1-18-96

SANDIA REPORT

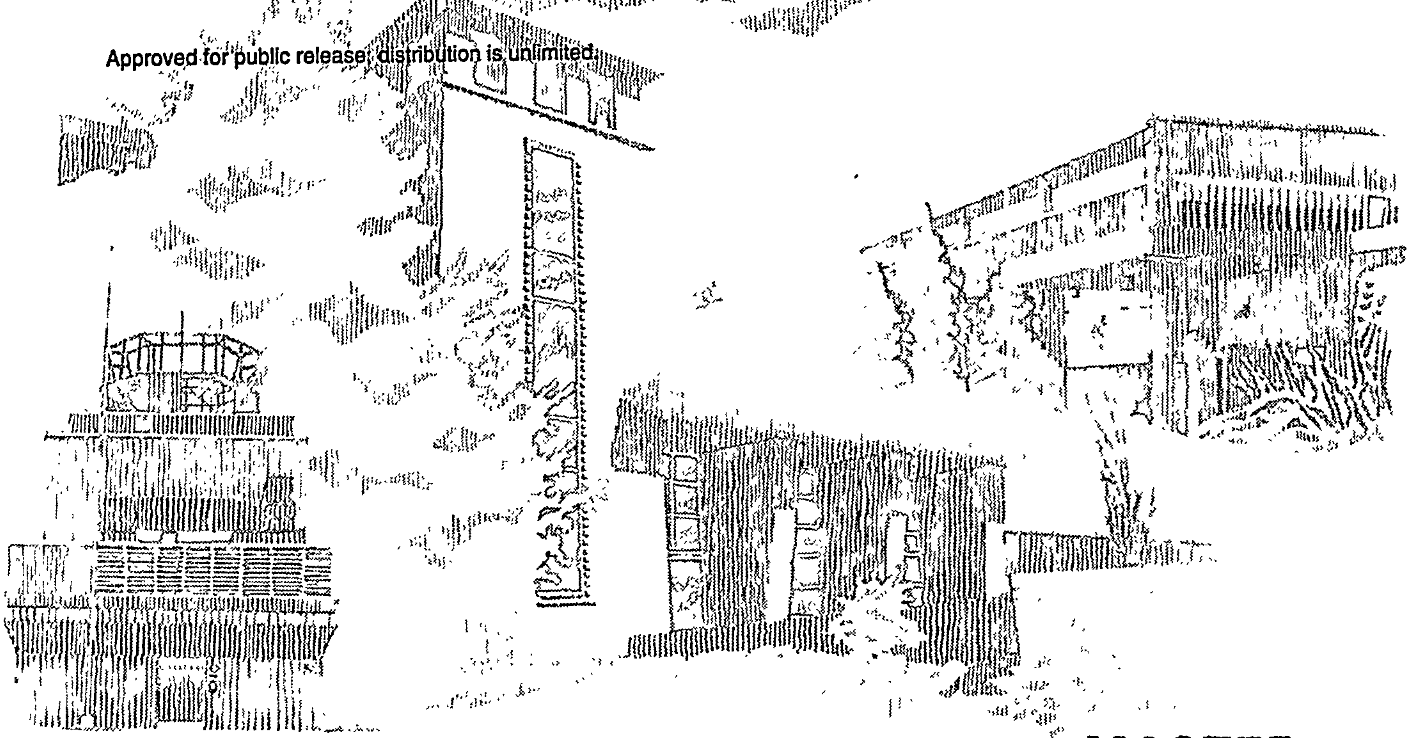
SAND95-3062 • UC-603
Unlimited Release
Printed December 1995

RECEIVED
JAN 30 1996
OSTI

Characterization, Monitoring, and Sensor Technology Catalogue

Rudolph V. Matalucci, Charlene Esparza-Baca, Richard D. Jimenez

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-94AL85000



SF2900Q(8-81)

MASTER

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831

Prices available from (615) 576-8401, FTS 626-8401

Available to the public from
National Technical Information Service
US Department of Commerce
5285 Port Royal Rd
Springfield, VA 22161

NTIS price codes
Printed copy: A14
Microfiche copy: A01

SAND95-3062
Unlimited Release
Printed December 1995

Distribution
Category UC-603

CHARACTERIZATION, MONITORING, AND SENSOR TECHNOLOGY CATALOGUE

Edited by:

Rudolph V. Matalucci
Security and Survivability Department 5822
Sandia National Laboratories
Albuquerque, New Mexico 87185

Charlene Esparza-Baca and Richard D. Jimenez
Applied Sciences Laboratory, Inc.
Albuquerque, New Mexico 87154

ABSTRACT

This document represents a summary of 58 technologies that are being developed by the Department of Energy's (DOE's) Office of Science and Technology (OST) to provide site, waste, and process characterization and monitoring solutions to the DOE weapons complex. The information was compiled to provide performance data on OST-developed technologies to scientists and engineers responsible for preparing Remedial Investigation/Feasibility Studies (RI/FSs) and preparing plans and compliance documents for DOE cleanup and waste management programs. The information may also be used to identify opportunities for partnering and commercialization with industry, DOE laboratories, other federal and state agencies, and the academic community. Each technology is featured in a format that provides: (1) a description, (2) technical performance data, (3) applicability, (4) development status, (5) regulatory considerations, (6) potential commercial applications, (7) intellectual property, and (8) points-of-contact. Technologies are categorized into the following areas: (1) Bioremediation Monitoring, (2) Decontamination and Decommissioning, (3) Field Analytical Laboratories, (4) Geophysical and Hydrologic Characterization, (5) Hazardous Inorganic Contaminant Analysis, (6) Hazardous Organic Contaminant Analysis, (7) Mixed Waste, (8) Radioactive Contaminant Analysis, (9) Remote Sensing, (10) Sampling and Drilling, (11) Statistically Guided Sampling, and (12) Tank Waste.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ACKNOWLEDGMENTS

The development of the Characterization, Monitoring, and Sensor Technology (CMST) Catalogue is the result of a team effort. The project was managed by Joseph Paladino, Program Manager in the DOE EM Office of Technology Transfer and Program Integration (EM-52). The work was tasked to Sandia National Laboratories (SNL), New Mexico, under TTP# AL2-1-41-03, and managed by Rudolph V. Matalucci, Principal Investigator. Applied Sciences Laboratory, Inc. (ASL) of Albuquerque, New Mexico, supported SNL in this effort. Critical roles were performed by Richard Jimenez, Charlene Esparza-Baca, John Reardon, David Castaneda, and Patricia Trujillo of ASL.

Appreciation is extended to Jeff Lenhert of the DOE Albuquerque Operations Office and to Paul Wang of DOE's Ames Laboratory, U.S. DOE, for their support and guidance. Marvin Anderson, Glenn Bastiaans, Bill Haas, and Tiffany Zachry, also of Ames Laboratory, Andee Rappazzo of BDM, and Simon Weavers of Science Applications International Corporation, are appreciated for technical review and editing contributions. Above all, special thanks are conveyed to the individual principal investigators and coworkers, who provided the latest available technical information concerning the technologies featured in this document.

TABLE OF CONTENTS

Abstract i

Acknowledgments ii

Preface ix

Introduction xi

1.0 Bioremediation Monitoring

Microbial Monitoring 3

2.0 Decontamination and Decommissioning

Associated Particle Imaging 9
Characterization of Radioactive Contamination Inside Pipes with the Pipe Explorer™ System 13
Coherent Laser Vision System 17
N-SCAN™ Prompt Gamma Neutron Activation Analysis 21
Portable Sensor for Hazardous Waste 25
Rapid Surface Sampling and Archival Record System 29
Three-Dimensional Integrated Characterization and Archiving System 35

3.0 Field Analytical Laboratories

Mobile Demonstration Laboratory for Environmental Screening Technologies 41
Rapid Transuranic Monitoring Laboratory 47

4.0 Geophysical and Hydrologic Characterization

Cross Borehole Electromagnetic Imaging 55
Crosshole Seismic Imaging 59
Electrical Resistance Tomography 63
Hydrologic Sensors for the Cone Penetrometer System 69
In Situ Permeable Flow Sensor 73
Magnetometer Towed Array 77
Post-Closure Monitoring 81
Rapid Geophysical Surveyor 85
Unsaturated Flow Apparatus 89

5.0 Hazardous Inorganic Contaminant Analysis

Laser-Induced Breakdown Spectroscopy for Metals in Soils and Groundwater 95
Sol-Gel Indicators 99
Stripping Analysis 103
X-Ray Fluorescence Spectroscopy 107

6.0 Hazardous Organic Contaminant Analysis

Chemical Fiber-Optic Sensor 113
Direct Sampling Ion Trap Mass Spectrometry 119
Field Portable Detection of VOCs Using a SAW/GC System 123
Field Raman Spectrograph for Environmental Analysis 127
HaloSnif Fiber-Optic Spectrochemical Sensor 133
In Situ Measurement of Volatile and Semivolatile Organic Compounds in the Subsurface 137
Miniature Chemical Flow Probe Sensors 141
Miniature GC for In Situ Monitoring of VOCs within a Cone Penetrometer 145
Multianalyte Sensor Arrays 149
Portable Acoustic Wave Sensor Systems 153
RCL Monitor, a Chlorinated Organic Vapor Monitor 157

7.0 Mixed Waste

Continuous Emission Monitor for Thermal Treatment Systems 163
Flow-Through Alpha Monitor 167
Laser Spark Spectroscopy for Continuous Metal Emissions Monitoring 171
Transient Infrared Spectroscopy 175
Waste Inspection Tomography 179

8.0 Radioactive Contaminant Analysis

Air-Quality Monitoring for Alpha Contamination: Long-Range Alpha Detection 189
Inductively Coupled Plasma - Mass Spectrometry for Analysis of Microliter Samples and Solids 193
In Situ Determination of Radionuclide Contaminants 197
Long-Term, Post-Closure Radiation Monitoring System 203
Portable High-Energy Beta Detector 207

9.0 Remote Sensing

Remotely Piloted Vehicles and Miniaturized Sensors 213

10.0 Sampling and Drilling

Directional Drilling Position and Locating Device 219
Heavy Weight Cone Penetrometer 223
Hybrid Directional Boring and Horizontal Logging 227

Miniature Pumps for the Cone Penetrometer 233
ResonantSonic^{SM} Drilling 237
SEAMIST™ Borehole Instrumentation and Fluid Sampling System 241
Zero-Tension Lysimeters to Monitor Colloid Transport in the Vadose Zone 245

11.0 Statistically Guided Sampling

Adaptive Sampling Program Support 253

12.0 Tank Waste

Acoustic Characterization of Wastes in Double-Shelled Underground Storage Tanks 259
Acoustic Wave Sensor for In-Situ Monitoring of Headspace Gases in Underground Storage Tanks 265
Fourier-Transform Infrared Photoacoustic Spectroscopy 269
Imaging through Obscurations During Sluicing Operations 273
In-Tank Interface Detection Using Time Domain Reflectometry 277

13.0 Additional Technology Information 283

14.0 Acronyms and Initialisms 285

Figures

A CMST Catalogue Development Process xxi
1.1 Enriched TCE Mineralization. 3
2.1a Overview of the Associated Particle Imaging System. 9
2.1b Top View of the Salt and Water Image Configuration. 11
2.1c 3-D Imaging Capabilities of API. 11
2.2a Sequence of Operation for Transporting Detectors into Contaminated Piping Using the Pipe Explorer™ Survey System. 13
2.2b INEL/ICPP Drain Line Mockup 14
2.3 Basic Fiber-Optic FMCW Coherent Laser Radar Configuration. 17
2.5a Block Diagram of ANET Analysis System. 25
2.5b Spectrum of D-B Discharge in the Absence and Presence of Added Hg. 26
2.5c D-B Discharge Spectra for Four Different Hg Mole Fractions. 26
2.6a Configuration of RSSAR System. 29
2.6b Total Extraction Amounts Versus Time-Derived from GC Analysis of Solvent Traps. 31
2.7a Scematic of the 3D-ICAS 35
3.1 Schematic of the LA-ICP-AES Analytical Technique. 41
3.2 Rapid Transuranic Monitoring Laboratory 47
4.1a Cross Borehole Electromagnetic Imaging. 55
4.1b Preliminary Tomographic Image on Vertical Plane Above the Northern Slant Hole at the "60s" Pits. 57
4.2 Example Quantitative Tomograph of a Fracture. 60
4.3 Schematic Diagram Showing the Data Collection Approach for ERT Measurements 63
4.5 Schematic of the In Situ Permeable Flow Sensor. 73

4.6 The Magnetometer Towed Array. 77
4.7a. Configuration. 82
4.7b Time Series Plot. 82
4.7c TDR and Neutron Probe Regression. 82
4.7d Configuration. 82
4.7e Time Series Plot. 82
4.7f TDR and Neutron Probe Regression. 82
4.8 Rapid Geophysical Surveyor 85
4.9 UFA™ Rotor and Seat Assembly with Large Sample and Ferromagnetic Seal Options. 89
5.1a Schematic of the Laboratory LIBS Apparatus. 95
5.1b Calibration Curve for Los Alamos Soil Spiked with Lead. 97
5.2 Response of SGI Uranyl Sensor at 118 ppm UO^{22+}. 99
5.3 Stripping Analysis. 103
5.4 Prototype XRF System. 107
6.1 Light Transmission Optrode. 114
6.3a Model 4100 Attached to a Cone Penetrometer. 123
6.3b Display Screen Presenting Visual and Numerical Results. 124
6.4 Optical Layout of the Near-infrared Echelle Spectrograph 127
6.5 HaloSnif Fiber-Optic Sensor 133
6.6a Down-Hole Sparging Vessel 138
6.6b Thermal Desortpion Device 138
6.7a Flow Probe Head. 141
6.7b Flow Probe Laboratory Configuration. 142
6.8 Cone Penetrometer GC Concept Sketch. 145
6.9a Schematic of the pH/Hydrocarbon Array. 149
6.9b Fluorescence Images of a pH/Hydrocarbon Array. 150
6.10a Schematic of a Portable Acoustic Wave Sensor. 153
6.10b In Situ PAWS Analysis with Above-Ground Comparison Data from a Separate PAWS System and a Commercial IR System for CCl_4 in a High Concentration Vadose Zone Well at DOE's Hanford Site. 154
6.10c In Situ PAWS Analysis with Above-Ground Comparison Data from a Separate PAWS System and a Commercial IR System for CCL_4 in a Low Concentration Vadose Zone Well at DOE's Hanford Site. 154

Tables

A Application to Focus Areas xv
2.3 Projected Performance of the 3D Demonstration System. 18
2.4 Projected Near-Surface Limits of Detection of N-SCAN™ System Based on a 50-Minute Run. 21
2.6 Anthracene, 2,4,5-trichlorobiphenyl, and Phenyldodecane Recovered by the Concrete Sampler Head from Concrete Cakes 4 and 6 and Measured by GC-FID. 31
2.7 Summary of Spectral Quality for a Number of Representative Samples from the Three Spectroscopic Methods Studied. 36
3.1 Summary of Field Demonstrations. 43
4.2 Tomographic Imaging Cost Estimates Based on a Single Well Pair. 60
4.6 Magnetometer Towed Array Specifications. 78
5.1 The LIBS 3 SDV Detection Limits for Selected Elements in a Los Alamos Soil Matrix. 97

PREFACE

The information provided in the descriptions and profiles of the characterization, monitoring, and sensor technologies contained in this catalogue represents a summary of the data available at the time of printing. This document is intended to serve as a means of disseminating timely data to engineers, scientists, the U.S. environmental industry, and interested stakeholders. The technology profiles were each reviewed by the principal investigators for accuracy of the data at the time of publication. Readers are encouraged to contact principal investigators or to use sources cited at the end of each profile and at the end of the document, to obtain more detailed information.

INTRODUCTION

The U.S. Department of Energy (DOE) Office of Environmental Management (EM) is responsible for management and cleanup of DOE wastes from past and current nuclear weapons production and operations. The EM mission is to minimize risk to the environment, human health, and safety posed by the generation, handling, treatment, storage, transportation, and disposal of wastes, and to bring all sites into compliance with federal, state, and local regulations.

In November 1989, DOE established the Office of Technology Development (EM-50) (renamed the Office of Science and Technology (OST) in 1995). EM-50 is charged with developing technologies that are safer, faster, more effective, and less expensive than current methods to meet DOE's environmental restoration and waste management goals. EM-50 works closely with DOE's Offices of Waste Management (EM-30), Environmental Restoration (EM-40), and Facility Transition and Management (EM-60) to identify, develop, and implement innovative and cost-effective technologies.

In January 1994, DOE announced "A New Approach to Environmental Research and Technology Development at the U.S. Department of Energy." Five major Focus Areas were identified to focus DOE-wide environmental research and technology development activities on DOE's most pressing environmental restoration and waste management problems. The Focus Areas were targeted for action on the basis of risk, prevalence, or need for technology development to meet environmental regulations and requirements. The five Focus Areas are:

- Plume Containment and Remediation
- Mixed Waste Characterization, Treatment, and Disposal
- High-Level Waste Tank Remediation
- Landfill Stabilization, and
- Decontamination and Decommissioning.

In addition, EM identified five categories of needs that crosscut all focus areas:

- Characterization, Monitoring, and Sensor Technology
- Efficient Separations and Processing
- Robotics
- Innovation Investment Area, and
- Pollution Prevention.

Two primary EM goals are to protect the health of DOE workers and the public during all environmental restoration and waste management activities, and to ensure cost-effective cleanup. These require that wastes and sites be characterized to determine the hazardous constituents present, the danger that these pose to site workers, and whether migration pathways exist that could allow hazardous materials to migrate off the site. The focus of this document is on characterization, monitoring, and sensor crosscutting technologies being developed by OST.

Purpose of the CMST Catalogue

This Characterization, Monitoring, and Sensor Technology (CMST) Catalogue features 58 crosscutting technologies being developed to provide site, waste, and process characterization and monitoring solutions required by the DOE EM Focus Areas. The purpose of this CMST Catalogue is to:

- provide performance data on OST-developed technologies to scientists and engineers responsible for preparing Remedial Investigation/Feasibility Studies (RI/FSs) and preparing plans and compliance documents for DOE cleanup and waste management programs; and
- identify opportunities for partnering and commercialization that may involve industry, DOE laboratories, other federal and state agencies, and the academic community.

The technologies featured include those funded under Cooperative Research and Development Agreements (CRADAs); Research Opportunity Announcements (ROAs); Program Research and Development Agreements (PRDAs); the DOE Small Business Innovation Research (SBIR) Program; and interagency agreements (IAGs) with other federal agencies.

The CMST Catalogue is also a valuable source of technical information for EM's international programs that are responsible for fostering EM cooperation with foreign governments, industries, and educational institutions. EM's international programs includes the import of innovative and cost-effective foreign environmental technologies for applications at DOE sites. Current efforts involve demonstrations of OST-sponsored technology development at foreign sites as a means of enhancing the knowledge and performance of OST technologies. An important secondary motivation for these technology demonstrations is to increase opportunities for technology export to the worldwide marketplace through commercial partnerships, licensing agreements and other arrangements that serve to enhance the competitiveness of the U.S. environmental industry.

This CMST Catalogue is a source of information on DOE emerging technologies that is being provided periodically by OST to the Interagency Federal Remediation Technologies Screening Matrix and the U.S. Environmental Protection Agency, U.S. Department of Defense, and various databases. The information is expected to be made accessible via the Internet through the Characterization, Monitoring, and Sensor Technology Crosscutting Program (CMST-CP) homepage and the DOE EnviroTRADE® Information System (see Section 13 of this Catalogue for details concerning Internet access).

Catalogue Development Process

The methodology used to develop the technology profiles is shown in Figure A. The process began with a list of approximately 60 technologies provided by Paul Wang, DOE Ames Laboratory, Program Coordinator for the CMST-CP. Information was then obtained from several sources, including technical reports, open literature, technical task plans, and principal investigators. Once sufficient information was gathered, an initial technology profile was drafted and reviewed internally by Sandia National Laboratories and Applied Sciences Laboratory, Inc. The initial drafts were revised, if needed, to fill information gaps, and were submitted to the appropriate principal investigator for a technical accuracy review. The profiles were further revised, as necessary, and submitted to DOE-HQ and CMST-CP personnel at Ames Laboratory for technical and editorial reviews, revision recommendations, and approval. Based on a final review by principal investigators, profiles were revised and submitted to DOE-HQ for publication and distribution.

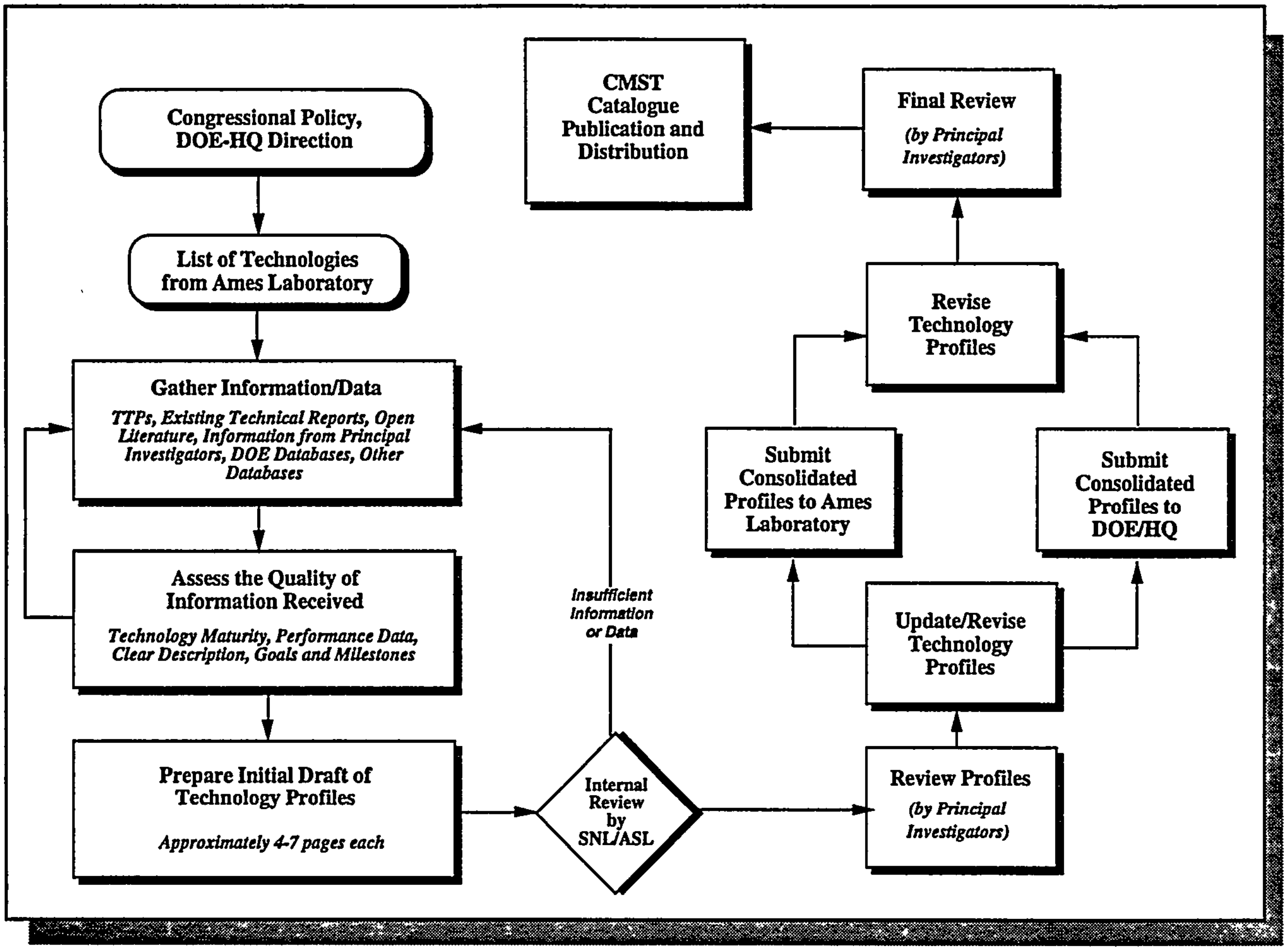


Figure A. CMST Catalogue Development Process.

Organization of Catalogue

Table A (at the end of this section) demonstrates the primary and secondary applications of each of the technologies with respect to the five Focus Areas. For example, the Portable Sensor for Hazardous Waste is a technology being developed that will have the capability to detect hydrocarbons, both chlorinated and non-chlorinated, transuranics, thorium, and heavy metals including mercury, chromium, cadmium, arsenic and lead. The primary application of this technology will be to the Decontamination and Decommissioning Focus Area for sensing radionuclides during decontamination and dismantlement of facilities. A secondary application of the technology is to the Landfill Stabilization Focus Area, where sensing of hydrocarbons will be important during remediation activities.

The characterization, monitoring, and sensor technologies listed in Table A and profiles presented in Sections 1 through 12 are grouped as follows:

1. Bioremediation Monitoring
2. Decontamination and Decommissioning
3. Field Analytical Laboratories
4. Geophysical and Hydrologic Characterization
5. Hazardous Inorganic Contaminant Analysis
6. Hazardous Organic Contaminant Analysis
7. Mixed Waste
8. Radioactive Contaminant Analysis
9. Remote Sensing
10. Sampling and Drilling
11. Statistically Guided Sampling
12. Tank Waste.

Each technology profile listed within the 12 groups contains information as follows:

- Description
- Technical performance and cost data
- Projected performance (1-3 years)
- Applicability
- Status
- Regulatory considerations
- Potential commercial applications
- Baseline technology
- Intellectual property
- Points-of-contact and references.

This information introduces the technology to the reader and provides a "snapshot" of its status with respect to performance and availability. More detailed information may be obtained from the sources cited in each profile.

Additional information about technologies being developed by OST may be obtained from sources cited in Section 13. A list of acronyms is provided in Section 14.

Table A. Application to Focus Areas.

p = primary application; √ = secondary application	PLUMES	TANK WASTE	MIXED WASTE	D&D	LANDFILLS
Bioremediation Monitoring					
Microbial Monitoring	p				
Decontamination and Decommissioning					
Associated Particle Imaging			√	p	
Characterization of Radioactive Contamination Inside Pipes with the Pipe Explorer™ System				p	
Coherent Laser Vision System		√	√	p	√
N-SCAN™ Prompt Gamma Neutron Activation Analysis	√		√	p	√
Portable Sensor for Hazardous Waste				p	√
Rapid Surface Sampling and Archival Record System				p	
Three-Dimensional Integrated Characterization and Archival Record System				p	
Field Analytical Laboratories					
Mobile Demonstration Laboratory for Environmental Screening Technologies	√				p
Rapid Transuranic Monitoring Laboratory	p	√	√	√	√
Geophysical and Hydrologic Characterization					
Cross Borehole Electromagnetic Imaging	p				√
Crosshole Seismic Imaging	p				
Electrical Resistance Tomography	√	p			√
Hydrologic Sensors for the Cone Penetrometer System	p				
In Situ Permeable Flow Sensor	p				
Magnetometer Towed Array	√				p
Post-Closure Monitoring	√				p
Rapid Geophysical Surveyor	√				p
Unsaturated Flow Apparatus	p				

Table A. Application to Focus Areas.

p = primary application; √ = secondary application	PLUMES	TANK WASTE	MIXED WASTE	D&D	LANDFILLS
Hazardous Inorganic Contaminant Analysis					
Laser-Induced Breakdown Spectroscopy for Metals in Soils and Groundwater	√	√	√	√	p
Sol-Gel Indicators	p	√			√
Stripping Analysis	p				√
X-Ray Fluorescence Spectroscopy	p				√
Hazardous Organic Contaminant Analysis					
Chemical Fiber-Optic Sensor	p	√			√
Direct Sampling Ion Mass Spectrometry	p				√
Field Portable Detection of VOCs Using a SAW/GC System	p				√
Field Raman Spectrograph for Environmental Analysis	p	√			√
HaloSnif Fiber-Optic Spectrochemical Sensor	p				√
In Situ Measurement of Volatile and Semivolatile Organic Compounds in the Subsurface	p				√
Miniature Chemical Flow Probe Sensors	p				√
Miniature GC for In Situ Monitoring of VOCs within a Cone Penetrometer	p				√
Multianalyte Sensor Arrays	p	√			√
Portable Acoustic Wave Sensor Systems	p		√		√
RCL Monitor, a Chlorinated Organic Vapor Monitor	p		√		√
Mixed Waste					
Continuous Emission Monitor for Thermal Treatment Systems		√	p	√	
Flow-Through Alpha Monitor		p		√	
Laser-Spark Spectroscopy for Continuous Metal Emissions Monitoring			p	√	√
Transient Infrared Spectroscopy		√	p		
Waste Inspection Tomography			p	√	√

Bioremediation Monitoring

Section 1.0

MICROBIAL MONITORING

DESCRIPTION

Microbial monitoring demonstrates the effectiveness of bioremediation and explains additional bioremediation benefits from other technologies (e.g., bioventing benefits from soil venting). Various advanced monitoring techniques, developed and applied (e.g., activity and biomass measurements, lipid analysis, DNA probe analysis) all contribute to documenting the necessary changes in microbial populations.

Microbial biomass is evaluated using measurements of colony-forming unit, most probable number (MPN) techniques for methanotrophic and methylotrophic populations, and phospholipid fatty acid (PLFA) analysis. Microbial activity is assessed using acetate-incorporation techniques and by measuring trichloroethylene (TCE) and tetrachloroethylene (PCE) degradation in enrichments. DNA probes are used to detect specific groups of bacteria such as methanotrophs, and toluene degraders. These techniques permit feedback during remediation efforts so that procedures may be changed (e.g., changing nutrients) to increase effectiveness of the remediation.

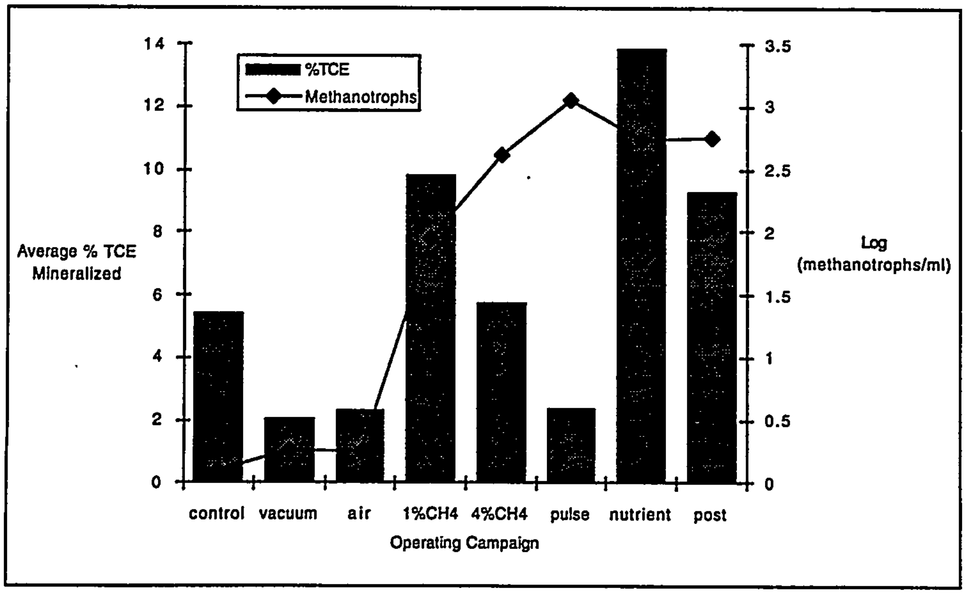


Figure 1.1. Enriched TCE mineralization.

TECHNICAL PERFORMANCE

Microbial monitoring of groundwater and sediments during a demonstration at the Savannah River Site (SRS) revealed significant changes in biological activity and microbial community structure that corresponded to changes in the operations of the bioremediation demonstration. The numbers of methanotrophs, which were shown to degrade TCE, increased three to five orders of magnitude with the addition of methane to the subsurface (Figure 1.1). Methanotrophic increases were also demonstrated by signature lipid biomarker technology and by DNA probing. With the addition of nutrients, the microbial population responses were less striking; however, the TCE-degradative capacities found in the groundwater increased dramatically (Figure 1.1). Nutrient supplementation caused a substantial and sustained increase in PCE degradation, as well. The activity of the existing microbial populations significantly increased in response to the nutrient addition. Bioreactor experiments indicated that in addition to TCE degradation, PCE could be degraded even with bulk phase aerobic conditions. As part of this work, several new DNA probes for methanotrophs were developed.

Microbial analyses can be completed in 2 days to 1 month, depending on the technique used.

Cost. Costs vary with the intensity of the monitoring techniques used. Costs at SRS were high because of the redundancy needed to develop data on the reliability of individual monitoring techniques. Costs for a more focused effort would be lower. Sample costs vary from less than $100 to greater than $500.

Adding nutrients to an established in situ remediation process is a minimal cost because the overall time to remediate the site will decrease. It is, therefore, important to monitor the microbial populations to maintain the efficiency of the degradation process.

PROJECTED PERFORMANCE

This technology demonstrated the efficient, effective, and accurate monitoring of specific microbial communities with increasingly aggressive measures to promote TCE degradation in the subsurface, and provided feedback during operations that increased the effectiveness of the bioremediation technologies.

APPLICABILITY

This technology is applicable to the monitoring of microbial populations that can degrade organic compounds.

STATUS

Materials and equipment are off-the-shelf. DNA probes are not commercially available, but can be made available.

The monitoring technologies developed during this demonstration were applied at Pacific Northwest Laboratory in Richland, Washington, and during the joint DOE-Remediation Technology Development Forum Project.

REGULATORY CONSIDERATIONS

This technology causes no ecological impacts. The potential exists for exposure to solvents and low-levels of radionuclides.

POTENTIAL COMMERCIAL APPLICATIONS

This technology has potential commercial application at any site undergoing bioremediation.

BASELINE TECHNOLOGY

The baseline technology is mass-balance measurements that are limited in monitoring critical changes in the microbial populations.

INTELLECTUAL PROPERTY

Patents: None

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Anthony V. Palumbo
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831
(423) 576-8002

DOE Program Manager
Kurt Gerdes
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7289

University Partners

University of Tennessee
Knoxville, TN

University of Minnesota
Minneapolis, MN

REFERENCES

1. Pfiffner, S.M., D.B. Ringelberg, D.B. Hedrick, T.J. Phelps, and A.V. Palumbo, "Changes in subsurface microbial communities and degradative capacities during in situ trichloroethylene bioremediation," Proceedings of the Third International Symposium In Situ and On-site Bioreclamation, San Diego, CA, 1995 (in press).

2. Pinkart, H.C., D.B. Ringelberg, J.O. Stair, S.D. Sutton, S.M. Pfiffner, and D.C. White, "Signature Lipid Biomarker Analysis of Extant Microbiota for Monitoring In Situ Bioremediation Effectiveness," Proceedings of the Third International Symposium In Situ and On-site Bioreclamation, San Diego, CA, 1995 (in press).

3. Jimenez, L., I. Rosario, J. Bowman, S. Koh, and G.S. Sayler, "Molecular Environmental Diagnostics of Trichloroethylene (TCE) Contaminated Subsurface Environments," R.E. Hinchee et al. (eds.), Bioremediation of Chlorinated and Polycyclic Aromatic Hydrocarbon Compounds, Lewis Publishers, Ann Arbor, MI, 1994, pp. 392-396.

4. Hazen, T.C., Preliminary Technology Report for In Situ Bioremediation Demonstration (Methane Biostimulation) of the Savannah River Integrated Demonstration Project DOE/OTD, WSRC-TR-93-670, 1994.

5. Phelps, T.J., S.M. Pfiffner, R. Mackowski, D. Ringelberg, D.C. White, S.E. Herbes, and A. V. Palumbo, "Application of Microbial Biomass and Activity Measures to Assess *In-situ* Bioremediation of Chlorinated Solvents," R.E. Hinchee et al. (eds.), Bioremediation of Chlorinated and Polycyclic Aromatic Hydrocarbon Compounds, Lewis Publishers, Ann Arbor, MI, 1994, pp. 404-408.

6. Palumbo, A.V., S.P. Scarborough, S.M. Pfiffner, and T.J. Phelps, "Influence of Nitrogen and Phosphorous on the In-situ Bioremediation of Trichloroethylene," Appl. Biochem. Biotech., 55/56: pp. 635-647.

7. Palumbo, A.V., T.J. Phelps, G.S. Sayler, D.C. White, and S.M. Pfiffner, "Integrated Demonstration of TCE Degradation: Biological Monitoring of Critical Populations," Information Exchange Meeting on Waste Retrieval, Treatment and Processing, Houston, TX, 1994.

8. Palumbo, A.V., T.J. Phelps, G.S. Sayler, D.C. White, and S.M. Pfiffner, "Integrated Demonstration of TCE degradation (Biological monitoring of critical populations)," Proceedings of the Information Exchange Meeting on Waste Retrieval, Treatment and Processing, DOE/CONF-930149, Houston, TX, March 1993, pp. 139-145.

9. Bowman, J.P., L. Jimenez, I. Rosario, T.C. Hazen, and G.S. Sayler, "Characterization of the Methanotrophic Bacterial Community Present in a Trichloroethylene-contaminated Subsurface Groundwater Site," Appl. Environ. Microbiol., 59(8), 1993, pp. 2380-2387.

