is due to the explosive properties of TNT and RDX. A study reported by Kristoff et al. (1987) indicated that soils contaminated with concentrations of 12% or greater of TNT or RDX were subject to detonation. In general, soil concentrations above 10% are considered reactive.

Acetone is a flammable organic solvent with a boiling point of 56°C (133°F), a flash point of –18°C (–0.4°F), and with flammable limits between 2 and 13% in air.

As such, it should not be used near an open flame or any extremely hot surface. The threshold limit value (TLV) for acetone in air is 1780 mg/m^3.

Potassium hydroxide is a strong base and contact with the skin should be avoided.

Eye protection should be used when using organic solvents such as acetone and stong base such as potassium hydroxide.

D. Critical parameters.

In order to obtain reliable TNT and RDX concentration estimates from these on-site methods, it is important to an establish extraction time based on the short kinetic study described in Section VII A 3 above. For some soils, a three-minute extraction time is adequate while for others a thirty-minute extraction time is necessary to obtain an extraction efficiency that approaches that for the 18-hour ultrasonic extraction used in the standard laboratory method (SW846 Method 8330).

The most critical parameters for the TNT test is to have at least 3% water in the acetone standards and extracts for full color development. The RDX method also requires at least 3% water for rapid color development. The other critical parameter for the RDX test is the contact time of the acidified extract with the zinc metal. If the contact time is too long, a low value for RDX will result. If contact times exceed 30 seconds for any reason, the sample should be reprocessed.

E. Anticipated results: Agreement of on-site methods with EPA Method 8330. Several studies have compared the agreement of the colorimetric TNT method with

those from analysis of separate subsamples using the reversed-phase HPLC method described in EPA Method 8330 (USEPA, 1995). Myers et al. (1994) compared results using 99 soil samples from the Naval Surface Warfare Center, Crane, Indiana. No false negatives were observed for the 14 samples with TNT concentrations above the detection limit of 1 mg/kg. The results for 66 samples analyzed by EPA Method 8330 were less than 0.3 mg/kg and, of these, the colorimetric method produced only two false positives. In another study, Jenkins et al. (1996) compared the agreement of results for 42 samples from six TNT-contaminated locations at three installations; concentrations in these samples varied over five orders of magnitude. Correlation analysis indicated that the agreement was excellent; the slope of the best fit linear regression line was 0.87 with a correlation coefficient of 0.979.

There has been less field validation for the RDX on-site method. However, Marcos et al. (1995) report that the procedure was adequate for characterization of soils from an explosives washout lagoon. More recently, Jenkins et al. (1997) compared the results using this colorimetric method for HMX determination versus those from using EPA Method 8330. A total of 84 samples was compared with concentrations between 1 and 2000 mg/kg. Correlation analysis was used and the slope of the best-fit linear regression line was 0.99 with a correlation coefficient of 0.971.

G. Time considerations. Total analysis time for either theTNT or the RDX determination using these protocols ranges between 30 minutes and an hour, depending on the extraction time used. Samples can be batched and processed in groups of six.

A single trained analyst can be expected to complete about 25 samples per day for TNT and RDX.

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Table 1. Detection limit, linear range, accuracy and precision for colorimetric on-site methods for TNT and RDX.

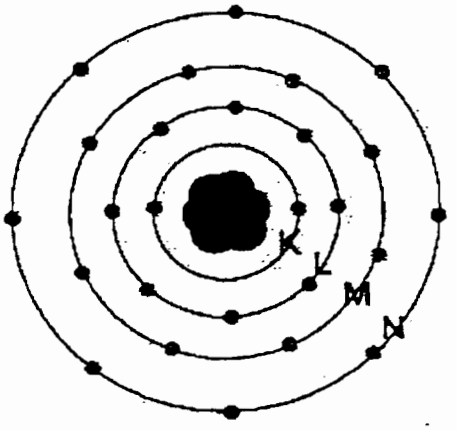
Method	MDL* (mg/kg)	Linear Range** (mg/kg)	Accuracy†	Precision (% RSD††)
TNT	0.7	0.7 – 22	0.919*** 1.05†††	14.7***
RDX	1.4	1.4 – 20	0.988†††	6.9†††

* Method detection limit
** Linear range without dilution of extract. Dilutions should be made with acetone containing 3% water.
† Slope of regression relationship between on-site method and SW846 Method 8330.
†† Pooled relative standard deviation
*** Jenkins et al. 1996
††† Jenkins et al. 1997

APPENDIX C

XRF Method

EPA Method 6200 and Field Portable X-ray Fluorescence



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A presentation developed for the EPA Technology Innovation Office and *On-Site In-Sights Workshops* for innovative field characterization technologies, 1998

Overview:

These training notes provide a brief introduction to x-ray fluorescence (XRF) analysis of soils. XRF has been used to characterize a broad range of materials for over twenty years. Recent advances in digital electronics and semi-conductor technology has yielded very portable XRF analyzers for field analysis of many sample types including soils. These notes will cover the following subjects:

1. Introduction to XRF, basic theory of operation
2. EPA Method 6200
3. Field use of XRF analyzers for soil
    - In-situ testing
    - Prepared sample (or ex-situ) testing
4. Basic quality assurance and sample preparation strategies

During the training session, most of the time will be spent performing measurements on prepared and unprepared soil samples with XRF instruments provided.

1. Introduction to XRF

Basic Atomic Structure:

A model of an atom is shown in Fig. 1. In this model, the atom consists of a nucleus occupied by protons and neutrons. Surrounding this nucleus are negatively charged particles called electrons. In this, the Bohr model of the atom, it is assumed that the electrons orbit around the nucleus of the atom in fixed orbits, much like the planets orbit the sun. While this atomic model is not phyiscally accurate, it is perfectly satisfactory to explain most of the principles encountered in x-ray fluorescence analysis. For an uncharged atom, the number of electrons equals the number of protons. For each element, the electrons are orbiting the nucleus at different energy levels. These "orbits" or "shells" each contain a specific number of electrons. The shells closest to the nucleus get filled first and the shells get filled from the inner-most to the outer-most shell. Shells are named with the inner-most being the K-shell, then L-shell, etc., alphabetically named. The K-shell electrons can be thought of as having the lowest level of stored energy. The further out the electron shells are, the higher the energy level they have stored (the L-shell electrons have more stored energy than the K-shell electrons, the M shell electrons have more stored than the L shell, etc.).

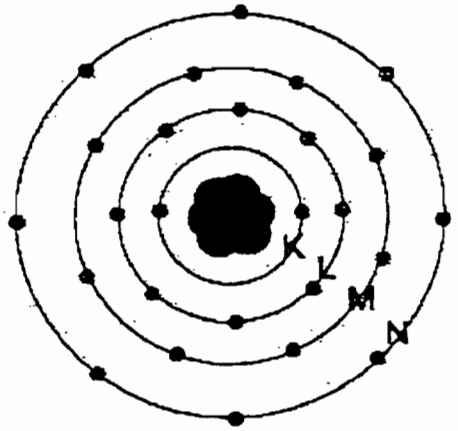


Figure 1. Bohr model of the atom, with nucleus of protons and neutrons. Nucleus is surrounded by electrons in orbit, much like the planets orbit the sun.

What is X-ray Fluorescence?

X-ray fluorescence can be viewed as a three step process. In the first step, as shown in Fig. 2, the atom is struck by a high energy photon, such as an x-ray or gamma-ray from a radioactive source.

In the second step, when the x-ray or gamma-ray has sufficient energy to knock electrons out of the atom, either a K-shell or L-shell electron may be ejected. The NITON XRFs measure these

fluorescent electrons. In the NITON XRF, the photons of energy that cause fluorescence is provided by either a cadmium-109 and/or an americium-241 radioactive source in the instrument. The cadmium-109 is a source of photons at 22.1 keV, 24.9 keV, and 88.0 keV. The americium-241 source provides 59.6 keV gamma-rays.

In the third step of x-ray fluorescence, the vacancy that is created from the electron being ejected is filled by a more outer shell electron. In dropping to the lower energy level, the electron gives off energy in the form of an x-ray. If a k-shell electron was ejected, the electron that jumps down to fill the vacancy emits a k-shell x-ray, if an L-shell electron was ejected, then the next highest electron in orbit emits an L-shell x-ray in order to jump down and fill the L-shell vacancy, etc.

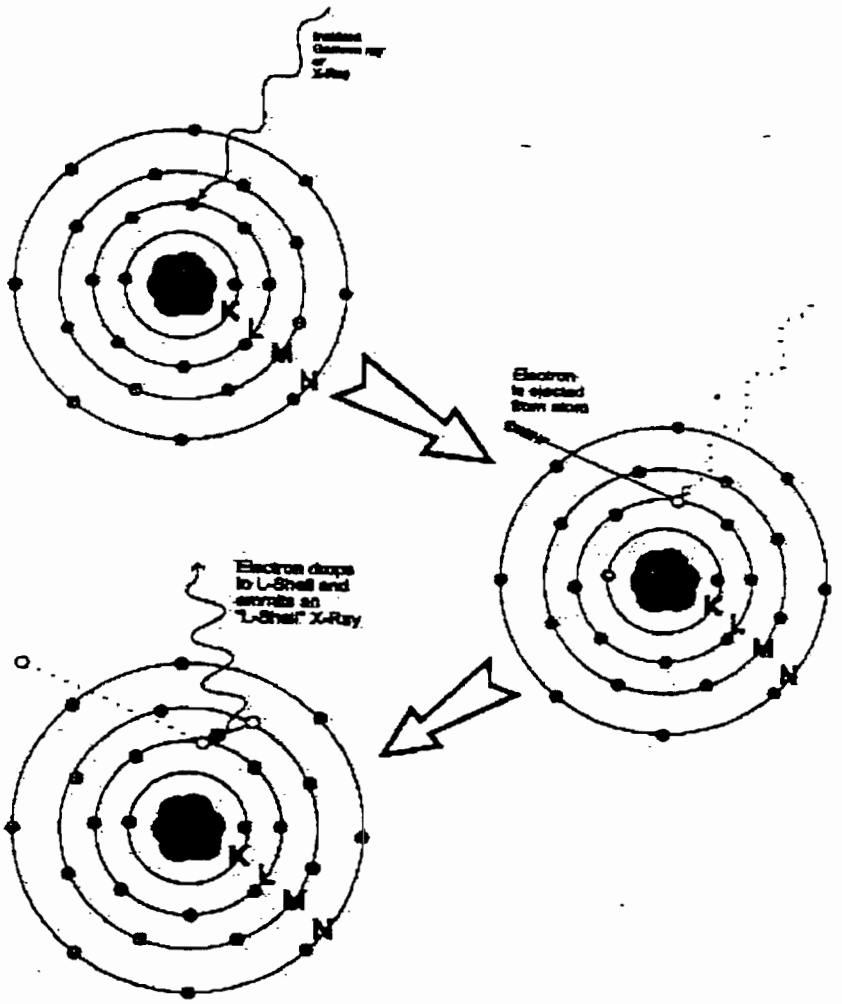


Figure 2. The three step process describing x-ray fluorescence.

The choice of radioactive source depends on what elements you are trying to measure. Cadmium-109 sources are suitable for excitation of the K-shell or L-shell energies of many other elements. Examples include five of the eight RCRA metals - arsenic, chromium, selenium via their K-shell x-rays and lead and mercury via their L-shells and K-shells. Other elements often tested with a cadmium-109 source include zinc, copper, nickel, iron via the K-shell x-rays and gold, uranium via the L-shell x-rays and K-shell x-rays. Americium-241 is used for K-shell fluorescence of cadmium, silver, barium, tin and antimony, but other elements are possible. For

environmental purposes, XRF instruments with both sources - cadmium and americium - are ideal since they produce x-rays from all eight RCRA metals.

Turning the x-ray fluorescence into something useful:

During testing, all the various metals within a soil sample are fluorescing. The XRF instrument must use this fluorescence to identify what elements are present and their concentrations in the sample.

XRF analyzers use x-ray detectors, electronics, and on-board microprocessors to quantify various levels of elements in a sample. Remember, each element produces a fluorescence x-ray at a unique frequency (or energy). Detectors respond differently to different frequencies of x-rays. The electronics connected to the detector use this differing response to determine the frequency of every x-ray that enters the detector, and how many x-rays at each frequency strike the detector. By determining the frequency, the XRF device knows what element emitted the x-ray since elements all have unique x-ray emission frequencies. By determining the total number of x-rays at a particular frequency during a given amount of time, the device can determine the concentration of that particular element in the sample.

2. Regulatory Status - EPA Method 6200:

An EPA Reference Method, incorporated into SW486 under RCRA, is now available for field portable XRF analysis of soils and sediments:

Method 6200 "Field Portable XRF Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.

Features of this method:

1. It is a field screening method, for analysis of in-situ or bagged samples. Developers of the method cite field studies indicating that variability in contaminate concentrations over small distances greatly exceeds instrument measurement variability. Thus, the method is used to thoroughly characterize a site. A large number of screening-level measurements provide a better characterization than a small number of measurements produced by sample removal and analytical analysis.

2. The method provides basic quality assurance methods, including calibration verification, determination of instrument precision, accuracy and limit of detection.

3. The method recognizes the some XRF instruments do not require site-specific calibrations by the operator, that is, the factory calibration provides appropriate data quality.

4. The method recommends that a minimum of 5% of all samples tested by XRF be confirmed by an outside laboratory using a total-digestion EPA analytical reference method.

The method **does not** provide a technique for sample preparation (NITON Corporation is authoring an ASTM Method for sample preparation), or a method to determine data quality of in-situ testing results. This manual provides that information in Sect. 4. Please

contact NITON Corporation for a copy of this method, or view it here.

3. Field Use of XRF Analyzers for Soil:

Field portable XRF is generally used in three ways to test for metals in soil:

- In-situ soil testing,
- Bagged soil sample testing
- Testing prepared soil samples.

In general, in-situ and bagged sample testing are considered field screening methods. *In-situ testing is still a very valuable technique because it is a very rapid testing method and screening methods can generate a great deal of data very quickly.* Common usage and benefits of in-situ testing are provided on the next page, in **Advantages of Field Screening with XRF.**

To achieve analytical-grade data quality operators usually (but not always) must prepare the sample by sieving and perhaps grinding it. It is important to understand your data quality objectives (DQO) in order to determine the appropriate mix of field screening versus prepared sample testing. Examples of in-situ testing and prepared sample testing are shown Figures 3 and 4.

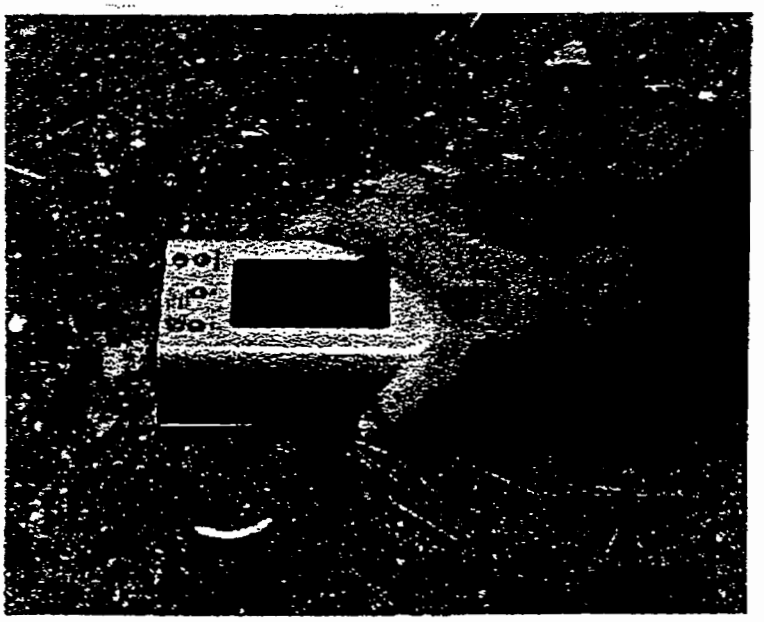


Fig. 3. In-situ testing of soil by placing XRF directly onto the ground. This type of testing is generally screening level data quality.

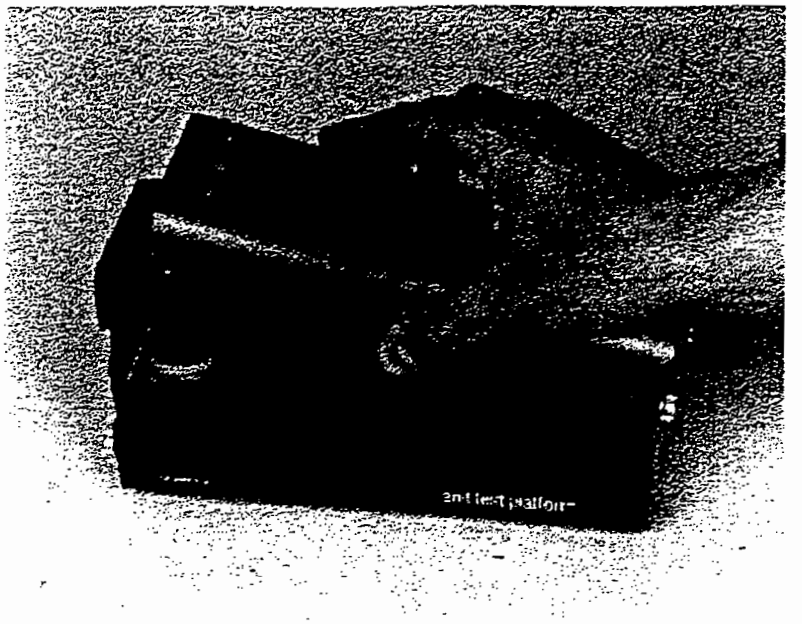


Fig. 4. Prepared sample testing using XRF. With proper sample homogenization, analytical grade testing data is usually achieved.

In-situ testing usually only provides screening-level data quality. This is because analytical testing always requires a uniform, homogeneous sample matrix. A laboratory achieves this by digesting the sample into a hot acid before analysis. Testing directly on the ground does not ensure uniformity is met. Two methods often used to determine the data quality of in-situ testing, relative to well-prepared samples, is given in the section titled **Basic Quality Assurance.**

Advantages of Field Screening with XRF

1. **Focus sampling for laboratory analysis.**

   Operators can profile a site with in-situ testing in order to determine a sampling plan. Sources of contamination can be located very quickly. Contamination boundaries can be established. Regions of low and high contamination can be delineated. Even main analytes of interest can be determined. Sample collection can then be concentrated in regions where contaminants are below or near cleanup levels. There is little need for off-site analysis of samples that the XRF reports as being above the clean-up levels. The cost reduction in off-site analysis easily justifies the up-front price of the XRF.

2. **Assure site meets clearance levels before contractors leave the site.**

   By combining in-situ and prepared-sample XRF testing, you can eliminate failed clearance tests. Before samples are sent to the lab for final clearance, XRF operators can prepare and test the same samples on-site because XRF is non-destructive. Provided the XRF reports levels below clean-up standards, operators can be assured that the lab will concur. XRF operators should always use prepared samples for this analysis. This procedure virtually guarantees clearance criteria will be met. Benefits include:

- The contractors can leave the site earlier thus reducing costs.

- Pre-testing prepared samples with XRF has assured that the lab will report levels below cleanup criteria, which reduces cost since the contractor will not be called back to the site for additional cleanup.

3. **Minimize volume of hazardous waste for treatment or disposal.**

   Samples can be constantly evaluated on-site with field portable XRF to be sure only soils with contaminant levels in excess of cleanup levels are being treated or removed. Also, samples can be analyzed on-site to determine if waste will pass/fail TCLP testing. Soils that pass this procedure can be disposed at a non-hazardous waste landfill, generating enormous savings.

4. Basic Quality Assurance and Sample Preparation Strategies

This section is intended to provide basic quality assurance steps for XRF testing. This is mainly on overview. All manufacturers provide training (usually free) to cover these topics in depth. Please contact the manufacturer of the instrument for a detailed quality assurance plan or to attend the next available training session.

Two Important Rules of Thumb:

1. Never report XRF results as being below cleanup levels based solely on in-situ XRF test results. Always perform some sample preparation to support these results. It is a good idea to confirm at least 5% of results via laboratory testing. In general in-situ XRF results will be lower than results from prepared samples, or from laboratory results. EPA Method 6200 recommends a minimum of 5% confirmatory analysis.

2. Always evaluate the data quality of in-situ testing results using one of the methods described in detail below.

Quality assurance can be broken into three main areas:

1. Proper verification of instrument operation

2. Determining data quality of in-situ testing, and amount of sample preparation required to achieve analytical data quality.

3. Proper sample preparation and testing for comparison to reference laboratory analysis.

1. **Instrument verification:**

   Quality assurance here constitutes testing of known standards to verify calibration, testing of blank standards determine limits of detection and to check for sample cross-contamination or instrument contamination. EPA Method 6200 provides a detailed procedure.

2. **Determining data quality of in-situ testing:**

For operators relying extensively on in-situ testing, it is extremely important to determine the data quality of this testing at a given site. XRF operators generally follow one of two procedures to determine data quality of in-situ testing:

1. Direct comparison of in-situ test results to laboratory results to determine correlation curve.

2. For subset of samples perform stepwise sample preparation to determine the effect of sample preparation on XRF testing results, and compare XRF test of fully prepared sample to laboratory analysis of the same sample.

Method (1) for determining data quality of in-situ test results:

Direct comparison of in-situ testing to laboratory testing

Operators will pick a number of testing locations and take several in-situ XRF measurements in that location. Or a sample can be collected and bagged, with several XRF tests performed directly into the bag. A sample is then collected from the testing region and sent to a laboratory for homogenization and analysis. (Or the bagged sample is sent). The average result from this series of XRF tests is plotted against the laboratory result. A correlation curve is determined, and this curve is used to "correct" future in-situ testing results from the site in question. The correlation curve developed from this analysis incorporates bias in the XRF result due to the lack of sample preparation. In this way, the bias from in-situ testing is removed, on average, from the in-situ test results.

As an example, in-situ testing data for zinc in soil is shown in Fig. 5. A direct comparison of the in-situ XRF results to the laboratory results reveals a consistent bias in the XRF data. Based on the least squares fit shown in the graph, the laboratory result is on average about 35% greater than the XRF result. This bias exists because the soil was not prepared before XRF testing, and particles like small pebbles in the soil surface "shielded" the zinc x-rays from reaching the detector. However, the comparison reveals a well-behaved correspondence between XRF and laboratory results. For this site, operators relied on extensive in-situ XRF analysis, but used the correction factor of 1.35 to correct in-situ results. This is a good example of using a direct comparison between initial in-situ XRF data and laboratory analysis to then gather a large amount of in-situ XRF data for off-line correction.

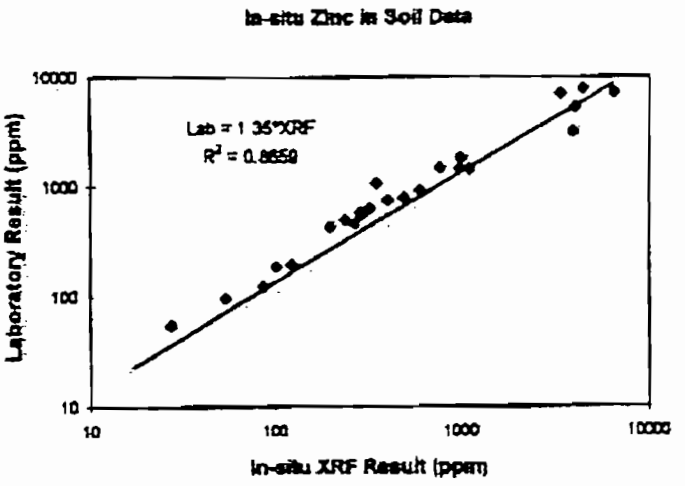


Figure 5. Comparison of in-situ XRF results for zinc in soil to laboratory results.

Method (2) for determining data quality of in-situ test results:

Stepwise sample preparation to determine data quality of in-situ testing.

The purpose of this protocol is to determine the amount of sample preparation required to get quantitative, as opposed to screening level, data quality. The basic strategy is to perform increasingly rigorous levels of sample preparation, followed by XRF analysis each time, until the XRF result stops changing. *This protocol is not intended for every sample, but rather for a small percentage of samples considered representative of the site.* If the operator can demonstrate that quantitative data is achieved with little or no sample preparation, then the site characterization will be completed much more quickly but correctly.

For example, an operator may be able to demonstrate that the XRF result changes considerably when samples are passed through a 2 mm sieve, but that XRF results do NOT change appreciably upon finer sieving. In this case the operator can conclude that good XRF data is achievable with only 2 mm sieving. Sieving only to this level requires far less time than a more robust sample preparation. A protocol to determine the appropriate level of sample preparation is the following:

1. Delineate a region of soil approximately 4" x 4".

2. Perform several in-situ tests in this area, or collect the top (approximately) quarter inch of soil from this region, bag the soil, test through the bag. In either case, average the results.

3. If you did not bag the in-situ test sample, collect the top (approximately) quarter inch of soil from this region and sieve through the 2 mm sieve provided. Otherwise sieve the bagged sample used for the in-situ test. Thoroughly mix the sieved sample, and place some of the sieved material into an XRF cup, and perform a test of this sample.

4. If the results of this prepared sample differ less than 20% with the average in-situ result, this indicates the soil in this region is reasonably homogeneous. The data quality in this case is probably at the semi-quantitative level, rather than just screening data.

5. If the results differ by more than 20%, this indicates the soil is not very homogeneous, and there are serious particle size effects affecting your in-situ measurements.

6. In this case, sieve the sample through the 250 ~m sieve. Mix this sample and place a sub-sample into an XRF cup for testing. If this result differs from the previous by less than 20% then this indicates that at a minimum the 2mm sieving is necessary to achieve higher data quality.

7. If this result differs by more than 20% from the sample sieved through 2 mm, then particle size effects are still affecting the XRF result. In this case samples should be sieved through 125 μm to assure data quality at the quantitative level. In our experience, sieving through 125 μm is always adequate to assure a quantitative data quality level.

3. **Comparison of prepared XRF samples to laboratory analysis.**

As shown in Fig. 6, comparison of XRF analysis of prepared soil samples generally yields very good agreement with laboratory analysis, provided proper sample preparation and handling is performed. The data shown is from a NITON 700Series XRF used within the EPA lead laboratory accreditation program (ELPAT). In this program participant laboratories (including field operators) receive quarterly samples for analysis. Results are reported, and compared to reference laboratory results as a means for laboratories to gauge their measurement accuracy.

The data shown below are several rounds of analysis where NITON operators participated in this program, to demonstrate that field portable XRF can routinely meet EPA lead laboratory accreditation requirements for prepared samples. It is important to note that samples sent to participant laboratories are homogenized and ground to 125 μm particle sizes or less.

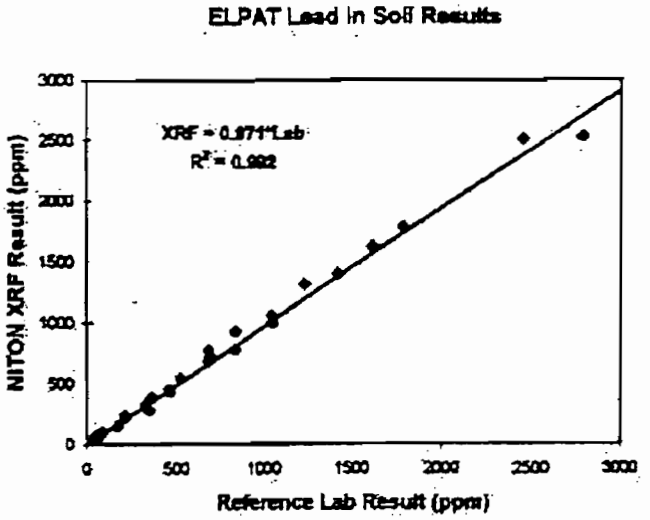
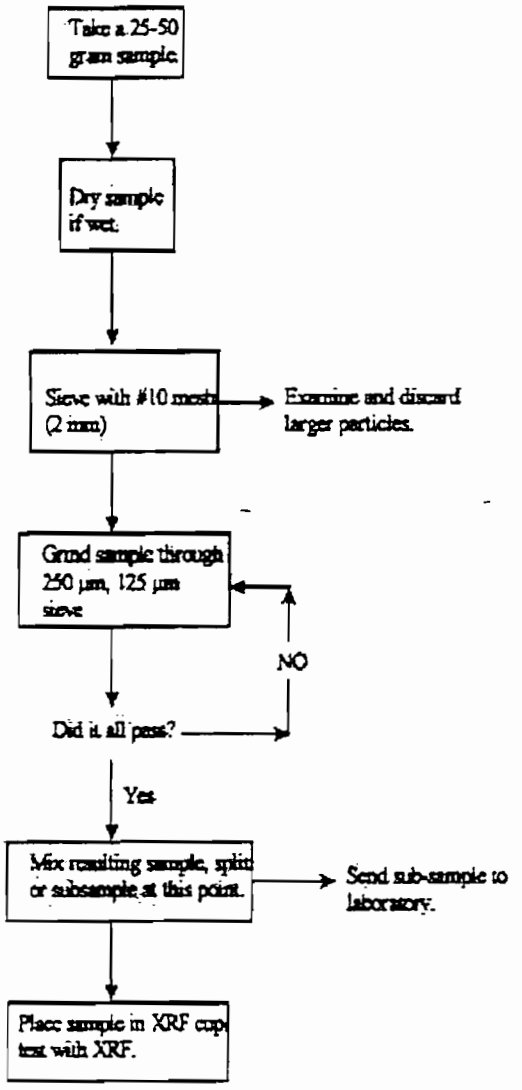


Figure 6. Comparison of XRF results to laboratory results for prepared soil samples.

Some XRF operators compare prepared XRF analysis to laboratory analysis to demonstrate the accuracy of XRF analysis. This is most often done to satisfy regulatory or client demands for defensible data. Please note this is different than the above comparison of in-situ results to lab results. In that case it is expected that the results will differ, and the goal is to determine an overall correction factor. For prepared samples the operator is attempting to make a direct comparison of the absolute XRF result to the laboratory result to show no further corrections to the data are required.

Sample preparation protocol.

For this type of comparison always use thoroughly prepared samples before XRF testing. One possible sample preparation protocol is described in Fig. 7 (next page). This protocol guarantees that the test results are being compared properly. Without such a preparation protocol there is no way to assure that the samples being compared are identical. Use of this protocol for prepared-sample XRF analysis generally provides analytical-level data quality.



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Comparing Field Portable X-Ray Fluorescence (XRF) To Laboratory Analysis Of Heavy Metals In Soil

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January 29-31, 1997

ABSTRACT

Field portable x-ray fluorescence (XRF) continues to gain acceptance as a complement to traditional laboratory testing of metal contaminated soil. The quality of data produced by field XRF varies with site conditions, soil composition, and sample preparation. Quality assurance protocols for the field method usually require that a number of field samples be split and sent to a laboratory for confirmatory analysis. This confirmatory analysis can provide valuable information of the effectiveness of the field methodology.

We present field and confirmatory data from a variety of contaminated sites that show the effectiveness of field XRF under different site conditions, with different methods of sample preparation. In general, we find that field sample preparation (drying, grinding, sieving, homogenization) significantly improves data quality, compared to unprepared, in-situ measurement. The level of data quality provided by rapid, low-cost in-situ or abbreviated preparation methods can be predicted in the field by the comparison of representative field samples to fully prepared split samples, and can be proven by laboratory confirmation.

We find that the method with which one performs sample splitting for confirmatory analysis can greatly affect the correlation of the field results to the laboratory results. Unexpectedly poor correlation often arises from the introduction of error in the confirmatory sample splitting and sample handling procedures, and which may be misinterpreted as a deficiency of the field method. We discuss

ways to avoid the introduction of such error. We also discuss how to use confirmatory analysis to determine the quality of field-obtained XRF data, and we discuss procedures for comparing the field XRF method to the laboratory method.

THE UTILITY OF FIELD METHODS

Field methods can offer significant advantages over laboratory methods, provided they are sufficiently accurate and well-documented to support field decision-making. Field analysis is frequently less expensive per sample than laboratory analysis because of less need for sample handling, transportation, and chain-of-custody documentation. In addition, the rapid analytical turn-around of a field method can provide timely support for field decision-making, and greatly reduce overall project cost. The lower cost-per-sample allows for denser, more complete sampling. And field methods offer the ability to rapidly delineate contaminated areas or "hot-spots", supporting interim control measures and guiding remediation.

Field portable x-ray fluorescence (XRF) is an exemplary field method, offering extremely rapid, cost-effective screening of heavy metals in soil by *in-situ* measurement. It is also versatile enough to provide *ex-situ*, prepared-sample analysis in the field with accuracy that can rival that of standard laboratory analysis. Even in cases where laboratory analysis is required, field XRF can be used to rapidly pre-screen samples (directly through the plastic sample bag), to obtain the optimal utility from the laboratory sampling effort. Since XRF is completely non-destructive, any sample collected and measured in the field can be retained for verification by a laboratory.

While field XRF cannot generally provide the low detection limits attained by laboratory methods, it can often provide detection limits well below regulatory levels. For example, field XRF can easily provide detection limits for lead-in-soil of less than 100 ppm, well below typical regulatory levels of 300 to 1500 ppm.[1,2,3]

FIELD SAMPLE PREPARATION FOR XRF

The in-situ XRF measurement requires little or no sample preparation. Although the instrument can measure undisturbed soil directly, we recommend a minimal preparation protocol. First, the field operator should remove any debris, such as leaves, twigs, grass, and stones, from the measurement surface. Second, the operator should loosen the soil to a depth of 1.5 to 2.5 cm over an area of at least 10 cm diameter, and stir the loosened soil to achieve some homogenization. The loosened soil may be allowed to dry in the sun for a few hours before the measurement, to improve accuracy. Just before the measurement, the operator should mix and level the loose soil and pack it down gently. For improved accuracy, the operator may screen or comb the loose soil with a 2 mm mesh to remove stones, roots, broken glass, metal fragments, paint chips and other such objects.

Ex-situ measurement offers a variety of sample preparation strategies. A core sampling device may be used to collect the sample to a well-defined depth. A composite sample may be formed by combining soil from several spots in the sample area, mixing thoroughly before measuring. The sample may be dried by spreading it out on a paper and exposing it to sunlight and air, or by using a small field stove or oven. The dried sample can be screened with a 2 mm mesh to remove large objects, and placed in a sample bag, or prepared further. The ultimate field sample preparation for XRF is to grind and sieve the soil to reduce the particle size to less than 0.250 mm (or preferably to less than 0.125 mm), homogenize well, and then sub-sample 3 to 5 grams of the dry, well-ground soil and place in an XRF sample cup for analysis.

The various stages of sample preparation require time and effort, but provide improved measurement accuracy. Core sampling improves the accuracy of the sample definition. Compositing increases the sample support, improving the sample's ability to represent a particular sample area, or "sampling unit". Drying the sample removes the diluting influence of moisture, and facilitates further sample preparation stages of grinding and sieving. Screening the sample with a 2 mm mesh removes the influence of large non-soil particles. Grinding facilitates thorough homogenization of the sample, reducing the effects of fundamental (particle) error and XRF particle-related bias. Sieving with grinding assures complete and accurate particle size reduction. Thorough homogenization assures accurate, unbiased sub-sampling. And the XRF sample cup assures consistent, accurate sample presentation to the XRF instrument. A companion paper[4] discusses the importance of particle-related effects and their control in detail.