Decontamination and Decommissioning

Section 2.0

DESCRIPTION

Associated Particle Imaging (API) is one of the most penetrating types of radiographic imaging, providing a wealth of information about the target identity. Although the neutron associated particle technique has been used since the 1950s for neutron flux measurements; its application to imaging is only very recent (1989), having been proof-of-concept investigated. The primary benefit of this technology is that it can be used to geometrically image and give an elemental analysis of materials located within shielded environments. Therefore, the API technology has the objective of providing a field deployable device for simultaneous 3-D imaging and isotopic composition of objects behind dense barriers (e.g., lead shields). API has applications to hazardous waste and contaminated facilities evaluation, as well as potential application to contraband interdiction.

A nuclear reaction, T(d,n)a, between deuterium (^{2}H) and tritium (^{3}H) produces a thermal neutron and an alpha particle having kinetic energies of 14.1 MeV and 3.5 MeV, respectively. The fast neutrons are produced when ionized deuterons are accelerated in the tube as a collimated beam to strike a scandium or titanium tritite target.

The API system makes use of the fact that the center of mass path of the neutron departure is opposite to the direction of the associated alpha particle departure. Consequently, position sensitive detection and timing of the alpha absorption correlates to the neutron path vector. There are uncertainties associated with this determination related to position resolution of the detector and interaction depth of the deuteron beam, which are minimized by engineering trade-off. These are discussed later. When a neutron collides with the object to be analyzed, one probable interaction is an inelastic scattering by an analyte atom producing a characteristic gamma-ray emission. The elapsed time between detection of the gamma-ray and detection of the alpha particle reveals the distance travelled by the neutron. This, together with directional information, enables the researcher to determine what part of the interrogated volume the gamma ray characterizes. This effect gives a multiplicity of information when integrated over many interactions. First, the detection of the gamma-ray spectra can be used to identify any element except hydrogen or helium. It is noted that there are also some application dependent spectral line overlaps or differences that may be difficult to resolve, but high resolution gamma-ray detectors are a part of this technology. Secondly, because the neutron departure vectors are correlated with associated

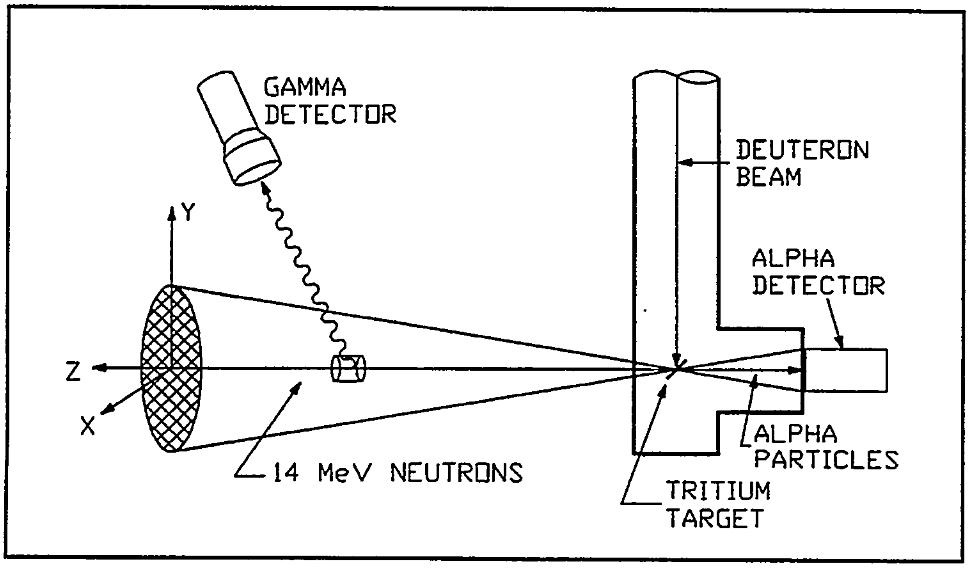


Figure 2.1a. Overview of the Associated Particle Imaging System.

alpha particle detection, the location of neutron scattering and, hence, the source of gamma emission may also be established. According to these physical principles, an array of spatially sensitive gamma-ray detectors can be used to produce a 3-D image of the analyzed target object (analyte). Figure 2.1a is an overview of the physical concepts of the API imaging system. Results can be presented in 2-D spectrographs, 2-D radiographs, and also as a color, fully manipulatable 3-D image.

Sealed Tube Neutron Generator. The API system consists of a state-of-the-art sealed tube neutron generator (STNG) that produces the 14 MeV neutrons.

Alpha Particle Detector. The alpha particle detector is composed of a fast (1.4 ns decay time) phosphor [ZnO(Ga)] film deposited on the inner surface of a fiber-optic window and a position sensitive photomultiplier tube (PMT).

Gamma-ray Instruments. These instruments will consist of BaF_2 and NaI photomultiplier detectors initially, with high purity Ge detectors used when high energy resolution is required.

TECHNICAL PERFORMANCE

API system performance depends on complex factors that are beyond the scope of this profile, but an attempt is made to describe key aspects. Fundamentally, the imaging performance is based on timing of individual neutrons and accurately identifying the interaction location where gamma-rays are produced. Therefore, neutron production rates must be kept low enough to minimize coincidence interactions (i.e., having two neutrons in flight at the same time). This counting rate limitation is theoretically about 2 x 106 n/s produced traveling in the direction of the target. This neutron rate has about 10% random coincidence rate for an image object that is 2 m from the n-source and the longest flight times are about 50 ns. The visibility of the object also depends on: (1) the probability of neutron scattering with associated gamma-ray production, (2) the density of shielding and analyzed materials, (3) the energy of produced photons, and (4) the distance of travel through dense materials. Other key aspects governing performance are: (1) the position resolution and response time of the alpha detector, (2) the energy resolution and efficiency of the gamma-ray detector, and (3) the computational speed of the data reduction algorithms. API provides copious information about the object being imaged. The image is resolved into many volume elements. There are 80 x 80 x 60 resolvable volume elements in x, y, z, respectively. This is more than 380,000 resolvable spatial elements, each of which has an associated gamma-ray spectrum for isotopic identification. It is the combination of the count-rate limitation and the spectral information requirements that dictates the data collection time for API.

Laboratory Tests. To date the API has been laboratory tested, and several models have been studied to optimize and predict the performance of the API in field demonstrations. Figure 2.1b and 2.1c show the experimental setup and the resulting fully manipulatable 3-D image of a laboratory test. The purpose was to show how two materials can be identified and geometrically distinguished. API was applied to image a container partially filled with NaCl and another filled with water. In the original image, colored voxels (group of pixels representing a finite volume in 3-D) are associated with each type of material as determined by gamma-ray energy.

The field deployable version of the API system was built and was deployed in May 1995. The STNG was updated to an all metal configuration to provide ruggedness and internal containment of high voltages. The full computer system with image analysis tools was obtained. Data enhancement is a recent addition (not applied in the Figure 2.1b). One of the programs increases the effective resolution of the API display by "de-blurring" the statistically determined aberration associated with particle imaging.

Cost Data. The basic API system will cost about \$750K. The price break down is: (1) basic components (STNG, HV power supply, computer system,

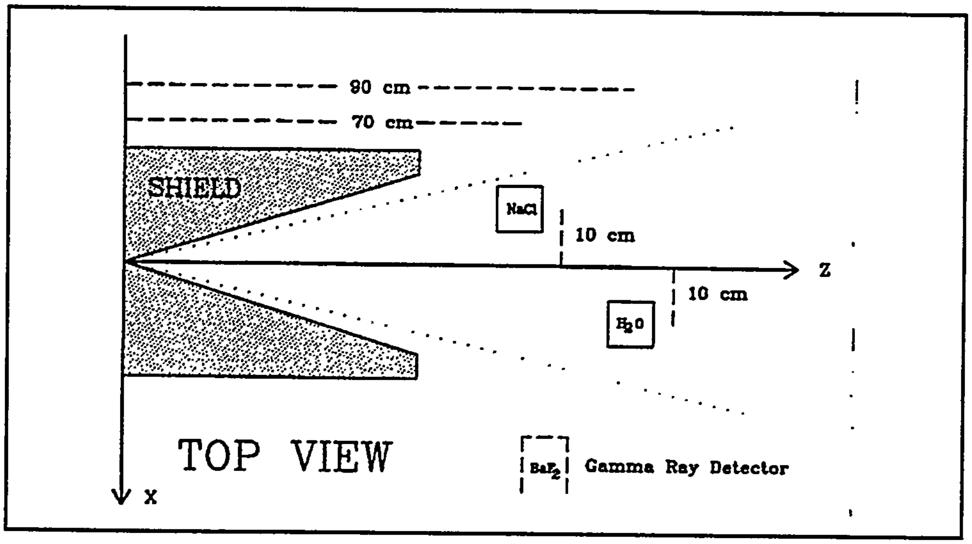


Figure 2.1b. Top view of the salt and water image configuration.

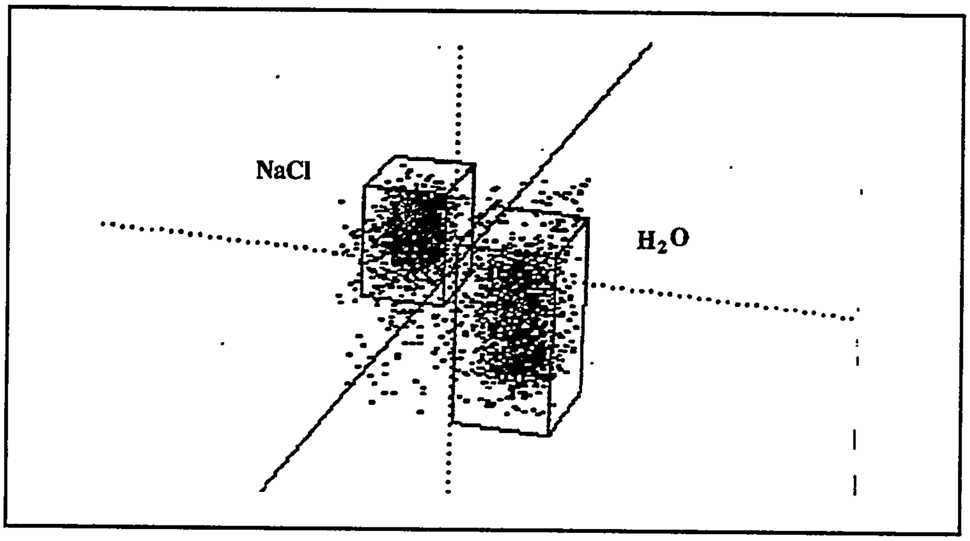


Figure 2.1c. 3-D imaging capabilities of API.

and miscellaneous hardware), $500K-600K; (2) NaI detector pods (two are recommended), $50K each; and (3) an HPGe (high purity germanium) detector (one is recommended), $60K each.

PROJECTED PERFORMANCE

The API system will be field tested in FY 1995; data results will be available shortly thereafter.

APPLICABILITY

This technology is applicable for imaging and characterizing contamination that exists in shielded environments. The high energy nature of produced gamma ray and the penetrating nature of neutrons make this applicable to situations where x-ray radiography may be insufficient. The neutron interrogation aspect of the technology enables elemental analysis of materials through radiation shielding while many imaging technologies must have physical access to both the front and backside of an interrogation region; API requires physical access to only one side.

The technology will produce elemental analysis and selected images of contaminants in concrete floors at a DOE site to be identified. Based on the results, API systems and experiments will be designed for future D&D measurements where 3-D information about enclosed volumes such as cascade pipes in gaseous diffusion pipes is a prime D&D requirement.

STATUS

This technology is in the prototype stage of development. Laboratory testing was performed but the first field demonstrations are not completed.

REGULATORY CONSIDERATIONS

Potential users may need a radiation license. Registration with the Nuclear Regulatory Commission or a similar regulatory agency may also be required depending on the rules of the state in which the system will be used.

POTENTIAL COMMERCIAL APPLICATIONS

A potential application for this technology is contraband interdiction. The petroleum industry is interested in the special neutron generator for providing more information of the subsurface via borehole logging than is currently available.

BASELINE TECHNOLOGY

There is no baseline technology for imaging and identification of materials behind thick radiation shielding.

INTELLECTUAL PROPERTY

A patent application was filed for a sealed tube neutron generator specialized for geophysical measurements.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigators

Paul Hurley and Laura N. Tunnell
Special Technologies Laboratory
5520 Ekwill Street, Suite B
Santa Barbara, CA 93111
(805) 681-2472; (805) 681-2411
(805) 681-2471 FAX

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

REFERENCES

1. Tunnell, L.N., Current Status of the Associated Particle Imaging System at STL, Special Technologies Report, EGG-10617-3008, January 10, 1992.

2. Tunnel, L.N., API Detection of UF_2O_2 Pipe Residue, 1994.

CHARACTERIZATION OF RADIOACTIVE CONTAMINATION INSIDE PIPES WITH THE PIPE EXPLORER™ SYSTEM

DESCRIPTION

A piping inspection system is being developed that couples gamma and beta scintillation detectors with an inverting membrane deployment system. The basic process involves inverting a tubular impermeable membrane under air pressure. The membrane is inverted inside the pipe from a pressurized canister located at the pipe's entrance. A radiation sensor is towed down the interior of the pipe by the membrane. The detector's signal is transmitted back to the canister through conductors enclosed in the tether. Count rates are recorded as a function of deployed depth in the pipe, and a multichannel analyzer provides energy discrimination of the gamma sources (see Figure 2.2a).

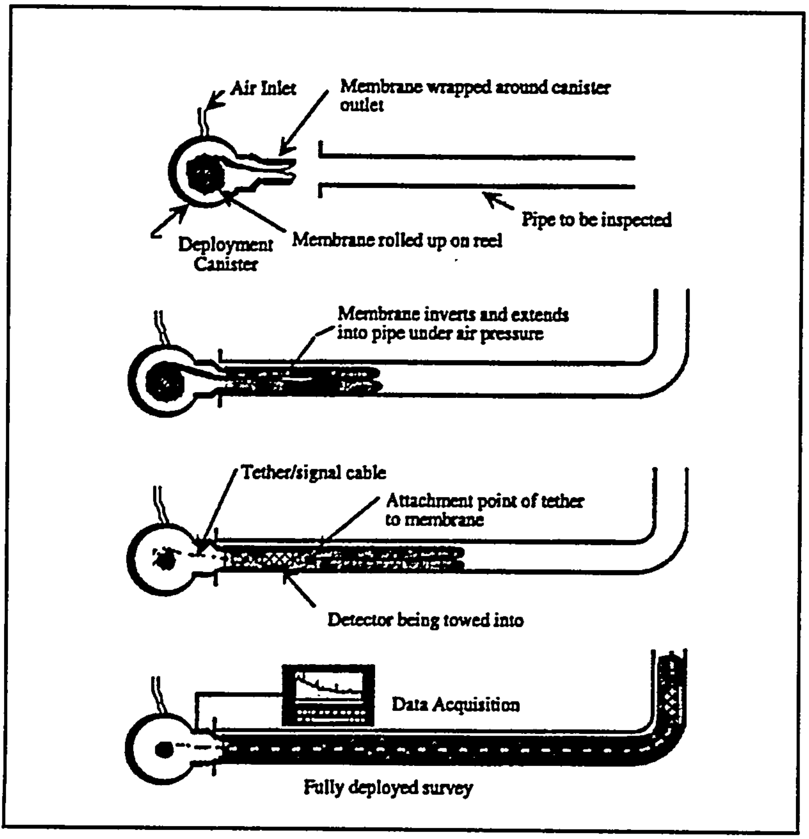


Figure 2.2a. Sequence of operation for transporting detectors into contaminated piping using the Pipe Explorer™ Survey System.

The Pipe Explorer™ system is versatile in that it can negotiate bends (90°) and limited obstructions, can travel horizontally and vertically, and can inspect pipes of smaller diameter than is possible with current pipe crawler technology. Emplacement and retrieval rates can be slow or fast (0.5 to 50 ft/min) and positional control is accurate with standard depth counting techniques. The system is unique in that the detector does not contact the contaminants.

TECHNICAL PERFORMANCE

An inverting membrane deployment system was designed and extensively tested in the laboratory. Various materials were tested to evaluate their ruggedness and deployment characteristics. Gamma and beta scintillation detectors were procured and tested with calibrated sources. Radiation transport modeling evaluated the measurement system's sensitivity to detector position relative to the contaminated surface, the distribution of the contamination, background levels, and source energy levels. An initial field demonstration was conducted at the Idaho National Engineering Laboratory (INEL) Idaho Chemical Processing Plant (ICPP) in 1994. During the summer of 1995, the system successfully surveyed drain lines at a DOE Formerly Utilized Sites Remedial Action Program (FUSRAP) site.

Deployment System. The deployment system consists of thin plastic film membranes, a pressurized canister assembly, a variable speed drive motor, an air source, and a remote control/monitoring system. The deployment system components allow the operator to select either deployment or retrieval at a specific rate. The system then controls the process within preset operational parameters until fully retrieved or deployed. Operational parameters monitored continuously include tether tension, detector location, and membrane pressure. The control system was tested extensively and worked as desired.

The deployment system was tested on various 1.5" to 6" diameter pipes with a maximum length of 200 ft. For the larger pipe diameter, four or more 90° elbows were negotiated in the 2", 200 ft long line. If shorter pipes are to be inspected, more elbows can be negotiated. Qualitative information was obtained with regard to pipe obstructions and in-line valves. Initial lab tests performed on 3" and 4" diameter pipes proved the ability of the deployment system and detector to negotiate 25% cross-sectional area obstructions with little or no difficulty.

The membranes selected for deployment are typically oversized by 20 to 50% of the pipe diameter. The best general purpose membrane used for deployment proved to be 100% low-density polyethylene (LDPE).

Radiological Measurements. The demonstration at the INEL/ICPP, FUSRAP site, and laboratory tests of the Pipe Explorer™ demonstrated the utility of the system to deploy radiation detectors into a variety of piping con -figurations. The detectors were successfully deployed with the system and were shown to have the sensitivity required to make very low-level (release level) measurements inside of pipes. For example, during a laboratory test a ^{60}Co source with an NIST traceable calibrated activity of 1,000 dpm/100 cm^2 was placed inside of 3" schedule 40 steel pipe. A 2" x 2" NaI detector used to survey the pipe showed that low activity radioactive sources are distinguishable from the background. Beta measurements of activity as low as 500 dpm/100 cm^2 have been demonstrated.

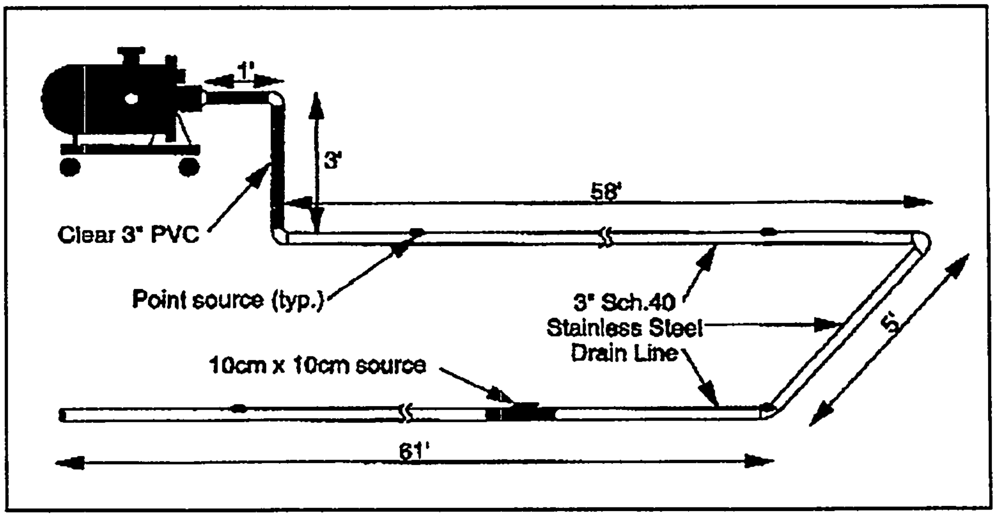


Figure 2.2b. INEL/ICPP drain line mockup.

The INEL/ICPP drain line mockup configuration (with calibrated sources mounted on the outer surface of the pipes) is shown in Figure 2.2b. The system clearly located the sources with the detector moving at 0.5 ft/min.

Cost. The LDPE membrane material ranges from $0.03 to $0.05 per lineal foot. Typically a 200 ft membrane costs less than $10 and consumes less than half a cubic foot in volume. Consequently, to consider the membranes disposable after each use is less expensive and produces less secondary waste. This also eliminates cross contamination measurement issues. Two operators are required to perform the survey.

PROJECTED PERFORMANCE

Future enhancements include adding an alpha measurement capability.

APPLICABILITY

This Pipe Explorer™ system is applicable to the inspection of piping, drain lines, and ducts for radionuclide contamination.

STATUS

The technology was successfully demonstrated in piping systems at INEL and a DOE FUSRAP site and will be demonstrated at additional DOE sites in 1995. These demonstrations will include deployment of a beta radiation detector, video survey, and pipe locating beacon.

REGULATORY CONSIDERATIONS

Regulatory considerations vary depending on where the technology will be used, the nature of the contaminants, and the intended application of the technology.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is applicable to inspection of piping in the nuclear industry.

BASELINE TECHNOLOGY

Radiological surveys of pipes are normally accomplished by passing a handheld radiological sampling instrument over the exterior surface of a pipe. For a complete survey, this requires personnel to gain access to the entire exterior surface of the pipe over its full length. Access is frequently restricted and the process is difficult, time consuming, potentially hazardous, and not readily capable of detecting threshold surface contamination values.

INTELLECTUAL PROPERTY

A patent application was filed.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

David Cremer
Science and Engineering Associates, Inc.
6100 Uptown Blvd., NE, Suite 700
Albuquerque, NM 87110
(505) 884-2300; (505) 884-2991 FAX

DOE Program Manager

Jerry M. Hyde
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7914

REFERENCES

1. "Pipe Explorer™, Detection of Radionuclide Contamination in Pipes for Nuclear Facility Decommissioning," Data Sheet, Science and Engineering Associates, Inc., Santa Fe, NM.

2. Lowry, W., D. Cremer, and E. Cramer, "Characterizing Internal Surfaces of Pipes for Radiological Contamination with Inverting Membrane Systems," Proceedings from Spectrum '94, Atlanta, GA, August 14-18, 1994.

3. Cremer, D., E. Cramer, T. Kendrick, W. Lowry, "Pipe Explorer™ - Field Demonstration at an Integrated Pipe Inspection System," ER '95 Proceedings, Denver, CO, August 1995.

COHERENT LASER VISION SYSTEM

DESCRIPTION

The Coherent Laser Vision System (CLVS) is a fiber-optic coupled FMCW coherent laser radar. It is an improvement over bulk optical versions previously developed by the Technology Research and Development Group of Coleman Research Corporation (CRC). A 3-D mapper consisting of a fiber-optic coherent laser radar with a precision mechanical scanner was recently completed. The CLVS with a no-moving-parts acousto-optic scanner is being developed for robotic applications. The CLVS will provide a substantial advance in accuracy for high speed 3-D imaging.

The CLVS will provide 3-D monitoring for situations in which it is necessary to update geometry of significant portions of the world model. The CLVS scanner will allow random access to the whole raster of pixels of a scene with transition time between pixels independent of pixel location. Thus, whole scene digitized data will be available to support operations in which robotic systems are altering the geometry of a scene as in waste removal, surface scarafying, equipment disassembly and removal, or autonomous vehicle operations.

The basic configuration is shown in Figure 2.3. A small portion of the output light is directed into the local oscillator (LO) path via a power tap. The remainder of the light is focused by the antenna lens into the range measurement area of interest. Light reflected from a surface in this area is recollected by the lens, directed into the return signal path by the optical circulator by means of a polarization diplexing scheme and mixed with the LO light at the second 3-dB coupler. By using two detectors and a differential amplifier, common mode rejection of amplitude noise is achieved.

TECHNICAL PERFORMANCE

The CLVS: (a) is not sensitive to lighting or surface shading, (b) is eyesafe (Class 1 device), (c) provides random order pixel addressability, and (d) provides pixel transition time independent of pixel location.

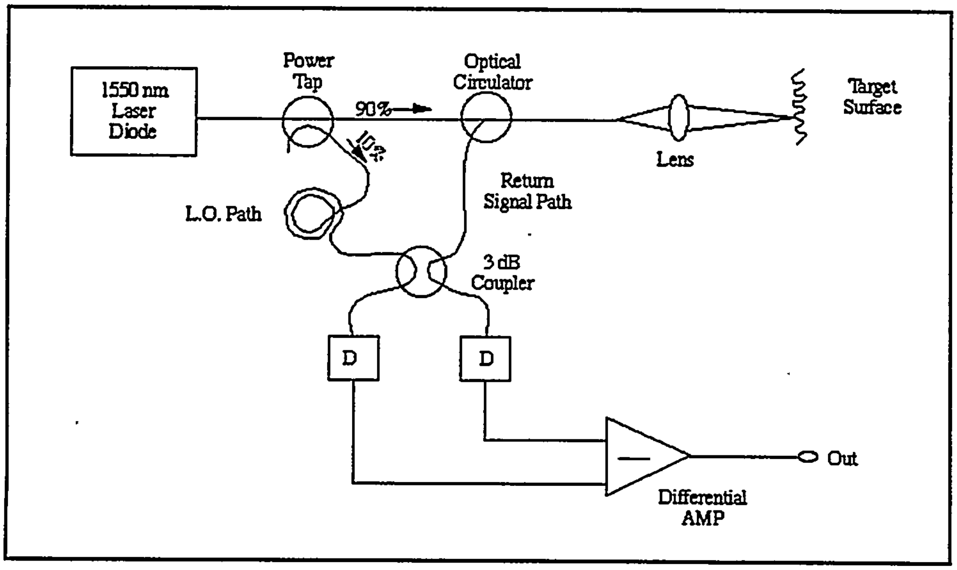


Figure 2.3. Basic fiber-optic FMCW coherent laser radar configuration.

PROJECTED PERFORMANCE

A CLVS field deployable prototype will be developed by CRC in a two phase program. Table 2.3 shows the projected performance specifications of the baseline 3-D vision demonstration system that is being developed during the first phase.

Table 2.3. Projected performance of the 3-D demonstration system.

Frame size:	(128 x 128) 3-D coordinates
Frame speed:	1 frame per second
Range accuracy:	$s_R = 1$ mm
Working range:	to 10 m
Instantaneous working range:	1.5m

During the second phase, the Phase I capability will be extended to a field deployable prototype 3-D vision system with expanded performance parameters including the ability to image (256 x 256) frame of 3-D measurements at a one frames per second rate. This instantaneous working range will be expanded to 5 m. This enhanced performance will be accomplished by the implementation of a "smart receiver" processing algorithms that maximize the use of a priori range information to streamline the real-time Coherent Laser Radar range processing computation. The effort will also yield a compact, no-moving-parts 3-D vision scanner. The fieldable prototype will output both range and intensity images.

The range accuracy and number of resolvable range values will be order of magnitude improvements over existing technology such as systems using pulsed or amplitude modulation sources and direct detection.

APPLICABILITY

The intended use of the CLVS is to generate raster scanned range images that provide a precision 3-D world model to support robotic operations. CLVS monitoring is intended for scene altering operations such as: (1) structure and equipment dismantling, (2) equipment moving or removal, (3) waste retrieval, (4) surface scarafacing (5) excavation, and, (6) autonomous vehicle operation.

STATUS

Phase I work is ongoing. A laboratory demonstration system is expected to be completed in November 1995 and the field deployable prototype in June 1996. The CLVS will be produced by CRC as a commercial/industrial system and will be available in 1996.

REGULATORY CONSIDERATIONS

The CLVS will have a Food and Drug Administration Class 1 certification. It is unconditionally eyesafe and is not expected to cause any environmental impacts.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include: (1) industrial robotics, (2) medical monitoring, (3) automatic personnel, or (4) object recognition.

BASELINE TECHNOLOGY

The existing technology is a programmable 3-D mapper that dwells longer for each range measurement (fewer than 10,000 measurements per second) and performs range measurements at a programmable, computer-controlled sequence of azimuth and elevation angles using a precision mechanical scanner. A 3-D programmable mapper can less frequently provide very high precision maps or track single objects such as robot end effectors.

INTELLECTUAL PROPERTY

Existing patents:

Frank E. Goodwin, "FM Laser Radar," Patent No.: 4,830,486, Patent Owner: Coleman Research Corporation.

Frank E. Goodwin and Dana Simonson, "3D Vision Using Coherent Optical Detection," Patent No.: 5,114,226, Patent Owner: Coleman Research Corporation.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Richard L. Sebastian
Coleman Research Corporation
6551 Loisdale Court, Suite 800
Springfield, VA 22150
(703) 719-9200; (703) 719-9229 FAX

DOE Project Manager

Vijay Kothari
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507-0880
(304) 285-4579

REFERENCE

1. Sebastian, R.L., R.B. Clark., D.L. Simonson, and A.R. Slotwinski, "Fiber Optic Coherent Laser Radar 3D Vision System," SPIE '94 Symposium, 1994.

N-SCAN™ PROMPT GAMMA NEUTRON ACTIVATION ANALYSIS

DESCRIPTION

A high signal-to-background approach to Prompt Gamma Neutron Activation Analysis (PGNAA), employing a pulsed source of neutrons and concurrent acquisition of multiple gamma spectra which have specified time correlation to the neutron pulses has been developed. The N-SCAN™ approach was developed specifically to address the non-intrusive, in situ detection and quantification of trace contaminant elements in host matrices (e.g., soil, concrete, or drummed waste). Applications include in situ characterization of soil or concrete, detection of trace contaminants in sealed drums or packages, and identification of chemical weapons (CW) agents in shells or other casings. The technology performance is excellent for mercury, chlorine, cadmium and boron, and is expected to be good-to-excellent for ^{235}U and ^{99}Tc. It is effective for most Resource Conservation and Recovery Act (RCRA) regulated metals at varying levels of sensitivity, depending on system configuration. The system performance for detection of ^{238}U or ^{232}Th through passive γ-ray spectroscopy capabilities is also excellent. The technology is being demonstrated for in situ measurement of contaminants in concrete floors or walls. In this application, N-SCAN™ is expected to provide significantly reduced cost and risk when compared to the alternative of core sampling and analysis using wet chemistry or other conventional methods.

TECHNICAL PERFORMANCE

The detection limits and measurement time are interrelated but several special cases are summarized in Table 2.4. The table entries are based on data taken from cement samples bearing trace contamination and well-understood scaling relations. Listed is the minimum uniform concentration in the region within a few inches of the surface, which would provide a measurement having 95% confidence in 50 minutes of interrogation. Note that these projections specifically use data from signature γ-rays of low energy, which would be indicative only of the contaminant burden in a layer near the surface. In most cases, other, more energetic signature gammas are also detected and could be used to project sensitivities for contaminant burdens at greater depths. Note also that ^{238}U and ^{232}Th are included; they are measured with the passive capability of the N-SCAN™ system.

The N-SCAN™ PGNAA approach requires sufficiently low neutron doses that within minutes of completion of the measurement, no radioactivity above background is detectable; thus, the technology generates no waste. The system performance is dependent on the nuclear properties of the contaminants of concern; however, dependence on surrounding conditions (e.g., water) is minimized through the use of a specially designed sensor configuration for near-surface interrogation. For deeper interrogation

Table 2.4. Projected near-surface limits of detection of N-SCAN™ System based on a 50 minute run.

Near-surface sensitivity data[a]	Contaminant							
	Hg	Cd	^{232}Th[c]	^{238}U[c]	Cr	Cl	^{99}Tc	^{235}U
Depth of interrogation [in] for quoted ppm sensitivity	2.5	3.0	2.1	3.5	3.3	3.5	2.0	3.0
Projected Limit of Detection,[b] ppm:								
From present system	35	10	18	140	2,220	370	1,100	300
From planned system upgrade	2	0.5	7	46	110	25	63	17

a Sensitivities for greater depths use data from higher energy γ–rays than cases shown
b volume-averaged concentration in quoted interrogation depth
c system in passive γ-spectroscopy mode

-- up to 1 foot in depth -- the water content of the matrix becomes a more important effect. However, the effective water content is available from the measurement, and self-consistent analytical corrections can be applied, if required. An analytical approach was also developed for extracting contaminant depth profiles from the results of a single irradiation.

The N-SCAN™ system is designed to be operable by two trained technicians. The system can use shielding materials or distance to ensure radiation safety, according to the requirements dictated by available space and customer access needs.

Cost. N-SCAN™ Field Assay will be provided through Scientific Ecology Group, Inc. (SEG), a wholly-owned subsidiary of Westinghouse. Upon commercial availability, rates will be available from SEG, and will vary according to workscope.

PROJECTED PERFORMANCE

Table 2.4 indicates the performance expected in the near term.

APPLICABILITY

The technology is well suited to hazardous (RCRA) elements, ^{235}U and ^{99}Tc. Applicability to other transuranic (TRU) isotopes is credible based on available nuclear data. The system in the subject program is specifically designed for in situ interrogation of concrete. However, configurations for drums, tanks or other applications can be developed.

STATUS

The system was developed to the pilot-scale. Initial full-scale applicability is planned for the end of the second phase of the current DOE-sponsored program. At that time, commercial availability is also expected, through SEG. In situ soil and concrete and ex-situ Chemical Weapons agent applications have been demonstrated.

REGULATORY CONSIDERATIONS

System operation requires a license for the site to temporarily possess the 2 Ci tritium inventory of the sealed neutron tube, and a license or permit to operate the system. The system was licensed and operated in Texas and Pennsylvania, and licensed for operation in Tennessee. A general license application is being prepared for submission to the U.S. Nuclear Regulatory Commission. Specific licenses are generally not required for operation on DOE or DoD sites.

In the current program, Westinghouse has established contact between the DOE and the USEPA's Office of Federal Facility Enforcement (OFFE) and Emerging Technology Initiative to prepare the path forward for eventual acceptance of N-SCAN™ results.

There are no environmental impacts from operation of this technology.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications of the N-SCAN™ technology include:

- In situ or ex-situ characterization of contamination in environmental samples.
- Noninvasive sorting of drummed waste for shipment or treatment.
- Pretreatment characterization of waste drums at processing facilities.
- Monitoring of remediation process line performance.
- Identification of Chemical Weapon (CW) or other agents for treaty verification.
- In situ identification of CW agents in non-stockpile applications.
- In-line monitoring of chemical process line performance.
- Detection of concealed explosives at government or private installations.

BASELINE TECHNOLOGY

The baseline technology for measurement of contaminants in concrete and walls is core sampling and analysis using wet chemistry or other conventional methods.

INTELLECTUAL PROPERTY

The N-SCAN™ approach to PGNAA and its use for in situ characterization of soil and concrete were developed by Westinghouse and are Westinghouse proprietary. Purchasing, leasing, and licensing arrangements for N-SCAN™ systems and services are negotiable through SEG.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Thomas Congedo
Westinghouse Electric Corporation
Science and Technology Center
1310 Beulah Road
Pittsburgh, PA 15235-5098
(412) 256-1084
congedo.t.v%wec@dialcomm.tymnet.com

DOE Contracting Officer Rep.

Scott Renninger
U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507-0880
(304) 285-4790

REFERENCES

Contact the Morgantown Energy Technology Center for the Phase I Final Report entitled "Treatability Study using Prompt Gamma Neutron Activation Analysis."

PORTABLE SENSOR FOR HAZARDOUS WASTE

DESCRIPTION

A field-portable monitor for sensitive hazardous waste detection using the technique of active nitrogen energy transfer (ANET) excitation of atomic and molecular fluorescence is being developed. The active nitrogen is made in a dielectric-barrier (D-B) discharge in nitrogen at atmospheric pressure. Figure 2.5a is a schematic of the instrument concept. Samples are fed into the D-B discharge region where the active nitrogen is generated, and where it transfers its energy to species in the sample, thereby exciting fluorescence from them. The pertinent fluorescence is then isolated by a small spectrograph or interference filter and is detected by a photomultiplier or diode array placed behind the filter or spectrograph. Signals from the detector are then processed by a computer and a report or screen display is generated.

ANET excitation generates only a few emission lines or bands for each hazardous species. Thus, spectral resolution requirements are greatly simplified over those of other techniques. Further, the power requirements are quite modest (<10 W) so that the unit can be powered by batteries, making the instrument readily portable.

TECHNICAL PERFORMANCE

Laboratory Study. The first phase of development of the portable sensor was a laboratory study of hazardous species detection in a D-B discharge in N_2 at atmospheric pressure. The primary activity involved characterizing the D-B discharge spectroscopically, both with and without added species, to gain an understanding of the basic operation of the discharge. When species were added, the fluorescence spectrum resulting from their addition was characterized, and in some instances, the variations in fluorescence intensities (characteristic of the additives) were determined as a function of concentration of the added species.

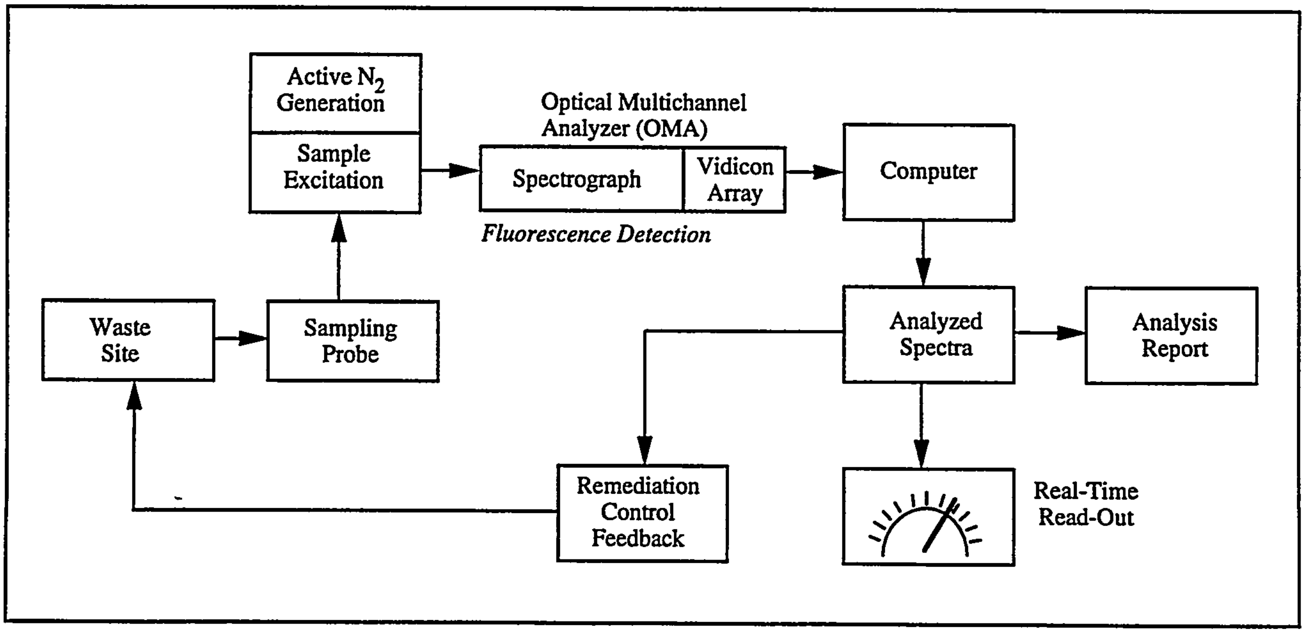


Figure 2.5a. Block diagram of ANET Analysis System.

An apparatus was constructed to perform laboratory experiments. The apparatus consisted of a D-B discharge lamp, a power source, an optical multichannel analyzer, and gas handling lines.

Figure 2.5b shows the spectral region in the vicinity of the mercury (Hg) 253.7 nm emission line. The Hg line is prominent in the spectrum, and is surrounded, but well separated from several bands of the NO gamma system. These bands are also excited by energy transfer from metastable nitrogen. The NO is formed in the discharge in reactions involving oxygen in the nitrogen. Figure 2.5c shows the D-B discharge spectrum when Hg at four different mole fractions was added to the discharge. The spectra are the difference between the D-B discharge spectrum with added Hg, and that in the absence of added Hg. The spectra illustrate qualitatively that the intensity of the Hg line increases in proportion to the mole fraction of Hg added.

Identical spectra of CN emissions were observed for a number of hydrocarbons including: hexane, acetone, methanol, isopropanol, 1,2-dichloroethane, trichloroethylene, 1-chlorobutane, and even bromotrifluoromethane.

The effect of adding small quantities of dust to the D-B discharge region was investigated to determine whether the presence of dust in the discharge region would compromise the operation of the D-B discharge and whether species adhering to dust could be detected. For the test, simulated-cement dust was spiked with a few drops of an aqueous Hg solution to 1 to 2g of dust. The powders used to make the particulate sample were generally 1μm or less in diameter. The resulting spectrum showed only one spectral feature of significance: the 253.7 nm emission from atomic Hg. Thus, it was demonstrated that ANET can be used to detect mercury adhering to particulate samples.

As a result of the laboratory study, the overall sensitivity of Hg and selenium was determined to be at sub parts-per-billion, and that for the organic species to be on the order of a few parts per billion. ANET: (1) can also differentiate between chlorinated and non-chlorinated organic species, (2) can detect different heavy metals simultaneously, (3) can differentiate elemental Hg from Hg tied up as chloride, and (4) can detect species adhering to particulates. In addition, ANET appears to have the potential for uranium detection.

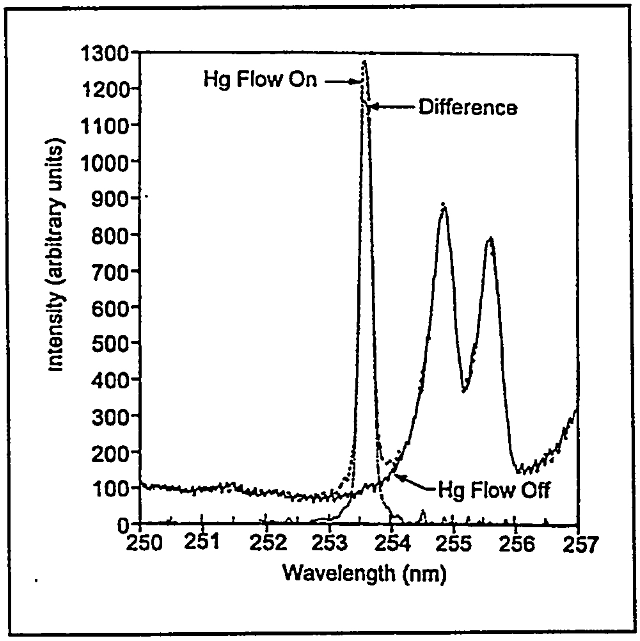


Figure 2.5b. Spectrum of D-B discharge in the absence and presence of added Hg.

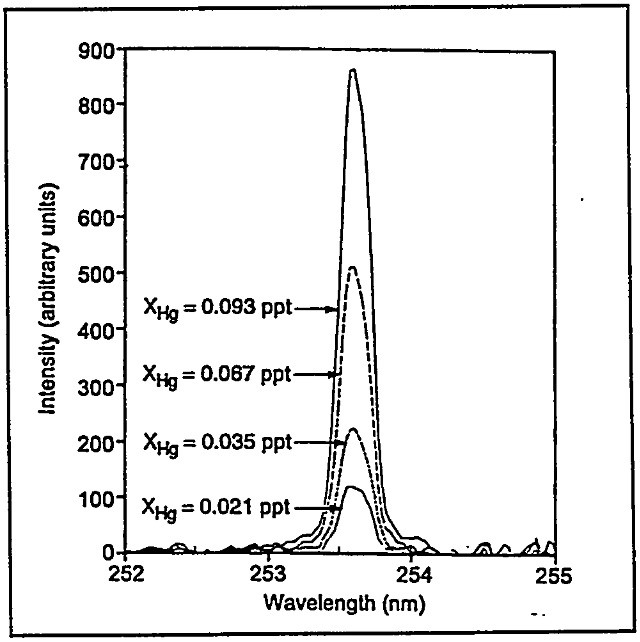


Figure 2.5c. D-B discharge spectra for four different Hg mole fractions.

PROJECTED PERFORMANCE

In the second phase of the development of the portable sensor, the focus will be on the important components and processes involved in the ANET analysis system. Software to automate instrument operation and data analysis will be developed. The following will be addressed: sample collection and introduction systems; active nitrogen source stability; fluorescence detection and analysis; measurement and calibration; and test procedures.

The third and final phase of the program will involve fabrication and field testing of the alpha-prototype instrument designed during the program's second phase.

APPLICABILITY

The portable sensor being developed will have the capability to detect hydrocarbons, both chlorinated and nonchlorinated; transuranics; thorium; and heavy metals including mercury, chromium, cadmium, arsenic, and lead.

STATUS

The first phase of work demonstrated that ANET technology holds great promise for development into a sensitive, multielement hazardous species monitor. During the second phase (beginning June 1995), a breadboard instrument will be developed and characterized under realistic conditions. The results will then be used to design, in detail, a first-generation, or alpha-, prototype instrument. During the third phase (scheduled to begin in February 1997) the alpha-prototype instrument will be built and field tested.

The ANET technology will be transferred to Spectrum Diagnostix, a subsidiary of Physical Sciences, Inc. (PSI). They have commercialized several instruments initially developed at PSI.

REGULATORY CONSIDERATIONS

This technology will not require any permits nor are there any regulatory barriers to its implementation, as it causes no environmental impacts.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include on-line monitoring of toxic heavy metal levels and chlorinated hydrocarbons at building sites, hazardous waste landfills, and from combustor flues.

BASELINE TECHNOLOGY

Analytical methods currently used require sampling and laboratory analysis which is time consuming and expensive.

INTELLECTUAL PROPERTY

The disclosure process for this technology was completed and a U.S. patent will be filed. PSI is the technology developer. Spectrum Diagnostix will be responsible for commercialization. The commercialization strategy may involve a partnership between Spectrum Diagnostix and a large industrial firm to achieve effective market penetration.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Lawrence G. Piper
Physical Sciences, Inc.
20 New England Business Center
Andover, MA 01810-1022
(508) 689-0003; (508) 689-3232 FAX

DOE Program Manager

Texas Chee
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874
(301) 903-7926

REFERENCE

1. Piper, L.G., H. Du, M.E. Fraser, and S.J. Davis, "Portable Sensor for Hazardous Waste," Proceedings of Opportunity '95 - Environmental Technology Through Small Business, V.P. Kotheri, ed., DOE/METC-95/1014. Available from NTIS (DE95000040), 1994, pp. 229-244.

RAPID SURFACE SAMPLING AND ARCHIVAL RECORD SYSTEM

DESCRIPTION

The characterization of equipment and building surfaces for the presence of contaminants as part of building decontamination and decommissioning activities is an immensely large task of concern to both government and industry. Because of the high cost of hazardous waste disposal, old contaminated buildings cannot simply be demolished and scrapped. Contaminated and clean materials must be clearly identified and segregated so that the clean materials can be recycled or reused, if possible, or disposed of more cheaply as nonhazardous waste.

By providing rapid analyses and a large number of accurate measurements of surface and subsurface contamination, the cost of remediation of large industrial sites will be dramatically lowered because both the characterization time and the material fraction that must be remediated will be reduced. The Rapid Surface Sampling and Archival Record (RSSAR) system is a portable instrument that can rapidly analyze structural material surfaces including concrete, steel, transite, and asbestos. The target contaminants include polynuclear aromatics, polychlorinated biphenyls (PCBs), and other semivolatile hydrocarbons.

The RSSAR system will be a modular instrument made up of several components including:

- Sampling heads for thermally extracting contaminants from concrete surfaces and steel surfaces.
- Quick-look detectors to give rapid (near real time) assessment of contamination levels. Both photoionization and ultraviolet detectors will be developed.
- Multisample trapping module to trap and store vaporized contaminants in a manner suitable for subsequent detailed lab-based analyses.

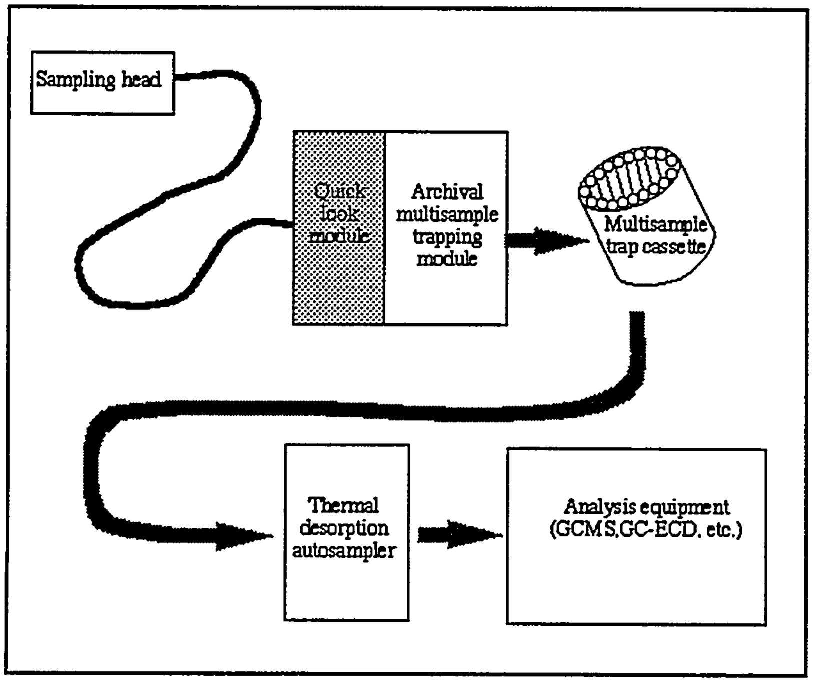


Figure 2.6a. Configuration of the RSSAR System.

The overall experimental configuration is shown in Figure 2.6a.

Thermal methods were demonstrated to be very effective at extracting semivolatile organics from porous solid matrices. A thermal sampling head was developed for contamination measurements on concrete surfaces. Future developments include a thermal sampling head for contaminants on steel surfaces. Samples will be collected using thermal desorption from surfaces warmed to approximately 250°C by radiant heat transfer. As an example, the concrete sampling head is connected to a "quick-look detector" whose purpose is to provide an immediate distinction between contaminated and uncontaminated surfaces. From the quick-look detector the contaminant-laden air is pulled through a sorption tube that provides long-term storage of contaminants for detailed analysis. In operation, the quick-look indication will be passed along with the sorption tube to indicate which tubes require detailed analysis and to permit avoidance of analysis of uncontaminated samples. It is intended that the sorption tubes will be held in a cassette capable of holding enough tubes for several hours of measurements, at a rate on the order of ten measurements per hour. Sample acquisition and analysis will be automated.

An archival multisample trapping module will be developed that will allow trapping of as many as 50 separate samples and will allow their transfer to a modified thermal desorption autosampler for subsequent analyses. The thermal desorption autosampler transfers sample records to various analyses including gas chromatography/mass spectrometry, tandem mass spectrometry, gas chromatography with electron capture detector, or a fast optical readout such as surface-enhanced Raman scattering. By manipulating sample and substrate size, quantities of PCBs of interest to the DOE (10 mg on 100 cm^2 surface) should easily be detectable.

TECHNICAL PERFORMANCE

Sampling Artifact Studies. The production of dibenzofurans (for example, dichlorodibenzofuran, DCBF) and dibenzodioxins during heating of concrete or other samples contaminated with PCB was a concern. Only one polychlorinated dibenzofuran (PCDF) congener was formed during all the thermal reactions studied in the temperature range 200 to 250°C. The parent PCB congener was 2,2',5,5'-tetrachlorobiphenyl. Other pathways for similar PCDFs were studied. Concrete is a very alkaline environment and certain pathways are probably favored under high pH. Even if PCDF formation rates near 200°C are found to be small, it may be necessary to control the thermal sampler heads to within fairly rigorous tolerances ($\leq$250°C surface temperature) to avoid formation of non-negligible amounts of PCDF.

Concrete Sampler Head. In its present form, initial thermal measurements support an expectation that the concrete sampler head will meet heating uniformity criteria over at least 60% of the sampling area. Sample thermal uniformity during heating is a design goal. Efforts to increase this fraction are underway and are expected to be successful with a proposed design change in the sample head geometry. The old head used a commercial 1,000 W filament in a spherically symmetric head cavity; the new proposed design will have a conic geometry with cylindrical symmetry and an IR source lamp instead of the previous visible source filament. Initial measurements indicate that peak temperatures are predictable within 10°C, in prepared samples. Provided that artifact effects can be controlled, the thermal performance of this equipment indicates that it should provide an excellent sampling method.

Concrete Sampler Head Functional Tests. The concrete sampler head was tested on concrete "cakes" that were prepared with contaminated sand. In total, seven concrete cakes were prepared that were 30 cm in diameter and 3.3 cm thick. One of the concrete cakes was prepared with clean sand, and was instrumented with thermocouples to enable the determination of settings necessary to bring the surface of the concrete to 250°C. It was determined that a 65 V input to the heating lamp was sufficient to bring the surface layer (top 1 mm) to 250°C in 4 minutes. This setting was used for subsequent tests.

The remaining six cakes were prepared using sand contaminated with anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane. These three compounds represent three typical kinds of environmental pollutants. The contaminated sand was mixed with clean sand, portland cement, and water and poured into cake molds. The concrete cakes were aged in 100% humidity for 7 days, then at 45% humidity for 6 months. The amount of contaminants recovered during thermal desorption experiments for cakes number 4 and number 6 are given in Table 2.6. This data is presented as an example for recovery during a five minute heating period over a 100 cm^2 heating area. Figure 2.6b shows two plots of concentrations calculated from the solvent trap measurements for cake number 6.

Bulk Sampler Head Design. The purpose of the bulk sampler head is to extract analytes from 1-5 mL of a bulk sample by thermal desorption. Typical bulk samples are drillings, pulverized concrete, and particulate waste. The bulk sampler can be used, for example, for deep sampling of concrete wherein the samples are acquired by drilling a concrete wall or floor. It can also be used to characterize general debris and soils. Another major use is to provide samples to test and calibrate quick-look modules and sorption devices. Consequent design requirements are rapid sample heating approximately 100 s, convenient cleaning and quick sample insertion, heated connection to the rest of the RSSAR system, and safe and rapid handling of samples. The performance was extensively tested in experiments on desorption with the photoionization detector (PID) and the UV absorption detector. In typical experiments, the majority of a 10 mg analyte such as phenyldodecane is evolved in about 4 minutes, after which the detection signal returns to background levels.

Near Vacuum UV Quick-Look Detector. The experimental results demonstrate clearly that minimum action levels of PCBs defined for wipe sampling are measurable with a conveniently sized NVUV absorption system. Sensitivity to oil and solvent surrogates is lower, which is desirable where PCBs are expected to be encountered with oils.

Table 2.6. Anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane recovered by the concrete sampler head from concrete cakes 4 and 6 and measured by GC-FID.

Cake	Compound	µg in 1 mm thickness	Total collected (µg)
#4	Anthracene	2116	355
	2,4,5-Trichlorobiphenyl	1888	1194
	Phenyldodecane	1888	1022
#6	Anthracene	529	121
	2,4,5-Trichlorobiphenyl	427	352
	Phenyldodecane	472	477

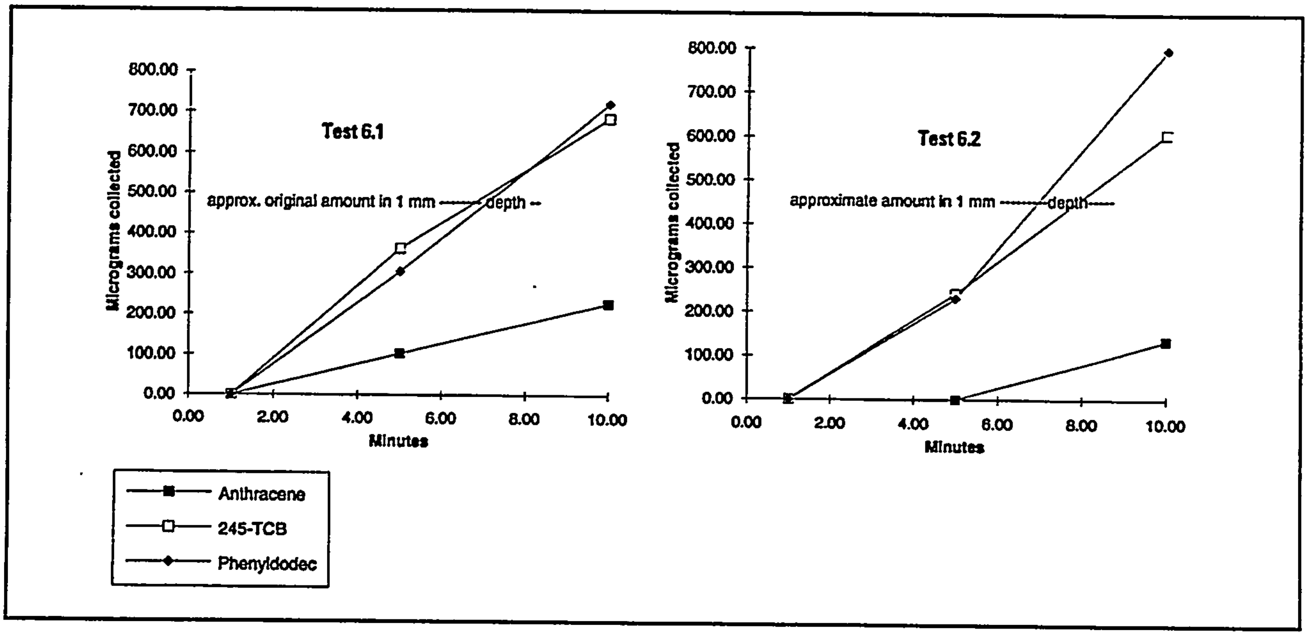


Figure 2.6b. Total extraction amounts versus time-derived from GC analysis of solvent traps. The first test number refers to the cake number and the second to the specific experiment. Two were run on each cake.

Sample Trapping Module. A key component of the RSSAR is the sample trapping module that holds a cassette of sampling tubes containing solid phase sorbent materials. When less efficient sorbents (Tenax GR, Carbopack B, Carbotrap C, XAD-2) were used significant breakthrough was observed, both in the presence and absence of water vapor. However, no detectable breakthrough was observed with the use of Carbopack 370 (trademark of Supelco, Inc.), including the cases where water vapor was evaporated along with the analytes, and in the experiment where Aroclor 1242 and transformer oil were trapped together. Based on these experiments, this material is the most effective sorbent among those tested for use in the RSSAR system. On the average, collection efficiencies greater than 80% were reported which exceeded Phase I performance requirements (>70% trapping efficiency) in all tested categories. During Phase II a multisample trapping module to replace the single sample trapping module demonstrated in Phase I will be developed. The sampler is capable of trapping up to 50 separate samples in a convenient manner, and transfer them to a modified commercially available thermal desorption autosampler for subsequent analysis.

Surface Enhanced Raman Spectroscopy. SERS presents advantages over normal Raman: (1) in the sensitivity and clarity of the spectra attainable, (2) in the ease of (automated) introduction of very small samples, (3) in its ability to quench fluorescence that would otherwise interfere with analyte detection, and (4) in its ability to partition the analyte from a mixed matrix. In Phase II, investigations will be performed using SERS as a quantitative method to evaluate environmental samples. Detecting PCBs is best done by using SERS coating technology, in which PCBs are partitioned from oil into a pentachlorothiophenol coating on a silver substrate. It was demonstrated that for a single congener in an oil contaminated mixture, quantitation at the detection limits of interest can be done.

Cost. The RSSAR system can potentially reduce the cost of measurements required for site remediation. Based on the types of contamination found at the Oak Ridge K-25 Site, the estimated cost for solid or wipe samples for oils and PCBs is $250/sample. The RSSAR system can provide results at an estimated cost of $32/sample, less than 15% of conventional methods.

Regulations proposed by the U.S. Environmental Protection Agency (December 6, 1995) would require sampling for PCBs at one meter intervals. This could require up to one million samples to characterize the floor, walls, and ceilings that encompass an area of approximately 1 km^2 at the K-25 site. The potential exists for millions of dollars in cost savings at this site alone.

PROJECTED PERFORMANCE

A fully integrated lab-scale system will be constructed in Phase II. A portable prototype system suitable for field operations will be designed and constructed during Phase III. A complete design of a production system will be prepared and two units built in Phase IV which is scheduled for completion in 1998.

APPLICABILITY

The RSSAR instrument system is being developed for the characterization of building and facility structural component surfaces for the presence of contaminants including polynuclear aromatics, PCBs, and other semivolatile hydrocarbons. The target building materials include concrete and similar porous building materials, steel surfaces, transite, and asbestos surfaces.

STATUS

Phase I of a four phase development schedule has been completed.

REGULATORY CONSIDERATIONS

Thermal desorption is not currently a EPA approved surface sampling methodology. However, thermal desorption sampling was proposed to the EPA for consideration in proposed changes to the PCB regulations covered under the Toxic Substances Control Act. This method has less adverse environmental impacts than current methods of using solvent soaked wipes with inherent waste disposal problems.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be used for characterization of surface contamination and bulk debris from building demolition, decontamination, and decommissioning activities at government and industrial sites. It can also be used for segregation of contaminated and non-contaminated waste and for characterization of contaminated soil.

BASELINE TECHNOLOGY

The most widely used current baseline method involves wipe sampling. In wipe sampling, the surface is wiped with a solvent-soaked piece of cloth, paper or the like, and the wipe is sent to an off-site laboratory for analysis. This method of analysis has a number of limitations:

- Very expensive and results are subject to human error and technique
- Does not provide real time information
- Tracking becomes a logistical nightmare because manual tracking is required when a large number of samples are involved
- Solvent usage raises safety issues
- Off-site analysis with manual sample preparation is expensive and time consuming
- Wipe method provides no way of effectively screening out a large number of the clean samples to reduce analysis costs.

INTELLECTUAL PROPERTY

Patent applications are being prepared. General Electric Corporate R&D owns the intellectual property.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Richard B. Sheldon, Ph.D.
General Electric Corporate R&D
Bldg K-1, Rm 3B35
P.O. Box 8
Schenectady, NY 12301
(518) 387-6565; (518) 387-7611 FAX

DOE Program Manager

Isiah Sewell
U.S. Department of Energy
Morgantown Energy Technology Center
12800 Middlebrook Road
Germantown, MD 20874
(301) 903-8459

REFERENCES

1. GE Corporate Research and Development, Rapid Surface Sampling and Archival Record (RSSAR) System, Phase 1 Final Report, Prepared for U.S. Dept. of Energy, Office of Fossile Energy, Morgantown Energy Technology Center, March 1995.

2. Barren, E., D.R. Berdahl, S.B. Dorn, S.F. Feldman, A.L. Ortiz, Jr., C.M. Penney, and P.R. Staver, "Thermal Sampling Head and System for Concrete Walls," 4th EPA and Waste Management Association International Symposium: Field Screening Methods for Hazardous Waste and Toxic Chemicals, Las Vegas, NV, February 1995.

THREE-DIMENSIONAL INTEGRATED CHARACTERIZATION AND ARCHIVING SYSTEM

DESCRIPTION

The Three-Dimensional Integrated Characterization Archiving System (3D-ICAS) is being developed to provide real-time, quantitative measurements of volatile organic compounds (VOCs) and radionuclides on bare materials consisting of concrete, asbestos, and transite. It will provide a 3-D display of the fusion of all measurement results, and it will archive the results for regulatory documentation. 3D-ICAS consists of two mobile robotic platforms (the sensor platform and the mapper platform) that operate in hazardous environments and are linked to an integrated workstation in a safe environment (Figure 2.7a). During characterization operations, the mapper, using its coherent laser radar (CLR), maintains its precise location and supports and reports the positioning of the multisensor probe by the sensor platform. The operator at the integrated workstation, using displayed 3-D map information, plans and directs the selection of surface areas to be characterized and the density of sampling to be employed. The 3D-ICAS then automatically samples the selected areas, and archives 3-D location, time, and contamination levels. The permanent archiving of the measurement data allows easy regulatory review of the characterization process and ensures data integrity.

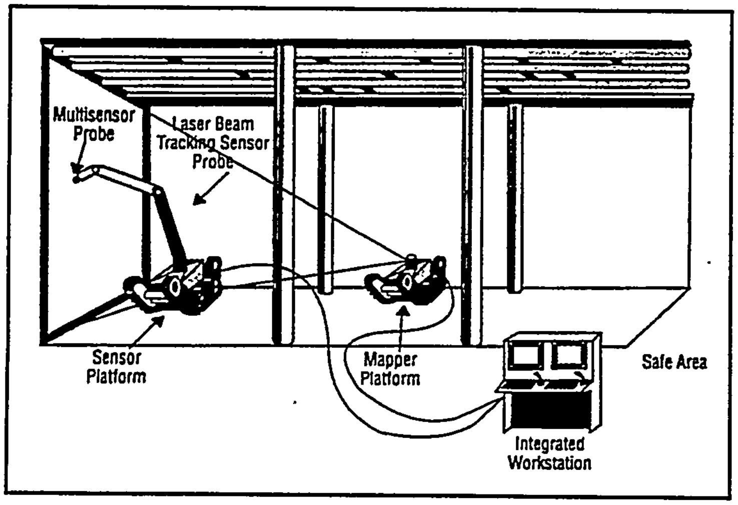


Figure 2.7a. Schematic of 3D-ICAS.

The dense, uniform surface sampling allows the straightforward establishment of the contour bounds of regions exceeding regulatory limits.

TECHNICAL PERFORMANCE

During Phase I, the 3-D CLR Mapper and a gas chromatograph (GC) were demonstrated, and molecular vibrational spectroscopic (MVS) sensors for inorganic base materials and organics were evaluated.

3-D CLR Mapper. Under Phase I, the 3-D Mapper demonstration system was capable of 3 degrees of freedom (3DOF) location (3-D location only) of a manually positioned GC sensor. During a demonstration, the GC was mounted on a manually positioned stage that could be moved along two axes, horizontal and vertical. Rotation was not allowed. The sensor head was manually moved a short distance and the position estimation system determined the vertical and horizontal position and range, in steps. The operator manually activated data acquisition, the location estimation processing, and contaminant measurement. Contaminant measurements were plotted on the 3-D map at the locations estimated for the sensor probe. The mean errors in vertical and horizontal coordinates were 0.0185 and -0.0102 inches, respectively. The standard deviations were 0.0164 and 0.0251 inches, respectively. Overall standard deviation was 0.0251 inches (0.64 mm).

High Speed GC Detection of Organic Contaminants. During Phase I, a high-speed, temperature-programmed GC developed by Thermedics Detection (TD) was adapted for the quantitative detection and classification of organic contaminants. The GC was used to detect polychlorinated biphenyls (PCBs) and other organic compounds on surfaces such as concrete. High speed GC separation was demonstrated using actual PCB target compounds rather than analogs. Chromatographic elution times ranging from 10 to 30 s were demonstrated. The modified GC system includes a newly developed sensor head and transport tube that, when combined with an available commercial mass spectrometer detection system, will be able to detect organic contaminants at the low parts per billion level at high speed.

Molecular Vibrational Spectroscopy. The University of Idaho performed experiments to determine the most suitable remote molecular vibrational spectroscopic technique for 3D-ICAS surface materials identification. The selected technique is a fusion of Near-Infrared (NIR) Raman spectroscopy and Mid-Infrared (MIR) Reflectance spectroscopy. Table 2.7 is a summary of results of a survey in terms of spectral quality (i.e., the combination of spectral contrast and signal-to-noise ratio). As shown, the majority of samples analyzed were not amenable to good spectral quality NIR analysis.

PROJECTED PERFORMANCE

During Phase II, using the NASA/DOE 3-D mapping system being completed with software enhancements, a robot arm borne multisensor package will be tracked with 6DOF (3-D location and orientation) while performing 3-D contamination mapping of surfaces. The new system will have at least 200X faster range and amplitude information to support the 6DOF tracking. The sample collection and GC system will be interfaced to a time-of-flight mass spectrometer and demonstrated with the robotic arm and multisensor probe. Detection of organic contaminants at regulatory levels (low parts per billion) is expected. A fused MIR/NIR Raman probe that combines commercially available instruments will be implemented for laboratory use. Neural net-based discrimination algorithms were implemented in software for FT Raman spectra, that can distinguish similar materials such as different species of wood. When extended to fuse MIR and Raman spectra, these techniques will easily distinguish the major surface types of interest to DOE decontamination and decommissioning (D&D) operations. The fused MVS sensor probe is projected to be effective in surface materials identification at a range of 1 mm, thus imposing no extra requirement for 3D-ICAS sensor positioning.

Table 2.7. Summary of spectral quality for a number of representative samples from the three spectroscopic methods studied.

Sample	Mid-IR	Near-IR	Raman
Concretes	G	P	P
Bricks	G	G	M
Woods	G	P	VG
Asphalt	M	P	VP
Asbestos	G	P	M
Porcelain	G	P	G
Polymers	M	P	VG
Organics	G	P	VG

VG = Very good, G = Good, M = Medium,
P = Poor, VP = Very poor

APPLICABILITY

The 3D-ICAS: (1) will provide real-time, quantitative measurements of volatile organics and radionuclides on bare materials consisting of concrete, asbestos, and transite, (2) will provide 3-D display of the fusion of all measurements, and (3) will archive the measurement results for regulatory documentation.

STATUS

During Phase I, the CRC team developed the component technologies and assessed their effectiveness as part of an integrated system. Phase II, as described earlier, runs from October 1994 through September 1995. Phase III, which follows, will develop a fieldable prototype system that will be demonstrated in 1996. The 3D-ICAS technology will then be ready for transfer to government and industrial facilities for characterization applications. At an earlier date (July 1995) the 3-D mapping technology will be ready for large-scale industrial metrology applications.

REGULATORY CONSIDERATIONS

The developers of 3D-ICAS are confident that meeting the U.S. Environmental Protection Agency's certified laboratory procedure (CLP) quantitation limits for PCBs, VOCs, and semivolatile organic compounds is possible. With proper engineering and tuning, the target detection limit of 160 picograms per GC peak should be readily attainable.

POTENTIAL COMMERCIAL APPLICATIONS

The 3D-ICAS technology will be applicable to contaminated industrial site characterization. The coherent laser radar 3-D mapping technology will be applicable: (1) to precision large-scale industrial assembly operations, (2) to quality control of large-scale manufacturing, and (3) to tooling calibration. The 3-D mapper is being tested by the Department of Transportation for bridge structural integrity assessment.

BASELINE TECHNOLOGY

The baseline technology is conventional sampling, storage, transportation, and analysis at an off-site laboratory.

INTELLECTUAL PROPERTY

Existing patents:

Frank E. Goodwin, "FM Laser Radar, " Patent No.: 4,830,486; Patent Owner: Coleman Research Corporation.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Richard L. Sebastian
Coleman Research Corporation
6551 Loisdale Ct., Suite 800
Springfield, VA 22150
(703) 719-9200; (703) 719-9229 FAX

DOE Program Manager

Jerry M. Hyde
U.S. Department of Energy
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7914

Industrial/University Partners

Thermedics Detection, Inc.
220 Mill Road
Chelmsford, MA 01824

University of Idaho
Moscow, Idaho

REFERENCES

1. Final Topical Report, Phase I: 3 Dimensional Integrated Characterization and Archiving System, Coleman Research Corporation, Springfield, VA, July 12, 1994.

2. Sebastian, R.L., R.B. Clark, D.L. Simonson, and A.R. Slotwinski, "Fiber Optic Coherent Laser Radar 3D Vision System," SPIE '94 Symposium, 1994.

Field Analytical Laboratories

Section 3.0

MOBILE DEMONSTRATION LABORATORY FOR ENVIRONMENTAL SCREENING TECHNOLOGIES

DESCRIPTION

The Mobile Demonstration Laboratory for Environmental Screening Technologies (MDLEST) is a completely self-contained mobile laboratory. The generic mobile laboratory concept is applied toward the objective of having a field laboratory to support screening and monitoring instruments at various DOE facilities. Computers and control systems, electrical power, potable water, cryogenic and high-pressure gases, and other utilities required to operate instrumentation are supplied by the MDLEST. A robotic surface sampling accessory (RSA) attaches to the rear of the MDLEST and includes the robotic arm, sampling head, closed circuit television cameras, and various control systems all tied to the MDLEST computers and a video monitor console. The complete MDLEST is housed in a 44 ft long fifth wheel trailer for transport by a medium duty truck. Within the context of the MDLEST, Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectrometry/Mass Spectrometry, LA-ICP-AES/MS, techniques are used to screen/characterize soils and concrete in situ to determine the extent of the contamination. Both heavy metals (e.g., chromium, nickel, barium, cadmium, lead, etc.) and radionuclides (uranium, thorium, etc.) are target contaminants for this technique. Sampling probes were developed and prototyped that will screen/characterize surface soils, concrete floors or pads (nondestructively), and also subsurface soils. The sampling probes, both surface and subsurface, contain the laser, associated optics and control circuitry to raster the laser ablation energy across one square inch (approximately 6.4 cm^2) of the sample surface. At one time, either the surface or the subsurface probe is connected by an umbilical, currently over 20 m long, to the MDLEST. The MDLEST trailer contains the ICP-AES/MS instrumentation to immediately analyze the samples generated by the laser ablation sampling system. The sample results are immediately available approximately 100 min.) for field remediation decisions. Figure 3.1 is a schematic of the LA-ICP-AES analytical technique.

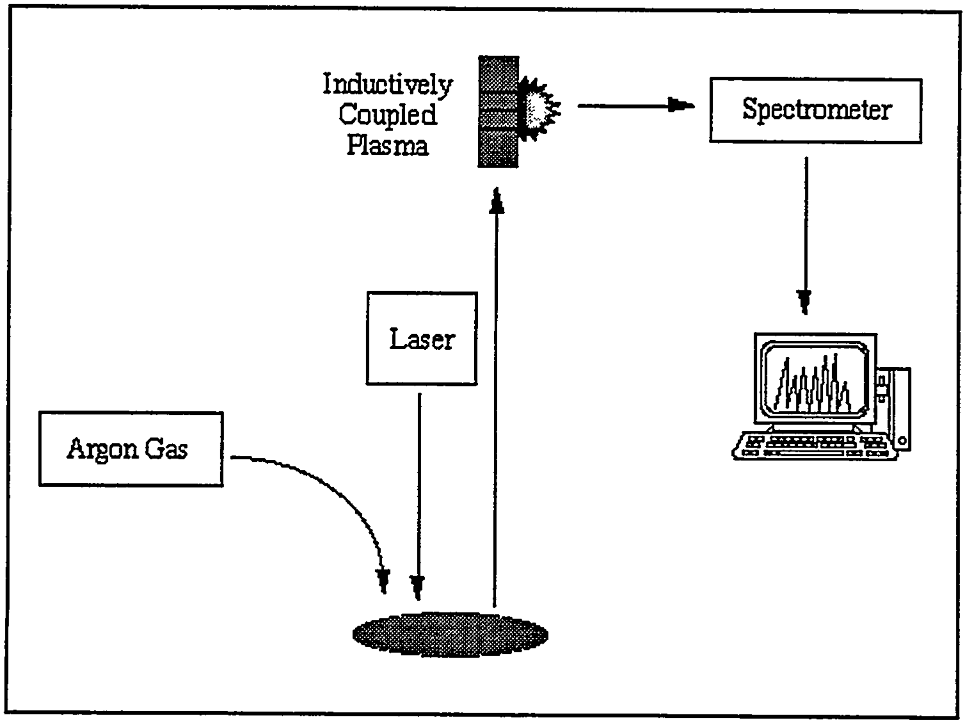


Figure 3.1. Schematic of the LA-ICP-AES analytical technique.