QUALITY ASSURANCE FOR THE LABORATORY AND FIELD METHODS

Quality assurance (QA) is a basic requirement of any analytical method. No measurement has value for decision-making unless its accuracy is known and understood. A quality assurance program should aim to assess the quality and accuracy of all stages of the measurement process, from sample selection and collection through sample handling and preparation and analysis. Significant levels of error can occur at all stages in the measurement process, and accuracy requires that errors at all stages be controlled. Laboratories concentrate a great deal of effort on their QA programs, which assess and control laboratory sample preparation and analytical error. At present, relatively little QA effort focuses on sample collection and sample handling. That is a pity, because much, if not most, of the overall measurement error occurs in the field, not the laboratory. If we do not assess the errors in the field stages, we cannot know the true accuracy of the laboratory-based measurement.

QA programs generally include calibration checks at several concentrations (typically at "background" or low-level, and at moderate to high level), and replicates (collocated or split samples) to assess variation. QA for a field method usually includes verification or confirmatory analysis of some samples, typically by laboratory. Laboratory confirmatory backup may be required for field methods used in decision-making, and assures that the field method is appropriate, effective, and of sufficiently accurate for its purpose. For in-situ XRF, the accuracy can vary significantly from site to site. Fully prepared ex-situ XRF offers the potential for field-based verification of the in-situ XRF method.

The laboratory confirmatory method should match the field method as well as possible. For example, since XRF is a total element method, the confirmatory method should also be a total element method. For lead, most laboratories use atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES). Both of these methods require that the soil sample be introduced to the instrument as a solution, so the lab must perform sample extraction or digestion. Laboratory analysis of total lead requires a strong acid total digestion to achieve complete dissolution of the sample. Weak acid extraction and leaching-based methods, such as the toxicity characteristic leaching procedure (TCLP), are not appropriate confirmatory methods for the total element XRF method. The most appropriate confirmatory method for XRF would completely digest silicaceous minerals, as does EPA draft method 3052. However, total digestion is relatively difficult and expensive, and seldom used in environmental analysis. More commonly used strong acid-based extractions such as EPA methods 3050 and 3051 generally recover most of the heavy metal content, but they cannot recover metals locked within an undissolvable silicate.

ASSESSING TOTAL MEASUREMENT ERROR

Error includes the components of bias and precision (or variation). It is difficult to determine the true measurement bias, because we do not generally know the true concentration of the contaminant in the sampling unit. Instead, we must be satisfied to compare our measurement results against confirmatory results. We can assess the total measurement precision by replicate sampling the sampling unit, and observing the variation of the resulting measurements. To avoid spatial bias in our assessment, we avoid taking replicates from identical sampling locations. Ideally, we select replicate sampling locations randomly throughout the sampling unit. The sampling unit is the volume of soil a particular sample is intended to represent. For example, suppose the sampling unit is a plot running along a 10 meter long wall, from the wall to 2 meters from the wall, and from the surface to a depth of 2.5 cm. The total area of the sampling unit is then 20 square meters, and the total soil volume is 0.5 cubic meters. If the sampling protocol calls for a composite sample of 6 randomly located cores, then replicates should be sampled and composited exactly the same way: as 6 randomly located cores. The greater the number of replicate samples, the more accurately we can determine the total measurement precision. For routine work, it may be sufficient to take only two replicates (that is, one duplicate pair) per sampling unit. The precision may be expressed in terms of relative standard deviation (RSD), or coefficient of variation (COV), which is simply the standard deviation of the set of replicate sample results divided by the mean of the set.

Total measurement variation may be substantially larger than you expect! It includes the variation in sample representation, sample collection, sample handling, sample preparation (including subsampling and homogenization), and analysis. Particle effects, including fundamental error, can generate serious variation in sampling and subsampling, depending on the particulate form of the contaminant. Soil contaminated by paint chips can exhibit severe particle effects, with relative errors easily exceeding 20 percent; this is discussed in detail in a companion paper.[4] Another significant contributor to total error is the representativeness of the sample collected. The contaminant is not likely to be distributed evenly through the sampling unit. If we ignore spatial variation and let a single point represent a large area, we can expect relative errors of at least 20 percent. To reduce the effect of spatial variation, we must "increase sample support"; composite a sample from several points in the sampling unit. The total measurement variance, σ_{total}^2, *is given by the sum of the individual component variances:*

$$\sigma_{total}^2 = \sigma_{sample\ representation}^2 + \sigma_{sample\ collection}^2 + \sigma_{sample\ handling}^2 + \sigma_{sample\ preparation}^2 + \sigma_{analysis}^2,$$

where the σ's denote the errors introduced at each stage of the measurement process. The error due to the analytical stage itself, $\sigma_{analysis}$, may be a minor, even negligible contributor to the total error.

Suppose our field method has an analytical error of 10 percent, while the lab method has an analytical error of only 1 percent. You might expect that your choice of field or lab method will seriously affect the total measurement error. Not necessarily so. Suppose the total relative error using the super accurate (1%) lab analysis is 30 percent. Then the total relative error using the field method (precision 10%) ought to be

$$\sigma_{total} = SQRT((30\%)^2 - (1\%)^2 + (10\%)^2) = 31.6\%.$$

The difference in total error (31.6% versus 30%) is of little or no practical significance. In general, a

component of error will affect total error only if it is large relative to the other components. If analytical error is much smaller than sampling and preparation-related errors (and it often is), then it will little affect total measurement error.

ASSESSING THE COMPONENTS OF MEASUREMENT ERROR

To assess the variation due to a particular stage of the measurement process, we prepare identical (replicate) splits and carry the replicates individually through the stage and the remainder of the measurement process. The variance due to a particular stage is calculated from the variance of the identical replicate results, minus the variances due to the remaining measurement stages.

The easiest meaurement stage to assess for precision is the final, analytical stage. Analytical replicates entering analysis must be as identical as possible. For XRF this condition is particularly easy to satisfy: replicates can be repeat measurements of the same sample. For the laboratory, analytical replicates can be splits from a well-mixed digestate liquid.

Variance due to the final subsample and packing of the XRF sample cup can be assessed by preparing replicate sample cups from a well-mixed container of ground, sieved sample material. The variance due to subsampling and cupping is the variance of the replicates minus the variance of the analytical replicates.

COMPARING AND CORRELATING DIFFERENT ANALYTICAL METHODS

If you want to compare two different analytical methods, the most accurate assessment of their equivalence will derive from the analysis of identical sample material. The sample material should be split as late as possible in the measurement process to assure that the two analytical methods see similar material. Otherwise, variance will be introduced in intermediate stages that will ultimately degrade the accuracy of the assessment, even if such variance is carefully measured and subtracted from the total.

Suppose we wish to compare two atomic spectrometry methods, AAS and ICP-AES. The sample preparation is identical; both require sample digestion. So we split the sample *after* the digestion. The two methods will measure identical liquid digestate. Any difference between the two measurement results can then be attributed to the analytical stage, not to the sample collection, sample handling, or sample preparation. If we wish to assess variation in the sample preparation stage, that assessment should be performed separately.

Suppose instead we wish to compare AAS with prepared sample XRF. We split the sample after the final stage of XRF sample preparation. The dried, ground, sieved and mixed material will split accurately, giving uniform analyte concentration to each method. Alternately, instead of splitting, we can send the analyzed XRF cup to the lab, assuring that the sample is truly identical. Of course, we do not compare XRF directly to AAS, but to the combination of the digestion method and AAS analysis. We can attribute differences in the results to the digestion and to the analytical methods, but not to variation in the sample collection and handling stages.

But if we wish to compare in-situ XRF with lab AAS, we must split the sample early in the measurement process, since the in-situ method requires so little sample preparation. We should still strive to make the sample splits as identical as possible. The in-situ XRF method measures a small area of ground, only a few square centimeters. As nearly as possible, the sample taken to the lab for

comparison to AAS should be removed from the same spot measured by the in-situ method.

When we observe differences between analytical methods, we must bear in mind that significant variation results from the sample collection, handling, and preparation stages. We should always consider the big picture: total measurement error. Unless two analytical methods differ by a more than a few percent, the impact on total measurement error will probably be insignificant.

EXPERIMENTAL DETAILS

The data presented in this paper come from the study of samples from three lead-in-soil sources. The first source was a site around a highway bridge in Smithtown, Long Island, New York. The soil around the bridge had been contaminated by leaded paint that had come off the bridge through the aging and weathering of the painted surfaces, and through bridge maintenance activities. We observed visible paint chips in many of the samples. The second source was an archive of Massachusetts residential lead-in-soil samples collected by Environmental Science Laboratory, Inc. We believe most of the lead in these samples was derived from paint chips. The third source was a low-income residential tract in Northbridge, Massachusetts where lead-in-soil had been determined to be the cause of 6 childhood lead poisoning cases. The Massachusetts Department of Environmental Protection (MA-DEP) was overseeing remedial activities in the neighborhood at the time the measurements were performed. Since paint chips were not visible in the soil at this site, we believe that most of the lead was contained in finely-dispersed particles. Many of the samples measured high in zinc as well as lead, indicating that the likely contaminant origin was paint. The samples from the three sources represented a variety of soil types and textures, from sandy to loamy to clayey.

All XRF data were collected with a NITON XL equipped with a 10 mCi cadmium-109 radioisotope source, silicon PIN diode detector, (750 eV resolution), and the Lead-In-Soil Analysis (LISA) software package. The LISA software reports concentrations in parts per million (ppm) for lead, arsenic, zinc, and copper in soil with matrix corrections determined by Compton normalization.[1] A newer model, the NITON 700, offers similar performance for lead, but with expanded multiple element capability.

In-situ XRF measurements were prepared minimally, by removing debris, loosening the soil, stirring the soil, and flattening the soil before measurement. The bridge samples of approximately 250 grams each were transported raw in heavy plastic bags and measured by the in-situ XRF method in the laboratory. In-situ measurements were 30 seconds in duration, adjusted for source decay. Ex-situ samples of approximately 100 grams each were field-prepared by air and/or sun drying, screening with a 2 mm sieve, then grinding and sieving to 0.250 mm or 0.125 mm. We measured prepared samples in Mylar window XRF cups for 120 seconds duration, adjusted for source decay.

Environmental Science Laboratory (Medway, MA), an ELPAT proficient and A2LA accredited laboratory, analyzed the Long Island bridge samples and the Massachusetts residential samples by flame-AAS. The MA-DEP Wall Experiment Station (Lawrence, MA) analyzed the Northbridge samples by ICP-AES. Both laboratories used microwave-assisted strong acid extractions, and achieved recoveries of 80 to 93 percent on reference materials (RMs). Since Wall Experiment Station reported results in mg/kg wet mass, we calculated mg/kg dry mass with water content determined by gravimetry. We adjusted both laboratory data sets by constant factors to give mean recoveries of 100 percent on RMs.

RESULTS AND DISCUSSION

The XRF method gave excellent performance on reference materials. (Graph 1) A set of 14 measurements on NIST Standard Reference Material (SRM) soils and Environmental Lead Proficient Analytical Testing Program (ELPAT) soils gave a linear regression slope of 0.996 and an R^2 of 0.996. For the 10 reference soils with more than 100 ppm lead, the mean recovery of the XRF was 0.992 and the standard deviation of the recovery was 0.058, for an RSD of 5.8 percent.

Fully prepared XRF samples showed excellent correlation with laboratory AAS for material split after the final grinding, sieving, and homogenization. (Graph 2) A set of 20 fully prepared XRF samples (oven dried, ground to 0.125 mm), including 11 bridge site samples, 6 residential lead samples, and 3 NIST SRM soils, gave a linear regression slope of 1.004 and an R^2 of 0.995. For the 17 samples with lead concentrations above 100 ppm, the mean recovery of the XRF relative to AAS was 0.952 and the standard deviation of the recovery was 0.068, for an RSD of 7.1 percent. The subset of 11 bridge site samples gave a linear regression slope of 0.958 and an R^2 of 0.994. The subset of 6 Massachusetts residential samples gave a linear regression slope of 1.010 and an R^2 of 0.994. We were pleased to observe such strong correlation of widely different analytical methods, especially considering the possibility of less than total lead recovery by the laboratory extraction.

The Massachusetts residential samples yielded an unexpected observation of variation due to standard laboratory protocol for sample preparation. These archive samples had already been dried and ground to pass a 0.500 mm mesh, subsampled, digested and measured by AAS according to standard lab protocol. We ground the samples further, to pass a 0.125 mm mesh, in order to prepare for XRF analysis. We then submitted a 1.0 gram subsample of the finely ground material to the lab for a second analysis, and it is that data which gave an impressive R^2 of 0.994 against XRF. Interestingly, when we compared the XRF data to the original lab data for the same samples, the correlation was decidedly less impressive: R^2 was only 0.958. In fact, the XRF readings correlated with the final AAS readings far better than the original AAS readings did! (Table 1) We believe the better correlation was due to better control of fundamental (particle) error in the laboratory subsampling by the reduction of particle size from 0.500 mm to 0.125 mm. The recovery of the original AAS readings versus the final AAS readings ranged from 0.962 to 1.226, with an RSD of 11.3 percent. This finding supports the argument that fundamental error in subsampling can have a major impact on the precision of the laboratory sample preparation method. If you require better precision than the standard laboratory protocol delivers, consider preparing the sample yourself, by drying, grinding, sieving, mixing, and subsampling, before submitting it to the lab.

Seven field-prepared composite samples (mixed, air and sun dried, ground to 0.250 mm or less) from the Northbridge site, when correlated against the adjusted lab ICP-AES values, gave a linear regression slope of 1.004 and an R^2 of 0.982. (Graph 3 and Table 2) The mean recovery of these 7 samples was 0.997 and the standard deviation of the recovery was 0.066, for an RSD of 6.6 percent.

As expected, in-situ XRF samples did not correlate with the lab as well as did prepared samples, and the performance of the in-situ method varied by site. (Graph 4) The bridge site in-situ method results had a slope of 0.548 and an R^2 of 0.737; negative bias was pronounced on the highest concentration samples. The bridge site in-situ data were all single, uncomposited in-situ readings. The Northbridge in-situ samples, given as mean values of several spots in the sampling unit and compared against a composite sample sent to the lab gave a regression slope of 0.969 and an R^2 of 0.915. We attribute the better in-situ performance at the Northbridge site to a well-dispersed, small particle contaminant.

To examine the effect of spatial variation on single spot in-situ measurements, we recorded indivdual readings for each of 5 to 6 spots in each of 5 sampling units at the Northbridge site. The five sampling units varied in area from a drip line approximately 10 m long by 0.5 m wide (5 m^2) to a rectangular yard of approximately 50 m^2 area. Compared with the lab analysis of the sampling unit composites, the set of 28 individual spot in-situ readings showed a mean recovery of 0.966 with a standard deviation of 0.320, giving an RSD of 33.1 percent. The means of the 5 to 6 spot in-situ readings per unit gave better correlation with the lab composites: mean recovery was 0.986 with a standard deviation of 0.150, giving an RSD of 15.2 percent. (Graph 5 and Table 2) By averaging 5 to 6 spot in-situs scattered through each sampling unit, we effectively "composite" a sample mathematically, improving sample support. We also retain the spatial data from the individual spot readings, giving us useful insight into site specific spatial variability and representativeness.

CONCLUSIONS AND RECOMMENDATIONS

Field prepared XRF can correlate extremely well with laboratory atomic spectrometry. The total measurement quality depends as much on sample support, collection, handling, and preparation procedures as it does on choice of analytical method. We can determine total measurement precision through replicate sampling within the sampling unit. We can better control overall measurement quality by paying close attention to sampling, handling, and preparation protocols. We can compare different analytical methods most effectively by splitting the sample as late as possible in the measurement process to eliminate variation caused by sample handling and preparation.

In-situ XRF provides rapid, low-cost measurement of heavy metals in soil with a minimum of sample preparation. While the in-situ XRF method is not generally as accurate as the ex-situ prepared sample method, it allows for more thorough sampling of an area to map out contamination patterns and assess spatial variation. The accuracy of the in-situ method depends on site-specific conditions of contaminant particle size and distribution; the accuracy can be assessed in the field by comparison to the prepared sample XRF method.

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Table 1: Massachusetts residential lead-in-soil samples measured by AAS before and after XRF sample preparation. The original samples had been dried and ground to 0.500 mm before subsampling for the microwave-assisted strong acid digestion and AAS analysis. Afterward, the dried ground samples were further ground to 0.125 mm, mixed, subsampled for XRF analysis, and then subsampled for a final microwave digestion and AAS analysis. Correlation coefficient (R^2) between the XRF and AAS values improved from 0.958 with the original AAS results to 0.994 with the final AAS results.

Sample	AAS-original (ppm)	XL-LISA (ppm)	AAS-final (ppm)
9502445	3251	2715	2652
9502446	508	549	524
9502557	605	500	535
9502448	2230	2310	2271
9502449	5487	6512	5704

Table 2: Northbridge samples first measured in-situ (composites averaged), then manually composited (where noted), field prepared and measured by XRF, then split and measured by laboratory ICP-AES. Agreement of in-situ XRF with field prepared XRF predicts agreement with the lab.

Sample	Composite sample?	In-situ XRF mean (ppm)	Field prep'd XRF (ppm)	Lab ICP-AES (ppm), adj.
Dripline C	Y	2561	3155	3004
Dripline 1	N	2512	2325	2354
Yard C	Y	1546	1637	1520
Yard 1	N	2347	2096	2217
Cover area C	Y	1132	1174	1328
Play area C	Y	942	796	774
Doghouse C	Y	932	944	940
Doghouse 1*	N	3632*	N/A*	15213*

*This sample was not dried and ground for field prepared XRF analysis before the laboratory split. Post-split preparation of the sample in a laboratory environment yielded an XRF reading of 12100 ppm. The sample came from a highly localized hot-spot which would not have been discovered without field XRF. Five in-situ method measurements of this non-composite sample ranged from 2976 ppm to 5885 ppm, indicating highly inhomogenous composition. The moisture content was 24.1 percent.

Graph 1: Performance of field portable XRF for lead-in-soil reference materials: NIST SRM numbers 2709, 2710, and 2711, and ELPAT soil samples from rounds 016 and 017.

NITON {GRAPH 1}

Graph 2: Comparison of fully prepared XRF (oven dried, screened, ground to 0.125 mm or less, and cupped) and laboratory AAS results on Long Island bridge site soil samples, Massachusetts residential lead-in-soil samples and NIST Standard Reference Materials.

NITON {GRAPH 2}

Graph 3: Comparison of field prepared XRF (field dried, screened, ground to 0.250 mm or less, and cupped) and laboratory ICP-AES for Northbridge lead-in-soil samples.

NITON {GRAPH 3}

Graph 4: Comparison of in-situ XRF results with laboratory AAS and ICP-AES. The Long Island bridge site in-situ measurements exhibit strong negative bias, probably due to the concentration of lead in relatively large particles (paint chips).

NITON {GRAPH 4}

Graph 5: Comparison of individual spot in-situ readings and averaged in-situ readings with laboratory ICP-AES measurement of composite samples. Samples from Northbridge site.

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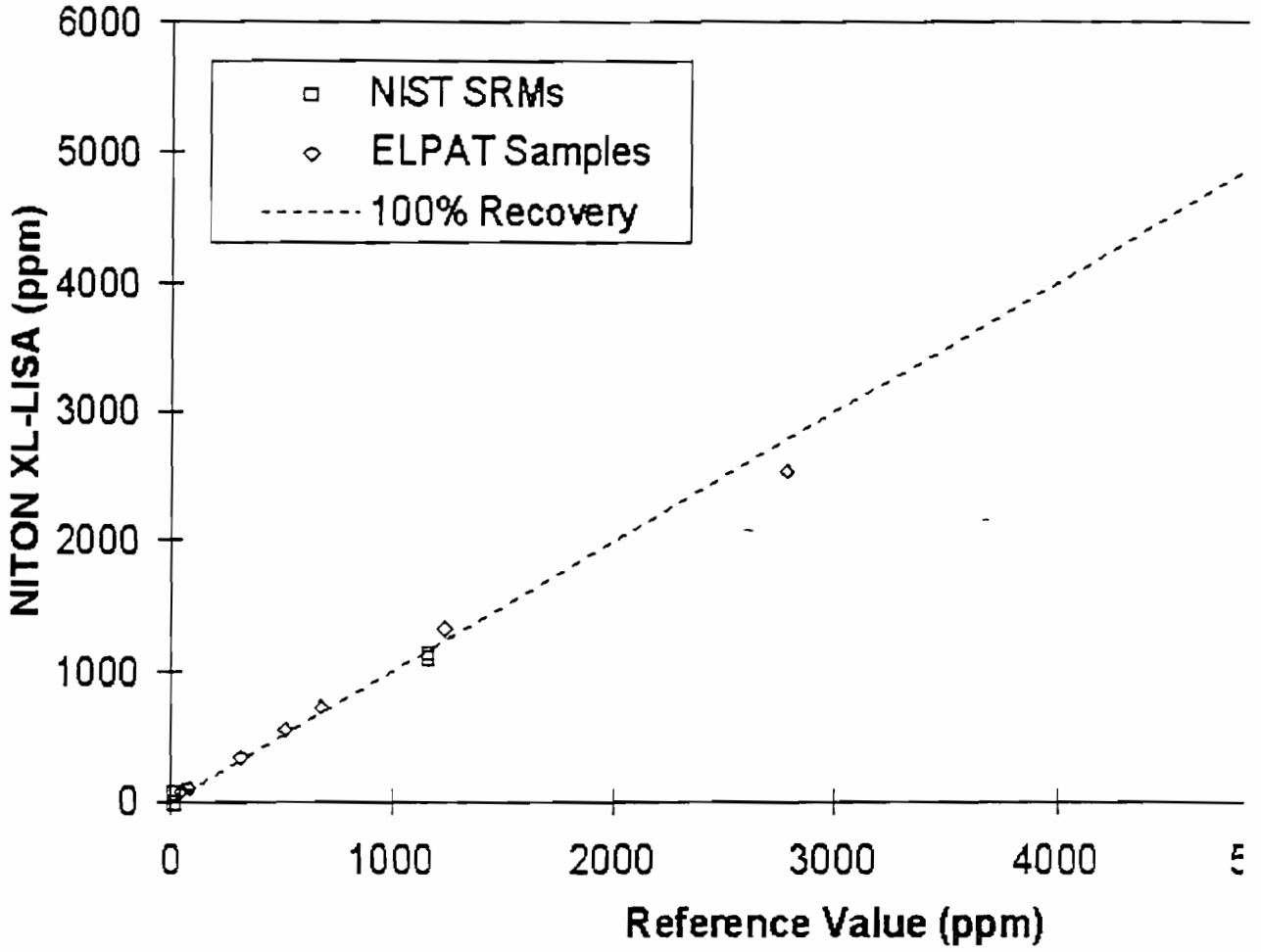
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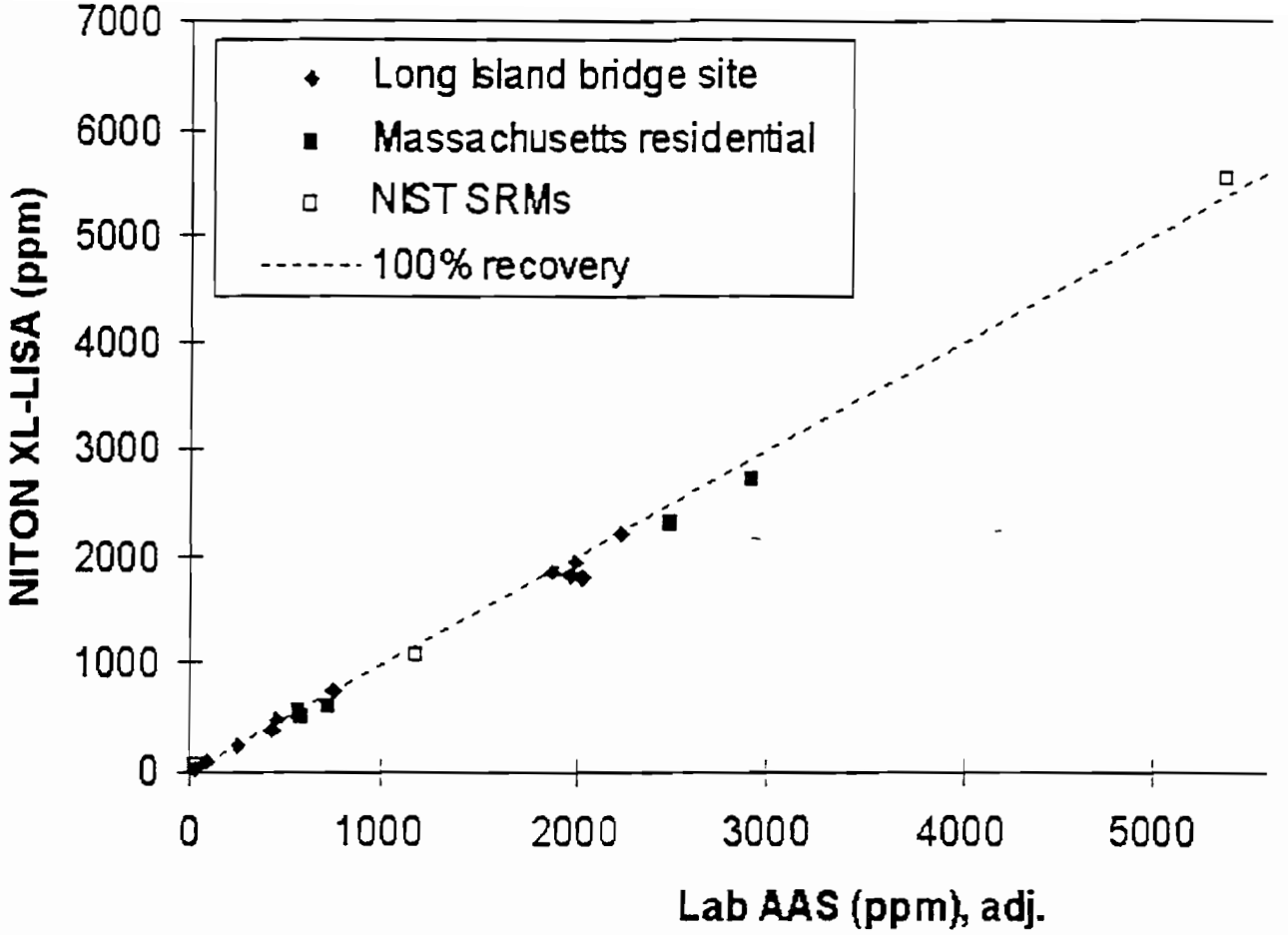
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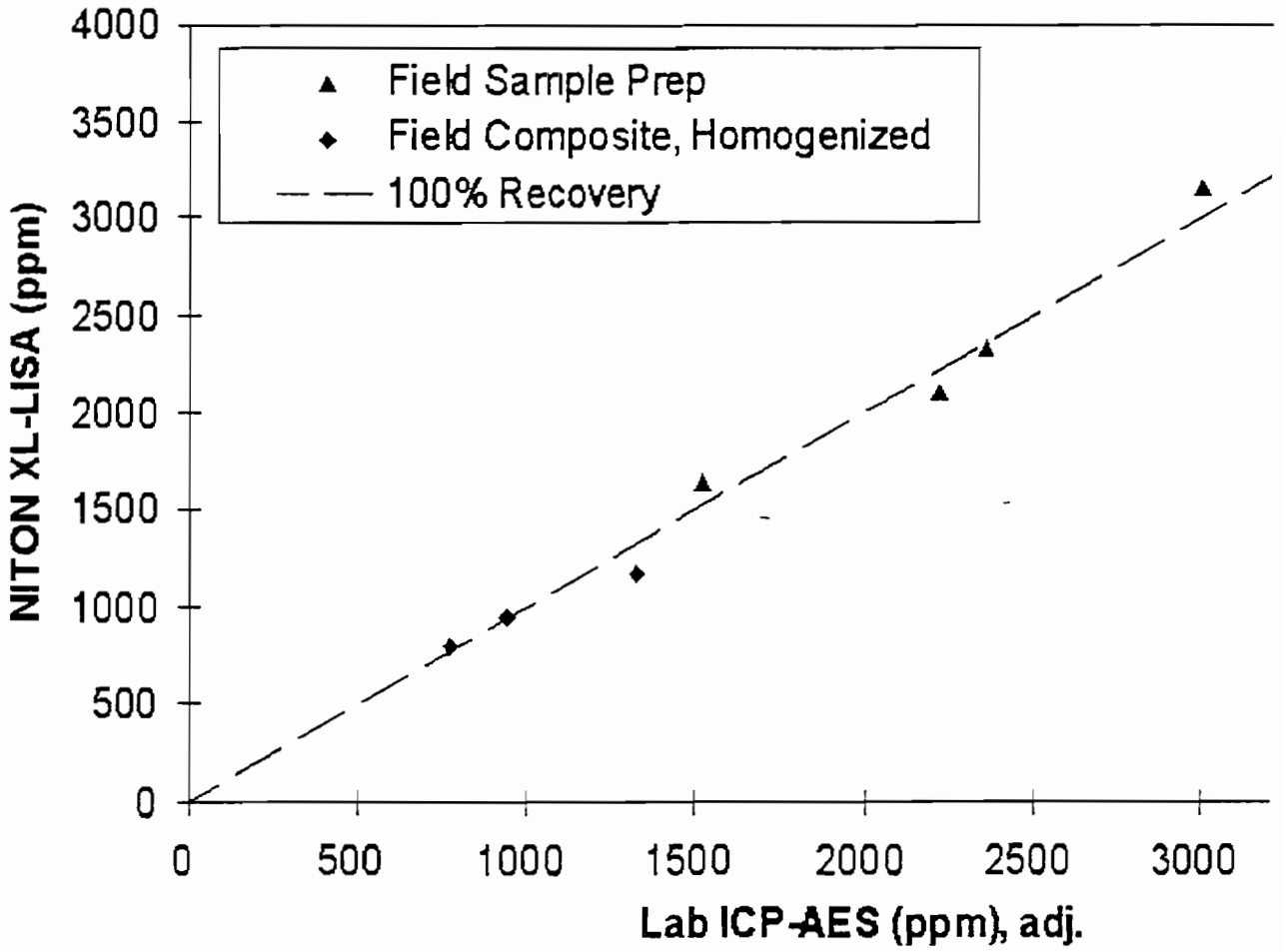
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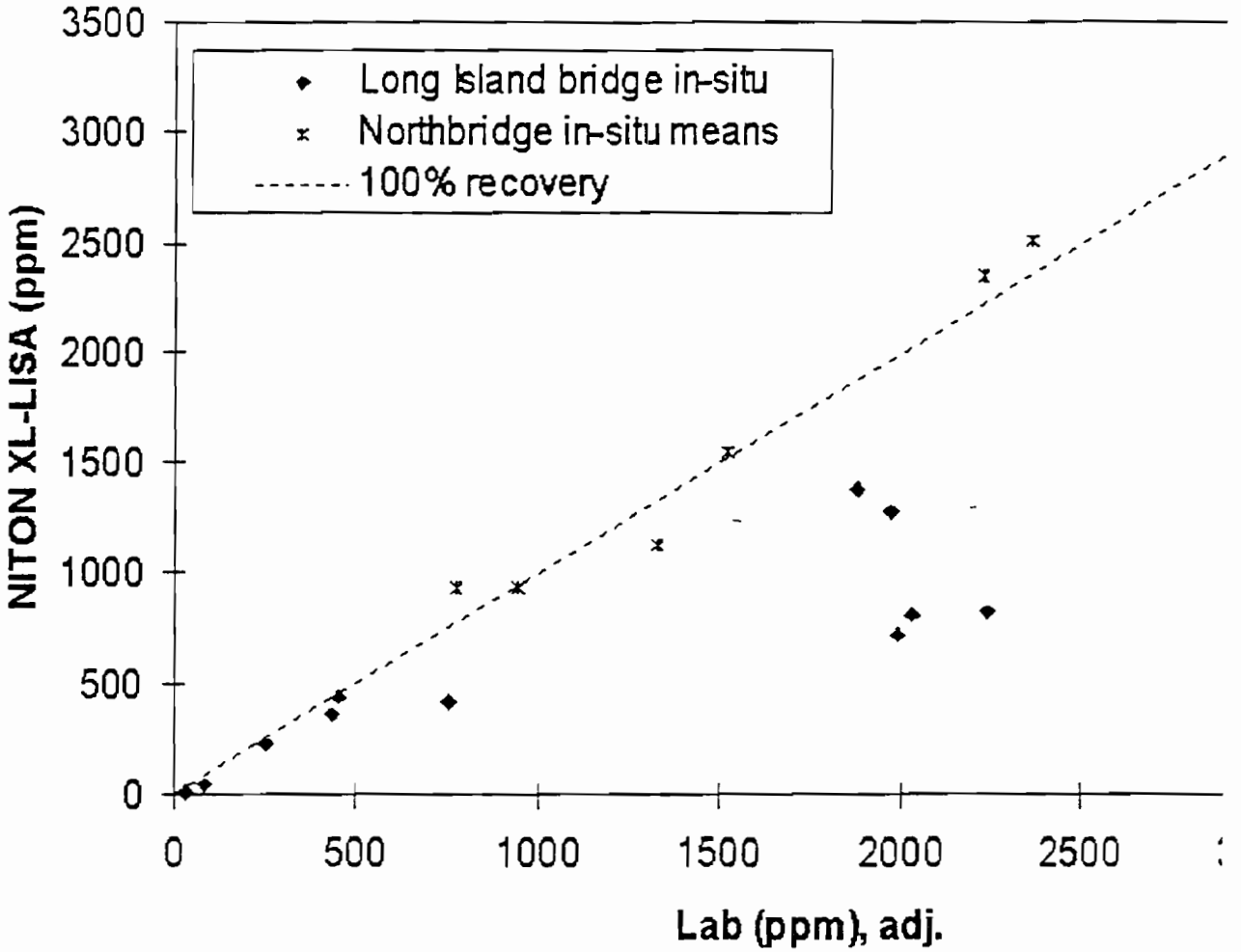
Long Island bridge in-situ
Northbridge in-situ means
100% recovery
NITON XL-LISA (ppm)
Lab (ppm), adj.
0
500
1000
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2000
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NITON

SAMPLE HANDLING STRATEGIES FOR ACCURATE LEAD-IN-SOIL MEASUREMENTS IN THE FIELD AND LABORATORY

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ABSTRACT

The inhomogenous lead-in-soil matrix can present serious obstacles to accurate sample collection and handling. In typical lead-in-soil measurement, particle size related errors in sampling and sample handling often exceed all other sources of error. The magnitude of error can vary widely depending on the particulate nature of the lead contaminant and the effectiveness of control measures. Large particle contaminants, such as lead bearing paint chips, pose a much greater challenge to accurate sample handling than do small particle contaminants, such as air dispersed industrial emissions. A sample handling protocol demonstrated to give reliable, valid data in small particle situations may prove entirely inadequate for large particle cases.

This paper focuses on the importance of fundamental error, a statistical consequence of particulate sampling. We discuss in quantitative terms the significance of fundamental error on the measurement of paint chip contaminated soils near a 400 ppm action level. On the basis of error estimates, we recommend that sample handling protocols control particle related errors by ensuring adequate sample size and sample definition, and by accomplishing sufficient particle size reduction and homogenization before subsampling. We discuss particle related errors and their effect on laboratory, field, and in-situ analytical methods. We recommend that quality assurance protocols aim to determine the overall measurement quality by evaluating error at all stages from sampling and sample handling through analysis.

SAMPLING DESIGN AND GEOSTATISTICS

The prerequisite of a well-designed study is a clear statement of the study's objectives for data quantity, quality, reliability, speed, and cost. The planner develops objectives with careful attention to the data's ultimate utility and the available resources of people, technology, and money. The objectives should be stated in quantitative terms, with exact figures to indicate the necessary precision and accuracy at and around the action or decision concentrations.