Although the MDLEST could be outfitted for other analytical methods, it currently contains the LA-ICP-AES/MS system. Laser ablation is a technique that enables sampling and analysis to be performed for solid samples without acid dissolution of the samples. The U. S. Environmental

Protection Agency (EPA) has certified ICP-AES/MS as a method for environmental contamination quantification when using solution chemistry (acid with microwave assisted dissolution) techniques with aerosol nebulization introduction of the analyte into the ICP torch. Now the MDLEST can be used to perform the EPA certified laboratory procedure (CLP) on-site with comparable results to offsite analysis, yet the laser ablation technique allows greater versatility and speed of analysis. As such, laser radiation is focused onto the surface of a sample to cause vaporization and ejection of material from the surface. The ablated material is transported in an inert argon gas stream to the ICP torch (approximately 8,000 K) where the analyte is subsequently vaporized, atomized, ionized, and electronically excited. Relaxation of this electronic excitation produces atomic and ionic emission spectra characteristic of the sample introduced into the ICP. The spectrum from the ICP is then analyzed using a 20 channel simultaneous atomic emission spectrometer (AES) or the mass spectrometer (MS).

The advantages of laser ablation sampling include direct analysis of the sample with little or no preparation and applicability to a wide variety of matrices. Because there is no limit on the type of solid material that can be subjected to laser ablation, a wide variety of samples were analyzed, including metals ceramics, and geological samples such as rocks, soils, and sediments. The results obtained using the laser ablation sampling process are less precise than those obtained using EPA-CLP methods involving solution nebulization sample introduction. This lack of precision in the results is caused by variations in the amount of sample introduced to the ICP. These variations are directly related to the laser energy density at the sample surface, energy scattering from the aerosol particles in the ablation cell, and variations in aerosol transport out of the cell through the transfer tubing to the ICP. New data quantitation methods for use with the laser ablation sampling technique have been investigated. A method combining aerosol mass measurements and solution standard additions techniques has successfully reduced the variations in sample quantitation and increased the agreement with EPA-CLP results.

TECHNICAL PERFORMANCE

Contaminated soils are in situ (directly) sampled by laser ablation. Once the surface of the site to be sampled has been cleared of organic debris, no additional sample preparation is required. The subsurface probe is used to a depth of 27 m (approximately 90 ft). The demonstration of the subsurface in situ sampling probe and immediate analysis was successfully demonstrated in August 1994 at a non-radioactive site in Denver, Colorado. The probe is fully functional, but has not been optimized in either size or function. Additional development is required to increase the operating efficiency and to downsize the probe for use with cone penetrometers and Geoprobes®. Laser ablation generates approximately 2 mg of sample.

The atomic emission spectrometer installed in the MDLEST is a standard production model Thermo Jarrell Ash, ICAP 61E Plasma Emission Spectrometer and can be used for samples introduced by either solution nebulization or laser ablation. The AES configuration of the MDLEST allows detection of 20 elements, simultaneously. The ICP-AES is capable of detecting and quantifying elements in real-time at the ppm level (μg/g) for direct sample injection (LA sampling). Using laser ablation sampling, the AES has a detection limit of 0.9 ppm (mass). A lower detection limit is achieved using samples prepared for solution nebulization where the detection limit is approximately 10 ppb (ng/g). It is possible to identify 70 elements using the AES. A standard production model (ELAN 5000 ICP-MS) mass spectrometer was obtained on loan from the Perkin-Elmer Corporation. The MS analysis provides detection of radionuclides (e.g., ^{238}U, ^{235}U, ^{234}U, ^{230}Th, and ^{232}Th) and is sensitive enough to provide isotopic separation. Using laser ablation, the MS instrument has the capability of multi-element determination of heavy metals including radioisotopes (total quantitation of 300 amu) at the (approximately 0.5 ppb (ng/g) detection limit; and a (approximately 0.03 parts-per-trillion (pg/g) detection limit is achievable using solution nebulization. At the DOE Gunnison, Colorado site, the lower detection limit of the LA-ICP-MS instrumentation was shown to be (approximately 0.45 ppb. The levels of ^{230}Th and ^{226}Ra must be detected to 15 pCi/g (approximately 0.80 and 0.05 ppb, respectively) to satisfy the Nuclear Regulatory Commission (NRC) remediation agreements for the Gunnison site. In particular, the MS instrument can detect the required ^{230}Th levels in the soil below the 15 pCi/g (0.8 ppb) level using laser ablation sampling.

Summary of Field Demonstrations. The MDLEST has participated in five field demonstrations. Each demonstration had a different objective and problem focus. The demonstrations and objectives are summarized in Table 3.1. Details of the investigations are available in the referenced documents.

In addition, a local feasibility test using the laser ablation in situ surface sampling technique to nondestructively sample concrete and determine the contamination level was performed. Preliminary results show this in situ technique is feasible for screening concrete floors and pads to determine if they have been contaminated by accidental spills, leaking waste storage drums, or tanks.

Cost. The MDLEST contains approximately $600K in instrumentation. The mobile laboratory with installed automation and instrumentation is estimated to cost $1.1M in capital and is expected to have a 5 year lifetime. Approximately 20 field surface samples (LA sampling) can be analyzed per day at a cost of $300 to $500 per sample, with a 15 minute sample turnaround. Sixteen subsurface samples with complete analysis per day can be achieved at a cost of $625 to $875 per sample. These costs cover the MDLEST crew (two scientists and two technicians) and the percussion hammer rig and crew.

PROJECTED PERFORMANCE

The ablation cell was optimized to a degree. Further improvements in signal intensity are possible if cell design parameters, particularly cell volume and geometry, are studied and optimized. Other future optimization work may include improvements to the gas flow and transport tube design, ICP torch design optimization for LA sample injection, and the raster pattern to provide higher ablation efficiency and

Table 3.1. Summary of field demonstrations.

Date of Demonstration	Objective
September 1992	Fernald, OH, detection and quantification of U in soil, the initial field trial of the MDLEST, and the first field use of the laser ablation sampling technique for in situ surface sampling.
June 1994	Returned to Fernald, OH, to participate with other state-of-the-art field sampling technologies to test a direct probability sampling plan.
November 1993	Gunnison, CO, Uranium Mill Tailing Remedial Action (UMTRA) Project to detect ^{230}Th levels in the soil after the mill tailing pile had been removed.
August 1994	Denver, CO, area to test the subsurface in situ sampling probe.
September 1994	St. Louis, MO, to participate in the Expedited Site Characterization (ESC) methodology at the St. Louis Airport Site (SLAPS) to evaluate the field capabilities of a broad range of characterization/monitoring technologies.

particle stream stability. These improvements will result in lower detection limits and reproducibility of the analyzed results, and will allow the ablation sampling system to satisfy the rigorous scrutiny of regulatory acceptance. In addition, sample acquisition time reduction in the case of subsurface characterization will be experienced with further development of the in situ subsurface sampling concept. Adapting the subsurface probe for use with cone penetrometers and Geoprobes® will greatly enhance its value as a characterization tool. Furthermore, development of a specialized probe to rapidly test large flat areas of concrete is also suggested. One of the important, nontrivial design problems that must be solved for this probe to operate rapidly is the design of a dynamic gas tight seal for the ablation cell moving over a concrete surface.

APPLICABILITY

This technology is applicable to the detection of more than 70 metallic elements and 300 isotopes which could exist as contamination in surface and subsurface soils or on concrete surfaces and foundation pads.

STATUS

This technology is developed and has participated in five field demonstrations. Commercialization of the technology is being pursued through the Technology Integration Program (TIP) at Ames Laboratory. Layne Environmental Services, Inc., who was the previous commercial partner in the 1994 Cooperative Research and Development Agreement (CRADA), would be a potential contract operator if a system becomes commercially available.

REGULATORY CONSIDERATIONS

The solution chemistry techniques for the ICP-AES/MS analytical system have been accepted by the EPA. Regulatory acceptance of the technology using the LA sample introduction system is being pursued. US-EPA and EMSL (Las Vegas) are aware of the progress of this technology.

POTENTIAL COMMERCIAL APPLICATIONS

A complete market survey has not been performed; however, several private sector manufacturing facilities may also have similar heavy metal and even radionuclide contamination in the surface and subsurface soils.

BASELINE TECHNOLOGY

The baseline technology is offsite analysis in conventional laboratories for heavy metal contamination or grab samples obtained from the surface or core samples from subsurface boreholes. The commercial gamma spectrometer/neutron borehole logging system is sometimes used as a baseline for cost comparison with the subsurface sampling probe; however, the boreholes are already in place. This commercially available baseline technology has per-sample charges that are 15 to 30 times the per-sample cost of the MDLEST system using LA-ICP-AES/MS analysis and can only detect the radioactive contaminants.

INTELLECTUAL PROPERTY

Patents are being pursued for certain components (including the ablation cell, the subsurface probe, and the calibration system). The Iowa State University Research Foundation (ISURF) owns the patents. Layne Environmental Services, Inc. has the patents rights to the casing components used with the subsurface probe. All patents are pending.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigators

Marvin S. Anderson and D. Thomas Noble
Ames Laboratory
TIP Office 125 S. 3rd St.
Ames, IA 50010-6739
(515) 294-6404

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 2 0874-1290
(301) 903-7672

Industrial Partner

Norm Mehlhorn
Vice President
Layne Environmental Services, Inc.
3610 E. Anne St.
Phoenix, AZ 85040

REFERENCES

1. Ames Laboratory, Final Report Ames Laboratory: The Development and Operation in a Mobile Laboratory for In Situ Real-Time Screening and Characterization of Soils Using the Laser Ablation Sampling Technique, IS-5115 UC-606, Iowa State University, Ames, Iowa, 1995.

2. Ames Laboratory, Laser Ablation ICP-Mass Spectrometry Determination of Th-230 in Soils at the Gunnison Colorado UMTRA Site, IS-5106 UC-606, Iowa State University, Ames, Iowa, 1994.

3. Ames Laboratory, Uranium in Soils Integrated Demonstration Site Characterization at Fernald, Ohio, September 1992, IS-5099 UC900, Iowa State University, Ames, Iowa, 1993.

4. Anderson, M.S., and E.J. Jaselskis, "Mobile Instrumentation Platform and Robotic Accessory for Real-Time Screening of Hazardous Waste," in Proceedings of the International Topical Meeting of Nuclear and Hazardous Waste Management Spectrum'92, Boise, ID, American Nuclear Society, La Grange Park, IL, August 1992, pp. 81-85.

5. Baldwin, D.P., D.S. Zamzow, A.P. D'Silva, "Aerosol Mass Measurement and Solution Standard Additions for Quantitation in Laser Ablation-Inductively Coupled Plasma Atomic Emission Spectrometry," Analytical Chemistry, Vol. 66, No. 11, 1994, pp. 1911-1917.

6. D'Silva, A.P., D. Zamzow, E. Jaselskis, and S. Weeks, "Remote, Real-Time Analysis of Hazardous Wastes through Laser Ablation Inductively Coupled Plasma Atomic Emission Spectrometry," Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management Spectrum'92, Boise, ID, American Nuclear Society, La Grange Park, IL, August 1992, pp. 409-413.

7. Goldner, H.J., "A Tale of 3 CRADAs," R&D, p. 47, October 1994.

8. Jaselskis, E.J., M.S. Anderson, P. D'Silva, D.P. Baldwin, and D. Zamzow, "In Situ Field Characterization Technique for Screening Contaminated Soils," Journal of Environmental Engineering, (in Press) 1994.

9. Purdy, M., "Mobile Lab Test Soil at PPB Level," Environmental Protection, February 1994 p. 20.

10. Zamzow, D.S., D.P. Baldwin, S.J. Weeks, S.J. Bajic, A.P. D'Silva, "In Situ Determination of Uranium in Soil by Laser Ablation-Inductively Coupled Plasma Atomic Emission Spectrometry," Journal of Environmental Science & Technology, 28, 1994, p. 352.

DESCRIPTION

Transuranic (TRU) contaminated rad-wastes have been stored in shallow pits and trenches at many DOE facilities, including the Idaho National Engineering Laboratory (INEL). It is anticipated that waste containers have degraded over the years and, consequently, a significant fraction of the backfill soil in these pits and trenches is now contaminated with TRU elements and long-lived fission and activation products. As an example, INEL has 57,000 m^3 of buried TRU waste material that would account for about 20% of the total volume of contaminated waste that must be removed. The Rapid Transuranic Monitoring Laboratory (RTML) was developed to support TRU waste retrieval efforts by continuously monitoring the air, soil, and deposited dusts for radioactive contaminants.

The RTML is a mobile, field deployable laboratory that can continuously monitor airborne TRU concentration and rapidly analyze soil, smear, and air filter samples for TRU isotopes, and fission products. The RTML consists of a collection of monitoring devices that are capable of measuring low-level concentrations of alpha- and photon-emitting contaminants. The laboratory is housed in two separate trailers that provide sample storage and preparation areas and counting laboratory space. The power can be supplied by portable 30 and 50 kW diesel generators in remote applications. One trailer (2.4 m x 7.3 m) houses the sample preparation laboratory that is equipped with a Class-A fume hood, having high efficiency particulate air (HEPA) filters, a gravity-flow drying oven, sieving equipment, two analytical balances, compressed air cylinders, hot plates, and a supply of sample planchets and containers. Samples are received and prepared for analysis in this trailer following specific procedures developed for the RTML.

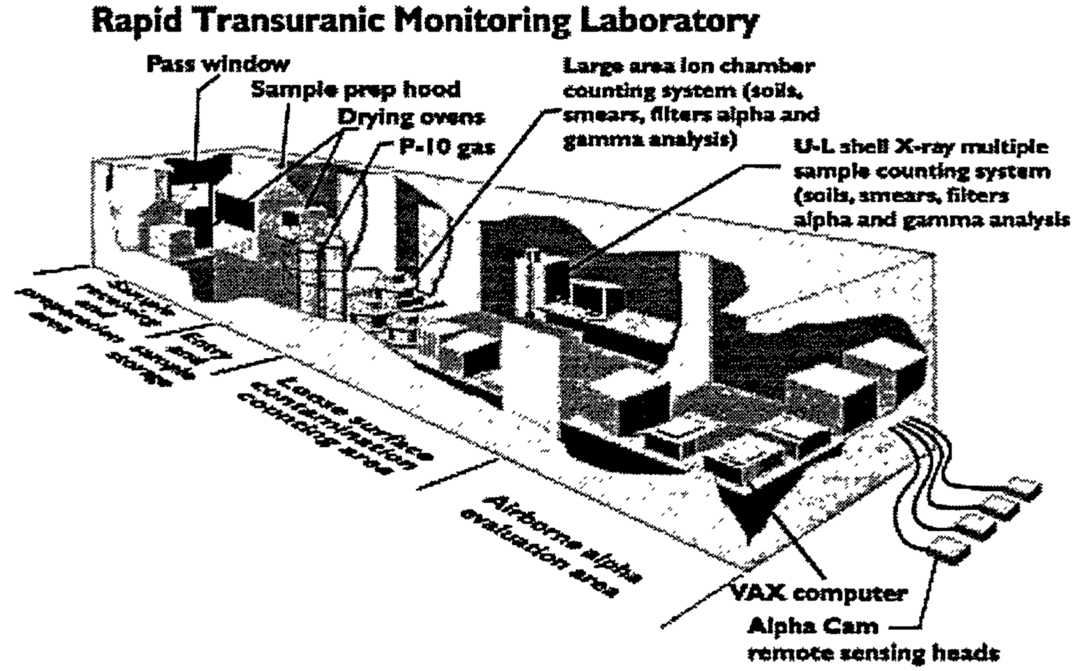


Figure 3.2. Rapid Transuranic Monitoring Laboratory.

The second trailer (2.4 m x 14.6 m) is equipped with: (1) a germanium photon spectrometer installed in an automatic sample changer, (2) two large-area ionization chamber alpha spectrometers, (3) a VAX 4000 model 100 computer, (4) four computer terminals with monitors, and (5) a laser printer. All three measurement systems are controlled from the VAX 4000-series computer that controls operation, analyzes spectral data acquired by the spectrometers, and displays and generates the analysis results reports. The RTML is also equipped with four alpha continuous air monitors (CAMs). The alpha CAMs can be operated up to 200 m from the trailer. See Figure 3.2.

TECHNICAL PERFORMANCE

Photon Analysis Spectrometer. The spectrometer consists of a 60 mm diameter, n-type, extended-range germanium detector capable of efficiently measuring both x-rays and gamma-rays. The gain is chosen to cover photon energies from about 10 to 1,380 keV with an 8,192 channel analyzer. The photon analysis spectrometer determines the presence of plutonium radioisotopes by counting the L-shell x-rays emitted by the uranium daughters. It also determines the presence of radionuclides such as ^{60}Co, ^{137}Cs, and ^{241}Am that emit gamma rays having energies below 1,380 keV. The gamma-ray and X-ray data are obtained in one spectrum, and two spectral analytical methods are applied simultaneously to the different regions of the spectrum.

Large Area Ionization Chamber Alpha Spectrometers. Two gridded ionization chambers constructed of nickel-plated milled steel are used. The chambers are rated to 100 kPa above atmospheric pressure. The sample holders are held in a reproducible geometric arrangement by fixed guides. The fixed guides have milled cutouts to hold both 254 mm circular pans, and 200 x 250 mm filters.

Alpha Continuous Air Monitors. The alpha CAMs are equipped with two-stage virtual impact detectors to remove the background radon progeny—improving the sensitivity. The impactor also concentrates the airborne TRU-bearing particulates. Each CAM has two air sampling pumps, two mass flow sensors, a 900 mm^2 detector with 4 mm thick collimator, a detector bias supply, a preamplifier, a linear amplifier, an analog-to-digital converter, a multiplexer, and the Canberra nuclear acquisition interface module (AIM). Because the preamplifiers are temperature sensitive and outside temperatures vary diurnally, the CAM sampling cabinets are insulated and equipped with a heater and an air conditioner to maintain constant temperature.

Sample Preparation. Each soil sample is baked 30 to 60 min at 175°C until the sample is dry, then sieved in a 50-mesh sieve. At this stage, 11 g of the sieved soil is weighed into a circular plastic container (3 mm x 64 mm diameter) for analysis using the photon spectrometer. Preparation for the ionization chamber alpha spectrometer is similar but also requires grinding of a 100 mg sieved soil sample in a diamonite mortar in an aqueous solution of 30% ethanol. The resulting suspension is transferred to an air operated sprayer and subsequently sprayed onto a preheated 254 mm diameter stainless steel pan.

Field Test Results. Field trials were conducted in the summer of 1993 as part of a remote retrieval demonstration involving a weather shield, remote retrieval equipment, and dust control equipment. The demonstration showed the capability of processing 100 samples per day of soil, filter, and smear samples at the stated lower levels of detection (LLD). During the field trial, hundreds of soil samples plus 20 specially prepared standards were analyzed by the RTML. The sensitivity and reliability to which alpha and gamma emitting radionuclides could be detected under field conditions were demonstrated by analyzing 20 soil standards containing known activities of ^{239}Pu, ^{241}Am, ^{60}Co, and ^{137}Cs. These standards were also randomly distributed among the cold test pit (CTP) soil samples for the blind test before delivery to the RTML preparation trailer.

Under field conditions, the lower detection limit (LLD) concentrations for ^{239}Pu, ^{241}Am, ^{60}Co, and ^{137}Cs by x-ray/gamma-ray spectrometry were confirmed to be 40, 1, 5, and 5 pCi/g, respectively, for 10 minute counts. The RTML unit can measure isotopic plutonium at 20 pCi/g using 15 minute counts. LLD concentrations for ^{239}Pu and ^{241}Am by large area ionization chamber alpha spectrometry were both 40 pCi/g. The LLD concentrations for the four RTML alpha CAMs were shown to be less than 1 derived air concentration (DAC) in 1-hr when airborne dust concentrations were below 0.01 mg/L.

None of the analyses in either the 143 CTP samples analyzed by photon spectrometry or the 96 CTP samples analyzed by ionization chamber alpha spectrometry showed manmade radiation. That is, there were no false positives for any of the 239 blank soil samples analyzed. The maximum number of samples analyzed in a 24-hour period with the photon spectrometer was 79; with the two ionization chambers, it was 33. Therefore, the total sample throughput rate was demonstrated to be 112 samples in 1 day, working one 8 hour shift. For an environmental restoration project such as a pit retrieval, 100 samples per day should be adequate to track contamination levels; therefore on-line tracking is essentially available. A true "on-line" tracking of ^{239}Pu content is presently not possible.

Cost. RTMLs can be procured for $500K. Operations and maintenance costs include four technicians and 10% time assistance from scientists. Life-cycle costs have not been estimated. Thermo Terratech estimated that using the RTML at DOE Formerly Utilized Sites Remedial Action Program (FUSRAP) sites will save the DOE $250K and 6 months in schedule.

PROJECTED PERFORMANCE

To provide the RTML the capability to directly measure ^{90}Sr in soil during FY 1994, two different large area beta detectors were developed and experimentally evaluated; a triple proportional counter beta detector operated in the coincidence mode, and a large-area scintillation beta detector. A third large-area beta detector (the real-time ^{90}Sr analyzer developed at Pacific Northwest Laboratories) was also experimentally evaluated. Of the three beta detectors tested, the triple proportional counter beta detector had the best sensitivity for ^{90}Sr in soil. Its LLD for a 10 minute count time was 1 pCi/g ^{90}Sr for a 150 g soil sample.

Alpha continuous air monitors equipped with a single fixed sample collection filter are not very reliable when the concentrations of airborne contaminants remain elevated over time. To provide a means of measuring at regular intervals (the total activity of each TRU isotope accumulated on the sample collection fiber) an alpha CAM was built that is equipped with two solid-state silicon detectors and three 47 mm diameter sample collection filters mounted at 120° intervals on a rotatable disk. The second detector intermittently measures the total activity of each TRU isotope accumulated on each of the three sample collection filters. A two-stage inertial impactor that samples at 283 L/minute removes most of the alpha-emitting radon and thoron daughters from the sample airstream before the airstream traverses the sample collection filter.

APPLICABILITY

The RTML monitors low-level concentrations of actinides and fission products in soils, fallout coupons, filters, air, and liquids.

STATUS

The RTML was field tested in FY 1993. The RTML unit was field deployable in 1994. It was transferred in March 1995 to Thermo Terratech of Albuquerque, NM, for use in monitoring radioactive contaminants at different DOE sites throughout the country that are being remediated under FUSRAP. The RTML was recently moved to the Oak Ridge National Laboratory for installation of additional analytical instrumentation; it will then be put into service at Savannah River Site.

REGULATORY CONSIDERATIONS

Ecological impacts are not anticipated from use of the RTM unit. Samples for the RTM unit will be standard health-physics wrapped and will be prepared under a Class A hood.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include monitoring of radioactive contaminated retrieval areas and separation, processing, and storage systems. The RTML could also be applied in accident mitigation and cleanup.

BASELINE TECHNOLOGY

The baseline for rapid monitoring during retrieval is "in laboratory" analysis and health-physics handheld instruments. Handheld instruments can provide gross alpha measurements on surface soils at the 5,000 to 10,000 pCi/g levels in minutes. Laboratory measurements can provide 4 samples per radiochemist per day at the 0.2 pCi/g level. Alpha CAMs "off the shelf" currently provide about 80 DAC-h sensitivities.

INTELLECTUAL PROPERTY

The following patents were issued or are pending:

- Photon spectrometer analysis system, U.S. Patent 5,206,174 issued April 27, 1993.
- Pulser for gamma-ray spectrometry, U.S. Patent 4,968,889 issued November 6, 1990.
- Alpha CAM, U.S. Patent Application S-81, 110.

The RTML technology was transferred to Thermo Terratech in 1995. An equipment loan agreement and a license agreement between Lockheed Idaho Technologies Company (which manages and operates INEL for the DOE) and Thermo Terratech was signed in March to set the terms and conditions for loaning the RTML to Thermo Terratech for one to five years.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigators

Charles V. McIsaac, Claude W. Sill, and
Robert J. Gehrke
Lockheed Idaho Technologies Company
P.O. Box 1625
Idaho Falls, ID 83415
(208) 533-4020, (208) 533-4024, and
(208) 526-4155

DOE Program Manager

Jaffer Mohiuddin
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7965

Industrial Partners

Ordella
Oak Ridge, TN

Thermo Terratech
Albuquerque, NM

REFERENCES

1. McIsaac, C.V., C.W. Sill, R.J. Gehrke, and L.O. Johnson, Rapid Transuranic Monitoring Laboratory Final Report, INEL/94-0246, April 1995.

2. Sill, C.W., "Rapid Monitoring of Soil, Water, and Air Dusts by Direct Large-Area Alpha Spectrometry," submitted to Health Physics, October 1994.

3. McIsaac, C.V., C.W. Sill, and R.J. Gehrke, Test Plan for Preparing the Rapid Transuranic Monitoring Laboratory for Field Deployment, EGG-WTD-11208, April 1994.

4. McIsaac, C.V., C. W. Sill, R.J. Gehrke, E.W. Killian, K.D. Watts, and C.R. Amaro, Field Test of Rapid Transuranic Monitoring Laboratory, EGG-WTD-10935, December 1993.

5. McIsaac, C.V., C.W. Sill and R.J. Gehrke, Operating Procedures for Rapid Transuranic Monitoring Laboratory, EGG-WTD-10898, October 1993.

6. DOE-ID, "Technology Information Profile (rev. 2), Technology Name: Rapid Transuranic Monitoring Unit," TTP Reference No. ID-121210, March 25, 1993.

7. McIsaac, C.V. and C.R. Amaro, Sensitivities of Five Alpha Continuous Air Monitors for Detection of Airborne ^{239}Pu, EGG-WTD-10314, July 1992.

8. Gehrke, R.J., et al., "Rapid Assay of Plutonium in Soils by Passive L X-ray Counting," Transcript of the American Nuclear Society, Vo.164, No. 94, 1991.

9. Sill, C.W., Rapid Monitoring for Transuranic Contaminants during Buried Waste Retrieval, EGG-WTD-9412, March 1991.

10. Loomis, G.G., and C.V. McIsaac, "Rapid Monitoring of Transuranic Contaminants during Buried TRU Waste Retrieval," Proceedings of Waste Management '91, Tucson, AZ, February 24-28, 1991.

11. McIsaac, C.V., et al., "Sensitivities of Alpha Continuous Air Monitors for Detection of Airborne ^{239}Pu," Proceedings of Waste Management '91, Tucson, AZ, February 24-28, 1991.

Geophysical and Hydrologic Characterization

Section 4.0

CROSS BOREHOLE ELECTROMAGNETIC IMAGING

DESCRIPTION

The objective of Cross Borehole Electromagnetic (EM) Imaging is to provide a "nonintrusive" characterization method for detection and quantification of underground waste forms with rapid coverage (acres per day). This technology is also useful for post-closure monitoring of waste sites and their associated geology; furthermore, it has an industrially relevant application as a "minimally intrusive" subsurface exploration and geologic and hydrogeologic property mapping tool. This tool uses the radio frequency imaging method to obtain 2-D tomographic maps, as well as 3-D combined images of the subsurfaces of various waste sites. Images are obtained from borehole-to-borehole (30 m deep with separations of 6 to 15 m) and surface-to-borehole configurations using vertical, horizontal, and slant boreholes. The tomographic data delineate the boundaries between alluvial facies at the meter scale (e.g., zones of granitic and limestone cobbles and variations in the consolidation and grain size). Geologic variations may control vertical and lateral contaminant migration at a given site. The method is sensitive to variations in electrical conductivity and the dielectric constant in the soil and rock at waste sites. Typical western United States geologies have been studied, that are composed of alluvial sand, gravel, and cobbles with small quantities of silts and clays. The waste forms at these sites included acids, oils, solvents, inorganic compounds, and other matter.

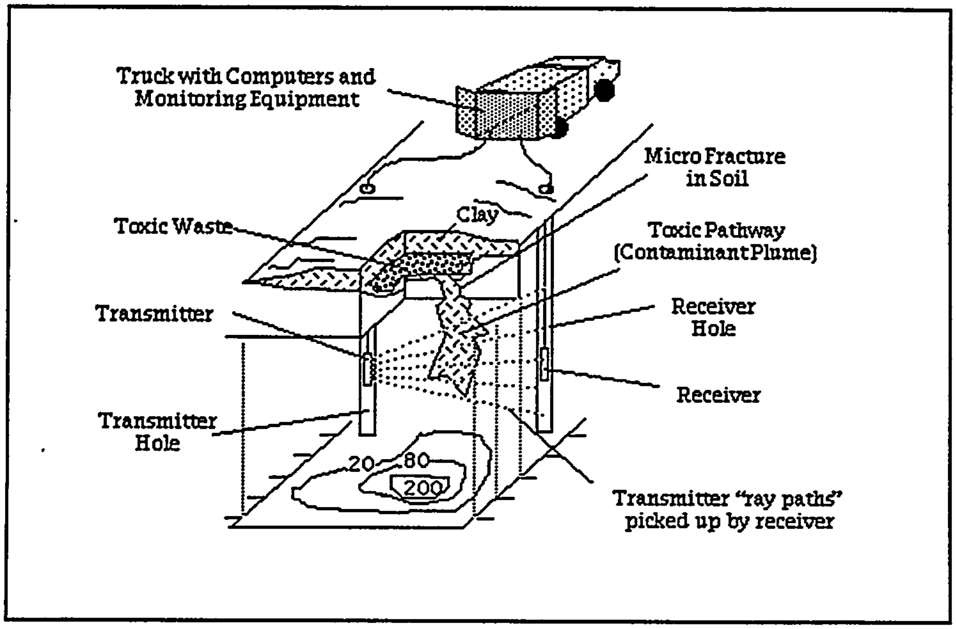


Figure 4.1a. Cross Borehole Electromagnetic Imaging.

The most recent form of the cross borehole EM imaging tool is called the RIM-II and uses radio frequency (RF) signals that are either continuous wave (CW) forms or pulsed wave (PW) forms. The continuous wave form (15 MHz signal) has a greater penetration depth than the time dependent wave (broad band). Therefore, the CW can be used between wells that are spaced farther apart (15 m) with a resolution of about 1 m. The pulsed wave must use closer spaced wells (6 m), but has an improved resolution (0.5 m). As the transmitted radio signal propagates through rock and soil mass, the electrical properties of the mass (e.g., conductivity and permittivity) cause attenuation of the wave (decrease in amplitude) along the path, and geometric and mass properties of the subsurface rock also cause a phase shift in the sinusoidal signal. The RIM-II system (developed by Sandia National Laboratories (SNL) and RIMtech Inc.) measures the magnitude and phase of the far field component of the EM wave, consequently making use of the fact that the radial wave impedance of a magnetic dipole immersed in a dissipative medium is largely imaginary and therefore stores energy in the near field. The way that this received data is mathematically interpreted to give 2-D tomographic images is described in the following paragraph. The pulsed wave technique is similar to the continuous wave in physical concept (attenuation, phase shift, etc.); however, the pulsed signal is broadband and the data is analyzed with respect to the time domain in contrast to the CW method which analyzes with respect to the frequency domain.

The imaging system (Figure 4.1a) consists of a transmitter and a receiver. The receiver has a 2 in diameter and is 6 to 12 ft long. The transmitter and receiver are placed in separate boreholes and lowered by fiber optic cables. The tomographic data is collected in a series of ray paths (the path directions resemble a fan). The ray path fan is a data set formed at a fixed location of the transmitter. The transmitter and receiver are lowered to a stationary location to make a measurement, the receiver is then moved to a different location in the borehole to make another measurement (approximately 2.5 to 5 ft apart). The receiver is again moved and the measurements are made repeatedly until the ray path fan is completed. Since the signals passing through a given cross-section are received from several directions, the data vectors can be manipulated to form a 2-D tomogram using the Radon transform (essentially equivalent to the Inverse Fourier integral transform). The resolution of the smallest object is roughly 0.05 times the interwell spacing (1.5 ft for the CWL demonstration). From the repeated and overlapping measurements of amplitude and phase-shift between boreholes, the distribution of electrical conductivity can be reconstructed in an isopleth map of conductivity. The signal properties are sensitive to changes in moisture content, permeability, and water chemistry and will, therefore, characterize changes in the landfill system and the zone between landfill and the water table. This tomographic method uses an RF source but is, nevertheless, very similar to several x-ray and gamma-ray imaging techniques known to the medical industry and other waste inspection technologies (see Waste Inspection Tomography).

There are several advantages to EM imaging: (1) it is faster because it optimizes sampling; (2) it is better because it fills in the "gaps" between boreholes and distinguishes between water soluble and organic contamination; (3) it is cheaper because of minimized drilling and sampling requirements; and, (4) it is safer as it does not require radioactive sources. The main challenge is how to perform and present the combination of 2-D images in the form a of 3-D image of a given waste site.

TECHNICAL PERFORMANCE

This technology requires only two people to operate. It can be used to generate three borehole-to-borehole images per day in 100 ft deep boreholes. One borehole-to-surface image can be obtained per day. This technology is sensitive to or adversely effected by stray electrical noise at some sites. There is a small amount of waste produced when the tool is decontaminated after withdrawal from the borehole. The typical application is in a 9 to 10 inch diameter borehole lined with the inflatable SEAMIST membrane.

Demonstrations. The Chemical Waste Landfill (CWL) at SNL was imaged in 1992 using borehole-to-borehole methods. During 1993, borehole-to-surface surveys were also completed of the "1960s" waste disposal pits at the CWL. These surveys delineated conductivity isopleths with three foot resolution when applied to the chromic acid plume and subsurface geology at the unlined chromic acid pit. The technology was also successful in mapping a series of trenches at the "60s Pits". Figure 4.1b is a sample of the images obtained in a borehole-to-surface tomogram taken through a vertical plane above the northern slant at the "60s Pits".

In 1992 and 1993, borehole-to-borehole imaging of the Unlined Chromic Acid Pit (UCAP) at SNL using the three UCAP wells was conducted. Although buried objects were not present in the UCAP, the methods indicate that soil units can be detected that have 0.5 m size consistent with DOE required performance criteria. The EM imaging method has delineated soil units which correlate to units interpreted from soil sampling in the UCAP boreholes. It is concluded that the characterization of environmen-

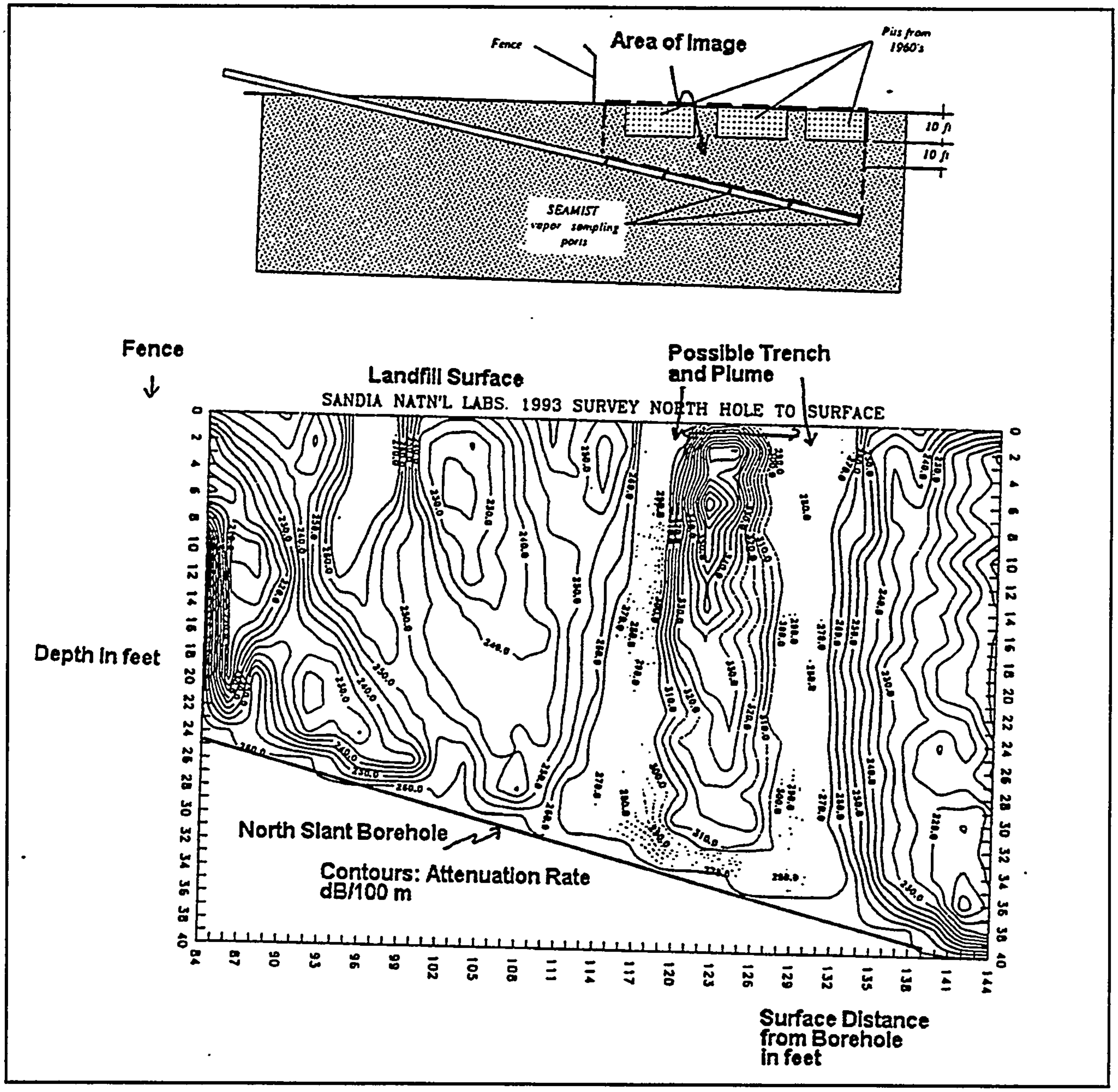


Figure 4.1b. Preliminary tomographic image on vertical plane above the northern slant hole at the "60s" Pits.

tally relevant geological and hydrogeological features relevant to the remediation effort can be elucidated, including the delineation of clay and low permeability zones, fracture zones, and changes in moisture content and porosity. The EM method appears to have detected portions of the plume beneath the disposal pit. The boundaries between the soil units or facies as defined by the image appear to control the distribution of chromium at the site.