In large projects with multimillion dollar budgets, such as some Superfund cleanups, statisticians develop a sampling design with the aid of geostatistical theory and preliminary data indicating the spatial variability of site contamination. The sampling design defines the number points to sample and the pattern. The statistician attempts to design a sampling effort that achieves the lowest possible cost of the total sampling, analysis, and remediation effort.[1,2,3] Geostatistics is an art of some subtlety; its effectiveness varies widely with the skill of the statistician.[4] Although, the application of geostatistics to sampling design is well beyond the scope of this paper, some of its principles (e.g. sample support) can be used to improve the effectiveness of small sampling projects.

SAMPLE HANDLING OPERATIONS

A typical soil sample experiences a number of physical manipulations at the sampling site and in the laboratory. According to the sampling plan, the field technician extracts soil from the ground, often by means of a core sampling device. The technician may combine soil collected from several points to form a composite sample. To avoid transporting unnecessarily large quantities of sample material, the technician may thoroughly mix, then split the sample, taking only the minimum necessary for the lab.

The laboratory technician unpacks the sample, weighs the sample, dries the sample (by oven or air-drying), re-weighs the sample, then screens the sample to remove stones, vegetable matter, and other particles larger than 2 mm in size. At this point the technician re-weighs the sample, then grinds the sample to reduce the particles to small enough size to pass a fine mesh sieve. When all of the sample passes the fine mesh sieve, the technician mixes and splits the sample for final sample preparation, or executes an additional stage of grind, sieve, mix, and split. The technician then carefully weighs the final sample for the analysis. If the analysis is to be performed by atomic absorption spectroscopy (AAS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES) then the technician will prepare the sample by acid digestion or extraction. If the analysis is to be performed by x-ray fluorescence spectrometry (XRF) then then sample may be prepared by flux fusion, press pelletizing, or simply by packing the ground sample in a plastic XRF sample cup. The technician then analyses the final prepared sample by instrument, and calculates the final result using the sample data and instrument output.

Accurate execution of these sample handling operations requires a great deal of skill and care. Every step of handling introduces a degree of error to the overall result. But every step is needed to ensure consistent overall precision, accuracy, and repeatability.

Errors Combine

Errors are generally expressed in terms of standard deviations, or "sigmas". Variance is the square of the standard deviation. The overall, or total, variance is the additive sum of the many individual variances created in each step of the process. The overall error (square root of overall variance) includes the contributions of sampling error, sample handling errors, sample preparation errors, and analytical error. Generally, you can most effectively reduce the overall error by reducing the largest

contributing error.

Analytical errors are usually well-characterized, well-understood, and well-controlled by laboratory quality assurance and quality control procedures. By contrast, sampling and sample handling errors are not usually well-characterized, well-understood, or well-controlled. Sampling programs frequently neglect to implement quality assurance measures. To control overall error, one must control sampling and sample handling errors as well as analytical errors.

THE PARTICULATE NATURE OF SOIL

Soil particles range widely in size from clay (less than 0.0039 mm diameter) to silt (0.0039 mm to 0.0625 mm) to sand (0.0625 mm to 2.0000 mm). Particles larger than 2 mm in diameter are classified as gravel.[5] Natural soils are mixtures of different particle types and sizes.

By general agreement and tradition, particles larger than 2 mm in diameter should be removed (by U.S. number 10 sieve) from a soil sample before analysis. The excluded particles are large enough to be examined and classified by eye or by magnifying glass. Contaminants can also be particulate. Lead-bearing particles in soil can vary in size from sub-micron aerosol deposits (less than 0.001 mm diameter) to lead paint chips and lead shot (up to the maximum 2 mm diameter). Generally, the largest particles create the greatest challenge in sample handing.

Particulate Sampling Theory

A theory of particulate sampling was developed by geologist Pierre Gy to improve the quality of data gathered in support of mineral exploration and mining.[6,7] The theory has since been adopted by environmental scientists. The theory recognises two major categories of sampling error: sampling bias and fundamental error. Both types of error are measureable and controllable.

In general, a sample is intended to represent the a particular sampling unit, or volume of material. The sampling unit may be a particular plot of land (e.g. a certain 10 foot by 10 foot square), to a particular depth (e.g. surface to 4 inches). Or a child's sand box. Or a rail car load of ore. A single sample represents the entire sampling unit.

The sampling methodology is considered unbiased and correct if all of the particles in the sampling unit have exactly the same probability of being selected for inclusion in a random sample. The perfectly unbiased methodology is a practical impossibility. To reduce sampling bias, we must recognise the difficulties presented by the sampling unit. It may exhibit grouping or segregation of particles. Denser particles may have settled toward the bottom. New contaminants may have recently settled onto the unit, and may not be mixed into the volume. The contaminants may be heavily concentrated on one side of the unit, or concentrated in "clumps".

One method for sampling from a plot of land is to go to the center of the unit and shovel out the requisite amount of sample. However, we can reduce bias substantially by using a core sampling probe to control the depth and profile of the sample. More importantly, we can take soil from several different parts of the unit and mix it together as a composite to "increase sample support". By increasing sample support, we create a composite sample which more accurately reflects the average contaminant concentration of the unit than that of any single point sample. The composite sample reduces bias and improves accuracy over single point sampling without the expense of additional analysis.

concentration in the alloy, the average lead content of a shot is 0.045 gram. Say we sample soil with a sample size of 100 grams, typical for lead-in-soil sampling. At an action level of 400 ppm, or 0.04%, we would have an expected shot count per sample of 100 grams times 0.04% divided by 0.045 shot per gram, or 0.89 shot per sample. So soil contaminated with an average of 400 ppm lead may have an average of less than one contaminant particle (shot) per 100 grams. This result is actually even worse than the single particle example that gave a 100% error. The relative error is greater than 100% due to fundamental error alone. Other errors only add to the fundamental error.

The only way to reduce fundamental error in sampling is to take a larger sample size. In this example, to reduce fundamental error to a manageable 10% (or 40 ppm), we must increase sample size by a factor of 112, which would amount to more than 11 kilograms (24 pounds)! What laboratory would be willing to process such a sample in its entirety?

A Single Chip

Paint on older buildings often has a lead loading of 20 mg/cm^2 or more. Imagine that a single chip of such paint the size of your thumbnail (2 cm^2) falls into in a 100 gram soil sample. The chip contains 40 mg, or 0.040 grams of lead, nearly the same amount of lead as in a 2 mm shot. Take 0.040 grams and divide by 100 grams and multiply by 1,000,000 to get 400 ppm. Your single paint chip raised the lead concentration of an entire 100 gram sample by 400 ppm. If the soil has a background level lead content of 20 ppm without the chip, then the chip raises it to 420 ppm, and above the 400 ppm action level.

Now imagine you are kneeling down next to a house to take a soil sample. You see the paint chip. Take it, or leave it? According to HUD's Soil Sampling Protocol,[9] "If paint chips are present, they should not be avoided and should be included in the sample." (item C.5) Later, under the heading "Laboratory Analytical Procedure", the same protocol states "Samples are to be sieved once with a number 10 sieve with a mesh size of 2 millimeters." (item E.3) So far, so good. It continues "Visible paint chips are disaggregated by forcing the paint chips and other large particles through the sieve by a rubbing motion." Disaster. Whether the sample passes or fails depends entirely on whether you take the chip. Or whether you notice the chip. What if the chip is just below the surface, invisible? Go back to the same spot and sample again, and again. You may never obtain the same result again.

The author suggests a different approach. Leaded paint chips are always a potential hazard; the hazard increases over long periods of time as chips decompose into the soil. To knowingly include large chips of leaded paint in a soil sample accomplishes nothing; the result is foregone. If you do not already know the lead content of the paint chips, do have the paint chips analysed, but separately. As for the soil itself, pass it through the 2 mm mesh, but without trying to break up the paint chips. Include only the soil that passes through the mesh. If you find paint chips that do not pass through, study them carefully; find out where they came from; test them for lead content; but do not include them in the soil sample.

FUNDAMENTAL ERROR IN THE LABORATORY

Now imagine you are the lab technician. You have the soil sample, 100 grams, dried and sieved through the 2 mm screen. You see little paint chips in the sample, all of them just small enough to pass through the sieve, about 2 mm on a side. If they are leaded like the thumbnail sized chip, how many chips will it take to exceed the action level? How much fundamental error should you expect?

The average area is 0.2 cm times 0.2 cm, or 0.04 cm^2. At 20 mg/cm^2, the average lead content per chip is 20 mg/cm^2 times 0.04 cm^2, which is 0.8 mg, or 0.0008 grams. Assuming that there are no other leaded particles in the soil, 400 ppm would imply a chip count of 400 divided by 1,000,000, times 100 grams per sample, divided by 0.0008 grams per chip. A total of 50 chips. For a mean chip count of 50, the standard deviation of the chip is the square root of 50, or about 7.1. Therefore the fundamental error is 7.1 divided by 50, or 14.1%. Remember, this is only 1-sigma confidence!

I have analysed in great detail a actual sample that was very similar to the example given. I do not believe that this type of sample is unusual or uncommon; it was one of the first soil samples that I ever examined in detail. The soil came from the drip line of a train depot built in 1874. Of the portion of the 100 gram sample that passed through the 2 mm mesh, more than half of the lead content was contained in particles between 1 mm and 2 mm in size. See Table 1.

The assumptions that lead to a fundamental error of 14.1% are plausible, but also arbitrary. You may imagine worse cases of fundamental error due to higher lead content per chip or smaller sample sizes. The higher lead content per chip may be caused by higher lead loading in the paint film (40 mg/cm^2, say) or larger area chips (a 4 mm by 2 mm chip can fit through the 2 mm mesh). So it is possible you may experience fundamental errors of worse than 14.1% from 100 gram soil samples with lead paint chips. Since smaller samples only exacerbate this error, I strongly discourage sampling less than 50 grams for lead-in-soil where paint chips may be present.

Subsampling Error

The laboratory has dried the sample and sieved the sample through the 2 mm screen. Sample digestion methods generally require between 0.2 and 1.0 grams of sample material.[10, 11] The sensitivity of atomic spectrometry is more than adequate to analyse such small amounts of material; using a larger quantity of sample material would require larger amounts of acid, increase cost, and raise safety concerns. So the laboratory subsamples.

Subsampling leads to another set of errors. Once again we have bias and fundamental error. Suppose we subsample 0.3 grams from the same example 100 gram sample. If we subsample without any regard to homogenization or particle properties, the result will be analytical disaster. The mean chip count in the subsample will go from 50 in the 100 g sample to 0.15 in the 0.3 g sample. The fundamental error in the subsample will then be the square root of 0.15, which yields 0.39, or 258%. What is worse is that the most likely outcome is that no lead will end up in the subsample at all, and the result will be 0 ppm. In the off chance that a 2 mm by 2 mm chip lands in the subsample, the result will be 0.0008 g divided by 0.3 g, which is 2667 ppm. There is no chance that the result will be even close to the correct 400 ppm.

Fortunately, we can reduce the particle size and homogenize the sample thoroughly before we subsample. Say we grind the 100 gram sample until all the particles pass a U.S. Number 60 sieve (0.250 mm). Then the average particle might be roughly spherical with a diameter of 0.250 mm. The volume of the sphere would be 0.0082 mm^3 or 0.0000082 cm^3. If the lead bearing particles each have a lead loading of 15% and a density of 2 g/cm^3, then each will have a total lead content of 0.00000245 g (or 2.45 g). In a 0.3 g subsample of our 400 ppm lead sample the expected particle count is then 0.3 times 400, divided by 1,000,000, divided by 0.00000245, which is 48.9. The fundamental error would be the square root of 48.9, which is 7.0 counts, or 14.3%. The fundamental error from subsampling

(14.3%) is actually slightly worse than what we calculated for the fundamental error from the original sampling (14.1%). Remember that the errors combine together (by adding the variances) to form an overall error that is worse than any of the several individual components. In the case of a sampling error of 14.1% and a subsampling error of 14.3%, the total error is 20.1%.

Realistic scenarios of subsampling could be even worse than those described. The lead content of dry paint film can be as high as 50%, far greater than 15%. Also, laboratories typically grind samples to a U.S. number 35 sieve (0.500 mm) rather than number 60 (0.250 mm) before subsampling. Larger particles translate to larger errors. With 50% lead content and 0.500 mm particles, the 0.3 g sub-sampling error could be as high as 74%!

One way to reduce subsampling error is to simply subsample and digest a larger amount. The ASTM method for sample digestion of soils for lead analysis[11], which is based on USEPA SW-846 Method 3050, calls for a 1.0 g subsample, more than three times larger than the 0.3 g subsample we calculated. In taking the larger subsample, the fundamental error from subsampling should be reduced by nearly half. But the method fails to deliver better performance, because it relaxes the grinding requirement from number 60 mesh (0.250 mm) to number 35 (0.500 mm). Doubling the particle diameter increases the volume of the spherical particle by a factor of 8, more than compensating the larger subsample. The fundamental subsampling error grows to 22.1%, and the total fundamental error becomes 26.2%.

Besides increasing subsample size, the laboratory can improve subsampling error by grinding the sample to a smaller particle size. Grinding to a 0.125 mm particle diameter, the laboratory reduces the fundamental error of the 0.3 g subsample from 14.3% to 5.1%. But grinding 100 grams of soil to such small particle size by hand methods (e.g. mortar and pestle) can be tedious and difficult. A method for speeding the particle size reduction without greatly increasing fundamental error is to grind and subsample in stages. If you grind the 100 g sample to 0.250 mm and subsample not 0.3 g, but 5 g, the fundamental error will be only 3.5% If you then grind the 5 g subsample to 0.125 mm and sub-subsample 0.3 g, the fundamental error will be 5.1%. Combining the subsampling and sub-subsampling errors, you have an overall error of 6.2%. By reducing only 5 g of the 100 g sample to the smallest particle size, you avoid much of the effort of grinding and sieving the whole sample.

Other errors related to subsampling include bias and homogenization errors. An accurate subsample must be unbiased; every particle should have an equal probability of being subsampled. If the ground, sieved sample is not properly homogenized, there can be substantial segregation of particles by composition, shape, size, and or density. Some types of particles (e.g. magnetic or electrostatic particles) tend to group or clump together. An improper method for homogenizing a sample can actually create segregation. Agitation or shaking a sample with particles of different size, shape, or density will likely cause stratification. With agitation, denser, smaller and rounder particles tend to drop to the bottom, while less dense, larger and flatter particles tend to rise to the top. Finely ground samples do not stratify as readily as the raw, unground sample.

One way to avoid homogenization error in subsampling is to make use of mechanical sample splitting devices. A riffle splitter, for example, can efficiently eliminate segregation errors in subsampling. If mechanical splitters are not available, then the manual cone-and-quarter method can reduce bias in subsampling.

OTHER LABORATORY ERRORS

A number of other laboratory errors affect the analysis of lead-in-soil. The sample should be dry;

water content should be no more than around 2 or 3% of the sample mass. For atomic spectroscopy requiring acid digestion of the sample, the the laboratory must measure the sample mass and solution volume, and record the data accurately. To avoid sample to sample cross contamination, the laboratory must clean tools and containers between samples. The lab must track each sample and follow every preparation step according to protocol, using the proper tools and properly maintained and calibrated equipment. Overall, laboratory error should be small and well controlled; otherwise, lapses in quality can easily lead to substantial error.

Sample Dissolution

An acid digestion or extraction procedure must achieve reproduceable results for the contaminant of interest in any of its likely physical or chemical forms. The procedure should allow ample time for the dissolution of the sample to finish. In general, reducing particle size speeds the dissolution to completion. Some chemical forms of lead tend to be difficult to dissolve. Of particular difficulty in this regard are the lead chromates, colored pigments commonly used in marine, exterior, and signage paints. Standard acid digestion procedures and suitable quality control will likely provide consistency to within a few percent under most circumstances.[10]

Instrumental Error

Instrumental errors generally fall into the categories of signal-to-noise and interference. Atomic spectrometry methods (AAS, ICP-AES) generally provide excellent sensitivity for the lead-in-soil application, with detection limits of 10 ppm or lower. Signal-to-noise ratios are correspondingly high. Matrix related interferences are also fairly low and well controlled in modern atomic spectrometry instruments. The overall instrumental sensitivity, precision, and accuracy are excellent, with errors in the range of nearly negligible compared to the other sources of error already discussed.

X-ray fluorescence (XRF) generally has worse sensistivity than AAS or ICP-AES, but with the compensating advantages of portability and less intensive sample preparation requirements. Matrix effects due to variable elemental composition can be a concern with XRF, but the lead-in-soil application is fairly benign in this regard. Sophisticated matrix correction methods (e.g. "fundamental parameters") have been developed and proven successful;[12,13,14] but even simple techniques, such as Compton Normalization, work surprisingly well in this application.[14,15,16]

XRF has an additional particle-related bias when the particle size becomes large compared to the attenuation length for the analyte's fluorescence x-ray.[15] In lead-in-soil analysis, large contaminant particles cause negative bias. For analysis using the lead 12.6 keV x-ray, particle size should be reduced to 0.125 mm or smaller to control this effect. [Table 2]. Of course, to avoid severe subsampling errors, you should already be grinding samples to small particle size.

Note that the larger subsample required for XRF (3 to 5 grams, typically) does not reduce the subsampling error of XRF relative to digestion based methods. Only about 0.3 grams of the typical XRF soil sample (approximately 1 mm depth in a 25 mm diameter XRF sample cup) produces the major part of the instrument response.[16] Therefore, the subsampling error is about the same as if a 0.3 gram subsample had been drawn rather than a 3 gram subsample.

The analytical error of field portable XRF is around 10 to 15 percent for lead-in-soil samples at 400 ppm. While this analytical error is far worse than that of laboratory atomic spectrometry, the overall

error of the methods may be fairly similar after taking into account sampling, sample handling, and sample preparation.[17]

THE SMALL PARTICLE CASE

If all the contaminant particles of the sample unit are very small, then fundamental errors greatly diminish, and sample handling can be simplified. Lead contamination from airborne sources (e.g. automobile emissions, smelter emissions, incinerator emissions, abrasive blasting of painted surfaces) and from chalking (powdery deterioration) of painted surfaces tends to be dispersed as fine particles. If the lead is found only in particles less than 0.032 mm (32 microns) in diameter, then the fundamental error for a 0.3 gram sample or subsample cannot be more than 4% at 400 ppm. In such a sample, grinding and sieving are not likely to make dramatic differences in the laboratory result. Sampling bias resulting from spatial variation is still a concern, so I always recommend careful attention to sampling design, sample support, and homogenization.

Even with the minimal sample preparation (dry, sieve 2 mm, mix), field portable XRF can perform very well in cases of small particle size.[18,19] The minimal sample preparation and high analytical throughput of XRF enable an investigator to collect large quantities of useful data in a short period of time, and at low cost. In many situations, the field XRF provides better overall decision making data than laboratory analysis by virtue of its ability to overcome spatial variability through massively increased sampling density.[20,21]

IN-SITU FIELD XRF

The in-situ capability of some field portable XRF instruments may be especially attractive for high speed, low cost screening and characterization. Depending on the nature of the contaminant and the soil matrix, the in-situ method can offer screening quality data with practically no sample preparation at all. To reduce bias and increase sample support, the field technician can mix and composite a sample on the ground before an in-situ XRF measurement.

Moisture and particle size effects can be especially pronounced for in-situ XRF, so quality assurance is especially important. The field technician may prepare one or more samples by the full protocol (dry, grind, sieve, split) in the field and compare the result to the in-situ measurement to determine if the soil conditions allow the in-situ XRF method to meet the data quality objectives. To back up field measurements, the technician should collect representative samples for laboratory analysis.

QUALITY ASSURANCE FOR SAMPLING AND ANALYSIS

Quality assurance programs usually include sample duplicates, replicates, spikes, blanks, and splits. To assess field based error (that is, error caused by sampling and sample handling), the sampling program should include field duplicates and replicates taken as early as possible in the sampling process. To assess the error due to spatial variation and sampling, the field technician takes duplicates or replicates according to the normal sampling protocol, but from spatially distinct points (sample points should be spread apart from each other) within the representative sampling unit. To assess the error due to sample handling, the technician makes several large field composites and splits them into duplicates or replicates before commencing any sample handling operations.

To assess the error due to final sample preparation and analysis, the field or lab technician splits

sample material into duplicates or replicates just before the final sample preparation (e.g. before digestion, or before putting material into XRF cup). Several splits may be sent to an independent laboratory for confirmatory analysis. Spikes and blanks serve to assess analytical recovery and bias. Of course, the quality assurance program should take care to use sample splitting methods that do not introduce significant bias. Chappel and Olsen[22] and Shefsky[23] give practical guidance for using confirmatory data to evaluate the quality of field data.

CONCLUSIONS AND RECOMMENDATIONS

The major goal of measurement in a environmental project is to provide accurate data for assessing risk and deciding on remedial action to lower risk to an acceptable level. The optimal sampling design accomplishes that goal while keeping the total of sampling, analysis, and remediation costs to a minimum. The quality of data provided for decision making depends on the overall error; that is, the combined errors of sampling, sample handling, and analysis. Field analysis often provides the best overall data quality by allowing for low cost, high density sampling of spatially variable sites.

All measurement projects should include a quality assurance program that evaluates error resulting from sampling, sample handling, and analysis. Sampling and sample handling are especially critical components to overall data quality. Sampling protocols must consider the important effects of sample definition, sample support, spatial variability, segregation and grouping bias, and fundamental error due to particulate sampling and subsampling.

In order to control sampling and sample handling errors for lead-in-soil, the author recommends that sampling protocols:

* Ensure data quality objectives (DQO's) are clear.

* Use a low-bias sampling method (e.g. core sampling) to define the sample.

* Use composite samples to increase sample support.

* Collect 100 grams; consider collecting more than 100 grams if paint chips may be present.

* Dry the sample, if possible.

* Exclude particles larger than 2 mm. Examine large particles separately.

* Reduce particle size (preferably to 0.125 mm or less) before subsampling.

* Use low-bias methods for sample splitting (e.g. riffle splitter, cone-and-quarter).

* Implement quality assurance for sampling and sample handling as well as analysis.

* Use confirmatory data to evaluate the effectiveness of field methods.

If the data quality objectives and site characteristics allow for relaxed field sample preparation or in-situ protocols, do take advantage of the higher analytical throughput to collect more data. But always proceed with a degree of caution and support your data with solid confirmatory analysis.

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APPENDIX A: STATISTICAL BASIS OF FUNDAMENTAL ERROR

For a sampling unit containing n contaminant particles, the probability P_x that an unbiased sample will contain x such contaminant particles is given by the binomial distribution:

$$P_x = \left(\frac{n!}{x!(n-x)!}\right) p^x (1-p)^{n-x}$$

where x is an integer and p is the probability that any particular particle will be in the sample. Note that the sum of all probabilities (the sum of P_x for x running over the range of 0 to n) is always 1. The probability for an individual particle, p, is simply the mass of the sample, m, divided by the mass of the sampling unit, M.

The mean or "expected" value for the number of contaminant particles in the sample, $\overline{x}$ can be found by summing the function xP_x over the range of $x=0$ to n. The resulting mean is simply $\overline{x} = np$, as one would reasonably expect.

The variance σ_x^2 of the number of contaminant particles around the mean $\overline{x}$ is found by summing the function $(x - \overline{x})^2 P_x$ over the range of x=0 to n. The resulting variance is $\sigma_x^2 = \overline{x}(1 - p)$. If the mass of the sample is much smaller than the mass of the sampling unit, then p = m / M will be much smaller than 1, and drops out of the formula, leaving $\sigma_x^2 \approx \overline{x}$. The standard deviation of x, or σ_x, will then be approximated by SQRT($\overline{x}$).

In calculating fundamental error for an even 50/50 sample split, where n is the number of contaminant particles in the whole sample (now considered the sampling unit for the splitting operation), $p = 0.5$, so

$$\overline{x} = 0.5\,n, \text{ and } \sigma_x^2 = 0.5\,\overline{x}.$$

In the limit as the sampling unit becomes extremely large, (n becomes extremely large, p becomes very small) the probability distribution simplifies to the Poisson formula:

$$P_x = \overline{x}^x e^{-x} / x!$$

where the mean, or expected value, is once again $\overline{x}$. As before, the variance, σ_x^2, *simplifies to* $\overline{x}$.

APPENDIX B: PIERRE GY'S PARTICULATE SAMPLING THEORY

An overview of Gy's sampling theory can be found in Ingamells and Pitard.[6] An important element of the theory is the concept of fundamental error. Fundamental error (FE) is an inherent property of the particulate nature of geological samples. FE can never be removed from a sample, but it can be reduced by controlling the maximum particle size allowed into the sample, and increasing the sample size.

FE is the product of a several factors. In terms of the variance, σ_{FE}^2,

$$\sigma_{FE}^2 = f\, g\, m\, b\, (u')^3 / w$$

where w is the sample weight, f is the shape factor, g is the particle size distribution factor, m is the mineralogical composition factor, b is the liberation factor, and u' is the maximum allowed particle dimension.

The shape factor f accounts for the typical shape of particles in a particular sampling unit. For cubes, f is exactly 1. For spheres, f is /6 (about 0.5). For flattened particles and flakes, f is less than 0.5, and for elongated particles f can be greater than 1.

The particle size distribution factor g accounts for the different sizes of particles in the sample. If all particles were the same size as the maximum allowed, g would be exactly 1; otherwise, g lowers with the presence of fine particles. Generally, g is much less than 0.5 for the original soil sample, rises to between 0.5 and 1.0 upon sieving. The factor g can never exceed 1.

The mineralogical composition factor m accounts for the presence of analyte (lead) in the ore mineral (contaminant material) and in the gangue mineral (background soil), as well as the density of the mineral components. If the contaminant particles contain much higher concentrations of lead than background and account for the largest share of the total lead, then m is approximately the density of the contaminant material times the ratio of the lead concentration in the contaminant to the concentration of the lead in the total sample.

The liberation factor b allows the ore mineral to be contained in completely separate particles from the gangue mineral (b is exactly 1), or in attached particles (b is less than 1).

The maximum allowed particle dimension u' for soil testing is 2 mm, the opening size of the U.S. Number 10 sieve. Reduction of particle size by grinding and sieving reduces maximum particle dimension u'.

Table1: Distribution of lead by particle size in a lead-in-soil sample from the dripline of an 1874 train depot. The sample contained visible paint chips.

Min. size (mm)	Max. size (mm)	mass (g)	ppm Pb	mg Pb
2.000	& above	8.605	NA	NA
1.000	2.000	7.530	7531	56.7
0.500	1.000	13.814	1317	18.2
0.250	0.500	24.315	297	7.2
0.125	0.250	21.716	236	5.1
0.063	0.125	10.996	323	3.6
0.000	0.063	12.462	630	7.9
	Totals:	99.438		98.7

Table 2: XRF particle effect for lead-in-soil derived from lead bearing paint. The original sample from the dripline of an 1874 train depot was separated by sieve into seven particle size ranges prior to independent analysis of the fractions. Recovery (%) is the response of the sample unground relative to the same sample ground to pass 0.032 mm. Note that analytical recovery is generally poor for the largest particle sizes.

Min. size (mm)	Max. size (mm)	Recovery (%)
1.000	2.000	3
0.500	1.000	31
0.250	0.500	46
0.125	0.250	70
0.063	0.125	90
0.000	0.063	100

Table 3: Example calculations of fundamental error in lead-in-soil sampling and subsampling based on realistic assumptions of concentration and density. Note that σ_{FE} is the calculated 1-sigma relative error at an average contaminant lead concentration of 400 ppm. We assume particles to be spherical, except for paint chips, which we assume to be flat squares. Since real-world contaminants vary widely in particle size, shape, and concentration, one should view these figures as rough approximations.

Contaminant particle	Assumptions	Sample or subsample size (grams)	σ_{FE} (%)
Lead shot, 2 mm dia.	95 % Pb, density 11.3 g/cm^3	100	>100
Paint chips, 2 x 2 mm	20 mg/cm^2 Pb	100	14.1
Paint chips, 1 x 1 mm	20 mg/cm^2 Pb	100	7.1
Paint, .500 mm (#35)	15 % Pb, density 2 g/cm^3	0.3	40.5
Paint, .500 mm (#35)	15 % Pb, density 2 g/cm^3	1.0	22.2
Paint, .250 mm (#60)	15 % Pb, density 2 g/cm^3	0.3	14.3
Paint, .250 mm (#60)	15 % Pb, density 2 g/cm^3	1.0	7.8
Paint, .125 mm (#120)	15 % Pb, density 2 g/cm^3	0.3	5.1
Paint, .125 mm (#120)	15 % Pb, density 2 g/cm^3	1.0	2.8

NITON
Return to XRF Instruments Home Page

SOP-1 XRF Analysis of Soil Samples for Lead

1-1.0 Objective

Soil samples will be collected for XRF field analysis of lead. This SOP contains specific details concerning the procedures and equipment necessary to properly collect soil samples and analyzed the samples. The analysis procedures are in accordance with the Niton Corporation User's Guide Version 5.0. The procedures for sample collection are detailed in the section 4.3 of the FSP.

1-2.0 Equipment And Materials

- Appropriate number and types of sample container coolers, sample label, and ice;
- Pre-cleaned stainless steel sample mixing dish;
- Sampling equipment decontamination supplies;
- Cotton swabs and soft cloth for cleaning XRF;
- Stainless steel trowel;
- Stainless steel hand auger;
- Appropriate field documentation (field log book, field data sheets, chain-of-custody forms, sample collection logs) and an indelible ink pen;
- Niton XRF; and
- Health and safety equipment, as specified in the SSHP.

1-3.0 Methodology

2) Soil samples will be analyzed as follows:

- Check that XRF is operational and leave the instrument on for at least 15 minutes prior to analysis.
- Perform the self-calibration check on the XRF;
- Analyze a "blank" sample to assess potential instrument noise;
- Analyze a Niton low-level sample to assess instrument accuracy;
- Analyze environmental samples and record all measurements;
- Correct the initial site sample measurement value by the "multiplier" determined in the correlation study; and,
- Perform the second self-calibration check on the XRF after the last sample analysis.

3) Collect 10% split samples for confirmation at a laboratory. Complete the sample labels accurately and legibly and affix to the sample bottles.

4) Clean the XRF. Use cotton swabs to clean the beryllium window. Use a soft cloth to clean the outer metal case. DO NOT use any water, detergents, or solvents to clean the instrument.

5) Record all pertinent information on the field logbook, and chain-of-custody (split samples).

1-4.0 Comments

The XRF is capable of accurately determining lead concentrations up to 10,000 mg/kg. The variability and correlation to laboratory data will be in the 200 mg/kg to 1,000 mg/kg lead range. This study will be performed prior to the field remediation effort.

If conditions in the field indicate that additional samples or techniques are required, the sampling program may change. This will be influenced by evidence of contamination, or nonhomogeneity of soils or other conditions observed during sampling events. Any changes to this SOP will be clearly communicated to the USACE.

NITON Corporation

XL-309

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*700*series

User's Guide Version 5.0 (HTML) Preface

Preface

This User's Guide is a detailed instruction and reference manual for NITON XL-309, 701, 701-A, 702, 702-A, 703 and 703-A owners and users. The operation and safety instructions in this Users Guide are complete. This User's Guide is intended to complement the instrument training that NITON provides free-of-charge.

Keep your NITON clean, particularly the beryllium window on the bottom of the instrument. If the beyllium window is dirty, the performance of your NITON will be affected. Clean the window gently with cotton swabs. Clean the instrument's metal case with a soft cloth. Never use water, detergents, or solvents. These may damage the instrument.

All Service except exterior cleaning must be performed by NITON Corporation. Do not

attempt to make repairs yourself. Opening the case of your NITON will void the instrument Warranty.

Never ship your NITON analyzer back to the factory for *any* reason without calling and obtaining a Return Authorization (RA) Number from NITON Corporation.

Users Guide conventions

Warnings: Provide information on how to safely operate the NITON.

Cautions: Provide information on how to avoid damaging the NITON.

Notes: Highlight other important information.

Warnings, cautions, and notes are printed in bold type.

Chapter summaries

Chapter summaries

Chapter 1, Unpacking your NITON

Supplies instructions for unpacking the shipping container.

Chapter 2, Operating your NITON

Includes basic operating instructions; an overview of NITON XRF test modes; and supplies instructions for instrument calibration, for taking a reading, for downloading data, and for charging and changing battery packs.

Chapter 3, Analyzing bulk samples

For users of 702, 702-A, 703 and 703-A model analyzers (for multiple elements).

For users of XL-309 with optional Lead in Soil Analysis Package (for lead only).

Supplies instructions for rapid, on-site, multi-element detection and analysis of a variety of bulk samples, including soils, house dust, sludges, and liquids.

Chapter 4, Analyzing thin samples

For users of 701, 701-A, 703 and 703-A model analyzers (for multiple elements).

For users of XL-309 with optional Dust Wipe Analysis Package (for lead only).

Supplies instructions for rapid, on-site, multi-element detection and analysis of a variety of thin samples, including filters, dust wipes and thin films.

Chapter 5, Analyzing lead paint

For users of 701-A, 702-A, 703-A and XL-309 model analyzers.

Supplies instructions for rapid, on-site detection and analysis of lead-based paint.

Chapter 6, Radiation safety

Includes an overview of radiation safety, instrument radiation profiles, and guidelines for safe operation of NITON XRF analyzers.

Chapter 7, Additional Information

Includes an overview of multi-element XRF analysis; tips to improve sampling and testing; a summary of safety warnings and equipment cautions; and NITON warranty information.

Chapter 8, Appendices

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Appendix B

Nitor Users Guide

NITON Corporation

XL-309

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*700*series

User's Guide Version 5.0 (HTML) Chapter 1

Chapter 1: Unpacking your NITON

1. Inspect the shipping carton for signs of damage such as crushed or water damaged packaging. Immediately notify the shipper and NITON Corporation if any damage is noted.

Note: The radioactive cadmium$_{109}$ source is completely sealed and extremely secure. It meets ANSI standard 33232.

2. Open the packing carton. If your NITON Spectrum Analyzer is not packed in its carrying case, please call NITON Corporation immediately at (401) 294-1234

3. Verify the contents of the shipping container against the packing list. Please record any

discrepancies and notify NITON Corporation.

4. Open the carrying case and visually inspect the instrument for damage before removing it from the case. Call the shipper and NITON Corporation if you find any damage to the case or its contents.

5. Save the shipping carton and all packing materials. Store them in a safe, dry area, Use when the spectrum analyzer is next shipped.

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NITON Corporation

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*700*series

User's Guide Version 5.0 (HTML) Chapter 2

Chapter 2: Operating your NITON

NITON **XL-309** and **700 Series** Spectrum Analyzers are hand-held, portable XRF detectors, designed to make fast, accurate measurements. The **XL-309** measures concentrations of lead, while **700 Series** instruments measure concentrations of many different elements simultaneously. NITON instruments measure the precision of each reading, store up to 3,000 readings with complete x-ray spectra, and download data quickly to a PC.

NITON designed the radioactive source and shielding of our analyzers with one guiding principle in mind: properly used, these will not expose the NITON user to levels of radiation significantly above natural background levels.

Note: The accuracy and precision of the data you collect with your NITON XRF will largely

depend on your familiarity with the instrument and your knowledge of the media you are testing.

Our free factory training is designed to give you the basic tools to use our instruments. This User Guide supplements our training. You can use it as both a quick reference and a detailed operating manual for any of our XRF analyzers.