During 1994, a 400 ft long borehole-to-surface tomographic survey of the Kirtland Airforce Base radioactive burial site, RB-11, was completed. The survey defined numerous disposal trenches and buried objects. The survey also detected a storm-caused infiltration event.

Cost. The estimated start-up costs for an EM Imaging system are $300K, in part to purchase the field receivers, transmitter cabling, hoist, and van.

Operations and maintenance costs are approximately $5K/day, which includes mobilization, equipment and manpower, for approximately 3 borehole-to-borehole images.

PROJECTED PERFORMANCE

The technology is commercially available; therefore, this section is not applicable.

APPLICABILITY

The targeted contaminants are metals, acids, aqueous plumes, and DNAPLs in arid soils and rock geologies.

STATUS

This technology commercially available through Physical Sciences Laboratory, New Mexico State University, and Raytheon Nevada.

REGULATORY CONSIDERATIONS

Regulators are aware of this technology. Specific requirements have not been defined.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include geologic and hydrogeologic exploration for natural resource identification or enhanced recovery.

BASELINE TECHNOLOGY

The major competitor to this technology is High Resolution Seismic Imaging.

INTELLECTUAL PROPERTY

The commercial rights have been purchased by Physical Sciences Laboratory of New Mexico State University. The patent for this technology is owned by Raton Technology Research.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

David J. Borns
Geophysics Dept.
Org. 6116/MS-0750
Sandia National Laboratories
Albuquerque, NM 87187-0750
(505) 844-7333; (505) 844-7354 FAX

DOE Program Manager

Skip Chamberlain
U. S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

Industrial Partners

RIMTech/STOLAR

REFERENCES

1. Borns, D.J., "Cross Borehole Electromagnetic Imaging of Chemical and Mixed Waste Landfills," Abstract, Session 143, Environmental Geology II: Geological Society of America, Land Use Impacts, 1992.

2. Borns, D.J., "Field Operations Report, Cross Borehole Electromagnetic Imaging of Chemical and Mixed Waste Landfills, SNL Report, TTP# AL-2211-23," August 23, 1993.

3. Borns, D.J., G. Newman, L. Stolarczyk, and W. Mondt, "Cross Borehole Electromagnetic Imaging of Chemical and Mixed Waste Landfills," Sandia Report, SAND-92-2296C.

CROSSHOLE SEISMIC IMAGING

DESCRIPTION

The objective of this technology is to measure the distribution of seismic wave velocity and attenuation in the ground. Seismic velocity depends on porosity, mechanical compressibility, shear strength, fracture content, density, fluid saturation, and clay content. The proper interpretation of the measured variables (seismic wave speed, direction, and attenuation) can be used to infer the geologic properties of the subsurface of a waste site on a volumetric scale. The most important use of seismic methods is mapping interfaces between materials of different velocities and providing high resolution images of the location of the main flow channels and soil types. The power of crosshole seismic tomography for petroleum reservoir characterization is now recognized, and will be equally important in hazardous waste site characterization. The key advances of this technology over standard mineral and petroleum engineering crosshole seismic imaging are listed below.

- Use of both compression (P-wave) and shear (S-wave) components of the seismic wave tensor to derive additional directional impedance information related to the subsurface geologic anisotropy.
- Use of higher frequency signals (1,000 to 10,000 Hz) to obtain better resolution, on the order of 1 m compared to baseline 400 Hz signals having resolutions of 3 m or worse.
- Use of air injection to highlight fractures by effecting a velocity change in an otherwise saturated subsurface.
- Application of "stiffness theory" to elucidate very thin discontinuities, less than 1/4 wave length.
- Application of innovative coupling and source clamping techniques to conduct seismic imaging at arid sites with dry and fragile borehole geologies.

The success of using seismic wave propagation as a monitoring tool will depend on the resolution obtainable. One usually thinks of the resolution of the seismic method in terms of 1/4 to 1/2 wavelengths. For frequencies of 1,000 to 2,000 Hz this translates to a maximum resolution of 0.5 to 1.0 m. However, recent theoretical and laboratory work shows that a single discontinuity (bedding boundary, lens structure, etc.) can significantly affect the propagation of seismic waves with wavelengths much larger than the discontinuity width. This is caused by slippage across the discontinuity or along the discontinuity as a seismic wave passes through it. These effects would be apparent in energy shift from P-wave to S-wave components of the seismic wave tensor. It is not so much the width of the feature that affects the seismic wave as it is the "stiffness" or compliance of the feature. The implication of this "stiffness theory" is that very thin discontinuities can have significant effect upon the propagation of an elastic wave. According to the stiffness theory, the lateral extent is still important, but the thickness of the features can be much less than the seismic wavelength.

An important element in characterizing fluid plumes is the in situ measurement of soil saturation. Soil saturation can be inferred from high resolution measurements of the seismic compressional (P) and shear (S) wave velocities. Consequently, portions of this work have focussed on the development of advanced seismic sources capable of high-frequency shear wave generation. A critical element of any S-wave source is the clamping mechanism in the borehole. A second method is the rotary source developed by Conoco, Inc., that relies on water coupling to the borehole. The SEAMIST™ (see profile featuring SEAMIST™) membrane borehole liner is also applied in this case to fill the borehole with fluid. The fluid may also be a "stiffer" (lower seismic impedance) gel material for improved seismic wave coupling. The SEAMIST™ technology can be used to clamp a string of receivers against a borehole wall.

TECHNICAL PERFORMANCE

High resolution (1,000 to 10,000 Hz) crosswell and single-well seismic surveys were performed in a shallow (25 to 40 m depth), saturated, fractured limestone sequence at Conoco's borehole test facility near Newkirk, Oklahoma. The objective was to develop seismic methods for imaging naturally fractured gas reservoirs. Crosswell surveys were performed before and after an air injection, that was intended to displace water from a fracture zone to increase the acoustic visibility of any fractures and to confirm previous hydrologic tracer test data that indicated a preferred pathway. The results indicated that the air did follow a preferred pathway. In addition, single-well seismic imaging also detected the fracture zone in a location consistent with the crosswell and hydrologic inversion results. An example of the imaging capabilities is presented in Figure 4.2 (the original image is in color with brightness colors representing largest amplitude of the signal).

Cost. Table 4.2 shows cost estimates for tomographic imaging based on a single well pair.

Table 4.2. Tomographic imaging cost estimates based on a single well pair.

Depth Scale (meters)	**Data Acquisition ($)**	**Data Processing ($)**
1-10	$5,000	$10,000
10-50	$10,000	$15,000
50-100	$20,000	$20,000
100-200	$25,000	$25,000

PROJECTED PERFORMANCE

Field and modeling studies have shown that such features as anisotropy, fluid content, and heterogeneity have a measurable effect on the propagation of seismic waves. It appears possible to use shear wave anisotropy and 3-D combination of tomographs to map the orientation, density, and spacing of these features in the field. Hence, the technology would be able to give the hydrologist/reservoir engineer useful information on the fluid flow regime. A few percent change in properties produces effects that are easily

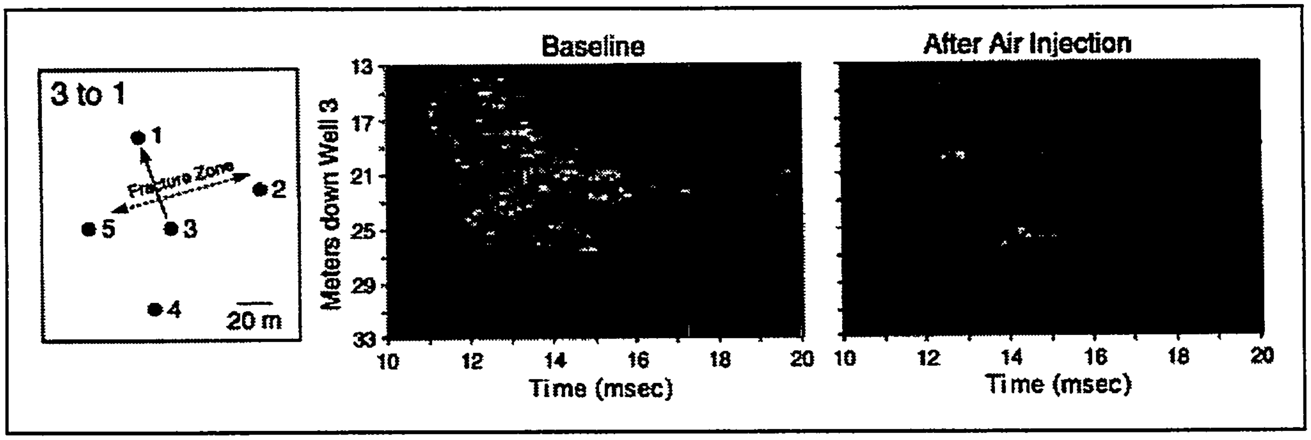


Figure 4.2. Example quantitative tomograph of a fracture. Field Test: Conoco's Newkirk, Oklahoma, Borehole Test Facility. The wave travel time is related to distance.

detectable. These seismic methods would be particularly informative if used in conjunction with electrical methods.

APPLICABILITY

This technology is applicable to characterization of subsurface geologies using boreholes at both arid and non-arid sites. This technology is mainly concerned with charting or correlating geologic features with seismic velocity tensor data (S- and P-waves). In addition to describing structure and anisotropy content, the technology also relates the seismic response of a rock mass to the hydrologic response. The idea is to tomographically map the variation in the P- and S-wave properties and relate the resulting anomalies to the actual density, orientation, and spacing of lithologic features. In addition to site characterization, a significant application of geophysical methods may be in performance assessment and in monitoring a repository with passive (or, if needed, active) seismology.

STATUS

This technology was field tested. Discussions are regarding transferring this technology to industry through SEA, Inc., are being conducted.

REGULATORY CONSIDERATIONS

The regulatory considerations pertinent to the drilling, completion, and maintenance of boreholes are applicable.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is applicable to subsurface exploration of petroleum, gas, mineral, and geothermal resources.

BASELINE TECHNOLOGY

The baseline technology is seismic characterization without tomography and without S-wave character in seismic analysis. The baseline was widely applied in the oil and gas industry and also other mineral explorations that have less demanding resolution requirements (approximately 8 m).

INTELLECTUAL PROPERTY

There are no patents for this technology.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Ernest Majer
Lawrence Berkeley Laboratory
University of California
1 Cyclotron Rd.
Berkeley, CA 94720
(510) 486-6709; (510) 486-5686 FAX

DOE Program Manager

Skip Chamberlain
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

Industrial Partners

Conoco, Inc.
Newkirk, Oklahoma

Amoco

Science and Engineering Associates, Inc.

REFERENCES

1. Datta Gupta, A., D.W. Vasco, and J.C.S. Long, "Detailed Characterization of a Fractured Limestone Formation Using Stochastic Inverse Approaches: SPE/DOE paper 27744," 71-86, 1994.

2. Gibson, R.L., Jr., "Radiation from Seismic Sources in Cased and Cemented Boreholes," Geophysics, Vol 59, 1994, pp. 518-533.

3. Harlan, W.S., "Tomographic Estimation of Shear Velocities from Shallow Crosswell Seismic Data," SEG Expanded Abstracts, 16th Annual Meeting, 1990, pp. 86-89.

4. Lines, L.R., K.R. Kelley, and J.H. Queen, "Channel Waves in Cross-Borehole Data," Geophysics, Vol. 57, 1992, pp. 334-342.

5. Majer, E.L., J.E. Peterson, S.M. Benson, and J.C.S. Long, "High Frequency Seismic Tomographic Imaging for Hydrologic Properties of Near-Surface Materials," Earth Sciences Division Annual Report 1990, Lawrence Berkeley Laboratory, Berkeley, CA, 1990.

6. Peterson, J.E., E.L. Majer, and T.M. Daley, J. Queen, P. D'Onfro, and W. Rizer, "Fracture Detection Using Crosswell and Single Well Surveys," Lawrence Berkely Laboratory, Berkely, CA.

7. Queen, J.H., and W.D. Rizer, "An Integrated Study of Seismic Anisotropy and the Natural Fracture System at the Conoco Borehole Test Facility, Kay County, Oklahoma," J. Geophys. Res., Vol 95, 1990, pp. 11255-11273.

DESCRIPTION

Electrical Resistance Tomography (ERT) is used to create 2-D or 3-D visualizations of in situ remediation processes such as air stripping, bioremediation, and subsurface heating. No alternative methods are currently available to image the fluid saturation distributions in true 2-D and 3-D cross-sections of the subsurface.

ERT employs buried electrodes to measure the potential distribution induced from applied electrical current. For the work reported here, arrays of electrodes were buried in two boreholes with some pairs acting as current-source electric dipoles and other pairs acting as potential-measuring dipoles (Figure 4.3). Several boreholes can also be used to produce a 3-D subsurface image.

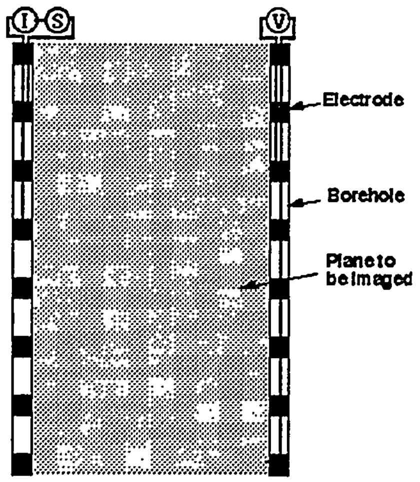


Figure 4.3. Schematic diagram showing the data collection approach for ERT measurements, where:
I = source current
S = current measurement
V = voltage.

The electrodes in each borehole are grouted in place to give quality electrical contact with the formation. Current is driven through the formation from one electrode pair, and the potential difference is measured between other electrode pairs (termed an electrode dipole) in the electrode array. The procedure is repeated for many combinations of source and receiver electrode dipoles. The data collection process can be automated because there are no probes to move within the boreholes (in contrast to other logging techniques).

Calculating the distribution of resistivity in the vicinity of the boreholes based on the measured transfer resistances is a highly nonlinear problem. The nonlinearity results because the current paths are dependent on the resistivity distribution. The ERT inversion process involves solving both the forward and inverse problems. The solution to the forward problem uses the finite element method to compute the potential electrical response in the soil due to the current source. The reverse problem is solved by an iterative inversion routine to approximate the resistivity distribution. The final product of the process is an image (tomograph) showing the distribution of resistivity in the plane between the two boreholes. By interconnecting a network of boreholes, a 3-D representation of the area being investigated can be developed. By analyzing the resistivity images before, during, and after a remediation process, useful 3-D subsurface images (e.g., as of saturation) can be inferred.

The inputs for this technology are switched-polarity, D.C. electric currents that are injected into the formation to measure electrical resistivity. Voltage used depends primarily on the electrical properties of the formation. The voltage used may be as low as 24 V or as high as 200 V. The outputs of the data collection process are measurements of resistance.

TECHNICAL PERFORMANCE

General. The data acquisition rate is sufficiently rapid for detailed measurement of large subsurface regions in reasonable amounts of time. For example, at the Savannah River Project, one cross-borehole data set could be obtained in approximately one hour. ERT is advanced enough to monitor remedial processes in almost real-time; at present the tomograph images are available for inspection a few hours after the data are collected. The sensors are cheap and robust—pieces of stainless steel buried in the ground to depths of hundreds of feet. Sensors can be placed in boreholes (alternatively they can be pushed into the ground, thereby reducing the need for drilling) and/or at the ground surface. True 3-D imaging is possible—not just a series of 2-D planes.

The data acquisition system is computer-controlled and can be operated by personnel with minimal training. Operation requires a technician to interact with the data collection system on a periodic basis to start the automatic program that performs data collection and to connect electrodes in other boreholes to the acquisition systems. Further development of the data collection system will allow unattended data collection and unattended connect/disconnect of electrodes in other boreholes. The data inversion algorithms need to be operated by professionals (such as engineers and physicists) proficient in the use of complex mathematical algorithms. The electrodes used are generally permanently grouted within the boreholes. These stainless-steel electrodes and attached wires can be left in the ground without harm to the environment. If electrodes are placed in radioactive soil or along a contaminated ground surface, they may need to be decontaminated upon removal.

Data inversions require the use of fast engineering workstations, whereas workstations are generally not needed to analyze well-logging data. Data collection times are longer than for the baseline technology (well logging) because more data are required. Finally, the results are relatively more sensitive to the presence of data noise than the baseline technology. Several field experiments were conducted to investigate the capabilities and limitations of ERT.

Monitoring Field Processes. The technology was successfully used at the Dynamic Underground Stripping Project at Lawrence Livermore National Laboratory (LLNL) during FY 1991-1992. The objective was to evaluate the ability of the technology to map the penetration of the steam flood as a function of space and time. Measurements were made during a four-week period (before and during steam injection). Twelve vertical planes were monitored during the test. Data from nine planes are considered reliable; three of the planes yielded unreliable data, which resulted in tomographs that are very different from all others obtained at the site and do not match lithologic columns or induction-well logs obtained in the same wells. These results were probably caused by loss of insulation on the wires connecting these electrodes to the ground surface.

ERT was also used at LLNL to monitor and evaluate subsurface-heating technologies such as six-phase electrical heating and in-situ radio-frequency heating.

ERT was also used to monitor the in situ radio-frequency heating process used for the remediation of volatile organic compounds from subsurface water and soil at the Savannah River Site near Aiken, South Carolina. A dipole antenna located in a horizontal well in the unsaturated zone was used to heat a contaminated clay layer. The heat-induced changes were tomographically imaged by their effects on the formation's electrical resistivity.

Leak Detection at the Hanford Reservation. Field experiments were performed under a 50 ft diameter steel tank mockup located at the Hanford Reservation (200 East Area). Two brine release experiments were conducted. About 1,000 gal of saline were released along a portion of the tank's edge and another 1,000 gal were later released near the tank's center. The solution was a 0.08 molar sodium chloride solution (much more dilute than typical tank liquids). The release rate averaged about 7 gal/hr for each leak. ERT images were made before, during, and after each brine release in each of eight horizontal planes beneath the tank. The image planes were arranged to provide a series of detailed images at many levels which, when assembled together, gave an overall view of the plume formed beneath the tank during the releases.

2-D tomographs collected during the side release experiment showed what areas of the image changed as a result of the brine spill. The changes observed increased in magnitude as the time and spill volume increased. Electrical noise measurements made during the test were used to calculate images that showed the magnitude of changes expected from measurement error. The measurements were then compared to resistivity changes observed during the release. Because the resistivity changes observed were substantially bigger than the changes expected from measurement error, it was concluded that the changes observed were caused by the brine release and not an unrelated phenomena such as measurement errors.

3-D images showing resistivity changes were also collected. In this case, the data were used to calculate resistivity changes within a block underneath the tank (instead of a series of 2-D slices). The 3-D images provide a better view of the changes caused by the leak because the flow regime is truly 3-D; there is no need for interpolation between adjacent 2-D slices. However, the 3-D images take longer to calculate (2 to 3 days per block) than the 2-D images (10 minutes per slice). The 2-D and 3-D images were generally in agreement.

ERT successfully detected the brine releases from both leak locations. The location, magnitude, and time behavior of the anomaly observed during the brine spill support the hypothesis that the anomaly was caused by the leakage and not by unrelated phenomena.

Cost. The hardware costs for data acquisition are approximately $50K. The cost for an engineering workstation to perform data inversions ranges between $10K and $20K. The cost of licensing the data inversion algorithm is negotiated by the DOE and the interested party. The life-cycle costs will depend on several factors, including the application of interest, frequency of use, degree of resolution desired, and flexibility to install electrodes in boreholes used for other types of measurements.

ERT tomographs used in conjunction with core sample information and well logging can be used to spatially extend borehole information much beyond the immediate vicinity of the boreholes. When used in this manner, ERT can reduce borehole drilling costs by at least 50%. This estimate includes the costs of obtaining and collecting ERT data. The analysis conservatively assumes that the unprecedented level of detail offered by ERT could be obtained from the conventional technology by drilling a few additional boreholes and interpolating/extrapolating the information beyond the borehole walls.

Time. It takes approximately two hours to install electrodes in each borehole. Data collection times generally range between 40 minutes and 2 hours per measurement plane; this time depends on the number of electrodes installed in each borehole. Data-processing times generally range from 20 minutes to several hours on a modern engineering work station; this time depends on several factors, including the area of the measurement plane being sampled, the number of measurements collected, and the presence of data noise.

PROJECTED PERFORMANCE

A test version 3-D ERT code was written that incorporates a new version of the forward solver, which is designed to be more accurate and faster than the current solver.

APPLICABILITY

ERT can be used to monitor the progress of subsurface environmental clean-up processes (e.g., air injection, steam injection, water flush, and radio-frequency and low-frequency heating) so that the processes can be adjusted and optimized in almost real time. ERT can also be used to map the movement of liquids in the subsurface; thus it can verify the emplacement and performance of surface and subsurface barriers such as grout curtains. It can also be used to detect leakage from holding tanks and liquid-waste ponds.

STATUS

The technology is near full development. The 2-1/2-D inversion algorithm was tested in several field demonstrations and is available for licensing. A prototype 3-D data inversion algorithm is available, but is being evaluated. An experiment will be conducted to image nonaqueous phase liquids at the Oregon Graduate Institute LEAP tank. The experiment will consist of releasing a DNAPL into a water-saturated sandy loam that has two low permeability clay layers to impede downward movement. ERT images will be made of both resistivity and chargability.

REGULATORY CONSIDERATIONS

Currently, the U.S. Environmental Protection Agency has no system for certifying sensor technology for site characterization or monitoring. Potential worker health and safety hazards are associated with electrical, physical, and chemical hazards of electrode installation. A potential exists for worker exposure to contaminant venting from the well head during electrode emplacement.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include subsurface geologic mapping for mining and petroleum industries. It is commercially applicable for the environmental applications discussed previously, such as monitoring soil heating, soil moisture during steam or gas injection/vacuum extraction, and aquifer perturbations during remediation activities. The technology is also applicable to the medical industry for tomographical imaging for various diagnostic techniques. It can also be used for nondestructive evaluation of large-scale structures such as dams.

BASELINE TECHNOLOGY

The baseline logging technology is measurement of fluid saturation along boreholes performed with any well established geophysical well-logging technique (e.g., neutron and resistivity logs). At least twice the number of boreholes at a closer spacing would be required to be able to observe the same level of detail. ERT directly measures a formation's electrical properties between boreholes using mathematical data reduction techniques; therefore, the tomographical method produces true 2-D and 3-D images. The conventional method of geophysical well logging requires that the measured values be interpolated between the boreholes. The ERT technology is ideally suited for field operations requiring minimal field personnel because, once the electrodes are installed, the data collection system can be designed to run automatically with minimal personnel intervention. In contrast, conventional well logging requires field personnel intervention since a physical probe must be moved vertically within a borehole for those techniques.

INTELLECTUAL PROPERTY

Several disclosures have been submitted on various applications of this technology. Two patents have been awarded. Three patents are in application. The basic ERT technology was transferred to RIMTech of Denver, Colorado, through a Cooperative Research and Demonstration Agreement. Several other companies are negotiating with LLNL to obtain rights to use the technology and to cooperate in further development.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigators

William Daily
Lawrence Livermore National Laboratory
P.O. Box 808, L-156
Livermore, CA 94551
(510) 422-8623; (510) 422-3013 FAX

Abelardo L. Ramirez
Lawrence Livermore National Laboratory
P.O. Box 808, L-206
Livermore, CA 94551
(510) 422-6909; (510) 422-3118 FAX

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

University Partners

Douglas LaBrecque
The University of Arizona
Tucson, AZ

Andrew Binley
University of Lancaster
Lancaster, England

REFERENCES

1. DOE ProTech Database, "Technology Information Profile (rev. 2) for ProTech," Technology Name: Electrical Resistance Tomography, TTP Reference No.: SF-221102, Information last revised July 15, 1993.

2. Daily, W., A. Ramirez, D. LaBrecque, and J. Nitao, "Electrical Resistivity Tomography of Vadose Water Movement," Water Resources Research, Vol. 28, No. 5, 1992, pp. 1429-1442.

3. Ramirez, A., W. Daily, K. LaBrecque, E. Owen and D. Chesnut, "Monitoring an Underground Steam Injection Process Using Electrical Resistance Tomography," Lawrence Livermore National Laboratory, Water Resources Research, Vol. 29, No. 1, 1993.

4. Ramirez, A.L., and W.D. Daily, Monitoring Radio-Frequency Heating of Contaminated Soils Using Electrical Resistance Tomography, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-115373, September 1993.

HYDROLOGIC SENSORS FOR THE CONE PENETROMETER SYSTEM

DESCRIPTION

Sensors which will allow real-time, continuous measurement of hydrogeologic parameters for use in contaminant transport modeling and risk assessments have been developed. The sensors are deployed in a cone penetrometer system composed of a push-rod assembly with down-hole sensors which, by the weight of the delivery vehicle, hydraulically pushes the push-rods into the subsurface for a minimally intrusive characterization hole (see profile titled "Heavy Weight Cone Penetrometer").

The sensor packages measure volumetric moisture content and unsaturated zone pore pressure with the cone penetrometer system. The moisture content sensor is based on electromagnetic pulsed wave form analysis techniques. The capillary pore pressure sensor is based on porous-polymer fiber-optic measurement techniques.

Moisture Content Probe. The moisture content sensor employs an electromagnetic pulse technique called Time Domain Reflectometry (TDR). TDR measurement of volumetric moisture content is based on the significant difference between the dielectric constant of soil and that of water. As the moisture content of the soil increases, the dielectric constant of the soil will increase. Dielectric constants are traditionally determined by measuring the transit time of an electromagnetic pulse propagating along parallel wave guides placed in the soil.

In order to adapt the TDR technique to a cone penetrometer application, the configuration of dipole elements was optimized to enhance the signal response of the electromagnetic wave pulse and to maximize the radius of influence on the probe. The radius of influence was determined in the laboratory. The majority of the electromagnetic response occurs within the first several centimeters about the probe assembly, with the radius of influence at approximately 10 cm.

Capillary Pore Pressure Probe. Soil-water potential or capillary pore pressure is a measure of the tenacity with which water is held by a soil matrix. A new fiber optic approach developed by Sandia National Laboratories (SNL) in cooperation with Geo-Centers, Inc., measures relative humidity (RH) without dew point estimates or temperature compensation methods. The fiber-optic pore pressure sensor uses a porous-polymer sensing element that includes a chemical sensitive material that changes color as a function of relative humidity (RH). The probe is calibrated to measure RH at very high sensitivities, between 98% and 100% RH, from which pore pressure is calculated.

TECHNICAL PERFORMANCE

The TDR moisture content probe and the fiber optic pore pressure probe were demonstrated and tested in two separate field trials as follows.

First Field Trial. The first field trial occurred at the Applied Research Associates' (ARA) cone penetrometer manufacturing facility in South Royalton, Vermont, in October 1994. The objectives were to: (1) test SNL hardware interfaces with test software developed for data acquisition from the TDR and RH probes, (2) test SNL hardware interfaces with ARA systems, (3) test the cone penetrometer TDR and RH probes in situ, (4) assess feasible data sampling rates and sampling efficiency, and (5) monitor for unwanted electrical energy (noise) interfering with measurements and eliminate it if found. Testing was performed at South Royalton so that any unforeseen technical difficulties could be corrected at the ARA laboratory before mobilizing the cone penetrometer rig SNL. Results of testing and calibration work were good, and no significant changes to the design or operation of the two probe configurations were required. However, the RH probe was not ideally suited to the moist soils in Vermont (as anticipated); it is more suitable to the drier soils of the southwest. In addition, the probe configuration selected for delivery of the RH sensor was a porous screen housing prone to plugging when pushed through fine-grained clayey soils.

Second Field Trial. The second field trial was performed at SNL in Albuquerque, New Mexico during November 1994. Most of the cone penetrometer pushes were done at a site where water had infiltrated several days before the testing. The site was chosen for contrasting moisture contents anticipated as a result of the infiltration and redistribution of the infiltration experiment. Approximately 75 meters of hole were pushed during the four day field trial, with each push between 18 and 14 meters in depth. Strong geological influences were apparent, controlling the movement and distribution of water. It was also apparent from the cone penetrometer results that finer scale features that affect the movement of water in a given geologic unit were evidenced by moisture movements, even though the lithology predicted from the geotechnical sensors suggested homogeneity.

PROJECTED PERFORMANCE

Although the RH sensors responded quickly in the laboratory, redesign is necessary to make the housing more suitable for "real-time" cone penetrometer applications.

Future work on these sensor packages may include adding other chemical-specific probes in the same fiber-optic assembly, coupling the TDR moisture probe to other chemical sensors that may require compensation for moisture effects (e.g., Laser Induced Fluorescence techniques), and integrating other hydrogeologic sensors (e.g., permeability or flow probes).

APPLICABILITY

The real-time sensor packages engineered into the cone penetrometer technology are applicable to measuring moisture content and pore pressure in subsurface environments for use in contaminant transport modeling, risk assessments, and remediation optimization (e.g., soil venting and bioremediation strategies). In addition, the moisture sensor may become a desired sensor for lithologic interpretations.

STATUS

The two probes have been prototyped, lab tested, and twice field tested. No major design changes are necessary for deployment to standard practice. The TDR moisture probe exceeded performance expectations. Because of the longer equilibrium times, the capillary pore pressure probe is better suited for longer monitoring measurements than real-time measurements. Technology transfer initiatives are underway to commercialize/license the technology. A transfer of the TDR moisture probe to the U.S. Navy cone penetrometer group is also being investigated.

A report detailing the field trials discussed earlier is scheduled to be completed by September 1995.

REGULATORY CONSIDERATIONS

Use of the cone penetrometer system requires compliance with regulations concerning subsurface access and characterization by well drilling.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is applicable to any environmental characterization project requiring subsurface moisture or pore pressure data for transport modeling, risk assessments, or optimization of remediation strategies.

BASELINE TECHNOLOGY

Conventional measurements of soil moisture content are performed using laboratory methods (i.e., oven drying) and field methods (i.e., neutron probe). The conventional approach to measuring capillary pore pressure in dry soils is a thermocouple psychrometer, which actually measures dew points and temperature to calculate relative humidity, which in turn is used to calculate pore pressure.

INTELLECTUAL PROPERTY

The sensors are being reviewed for patent/copyright protection. Geo-Centers, Inc., developed the patented/proprietary fiber-optic sensor package.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Robert Knowlton
Sandia National Laboratories
P.O. Box 5800, MS-0715
Albuquerque, NM 87185-0715
(505) 844-8533; (505) 844-9449

DOE Projects Manager, CMST-CP

Eric Lightner
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7935

Industrial Partners

Bruce Nelson
Geo-Centers, Inc.
Seven Walls Avenue
Newton Center, MA 02159
(617) 964-7070, FAX (617) 597-7592

Wes Bratton
Applied Research Associates, Inc.
RR#1, Box 120-A, Waterman Road
South Royalton, VT 05068
(802) 763-8348; (802) 763-8283 FAX

REFERENCES

1. Knowlton, R., W. Strong, J. Onsurez, and E. Rogoff, "Advances in Hydrologic Measurement Techniques - In Situ and Cone Penetrometer Applications," Proceedings of the European Symposium on Optics for Environmental and Public Safety, Munich, Germany, June 19-21, 1995 (in press).

2. "Hydrologic Sensors for the Cone Penetrometer System," Technology Applications Program Brochure, Sandia National Laboratories, Albuquerque, NM, February 1995.

3. Knowlton, R.J. Onsurez, S. Bayliss, and W. Strong, "Environmental Applications of Time Domain Reflectometry at Sandia National Labs," Symposium and Workshop on Time Domain Reflectometry in Environmental, Infrastructure, and Mining Applications, Northwestern University, Evanston, Illinois, Special Publication SP 19-94, September 7-9, 1994, pp. 183-192.

4. Knowlton, R., L. Everett, S. Bayliss, S. Cullen, J. Kramer, J. Onsurez, E. Rogoff, and W. Strong, "Environmental Monitoring Techniques for Characterization and Post-Closure Monitoring Needs," First Hawaii National Technologies Conference: Remediation and Environmental Monitoring, Honolulu, Oahu, Hawaii, September 12-16, 1994.

DESCRIPTION

Groundwater flow is perhaps the most important mechanism for the dispersal of many types of toxic contaminants once they have been released into the subsurface. Accurate information about the groundwater flow is critical to the characterization of contaminated sites, the monitoring of remediation activities, and the monitoring of post-closure performance of remediated sites. In situ permeable flow sensors can measure the full three-dimensional groundwater flow-velocity vector at a point in a saturated, permeable, unconsolidated medium using only one hole. In situ permeable flow sensors require only very crude estimates of the hydraulic conductivity; thus, they eliminate costly testing to determine hydraulic conductivity. The flow sensors measure the velocity characteristic of a very small volume of material, on the order of 1 m^3. The sensors are simple to install and can be monitored remotely for extended periods of time without requiring personnel in the field. Use of this technology at a site does not preclude using any other technology at the same time or at some future date. Figure 4.5 is a schematic of the In Situ Permeable Flow Sensor.

A thin cylindrical heater is buried vertically in the ground, at the point where the groundwater flow velocity is to be measured. If the heat flux out of the cylinder is uniform over the surface of the cylinder, then the temperature distribution on the surface of the cylinder will vary as a function of the direction and magnitude of the groundwater flow velocity past the cylinder. In the absence of any flow past the device, the temperature on the surface of the probe will be independent of the azimuth and symmetric about the vertical midpoint of the probe. The vertical midpoint will be warmer than the ends of the probe because heat transfer away from the ends of a finite length cylinder is more efficient than from the midsection of the cylinder. Groundwater flow past the device perturbs the surface temperature distribution, with the pattern and magnitude of the temperature variations reflecting the direction and magnitude of the groundwater flow. Relatively warm temperatures will be observed on the downstream side of the instrument and relatively cool temperatures on the upstream side as the heat introduced into the formation by the heater is conveyed away by the groundwater flow.

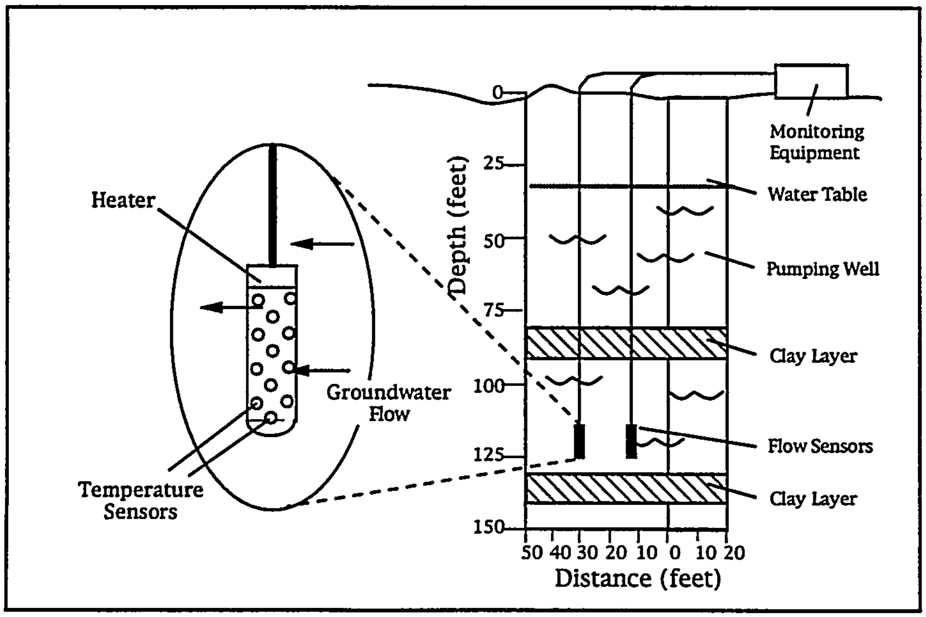


Figure 4.5. Schematic of the In Situ Permeable Flow Sensor.