This is your NITON XRF Spectrum Analyzer

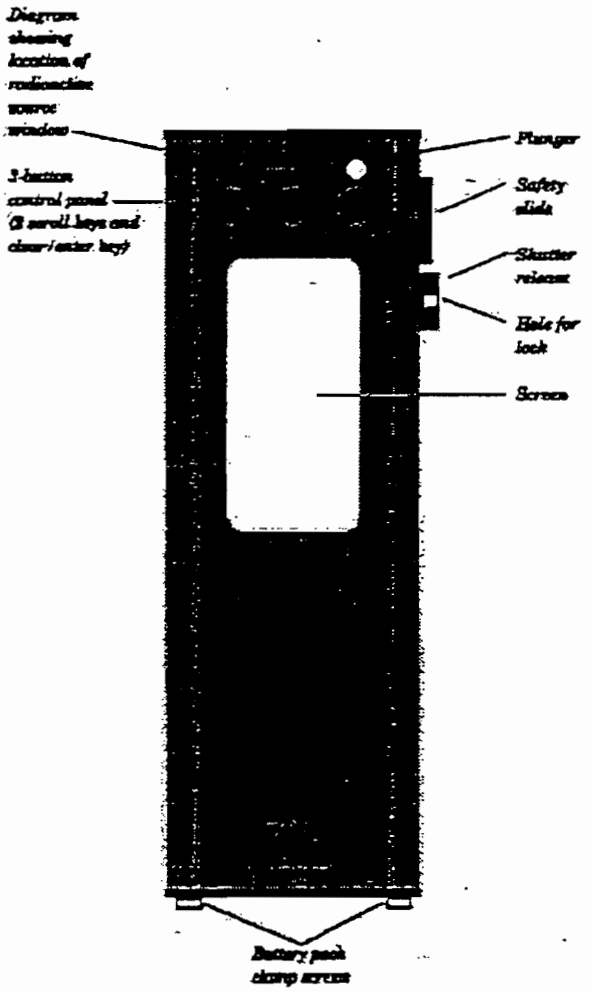


Fig. 2.01 Front view of the NITON 700.

Fig. 2.02
Top view of the your NITON.

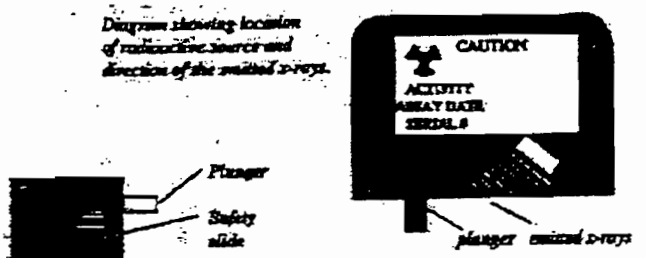


Fig. 2.03
Right side view of your NITON.

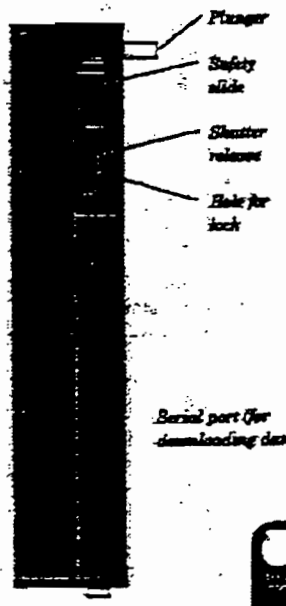
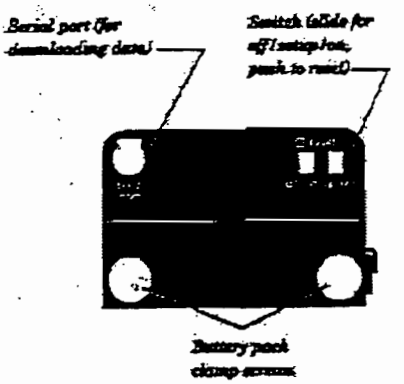


Fig. 2.04
Back view of your NITON



NITON Spectrum Analyzers operate in the following modes:

Modes of operation, by model

Model	Bulk Mode	Thin Sample Mode	Paint Modes
• 701	• No	• Yes	• No
• 701-A	• No	• Yes	• Yes
• 702	• Yes	• No	• No
• 702-A	• Yes	• No	• Yes
• 703	• Yes	• Yes	• No
• 703-A	• Yes	• Yes	• Yes
• XL-309	• Opt (lead only)	• Opt (lead only)	• Yes

Turning on your NITON

1. Turn on the instrument. Depress and slide the **On/Off switch** on the bottom of the instrument to the **on** position (**Figure 2.04**). Sometimes the instrument's battery saving features momentarily delay start up. If your NITON does not turn on immediately, turn it off, wait a few seconds, and turn it on again. Each time the NITON is turned on, the **Main menu** appears (**Figure 2.05**).

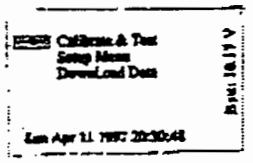


Fig. 2.05 Main Menu

2. The control panel consists of three buttons (**Figure 2.06**). These buttons allow you to navigate all of your NITON's screens and menus. Press the **Clear/Enter** button to *select* the function indicated by the screen arrow. When you turn on your NITON, the **Screen arrow** is on

Calibrate & test.

Note: You can begin to test immediately in whatever mode you *last* tested in by pressing the Clear/Enter **button.**

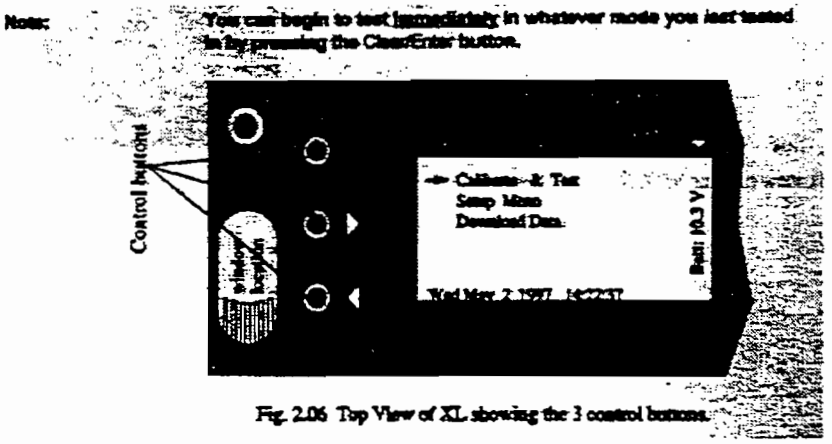


Fig. 2.06 Top View of XL showing the 3 control buttons

Getting started

The XL-309 and 700 Series Instruments are highly sophisticated, electronic spectrum analyzers. The more familiar you are with your NITON's operation, the better your measurements and reports will be. Here, in brief, is an outline of how to do various kinds of testing using your NITON. More detailed information is offered in subsequent chapters.

1. Turn on the instrument. When testing in **Bulk Sample** or **Thin Sample modes**, leave your NITON on for fifteen minutes prior to testing. ***This is not necessary if you are going to test in any of the Paint Modes***. Go to the **Setup Menu** (**Figure 2.07**) and set the .mode you wish to test in.

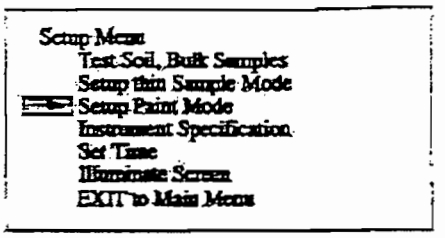


Fig. 2.07 Setup Menu

2. Press **Clear/Enter** to begin self-calibration.

3. When the NITON beeps, calibration is complete. You are now ready to test. For instructions on how to take a measurement, depending on the nature of the media you will be measuring, turn to one of the following chapters: **Chapter 3: Analyzing Bulk Samples**; **Chapter 4: Analyzing Thin Samples**; or **Chapter 5: Analyzing Lead Paint.**

Note: Check your instrument's calibration with testing standards before and after testing and at least once per hour during testing.

The Setup Menu

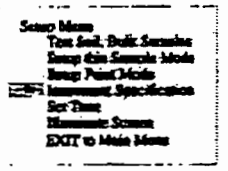


Fig. 2.08 Setup Menu

Use the **Setup Menu** (**Figure 2.08**) to check your instrument specification; to set the date and time; to illuminate the screen continously; or to select a different testing mode. Select the **Setup Menu** from the **Main Menu** with the **Arrow buttons**; enter the **Setup Menu** by pressing **Clear/Enter**.

Instrument Specification

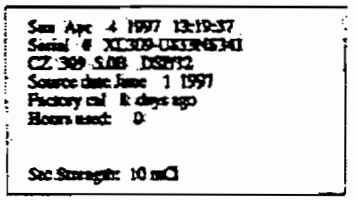


Fig. 2.09 Instrument Specifications

To check the source strength of your instrument and other useful information, select the **Instrument Specification** screen (**Figure 2.09**) from the **Setup Menu** with the **Arrow buttons**. Press **Clear/Enter**. The screen displays the following information:

1. The **Day, Month, Date, Year** and **Time** (hours, minutes and seconds).

2. The **Instrument Serial Number**

3. The instrument **Model**; and the versions of **Firmware** and **DSP software** installed on the instrument.

4. The **Source Date**, the assay date of the cadmium$_{109}$ source.

5. The number of days since the last factory calibration of the instrument.

6. The **Hours used**, the number of hours the instrument has been used since the last factory calibration.

7. The **Source Strength**, the current strength of the instrument's cadmium$_{109}$ source, in millicuries (mCi).

To exit the **Instrument Specification** screen to the **Main Menu**, press the **Clear/Enter** button.

Setting the time and date on your NITON

NITON sets the date and time (EST) on each instrument before it is shipped. Reset as needed when changing time zones, daylight savings time begins and ends, or whenever the time or date is wrong.

Caution: Check the Date and Time displayed on the Ready to Test screen. If they are not correct, reset them before taking any measurements. Your readings will not be accurate unless the date and time are correct.

To reset the date and time from the **Setup Menu**, do the following steps:

1. Use the the **Arrow buttons** to scroll to **Set Time** (**Figure 2.10 a,b**).

2. Press **Clear/Enter** to select it. The **Date** and **Time** appear as follows:

Month-Day-Year-Hour-Minute-Second

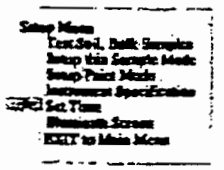


Fig. 2.10a Setup Menu Set Time

Press Clear/Enter to bring up the Set Time screen.

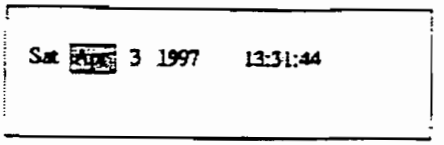


Fig. 2.10b Set Time screen

Month-Day-Year-Hour-Minute-Second

The cursor starts at **Month** and moves to the right. To change the time and date, move from left to right on the screen. For example, To change the **hour** and **seconds**:

1. Press **Clear/Enter** three times to move the cursor to **Hour**.

2. Use the **Arrow buttons** to change the hour to the desired hour. Press **Clear/Enter**.

3. The cursor automatically moves to the next field: **Minute**. Use the **Arrow buttons** to change the minutes to the desired minutes. Press **Clear/Enter** again to move the cursor to **Second**.

4. Use the **Arrow buttons** to change the seconds to the desired seconds. Press **Clear/Enter.**

5. After selecting **Seconds**, the **Main Menu** screen is again displayed, set to **Calibrate & Test.**

Note: If the year is incorrect, set it first. Use Clear/Enter **to move to the year position and the** Arrow buttons **to set the year. Then press** Clear/Enter ***five*** **more times and set the remaining fields as described above.**

Lighting the LCD screen

In its default mode, your instrument's LCD screen remains back-lit for 15 seconds after any of the three buttons is pressed. You can light the screen any time the instrument is turned on by pressing any of the three buttons. When working in a dark place, you also have the option of lighting the screen continuously.

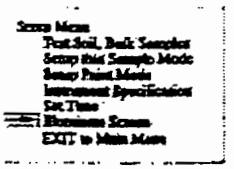


Fig. 2.11 Setup Menu
Illuminate Screen

Take the following steps to either light the screen continuously, or turn off continuous screen lighting if it is currently activated:

1. Use the **Arrow buttons** to select **Illuminate Screen** from the **Setup Menu** (**Figure 2.11**).

2. Press the **Clear/Enter button** to turn continous screen lighting on or off. The instrument will then return automatically to the **Main Menu.**

Overview of test modes

The **Setup Menu** allows you to choose the pre-programmed test mode best suited for the type of testing that you will be doing. A full chapter is devoted to each mode later in this User's Guide.

Note: The Setup Menu shows <u>all</u> NITON analyzer modes for all instruments. If you select a test mode which is not available on your NITON instrument, a reminder message will be displayed on the sceen.

Please contact NITON instrument sales at (800) 875-1578 or your local NITON sales representative to enquire about upgrading your NITON analyzer to add capabilities.

Use the **Arrow buttons** to select the mode you wish to test in. Press **Clear/Enter** to select the mode.

The Bulk Sample mode

Bulk Sample Mode can be used to measure concentrations of contaminants in any fairly homogeneous, fine-grained medium such as soil, ground-up paint chips, a liquid or many other kinds of bulk materials.

To test in Bulk Sample Mode:

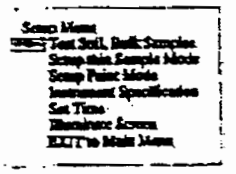


Fig. 2.12 Setup Menu
Bulk Samples

1. Use the **Arrow buttons** to select

Test Soil, Bulk Samples

from the **Setup Menu** (**Figure 2.12**). Press the **Clear/Enter** button.

2. The instrument will return to the **Main Menu** ready to **Calibrate & Test** in Bulk Sample Mode. Press the **Clear/Enter** button.

3. The instrument will initiate self-calibration. This will take one to two minutes. When self-calibration is complete, the instrument will **beep** and display the **Ready to Test** screen for Bulk Sample Mode (**Figure 2.13**).

4. See **Chapter 3: Testing Bulk Samples** for details on how to test particular kinds of bulk samples.

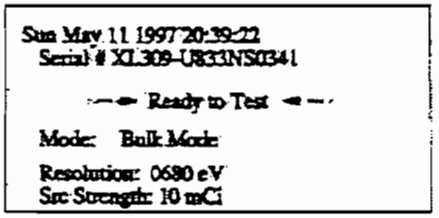


Fig. 2.13 Ready to Test, Bulk Mode

The Thin Sample modes

Thin Sample Modes can be used to measure concentrations of contaminants in a variety of thin layers, including deposits on dust wipes, filters and many other substrates, including, for example, thin layers of uranium on concrete.

Caution: The Standard Thin Sample Mode should not be used for quantitative lead-paint testing. Use only the three Paint Testing modes to test lead-based paint.

There are five Thin Sample Testing modes, each designed for a different type of test media:

1. **37 mm CE Filters**: Used for 37 mm diameter filters (fiberglass or cellulose-ester) used in personal exposure monitoring. This mode can also be used for 37 mm filters used to analyze dust in Dust Vacuum Methods. In this Thin Sample Mode, three measurements are taken, weighted, and summed for each filter.

2. **TSP/PM Filters**: Used for the larger filters to monitor the concentration of metals in air. In this mode, the instrument averages the measurements you take on the filters.

3. **Dust Wipes**: Used for dust wipes to take samples by wiping surfaces following HUD guidelines for risk assessment and clearance testing for lead in dust.

4. **Standard Thin Sample**: Used for taking single measurements of samples or coatings. In this mode, results are displayed, in micrograms/cm^2.

5. **User-Definable Thin Samples**: User-definable testing gives you the flexibility to specify custom thin sample measurement protocols.

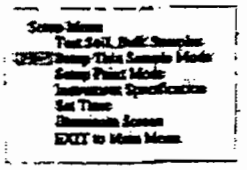


Fig. 2.14 Setup Menu
Thin Sample Mode

Testing in the Thin Sample Modes:

1. Use the **Arrow buttons** to select

Setup Thin Sample Mode

from the **Setup Menu**. Press **Clear/Enter**.

2. The **Choose Operation Mode for Thin Samples** screen will appear (**Figure 2.14**)

3. Use the **Arrow buttons** to select the mode appropriate for the kind of thin samples you are going to test. Press **Clear/Enter**.

4. The **Choose Operation Mode for Thin Samples** screen will *highlight* the thin sample mode you have selected and the cursor will move to **Exit to Main Menu** (**Figure 2.15**). Press the **Clear/Enter** button to return to the **Main Menu**. Press the **Clear/Enter** button again to initiate **Calibration & Testing** in the thin sample mode you have selected.

5. The instrument will initiate self-calibration. This takes one to two minutes. When calibration is complete, the instrument will **beep** and display the **Ready to Test** screen for the thin sample mode you have selected (**Figure 2.16**).

6. See **Chapter 4: Testing Thin Samples**, for details on how to test thin samples.

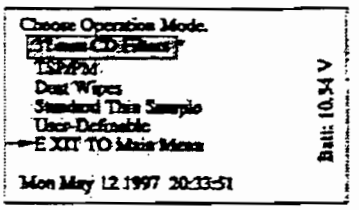


Fig. 2.15 Operation Mode
Select 37 mm CD Filters

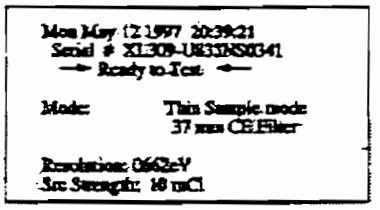


Fig. 2.16 Ready to Test
37 mm Filter Mode

The Paint modes

All three **Paint Modes** can be used interchangeably to measure lead concentrations in paint in mg/cm^2. In all paint modes, NITON analyzers simultaneously measure and analyze both K-shell and L-shell lead x-rays to determine (1) the numerical value of the lead in mg/cm^2 present in the sample; (2) the 95% confidence interval; and (3) whether the sample has a lead concentration that is **greater-than-or-equal-to** ("**Positive**") or **less-than** ("**Negative**") the lead **Action-level** (in mg/cm^2) that has been entered.

Standard Paint Mode

In **Standard Paint Mode**, the instrument reads until a 95% confident reading of "**Positive**" or "**Negative**" versus the **Action-level** is achieved. Then the instrument displays either **Positive** or **Negative**, the **Result** in mg/cm^2, and displays **Surface lead** for all **Positive** readings where the lead is not shielded by overlying layers of non-leaded paint.

In **Standard Paint Mode**, testing times will vary somewhat from sample to sample. The instrument will measure *only* until a 95% confident reading of "**Positive**" or "**Negative**" (versus the **Action-level** you have set) has been attained. Most readings take 10 seconds or less.

Standard Mode + Spectra

Standard Mode + Spectra is identical to **Standard Paint Mode** except that the x-ray spectrum is displayed with each reading.

K & L + Spectra Mode

In **K & L + Specra Mode**, the instrument displays the complete test information *continuously*, from the beginning of each reading, including the K-shell reading with two-sigma confidence interval, the L-shell reading with two-sigma confidence interval, the combined reading (Pb) with two-sigma confidence interval, and the full x-ray spectrum. With each reading, a **Null** result is displayed until a **Positive** or **Negative** result is determined.

In **K & L Mode + Spectra**, you may continue readings indefinitely after a **"Positive"** or **"Negative"** result is obtained, until you have attained a desired measurement time or degree of precision.

Note: In all paint testing modes, if a test is stopped *before* a "Positive" or "Negative" determination has been made, you will get a "Null" test result.

Testing in the Paint Modes:

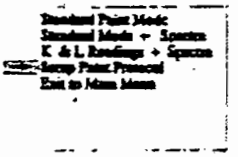


Fig. 2.17 Setup Paint Mode Arrow on Paint Protocol

1. Use the **Arrow buttons** to select

Setup Paint Mode

from the **Setup Menu**. Press **Clear/Enter**. The **Setup Paint Mode** menu screen will appear (**Figure 2.17**)

2. Use the **Arrow buttons** to select

Set up Paint Protocol

. Press **Clear/Enter**. The **Paint Protocol** screen will appear (**Figure 2.18**)

3. Use the **Arrow buttons** to adjust the times for the **1st beep**, the **2nd beep** and the **3rd beep** signals for **K & L Mode + Spectra** and to set the **Action level**. Use the **Clear/Enter** button to enter each selection.

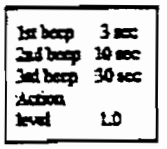


Figure 2.18: Paint protocol screen

4. When the **Action-level** has been entered, the **Setup Paint Mode** screen will re-appear (**Figure 2.17**). Now use the **Arrow buttons** to select a Paint Testing Mode. Press **Clear/Enter**.

5. The **Main Menu** will appear, with the instrument ready to **Calibrate & Test** in the paint mode you have selected. Press**Clear/Enter**.

6. The instrument will self-calibrate in one to two minutes. When self-calibration is complete, the instrument will **beep** and display the **Ready to Test** screen for the paint mode you have selected (**Figure 2.19**).

7. See **Chapter 5: Testing Paint Samples**, for detailed descriptions of all three paint testing modes.

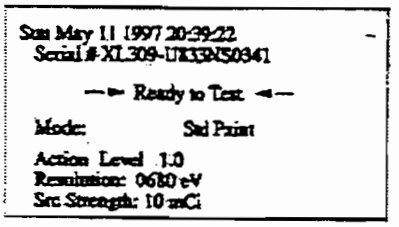


Fig. 2.19 Ready to Test. Paint Mode

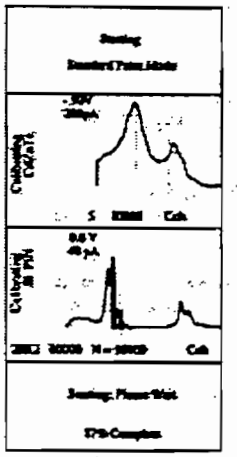
Calibrating your NITON

Your NITON has been thoroughly calibrated at the factory. To further assure the best Quality Assurance/Quality Control, your NITON performs a second self-calibration check every time you turn on or reset the instrument.

In addition, NITON has provided you with several standard samples so you may check both calibrations. These tests against known standards insure that the instrument is functioning properly and buttress your results with a permanent record of regular calibrations.

Instrument self-calibration

When the **screen arrow** (->) is on **Calibrate & test**, press **Clear/Enter** to start the self-calibration process (**Figure 2.20**). Self-calibration takes one to two minutes. When it is completed, the instrument will beep and the **Ready to Test screen** will appear.



Caution:

The ready to test screen

The **Ready to Test screen** (**Figure 2.19**) displays the following fields:

1.The current **Date** and **Time.**

Caution: Check the Date and Time. If they are not correct, reset them before taking any measurements (see page 10)**. Your readings will not be accurate unless the date and time are correct.**

2. The instrument **Serial Number.**

3. The indication that the instrument is **Ready to Test**

4. The testing mode the instrument is ready to test in.

5. The **Action-level** the instrument will use to make either a "Positive" or "Negative" determination of lead in paint testing. The **Action-level** is only used in paint testing modes.

6. The **Energy Resolution**. The lower the number (in eV), the better the instrument will perform.

Caution: If you try to calibrate the instrument and it does not calibrate successfully, push the Reset Button on the bottom of the instrument and recalibrate. If your NITON does not calibrate successfully in three attempts, please call the NITON Service Department at (401) 294-1234.

7. The **Source Strength** (**Src Strength**). The Source Strength indicates the current activity of the cadmium$_{109}$ source in your instrument, in millicuries. Your NITON compensates automatically for the decay of the source.

Re-calibrating your NITON during testing

To insure the accuracy and precision of your NITON, it is recommended that you re-calibrate hourly during testing. To recalibrate:

Press the **reset** button on the bottom of your NITON.

or turn the NITON off, then on, and press the **Clear/Enter** button.

Note: Occasionally, your NITON may refuse to take further readings and the screen will display the following message:

YOU MUST RECALIBRATE.

Typically, this will occur when there is a sudden, very large change in the ambient temperature. When this occurs, recalibrate and continue testing.

How to use your NITON standard samples

NITON provides sets of standard samples for each testing mode. These are used to check the calibration of the instrument:

1. For **Bulk Sample Mode**, there is a set of three NIST soil standards

2. For **Thin Sample Mode** there is a set of three thin film standards: lead, copper, and iron.

3. For **Lead Paint Mode**, there is a set of government-traceable lead paint films.

Note: Although the standards do not contain every element our multi-element analyzers test for, when an instrument correctly measures the standards you have have received with your 700, your NITON will correctly measure the other elements.

Test the standards regularly. First, immediately after the instrument finishes self-calibration. Then test the standard samples appropriate to the type of tests you are conducting, and once every 1-2 hours thereafter.

Warning: Tampering with the 5,500 ppm lead-in-soil standard may cause exposure to lead dust. Keep all standards out of reach of children.

Caution: Never tamper with Test Standards. They should not be used unless they are completely intact.

Soil and Thin Film standards

To test soil or thin film standards, place the sample in the test platform receptacle and proceed to test as with any prepared sample. The NITON standard soil samples provided with your instrument contain known amounts of several elements. Do not contaminate the thin film samples with your fingerprints. Handle them by the edges with clean hands.

Lead paint standards

1. Place the NITON standard with the colored side face up. Choose the RED strip labelled 1.0 +/- 0.1. Take a reading of that standard. Place the instrument on the standard so that the instrument window is fully on the standard. Your NITON should display a value between 0.9 and 1.1 mg/cm^2 and should indicate **Surface lead.**

2. Place the same standard with the colored side down. Take a reading of the standard (buried beneath the equivalent of 5-6 coats of non-lead paint). Your NITON should still display a value between 0.9 and 1.1 mg/cm^2 and should not display **Surface lead.**

Note: If your instrument is testing high on Standard samples, check the surface the Standards are resting on. The surface may contain lead.

When you test the Standard samples, your instrument should give readings which approximate the certified values. Your instrument should give consistent readings for each sample.

Downloading data

Your NITON stores up to 3,000 measurements plus their spectra. You can download this data to a computer for reporting or insertion in a database.

Note: Downloading data does not erase readings. To make room for the next set of data, erase readings after verifying that the data was downloaded successfully (see next section).

The RS-232 port, on the back of your NITON, accommodates a 4-pin LIMO connector. A LIMO to 9-pin RS-232 connector cable is provided with your NITON. Your NITON can communicate with either a "dumb" or an "intelligent" terminal, such as a VT100 connected to a mainframe computer or a PC-compatible computer.

Fast data dump

You can download up to 3,000 measurements, their descriptions, and spectra (4-90 keV) in *minutes* using the high-speed compressed format, **NITON/Mid-Hudson Downloading Software**, provided with your instrument.

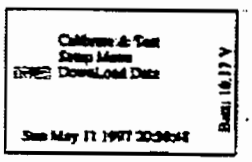


Fig. 2.21 Main Menu DownLoad Data

1. Connect your NITON to your computer with the RS-232 port cable that is provided.

2. Using the **Arrow buttons**, select **Download Data** from the **Main Menu** and press **Clear/Enter**

(Figure 2.21).

3. Select **Fast Data Dump** from the **Download Data menu** (**Figure 2.22**)and press **Clear/Enter**. Select the first to the last readings you wish to download. The **default** setting will download all readings currently stored in memory.

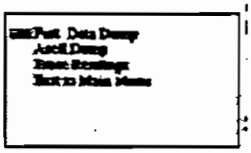


Fig. 2.22 Download Data
Fast Data Dump

4. When the instrument finishes downloading, it will return to the **Main Menu**.

ASCII data dump

For users who wish to download data in ASCII format, the NITON can dump its data as an ASCII file to any terminal emulator program.

1. Connect the NITON to your computer with an RS-232 cable.

2. In the **Download Data screen**, press the **Arrow buttons** to scroll to **ASCII dump** (**Figure 2. 23**). Press **Clear/Enter**.

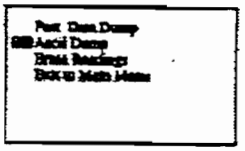


Fig. 2.23 Download Data
Ascii Dump

3. When the instrument finishes downloading, it will return to the **Main Menu**.

Erasing readings

If you do not erase your data, the NITON will continue to record data until the memory is completely full. Then the NITON will start to overwrite older data. Any data that is overwritten in this way will be lost.

Your NITON can store data on up to 3,000 measurements in all **Paint modes**, or 1,000 readings in **Bulk Sample** or **Thin Sample modes**.

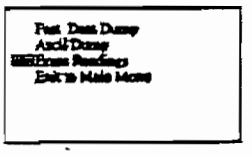


Fig. 2.24 Download Data
Erase Readings

Note: Download your data before the memory is completely full. Clear the memory after downloading.

The erase readings function is designed to protect you from accidentally erasing readings. To erase readings:

1. In the **Download Data** menu, use the **Arrow buttons** to scroll to **Erase Readings** (**Figure 2.24**). Press **Clear/Enter.**

2. The **Erase Readings** screen (**Figure 2.25**) appears with the following choices:

ERASE all readings

-> CANCEL do not erase

EXIT to Main Menu

The screen arrow defaults on **Cancel do not erase**, so that if you select it by mistake, you will not erase any readings.

3. To **Erase Readings**, use the **Up-Arrow button** to go to **ERASE all readings**. Then press **Clear/Enter**. When you enter either **ERASE all readings** or **CANCEL do not erase** your instrument will return to the **Main Menu**, ready to take and store more readings.

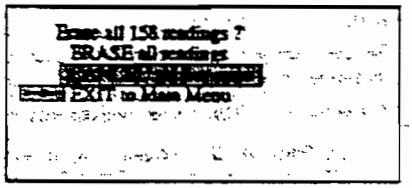


Fig. 2.25 Erase Readings Screen
Default is: CANCEL, do not erase

Battery packs and battery charger

Fully charged, each Nickel Metal Hydride battery pack gives eight or more hours of continuous use. It takes about 2.5 hours to fully recharge a spent battery pack if the batteries have been recently used. If the NITON has not been used for several weeks, or if the batteries are completely discharged, they must be pre-charged before they can be recharged. See **Battery Charger**, below.

NITON Battery packs can be recharged at least 500 times. They are warranted to be free of defect when shipped. They are not further covered by manufacturers' warranty. When they need to be replaced, new battery packs may be purchased from NITON.

Note: Before beginning a test, be certain the battery pack has sufficient charge. It is always a good idea to carry a spare battery pack.

Caution: NITON's Nickel Metal Hydride battery packs discharge at a rate of about 2% per day when not in use.

Battery pack routine maintenance

Some guidelines:

* Don't leave battery packs on the charger *all* the time. Overnight recharging is recommended.

* For longest battery lifetimes, use a battery until completely discharged, and then recharge.

* Don't recharge a fully charged battery pack. If you want to charge a partially charged battery, run the Discharge cycle before recharging.

* Store the charger and battery packs in a cool, but not cold, place, away from direct sunlight.

* When a battery pack is not used for a long period of time, it will lose its charge completely. Fully recharge it before use.

Note: The lithium battery inside your NITON will prevent any loss of data if you need to change the battery pack before downloading readings.

Changing battery packs

Removing a battery pack

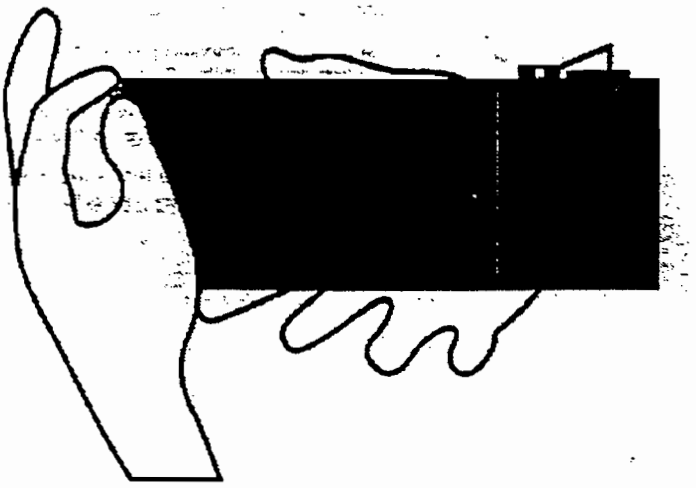


Fig. 2.26.
Loosen clamp screws to remove the battery pack. The clamp screws stay attached to the battery pack.

1. Avoid changing the battery pack outdoors. Moisture and dirt can damage a battery.

2. Rest the NITON on a clean surface.

3. Loosen the (2) clamp screws. They do not come off (**Figure 2.26**).

4. Pull the battery pack away from the instrument by grasping the knurled screws and gently rocking the battery pack from side to side while removing it.

Installing a battery pack

1. Rest the NITON on a clean surface, as before.

2. Slip the notch at the bottom of the battery pack into the wide slot.

3. Gently push the battery pack in, taking care that the battery pack connector is seated properly to the instrument.

4. Tighten the (2) knurled screw clamps that fit into holes on the NITON. If the screw clamps do not tighten, the connectors are not lined up properly. These screw clamps must be tight for a secure connection.

Recharging battery packs

Recharging with the AC adapter

1. Lay the battery pack on top of **Battery Charger**. Fit connectors together snugly (**Figure 2.27**).

2. Plug one end of the AC adapter into the power port on the bottom of the charger. Push the plug in, making sure it seats fully.

3. Power up the charger: Plug the other end of the AC adapter into a 110V outlet. The yellow ***Power*** light will come on and stay on throughout. The green ***Charge*** light will also come on. It will blink slowly at first, indicating that the battery is on **Pre-charge**, and then stay on with a steady light, indicating that the battery is on **Full Charge**.

4. In **Full Charge** mode, the green ***Charge*** light will stay on with a steady light while the battery is being charged. It is normal for the charger to make some noise in **Full Charge** mode.

5. In **Trickle Charge mode:** When the battery is fully charged, the charger will automatically switch to **Trickle Charge** mode and the green ***Charge*** light blinks rapidly.

Caution: Do not leave battery packs on the Battery Charger longer than necessary.

Battery charger

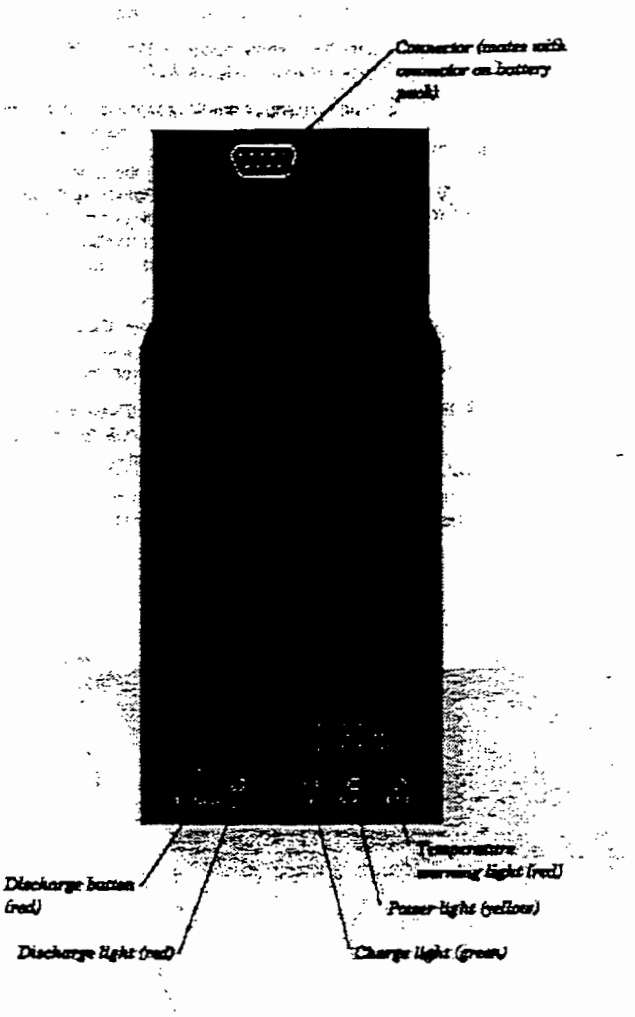


Fig. 2.27. Front view of the battery charger.

Discharge cycle

Put battery packs on the **Discharge Cycle** only if they are not holding a charge; or, if they are partially charged, run the **Discharge Cycle** before recharging. It takes about eight hours to fully discharge a battery pack. To discharge a battery pack, place it on the charger and:

1. Press the red **Discharge** button. The red **Discharge light** goes on, and the green **Charge** light blinks slowly, showing charger is in **Discharge** mode.

2. After a full Discharge cycle, the charger automatically recharges the battery.

3. The red **Discharge** light goes out and the green **Charge** light will blink rapidly, showing it is in the **Trickle Mode**.

Pre-charge

If your NITON battery packs run all the way down, they must be pre-charged before they can be re-charged. The process can take up to 5 hours. A battery is pre-charging when the green **Charge** light on the battery charger is blinking slowly, and the **Discharge** and **Temperature** lights are off.

Overheating during charge

Caution: If the red Temp light comes on repeatedly when a battery pack is on the battery charger in the Full Charge cycle, call NITON Customer Service at (401) 294-1234.

Caution: Do not store the battery packs or battery charger in direct sunlight.

Using your vehicles 12V DC outlet

[yen] A 12V DC Adapter is provided with your NITON. Instructions are the same as for using the 110V AC Adapter. When you have seated all connections well, the yellow **Power** light will come on.

[yen] Do not use the Discharge Cycle while on the DC outlet.

[yen] Secure the charger so the power cord does not get pulled out while the vehicle is in motion.

[yen] The plug of the DC Adapter has a 5A internal fuse. To check the fuse, unscrew the cap that retains the contact from the end of the plug. Replace this fuse only with a 5A fuse of the same size. If the fuse in the 12V Adapter burns out frequently, call NITON's Service Department at (401) 294-1234.

Note: Please do not throw away spent battery packs. Return spent battery packs to NITON so we can dispose of them properly.

Maintenance, cleaning and repairs

NITON Corporation welcomes any questions or comments you may have about your NITON analyzer. Please do not hesitate to call us at either our Main Office number: (781) 275-9275 or at our Rhode Island Service Facility number: (401) 294-1234.

Caution: All Service except exterior cleaning must be performed by NITON Corporation. Do not attempt to make repairs yourself. Opening the case of your NITON will void the instrument Warranty.

Keep your NITON clean, particularly the beryllium window on the bottom of the instrument. If the window is dirty, the performance of your NITON will be affected. Clean the window gently with cotton swabs. Clean the instrument's metal case with a soft cloth. Never use water, detergents, or solvents. These may damage the instrument.

Note: Never ship your NITON analyzer back to the factory for *any* reason without calling and obtaining a Return Authorization (RA) Number from NITON Corporation.

Storage, transport, and shipping

Storing and transporting your NITON

All NITON instruments come in waterproof, drop-proof carrying cases with padlocks. NITON instruments can be transported by car or plane or shipped as an ordinary package. There are no restrictions for tunnels or bridges. No notification is required for transportation except the following: There may be disclosure and/or licensing requirements if you take your NITON instrument across state or national boundaries. Please check with the appropriate agencies for details.

No special labelling is required on the outside of case or packaging. A compliance statement must be kept with the instrument case. *Always* transport the unit in its carrying case, and keep the NITON in its case whenever it is not being used. Store the instrument, in its case, in a secure area.

Shipping your NITON

All NITON instruments must be packed in their original padded carrying cases for shipment. Pack the NITON in its carrying case and ship in either the original carton and packing material or their equivalent.

Caution: Do not ship your instrument back to NITON for any reason without first notifying NITON Corporation and receiving a Return Authorization Number.

Caution: If you return your NITON without the carrying case you will void the instrument warranty. You will also be billed for a replacement case plus any repairs resulting from improper shipping.

Always enclose a copy of a current leak test certificate when you ship your instrument back to NITON.

Caution: NITON's license prohibits repairing or upgrading any XRF instrument without a current leak test certificate. If you return an instrument without a current leak test certificate, NITON will perform a leak test and bill you for the leak test.

Note: Keep a copy of the following statement in the NITON case whenever the instrument is shipped:

THE NITON SPECTRUM ANALYZER CONFORMS TO THE CONDITIONS AND LIMITATIONS SPECIFIED IN 49 CFR 173.422 FOR EXCEPTED RADIOACTIVE MATERIAL, INSTRUMENTS AND ARTICLES, N.O.S. UN-2910. THIS PACKAGE CONTAINS NO MORE THAN 50 mCi $CADMIUM_{109}$ IN A PLATED, SOLID, SEALED SOURCE INSTALLED IN AN X-RAY FLUORESCENCE ANALYZER.

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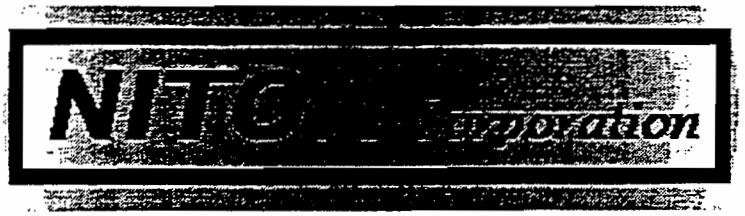


NITON Corporation

XL-309

&

*700*series

User's Guide Version 5.0 (HTML) Chapter 3

3: Analyzing bulk samples

Overview

The NITON XL-309 may be used to test lead in soil and ground-up paint chips if equipped with optional Lead In Soil Analysis software and hardware. 702, 702-A, 703 and 703-A Model Spectrum Analyzers are multi-element analyzers for bulk media, thick samples of materials such as soil, sludge, and various liquids. Applications include:

- in-situ soil testing,
- in-situ materials testing (e.g., contaminated concrete)

- bagged soil sample testing
- testing sludge, sediments, liquids, and dust in cups,
- testing prepared soil samples.

Choose the **Bulk Sample mode** from the **Setup screen** (**Figure 3.01**).

Note: Before testing in Bulk Sample mode, turn your NITON on at least 15 minutes prior to testing. This will give you more precise measurements.

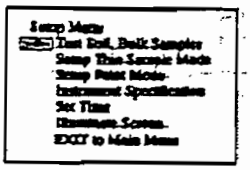


Fig. 3.01 Setup Menu: Test Soil, Bulk Samples

In general, testing methods for bulk media are of two types: Field screening and testing prepared samples. Understanding the difference between these two types of analysis is crucial to getting good data.

Field screening should be used to profile an area, to locate sources of contamination, to determine the boundaries of contamination, or to gather data that will subsequently be used to design a sampling plan. Field screening is usually only approximate; field screening will correlate very well with lab analysis for a highly-homogeneous sample, but may correlate extremely poorly for a non-homogeneous sample.

Note: For performance evaluation of field XRF results by comparing them to laboratory results (done to justify XRF usage), never use in-situ testing; always gather samples and prepare them before testing.

When comparing field screening to laboratory analysis, try to compare the same samples. For best results, collect a large sample in a zipper locking storage bag. Shake the bag to mix the sample. Test the bagged sample several times using the NITON and average the readings. Then compare this average reading with lab results.

If you must test in-situ for performance evaluation, take several XRF readings bracketing a spot. Then take a sample for laboratory testing from that spot. For further discussion of field screening, see EPA Method 6200, "Field Screening Using a Field-Portable XRF." Contact NITON for a copy. The EPA accepts field screening using the NITON if the screening is performed using Method 6200. Most states accept EPA Method 6200.

The measurement screen

On NITON XL-309s with optional Lead in Soil Analysis, *only* lead is displayed in bulk sample testing. On 700 models, only the two highest-concentration elements are displayed (in ppm, with the

two-sigma confidence intervals) on the first **Measurement screen** (**Figure 3.02a**), with the x-ray spectrum. The black bars on the spectrum display highlight the presence or absence of lead or iron in the sample. The test time is also displayed in nominal (source) seconds.

The summary screen

When you end a reading, the **Measurement Screen** is replaced by the **Summary Screen** (**Figure 3.02b**). On 700 models, results are displayed for 14 elements. The elements are divided into two groups: elements that were detected in the sample, and elements that were not detected. Press the **Arrow buttons** to scroll through the elements.

Detection Limit: For an element to be detected by the NITON in a given sample, the measured concentration of the sample must be at least three times the standard deviation of the measurement. This detection limit will depend on the composition of the sample.

Precision: The measurement precision for each element displayed appears to the right of the measured concentration, under the heading "+-". The **precision** of each measurment is two times the standard deviation (sigma). An element is classified **detected** if the measured concentration (in ppm) is at least 1.5 times the precision.

Detected elements are displayed as in the Measurement screen. Non-detected elements are shown as **< xx**, where **xx** is the detection limit for that sample. The detection limit for each element is calculated from each sample.

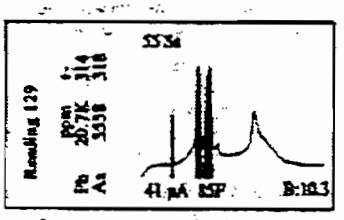


Fig. 3.02a Measurement Screen
Bulk Mode, In-progress screen.

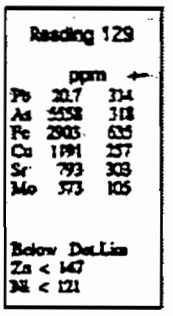


Fig. 3.02b Bulk Mode
Summary Screen

In-situ surveys

Before you take your first measurement, you must decide whether to test the bulk material

- in-situ (in-place),
- as bagged samples (or, for liquids and sludge, in cups) with a minimum of preparation, or
- in an XRF cup after careful preparation.

Note: More sample preparation (drying, milling and sieving) will yield greater accuracy. The drier, finer, and more homogeneous the particles, the better the measurements.

If you are primarily interested in determining whether an element is present (rather than in accurately measuring how much is present), direct measurement is the quickest, simplest way to proceed. Even if you intend to take samples, preliminary direct measurements will help you to survey the site. The analysis of bagged samples is another screening technique.

The NITON test guard

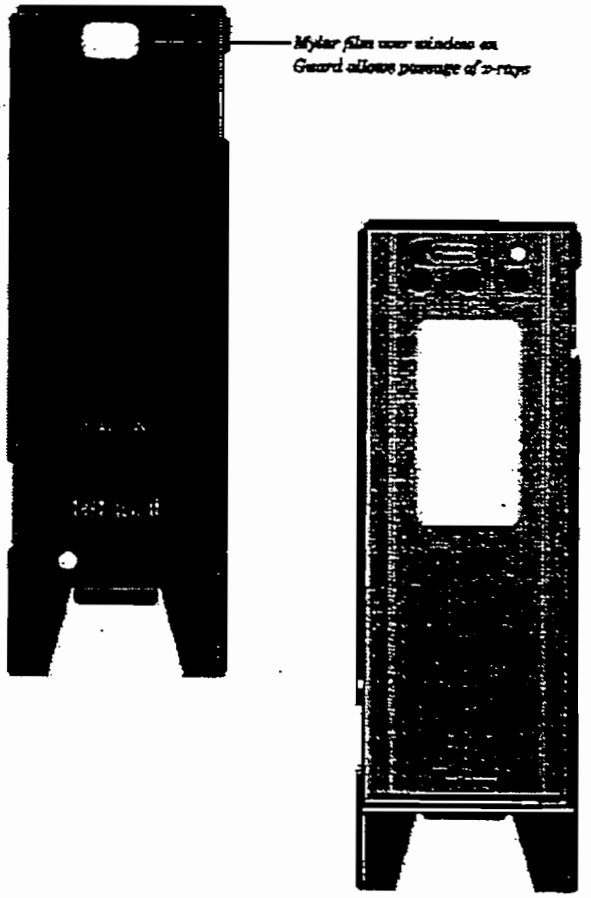


Fig. 3.03
The NITON
Test Guard

The NITON **Test Guard** (**Figure 3.03**) is a formed metal plate designed to be placed directly between the ground or other bulk media and the NITON. Use the **Test Guard** for surveys of bulk media *in-situ* or for testing bulk samples in bags. The **Test Guard** shields the unit from contamination and damage.

Testing in-situ

Warning: When taking samples from a site where toxic chemicals may be present, always use gloves and respiration equipment for your own protection.

1. Select a measurement site. Lead-in-soil from paint, for instance, will be concentrated within a few feet of the painted structure. Valid results will depend on a sufficient and appropriate selection of sites to sample.

2. Clear any surface debris or vegetation. Use a flat area so that the NITON will contact the test medium. The finer and more homogeneous the material, the more accurate the measurement. (You can increase your accuracy when testing soil by loosening the soil and letting it dry in the sun before testing.)

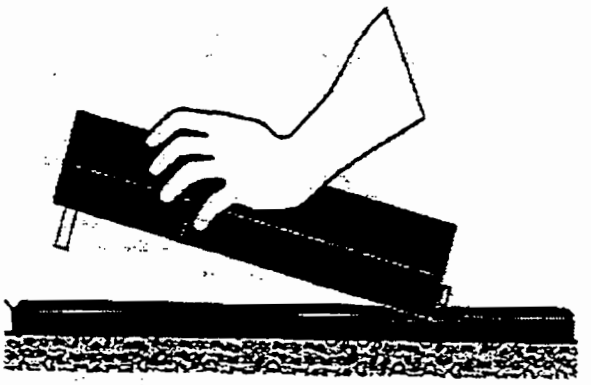


Fig. 3.04a
Place your NITON on the Test Guard.

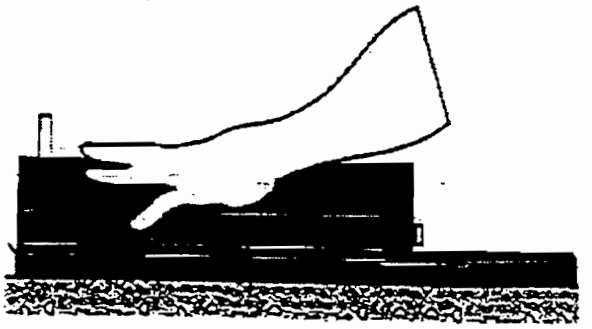


Fig. 3.04b
Firmly press your NITON flat against the surface.

3. Place the test guard on ground. Keep the top of the test guard clean.

4. Hold the NITON in one hand.

Warning: Always treat radiation with respect. Do not put your hand on the end plate of the NITON while measuring. Never point the NITON at yourself or anyone else when the shutter is open.

5. Push the safety slide (that locks the shutter release) out from under the shutter release. If the slide is still tucked in, you cannot press in the release nor will the instrument fit on the test guard correctly.

6. Place the NITON on the test guard so that the rectangular opening on the test guard is under the window of the NITON, squeeze the shutter release, and firmly press the instrument flat against the surface of the test guard (**Figure 3.04 a,b**). If you don't squeeze the shutter release, the plunger will not depress. If the plunger is not fully depressed, the window is not fully open and the NITON cannot measure accurately. The back of the unit must be flush with the test guard.

Note: During the measurement, you do not need to squeeze the shutter release continuously. Hold the NITON firmly against the test guard surface and it will continue to read. Once you lift the instrument, the plunger will back out the bottom, the shutter will close, and the test will be finished.

7. Watch for indications to decide when the test has reached the desired level of accuracy. A typical screening test will last 20-30 source seconds.

Warning: In the unlikely event that the plunger gets stuck in the open position, simply push it closed. Then call the NITON Service Department at (401) 294-1234.

In-situ depth profiling

An XRF soil test examines only the top millimeter or so of soil. To do depth profiling, simply remove a vertical slice of soil and test several samples from different depths. Doing so rapidly yields information about the depth of contamination.

Analysis of bagged bulk samples

Sometimes it is convenient to collect samples in plastic bags. Without further preparation of the sample, you can screen the site by testing each bag. Because you are testing through a bag, test results will tend to be 5-10% lower than test results obtained from direct analysis.

Taking bagged samples

1. Before sampling a site, size it up for differences in soil characteristics. Valid results depend on a sufficient and appropriate selection of sites to sample. Consider the site's topography, texture, drainage, color of topsoil, and past use.

2. Take a composite sample from each predetermined area. Do not combine samples from areas with different compositions or history. **A composite sample made up of samplings from two distinctly different areas is not representative of either area.**

Mix the sample. If it is too large, reduce the sample. Some techniques for reduction and homogenization are described in the section on analysis of prepared samples.

3. Fill a clean plastic bag with 50-100 grams of soil and close it securely (with a twist tie). The accuracy of your measurements will be limited by the thickness of the plastic in the bag you use. 1 mil-thick Polyethylene bags offer a reasonable compromise between accurate readings and bag durability. Be sure to label each bag with your name and the location of the sample site.

Testing samples in bags

Shape the bag of soil to form a continuous uniform layer of at least 1 cm. (0.4 inch) thickness. Place the NITON test guard on the bag (**Figure 3.05**). Then follow testing in-situ instructions.

Warning: Do not hold bagged bulk samples in your hand during testing.

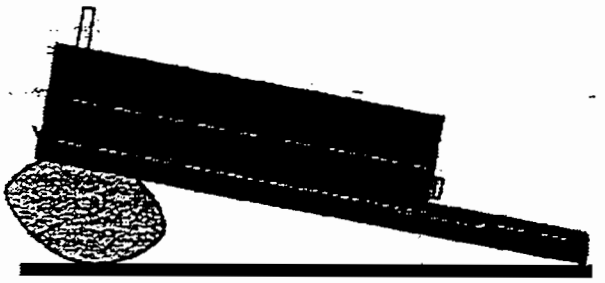


Fig. 3.05
To test a bag of soil, firmly press your NITON plus Test Guard flat against the surface of the bag (which should rest on a firm surface -- not on your hand).

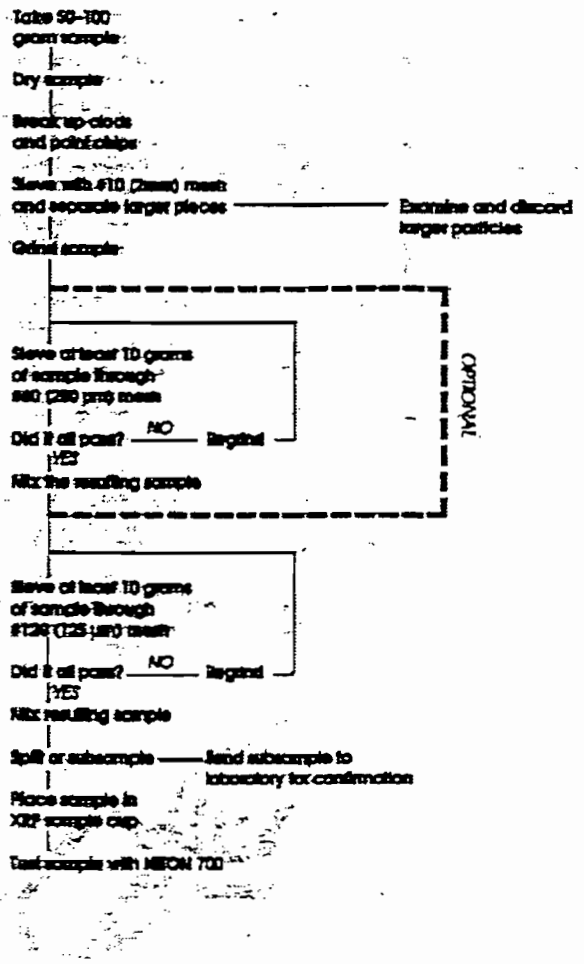
Analysis of prepared bulk samples

Prepared sample analysis is the most accurate method for determining the concentration of elements in a bulk medium using your NITON. Sample preparation will minimize the effects of moisture, large particle size and variations in particle size.

Warning: For your protection, when taking samples from a site where toxic chemicals may be present, always use gloves and respiration equipment.

NITON recommends a specific sample protocol. Following this protocol for preparing and testing samples is vital for achieving a level of accuracy comparable with laboratory results. See **Figure 3.06** for a flow chart of the protocol.

Fig. 3.06 Flow chart of sample preparation protocol recommended by NITON.
Use of the #60 mesh sieve is optional.



Taking bulk samples

Note: When testing for lead-in-soil in a residential setting, it is standard practice to sample the top 4 to 6 inches of soil.

The soil probe or sampling tube is a very convenient sampling tool. It not only allows speed but it makes more accurate composite samples than any other tool as it may always be inserted to a marked depth and it removes the same amount of soil at each insertion. There are core sampling devices that remove an intact cylinder of undisturbed material.

A shovel, spade, dibble, narrow (1-1/2 inch) garden trowel, or other sampling tool can do the job. Take a half-inch soil slice. A satisfactory soil auger may be made by welding a 1-1/4 or 1-1/2 inch wood bit into a 1/2 inch pipe equipped with a T-handle.

Take 50-100 gram sample to insure that you have a sample large enough to be representative and unbiased after mixing, grinding, and straining it.

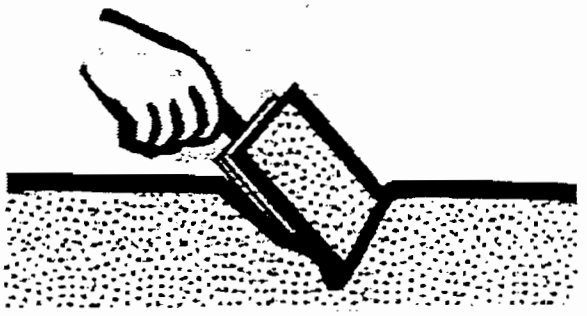
1. Before sampling a site, evaluate it for differences in soil characteristics. Valid results depend on a sufficient and appropriate selection of sites to sample. Test results may be worthless, even highly misleading, unless the samples tested actually represent the area.

Consider topography, texture, drainage, color of topsoil, and past use. Lead, for instance, is usually concentrated near a building with lead paint (within 4-6 feet).

2. If the individual samplings are taken with a spade or trowel, (**Figure 3.07**) reduce the samples by taking a vertical slice (so it is representative of the entire spadeful) about one inch wide.

Place the reduced samples in a clean pail. Then mix the sample thoroughly by stirring and by rotating the pail at an angle of 45 degrees. Don't shake. (You do not want to stratify the sample by weight).

Fig. 3.07
Use a spade, trowel or garden dibble to take a half-inch thick slice of soil.



3. Take a composite sample from each predetermined area. Do not combine samples from areas with different compositions or history. A composite sample made up of samplings from two distinctly different areas is not representative of either area.

From each predetermined area, prepare a composite sample by taking several samplings consisting of vertical columns of material approximately 1 inch in diameter. The length of each column should be about 6 inches. Lead from paint is usually concentrated within the top 1-4 inches. The elements you wish to measure and the local history will determine how deep you need to sample.

Package samples from the following areas separately: samples close to painted structures, close to roads, samples close to where various types of waste have been stored, or near pressure-treated lumber.

4. Fill a clean plastic bag and close it securely (with a twist tie). Be sure to label it with the date, the site and the location where you took the sample

Preparing bulk samples

The equipment you need to prepare samples is included in your kit. Among these are a mortar and pestle (for the XL-309 with lead-in-soil-analysis), an electrically powered grinding mill (included with 700s), and several sized-sieves.

Caution: Keep all test equipment clean to prevent contaminated samples.

The mortar, pestle, and grinding mill may be cleaned with dry paper towels. Water will also clean the mortar, pestle, and the mill's container, but be sure each is absolutely dry before you use them on another sample. The mortar and pestle may be cleansed by grinding clean dry sand in the mortar. Use the short bristle brushes (included in your Bulk Testing Kit) to clean the sieves. When Soil Grinder blades wear out, unbolt the worn blades and replace.

Cone and quartering

At various times while preparing a sample you may need to divide it. Cone and quartering is a method for splitting the sample into homogenous quarters. Slowly and carefully pour the dry material onto a flat sheet or pan forming a symmetrical cone. Using a flat thin-bladed tool, such as a knife or ruler, divide the cone into equal piles. Divide these in half again. Now you have four samples, each one-quarter the size of the original and each more homogenous than the original.

1. If the sample is moist and cohesive, dry it. To best prepare a sample for presentation to the XRF, the material should be dry and well homogenized. Ideally, the entire sample should be dried to constant weight, sieved to remove gravel and debris, and ground or milled to a fine powder.

The sample can be dried in any of several ways. Choose one of the following: Oven dry the sample for approximately 2 hours at 150° C., until the sample reaches a constant weight; air dry the sample overnight at room temperature in a shallow pan; gently stir and warm the sample in a pan over a hot plate or burner.

Oven drying is inappropriate when volatile compounds may be present in the sample. For example, lead present as tetraethyl lead would be driven off by the heat of drying. Some forms of mercury and arsenic are volatile. Air drying will preserve more of these volatile substances.

2. Grind the sample to break up dirt clods and/or paint chips.

3. Sieve with the #10 (2mm) mesh and separate out the larger pieces (stones, organic matter, metallic objects, etc. Examine the larger particles by eye (look for paint chips), but do not include in the sample.

4. Grind the sample so its particles will be finer and more homogenous. Use mortar and pestle, or an electrically powered grinding mill.

Warning: Grinding-and-sieving dried samples produces dust. Even clean soil contains silica, which may be hazardous when airborne. Prepare all samples in a ventilated area; wear a mask, gloves, and an apron; and spread a drop cloth.

5. Sieve at least 10 grams of the sample through #60 (250 um) and #120 (125 um) mesh. Re-grind the unpassed material until the required fraction is able to pass.

6. Mix the resulting sample.

Putting the sample in an XRF sample cup

The container holding the sample affects the accuracy of the measurement. Use a container with as thin-walled a window as is convenient and use the same kind of container and window for each sample. Consistency and careful attention to detail are keys to accurate measurement.

Note: The sample container should be a sample cup of a type that can be filled from the rear; that is, the side opposite the window (e.g. Chemplex #1330). NITON recommends using a 1/4 mil mylar film window (Figure 3.08)**. A supply of cups and windows are included.**

1. Place a circle of mylar film on top of an XRF sample cup. The window goes on the end of the cup with the indented ring. Note that the window may be prepared ahead of time.

2. Secure the film with the collar. The flange inside the collar faces down and snaps into the indented ring of the cup. Inspect the installed film window for continuity and smooth, taut appearance.

3. Set the cup, window-side down, on a flat surface. Fill it with at least three grams of the prepared sample (no more than half-full). Take care that there are no voids or layering.

4. Placing the cup film-side down on a flat surface, tamp the sample into the cup. The end of the pestle makes a convenient tamper. If you intend to re-use the sample, you can, alternatively, place a filter-paper disk on the sample before tamping it.

5. Fill the cup with polyester fiber stuffing to prevent sample movement. Use aquarium filter or pillow filling as stuffing. A small supply of stuffing comes with your bulk sample kit.

6. Fasten the cap on the cup (**Figure 3.09**). Using an indelible pen, write an identifying number on the cup. Keep a record of the sample number, the site and location, the date of the sample, and any other relevant comments.

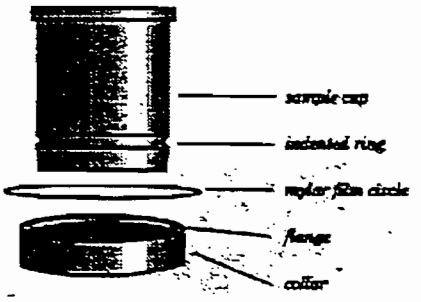


Fig. 3.08 Secure the film by snapping the collar on to the cup.

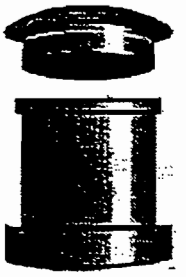


Fig. 3.09 Fasten the cap on the cup.

Preparing samples of liquids, sludges or dust

Liquids:

Fill an XRF sample cup with the liquid to be tested (Use no cotton). It is best if some overflows when the cap is put on, since the cup must be full.

Sludge:

Sludge can be placed directly in an XRF cup for screening. This is considered in-situ testing because no attempt has been made to prepare the sample. For more accuracy, the sludge can be dried, sieved, and ground.

Screening dust:

Use large dust samples taken from a home vacuum cleaner bag. Remove fibers, hairs, and debris. At least three grams of dust are needed to assure accurate analysis. Samples as small as one or two grams may be measured with less accuracy. Even smaller samples (0.3 to 1.0 grams) can be analyzed by applying a weight correction factor and by using a funnel to place the sample in the center of the sample cup.

Prepare in an XRF sample cup and test the same way you would with a soil sample. For risk analysis, it is advisable to use a 60-mesh sieve to isolate and test only fine particles.

The bulk testing platform

The test platform (**Figures 3.10a,b**) is an accessory fixture for holding bulk samples (such as soil or ground paint chips) in standard film-window XRF cups. This fixture snaps quickly and securely to your NITON instrument.

The platform latch screws underneath for storage. Before using the test platform, unscrew the latch and rescrew it on the end of the platform nearest the receptacle for the sample cup.

The test stand securely holds the XRF sample cup in place.

Testing the sample;

Set the NITON test platform on a flat, solid surface. Place the sample cup in the receptacle of the sampler. Included in your kit are some foam disks that you can put in the receptacle under the cup for firmer contact between the NITON and the sample cup window. Attach the NITON to the test stand and follow in-situ bulk sample instructions (**Figures 3.11 a,b**).

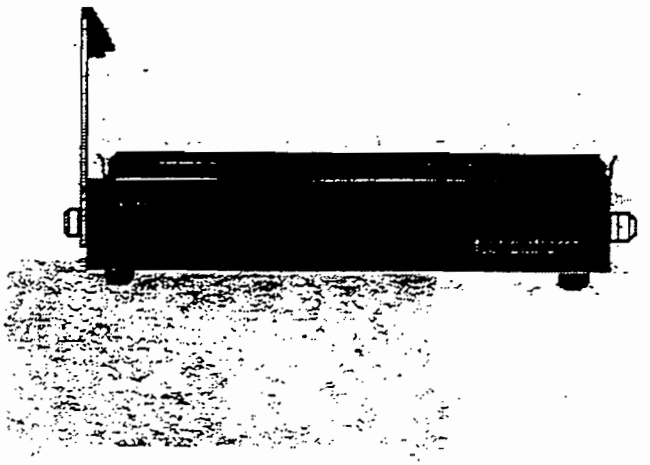


Fig. 3.10a
The Niton
Test Platform

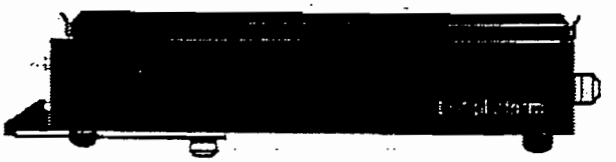


Fig. 3.10b
The Niton
Test Platform
with its latch in
the stored position.

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NITON Corporation

XL-309

&

*700*series

User's Guide Version 5.0 (HTML) Chapter 4

Chapter 4: Analyzing thin samples

Overview

The NITON XL can test dust wipes and other thin samples for lead if equipped with optional Dust Wipe Analysis Software and Hardware. The 701, 701A, 703 and 703A Model Analyzers are multi-element analyzers for a wide range of thin samples. Examples of thin samples include:

- 37 mm filters used for exposure monitoring filters, and filters used for Dust Vacuum methods
- Total Suspended Particulate (TSP) and Particulate Monitoring (PM) filters,
- dust wipes,

- filters used for measuring suspended and dissolved metal concentrations in liquids, and
- thin coatings deposited on substrates.

Contamination captured on filters or wipes is not usually deposited uniformly, and the filters and wipes are several times larger that the 1 cm x 2 cm scanning window of the instrument. To produce meaningful results, several readings must be taken for each thin sample measurement. Readings are then summed or averaged.

The number of readings, the weight given each reading, and whether the readings are summed or averaged depends on the application. For example, the procedure for testing dust wipes is different from the procedure for testing 37 mm personal exposure filters. The instrument follows a unique procedure for each application. Simply choose the appropriate Thin Sample Mode from the Thin Sample Setup Menu. (See **Figure 4.01**). See the section titled "Setup Thin Sample Mode".

Note: Before testing in Thin Sample Mode, turn your NITON on at least 15 minutes prior to testing. This will give you more precise measurements.

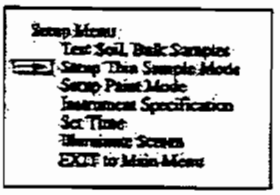


Fig. 4.01 Setup Menu, Thin Sample Mode.

The dust wipe and filter test platform

The Dust Wipe and Filter Test platform is an accessory fixture for holding 37 mm personal exposure filters, larger contamination monitoring filters, and dust wipes (**Figures 4.02, 4.03**). The test platform snaps quickly and securely to your NITON-and detaches just as quickly. It also protects personnel from exposure to radiation.

The front end of the platform is designed to facilitate testing 37 mm personal exposure filters. The test stand securely holds the filter in place in each of the three test positions required for these filters. The clamp holds the instrument.

When testing larger TSP and PM filters, remove the front end. Use the plunger shield to protect the filter from being punctured by the NITON's plunger. The velcro strap on the filter test platform holds the instrument in place and loosens easily to permit you to reposition the filter between each reading.

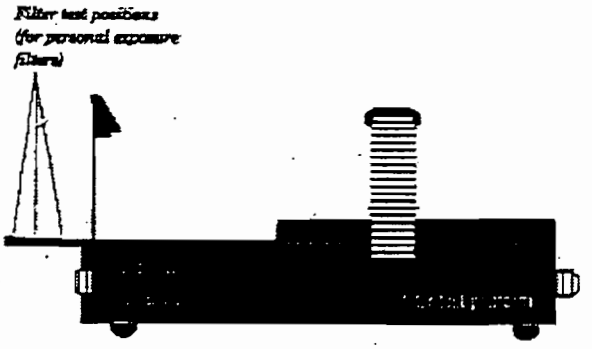


Fig. 4.04 Operation Mode
Select 37 mm CD Filters

Figure 4.02
The NITON Thin
Sample test platform.

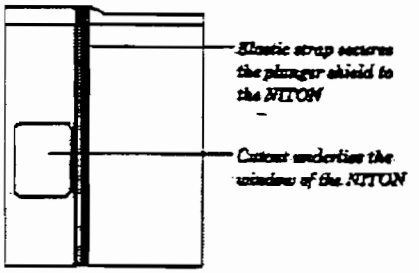


Figure 4.03
The NITON plunger
shield protects PM
and TSP filters from
puncture.

37mm CE and fiberglass filters

Before testing 37mm filters, access the **Setup Menu**, selecting **Setup Thin Sample mode**, and then select **37mm CE Filters** (**Figure 4.04**). See the following sections for details: "Setup" and "Setup Thin Sample mode".

Preparing a filter

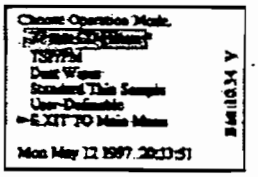


Fig. 4.04 Operation Mode
Select 37 mm CD Filters

37 mm filters are often used for monitoring personal exposure. Dust vacuum measures (DVM) use the same size filters and are tested in much the same way. To prepare the filter for testing, remove it from the air sampling cassette and load it in a filter sleeve.

The plastic air sampling cassette (**Figure 4.05**) is closed-face; an open-faced cassette would be missing the top section and plug. The filter sleeve is a piece of cardboard sandwiched between two layers of thin plastic film (**Figure 4.06**). The cardboard has a circular cutout of slightly larger cutout than the filter.

Note: To avoid contaminating the test results, wear clean surgical gloves. Take a sleeve. Peel

back the top layer of film. Set the sleeve down on a clean surface.