If the groundwater flow has a vertical component, the vertical temperature distribution on the surface of the probe will no longer be symmetric about the vertical midpoint of the probe, but will be skewed in the direction of the flow. The surface of the downstream end of the probe will be warmer than the upstream end. If the flow velocity has a significant horizontal component, the surface temperature distribution will not be independent of the azimuth, but will vary approximately as the cosine of the azimuth, with the downstream side of the probe being warmer than the upstream side. The magnitude and direction of the three-dimensional flow velocity are determined from the magnitude and the pattern of the temperature variations on the surface of the probe, respectively.

Electric power, either from line power or a generator, is required. For remote monitoring, access to a telephone line or cellular phone service is also desirable (data transfer by radio frequency transmission is presumably possible).

TECHNICAL PERFORMANCE

The way in which probes are fabricated and deployed in the ground is critical to obtaining a valid measurement. The current strategy involves constructing very simple, inexpensive probes that can be permanently buried in saturated, unconsolidated sediments. Each probe consists of a rod of low thermal conductivity, closed cell, polyurethane foam, 30 inches long by 2 inches in diameter, surrounded by a thin film, flex circuit heater, an array of 30 degree, carefully calibrated thermistors and a waterproof jacket. The design seeks to achieve a high uniformity heat flux from the probe and sufficient temperature sensors to adequately characterize the temperature distribution on its surface. The thermistors are calibrated such that the temperature differences between sensors are accurate to within ±0.01°C.

The in situ permeable flow sensor can measure groundwater flow velocities in the range of approximately 0.01 to 3 ft/d depending on the thermal properties of the formation.

Failure occurs when the waterproof coatings ultimately leak, allowing water into the probe where it shorts out the electronics. Failure of the probe does not present any serious consequences other than the fact that useful flow-velocity measurements will no longer be available.

The sensor measures the velocity at essentially a point. Sometimes the average velocity over a wider area is desirable. The standard technique measures a velocity that is an average of the velocity over a much broader region, one whose dimensions are characterized by the separation of the boreholes.

Field Tests. Field tests conducted at the Savannah River Site (SRS) assessed the accuracy of the technology by directly comparing flow velocity measurements obtained with the flow sensors to velocities estimated using standard hydrologic techniques. Two flow sensors were deployed in a confined aquifer. The well was subsequently pumped at four different pumping rates (3, 6, 9, and 15 gpm). As predicted by theoretical considerations, the magnitude of the horizontal component increased linearly with pumping rate. Results of the tests indicated that the technology is capable of measuring groundwater flow velocities as low as a few hundredths of a foot per day in saturated, unconsolidated geologic materials and the probes are simple to install and monitor. In addition, data from a number of probes at the same site can be collected and sent via modem to computers at a remote site. After installation the system can be operated remotely for extended periods of time with only occasional maintenance.

Flow Velocity Measurements. In July 1994, an in situ permeable flow sensor was deployed within a sand-filled conduit in a salt dome directly beneath a sinkhole that was discovered above a Strategic Petroleum Reserve storage facility at Weeks Island, Louisiana, in 1992. The flow sensor measured substantial groundwater flow directed vertically downward into the salt dome. The data obtained with the flow sensor provided critical evidence that was instrumental in assessing the significance of the sinkhole in terms of the integrity of the oil storage facility.

Cost. Each flow sensor is estimated to cost between $2.5K and $3K. In remote-monitoring applications, approximately one-tenth of a person's time is required to collect and analyze the data.

PROJECTED PERFORMANCE

In future deployments the challenge will be to find ways to install the probes so that disturbance of the hydrologic and thermal properties of the medium is minimized. Alternative drilling methods such as cone penetrometer emplacement, and more careful well completion (i.e., grouting the hole above the flow sensor) will be considered.

APPLICABILITY

This technology is specifically used for obtaining groundwater flow-velocity information at contaminated sites.

STATUS

Virtually all of the components for the sensors and the data acquisition system are available commercially. The system was successfully demonstrated and the technology is licensed to SIE, Inc. of Ft. Worth, Texas for commercialization. Systems are available for purchase.

REGULATORY CONSIDERATIONS

Compliance with the Occupational Safety and Health Administration regulations is required for hazardous-waste operations and protection of workers from electrical power. In addition, permits may be required for drilling at contaminated sites.

POTENTIAL COMMERCIAL APPLICATIONS

The in situ permeable flow sensor can be useful at a wide variety of sites and with several different remediation processes. They can be used at any site where information on groundwater flow velocity is necessary. Such information is critical to the characterization of waste sites, the monitoring of remediation activities, and the monitoring of post-closure performance of remediated sites.

BASELINE TECHNOLOGY

The baseline technology uses hydraulic head gradients and hydraulic conductivities in boreholes to determine flow velocity. Three holes are required for a measurement using this technique, in comparison to only one hole with the in situ permeable flow sensor. Information about the hydraulic conductivity of the medium is required in the standard technique. This is generally determined using a pump test in which large quantities of water are pumped from the well. At contaminated sites, disposal of this water can be difficult and expensive. The flow sensors measure the velocity characteristic of a very small volume of material, on the order of 1 m^3. The standard technique measures a velocity that is an average of the velocity over a much broader region, one whose dimensions are characterized by the separation of the boreholes.

INTELLECTUAL PROPERTY

This technology is in the public domain. Sandia National Laboratories has applied for copyrights on engineering drawings and on the software that interprets flow-sensor data.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Sanford Ballard
Sandia National Laboratories
P. O. Box 5800, Org. 6116
Albuquerque, NM 87185-5800
(505) 844-6293; (505) 844-7354 FAX
email: sballar@sandia.gov

DOE Program Manager

Kurt Gerdes
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7289

Industrial Partner

Jim Gibson
SIE, Inc.
7450 Winscott Road
Ft. Worth, Texas 76126
(817) 249-7200; (817) 249-7222 FAX

REFERENCES

1. Ballard, S. and J. Gibson, "Groundwater Flow Velocity Measurements in a Sinkhole at the Weeks Island Strategic Petroleum Reserve Facility, Louisiana," Proceedings of the Symposium on the Application of Geophysics to Environmental Engineering Problems, Orlando, FL, April 23-26, 1995.

2. Ballard, S., In Situ Permeable Flow Sensors at the Savannah River Integrated Demonstration: Phase II Results, Sandia Report, SAND94-1958, August 1994.

3. Ballard, S., G. T. Barker, and R. L. Nichols, The In Situ Permeable Flow Sensor: A Device for Measuring Groundwater Flow Velocity, Sandia Report, SAND93-2765, March 1994.

4. Ballard, S., In Situ Permeable Flow Sensors at the Savannah River Integrated Demonstration: Phase I Results, Sandia Report, SAND92-1952, October 1992.

5. Ballard, S., T. Baker, and R.L. Nichols, "A Test of the In Situ Permeable Flow Sensor at Savannah River, SC," accepted by the Journal of Groundwater, (in press).

6. Ballard, S., "The In Situ Permeable Flow Sensor: A Groundwater Flow Velocity Meter," accepted by the Journal of Groundwater, (in press).

MAGNETOMETER TOWED ARRAY

DESCRIPTION

The Magnetometer Towed Array (MTA) is a nonintrusive system for the detection and quantification of buried wastes. MTA was developed by the U.S. Naval Research Laboratory and the U.S. Department of Energy (DOE). A commercial version was developed by the Search Technology Division of Geo-Centers, Inc., of Newton, Massachusetts. It was built to detect ordnance and has been adapted to help characterize buried hazardous-waste sites.

The MTA is a high-technology geophysical survey device consisting of a vehicle-towed sensor array containing seven magnetometers integrated with a state-of-the-art Global Positioning System (GPS). A computer aboard the rugged off-road tow vehicle simultaneously collects magnetic data and navigation data at a density of about 100,000 points per acre, 100 times greater than with conventional manual technologies. The acquired data are processed to produce high resolution magnetic image maps of the surveyed area that are analyzed on a Unix workstation via the automated target analysis software. The user selects an anomaly in the data and the software performs an automated least-squares model match to determine the position, depth, and size of the isolated target. Figure 4.6 shows the vehicle based environmental system. Specifications for MTA are listed in Table 4.6.

TECHNICAL PERFORMANCE

This technology was successfully demonstrated at the RB-11 Landfill at Kirtland Air Force Base, New Mexico, and was used in commercial surveys at Sandia National Laboratories (SNL), New Mexico; Rocky Mountain Arsenal, Colorado; and the DOE Grand Junction Projects Office, Colorado, to name a few.

Sandia National Laboratories Field Tests of MTA. In September 1993, MTA was used to characterize buried wastes at the Sandia National Laboratories (SNL) Technical Area 2. With a 0.5 m spacing between magnetometers and each magnetometer operating at 20 Hz, the effective survey grid (per sensor) at 5 mph is 0.12 m by 0.5 m. Consequently,

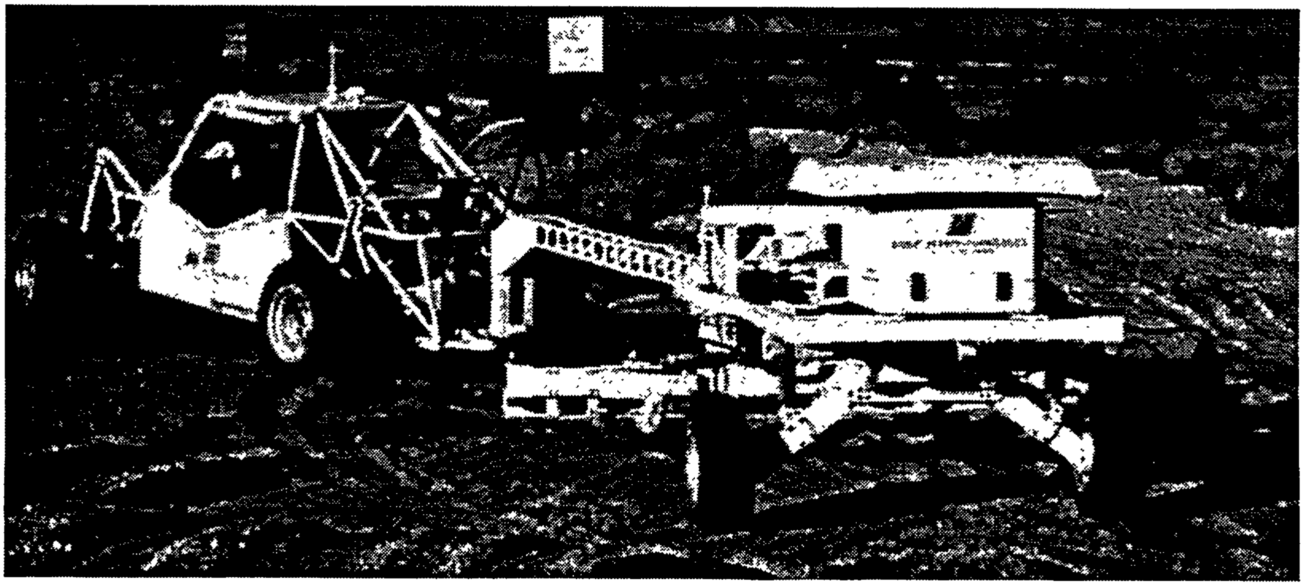


Figure 4.6. The Magnetometer Towed Array.

Table 4.6. Magnetometer Towed Array specifications.

Type	Cesium vapor (7 each)
Survey Rate	3.5 - 5 mph (5.6 - 8 km/hr)
Coverage	10 - 15 acres/day
Data Density	100,000 points/acre @3.5 mph
Position Accuracy	<0.5 meters
Power Supply	120 Volt, 1,000 Watt

MTA maps provide outstanding resolution. At Technical Area 2, buried objects such as culverts, pipes, and a septic system were delineated along with several previously unknown anomalies. Additionally, MTA was deployed at the SNL Chemical and Radioactive Waste Landfills. The system detected and characterized in terms of location, size, and depth, several objects including roadbeds, fence posts, pipes, barrels, and trenches containing waste containers.

RB-11 Test of MTA. During the week of September 7, 1993, the commercially available system was demonstrated at the RB-11 Landfill. Less than 2 hours was required to actually survey the 4.5 acre site. Among the findings were: (a) previously unidentified, large (1 in diameter) electrical cable was buried across some of the pits at a depth of about 3 ft, (b) the collapsing trench was found to contain ferrous metal, and (c) one of the northern pits was found to extend much further north than previously believed.

Geophysics Performance Evaluation Range (GPER). The DOE GPER is located in Rabbit Valley, 30 miles west of Grand Junction, Colorado. The purpose of the range is to provide a test area for geophysical instruments and survey procedures. A magnetic survey was conducted with the commercial MTA in September 1993 to assess the equipment's accuracy, resolution, and target detectability; and, to establish a large-scale baseline data set on the undisturbed areas for comparisons as more artifacts are buried in the future. The system acquired data over approximately 30 acres in four days. Overall, the MTA system detected three ferromagnetic objects, several other major magnetic anomalies above background, and other smaller anomalies. The three objects identified corresponded to known buried artifacts. The position error was less than 0.5 m.

Cost. The MTA is commercially available from Geo-Centers, Inc. Costs vary depending on site access, site size, health and safety requirements, and topographical characteristics, etc. The vehicular based system can collect high fidelity data at a maximum velocity of 20 mi/hour. Most experience to date has been at rates ranging from 3 to 6 mi/hr. When an average velocity of 5 mi/hr can be maintained, 25 acres per day can be surveyed. Prices charged for this rate of coverage are less than $900 per acre. Operation costs are more than competitive with conventional technology on larger sites and provide same-day, high-resolution data. Detailed cost data may be obtained from Geo-Centers, Inc.

PROJECTED PERFORMANCE

Geo-Centers, Inc., has incorporated several significant additions to the technology that are expected to improve performance, including:

- Multi-sensor, multi-modal survey capability

  This sensor suite was designed to maximize the probability of detection over the entire range of possible buried items, while minimizing false alarms caused by clutter.

- Increased modeling capabilities

  New parameter estimation techniques based on empirical model matching, and the Geographical Resource Analysis Software System (GRASS) originally developed by the Army Corp of Engineers, have been implemented to manipulate, correlate and manage all digital spatial data.

- Increased capabilities through increased data quality

Modifications to the vehicle and systems power supply, incorporation of selected materials, redefinition of sensor geometry, and replacement of electromagnetic system electronics have reduced the noise level of the system by one order of magnitude. This improvement has resulted in a significantly higher overall detection ratio for small targets and large deep targets.

- Improved RTK Global Positioning System

APPLICABILITY

This technology is applicable for detection and identification of metallic objects (e.g., ferrous material) in the subsurface at any site that can be traversed by the MTA.

STATUS

Work with SNL will be completed in FY 1995.

The MTA is available for commercial surveys through Geo-Centers, Inc. A portable version is also available.

REGULATORY CONSIDERATIONS

This technology is nonintrusive and passive. The vehicle is driven across the site and measures the Earth's natural magnetic field. As with any operation at a hazardous waste site, health and safety protocol must be followed. No specific permits are required to use this equipment and technology.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be used for any site needing characterization and for buried hazardous wastes such as buried drums of waste, utility lines, fence posts, etc.

BASELINE TECHNOLOGY

Current technology requires a person to walk a grid and take measurements by hand. The data are then transferred to a contouring package for plotting. The resulting plots are then visually interpreted. A typical survey grid is 5 ft x 5 ft or 10 ft x 10 ft, with survey rates of an acre or two per day. The time-consuming nature of the survey usually prevents large areas from being surveyed (e.g., outlying burials are missed). Further, the coarse grid does not allow the boundaries of burials to be adequately determined and may miss small, isolated targets.

INTELLECTUAL PROPERTY

Geo-Centers, Inc. has several patent applications in process. This technology is a commercial service offered by Geo-Centers, Inc. U.S. Naval Research Laboratory and Sandia National Laboratories' work are both public domain.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
John R. Cochran
Sandia National Laboratories
P. O. Box 5800, Org. 6331
Albuquerque, NM 87185-1345
Phone: (505) 848-0415;(505) 848-0764 FAX

DOE Program Manager
Skip Chamberlain
U. S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

Industrial/Laboratory Partners

Richard J. Russell
Geo-Centers, Inc.
7 Wells Avenue
Newton, MA 01824
(617) 964-7070; (617) 527-7592 FAX

Jim McDonald
Code 6110
U.S. Naval Research Laboratory
Washington, DC 20375-5000
(202) 767-3340

REFERENCES

1. Geo-Centers, Inc., "STOLS™ Magnetic Survey at Sandia National Laboratory Technical Area 2," October 1993.

2. Foley, J.E., "Environmental Characterization with Magnetics and STOLS™," Proceedings of the IEEE, Vol. 82, No. 12, December 1994.

3. McDonald, J.R., R. Robertson, and J.R. Cochran, Results of a Magnetometer Towed Array Survey and Sub-System Testing at Site RB-11, Kirtland Air Force Base, Albuquerque, NM, Naval Research Laboratory, NRL/PU/6110-94-257, May 9, 1994.

4. McDonald, J.R., H.H. Nelson, and R. Robertson, Microwave and Differential GPS Navigation Systems: Field Performance Tests, Naval Research Laboratory, NRL/PU/6110-93-244, July 1993.

5. Magnetometer & Radar Evaluations of Toxic and Hazardous Waste Sites at the Sandia National Laboratories, Naval Research Laboratory, NRL Prob. No. 61-M213-X-1, April 30, 1992.

6. Sandia Technology, Engineering and Science Accomplishments, February 1994.

7. Sandia Science News, February 1994.

8. Environment Today, January 10, 1994.

9. Hazmat World, January 1994.

10. Environmental Remediation Technology, Vol. 1, No. 6, December 1, 1993.

POST-CLOSURE MONITORING

DESCRIPTION

Post-closure monitoring for soil moisture and contaminant transport is of cardinal importance to the containment remedial option. Two aspects of this technology are the evaluation of water saturation and chemical transport. Soil moisture is a critical variable influencing chemical transport in landfills. The objective of the Post-Closure Monitoring (PCM) task is to design, construct, install, field test, and evaluate an automated state-of-the-art soil moisture and chemical transport monitoring system for measuring the hydrologic performance of migration barriers and advanced surface covers for remediating landfills.

Field experiments have focused on evaluation of water saturation and chemical transport monitoring technologies. Comparison of the established, conventional neutron probe technique for measurement of water saturation with recent developments in state-of-the-art Time Domain Reflectometry (TDR) probe systems is being used to evaluate opportunities for automated and more detailed characterization. Soil water content measurements have been collected using neutron probe technology by the Environmental Sciences Group (EES-15) of Los Alamos National Laboratory for the past 15 years. With the arrival of Time Domain Reflectometry and its comparative ease of installation, use and adaptability to automated data collection, many field endeavors that formerly employed neutron probe measurements are now being monitored with TDR. A comparison of the two techniques is desirable to determine if the data collected by the TDR technique is a valid replacement for the more labor intensive but reliable and accepted neutron probe method.

Chemical transport is being evaluated through the detection of contaminant and chemical tracers. Application of tagged tracers allows the evaluation of both barrier system effectiveness and potential contaminant transport pathways or imminent arrival. Tracers for the permeable barrier experiments include low concentrations of common anions (e.g., bromide), soluble organic acids, semivolatile organic acids, fluorescein, chromium, and EDTA. The tracer/pseudo-contaminant for the bio-barrier experiments focused on toluene labeled with carbon-13 to allow specific characterization of transport and biodegradation processes as a function of plant cover and fertilization.

TECHNICAL PERFORMANCE

The results of a ten-month study to compare TDR and Neutron Probe measurements of soil water content are presented and indicate good comparability overall; however, there are two notable instances where the results diverge. Two field plots constructed of homogeneous crushed Bandelier tuff were used for this study. Each plot has three access tubes evenly spaced on the longitudinal axis of the plot. Near two of the neutron probe tubes of each plot, a series of TDR waveguides and temperature probes were placed at various depths with either a vertical or a horizontal orientation to approximate the neutron probe interrogation zones. The TDR system consists of TDR rod pairs connected to a Campbell Scientific (Logan, Utah) multiplexer (model SDMX-50) by coaxial cable. All electronic components were mounted in weatherproof housings and the entire system was powered by a Campbell Scientific 18 watt solar panel. A Campbell Pacific Nuclear Corp. (Martinez, California) model 503DR hydroprobe was used to collect neutron probe data. The probes use an encapsulated ^{241}Am/Be source. The calibration employed for converting gross counts to volume percent water content was derived from previous monitoring on the plots.

Several comparisons were made with various combinations of neutron probes at 15, 30 and 45 cm depths with either horizontal or vertical TDRs at 15, 30, 45 and 60 cm depths. Two of these comparisons are presented as an example. The first comparison shown in Figure 4.7a shows the neutron probe located at a 30 cm depth having a spherical interrogation volume of an assumed 30 cm diameter. The average measurements of three horizontal TDR wave guides installed at 15, 30, and 45 cm depths are intended to approximate the neutron probe interrogation volume. Figure 4.7b is a composite plot of the soil water content data by the neutron probe (at 30 cm) and averaged TDR data (horizontal TDRs, 15, 30, and 45 cm) for this configuration. Figure 4.7c illustrates a good degree of correlation between the TDR moisture measurements and neutron probe moisture measurements.

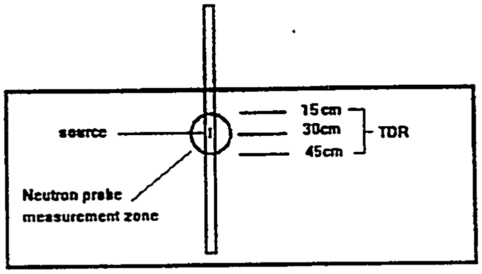


Figure 4.7a. Configuration.

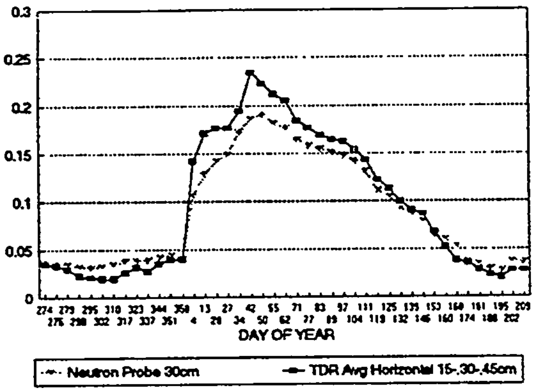


Figure 4.7b. Time series plot.

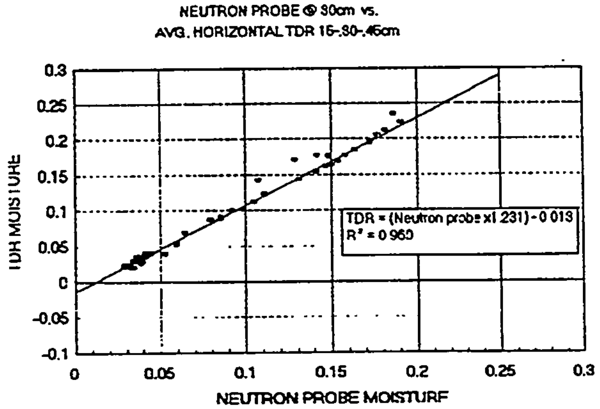


Figure 4.7c. TDR and neutron probe regression.

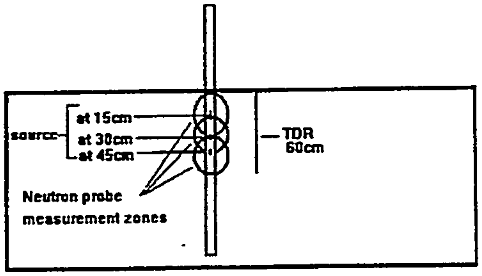


Figure 4.7d. Configuration.

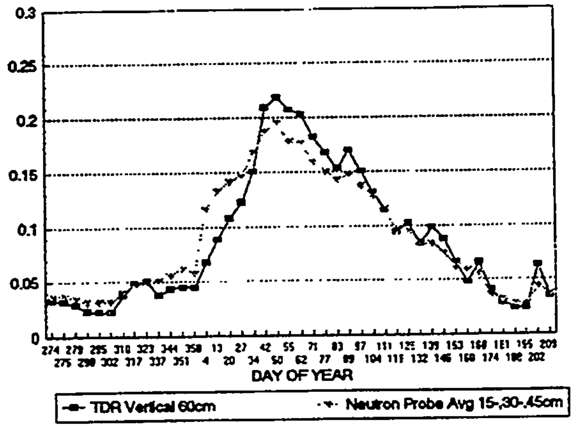


Figure 4.7e. Time series plot.

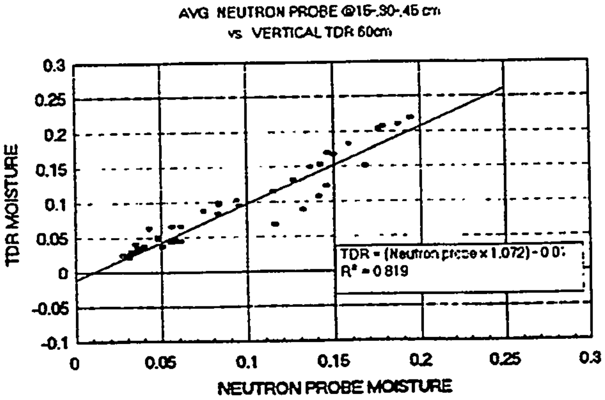


Figure 4.7f. TDR and neutron probe regression.

A contrasting comparison had neutron probe measurement at 15, 30 and 45 cm depths with a single vertical TDR probe of 60 cm length as shown in Figure 4.7d. The composite time series plot for soil moisture by both TDR and neutron probe methods is shown in Figure 4.7e.

It is obvious that the spherical interrogation regions of the neutron probes are different from the linear, vertical (or cylindrical) interrogation region of the TDR and this may contribute to some degree to discrepancies shown in the composite series plots. While overall there is a good degree of correlation, there are at least two unique variances that can be seen. In Figure 4.7e (for days 279-358), it appears that when the soil temperatures were below freezing there was a suppressing effect on vertically placed TDRs. The suppression was reflected in the low correlation coefficients of all comparisons involving vertical TDRs (R^2 values between 0.815 and 0.852). Horizontally placed TDR averages were affected by freezing but to a much lesser degree. It is most probable that freezing conditions only effect horizontal TDRs closest to the surface and vertical TDRs because they penetrate the surface; this is suggested by comparison of Figures 4.7b and 4.7e. In contrast, as the water content values approached 20%, the neutron probe readings appear to attenuate while TDR readings continue to rise. Whether this discrepancy is caused by the calibration used on the neutron probes or some other factor has not been determined.

Cost. Cost estimates were not available at this writing.

PROJECTED PERFORMANCE

Recent results for the contaminant migration monitoring studies were not available at the writing of this profile. Cost and performance competitive results for the six TDRs studied in the past will be available in late 1995.

APPLICABILITY

TDRs and neutron logging moisture probes are applicable to determining the moisture content in porous media such as soils. Also, TDRs have also been studied for application to liquid volume determinations in remnant salt cake waste at the Hanford underground storage tanks. TDRs have been applied in liquid level determination in other critical storage tank applications.

STATUS

The TDR probes are state-of-the-art internal radar devices that are commercially available in both domestic and international markets. However, their application to replace neutron probes in PCM situations is recent and experimental verification is justified. A demonstration has been initiated at Keneohe Marine Corp Base, Hawaii, using an automated system with off-the-shelf technology. Neutron probes are also commercially available and have been extensively studied and demonstrated as well as applied for soil moisture studies and in PCM applications.

REGULATORY CONSIDERATIONS

TDR probes do not require any specific permits and are not expected to cause any environmental impacts. Neutron probes require U.S. Department of Transportation certification for transport.

POTENTIAL COMMERCIAL APPLICATIONS

PCM using TDR and/or neutron logging is potentially applicable to a large number of municipal- and industrial-waste landfills.

BASELINE TECHNOLOGY

The baseline technology for moisture monitoring in soils is the neutron probe. TDRs may be much more suited for monitoring applications because of their comparative ease of installation and adaptability to automated data logging.

INTELLECTUAL PROPERTY

None.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Ken Bostick
Los Alamos National Laboratory
MS-J495, EES-15
P.O. Box 1663
Los Alamos, NM 87545
(505) 667-8483

DOE Program Manager
Skip Chamberlain
U. S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

REFERENCE

1. Schofield, T.G., G.J. Langhorst, G. Trujillo, K.V. Bostick, and W.R. Hansen, Comparison of Neutron Probe and Time Domain Reflectometry Techniques of Soil Moisture Analysis, Los Alamos National Laboratory Report, LA-UR-94-981, September 1994.

RAPID GEOPHYSICAL SURVEYOR

DESCRIPTION

The Rapid Geophysical Surveyor (RGS) is a passive, nonintrusive measurement system that automates the collection of high-spatial-resolution geophysical data. Closely spaced data are required to adequately characterize complex buried-waste areas commonly found in the Department of Energy, Department of Defense (DoD), and private sectors. The system measures and associates the local magnetic field with precision positioning in a systematic fashion. Variations in the Earth's local magnetic field are indicative of subsurface ferromagnetic material which is a common component of buried wastes.

The RGS consists of magnetic-field sensors, a calibrated measuring wheel, and a microprocessor-based data logger mounted on a hand-pushed, nonferrous vehicle. The data logger uses menu-driven software so that the key survey parameters can be configured by the user. The user pushes a 20 lb cart to collect magnetic data (see Figure 4.8). Magnetic data are automatically collected and stored at user-specified intervals as close as 2 in apart along survey profile lines. These data form a high-resolution database capable of locating individual objects and potentially determining object orientation, shape, and depth to burial. No input is required for this passive system, and the output of the RGS is a set of spatially correlated magnetic data.

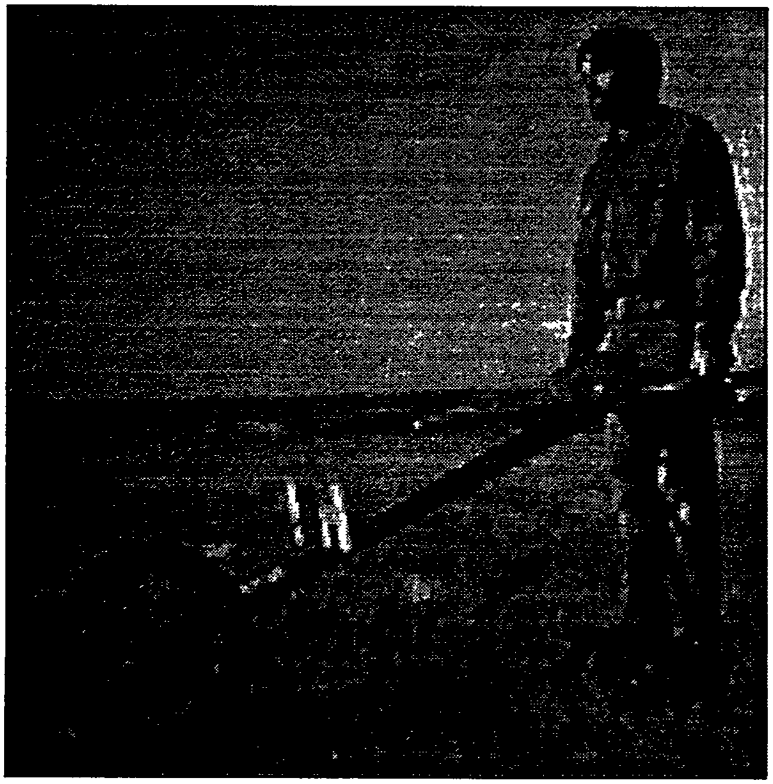


Figure 4.8. Rapid Geophysical Surveyor.

TECHNICAL PERFORMANCE

Field Demonstration. The RGS was initially field tested in September 1992 at the Subsurface Disposal Area (SDA) at the Idaho National Engineering Laboratory (INEL). The system functioned so well that a production survey of the Pit 9 area within the SDA was performed with the prototype RGS in October 1992. Since then, the RGS has been used on many sites within the INEL and for outside agencies, including the DoD and the Environmental Protection Agency (EPA). The RGS was successfully used to locate waste trenches and pits, underground storage tanks, and underground utilities. It was used with success in isolated areas and in the proximity of buildings and above-ground utilities where magnetic noise is a concern for conventional magnetic instruments and surveys.

The RGS has demonstrated data-collection rates of up to 30,000 data points per hour compared to a maximum of about 200 data points per hour for baseline, handheld magnetometer technologies. Also, because the RGS automates data collection, errors caused by human fatigue are greatly reduced, improving field efficiency and overall accuracy. The RGS is a self-contained unit, drawing all power from a single 12 volt, 7 amp-hour gel cell battery that supports 8 hours of continuous operation before a battery recharge is required.

Cost. Survey cost with the RGS is proportional to site size and is essentially the man-hours required to perform the survey, as the capital investment in the equipment is very small. The initial development cost of the RGS was $80K. It is anticipated that the cost of a commercial version of the RGS would be well under $10K.

PROJECTED PERFORMANCE

Potential enhancements include the addition of a remote absolute positioning system that would preclude the use of the measuring wheel to track relative distance travelled by the RGS. A number of technologies have potential application, such as microwave interferometry, ultrasonics, optical techniques, and global-positioning systems.

APPLICABILITY

The RGS is applicable to all problems where ferromagnetic material is included in the waste search target. This includes waste pits and trenches in landfill scenarios and underwater applications. This concept can also be expanded to include other nonintrusive geophysical instruments such as electromagnetic devices.

STATUS

The RGS is commercially available to the private sector as a service through Sage Earth Science.

REGULATORY CONSIDERATIONS

Regulatory issues are expected to be minimal. Because this is a nonintrusive characterization technique, there is no subsurface disturbance or process waste, and little or no requirement for decontamination of equipment is anticipated. No health hazards originate from the RGS; however, exposure to hazardous materials at survey sites is possible. The RGS concept sets a new standard for geophysical surveys, and it is conceivable that this new standard may be incorporated into EPA standard practices for environmental surveys.

POTENTIAL COMMERCIAL APPLICATIONS

Expected commercial applications include underground storage-tank detection and location, pre-transaction real-estate environmental surveys, underground-utility location, and industrial-site environmental surveys.

BASELINE TECHNOLOGY

Handheld instrumentation represents the current method for collecting magnetic and electromagnetic geophysical data. Hand-positioned magnetometer surveys are labor-intensive. In contrast, the RGS can perform geophysical magnetic surveys more quickly (30 to 300 times faster) and more economically ($.25 versus $5 per datum point) than handheld instruments can. The RGS raises the standard for environmental surveys by providing the ability to collect spatially dense data sets at an affordable cost. To date, cost has been the primary concern and limitation when planning and budgeting environmental surveys, especially in the private sector.

INTELLECTUAL PROPERTY

A patent disclosure has been made.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator

Lyle G. Roybal
Lockheed Idaho Technologies Company
Applied Geosciences Unit, MS 2107
P.O. Box 1625
Idaho Falls, ID 83415-2107
(208) 526-5744; (208) 526-0875 FAX

DOE Program Manager

Jaffer Mohiuddin
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7965

Industrial Partner

Glen Carpenter
Sage Earth Science
2300 North Yellowstone Hwy., Suite 206
Idaho Falls, ID 83401
(208) 522-5049

REFERENCE

1. DOE-ID, "Technology Information Profile (rev. 2) for ProTech, Technology Name: Rapid Geophysical Surveyor (RGS)," DOE ProTech Database, TTP Reference Number: ID-121213, July 15, 1993.

DESCRIPTION

The Unsaturated Flow Apparatus (UFA™) is a laboratory instrument that simulates the migration of various compounds (e.g., volatile organic compounds), microbial nutrients, and water in the subsurface environment. Knowledge of the transport properties of soils, sediments, and rocks under unsaturated and saturated conditions, particularly hydraulic conductivity as a function of moisture content, is required for accurate modeling of the transport of contaminants in subsurface materials surrounding hazardous and mixed-waste sites. Traditionally, it has been difficult to obtain transport data on unsaturated and multicomponent systems because of the long experimental durations necessary for achieving hydraulic steady state. The UFA™ is based on open-flow centrifugation and provides a technique in which hydraulic steady-state can be achieved in a matter of hours in most geologic materials (even at very low water content). Therefore, the UFA™ provides the means to experimentally measure transport parameters in a very short time frame under the wide range of conditions found in the field (see Figure 4.9).

The advantage of using centripetal acceleration as the fluid-driving force is that it is a body force similar to gravity and acts simultaneously over the entire system and independently of other driving forces (e.g., matrix suction). The system is the most rapid method for obtaining transport data. The UFA™ can address any flow-transport problem involving any fluid in any porous media under many conditions. The UFA™ improves the ability to predict VOC migration and increases the probability of choosing a successful restoration strategy for site-specific conditions. The technology can also be used for quick screening and can provide data to describe field conditions. As an example, more than 500 values of hydraulic conductivity on about 50 samples were measured in less than 6 months using one UFA™ instrument. The data were used to extend the understanding of subsurface interactions under actual field conditions at the Hanford Site for characterization, remediation, and predictive modeling. The database could not have been developed without using the UFA™ method.

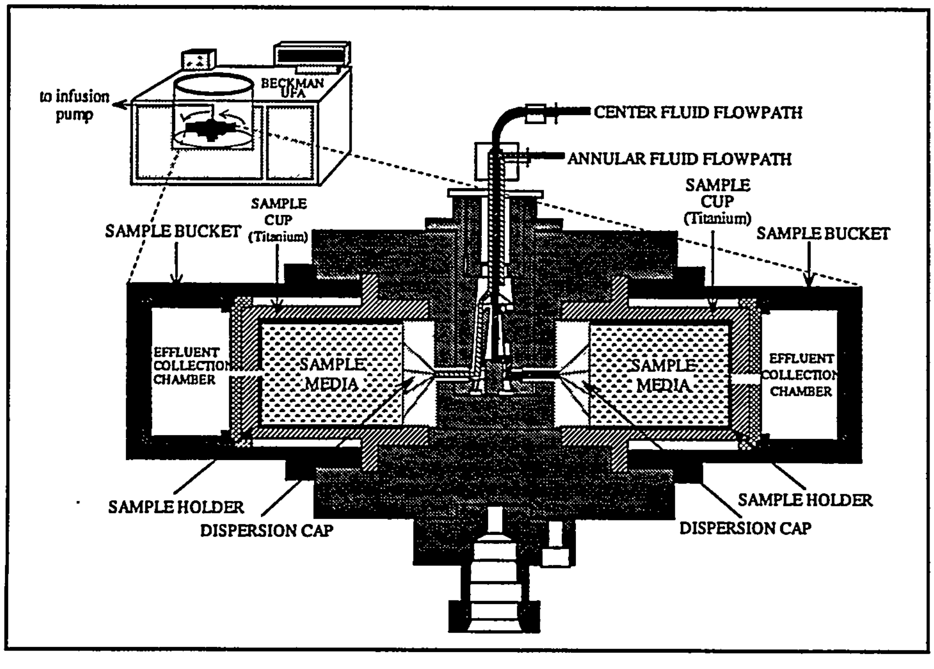


Figure 4.9. UFA™ rotor and seat assembly with large sample and ferromagnetic seal options.

TECHNICAL PERFORMANCE

The UFA™ consists of an ultracentrifuge coupled with a constant, ultra-low-flow-rate pump that can provide liquid to the sample surface through a rotating seal assembly and microdispersal system. The flow rates can be adjusted to as low as 0.001 ml/hr. Sample accelerations up to 20,000 g are attainable at temperatures from -20 to 150°C. The effluent is collected in a transparent, volumetrically calibrated container at the bottom of the sample assembly that can be observed during centrifugation using a strobe-light assembly. The UFA™ measures transport parameters at water contents as low as a few percent and hydraulic conductivities down to 10^{-10} cm/s in a few days. As an example, a silt sample (from Hanford) accelerated to 2,000 rpm with a flow rate of 3 ml/hr reached hydraulic steady state in two hours at the target volumetric water content of 22.4% and unsaturated conductivity of 2.5×10^{-7} cm/s. For homogeneous samples run in the UFA™, moisture distributions are uniform to within 3%. The rotational speed and flow rate into the sample are chosen to obtain the desired values of flux density, water content, and hydraulic conductivity within the sample.

Several studies were made to compare the UFA™ method with other experimental and estimation methods for determining hydraulic conductivity. All of the UFA™ measurements were conducted in only 3 days. In comparison, direct measurements of the hydraulic conductivity by traditional column-flow experiments under unit-gradient conditions took approximately a year of experimental time. The second method used data obtained over 13 years from a field lysimeter. The third method was an estimation derived by using the Campbell relationship to fit laboratory-determined water-retention values to matrix-potential values to generate the Maulem relationship. The agreement of the UFA™ data with all three methods is excellent and demonstrates not only the feasibility but also the time saved by using the UFA™ method.

Cost. The present cost of the UFA™ and support equipment is about $100K. The annual operating and maintenance cost is $10K, including the maintenance contract and sample holders. The operating life of the system is up to 30 years.

PROJECTED PERFORMANCE

A new generation UFA™ is being developed. Soil samples will be collected from the Hanford Site using cable-tool drilling/split-spoon sampler technology. The soil or bedrock samples are transferred to a specially designed titanium canister and subjected to as much as 20,000 g. A rotating-seal assembly fitted to the canister allows an ultra-low-flow pump to deliver liquid (carbon tetrachloride, in this case) to the sample surface during centripetal acceleration. When steady-state conditions are reached (within a matter of hours), three transport parameters will be evaluated: (1) hydraulic conductivity to measure permeability, (2) diffusion coefficient, and (3) breakthrough retardation. Transport data and a compilation of data for Hanford sediments will be final output elements.

Modification may necessary for application of this technology in radioactive environments.

WASTE APPLICABILITY

The UFA™ can address all flow transport problems involving fluid in any porous medium under almost every condition. This technology is applicable to VOCs, microbial nutrients, water in the subsurface, tank-waste sludges, fluid behavior in ceramics, and other fluid/substrate systems.

STATUS

The UFA™ is available commercially. The UFA™ was developed and has been deployed in a number of Pacific Northwest Laboratory programs since 1991. Improvements to the UFA™ continue.

REGULATORY CONSIDERATIONS

Environmental regulations are not expected to impact this technology. Proper laboratory procedures will be followed to minimize workers' exposure to contaminants.

POTENTIAL COMMERCIAL APPLICATIONS

The UFA™ supports the development of restoration technologies such as vapor extraction (e.g., estimate vapor-migration rates) or bioremediation (e.g., estimate nutrient-delivery rates) for unsaturated soils. In addition, the UFA™ technology is a predictive tool, that is, a "time machine" that can be used: (1) to validate the predictive models of subsurface contaminant migration, and (2) to screen the performance of various remediation technologies in the field. The UFA™ is also being used to investigate tank waste sludges.

The concrete industry has expressed interest in this technology to test reactivity of concrete aggregate to alkaline solutions. Extraction of pristine pore fluid from highly unsaturated materials and highly impermeable materials is possible with the UFA™.

BASELINE TECHNOLOGY

The baseline technology is traditional column experiments or in situ analysis such as lysimeter measurements that require months to years to achieve results. UFA™ data have been shown to be in complete agreement with data generated using traditional column experiments.

INTELLECTUAL PROPERTY

Beckman has the intellectual property rights.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigators

James L. Conca
Washington State University Tri-Cities
100 Sprout Road
Richland, WA 99352
(509) 375-3268

Judith Wright
NESTT
2000 Logston Blvd.
Richland, WA 99352
(509) 375-4787

DOE Program Manager

Rashalee Levine
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7920

Industrial Partner

Beckman Instruments, Inc.
Palo Alto, CA

REFERENCES

1. Conca, J.L., and J.V. Wright, "Direct Determinations of Unsaturated Flow and Transport," Proceedings of the 12th Annual Hydrology Days Conference, Fort Collins, CO, 1992, pp. 103-116.

2. Conca, J.L., and J.V. Wright, "Flow and Diffusion of Unsaturated Gravel, Soils and Whole Rock," Applied Hydrogeology, International Association of Hydrogeologists, Vol. 1, 1992, pp. 5-24.

3. Conca, J.L., and J.V. Wright, "A New Technology for Direct Measurements and Unsaturated Transport," Proceedings of the Nuclear and Hazardous Waste Management Spectrum '92 Meeting, American Nuclear Society, Boise, ID, Vol. 2, 1992, pp. 1546-1555.

4. DOE-RL, "Technology Information Profile (rev. 2), Technical Name: Unsaturated Flow Apparatus (UFA™) Centrifuge," DOE ProTech Database, TTP Reference Number: RL-321105, March 30, 1993.

5. Wright, J.V., J.M. Leather, and J.L. Conca, "The UFA™ Method for Site Characterization and Remediation," Proceedings of the Environmental Remediation '93 Conference, Augusta, GA, Vol. 2, 1993, pp. 819-826.

Hazardous Inorganic Contaminant Analysis

Section 5.0

LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR METALS IN SOILS AND GROUNDWATER

DESCRIPTION

The Laser-Induced Breakdown Spectroscopy (LIBS) technology is being developed for rapid analysis of hazardous metals in soils. The technology is applicable to both hazardous waste sites and mixed waste sites. Initially, its application is to an extracted drill string, but future developments will include fiber-optic transport of the laser radiation to in situ analytical locations. Development is focused on producing a field deployable instrument; therefore, results will not match the highest quality achievable by laboratory high pulse energy lasers. The field deployable laser will be small and portable with a weight of about 2 lbs. The data quality is such that the instrument could be used as a field analytical method during site characterization. In the initial investigation, detection limits of Resource Conservation and Recovery Act (RCRA) metals were determined for elements of primary concern to the Component Development Integration Facility (CDIF) in Butte, Montana. These primary analytes of interest are arsenic (As), lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn); furthermore, regulatory drivers make silver (Ag), chromium (Cr), iron (Fe), and manganese (Mn) of interest, as well.

The physical basis of the technology is very similar to inductively coupled plasma spectroscopy although the plasma is initiated on a micro-scale by a laser. In the LIBS method (see Figure 5.1a), sample atomization and excitation is provided directly by a laser spark. Notably, time consuming, hazardous, and potentially adulterating sample preparation is eliminated. The spark is produced by focusing pulses of laser light on the material of interest using either a cylindrical or spherical focusing lens that generates a small, short lived microplasma. The plasma temperatures initially exceed 10,000K, so the material in the plasma is efficiently vaporized, reduced to its elemental constituents, and the resulting atoms are electronically excited. Subsequent light emissions will be characteristic of the elements in plasma volume (about 0.01 to 0.5 mm^3). LIBS instrumentation is quite compact and only requires line-of-site access to a material. The method lends itself to integration with other instruments and several instrument configurations (vis, cone penetrometer testing).

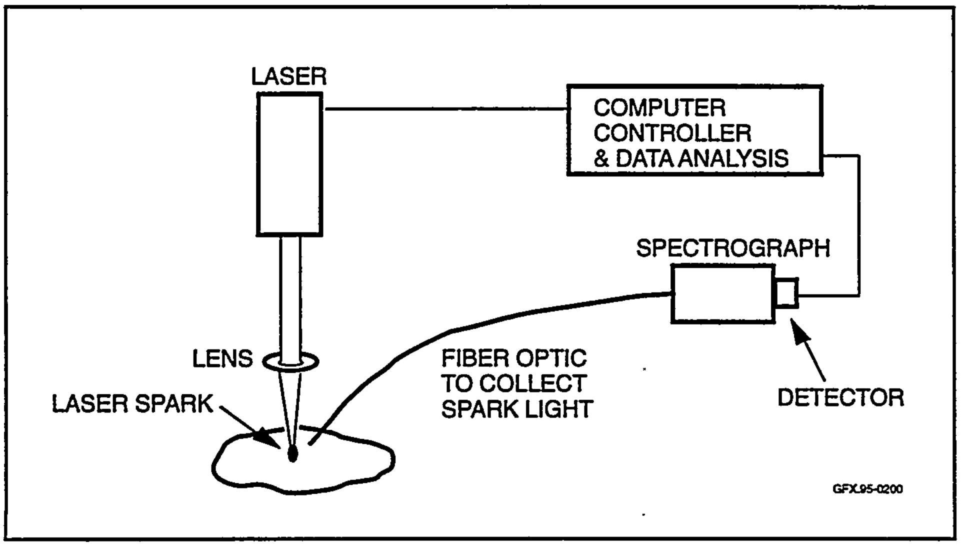


Figure 5.1a. Schematic of the laboratory LIBS apparatus. The sample is mounted on a motorized translation stage and translated as the laser fires.

Advantages of the LIBS technology for field analysis of soils are:

- Materials can be analyzed directly in the field. Little or no sample preparation is required. Adulteration of the sample by improper handling is minimized or eliminated entirely.

- Rapid analysis. A complete spectrum can be obtained in a single laser shot. The technique is as rapid as the laser pulse rate and the detection apparatus will allow.

- Simplicity. Skilled operators are not required once the analytical line, linear range, and detection limit database is completed by the developers.

- Portability. Lasers with the necessary pulse energy for LIBS that weigh less than 2 lbs are now available. Compact detection systems are also available. One complete apparatus including power supplies, detection apparatus, and a portable computer is the size of a small suitcase. The active sampling unit, which includes the laser head and optics, is also handheld.

- Simultaneous multi-element analysis. All elements in the microplasma are electronically excited and can, in principle, be detected simultaneously. Proper application will help avoid cases where certain analytical spectra lines coincide.

- Spatial discrimination. The analytical region for LIBS from a single laser pulse is the size of the induced spark. In practice, with lasers of convenient size, this region can be as small as 0.01 mm^3- 0.5 mm^3. Larger regions are analyzed by rastering of the laser beam.

- Remote detection. The spark is produced by focused optical radiation. Thus, only optical access to the sample is required. The utility of delivering the laser light to an in situ subsurface location via a fiber-optic cable is being investigated. Some results indicate that the LIBS spectra can be analyzed at distances as great as 80 ft from the material being analyzed.

- Sensitivity. Detection limits should be suitable for field-screening data and for many elements of interest. Improvement of the detection limit for specific elements is being pursued.

TECHNICAL PERFORMANCE

Laboratory experiments were conducted in FY 1994 to identify the interferences from elements typically found in soils for the analytes of interest. Furthermore, the detection limits, sensitivity, and precision of the best analytical lines were determined for soils spiked with single elements of interest. The best instrument parameters that could be incorporated into the field were used.

Optical microscopic studies (100x) of the 500 mm (0.02 in) wide laser track in a post-test soil sample showed that the underlying soil crystal structures remained intact. It was concluded that the surface material on the soil particle is the material that is vaporized. Furthermore, scanning electron microscopy (SEM) of NIST standard reference materials 2709, 2710, and 2711 showed heterogeneities on the microscale (on the order of 10 microns) which are effectively averaged by bulk type analytical reference techniques such as X-Ray Fluorescence (XRF). Because the heterogeneities exist on a comparable scale to the microplasma volume, LIBS requires multiple measurements to mechanically average any heterogeneities over the analytical volume. The rate of repeated measurements can be as rapid as the repetition rate of the laser and detection apparatus will allow. Typical instrument times for a statistical representation is about 1 minute.

Optimum detection limits are functions of several instrument parameters including detection time (usually 3 s), pulse energy (typically 125 mJ), type of focusing lens, the type of analytical line chosen, its peak intensity, and the type of local interference by the matrix materials or by the internal standard. Each element has several possible analytical lines which are referred to by the wavelength of the emitted light. For most experiments, a 100 mm focal length spherical lens was used but in some cases a cylindrical focusing lens was used. A typical calibration curve for detection of Pb using the 4057.8 Å analytical reference line is shown in Figure 5.1b. The Pb analytical line has nearby interferences from Mn on both the blue side, and more severely, on the red side.

The strength of the line overcomes the interference, however, and results in a good detection limit. Using the Fe-I lines at 3997.39Å and at 3998.05Å as an internal reference, 3 sdv detection limit was found to be 15 ppm. A summary of 3sdv detection limits using LIBS for selected elements is shown in Table 5.1.

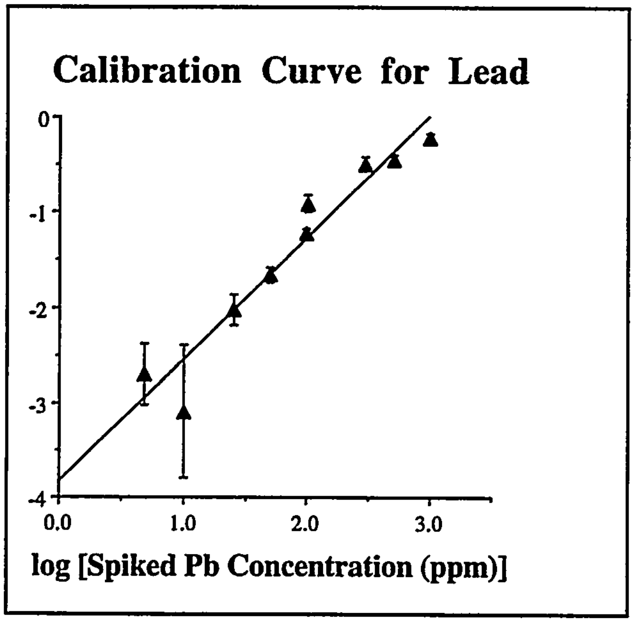


Figure 5.1b. Calibration curve for Los Alamos soil spiked with lead. Error bars are one standard deviation. The resulting detection limit is 13 ppm based on 2 standard deviations of the blank.

Cost Data. Estimated cost for a LIBS instrument range from \$30K for a single element, single matrix instrument to the approximately \$90K to \$100K for the more broadly applicable instrument being constructed for the CDIF demonstration. These costs are for parts and components and do not include labor or profit (for the case of a commercial entity).

PROJECTED PERFORMANCE

Some preliminary work was done on cesium. The moderately strong line of Cs-II at 4526.74Å was sought and could not be found. The strongest line of the atomic species at 6973.297Å was observed along with weaker lines at 6870Å and 6983.49Å. Measurements to develop a full calibration curve at this wavelength and a search for the more intense Cs lines will be conducted in the near future. A second goal of future development is to improve the Cd detection limit to 10 ppm. A prototype of the LIBS system is scheduled for delivery and field testing at CDIF in FY 1995.

Table 5.1. The LIBS 3 SDV detection limits for selected elements in a Los Alamos soil matrix.

Analyte	Analyte Line	Int-Std	Std Line(s)	3 sdv Detection Limit	Comments
	(Å)		(Å)	(ppm)	
As-I	2349.84	Fe-II	2395.408+2395.627	705	
Ba-II	3130.42+3131.07	Ca-II	3179.33	2	contaminated soils
Be-II	3130.42+3131.07				
Cd-I	5085.822	Fe-I	5110.357	73 141	spherical lens cylindrical
Cr-I	4254.35	Fe-I	4250.787+4250.12	23 67	125 mJ Pulse 20 mJ Pulse
Pb-I	4057.6	Fe-I	4063.594	18 9	125 mJ Pulse Peak Fit
Sr-I	4607.33	Fe-I	4476.0206	80	
Sr-II	4215.52			24	
Zr-II	3572.47	Fe-I	five lines (3526.2)	86	

APPLICABILITY

This technology is applicable to field analysis and characterization of hazardous metal contamination in soils at hazardous and mixed waste sites. The initial prototype instrument is being developed for application at the CDIF site. The elements of interest at the CDIF site are: As, Pb, Cd, Cu, Zn, Ag, Cr, Fe, Mn.

STATUS

This technology was laboratory tested for several elements of interest as described in previous sections. A prototype instrument which will be capable of detecting as many of the above mentioned elements is scheduled for delivery to the CDIF in late FY 1995.

REGULATORY CONSIDERATIONS

Contact the principal investigator for regulatory information.

POTENTIAL COMMERCIAL APPLICATIONS

There are potential commercial applications to mining and milling operations that frequently involve hazardous metal contamination.

BASELINE TECHNOLOGY

There is no baseline technology for field measurements of hazardous metals. The current method uses grab samples and (off-site) laboratory analysis.

INTELLECTUAL PROPERTY

Contact the principal investigator for intellectual property information.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Aaron Koskelo
Los Alamos National Laboratory
P.O. Box 1663, MS-J565
Los Alamos, NM 87545
(505) 665-4463; (505) 665-6095 FAX

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 10874-1290
(301) 903-7672

Industrial Partner

MSE, Inc.

REFERENCE

1. Koskelo, A. and D.A. Cremers, RCRA Metals Analysis by Laser-Induced Breakdown Spectroscopy: Detection Limits in Soils, Report Number LA-UR-94-1544, Los Alamos National Laboratory, Los Alamos, NM, 1994.

SOL-GEL INDICATORS

DESCRIPTION

Increased emphasis in recent years on environmental analyses has fueled a need for field-portable and remote monitoring instruments. From the commercial sector, there has been increased emphasis on in-situ and on-line measurements for process control. In both of these arenas, cost reduction and automation of analyses have been key drivers. An important contribution to these efforts was the development of portable fiber-optic diode array spectrophotometers (DAS) and associated fiber-optic probes. These probes contain the sensing element or function as a measurement cell and are small, rugged, and easily deployed. Sol-gel indicator (SGI) composites are being developed and used by the Savannah River Technology Center as sensor elements to measure a variety of conditions and species. The technology is based on incorporation of indicator materials into specially prepared porous silica, alumina, or titania glass matrices. The SGIs change color in response to analyte concentration. Sensors are prepared by coating SGI composites on optical components so that photometric measurements can be made. Pore sizes of the sol gel can be controlled during synthesis to allow the desired analyte to react with the indicator molecule, while keeping the indicator trapped within the glass matrix. Sol-gel technology has the advantage of being able to distribute and incorporate the indicator in a chemically durable matrix at room temperature and, hence, avoid the high temperatures in conventional glass manufacture that would degrade organic indicator molecules. Sol-gel indicators have also been incorporated into flow injection analysis flow cells, thus eliminating one reagent stream from the system and making possible on-line measurement of a process sample without the addition of reagents. This allows the sample to be returned to the process unchanged and reduces waste significantly.

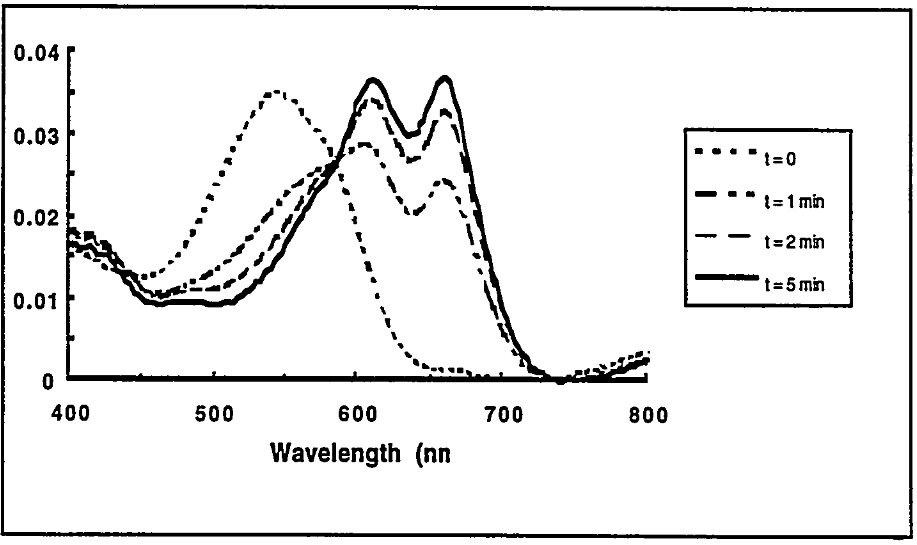


Figure 5.2. Response of SGI uranyl sensor at 118 ppm UO_2^{2+}.

Sensors were prepared to measure pH and uranium and were integrated into an analytical measuring system. The response of the uranium SGI sensor is shown in Figure 5.2. Work is in progress on a sensor for chromium (VI). Future target analytes could include other heavy metals or organic contaminants in aqueous media and gases.

TECHNICAL PERFORMANCE

- SGI sensors were prepared with pH indicators such as bromophenol blue.
- Many of the SGI pH sensors respond over a wider range relative to aqueous solutions of the indicator.

- Depending on the indicator selected, pH values from 0 to 10 are accessible with silica-based sol gels.

- All SGI pH sensors are reversible and respond to pH changes quickly.

- Nine different pH sol-gel indicators have been successfully incorporated into flow injection analysis flow cells.

- A SGI sensor for uranyl has been prepared using the indicator arsenazo III.

- SGI uranyl sensor response time is approximately 5 minutes; detection limit is 1 ppm.

- A treatment for reversal of the uranyl sensor has been developed so that it can be reused.

- SGI coatings were shown to be viable for at least 6 months; optical probes may be cleaned and recoated with new SGI, if needed.

- Multiple sensors may be multiplexed to a single spectrophotometer system.

Cost. SGI coatings cost pennies to produce. For a complete system, an optical probe costs $200 and a portable spectrophotometer costs $6K. Use of SGIs with a cheaper two wavelength filter photometer is also possible. The time to develop a sensor for a new analyte is about 9 to 12 months at a cost of $75K to $125K

PROJECTED PERFORMANCE

Additional refinement of the coating process is needed to improve fabrication reproducibility -- an important requirement for commercialization of the technology.

APPLICABILITY

This technology will prove useful as a screening tool and in field measurements (wells, lakes, streams, etc.) of properties such as pH and dissolved heavy metals content. Measurements of this type are needed at many sites (nationwide) that require environmental remediation. Sol-gel indicators may also be used in gaseous media. Potential analytes include metal ions, pH, organics (in air or water), and gases (e.g., NH_3, CO_2, HCl).

STATUS

This technology is moving from basic research into more applied research; although some basic research must be done with each new indicator/analyte. Current work is focusing on development of a SGI sensor for Cr (VI). Two new CRADAs with industrial partners have been developed to facilitate testing and commercialization of specialty SGI systems.

REGULATORY CONSIDERATIONS

None.

POTENTIAL COMMERCIAL APPLICATIONS

Many companies with applications in environmental remediation, waste water monitoring, and process monitoring have expressed interest in this technology. It is licensed by four companies; future joint efforts are being negotiated.

BASELINE TECHNOLOGY

Currently available technology for field analysis of pH and metal ion concentrations includes pH meters and wet-chemical field test kits. The field test kits require transport of various reagents and are not reusable. They require that a sample be pulled from a well or surface body, and may not be used in situ. The SGI probes are more easily deployed down a well than a pH electrode, require less frequent calibration, and may be multiplexed so that other analytes may be measured at the same time. The SGI probes are compatible with existing portable fiber-optic spectrophotometers.

INTELLECTUAL PROPERTY

- U.S. Patent #796974 in prosecution.
- Four private-sector companies have licensed this technology.
- One CRADA has been completed; two others are in progress.
- Additional industry contacts/collaborations are being negotiated.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

George Wicks
Westinghouse Savannah River Company
Bld. 773-A
Aiken, SC 29808
(803) 725-3190; (803) 725-8136 FAX

Sol-gel Team

Lewis Baylor
Mike Whitake
George Wicks (coordinator)
Westinghouse Savannah River Company

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

REFERENCES

1. Livingston, R.R., L.C. Baylor, and G.G. Wicks, Development of Novel Sol-Gel Indicators (SGIs) for In-Situ Environmental Measurements: Part I - Program and a New pH Sol-Gel Indicator (U), Westinghouse Savannah River Company Report, 1992.
2. Odom, M.B., G.G. Wicks, R.R. Livingston, L.C. Baylor, and M.J. Whitaker, Sol-Gel Indicator Demo Kit (U), Westinghouse Savannah River Company Report No. WSRC-RP-93-645, 1993.

STRIPPING ANALYSIS

DESCRIPTION

Stripping Analysis (SA) has been demonstrated in the field to measure the concentrations of leachable chromium (Cr), lead, calcium, copper, nickel, and zinc in soils and sediments. The demonstration was conducted at the Chemical Waste Landfill (CWL) at Sandia National Laboratories (SNL) in Albuquerque, NM. Samples are taken from beneath the CWL during drilling operations and analyzed in a portable laboratory at the site. This technique allows decisions to be made in the field during characterization and remedial activities by determining the areal and vertical extent of contamination within hours of the sampling.

Stripping voltammetry has been used for several decades in the laboratory. Recent advances associated with nonelectrolyte (i.e., adsorptive) pre-concentration schemes and the development of miniaturized electrodes have increased the potential for practical use of the technique in the field.

In this program, the samples are dried with a microwave system and digested with a nitric acid leachate. The resulting solution is diluted with distilled or deionized water and analyzed using the SA technique. For a particular analysis, an electrode(s) is immersed in the solution. The voltammetric response (potential change) of the adsorbed species during the stripping is a function of the concentration of the specie on the electrode. This, in turn, is directly related to the bulk concentration of the specie in the solution through the adsorption isotherm (see Figure 5.3).

The SA equipment uses 10 A at 120 VAC (120 W). Ten square feet of bench space and a vent hood are also required for operation in the field. Since a different coating procedure must be used on the electrode for a particular specie, SA is not suitable for pre-screening a site to identify the contaminants, but it is capable of measuring the concentration of select contaminants after they have been identified by other techniques or from a priori knowledge.

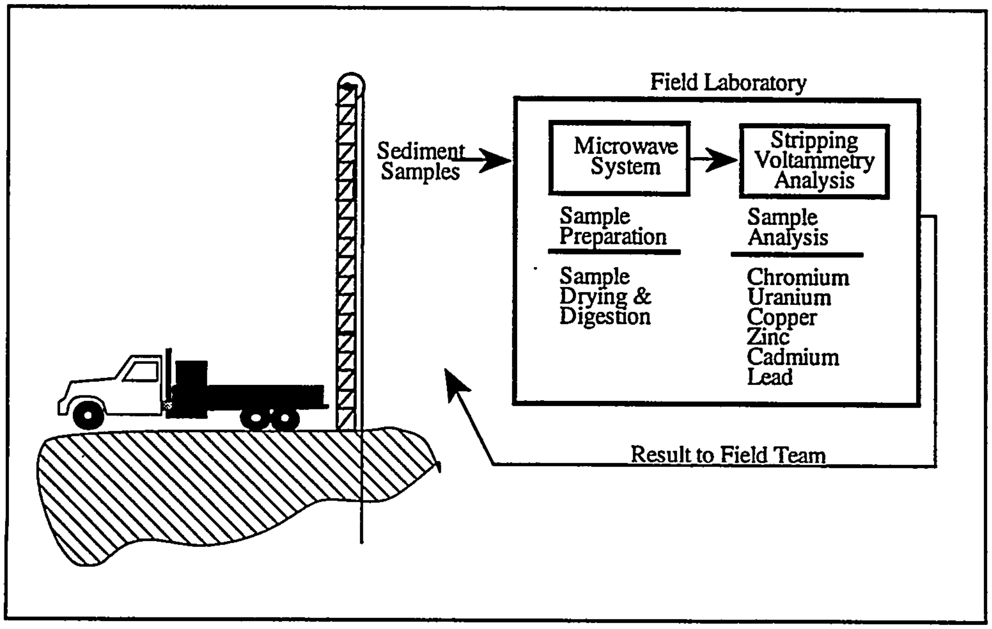


Figure 5.3. Stripping Analysis.

TECHNICAL PERFORMANCE

The SA system has a detection limit of 10^{-10} to 10^{-11} moles/l. Concentrations of chromium and uranium have been measured in solution to 1 ppb in both laboratory and field testing.

The concentrations of two or three trace metals may be measured simultaneously from a single analysis. A four-hour test is typical for obtaining the results in the field for 12 samples. However, the time required for a single analysis is very test-specific. For example, 20 to 30 minutes were required to determine the concentrations of Cr(III) and Cr(VI) from a single sample in a field test. However, when only Cr(VI) is measured, only eight minutes were required to measure the total concentration of chromium.

Cost. Start-up cost depends on the analytical requirements of the specific task. The cost for the stripping voltammetry equipment would range from $5K for single-element to $37K for multi-element, multi-sampling capability. A microwave digestion unit is approximately $12K. The operations and maintenance costs are dominated by the need for two operators, one of whom may be a technician. The annual cost for chemicals and supplies ranges from $1K to $2K. Life-cycle costs without labor would vary from $20K to $50K for a single SA system.

PROJECTED PERFORMANCE

The SA technique has the potential to measure trace concentrations of approximately 9 metals in addition to those associated with the CWL (as shown in the Table 5.3). Improvements in the detection limits for some metals may be anticipated.

Modifications to the electrodes and processes have also resulted in demonstrated capability of measuring trace levels of electroactive drugs (anti-cancer antibiotics, cardiac glycosides, etc.) and large macromolecules such as insulin and ferritin.

Table 5.3 shows trace metals measured in laboratory and field tests.

APPLICABILITY

The SA technique is being developed specifically to measure trace concentrations of metals in soils and sediments. However, it can be extended to make contaminant measurements in ground and surface water.

Table 5.3. Trace metals measured in laboratory and field tests.

Field Tests at CWL	**Laboratory Results[1,2]**	
Chromium (Cr)[3]	Aluminum (Al)	Technetium (Tc)
Cadmium (Cd)[4]	Iron (Fe)	Uranium (U)
Copper (Cu)[4]	Gold (Au)	Silver (Ag)
Lead (Pb)[4]	Arsenic (As)	Selenium (Se)
Zinc (Zn)[4]	Mercury (Hg)	-

1. Reference 4.
2. Includes metals tested in the field.
3. Measured at CWL in 1992.
4. Measured at CWL in 1993.

STATUS

The concentration of chromium was measured to the 1 ppb level and the ability to distinguish between Cr(III) and Cr(VI) was demonstrated during field tests in June 1992 (at the CWL site). During FY 93, the SA technique was scheduled for extension to the other four trace metals listed in Table 5.3.

REGULATORY CONSIDERATIONS

Dilute (1%) nitric acid and very small amounts of elemental mercury (50 ml) are contained in the 100 ml sample used for each analysis. Because of these small quantities, no environmental impacts or risks to the public are anticipated for the SA process.

POTENTIAL COMMERCIAL APPLICATIONS

All the equipment used for the SA analysis is "off-the-shelf" and at the conclusion of the demonstration the technology will be transferred to an operational system. Thus, the SA technique is available to the commercial sector for use in measuring the concentration of metals in water, soils, and sediments.

The capabilities of the SA system could also be extended to the metals that have been laboratory tested and are listed in Table 5.3. Additional applications in the fields of medicine and pharmacology are possible.

BASELINE TECHNOLOGY

The baseline technologies are acid digestion plus inductively coupled argon plasma (ICAP) or atomic adsorption (AA) analyses; both require the use of an off-site laboratory. In addition to being less convenient for field work than SA, they are slower. They are also less sensitive. For example, experiments with chromium indicated that the detection limit for the ICAP technique was an order of magnitude greater than that for SA.

INTELLECTUAL PROPERTY

Patent Ownership: None

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Khris S. Olsen
Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352
(509) 376-4114; FAX (509) 376-5368

DOE Program Manager

Skip Chamberlain
U. S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

Participating DOE Laboratory

Sandia National Laboratories
Albuquerque, NM 87185

University Partner

Joseph Wang
Department of Chemistry
New Mexico State University
Las Cruces, NM 88003
(505) 646-2140

REFERENCES

1. Wang, J., J. Lu, and K. B. Olsen, "Adsorptive Stripping Voltammetry of Trace Uranium-Critical Comparison of Various Chelation Agents," Anal. Chem. Act., in press, 1994.

2. Wang, J., J. Lu, and K.B. Olsen, "Ultratrace Measurements of Chromium," Analyst, 1993, p. 117.

3. Olsen, K.B., and J. Wang, "Field Screening of Sediment Samples for Chromium by Stripping Voltammetry," (unpublished White Paper), October 1992.

4. Olsen K.B., "On-Site Analysis of Metals in Soils Using Stripping Voltammetry," TTP Reference No. RL-3211-12, Briefing Chart, Pacific Northwest Laboratory, Richland, WA, November 11, 1992.

5. Wang, J., "Recent Advances in Stripping Analysis," Fresenius' Journal of Analytic Chemistry, 337, Springler-Verlag, 1990, pp. 508 - 511.

6. "TTP Overview - On-Site Analysis of Metals in Soils Using Stripping Voltammetry," Technology Needs Crosswalk Report, Vol. 3, DOE/D/12584-117, Ed. 1 GJPO-109, Chem-Nuclear Geotech, Inc., Grand Junction, CO, January 1993.

7. DOE-RL, "Technology Information Profile (rev. 2), Technology Name: On-Site Analysis of Metals in Soils Using Stripping Voltammetry," DOE ProTech Database, TTP Reference No. RL-3211-12, June 22, 1993.

8. DOE-RL, "On-Site Analysis of Metals in Soils and Sediments," FY 1992 Technical Task Plan, TTP Reference No. RL-MWLID-05, October 7, 1991.

X-RAY FLUORESCENCE SPECTROSCOPY

DESCRIPTION

Downhole x-ray fluorescence spectroscopy is a method for detecting and quantifying inorganic (i.e., metal) contaminant concentrations in soils above the water table using a photoelectric process. The x-ray fluorescence (XRF) instrument is a downhole probe consisting of an x-ray source and a photon detector (see Figure 5.4). The instrument probe is placed in a lined borehole. The surrounding soil and the detector are then irradiated with the source x-rays for a specified period of time. The detector receives a combination of Compton backscatter photons, as well as fluorescence photons emitted by atoms in the soil. Real-time assays of soil constituents can be performed when the instrument system is properly calibrated. The system also includes an onboard amplifier, an analog-to-digital converter, a multichannel analyzer, and a computer processor. Calibration of the instrument for a particular element and observation of the number of counts appearing in a specific fluorescence range of the energy spectrum results in a quantitative determination of the concentration of the element in the soil. Multi-element calibration is possible.

Fluorescence occurs when the source x-ray energy is greater than the electron-binding energy of the K or L shell in the target atom. The source photon collides with the target atom and causes an electron vacancy in, for instance, the K shell. This vacancy is filled by a transition of an L electron into the K shell and the emission of either a K_α x-ray photon (especially in heavy elements) or an Auger electron (especially in light elements). The competition between the two processes is described by the fluorescence yield. The probability that a K_α x-ray will be emitted approximates unity in high-atomic-number (Z) elements and approaches zero in low-Z elements. Typically, x-ray fluorescence is useful for elements with a $Z > 20$.