Remove the bottom plug from the air sampling cassette. Separate the sections of the cassette so you can reach the filter. Using tongs, poke the filter and filter pad through the plug hole to release it from its seat in the cassette. Touching only the edges of the filter and pad, gently separate one from the other with your finger. Then, using the tongs, lift the filter from the cassette and place it on the sleeve in the cutout. Close the sleeve. It doesn't matter if the sleeve wrinkles some.

Note: It is advisable to practice with several blank filter cassettes before using real samples.

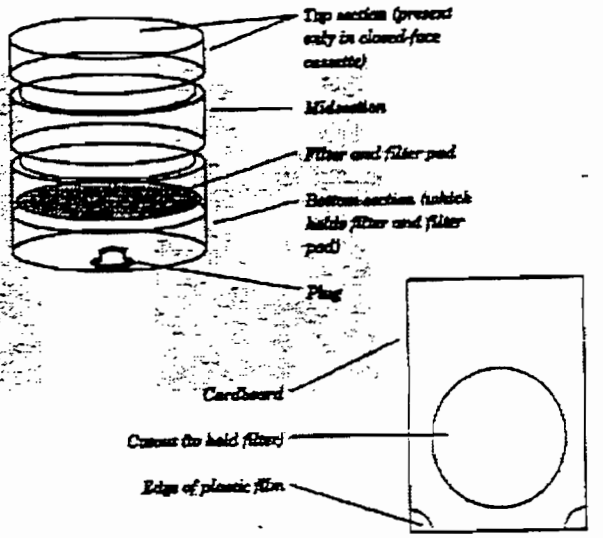


Figure 4.05 (right) An air sampling cassette.

Figure 4.06 (far right) Place the filter in the cardboard filter-sleeve for testing.

Positioning a filter

Place the sleeve on the test platform. The test platform has a built-in filter holder, designed to hold 37 mm filters securely under the test window of the instrument.

To accurately determine the concentration of elements on the filter, you must take three readings, each from a different area of the filter (**Figure 4.07**). The XL or 700Series will automatically calculate the total loading, in micrograms, when you complete the three readings. The filter holder has ridges that hold the filter in position for each of the three required readings.

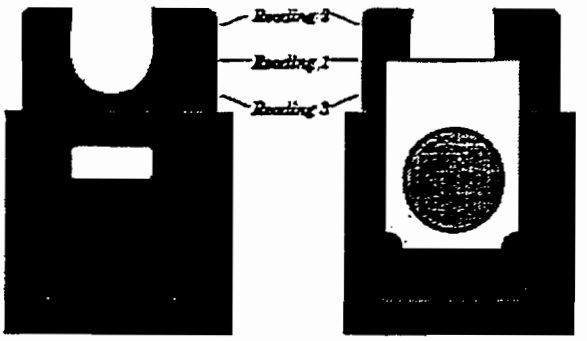
You must measure the center of the filter first (Figure 4.08). Place the filter against the middle ridge of the filter holder. This reading is multiplied by a different coefficient than either of the other reading, hence the order is important. Take the first measurement as described in the section *Taking One Reading*.

Note: The order is important: The middle-of-the-filter reading must be done first.

Next, slide the filter to the outermost ridge. Take the second measurement (the top of the filter). Finally, slide the filter to the innermost ridge. Take the third measurement. The order of these last two measurements is not important.

Figure 4.07 (left) Detailed diagram of filter test platform from above. Note three test positions.

Figure 4.08 (right) Filter-sleeve in the Middle position(the first reading) The filter is in the sleeve cutout.



Taking a reading

1. Set the test platform on a flat, solid surface.

2. Holding the NITON in your hand, place it on the test platform so that the filter is under the test window. Squeeze the shutter release, pull back the latch on the platform with your left hand, and firmly press the instrument flat against the platform surface. If you don't squeeze the shutter release, the plunger will not depress. If the plunger is not fully depressed, the window is not fully open and the NITON cannot measure accurately. The window opening must be flush with the test platform to get an accurate reading.

The test platform latch will continue to hold the NITON flush against the sample until you lift it off.

Note: During the measurement, you do not need to hold the NITON or squeeze the shutter release continuously. Your NITON will continue to test until you lift the instrument from the test platform.

3. Watch for indications of lead on the screen to decide when the test has reached the desired level of accuracy. A typical test for the quantitative measurement of lead takes 60 nominal, or source seconds. The instrument will beep at 60 nominal seconds.

4. After the desired interval, pull back on the platform latch to release the NITON and lift from the test platform to end the test. The shutter will close automatically. The plunger should be fully extended.

Warning: In the unlikely event that the plunger gets stuck in the open position, simply push it closed. Then call the NITON Service Department at (401) 294-1234.

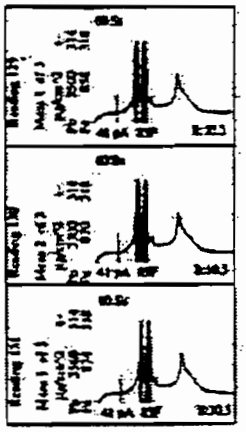
Reading the display

The Measurement screen

The Measurement screen is displayed during each test and is accessible after the test is complete. For the XL, the screen shows each of the three measurements in micrograms/cm^2 of lead (**Figures. 4.09 a-c**).

Note: On multi-element models, the initial Measurement Screen always shows lead because lead is the element most commonly measured in Thin Sample mode. The element with the next highest concentration (in micrograms/cm^2) is also shown. To see the other elements, press and hold Clear/Enter **for two seconds** (Figure 4.09 d). **Use the** Arrow buttons **to scroll through the list of results for all elements.**

The Final Result screen



The **Final Result** screen (**Figure 4.10**) is displayed only after all three measurements are complete. Final results are in units of micrograms. On 700 Series instruments, the screen shows 14 elements, whether they were detected, and how much of each element that was detected on the filter (in micrograms). The **Final Result** screen is given the next reading number.

This screen is divided into three parts. The first shows the metals detected. For the XL, only lead is listed. For the 700 Series, all of the detected elements are listed, in order of decreasing amounts. Next is a list of elements where the result was less than the calculated detection limit. The XL (for lead) and the 700 Series calculates the detection limit for every sample. Each is shown as being less than a number, representing the detection limit for that element, for that sample. The detection limit is calculated using EPA protocols, that the detection limit is three times the standard deviation. Finally, there is a list of these same undetected elements displaying for each the weighted sum and twice the standard deviation (95% confidence level) that the instrument calculated.

These three lists will not fit on the screen at one time. Use the **Arrow buttons** to scroll up or down the screen.

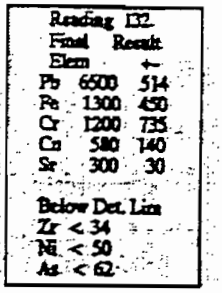


Fig. 4.10
Final Result Screen

TSP and PM Filters

These filters are often used for air monitoring. They are about 8 x 10 inches in size. The samplers are designed for uniform filter deposition. The purpose of the XRF measurement is to determine total micrograms of lead and other metals on the filters. Because the samplers are designed for uniform deposition onto the filters, two measurements are taken on these filters. The choice of two measurements resulted from original testing conducted by NITON Corporation, Galson Corporation, and the New York State Department of Transportation (NYSDOT). Because deposition on the filter is presumed uniform, the NITON averages the two readings.

Preparing to take a measurement

1. Wear clean surgical gloves

2. Remove the front end of the filter test platform (**Figure 4.11**).

3. Place the plunger guard over the NITON. The elastic strap of the plunger guard should be between the buttons and screen of the instrument.

4. Place one corner of filter over the hole in filter test stand (which corresponds to the position of the test window on the NITON). Measure about two inches in from the edge of the contamination on the filter. Take the first measurement.

5. Take one reading from one quadrant of the filter (**Figure 4.12**). Wipe the bottom of the instrument and test guard after each filter.

Note: Initial studies have shown that, after two readings, about 1 to 2% of the lead on a filter is removed from the filter and redeposited on the instrument. Hence, wipe the bottom of the instrument to avoid compromising future tests. You may want to have the wipes analyzed. Note that since the accuracy for this method (*and* for laboratory analysis) is 10-20%, the small error due to removing dust is negligible and can be ignored.

Taking a Reading

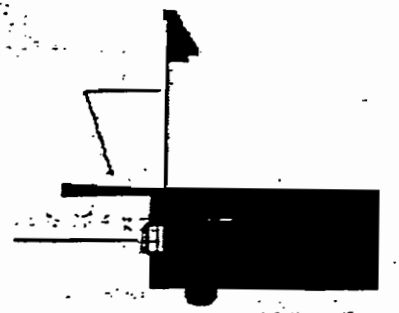


Figure 4.11
Before testing TSP or PM filters, take off the front part of the test platform by removing the two attachment screws.

See **Taking a Reading** for 37 mm filters **(Page 49)**.

Testing TSP and PM filters on the sampler

With your NITON, it is possible to test filters while they are still on the sampler (e.g., a Graseby Sampler). First, shut off the sampler. Then place the plunger guard over the NITON. The NITON (with plunger guard) will fit inside of the frame holding the filter.

Take two measurements, as described in the previous section. You will need to hold the NITON against the filter for the length of each test. The test will end when you lift the NITON from the filter. Wipe the instrument and guard after testing each filter.

The official protocol for this procedure is under evaluation by the NYSDOT.

Note: Only test for lead, zinc, and arsenic when testing filters directly on a sampler. The steel grid supporting the filters makes it impossible to measure small concentrations of other elements.

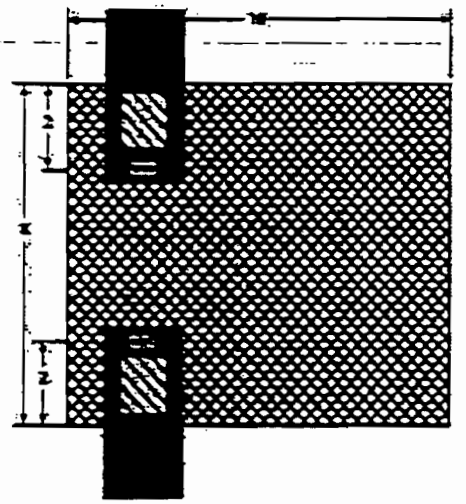


Fig. 4.12 Measurement Positions for TSP and PM Filters.

Reading the display

The Measurement screen

The Measurement screen is displayed during each test and is accessible after the test is complete. The screen shows each of the two measurements in micrograms/cm^2 of lead (**Figure 4.13 a,b**).

When the two measurements are complete, the XL or 700Series automatically averaged the results to yield the average loading in micrograms/cm^2. The average is multiplied by 404 cm^2 to yield the total lead and other metals, in micrograms. These results are displayed on the **Final Result** screen (**Figure 4.13c**).

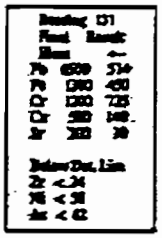
Note: Even on multi-element analyzers, lead is always displayed on the first screen. Lead is the element most commonly measured in Thin Sample mode. To display the next screen, which shows the results for other elements, press and hold Clear/Enter **for two seconds. Use the** Arrow buttons **to scroll through the list of results for all elements.**

The Final Result screen

The Final Result screen (**Figure 4.13c**) is displayed only after both measurements are complete. Final results are in units of micrograms. On 700Series instruments, the screen shows 14 elements, whether they were detected, and how much of each element that was detected on the filter (in micrograms). The Final Result screen is given the next reading number.

This screen is divided into three parts. The first shows the metals detected. For the XL-309, only lead is listed. For the 700 Series, all of the detected elements are listed, in order of decreasing amounts. Next is a list of elements where the result was less than the calculated detection limit. The XL-309 (for lead) and the 700 Series calculate the detection limit for every sample. The detection limit is calculated using EPA protocols, that the detection limit is three times the standard deviation. Finally, there is a list of these same undetected elements displaying for each the weighted sum and twice the standard deviation (95% confidence level) that the instrument calculated.

These three lists will not fit on the screen at one time. Use the **Arrow buttons** to scroll up or down the screen.



Other air-monitoring filters

Low-volume air-sampling techniques use 47 mm diameter filters. The NITON can test these as well. The filters are usually very uniform, so taking a single measurement of the center of the filter is a viable option. Use the **Standard Thin Sample mode** (**See Page 59**) for this. Results are given in micrograms/cm^2. The operator should multiply by the area of the filter to obtain results in micrograms. Sum or average several readings, or have the results automatically multiplied by using the **User-defineable Thin Sample mode** to specify a protocol that satisfies your requirements (**See Page 60**).

Dust Wipes

This section describes the testing of dust wipes. The wipe, recommended by NITON and used in the ELPAT program, is the PaceWipe. It is available from:

Pace Environs
207 Rutherglen Drive
Cary, NC 27511
(800) 361-5323

NITON is developing a procedure for measuring dust wipes that will be reviewed for regulatory approval. What is presented here works in company tests, but is nonetheless tentative pending approval. The NITON displays levels of contamination in micrograms per wipe. The wipe reflects the contamination of the area wiped. Current regulations require lead contamination below 100 micrograms/ft^2 on floors, 500 micrograms/ft^2 on window sills, and 800 micrograms/ft^2 in window wells.

Note: For the current software release (Version 5.0) the XL and 700Series provide quantitative results for lead only. You may use the 700 Series for screening of other metals on dust wipes, but element-specific correction factors must be implemented in the firmware to make non-lead measurements quantitative. Please contact NITON regarding timetables for new firmware releases that will offer this feature.

NITON assumes that the operator follows the HUD guidelines for taking a dust wipe that are summarized here. To use the wipe, measure a known area of the surface, preferably one square foot. Wear clean surgical gloves. Wipe the measured square with parallel strokes. Fold the wipe in half. Wipe in strokes 90° to the original direction. Fold the wipe in half again. Thus far, you have followed one of the HUD procedures for taking a wipe test. For more information on taking dustwipes, please refer to "Guidelines for the Evaluation and Control of Lead-Based Paint Hazards in Housing," Chapter 7.

Now, fold the wipe in half three more times (**Figure 4.14**). You now have a pad measuring about 1 x 1.5 inches (2.5 x 3.7 cm). It is important to fold the wipe neatly, so the final wipe is very nearly a neat square measuring about 1 x 1.5 inches.

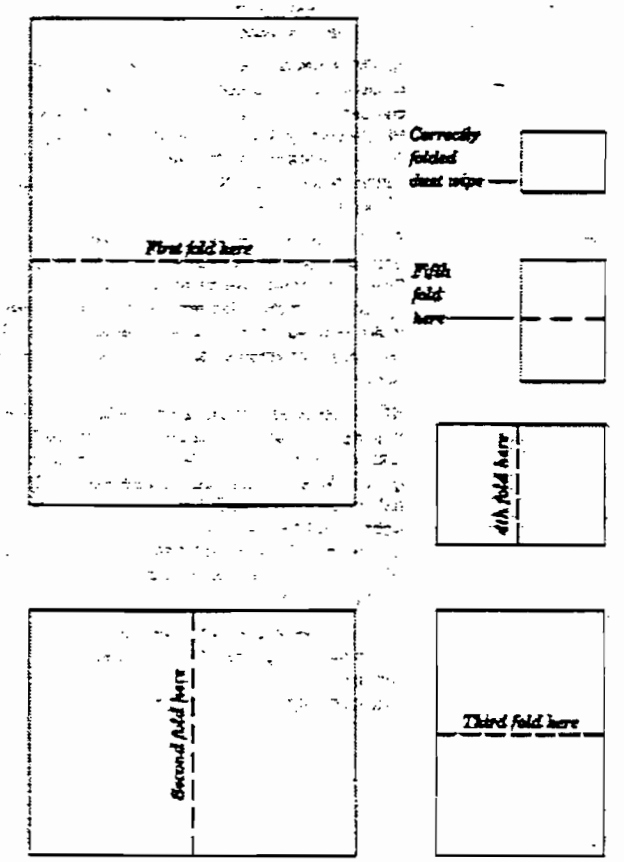


Fig 4.14
Folding the dust wipe. Start at the top left and proceed counterclockwise, making five folds.

Then put the folded wipe in one of the plastic baggies provided, and place the wipe, in the baggie, in the metal dust wipe holder (**Figure 4.15**). The dust wipe is now ready to test. NITON recommends that the plastic bags NOT be re-used, to eliminate the chance of cross-contamination of subsequent wipes.

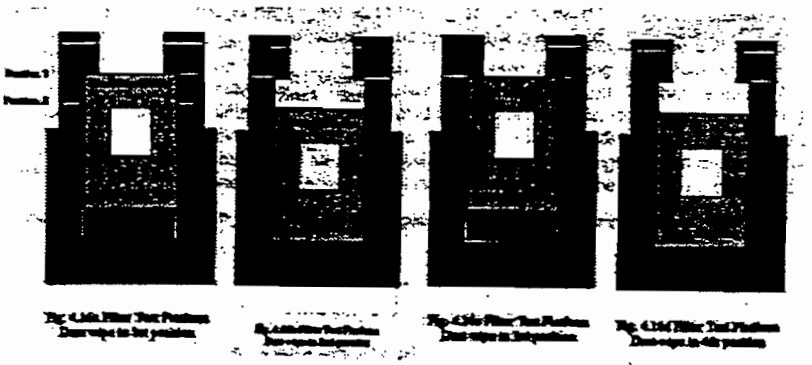
Taking dust wipe measurements

Take four measurements, positioning the metal dust wipe holder on the number one position of the test stand, then the number two position of the test stand; then rotate the dust wipe holder 180 degrees (without turning the holder over) and again test on the number one position followed by the number two position (**Figure 4.16**). This procedure assures that the entire area of the folded dust wipe is measured by the analyzer.

Taking a reading

See Taking a Reading for 37mm Filters (**See Page 49**).

Fig. 4.15 Metal dust wipe holder



Reading the display

The Measurement screen

The Measurement screen is displayed during each test and is accessible after each test is complete. For the XL, the screen shows each of the four measurements in micrograms/cm^2 of lead (**Figure 4.17a-d**). When all four measurements are complete, the NITON automatically sums the four test results to achieve the correct reading. This result is given in the **Final Result** screen (**Figure 4.17e**).

Note: Even on 700 Series instruments, only two elements are displayed on the first screen: lead and the element with the highest concentration (other than lead).

To display the next screen, which shows the results for other elements, press and hold **Clear/Enter** for two seconds. Use the **Arrow buttons** to scroll through the list of results for all elements.

The Final Result screen

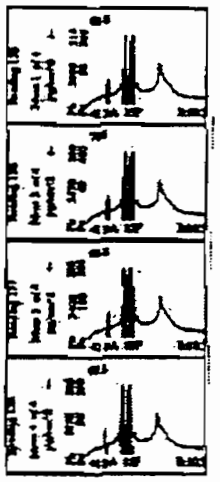


Fig. 4.17e-d
Measurement Screens
Dust Wipe Measurements

The Final Result screen (**Figure 4.17e**) is displayed only after all four measurements are complete. Final results are in units of micrograms. On 700 Series instruments, the screen shows 14 elements, whether they were detected, and how much of each element that was detected, on the filter (in micrograms). The Final Result screen is given the next reading number.

This screen is divided into three parts. The first shows the metals detected. For the XL, only lead is listed. For the 700 Series, all of the detected elements are listed, in order of decreasing amounts. Next is a list of elements where the result was less than the calculated detection limit. The XL (for lead) and the 700 Series calculates the detection limit for every sample. Each is shown as being less than a number, represneting the detection limit for that element, for that sample. The detection limit is calculated using EPA protocols, that the detection limit is three times the standard deviation. Finally, there is a list of these same undetected elements displaying for each the weighted sum and twice the standard deviation (95% confidence level) that the instrument calculated.

These three lists will not fit on the screen at one time. Use the **Arrow buttons** to scroll up or down the screen.

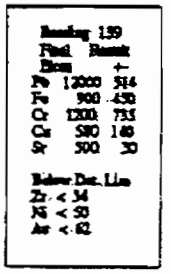


Fig. 4.17e Final Result Screen

Standard thin sample mode

The Standard Thin Sample mode should be used to test thin samples that have uniform contamination or deposition. These include many filters for liquids and gases, various types of coatings, and the leaves of plants. Operators who want to make a single measurement and obtain a result in units of micrograms/cm^2 should use Standard Thin Sample mode.

Caution: The Standard Thin Sample Mode should not be used for quantitative lead-paint testing. Use only the three Paint Testing modes to test lead-based paint.

In the Standard Thin Sample mode, each measurement is a separate test. For this reason, there is no **Final Result** screen in this mode. The results of each test are given in micrograms/cm^2 for lead only (XL) or for up to 14 elements (700Series).

Note: Using Standard Thin Sample Mode to test any coating may yield lower-than-actual test results.

Standard Thin Sample Mode does not correct for shielding caused by the presence of overlaying coatings. Thus, for coatings testing, the results should be viewed as the *minimum* amount of contaminants present. If an element is not detected, it may be that the element is present but entirely shielded by overlaying coatings. Beware. Do not rely on negative results when testing paints and other coatings in this mode.

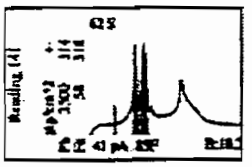


Fig. 4.18 Measurement Screen Standard Thin Sample Mode

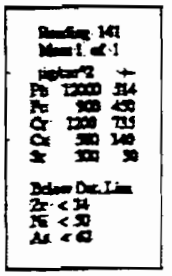


Fig. 4.19 Final Result Screen Standard Thin Sample Mode

The Measurement screen

The Measurement screen is displayed during each test and is accessible after each test is complete. For the XL, the screen shows the measurements in micrograms/cm^2 of lead (**Figure 4.18**). For the 700 Series the screen displays lead and the element with the highest concentration other than lead, in micrograms/cm^2. When the measurement is concluded, the display is changed to show all the elements, in micrograms/cm^2 (**Figure 4.19**). Use the **Arrow buttons** to scroll through the list of elements.

This screen is divided into three parts. The first shows the metals detected. For the XL, only lead is listed. For the 700 Series, all of the detected elements are listed, in order of decreasing amounts.

Next is a list of elements where the result was less than the calculated detection limit. The XL (for lead) and the 700 Series calculates the detection limit for every sample. Each is shown as being less than a number, representing the detection limit for that element, for that sample. The detection limit is calculated using EPA protocols, that the detection limit is three times the standard deviation. Finally, there is a list of these same undetected elements displaying for each the weighted sum and twice the standard deviation (95% confidence level) that the instrument calculated.

Note: In Standard Thin Sample mode all results are in units of micrograms/cm^2.

User-definable thin sample testing

User-definable Thin Sample mode allows you to set up your own protocol for testing thin samples. The user defines the number of measurements that constitute a set, the coefficient applied to each, and whether the measurements are to be summed or averaged.

Specifying a Protocol

You specify your own measurement protocol in this mode. When you select **User-Definable** from the **Setup Thin Sample Mode menu**, the screen (**Figure 4.20a**) is displayed. The menu allows you to customize an application. You can average or sum your choice of up to 9 of readings.

In most custom applications, where deposits on a thin sample are not uniformly spread across the sample, readings should be averaged or summed. Using this screen's menu, you can customize how readings are summed or averaged for a particular application.

Note: Whatever configuration you enter will be saved in the instrument's memory. When you select the User-Definable mode, the last configuration entered will be recalled.

To Define a Protocol:

* **Avg or Sum**: Use the **Arrow buttons** to select either **Avg** or **Sum**. Press **Clear/Enter**. Your choice will be shaded. If **Avg** is chosen, your NITON will average the number of readings you have specified. If **Sum** is chosen, readings will be summed instead of averaged. (Refer to **Figure 4.20a.**)

* **# readings:** To tell the instrument how many readings to use when calculating an average or sum: Use the **Arrow buttons** to increase or decrease the number of readings you wish to average or sum. Press **Clear/Enter**. The number must be between 1 and 9. (Refer to **Figure 4.20b.**)

* **Range:** This allows the operator to set the numeric range of the coefficents, from 0.0001 to 9999. The same range must be used for all coefficients. First, set the decimal place by using the **Arrow buttons**. The decimal place determines the range of possible values for the coefficients. When the decimal place is set press **Clear/Enter.** (Refer to **Figure 4.20c.**)

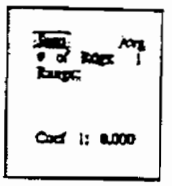


Fig. 4.20a This Sample User Defined Screen

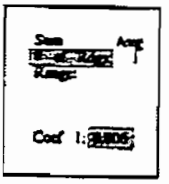


Fig. 4.20b This Sample Set # of Readings

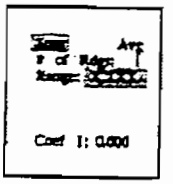


Fig. 4.20c This Sample Setting Range

* **Coefficients:** (Refer to **Figure 4.20d**). Enter each coefficient. Moving from left to right, set the value of each digit that constitutes the coefficient. First use the **Arrow buttons** to set the value, then press **Clear/Enter** to move to the next digit to the right. To move to the next digit without changing the current digit, press **Clear/Enter**. Repeat this process until every digit of the coefficient has been set. After every digit has been set, press **Clear/Enter** to move to the next coefficient. When finished with the last coefficient, press **Clear/Enter** to return to the **Main Menu**. By setting coefficients, you can calculate a *weighted sum*, in which the result of each reading is multiplied by the coefficient entered for that reading. For a simple (un-weighted) sum, set each coefficient to 1.0. All unused coefficients should be set to 0.0 (0.0 is the **default** setting).

From the **Main Menu**, enter **Calibrate and Test**. When the NITON is finished self-calibrating, you may begin testing.

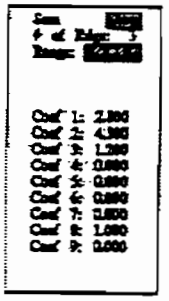


Fig. 4.20d This Sample User Defined

Example:

Suppose you would like to perform a weighted sum of three consecutive measurements, using the formula:

(2.800 x Measurement 1) + (4.5 x Measurement 2) + (1.2 x Measurement 3)

The screen for setting up the protocol should appear as follows:

Sum

# of Rdgs = 3

Range: X.XXX

Coef 1: 2.800

Coef 2: 4.500

Coef 3: 1.200

Note: In User-Definable Thin Sample mode, you must take exactly the number of readings that you have specified for each test in this mode before proceeding to the next test.

When you conclude each measurement within the protocol, the analyzer will display the results, in micrograms/cm^2 (**Figure 4.09a**). When the protocol is complete, the analyzer will display a **Final Result** screen (**Figure 4.09d**).

Note: The units of measurement will be determined by the coefficients you have chosen. In "User-Definable" Mode, the units are not necessarily micrograms.

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NITON Corporation

XL-309

&

*700*series

User's Guide Version 5.0 (HTML) Chapter 5

Chapter 5: Analyzing lead paint

Overview

Lead paint mode is standard on NITON XL-309, 701-A, 702-A and 703-A Spectrum Analyzers. In addition to the silicon PIN-diode detector standard in all NITON analyzers, all NITON analyzers equipped to test lead in paint have a second detector: a cadmium-zinc-teluride (CdZnTe) detector optimized to measure lead K-shell x-ray fluorescence.

Caution: The Standard Thin Sample Mode (on 701, 701-A, 703 and 703-A analyzers, and available as an option on XL-309s) should not be used for quantitative lead-paint testing. Use only the three Paint Testing Modes (on 701-A, 702-A, 703-A, and XL-309 analyzers) to test lead-based paint.

Getting started

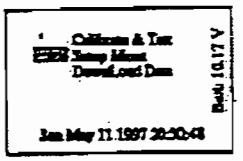


Fig. 5.01 Main Menu Setup Menu

1. Turn on your NITON Analyzer

2. Use the **Arrow buttons** to select

Setup menu

from the **Main menu**. Press **Clear/Enter** (**Figure 5.01**).

3. Use the **Arrow buttons** to select

Setup Paint mode

from the **Setup menu**. Press **Clear/Enter** (**Figure 5.02**).

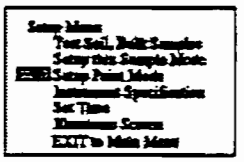


Fig. 5.02 Setup Menu Setup Paint Mode

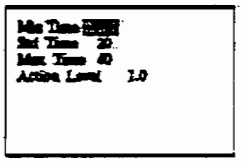


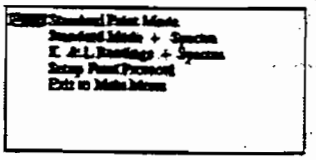
Fig. 5.03 Paint Protocol Screen

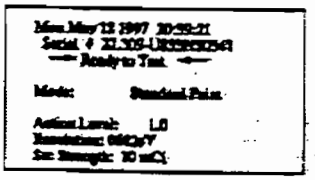
4. Go to *step 5* unless you want to change the **Action-level** or ***beep* time** settings. If they are not changed, the NITON will default to the last settings entered. To change settings, enter **Setup Paint Protocol** from the **Setup Paint screen**. The **Setup Paint Protocol screen** allows you to set the **Action-level** and ***beep* times** (**Figure 5.03**). When you have set the paint protocol, the instrument will return automatically to the **Setup Paint** screen.

5. From the **Setup Paint** screen (**Figure 5.04**), select one of the three paint testing modes: **Standard Paint Mode, Standard Mode + Spectra** or **K & L Readings + Spectra**. When you have selected a paint testing mode, the instrument will return automatically to the **Main Menu**.

6. Select **Calibrate and Test**. The instrument will then initiate its auto-calibration sequence. This will take one to two minutes. When calibration is complete, the instrument will beep and display the **Ready to Test** screen for whichever of the three paint modes you selected in *Step 5* (**Figure 5.05**). The **Ready to Test** screen displays the paint testing mode you have selected, the date and time, the instrument serial number, the action-level, the instrument energy resolution and the current source strength.

Caution: Check the *Date* and *Time* displayed on the Ready to Test screen. If they are not correct, reset them before taking any measurements. Your readings will not be accurate unless the date and time are correct.

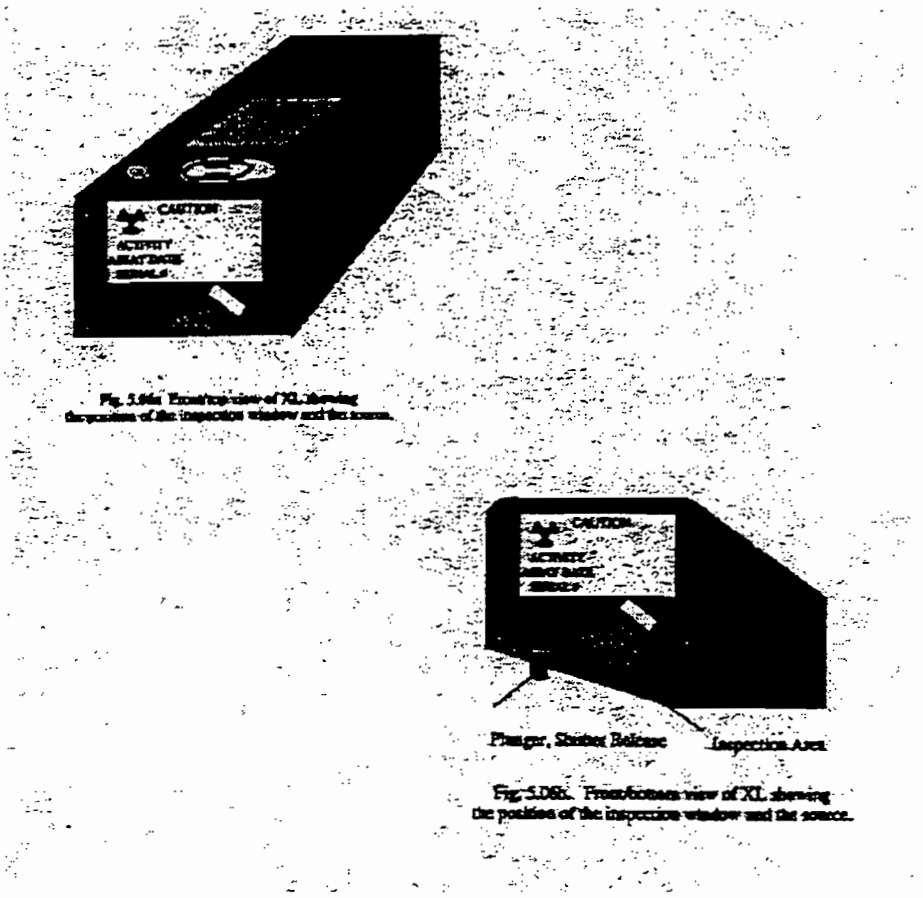




Taking a measurement

Warning: Always treat radiation with respect. Do not put your hand on the end plate of the NITON while measuring. Never point the NITON at yourself or anyone else when the shutter is open.

Caution: When testing the *exterior* of the window sash from the inside of a room, avoid standing in the path of the NITON's radiation beam. The direction of the beam is drawn on the cover of the instrument (Figure 5.06 a,b). It is easier to avoid the radiation beam if you hold the instrument in your right-hand.



How to take a measurement

1. Push the safety slide (that locks the shutter release) out from under the shutter release. When the slide is in place, you cannot press in the release (**Figure 5.07**).

2. **When you are using the Barcode Data Entry System:** Attach the light pen bar-code reader and wrist-mounted bar codes. Flick the **Barcode Reader** across one of the bar codes to display the **Data Entry screen** (**Figure 5.08**). Enter the test location and other test information with the **Barcode Reader.**

3. Place the NITON on the painted surface, squeeze the shutter release, and press the NITON against the surface.

Note: The shutter-release trigger must be activated and the window at the back of the instrument must be flush against the surface for instrument to take reliable readings. The instrument must be held against the surface throughout each measurement. You do not need to hold the shutter release continuously.

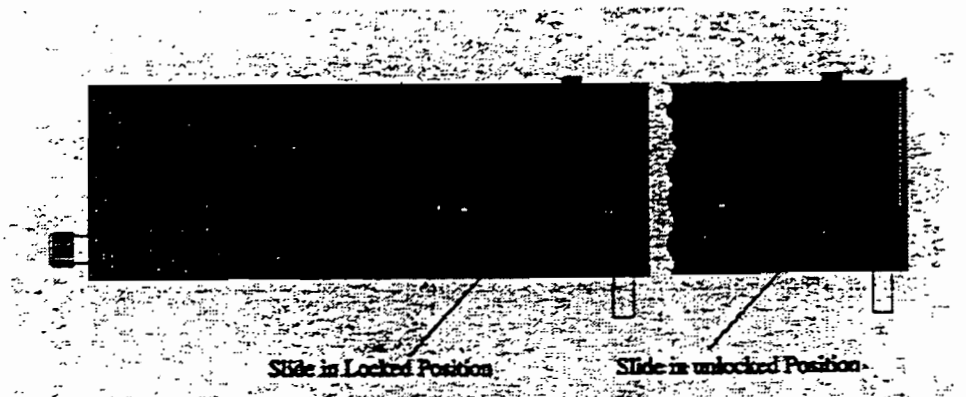


Fig. 5.07 Slide lock shown in locked position (left) and unlocked position (right).

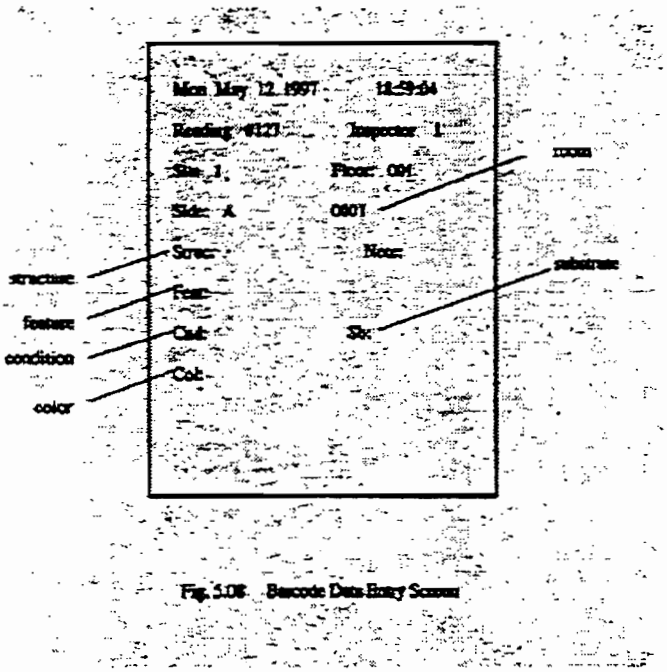
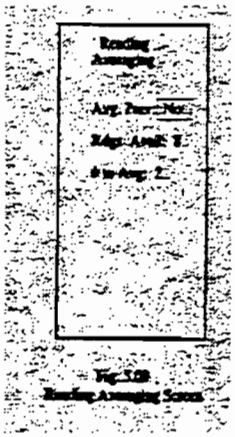


Fig. 5.08 Barcode Data Entry Screen

4. Please refer to **Reading the display** (see Page 69) for screen descriptions in each paint mode.

5. When the test is finished, lift the NITON from the surface. The shutter will close automatically.

Warning: In the unlikely event that the plunger gets stuck in the open position, simply push it closed. Then call the NITON Service Department at (401) 294-1234.



6. Your NITON Analyzer can average up to 100 readings at a time. To set up the **Averaging Screen,** hold down the **Clear/Enter** button to toggle through the testing and data entry screens to the **Reading Averaging** screen (**Figure 5.09**). If you select **Yes** to average readings, you will be prompted to select the number of readings you wish to average. To take additional readings, simply repeat steps 3 through 5. Your NITON will display both the average of the current and previous readings and the number of readings being averaged.

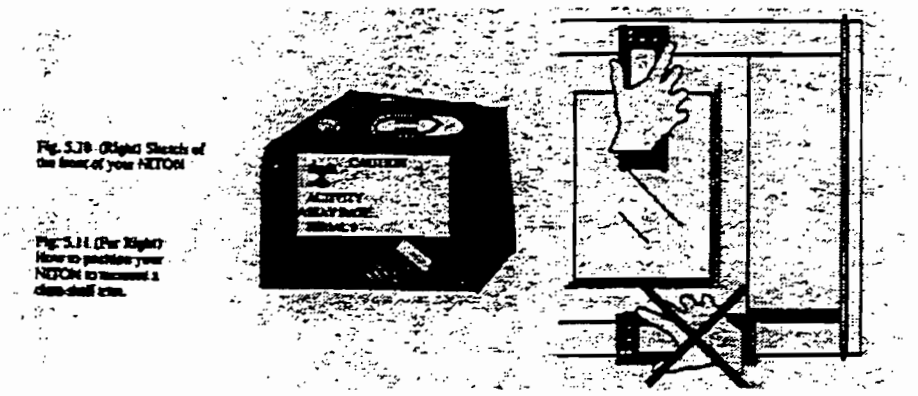
Using the NITON on flat and curved surfaces

Using your NITON, you can take measurements of any surface a child can mouth; only $^{5}\acute{U}8$ inch (1.6 cm) is required.

1. A sketch of the window is printed on the front of the NITON's case so you can position the instrument properly (**Figure 5.10**) The window of the instrument must be flat against the paint surface or it cannot read properly.

3. Your NITON Analyzer can measure accurately many curved surfaces. Position the instrument so that its window is flat on the surface. The rest of the instrument doesn't have to lie flat. E.g., on slightly rounded clam shell trim, turn the NITON at right angles to the trim so that its window runs parallel with the length of the trim (**Figure 5.11**). On a cast iron radiator, find a spot againt which the NITON's window can lie flat.

Note: On *very* highly curved surfaces (such as quarter-round moldings or balusters) the NITON will tend to underestimate the amount of lead present. On very highly curved surfaces, your NITON can only be used to positively identify high concentrations of lead.



How long is a Test

In any of the three paint testing modes, your NITON can measure paint samples in as little as one second; most readings take less than ten seconds. The testing time will depend primarily on the amount of lead in the sample that you are testing compared to the action level you have set. The closer the actual lead concentration in the sample is to the action level, the longer it will take the NITON do make a 95% confident "Positive" or "Negative" determination.

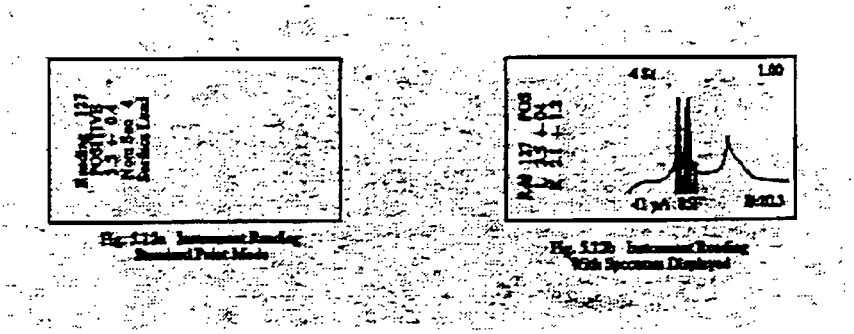
In **Standard Paint Mode** and **Standard Paint Mode + Spectra**, the instrument will measure the paint sample only until a 95% confident reading of "Positive" (greater-than-or-equal-to) or "Negative" (less-than) versus the action-level you have set has been attained. In **K & L Mode + Spectra**, the instrument will also display a "Positive" or "Negative" result and will beep as soon as a 95% confident reading is attained. You then have the option to continue readings until you have achieved a given reading time or degree of precision.

Note: For all paint testing modes, if you terminate a test *before* a "Positive" or "Negative" determination is attained by the instrument, it will display a "Null" test result.

Reading the display

In **Standard Paint mode**, the instrument displays **Please Wait** until a 95% confident reading is achieved. If there is lead in the sample, the instrument will indicate **Lead present** on the **Please Wait** screen.

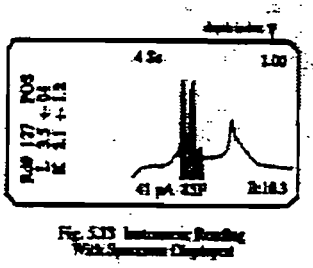
When a 95% confident reading is achieved, the instrument will display the reading number; either a "Positive" or "Negative" reading; the result in mg/cm^2; the reading time in nominal (source) seconds; and will display **Surface lead** for all positive readings where the lead is not shielded by layers of non-leaded paint (**Figures 5.12 a,b**).

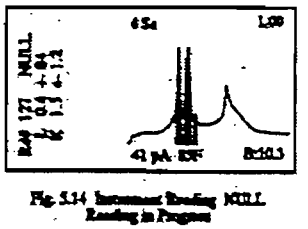


Standard Mode + Spectra is identical to Standard Mode except that the x-ray spectra is displayed with each reading.

In **K & L Mode + Spectra**, the instrument displays the following information, updated continously during each reading: the **reading number**, the **nominal seconds**, the **L-shell reading** (displayed as L) with the two-sigma confidence interval, the **K-shell reading** (displayed as K) with the two-sigma confidence interval, the **combined reading** (displayed as **Pb**) with the two-sigma confidence interval, the **full x-ray spectrum**, and the **Depth Index** (**Figure 5.13**).

Note: During each reading in K & L + Spectra mode, *before* a 95% confident Positive or Negative determination has been made, the instrument displays a "Null" test result (Figure 5.14). **When a 95% confident determination has been made, the instrument beeps, and the reading classification switches from** Null **to either** Positive or Negative.





The Depth Index (K & L + Spectra mode)

The **Depth Index** (DI) is a numerical indication of the amount of non-leaded paint covering the lead detected by the instrument. The position of the DI on the screen is indicated by an arrow painted on the front of the NITON (**Figure 5.13**). A DI less than 1.5 indicates lead very near the surface layer of paint. A DI between 1.5 and 4.0 indicates moderately covered lead. A DI greater than 4 indicates deeply buried lead.

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Chapter 6: Radiation Safety

NITON has designed its XRF analyzers so that there is virtually no measurable radiation external to any part of the instrument when the shutter is closed. When our instruments are used according to instructions, there is minimal radiation exposure even with the shutter open. NITON XRFs contain sealed cadmium$_{109}$ radioactive sources. The source is designed to remain secure even under extreme conditions, so that even if the instrument is broken, crushed or burned, there will be no leakage of radioactive material.

During manufacturing, each sealed source is placed in a solid metal source holder. A plug is screwed into the access hole and secured with a set screw and Locktite. The source is completely secure in its housing beacause the aperture at the other end of the housing is smaller than the source. The small aperture is sealed with a beryllium metal window that is transparent to the cadmium x-rays and gamma-rays. The source assembly is secured in the NITON's aluminum case. The case has tamper

proof screws.

The following table lists typical radiation doses encountered in everyday living and lists the annual occupational radiation dosage limits for adults set forth in NITON's Materials license from the Rhode Island Radiation Control Agency, Section A.2.3.

Minimum detectable dose on a standard film badge

- Typical Radiation Doses in mR (NCRP, 1987)

• Average total dose in US. (annual)	• 360 mR
• Average worker exposure (annual)	• 210 mR
• Average exposure for underground miner (annual)	• 400 mR
• Exposure for airline crew (1,000 hours at 35,000 ft)	• 500 mR
• Additional from living in Denver at 5300' (annual)	• 25 mR
• Additional from 4 pCi/l radon in home (annual)	• 1,000 mR
• Typical chest x-ray	• 6 mR
• Typical head or neck x-ray	• 20 mR
• Typical pelvis/hip x-ray	• 65 mR
• Typical lumbar spine x-ray	• 130 mR
• Typical upper G.I. x-ray	• 245 mR
• Typical barium enema x-ray	• 405 mR
• Typical CAT scan	• 101 mR
• 5 mR	

- Annual occupational dosage limits:

• Maximum allowable for the general public (annual)	• 500 mR
• Annual Occupational Dose Limits for Adults:	
• The lesser of (1) total effective radiation dose	• 5 ,000 mR
• or the (2) sum of the deep dose equivalent plus the committed dose equivalent to any individual organ or tissue *other* than the lens of the eye	• 50,000 mR.
• For a pregnant worker or a minor	• 500 mR.
• Eye dose equivalent	• 15,000 mR.
• Shallow dose equivalent to the skin or any extremity	• 50,000 mR.

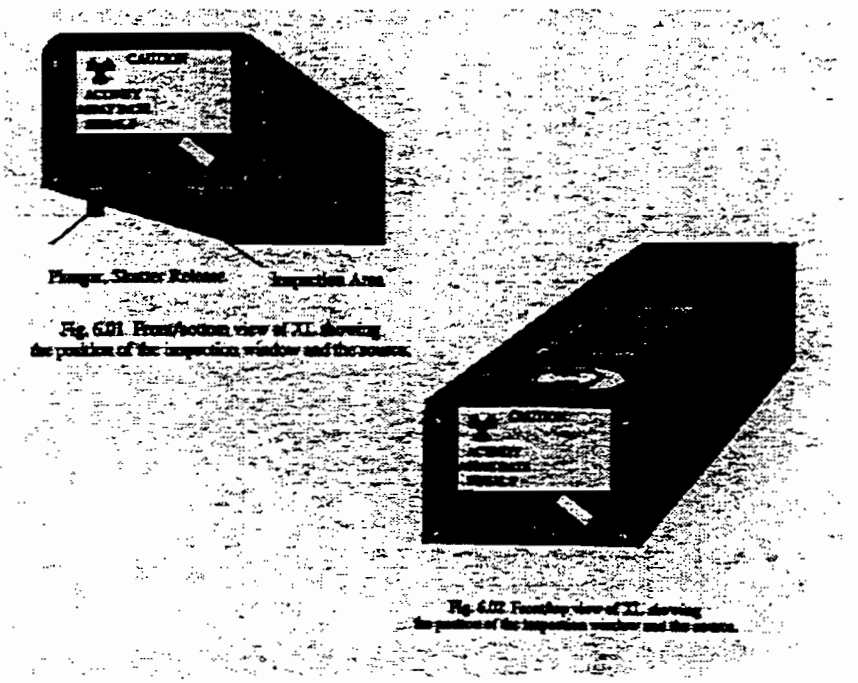
How to use your NITON safely

Each NITON is designed to be safe as possible. However, we strongly recommend that you follow these precautions to insure your safety and the safety of those around you:

- Always be aware of the location of your instrument's radioactive source and the direction of its beam of x-rays. The location of the source and the direction of its beam are both clearly marked on the front (**Figure 6.01**) and top side (**Figure 6.02**) of your NITON.

- Open the shutter *only* to do a test.

During testing, a strong beam of radiation (gamma-rays and x-rays) is continuously emitted through the beryllium window at the bottom of the NITON. There will be some radiation at the front and top-front of the instrument. There is negligible radiation where your hand should be holding the instrument.



Warning: Always treat radiation with respect. Do not put your hand on the end plate of the NITON while measuring (Figure 6.03)**. Never point the NITON at yourself or anyone else when the shutter is open.**

Caution: When testing the *exterior* of the window from the inside of a room, avoid standing in the path of the NITON's radiation beam. The direction of the beam is drawn on the cover of the instrument (Figure 6.03). It is easier to avoid the radiation beam if you hold the instrument in your right hand.

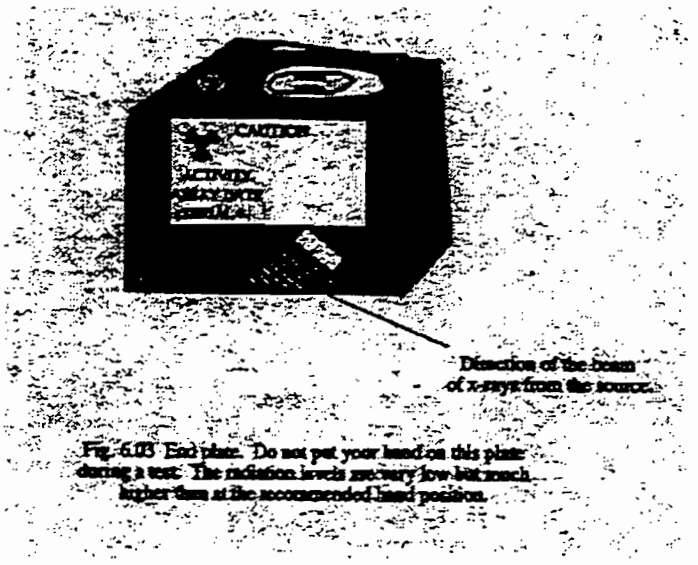


Fig. 6.03 End plate. Do not put your hand on this plate during a test. The radiation levels are very low but much higher than at the recommended hand position.

Shutter safety

Your NITON is designed so you cannot accidently open the shutter or leave it open accidentally when you lift the instrument from a surface.

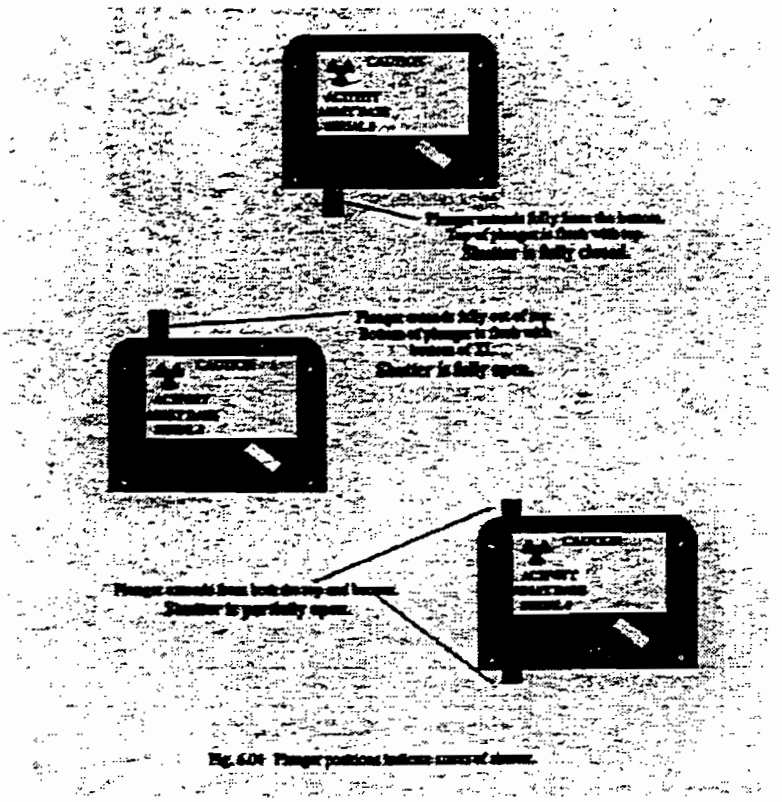
To open the NITON's shutter and to keep it open, the instrument must be held against a surface. The shutter will close as soon as you cease to hold your NITON against a surface.

1. The shutter should be open only during a test.

2.Under no circumstances should the shutter be open when the instrument is not in use.

3. Your NITON clearly indicates any time the shutter is open (**Figure 6.04**). The plunger will stick up through the instrument case whenever the shutter is open.

Warning: In the unlikely event that the plunger gets stuck in the open position, simply push it closed. Then call the NITON Service Department at (401) 294-1234.



Monitoring your radiation exposure

There is virtually no measurable radiation from a NITON when its shutter is closed. The maximum dosage to which you are exposed when properly operating your NITON is 0.1 mR/hr on the fingers of the hand holding the instrument with the shutter open.

As an additional precaution to insure that your radiation exposure is always minimal, NITON strongly recommends that you wear a dosimeter at all times when using the instrument.

Note: Your state may have regulations concerning radiation monitoring.

A dosimeter badge is usually worn close to the parts of your body that are most sensitive to radiation, such as your reproductive organs and your eyes. These badges are available from many companies. One company selling dosimeters is:

Landauer, Inc.
2 Science Road
Glenwood, IL 60425-9979.

Each month, your radiation badge company will send you a new badge.

Warning: Wearing a dosimeter badge does not protect you against current exposure. A dosimeter badge measures your exposure after the fact. If, at any time, you find measurable exposure, call NITON immediately at (401) 294-1234.

The principles of radiation safety

Your exposure to radiation is related to three factors: time, distance, and shielding. Human exposure to radiation is typically measured in rems, or in one-thousandths of a rem, called millirems (mR).

As noted previously in this chapter, the allowable limit in the US. for occupational exposure is 5,000 mR/year for a whole-body and 50,000 mR for shallow penetration of extremities. Exposure from a properly-used NITON will be less than 50 mR per year, even if the instrument is used 2,000 hours per year.

Warning: Pregnant female workers may want to take special precautions to reduce their exposure to radiation. Qualified scientists have recommended that the radiation dose to pregant women should not exceed 500 mR/year because of possible risk to the fetus.

For a given source of radiation three factors will determine the radiation dosage you receive from the source:

Duration of Exposure

The longer you are exposed to a source of radiation the more radiation strikes your body and the greater the dose you receive. Dosage increases in direct proportion to the length of exposure.

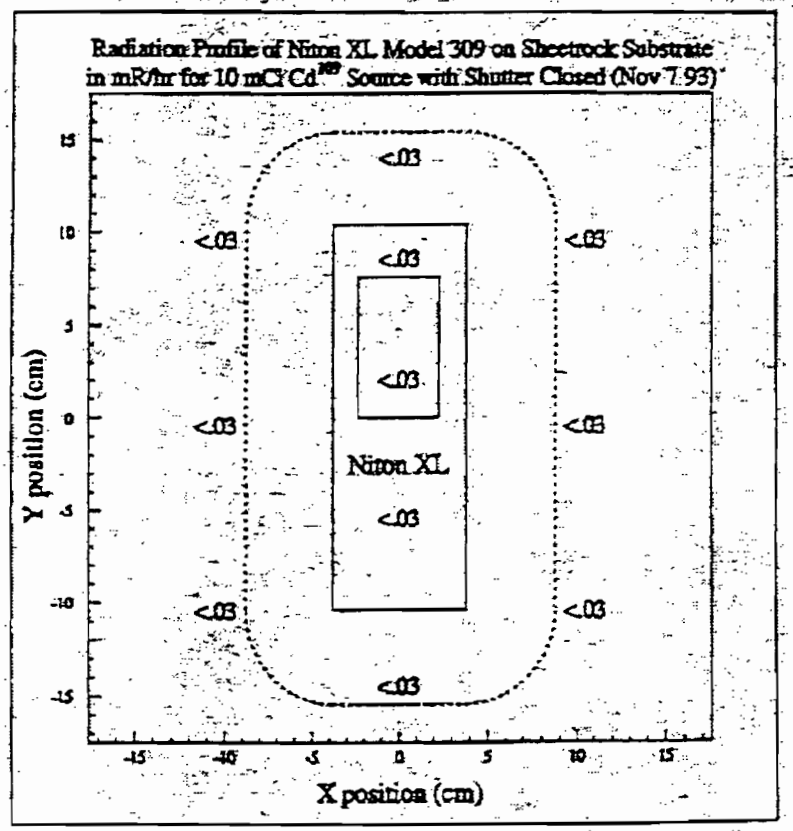
Distance from the source

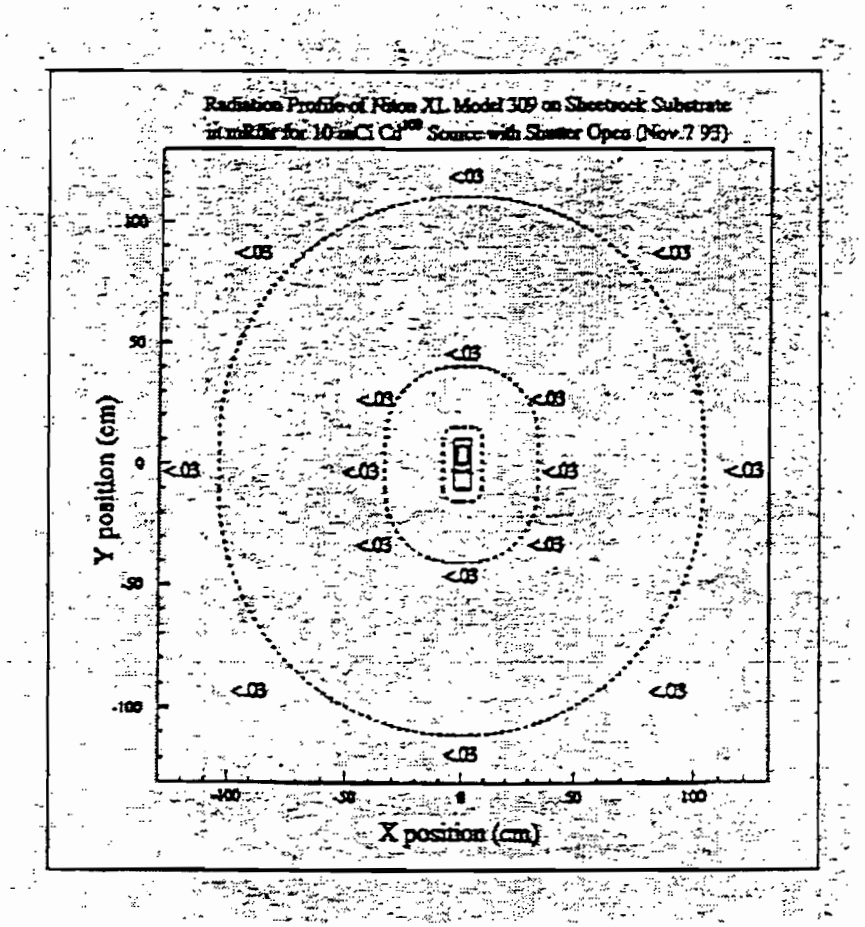
The closer you are to a source of radiation, the more radiation strikes you. The dosage increases in inverse-squared relation to the distance from the source. For example, the radiation dose one inch from a source is *nine* times greater than the dose three inches from the source, and *144* times greater than the dose one foot from the source. Keep your hand away from the source-end of your NITON when the shutter is open to minimize your exposure.

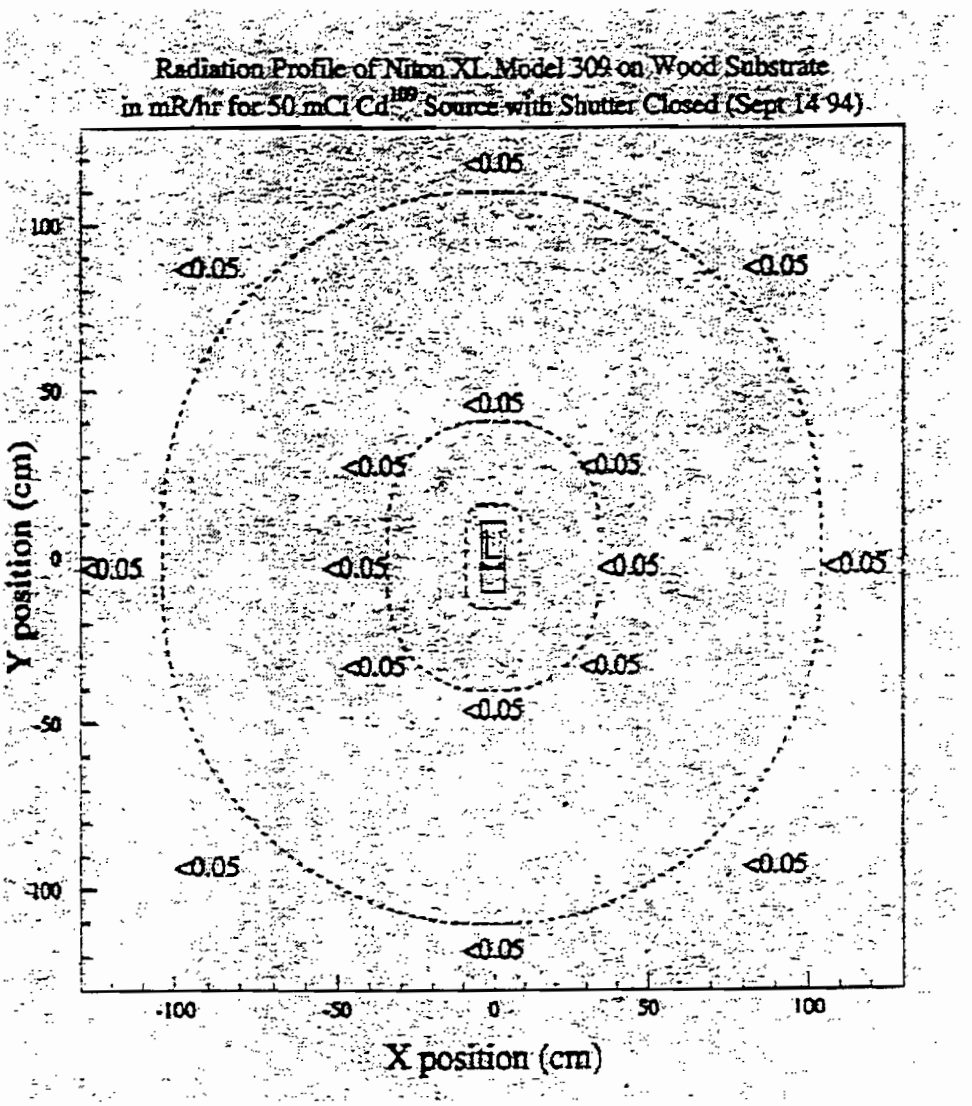
Shielding

Every NITON XRF emits virtually no radiation with the shutter closed because the cadmium$_{109}$ source is thoroughly shielded in every direction. This shielding absorbs nearly all of the radiation produced by the source - except when the shutter is open during testing. With the shutter open, the instrument emits a directed radiation beam of about one mR/hr intensity; the direction is clearly indicated by the diagram on the front of the NITON. Always hold your NITON so as to avoid the radiation beam.

Instrument radiation profiles




Radiation Profile of Niton XL Model 309 on Sheetrock Substrate
Y position (cm)
X position (cm)
<.03



Instrument radiation profiles

Wipe testing

The shielding on your NITON is designed to hold up even under extreme conditions, including the instrument's being crushed or burned. The continued effectiveness of the instrument's radiation shielding should be tested every six months with a thorough leak test of the instrument (**Figure 6.05**).

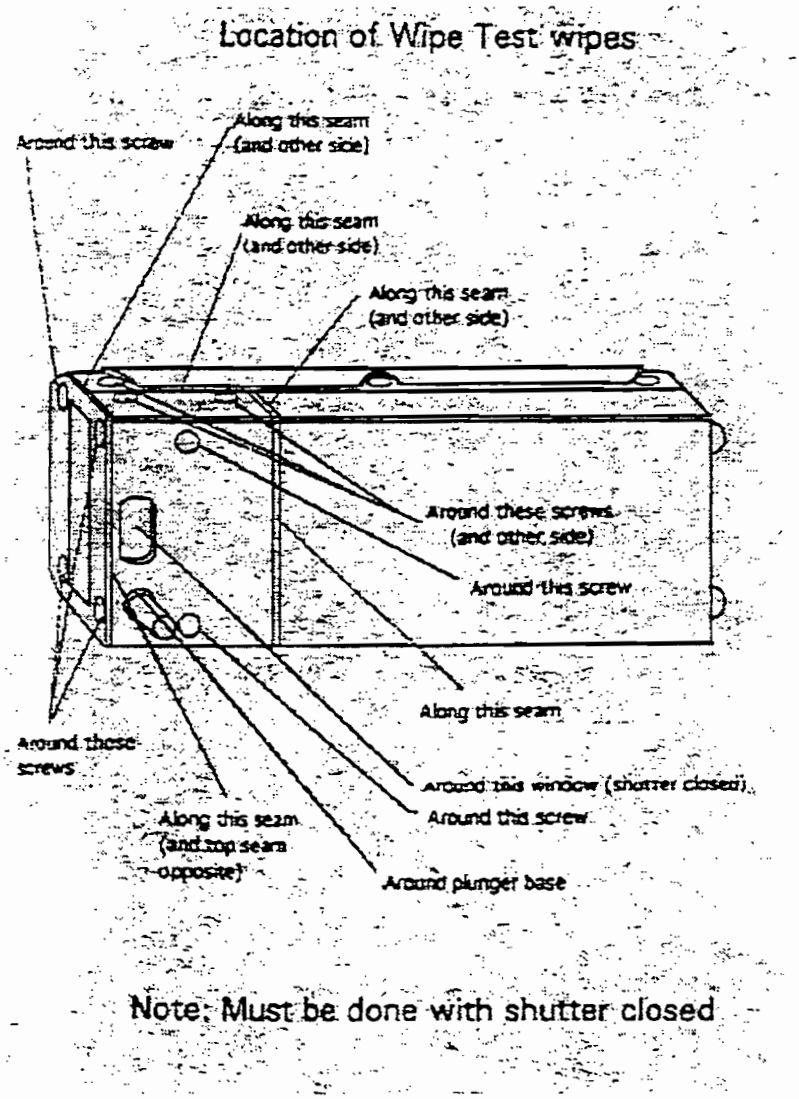
NITON's license requires that leak tests be done every 6 months. Leak test kits, with full instructions, are available from several vendors. These vendors will remind you when it's time to do another semi-annual leak test on your NITON. Please follow the accompanying instructions and promptly mail the test sample to the laboratory. The following are just a few of the labs that offer leak tests:

Applied Health Physics
2986 Industrial Blvd.

Bethel Park, PA 15102
Tel: (412) 835-9555

Stan A. Huber Consultants
200 N. Cedar Road
New Lennox, IL 60451
Tel: (800) 383-0468

Valley Safety Services
330 Old Enfield Road
Belchertown, MA 01007
Tel: (413) 323-9571



If your NITON is damaged, destroyed, lost or stolen:

Immediately

- Notify the Office of Radiological Safety in your state Dept. of Health.

Telephone: _____

- **Notify NITON Corp's Radiation Safety Officer, Dr. Don Sackett.**

During regular business hours: (800) 875-1578

Evenings and weekends: (617) 275-1424

- If your NITON is lost or stolen, or damaged in a car accident:

Also immediately notify your state police.

Telephone: _____

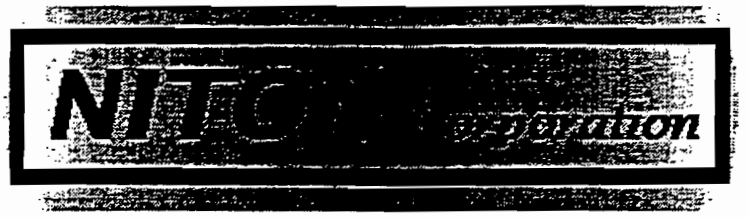
- If your NITON is damaged in a fire or an explosion:

Also immediately notify your local fire department.

Telephone: _____

Please fill in the phone numbers on this page today. Keep copies where you can find them in case of an emergency.

Back to the Table of Contents



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Chapter 7: Additional Information

Multi-element analysis (700 Series only)

Overview

700 Series analyzers can quantify concentrations of many elements. The normally displayed elements are: arsenic, barium, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, rubidium, strontium, zinc and zirconium. The best detection limits are for molybdenum, rubidium, strontium and zirconium, as well as niobium and yttrium, which are not ordinarily displayed. 700's also have excellent detection limits for lead and mercury, as well as for gold, tungsten and uranium, which are not ordinarily displayed. 700's detect barium, chromium, cobalt, iron, manganese, and nickel with somewhat less sensitivity; the same applies to calcium, scandium,

titanium, and vanadium, which are not ordinarily displayed. Finally, 700's detect arsenic, copper and zinc, but there are sometimes problems associated with the measurement of these elements due to cross-element interference. In particular, when zinc and copper are both present in a sample, the element with the higher concentration of the two can be measured more accurately.

Cross-Element Interference

700 Series users should be aware that interference between elements can reduce the sensitivity of the 700 to certain elements in certain situations. Interference occurs when the spectra of two or more elements partially or totally overlap (that is, the elements have nearly identical x-ray flourescent energies).

Note:

All NITON analyzers correct automatically for cross-element interference in all modes. These corrections are performed automatically and continuously, throughout each test.

NITON instruments correct for these cross-element interferences in all modes. In some instances, however, these corrections will worsen the detection limits and precision of the instrument in **Bulk Sample** and **Thin Sample** modes. For example, in the presence of high concentrations of zinc (>10,000 ppm), the 700 Series analyzer will be unable to detect slight trace concentrations of copper that would be detected if a large amount of zinc was not present. Another example: Very high concentrations of iron (>30,000 ppm) may produce false-positive readings for very small concentrations of manganese and/or cobalt.

Tips for better testing

Define Data Quality Objectives (DQOs)

Before implementing a sampling and analysis program, consider the data quality objectives (DQOs) for the particular site and job. For what purpose is the data being collected? What types of decisions will be made as a result of the data? What are the action-levels for the analytes you are testing at the site? What is known about the extent and distribution of the contaminant? What are the implications of possible mis-classification of samples?

The answers will help to determine the precision and accuracy you need to attain for different phases of the program. These in turn will help you to determine sample-collection procedures, sample preparation methods, sample measurement times, and your requirements for quality assurance and laboratory support.

Standard Operating Procedures

To obtain good test data in your study, it is essential to develop a written Standard Operating Procedure for sampling, measuring, and reporting data. A systematic procedure will help you to produce data of uniform quality. Typically, the Standard Operating Procedure is a written document that details the steps to be taken in handling the samples, standards, equipment, and data, including quality assurance measures, such as calibration checks and laboratory confirmation.

Warm up and calibration checks

All Niton analyzers should be turned on at least 15 minutes prior to testing in **Thin Sample** or **Bulk Sample** modes. This procedure is not necessary in any of the paint testing modes.

Note: Your instrument should be calibrated before and after testing and at least once per hour during testing.

Check your instrument by testing **Standard Samples** of known concentration every time you calibrate. Check both a low-level standard (or "blank"),and a high-level standard, (or "spike") of known concentration. Tests of **Standard Samples** should be recorded and kept with the sample test data.

Compare samples with and without preparation

Set aside part of a sample and prepare the rest. Measure both the prepared and the unprepared portions. Small differences (+/-30%) are to be expected.

Send samples to a lab for confirmation

Have some samples measured by atomic absorption spectrophotometry by a certified laboratory. This will verify the correctness of your technique and alert you to any site-specific biases.

Split some samples and analyze each sample with both the XRF and with atomic absorption spectrophotometry in a lab. Your Standard Operating Procedure should specify the number of confirmatory samples (perhaps 10 percent of all samples), what actions will be taken in response to the results, and what records will be kept.

Range, precision and limits

Range of accurate measurement

NITON XRFs are calibrated to give accurate values for most elements in concentrations of 10,000 ppm or less. This is because the linear range of the Compton Normalization Method is from 0 ppm to approximately 10,000 ppm (1%). For actual concentrations of 10,000 ppm to 20,000 ppm (1% to 2%), NITON's may overstate the elemental concentration. For content above 20,000 ppm (2%), readings may exhibit even greater deviation.

This deviation results from the extreme x-ray absorption of lead relative to the typical matrix. In terms of x-ray properties, the sample with greater than 20,000 ppm (2%) lead behaves more like lead than the matrix. It may be possible to develop a calibration curve for a specific soil matrix with a very high concentration of lead. If you wish to measure lead in such matrices, please contact Dr. Don Sackett at NITON Corporation for further information at (617) 275-9275.

95% confidence intervals

The precision of a measurement is expressed as the uncertainty or error of the measured result. For

every measurement, the NITON gives an uncertainty range that represents a 95% (or "2-sigma") confidence interval. The 95% confidence interval is the interval between the measured-result-minus-the-uncertainty-range to the measured-result-plus-the uncertainty-range. For example, if you took 100 measurements of a sample, you would expect 95 of the measurements to fall within the 95% confidence interval.

Detection limits (DLs)

The detection limit (DL) is the lowest concentration of analyte in a sample that can reliably be distinguished from zero concentration in a sample. In XRF, the DL is usually defined as three times the standard deviation (sigma) of fluctuation in the background.

A estimate of the DL can be obtained by measuring a blank standard. Use a standard measurement time (e.g. 60 source seconds). The estimated DL is 1.5 times the two-sigma precision of the measurement.

The method detection limit (MDL) may be a more realistic measure of sensitivity in actual field conditions. The MDL can be determined by replicate analysis of a blank or low level soil standard. This procedure may be carried out in the laboratory or field. The number of replicate blank measurements should be at least 7. If the replicate blanks are interspersed with the regular measurements as part of the continuing calibration verification (CCV), then the MDL will include the error resulting from instrument drift. Calculate the mean and standard deviation of the replicate measurement series. The bias is the mean minus the standard's known concentration. The MDL is 3 times the standard deviation. The MDL should be reasonably close to the estimated DL. Conservatively, one should report the DL to be the largest value among the estimated DL, MDL, and bias.

In actual usage, a measurement result that exceeds the DL is considered strong evidence of the analyte's presence in the sample. A measurement result that does not exceed the DL for an analyte is reported as "not detected."

Quantitation limit (QLs)

The quantitation limit (QL) is the lowest concentration of analyte that can be reliably measured at high enough precision to allow comparisons among measurements. The XRF industry usually defines QL as 10 times the standard deviation (or "10-sigma") or fluctuation in the background level. QL is therefore 3.33 times the DL. Similarly, the method quantitation limit (MQL) is simply 3.33 times the MDL.

Regulatory bodies often require analytical methods used to establish compliance with a standard or action level to achieve a quantitation limit (QL) equal to or below the standard or action level.

Summary of warnings

Warning: Always treat radiation with respect. Do not put your hand on the end plate of the NITON while measuring. Never point the NITON at yourself or anyone else when the shutter is open.

Warning: Wearing a dosimeter badge does not protect you against current exposure. A dosimeter measures your exposure after the fact. If, at any time, you find measurable exposure, call NITON immediately at (401) 294-1234.

Warning: Pregnant female workers may want to take special precautions to reduce their exposure to radiation. Qualified scientists have recommended that the radiation dose to pregnant women should not exceed 500 mR/year because of possible increased risk to the fetus.

Warning: In the unlikely event that the plunger gets stuck in the open position, simply push it closed. Then call the NITON Service Department at (401) 294-1234.

Warning: Tampering with the 5,500 ppm lead-in-soil standard may cause exposure to lead dust. Keep all standards out of reach of children.

Warning: Always use gloves and respiration equipment for your protection when taking samples from a site where toxic chemicals may be present.

Warning: Grinding and sieving dried samples produces dust. Even clean soil contains silica, which may be hazardous when airborne. Prepare all samples in a ventilated area; wear a mask, gloves, and an apron; and spread a drop cloth.

Warning: Do not hold bagged bulk samples in your hand during testing.

Summary of cautions

Caution: Do not attempt to make repairs yourself. All Service except exterior cleaning must be performed by NITON Corporation. Any attempt to open your NITON instrument will void the instrument warranty.

Caution: Do not return your NITON without the carrying case. You will void the instrument warranty. You will also be billed for a replacement case plus any repairs resulting from improper shipping.

Caution: Do not return your instrument to NITON without a current leak test. NITON's license prohibits us from repairing or upgrading our instruments without a current leak test certificate. If you return an instrument without a current leak test certificate, NITON will perform a leak test and bill you for the leak test.

Caution: Do not ship your instrument back to NITON for any reason without first notifying NITON Corporation and receiving a Return Authorization Number.

Caution: Do not store the battery packs or battery charger in direct sunlight.

Caution: Do not leave battery packs on the battery charger longer than necessary.

Caution: If the red Temp light comes on repeatedly when a battery pack is on the Battery Charger in the Full Charge cycle, call NITON Customer Service at (401) 294-1234.

Caution: NITON's Nickel Metal Hydride battery packs discharge at a rate of about 2% per day when not in use.

Caution: If you try to calibrate the instrument and it does not calibrate successfully, push the Reset Button on the bottom of the instrument and recalibrate. If your NITON does not calibrate successfully in three attempts, please call the NITON Service Department at (401) 294-1234.

Caution: Check the **Date** and **Time** displayed on the Ready to Test screen. If they are not correct, reset them before taking any measurements. Your readings will not be accurate unless the date and time are correct.

Caution: Never tamper with Test Standards. They should not be used unless they are completely intact.

Caution: The Standard Thin Sample Mode should not be used for quantitative lead-paint testing. Use only the three Paint Testing modes to test lead-based paint.

Caution: When testing the *exterior* of the window sash from the inside of a room, avoid standing in the path of the NITON's radiation beam. The direction of the beam is drawn on the cover of the instrument. It is easier to avoid the radiation beam if you hold the instrument in your right-hand.

Caution: Keep all test equipment clean to prevent contaminated samples.

Warranty

NITON will warranty parts and labor for any manufacturer's defects for 15 months. No precision instrument is warranted if crushed, dropped on the floor or in a bucket of water. All service, including repair, maintenance and source replacements, must be performed by NITON Corporation. Any attempt to open the metal case of your NITON instrument will nullify this warranty.

Limited Warranty Provision for Use with Purchase and License Agreement for NITON Corporation XRF Detection instruments:

(a) Except as otherwise agreed in writing, NITON Corporation warrants, under normal conditions of operation, each product sold (except for components not of its manufacture) against defects of material and workmanship, provided that such product has been properly utilized. This warranty applies to the original purchaser only and shall commence to run from the date of shipment and shall continue for a period of fifteen (15) months. In any event, NITON Corporation's liability for any such defects of material and workmanship shall not exceed the cost of replacement of defective parts upon timely notification of such defect in writing delivered to NITON Corporation's home office. NITON Corporation shall not be liable for damage or destruction caused during delivery or caused other than by employees of NITON Corporation.

(b) Material, accessories, parts, or items of equipment furnished by suppliers to NITON Corporation

and used in the manufacture of NITON Corporation products are guaranteed by NITON Corporation only to the extent of the original manufacturer's express warranty to NITON Corporation for a period not to exceed the warranty period described in paragraph (a) above and provided that the purchaser shall have notified NITON Corporation so as to enable NITON Corporation to avail itself of its rights under such original manufacturer's express warranty.

(c) NITON Corporation shall, at its option, repair such defects or replace the parts or products found defective. All defective parts are to be returned, freight prepaid, immediately to NITON Corporation for inspection and credit. NITON Corporation will make no allowance for repairs or alterations made by the purchaser unless made with the advance written consent of NITON Corporation. NITON Corporation assumes no liability for costs of disassembly of defective parts and equipment. Shipment by purchaser of all repairs and replacements under this warranty are F.O.B. NITON Corporation's factory or authorized service representative and method of shipment will be determined by NITON Corporation. The purchaser will pay shipping costs and insurance in both directions of products, parts, or components shipped for warranty service hereunder. The purchaser will be responsible for risk of loss in both direction. Replaced parts or components will become the property of NITON Corporation. Replacement parts or components may contain recycled, refurbished, or remanufactured parts equivalent to new parts and shall be warranted for the remainder of the original warranty period for the products.

(d) NITON Corporation shall not be liable for delays, deprivation of use, or any other damages, direct or indirect, which may result to the purchaser because of defects in the product or because of the purchaser's inability to operate it or use it to his satisfaction. NITON Corporation will not be liable to anyone for special or consequential damages of any kind. NITON Corporation neither assumes nor authorizes any person to assume for it, any other obligation or liability with respect to NITON Corporation products.

EXCEPT FOR THE FOREGOING EXPRESS WARRANTY, THERE ARE NO WARRANTIES, REPRESENTATIONS, OR GUARANTEES, EXPRESS OR IMPLIED, EXCEPT AS ARE EXPRESSLY SET FORTH HEREIN. THE FOREGOING WARRANTY IS THE ONLY WARRANTY MADE BY NITON CORPORATION. ANY IMPLIED WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE ON THIS PRODUCT IS LIMITED IN DURATION TO THE TWO YEAR DURATION OF THIS WRITTEN WARRANTY. SOME STATES DO NOT ALLOW LIMITATIONS ON HOW LONG AN IMPLIED WARRANTY LASTS OR THE EXCLUSION OF LIMITATION OF INCIDENTAL OR CONSEQUENTIAL DAMAGES SO THE ABOVE LIMITATIONS OR EXCLUSIONS MAY NOT APPLY TO YOU. THIS WARRANTY GIVES YOU SPECIFIC LEGAL RIGHTS AND YOU MAY ALSO HAVE OTHER RIGHTS WHICH VARY FROM STATE TO STATE.

APPENDIX D

N-Trak® Test Kit Instructions

1468-87

Nitrate Test Kit
Trousse d'analyse nitrate
Nitrat Test Kit
Kit para el análisis del contenido en nitratos

0-30 mg/L NO_3-N
Mod. NI-11
1468-03

WARNING

Handling chemical samples, standards, and reagents can be dangerous. Review the Material Safety Data Sheets before handling any chemicals.

ATTENTION

La manipulation des échantillons chimiques, étalons et réactifs peut être dangereuse. Lire les fiches de données de sécurité des produits avant de manipuler tous produits chimiques.

WARNUNG

Die Handhabung chemischer Proben, Standards und Reagenzien kann gefährlich sein. Bitte lesen Sie die Materialsicherheitsdatenblätter durch, bevor Sie Chemikalien handhaben.

ADVERTENCIA

El manejo de muestras químicas, patrones y reactivos puede resultar peligroso. Revise las hojas de información de seguridad del material antes de manipular cualquier producto químico.

HACH

Measuring Hints and General Test Information

- Samples containing more than 50 mg/L nitrate nitrogen can be tested by diluting the sample before testing. A 1:5 dilution is made by using 1 mL of sample water and 4 mL of Deionized Water (Cat. No. 272-42, not included in this kit. See *Optional Reagents and Equipment.*). Use the calibrated dropper provided in this kit for the dilution. Multiply the test results by 5 to obtain the correct mg/L nitrate nitrogen. The results of other dilutions will follow a similar procedure; for example, the results of a 1:3 dilution would be multiplied by 3 to obtain the correct mg/L nitrate nitrogen.
- Wash all labware between tests. Contamination may alter test results. Clean with a non-abrasive detergent or a solvent such as rubbing alcohol. Use a soft cloth for wiping or drying. Do not use paper towels or tissue on plastic tubes as this may scratch them. Rinse with clean water (preferably deionized water).
- Rinse all viewing tubes thoroughly with the sample water before testing.
- To open PermaChem® Powder Pillows:
  1. Tap the bottom of the pillow on a hard surface.
  2. Tear open the pillow along the dashed line.
  3. Open the pillow and form a spout by squeezing the side edges.
  4. Pour the contents into the sample.
- Accuracy is not affected by undissolved powder.
- Hach strongly recommends that, for optimum test results, reagent accuracy be checked with each new lot of reagents. Use the standard solution included in this kit or listed in the *Optional Reagents and Equipment* section. Follow the instructions included with each standard solution.

Conseils pour les mesures et informations générales sur l'analyse

- Les échantillons contenant plus de 50 mg/L d'azote peuvent être analysés en diluant l'échantillon avant l'analyse. Une dilution au 1/5 est réalisée en utilisant 1 mL d'échantillon et 4 mL d'eau déionisée (Réf. No. 272-42, non contenue dans la trousse. Voir *Réactifs et Equipements optionnels*). Utiliser le compte-gouttes gradué fourni dans la trousse pour la dilution. Multiplier le résultat par 5 pour obtenir la concentration correcte d'azote. Pour les autres dilutions, suivre une procédure similaire; par exemple, le résultat d'une dilution au 1/3 doit être multiplié par 3 pour obtenir la concentration correcte d'azote.
- Laver toute la verrerie entre les analyses. La contamination peut fausser les résultats d'analyses. Laver avec un détergent non abrasif ou un solvant tel que l'alcool à brûler. Utiliser un tissu doux pour essuyer ou sécher. Ne pas utiliser de tissu ou papier d'essuyage sur les tubes en plastique pour ne pas les rayer. Rincer à l'eau propre (de préférence de l'eau déionisée).
- Rincer soigneusement tous les tubes colorimétriques avec l'échantillon d'eau avant l'analyse.

- Pour ouvrir les sachets PermaChem®:
  1. Taper le bas du sachet sur une surface dure.
  2. Déchirer le sachet en suivant le pointillé.
  3. Ouvrir le sachet et former un bec en rapprochant les bords latéraux.
  4. Verser le contenu dans l'échantillon.
- L'exactitude n'est pas affectée par la poudre non dissoute.
- Pour de meilleurs résultats, Hach recommande vivement de vérifier la validité du réactif pour chaque nouveau lot de réactifs. Utiliser la solution étalon contenue dan cette trousse ou listée dans la partie *Réactifs et Equipements optionnels*. Suivre les instructions fournies avec chaque solution étalon.

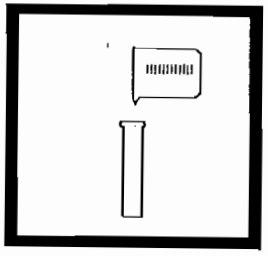
Meßtips und Allgemeine Testinformationen

- Proben, die über 50 mg/L Nitratstickstoff enthalten, können durch Verdünnen der Probe vor dem Test geprüft werden. Eine 1:5-Verdünnung wird unter Verwendung von 1 mL Probenwasser und 4 mL entsalzt Wasser (Deionized Water, Kat.-Nr. 272-42, nicht im Lieferumfang dieses Kits enthalten. Siehe *Zusätzliche Reagenzien und Zubehör.*) hergestellt. Verwenden Sie die in diesem Kit mitgeliefert kalibrierte Tropfpipette für die Verdünnung. Multiplizieren Sie die Testergebnisse mit 5, um die richtigen mg/L Nitratstickstoff zu erhalten. Die Ergebnisse anderer Verdünnungen folgen einem ähnlichen Verfahren. So werden zum Beispiel die Ergebnisse einer 1:3-Verdünnung mit 3 multipliziert, um die richtigen mg/L Nitratstickstoff zu erhalten.
- Waschen Sie alle Laborartikel zwischen den Tests. Verunreinigung kann die Testergebnisse verfälschen. Reinigen Sie sie mit einem nicht scharfen Detergent od einem Lösungsmittel wie zum Beispiel Isopropylalkohol. Verwenden Sie für das Abwischen oder Abtrocknen ein weiches Tuch. Verwenden Sie bei den Plastikröhrchen keine Papierhandtücher oder Tissue-Papier, da dieses sie zerkratze kann. Spülen Sie mit sauberem Wasser (vorzugsweise entsalzt Wasser).
- Spülen Sie alle Prüfröhrchen vor dem Test gründlich mit dem Probenwasser.
- Öffnen der PermaChem®-Pulverkissen:
  1. Klopfen Sie mit dem Boden des Kissens auf eine harte Oberfläche.
  2. Öffnen Sie das Kissen und bilden Sie durch Drücken der Seitenkanten einen Ausgießer.
  3. Schütten Sie den Inhalt in die Probe.
- Die Genauigkeit wird durch unaufgelöstes Pulver nicht beeinträchtigt.
- Hach empfiehlt dringend, für optimale Testergebnisse die Genauigkeit des Reagenz bei jeder neuen Charge von Reagenzien zu überprüfen. Verwenden Sie dazu die diesem Kit beiliegende Standardlösung oder die im Abschnitt *Zusätzliche Reagenz und Zubehör* aufgeführte Standardlösung. Befolgen Sie die Anweisungen, die jede Standardlösung beiliegen.

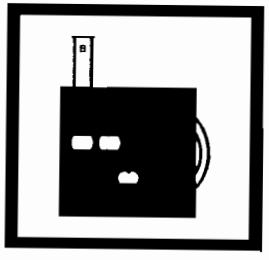
Consejos para la medición e información general sobre el análisis

- Las muestras que contengan más de 50 mg/L de nitrógeno en forma de nitratos pueden ser analizadas si se diluyen antes de proceder al análisis. Diluya 1 mL de muestra de agua en 4 mL de agua destilada (N° Ref 272-42, no incluida en este kit, véase *Reactivos y Equipamiento opcionales*) para obtener una dilución al 1:5. Utilice la pipeta graduada que se suministra con este kit. Multiplique los resultados obtenidos por 5 para obtener la concentración de nitrógeno en mg/L. Proceda del mismo modo para otras diluciones. Por ejemplo, los resultados de una dilución al 1:3 se multiplicarán por 3 para obtener la concentración correcta de nitrógeno en forma de nitratos.
- Lavar todo el material del laboratorio entre los análisis. Su contaminación puede alterar los resultados. Limpiar con detergentes no abrasivos o con un disolvente como el alcohol de quemar. Utilizar un paño suave para limpiar o secar. No utilizar ni toallitas ni pañuelos de papel para limpiar los tubos de plastico para no rayarlos. Aclarar con agua limpia (preferentemente agua destilada).
- Aclarar todos los tubos para colorimetría abundantemente con la muestra de agua antes de realizar el análisis.
- Para abrir las Cápsulas de Reactivo PermaChem® proceda del siguiente modo:
  1. Golpee ligeramente la parte inferior de la cápsula contra una superficie dura.
  2. Tire de la línea de puntos para abrir.
  3. Abra la cápsula y presione sobre los laterales de la misma hasta que se forma un pico.
  4. Vierta el contenido en la muestra.
- La exactitud del análisis no se verá afectada por restos de polvos de reactivo sin disolver.
- Para obtener mejores resultados, Hach recomienda encarecidamente comprobar la validez del reactivo con cada nuevo lote. Utilice para ello la solución patrón incluida en este kit o relacionada en la sección de *Reactivos y Equipamiento opcionales*. Siga las instrucciones que se incluyen en cada solución patrón.

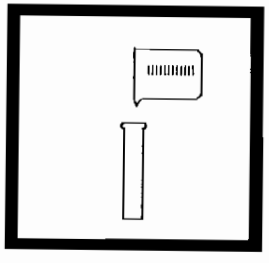
• Procedure • Technique • Verfahren • Procedimiento



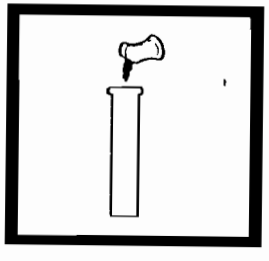
1. Fill a viewing tube to the first (5-mL) line with sample water. This is the blank.
- Remplir un tube colorimétrique jusqu'au premier trait (5-mL) avec l'échantillon d'eau. Ceci est le blanc.
- Füllen Sie ein Prüfröhrchen bis zur ersten (5-mL) Linie mit Probenwasser. Dieses ist die Blindprobe.
- Llene un tubo para colorimetría hasta la primera marca (5-mL) con la muestra de agua. Esto constituye el blanco



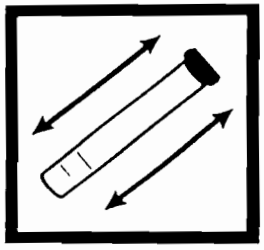
2. Place this tube in the top left opening of the color comparator.
- Placer ce tube dans l'ouverture supérieure gauche du comparateur.
- Stellen Sie dieses Röhrchen in die obere linke Öffnung d Farbkomparators.
- Coloque este tubo en la abertura superior izquierda del comparador.



3. Fill another viewing tube to the first (5-mL) line with sample water.
- Remplir un autre tube jusqu'au premier trait (5-mL) avec l'échantillon d'eau.
- Füllen Sie ein weiteres Prüfröhrchen bis zur ersten (5-mL Linie mit Probenwasser.
- Llene otro tubo para colorimetría hasta la primera marca (5-mL) con la muestra de agua.

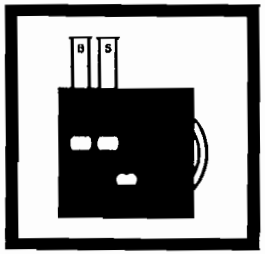


4. Add the contents of one NitraVer® 5 Nitrate Reagent Powder Pillow to the second tube.
- Ajouter le contenu d'un sachet de réactif nitrate NitraVer® 5 au second tube.
- Geben Sie den Inhalt eines NitraVer® 5 Nitrat Reagenz Pulverkissens in das zweite Röhrchen.
- Vierta el contenido de una de las cápsulas NitraVer® 5 de reactivo de nitratos en el segundo tubo de los preparados anteriormente.



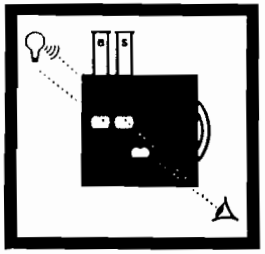
5. Cap the tube and shake vigorously for exactly one minute. Allow this sample to sit undisturbed for one minute. An amber color will develop if nitrate is present.

- Boucher le tube et agiter vigoureusement pendant exactement une minute. Laisser reposer le tube pendant une minute. En présence de nitrate, une coloration ambre se développe.
- Verschließen Sie das Röhrchen mit einer Kappe und schütteln Sie es genau eine Minute lang kräftig. Lassen Sie diese Probe ungestört eine Minute lang stehen. Eine bernsteingelbe Farbe wird sich entwickeln, wenn Nitrat vorhanden ist.
- Tape el tubo y sacuda vigorosamente durante un minuto exacto. Deje que la muestra se decante un minuto. Si hay nitratos en la muestra de agua aparecerá un color ámbar.



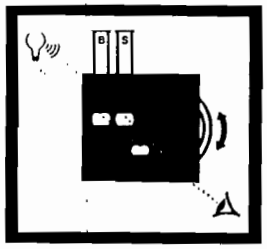
6. Place the second tube in the top right opening of the color comparator.

- Placer le second tube dans l'ouverture supérieure droite du comparateur.
- Setzen Sie das zweite Röhrchen in die obere rechte Öffnung des Farbkomparators.
- Coloque el segundo tubo en la abertura superior derecha del comparador.



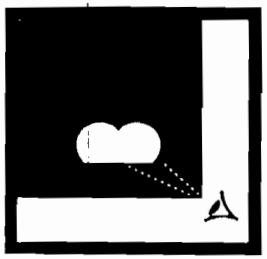
7. Hold comparator up to a light source such as the sky, a window or a lamp. Look through the openings in front.

- Tenir le comparateur face à une surface uniformément éclairée (ciel, lampe, fenêtre) et regarder par les ouvertures de la face antérieure du comparateur.
- Halten Sie den Komparator gegen eine Lichtquelle, wie zum Beispiel den Himmel, ein Fenster oder eine Lampe. Sehen Sie durch die Öffnungen vorn.
- Lleve el colorímetro hasta una fuente de luz, tal como el cielo, una ventana o una lámpara. Mire a través de las aberturas frontales del colorímetro.



8. Rotate the color disc until the color matches in the two openings.

- Tourner le disque jusqu'à égalité des teintes dans les deux ouvertures.
- Drehen Sie die Farbscheibe, bis die Farbe in den beide Öffnungen übereinstimmt.
- Gire el disco hasta que el color coincida en ambas aberturas.



9. Read the mg/L nitrate nitrogen in the scale window.

- Lire la concentration de nitrate en mg/L d'azote (N) da la fenêtre de l'échelle.
- Lesen Sie die mg/L Nitratstickstoff im Skalenfenster a
- Lea la concentración de nitratos en mg/L la ventanilla la escala.

Note: Multiply the mg/L nitrate nitrogen value by 4.4 t obtain the mg/L nitrate.

Note: Multiplier par 4.4 la lecture en mg/L d'azote pou obtenir la valeur en mg/L de nitrate.

Anmerkung: Multiplizieren Sie den mg/L-Nitratstickste wert mit 4,4, um die mg/L Nitrat zu erhalten.

Nota: Multiplique por 4,4 la lectura en mg/L de nitróge para obtener el valor en lmg/L de nitratos.

REPLACEMENTS

Description	Unit	Cat. No.
Color Comparator Box	each	1732-00
Color Viewing Tube, plastic, with cap	4/pkg	46600-04
Dropper, glass, 0.5- and 1.0-mL marks	5/pkg	14197-05
Color Disc, Nitrate Nitrogen, 0–50 mg/L	each	14038-00
NitraVer® 5 Nitrate Reagent Powder Pillows	100/pkg	14035-99

REACTIFS ET PIECES DE RECHANGE

Désignation	Unité	Réf. Nº
Comparateur	1	1732-00
Tube colorimétrique en plastique avec bouchon	4/paq	46600-04
Compte-gouttes en verre, marqué 0,5- and 1,0-mL	5/paq	14197-05
Disque coloré Nitrate , 0–50 mg/L N	1	14038-00
Réactif nitrate NitraVer® 5 en sachets	100/paq	14035-99

VERBRAUCHSMATERIAL UND ERSATZTEILE

Beschreibung	Einheit	Kat. Nr.
Farbkomparator	jeweils	1732-00
Farbprüfröhrchen, Plastik, mit Kappe	4/Stck	46600-04
Tropfpipette, Glas-, mit 0,5 mL- und 1 mL-Markierungen	5/Stck	14197-05
Farbscheibe, Nitratstickstoff, 0-50 mg/L	jeweils	14038-00
Nitratreagenz-Pulverkissen	100/Stck	14035-99

REACTIVOS Y MATERIALES

Descripción	Unidad	Nº Ref.
Colorímetro	1	1732-00
Tubo Para Colorimetría de plástico, con tapa	4/lote	46600-04
Pipeta, de vidrio, graduada (divisiones de 0,5 y 1,0 mL)	5/lote	14197-05
Disco de color, nitrógeno en forma de nitratos, 0- 50 mg/L	1	14038-00
Cápsulas NitraVer® 5 de reactivo de nitratos	100/lote	14035-99

OPTIONAL REAGENTS AND EQUIPMENT

Description	Unit	Cat. N
Caps, for plastic Color Viewing Tubes 46600-04	4/pkg	46600-
Color Viewing Tube, glass	6/pkg	1730-
Instructions, Color Viewing Tube	each	46600-
Nitrogen-Nitrate Standard Solution, 12 mg/L, 2-mL PourRite™ Ampule	20/pkg	25587-
Stoppers, for glass Color Viewing Tubes 1730-06	6/pkg	1731-
Water, Deionized	100 mL	272-

REACTIFS ET EQUIPEMENTS OPTIONNELS

Désignation	Unité	Réf.
Bouchons pour tubes en plastique 46600	4/paq	46600-
Tube colorimétrique en verre	6/paq	1730-
Instructions pour tubes colorimétriques	1	46600-
Solution étalon Nitrate, 12 mg/L d'azote (N), ampoule PourRite™ 2 mL	20/paq	25587-
Bouchons pour tubes en verre 1730	6/paq	1731-
Eau déionisée	100 mL	272-

ZUSÄTZLICHE REAGENZIEN UND ZUBEHÖR

Beschreibung	Einheit	Kat. N
Kappen, für Plastik-Farbprüfröhrchen 46600-04	4/Stck	46600-
Farbprüfröhrchen, Glas	6/Stck	1730-
Gebrauchsanweisung für Farbprüfröhrchen	jeweils	46600-
Stickstoff-Nitrat-Standardlösung, 12 mg/L, 2 mL-PourRite™-Ampulle	20/Stck	25587-
Stopfen für Glas-Farbprüfröhrchen 1730-06	6/Stck	1731-
Wasser, entsalzt	100 mL	272-

REACTIVOS Y EQUIPAMIENTO OPCIONALES

Descripción	Unidad	Nº R
Tapas para los tubos para colorimetría de plástico 46600-04	4/lote	46600
Tubos para colorimetría de vidrio	6/lote	1730
Instrucciones para los tubos para colorimetría	1	46600
Solución patrón de nitratos, 12mg/L. Ampolla PourRite™ de 2mL	20/lote	25587
Tapones para los tubos para colorimetría de vidrio 1730-06	6/lote	1731
Agua destilada	100 mL	272

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APPENDIX E

LL-11 IRA Ordinance Avoidance Plan

STATEMENT OF WORK FOR ORDNANCE AVOIDANCE AT LOAD LINE 11, RAVENNA ARMY AMMUNITION PLANT, RAVENNA , OHIO

1. **General.** MKM Engineers, Inc. Unexploded Ordnance (UXO) staff personnel will provide a two-person Unexploded Ordnance (UXO) team to provide on-site UXO support during all sampling activities. The UXO team will not destroy any UXO encountered. The UXO team will report all located UXO to Mark Patterson, Environmental Manager, Ravenna Army Ammunition Plant, Ravenna, Ohio, for disposition and guidance

2. **Definitions.**

   a. **Ordnance and Explosive (OE).** Bombs and warheads, guided and ballistic missiles, artillery, rocket and mortar ammunition, small arms ammunition, anti-personnel and anti-tank mines, demolition charges, pyrotechnics, grenades, containerized and uncontainerized explosives and propellants, military chemical agents and all similar and related items or components, explosive in nature or otherwise designed to cause damage to personnel or material. Soils with explosive constituents are considered to be OE if the concentration is sufficient to be reactive and present an imminent safety hazard.

   b. **Unexploded Ordnance (UXO).** An item of explosive ordnance that has failed to function as designed or has been abandoned, discarded or improperly disposed of and is still capable of functioning and causing damage to personnel or materials.

   c. **Inert Ordnance.** An item that has functioned as designed, leaving an inert carrier. An item manufactured to serve a specific training purpose. Fragments from UXO.

   d. **Explosive Ordnance Disposal (EOD) Personnel.** Active duty military EOD personnel.

   e. **UXO Personnel.** Former EOD personnel employed by a contractor.

   f. **Recovered Chemical Warfare Materiel (RCWM).** RCWM is defined as chemical agent material and/or associated equipment and surrounding contaminated media discovered either by chance or during deliberate real estate recover/restoration operations that was previously disposed of as waste. RCWM is classified as hazardous waste by the Army and not within the scope of the Army Chemical Surety Program.

   g. **Chemical Event.** Discovery of an actual or suspected chemical agent or container that may require emergency transportation or disposal.

3. UXO Team Composition and Qualifications. UXO Team shall consist of two members with the following qualifications:

a. **UXO Team Leader.** The UXO supervisor for this project will be Mr. Dewey Thedford. He will be the technical lead for all UXO operations on the site. Mr. Thedford is qualified for this project by virtue of training and experience. He has over 25 years of military and civilian experience. He has served as a Senior UXO Supervisor, UXO Supervisor, Safety Officer and Quality Control Specialist. Duties and assignments include range clearances as EOD Range Control Officer and Range Supervisor of multiple team operations and civilian UXO experience including performance as a Senior UXO Supervisor for OE removal operations.

b. **UXO Specialist.** The UXO specialist for this project will be Mr. Bill Howell. Mr. Howell has 20 years military and civilian experience. He has served as EOD Demolition Supervisor, Safety Officer and Senior UXO Supervisor for OE removal operations.

4. Responsibilities and Authority. The UXO Team will provide the explosive ordnance recognition, location and safety functions for the operation. The UXO team leader has the final authority for on-site personnel regarding all matters concerning UXO.

5. Work and Safety Plans. The UXO team will assist in the development of the site safety and health plan and the work plan. The UXO team leader will conduct UXO safety briefings for all site-personnel and visitors.

6. Access Routes to Sampling Locations.

a. Prior to commencement of operations at specific sites, the UXO team will conduct a reconnaissance of the sampling area. The reconnaissance shall include locating a clear path for the sampling crews, vehicles and equipment to approach the site. The approach path, at a minimum, will be twice the width of the widest vehicle. MKM UXO personnel will clearly mark all boundaries of the cleared approach path to prevent personnel from straying into uncleared areas. The path will be marked utilizing red pin flags spaced no more than fifteen (15) feet apart or as visibility dictates. No personnel shall be allowed outside the cleared paths.

b. If UXO is encountered on the surface, divert the approach path around the UXO, clearly mark the area and report the UXO.

c. A Schonstedt magnetometer will be used to insure there is no subsurface UXO within the approach path. If a magnetic anomaly is encountered. assume it to

be a UXO and divert the path around the anomaly. Only UXO personnel shall handle UXO and operate the magnetometers.

7. Soil Sampling and Well Drilling Sites

a. The UXO team will locate magnetic anomaly free areas for soil samples and GEOPROBE operations. If a pre-selected area indicates magnetic anomalies, a new sampling site will be chosen.

b. The UXO team will clearly mark the boundaries of the cleared soil sampling or well drilling sites. Personnel will not go outside the cleared areas. As a minimum, the cleared area will be square, with a side dimension equal to twice the length of the largest vehicle or piece of equipment to be brought on site.

c. Prior to drilling equipment being moved to the proposed drilling site, the UXO team will locate a magnetic anomaly free site. This shall be accomplished using a Schonstedt GEOMAG. The UXO team shall start the borehole with a hand held or portable auger. At not more than a two-foot depth, the auger will be withdrawn and the magnetometer probe will be lowered into the hole. This procedure will be used to ensure that smaller items of UXO, undetectable from the surface can be detected. If no magnetic anomalies are found, the procedure will be repeated at two-foot intervals to the maximum depth of the auger, but not less than six feet. If the proposed drilling site is still free of magnetic anomalies, the drilling equipment may be brought on site and utilized. Borehole monitoring with the GEOMAG shall continue at two-foot intervals, until virgin soil is encountered.