TECHNICAL PERFORMANCE

Several factors affect the minimum detectable concentration of an element. First, the source x-ray energy must be greater than the electron-binding energy in the K or L shell of the target atom. The excitation process is increased when the source and fluorescence energies are closely matched. Second, greater-atomic-number elements (higher-Z elements) have increased probabilities of K_α (photon) emission compared to Auger electron emission that dominates in lower-Z elements. Third, the detector quantum efficiency

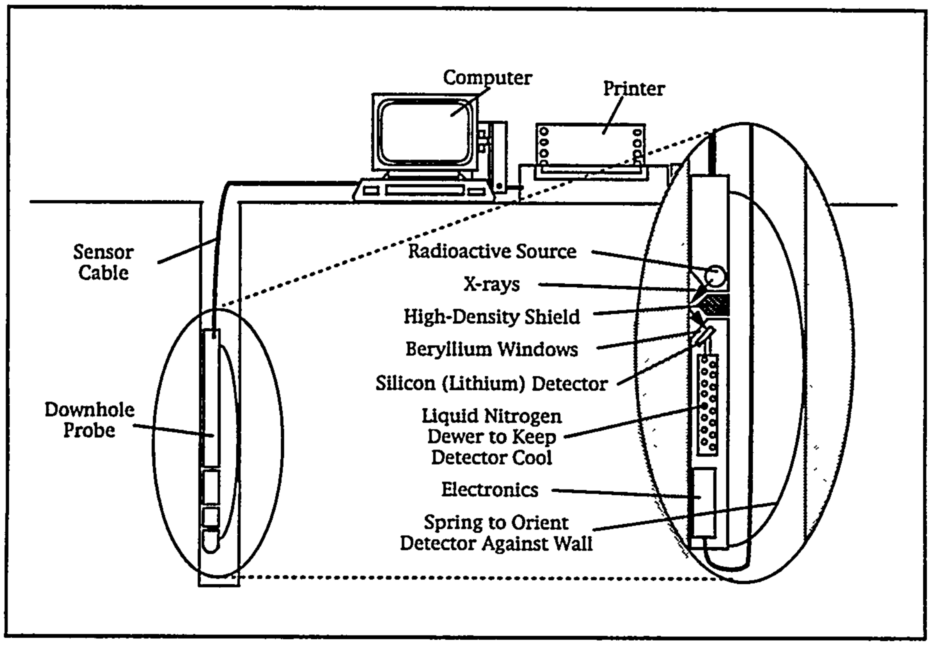


Figure 5.4. Prototype XRF System.

depends on the atomic number of the anticipated target atom.

Fourth, the energy-band resolution becomes increasingly important to achieve signal discrimination when neighboring elements are present in the soil media (e.g., chromium Z=24, iron Z=26). Finally, attenuation of low-energy x-rays limits the volume of soil that can be probed, but when the element under consideration increases in Z, then a greater volume of soil can be analyzed with increased accuracy. The accuracy is directly related to the minimum-detectable contaminant-concentration level.

A field test of an XRF system was conducted at Sandia National Laboratories (SNL) Chemical Waste Landfill (CWL) by Pacific Northwest Laboratories (PNL) in 1992 and 1993. In 1992, a commercial downhole probe manufactured by Scitec Corporation was employed for measurements of chromium concentration in three 9 in diameter boreholes, each 100 ft deep. These boreholes were in a landfill lined with high-density polyethylene material and a nylon cloth outer liner. Both copper and chromium were observed; however, the resolution was not acceptable for waste-characterization applications. In 1993, PNL demonstrated a new prototype downhole XRF probe featuring a liquid-nitrogen-cooled Si(Li) detector and onboard signal processing electronics. In addition, both a radioactive isotope and an x-ray tube were used as sources for excitation x-rays. The probe was demonstrated in the same boreholes as before, and much improved contaminant detection capability was obtained, with chromium detectable at around the 50 to 100 ppm level. However, the detector resolution can still be improved.

Cost. For a commercial Scitec instrument, the cost is estimated to be $50K.

PROJECTED PERFORMANCE

In 1994 and 1995, an instrument will be developed that will have improved detector resolution and higher count-rate capability. It will have a higher resolution Si(Li) detector and will retain the onboard signal-processing capability. Excitation x-rays can come from either an x-ray tube or an isotopic source. In addition, it will be greatly reduced in size and weight. The outside diameter will be about 1.25 inches with an overall instrument height of about 3 ft. It is designed to operate in combination with a cone penetrometer. It will be capable of analyzing any soil type, but the boreholes must be bare or lined with thin membranes, such as the SEAMIST™ liner.

APPLICABILITY

The XRF spectroscopy method of detection and quantification of contamination is appropriate for high-Z metals and all other elements where $Z > 20$. The penetration thickness into the soil is limited by x-ray attenuation for low-energy radiation. The low-energy x-rays are likely to be used when the target atom has a low atomic number (lower-Z). However, when higher-Z atoms are to be detected, higher energy x-rays will be used, and the volume of probed/analyzed soil is increased. The applicability of this technology is largely dependent on the desired minimum-detectable concentration, the atomic number of the contaminant, the site characteristics (such as high levels of a natural element with an atomic number close to a contaminant's atomic number), and the resolution of the detecting device.

STATUS

This is a developing technology with respect to low-concentration detection (ppm concentrations) and low-Z element detection such as chromium (Z=24). The technology has been demonstrated on a field scale with good success, but some improvements are necessary in terms of size reduction and instrument performance.

REGULATORY CONSIDERATIONS

Compliance with the Occupational Safety and Health Administration regulations is required for hazardous-waste operations and protection of occupational workers from ionizing radiation. In addition, permits may be required for drilling at hazardous waste sites.

POTENTIAL COMMERCIAL APPLICATIONS

This technology could be used to detect metallic contamination near industrial sites. Examples would be Environmental Protection Agency (EPA)-required testing, post-closure monitoring, site investigation, or follow-up soil analysis after structural lead-paint stripping. XRF could also be used in experimental situations to determine concentrations of metals in an aerosol or aerosol filter (radioactive spent-fuel aerosol experiments). In countries that have dated steel-processing facilities (such as Poland), the soil surrounding an industrial plant can be analyzed for metallic contamination, specifically lead. Municipal solid-waste processing and/or disposal facilities can be monitored for undesirable, toxic, or hazardous metallic waste. Other applications may include decontamination/decommissioning and post-closure monitoring for all types of industrial sites (i.e., nuclear, coal , diesel, natural-gas-fired power plants, decommissioned transformers, and others). In addition, application to the mining industry is expected for characterizing ore bodies.

BASELINE TECHNOLOGY

The baseline technology for analysis of heavy metals is conventional laboratory analysis such as inductively coupled plasma spectroscopy or atomic absorption. Each requires laboratory sample preparation and data evaluation to detect contaminants in soil. XRF was used previously used in the mining industry to detect soil constituents in concentrations greater than 1%. The use of XRF in environmental site characterization is a recent application. It provides a qualitative indication of heavy-metal content with minimal sample preparation and data evaluation.

INTELLECTUAL PROPERTY

PNL and Scitec have entered into a Cooperative Research and Development Agreement (CRADA) to develop the probe. All intellectual-property rights will be shared among the Department of Energy (DOE), PNL, and Scitec.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Chester L. Shepard
Pacific Northwest Laboratory, Battelle NW
P.O. Box 999
Richland, WA, 99352
(509) 375-3675

DOE Program Manager
Skip Chamberlain
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

Industrial Partner
Bill Boyce
Scitec Corporation
415 N. Quay
Kennewick, WA 99379
(509) 375-5000

REFERENCES

1. Evans, R.D., The Atomic Nucleus, Krieger Publishing Company, Malabar, FL, 1982, pp. 565, 688-691.

2. Shepard, C.L., "Test Results from the Sandia National Laboratory Chemical Waste Landfill Using Downhole X-Ray Fluorescence," prepared for the U.S. Department of Energy under contract DE-AC06-76RLO 1830, Pacific Northwest Laboratory, Richland, WA.

3. Reeves, J.H., R.J. Arthur, R.L. Brodzinski, and C.L. Shepard, "A Tube Excited X-Ray Fluorescence Spectrometer for use in Small-Diameter Boreholes," Journal of Radioanalytical Nuclear Chemistry (in press).

Hazardous Organic Contaminant Analysis

Section 6.0

CHEMICAL FIBER-OPTIC SENSOR

DESCRIPTION

Current U. S. Department of Energy policy requires characterization of sites where trichloroethylene (TCE), carbon tetrachloride (CCl_4), and other species have been discharged into the soil and groundwater. Contaminated samples are commonly collected and analyzed by an outside laboratory. An expensive and time-consuming process. An alternative is to use a fiber-optic chemical sensor that can be put down an existing monitoring well or punched into the soil using a penetrometer-type device. Accordingly, measurements can be made continuously and at a relatively low cost.

Generally, the chemical species of interest in environmental analysis do not absorb visible light or produce fluorescent emissions even when the contaminants are highly concentrated. Therefore, detecting analytes at the relatively low concentrations (e.g., ppm levels) that exist in many contaminated environments requires an indirect method. In this regard, there are three phenomena useful to chemical sensing with fiber-optics that may be appropriate in various contaminant-detection applications. These include the following :

- Incident monochromatic light producing Raman or fluorescent scattering (i.e., direct spectroscopy).
- Chemical-reaction-modulated fluorescence. Reaction between trace contaminant and organic fluorescing dye modulates the fluorescence properties of the dye.
- Chemical-reaction-inhibited light transmission. Reaction between trace contaminant and optrode dye reagent induces wavelength-dependent light absorption.

The latter phenomenon will be discussed in this profile. An optical device is being developed that incorporates fused quartz optical fibers as a wave guide to conduct light to and from a downhole probe. A chemical reagent in the fiber-optic tip of the optrode reacts with trace chemical contaminants to effect a change in the light transmissibility or fluorescing properties of the fluid in the optrode. The chemical reagent in the probe is an "organic transducer" as its photophysical properties change with contaminant concentration, thereby enabling detection.

Light Transmission Optrode. The light transmission optrode was developed by the Lawrence Livermore National Laboratory (LLNL) with cooperation from the University of California which has a patent pending. The target application is TCE detection. The light transmission optrode was demonstrated in two different configurations at the Savannah River Site in Aiken, South Carolina.

This device works by absorbing a small amount of TCE-contaminated vapor into the optrode tip where it reacts quantitatively with the pyridine reagent (see Figure 6.1). The principle of detection is that fluid in the optrode (chemical reagent) becomes increasingly red (absorbs light) when reacted with specific chlorinated compounds. The pyridine reagent is specific to detection of TCE, chloroform, bromoform, bromodichloromethane and chlorodibromoethane. The unknown concentration level of these compounds can be measured because absorption of light relative to the reaction time is directly proportional to contaminant concentration. This light-absorbing sensor has demonstrated dramatically improved performances over previously reported fluorescence-based sensors (light-producing chemical reaction). The input of the device is a small amount of sampled contaminated vapor, and the physical output involves a small amount of contaminated pyridine reagent (<50 ml/measurement).

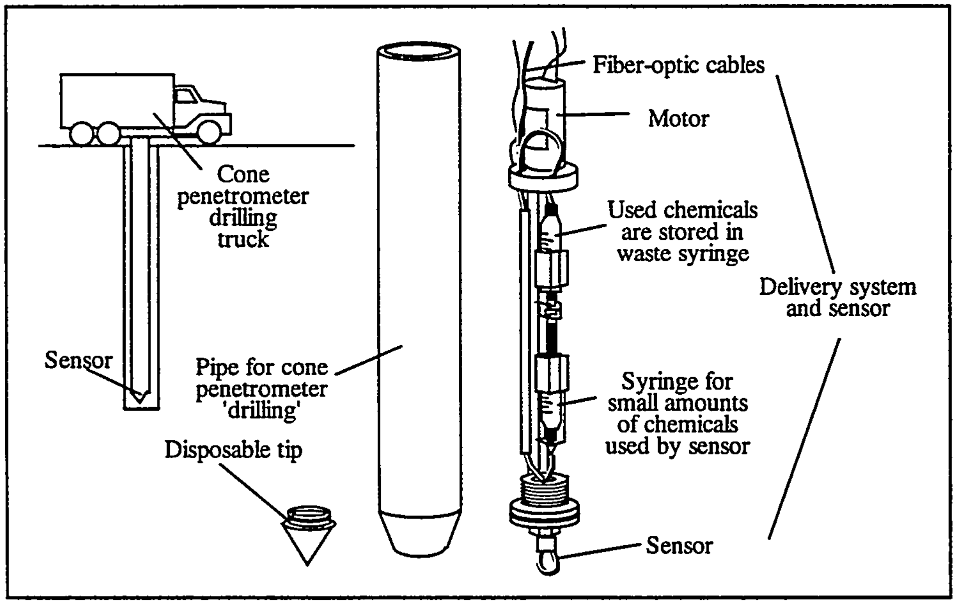


Figure 6.1. Light Transmission Optrode.

Vapor can be sampled from groundwater or unsaturated soils zones, but groundwater monitoring requires groundwater isolation in a headspace. The sensitivity of groundwater analysis is related to the Henry's law constant for equilibrium vapor concentrations. Sensitivity to 5 ppb has been demonstrated for vapor-phase TCE and chloroform detection.

TECHNICAL PERFORMANCE

General. Technologies using chemical fiber-optic sensors have been in existence for more than 10 years. The foundations for developing the TCE (light transmission) optrode originated 3 to 4 years ago at LLNL. The light transmission optrode is unique in that the chemistry remains in solvent form rather than being bound in a matrix. The sensor can thus be used continuously despite the irreversible nature of the chemical reaction. The chemical fluorescent optrode has a chemical fluorescence dye inside the optrode, and the reaction is reversible. Specifications of the light transmission chemical sensors are shown in Table 6.1a.

Field Tests. Field-test and demonstration results are available in the literature cited. The sensor's detection limit for TCE is about 150 ppb (v/v) in vapor and 5 ppb (w/w) in groundwater. The level of detection of this sensor is within OSHA permissible-exposure limits. Less than one hour is required to emplace a probe using a cone penetrometer. The probe has been placed to a depth of over 100 ft in under one hour using a cone penetrometer. For use in a vadose zone well, the implementation is even faster.

Table 6.1b contains a list of field tests and descriptions of the tests or developmental accomplishments.

Table 6.1a. Specifications for chemical sensors.

Aspect	**Specification**
Medium	vapor phase VOCs
Range	5-1000 ppb low range reagent 1-100 ppm high range reagent
Sensitivity	5 ppb
Contaminants	TCE, chloroform, other chlorinated hydrocarbons
Sampling frequency	Three minutes per measurement
Repeatability	±5%
Accuracy	±10% (Compared to gas chromatograph / ECD)
Calibration	Recommended once per week
Reagent usage	20 microliters/sample
Power required	110 V, 5 amps

Cost. The start-up cost for this monitoring system is $10K. Operation should require less than one hr/wk with minimal maintenance necessary to replenish the reagent every several months. The life-cycle cost depends largely on the frequency with which measurements are made. The individual sensors will be comparatively inexpensive and should cost less than $100. The costs associated with fiber-optic sensors will depend on the protocols and application for which the technology will be used. The life-cycle costs are estimated at $25K/yr (5 yr) and $1.25K/yr (10 yr).

PROJECTED PERFORMANCE

Future work includes developing alternative reagents specific to other VOCs and developing a downhole device for isolating headspace in groundwater applications. As yet, direct measurement of VOCs dissolved in water has not been accomplished, and all measurements have been made in the vapor phase above contaminated aqueous solutions. Therefore, sensitivity to measurement in aqueous solutions is dependent on the Henry's law constant for vapor/aqueous equilibrium, as well as the measurement sensitivity in the vapor phase. However, the issue of direct measurement of VOCs in water will be addressed in future development.

APPLICABILITY

The fiber-optic chemical sensors are generally applicable to VOCs in soil and groundwater. Application to groundwater sensing is indirect by measuring the vapor phase above the contaminated aqueous phase. A pyridine reagent was developed for the light transmission optrode that is applicable for selective TCE detection. The pyridine is also applicable to a narrow range of compounds including chloroform, bromoform, chlorodibromoethane, and bromodichloromethane. The reaction fluorescence sensors are applicable to carbon tetrachloride, toluene, xylene, and similar compounds in unsaturated soils.

The initial sensors are not intended to be general analytical instruments. Rather, the initial products are designed to be used as real-time continuous

Table 6.1b. Field tests information.

Test Date	Location	Description
September 1991	Westinghouse, SRS, Aiken, SC	Measurement of TCE in a soil-vapor well.
March 1992	Westinghouse, SRS, Aiken, SC	Measurement of TCE in a soil-vapor well and two groundwater wells.
April 1992	Westinghouse, SRS, Aiken, SC	Penetrometer placement of TCE sensor.
April 1992	LLNL Site 300, Livermore, CA	Measurement of TCE in conjunction with an above-ground soil-gas treatment process.
August 1992	Ft. Lewis, WA	Measurement of TCE in three groundwater wells.
April 1993	Westinghouse, SRS, Aiken, SC	Delivery of complete stand-alone monitoring system for long-term evaluation.
October 1993	LLNL Site 300, Livermore, CA	Measurement of TCE in a groundwater well using Burge Instrument Company-developed in situ water sampler and head-space sensor.

monitors during site screening or remediation. Other uses are long-term well monitoring, industrial processing, or laboratory screening. The sensor also can be used in conjunction with remediation technologies either in situ in the soil column or above ground as a process-tracking aid.

STATUS

Above-ground and penetrometer applications are available now. The light-transmission chemical sensor technology is fully developed and ready for commercialization. A fully operational in situ device for long-term monitoring of vadose zone wells was transferred to the SRS in FY 1993. Packaging and software for long-term monitoring was made available in June 1993. The reaction-fluorescence optrode is also available.

REGULATORY CONSIDERATIONS

Interconnection to an aquifer could occur during probe placement, leading to environmental impact (i.e., if a penetrometer is used for probe insertion, the borehole that is produced could provide access for contamination to spread vertically from the aquifer). The detection level of the sensor is compatible with regulatory cleanup milestones. Currently, EPA has no system for certifying sensor technology for site characterization.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include cost effective site characterization and monitoring for any industry which may have TCE, CCl_4, or other applicable contamination (other VOCs are detectable with further reagent development). LLNL has reached agreement with Burge Instrument Company and Purus, Inc., for the commercialization of the light transmission-based chemical-sensor technology. Both companies plan to introduce commercially available environmental-monitoring instrumentation for the detection of chlorinated hydrocarbons using the fiber-optic sensor.

BASELINE TECHNOLOGY

The baseline technology is purge and trap gas chromatography of grab samples. In contrast, this fiber-optic chemical sensor technology allows trace quantities of TCE, for example, to be measured on a continuous in situ basis. The sensor can be automated to provide a database of fluctuating contaminant concentration over time to aid in ongoing remediation efforts. It is as selective and sensitive as GC and is faster and cheaper. The TCE optrode (light transmission measurement) does not provide as much information as GC in situations where multiple volatile organic compounds are present.

INTELLECTUAL PROPERTY

The University of California has a patent pending for the light-transmission optrode for TCE detection.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Fred Milanovich
Lawrence Livermore National Laboratory
P.O. Box 808, MS L-524
Livermore, CA 94550
(510) 422-6838; (510) 422-8020 FAX

DOE Program Manager

Kurt Gerdes
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7289

Industrial Partners

Purus, Inc.
San Jose, CA

Burge Instrument Company
Tempe, AZ

REFERENCES

1. Milanovich, F.P., S.B. Brown, B.W. Colston Jr., P.F. Dailey, and K. Langry, "A Fiber-Optic Sensor System for Monitoring Chlorinated Hydrocarbon Pollutants," UCRL-JC-115898, Rev. 1, submitted to the Journal Talanta, April 1994.

2. Milanovich, F.P., S.B. Brown, and B.W. Colson, "Penetrometer Compatible, Fiber-Optic Sensor for Continuous Monitoring of Chlorinated Hydrocarbons - Field Test Results," Chemical Sensors Symposium, Honolulu, HI, May 16-21, 1993.

3. DOE ProTech Database, "Technology Information Profile (rev. 2) for ProTech," Technology Name: Chemical Fiber Optic Sensor, TTP reference number: SF-2211-01, Information last revised July 15, 1993.

4. Milanovich, F.P., K.C. Langry, J.N. Roe, and B.W. Colston, "Preliminary Field Demonstration of a Fiber Optic TCE Sensor," SPIE Proceedings, Vol. 1368, Chemical, Biomedical, and Environmental Fiber Sensors II, San Jose, CA, September 19-21, 1990.

5. Daley, P.F., B.W. Colston Jr., S.B. Brown, K. Langry and F. P. Milanovich, "Fiber Optic Sensor for Continuous Monitoring of Chlorinated Solvents in the Vadose Zone and in Ground Water: Field Test Results," SPIE Proceedings International Symposium on Chemical, Biochemical, and Environmental Sensors, Boston, MA, September 3-6, 1991.

6. Colston, B.W. Jr., S.B. Brown, P.F. Daley, K. Langry, and F.P. Milanovich, "Monitoring Remediation of Trichloroethylene Using a Chemical Fiber Optic Sensor: Field Studies," Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, Vol. 1, August 1, 1992, pp. 393-396.

DIRECT SAMPLING ION TRAP MASS SPECTROMETRY

DESCRIPTION

Direct Sampling Ion Trap Mass Spectrometry (DSITMS) is based on using an ion trap mass spectrometer (ITMS) as a continuous real-time monitor of multiple chemicals simultaneously as they are being introduced into the ion trap cell. No or minimal sample preparation or chromatographic separation is required. Volatile Organic Compounds (VOCs) in water, for example, are measured by purging the sample of water with helium and routing the purge stream directly into the ITMS. The ITMS generates approximately ten mass spectra per second and the spectra are recorded. The ion intensities of the masses corresponding to the chemicals present are integrated over the purge period to provide measures of their quantities. Additional selectively is achieved using chemical ionization or using multiple stage mass spectrometry, if necessary. DSITMS is made possible by modifying commercially available ion trap mass spectrometers to employ direct sampling inlets and operating conditions developed at the Oak Ridge National Laboratory (ORNL).

The principle advantage of DSITMS is that it allows analyses to be performed very rapidly. This allows more samples to be analyzed per unit time; thus resulting in a lower cost per analysis. The continuous monitoring capability of DSITMS allows studies not previously possible. Examples include the real-time monitoring of groundwater remediation and soil venting processes.

DSITMS technology is most advanced for the measurement of VOCs in water, soil, and air (ambient, soil gas, headspace). Pilot studies suggest similar applicability to many semivolatile organic compounds (SVOCs) and VOCs in wastes. Both laboratory-based and fieldable instruments are available. No unique facilities are required to operate the system. Troubleshooting and the analysis of some complex materials requires experience in ITMS but normal operation can be carried out by competent technicians.

TECHNICAL PERFORMANCE

U.S. Environmental Protection Agency (EPA) Method Detection Limits (MDLs) of 1-5 parts per billion are documented for the 34 Target Compound List (TCL) VOCs in water using purge periods of 3 minutes. Data can be acquired and concentrations estimated for up to 20 samples per hour. Current technology requires off-line computation of exact concentrations reducing the throughput to approximately 10 samples per hour. The same method is applicable to soils and sediments by adding water to produce a purgeable slurry. VOCs in air can be monitored in real-time down to concentrations of 50 parts per billion by volume and often less. Additional sensitivity can be achieved by collecting a sample on solid sorbent traps and analyzing the traps by thermal desorption DSITMS. Common operating conditions allow the detection and measurement of preselected VOCs in water at concentrations of 100 per trillion or less. Excess analyte in the purge stream can be collected on a solid sorbent to provide samples for confirmatory analyses, if necessary, or for quality assurance purposes.

Laboratory Demonstrations. Approximately 100 groundwater samples from the local Y-12 Plant have been analyzed for VOC content by DSITMS in the laboratory for comparison with the results using standard EPA-approved methods. Agreement between the methods was excellent. The method is similarly applicable to VOCs in soils. Gasoline Range Organics (GROs) were measured by laboratory DSITMS in blind spiked water samples with very good success. Comparison with the standard method using actual samples was good except for those cases where the standard method overestimates GROs because the presence of interferants. Thermal desorption DSITMS was shown capable of detecting polychlorinated biphenyls and other thermally stable SVOCs; but quantitative methods have not been developed.

Field Demonstrations. Field DSITMS has been demonstrated as a rapid batch analyzer and as a continuous monitor. VOCs in water and soil samples have been determined with good success on the Oak Ridge Reservation, at the Savannah River Laboratory, at Arnold Air Force Base, and elsewhere. Continuous monitoring features of DSITMS for VOC's have been demonstrated by real-time measurement during a cone penetrometer push, monitoring water undergoing photocatalytic remediation, and in situ groundwater well sampling. Pilot studies at the local Toxic Substances Control Act Incinerator at Oak Ridge suggest that DSITMS is a promising approach for monitoring stack effluents.

Cost. The cost of a commercial ion trap mass spectrometer ranges from approximately $70K to $100K depending on the features desired. The direct sampling interface and inlets for soil/water purge, air monitoring, and thermal desorption costs approximately $20K. Additional costs for modifications for field use are approximately $20K. Operating and maintenance costs are the same as for conventional commercial gas chromatography/mass spectrometry instruments.

PROJECTED PERFORMANCE

Applicability to SVOCs and validated application of continuous real-time monitoring capabilities will be demonstrated in the near-term (1 to 3 years). Additional work is required to achieve the near-term objectives, reduce the cost of the instrument, and automate data processing. Basic research and development is required to extend the technology to the measurement and monitoring of low molecular weight isotopic and radioisotopic gases and other speciality chemicals of importance to the DOE.

APPLICABILITY

DSITMS is currently applicable to the measurement of VOCs in water, soil, and air. It is especially useful: (a) as a no-false-negatives screen to avoid subjecting uncontaminated samples to costly standard laboratory analysis; and (b) as a rapid field method to support well-siting and remedial action activities. It is also currently useful for routine monitoring of waters and soils which have previously been characterized by standard EPA methods.

DSITMS is ideally suited for the rapid measurement and real-time monitoring of VOCs. It promises to be similarly applicable to many SVOCs. The use of external ionization accessories is likely to allow its application to trace elements. DSITMS has been shown applicable to the analyses of waters, soils, sediments, and air (ambient, soil-gas, well headspace). It should be equally applicable to wastes and the headspace of contained wastes.

STATUS

Instruments configured by ORNL are in place at the DOE Hanford Site, the DOE Savannah River Laboratory, the Army's Rocky Mountain Arsenal, and ORNL. First steps toward commercialization are being taken under an ARPA-Technology Reinvestment Project led by Teledyne Electronic Technologies and involving Phillips Petroleum, Monsanto Chemical, and two small businesses. ORNL is funded by the DOE Environmental Remediation/Waste Management program and the Army Environmental Center to demonstrate and facilitate deployment of DSITMS. Funding is not allocated for research and development to extend or improve the technology.

REGULATORY CONSIDERATIONS

Regulatory agency approval is required to substitute DSITMS for standard EPA methods when applied to compliance issues. The determination of VOCs in water by DSITMS has been approved by the organic chemical methods subgroup of EPA/OSWER and is scheduled to be incorporated in a future update of the SW846 manual as method number 8265. State (Tennessee) and EPA Region IV regulatory personnel are being briefed on the technology. DSITMS will be included in an EPA-coordinated validation study of field methods scheduled for the summer of 1995.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include monitoring of feedstock, process, product, and emissions. Interest in the technology has been expressed by companies and organizations from the following industries: (1) petroleum, (2) chemical, (3) pharmaceutical, (4) automotive, and (5) semiconductor. The companies have most often been interested in environmental- and process-monitoring.

BASELINE TECHNOLOGY

Gas chromatography/mass spectrometry (GCMS) is the baseline technology for the analysis of discrete samples. High speed GCMS, membrane introduction mass spectrometry, and ion mobility spectrometry are the baseline technologies for continuous monitoring.

INTELLECTUAL PROPERTY

Finnigan MAT, Inc., and Teledyne Electronic Technologies, Inc., hold licenses to an ORNL patent (Patent No. 4,989,678, February 5, 1991) on the direct sampling interface and sampling modules.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Marcus B. Wise
Oak Ridge National Laboratory
Bldg. 4500S, MS-6120
P. O. Box 2008
Oak Ridge, TN 37831-6120
(423)574-4867; (423)574-4902 FAX
e-mail: wisemb@ornl.gov

DOE Program Manager

Kurt Gerdes
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7289

REFERENCE

1. Wise, M.B., C.V. Thompson, M.V. Buchanan, R. Merriweather, and M.R. Guerin, "Direct Sampling Ion Trap Mass Spectrometry," Spectroscopy, 8(5), 1993, pp. 14-22.

FIELD PORTABLE DETECTION OF VOCS USING A SAW/GC SYSTEM

DESCRIPTION

The system (Model 4100) is a single operator, portable, field transportable system at low cost, with accurate vapor detection and analysis. Its purpose is to provide a low cost instrument for identifying hazardous materials and for monitoring Department of Energy (DOE) waste site cleanups throughout the United States. Other applications include workplace monitoring of environmental conditions.

The Model 4100 uses a patented piezoelectric Surface Acoustic Wave (SAW) resonator device and capillary gas chromatography. The result is a portable system that provides detection specificity, selectivity, and sensitivity. The SAW resonate sensor has excellent recovery characteristics and provides a trace analysis in less than 30 s.

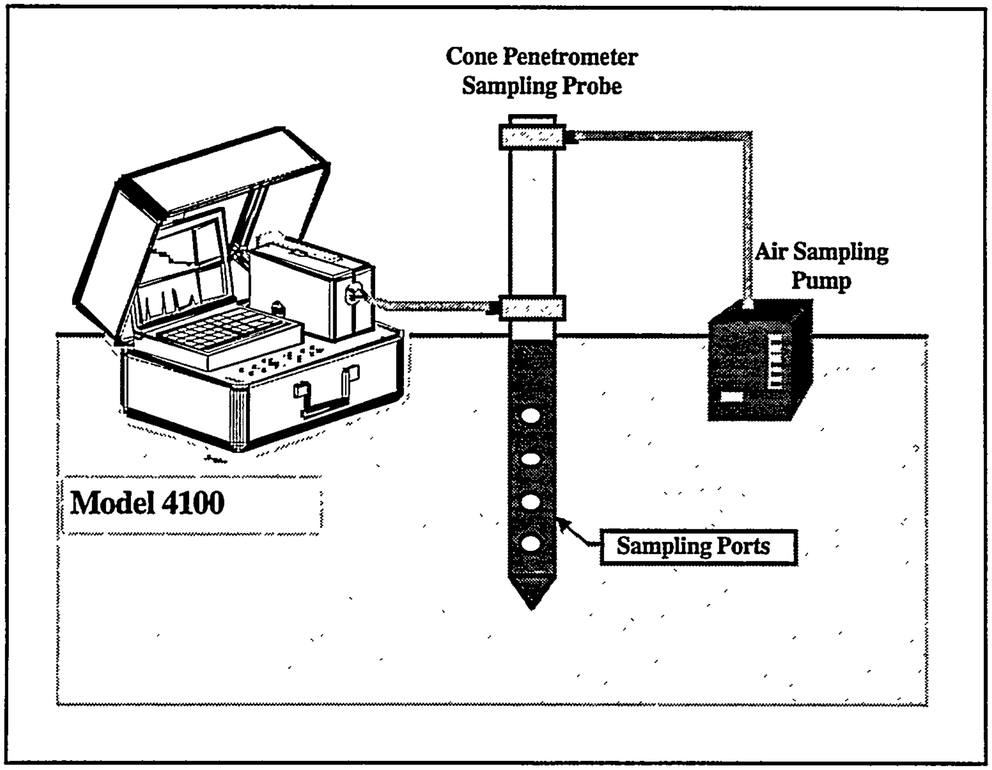
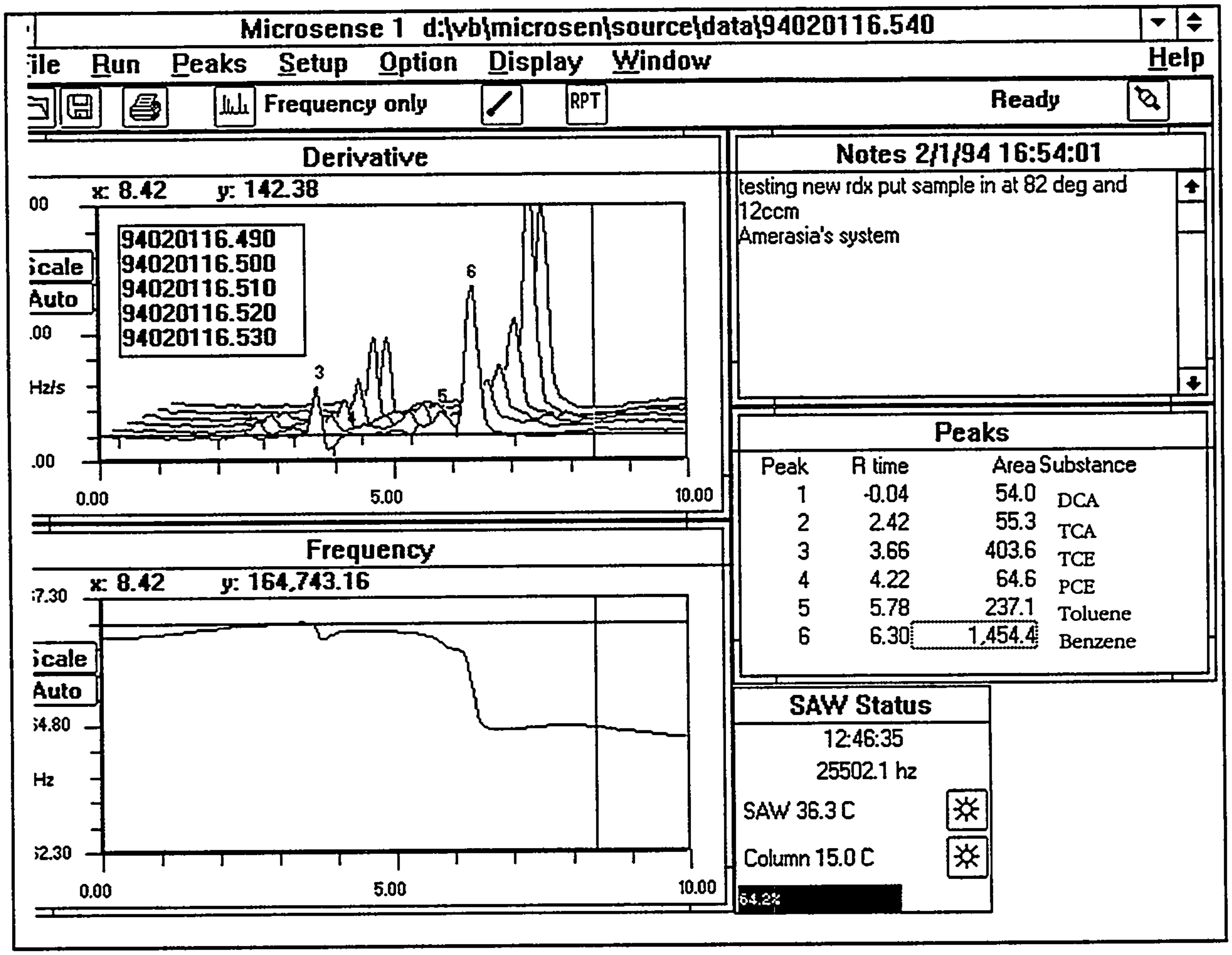


Figure 6.3a. Model 4100 attached to a cone penetrometer.

Figure 6.3a displays the Model 4100 attached to a cone penetrometer sampling tube for ground sample analysis. The Model 4100 consists of a portable Gas Chromatograph (GC), a SAW sensor, and a dynamic particle/vapor capture head. The three components are shown mounted in a rugged field portable fiberglass carrying case. The Model 4100 captures the sample in a cyro focus chamber. The chamber deposits it upon the SAW sensor. The SAW sensor determines the change in its mass density and reports it to the database maintained in a laptop 486 computer. The Model 4100 database identifies the suspect sample through an analysis of the numerous chemical signatures it has previously identified and recorded. The analysis is then displayed (Figure 6.3b).

Figure 6.3b shows a sample display screen presenting both visual and numerical data results (the actual screen is in color). The operator also has an electronic scratch pad to enter any notes or comments. The system uses software (developed by Amerasia) that integrates a proprietary database system with Microsoft Windows.

Based upon the application, it responds to both vapor and particle material media. Detection and analysis parameters are determined by the user's need. The system can be configured for standalone uses or can be integrated with other systems.



Notes 2/1/94 16:54:01

testing new rdx put sample in at 82 deg and 12ccm
Amerasia's system

Peaks

Peak	R time	Area	Substance
1	-0.04	54.0	DCA
2	2.42	55.3	TCA
3	3.66	403.6	TCE
4	4.22	64.6	PCE
5	5.78	237.1	Toluene
6	6.30	1,454.4	Benzene

SAW Status

12:46:35
25502.1 hz
SAW 36.3 C
Column 15.0 C
54.2%

Figure 6.3b. Display screen presenting visual and numerical results.

The Model 4100 is successful using water, soil, vapor, and particle mediums. It is used in three situations:

- Laboratory analysis and testing, both multiple and single gas analyzing.
- Field and on-site test and analysis, both multiple and single gas analyzing.
- Remote sensing, both within buildings and in hostile environmental locations.

TECHNICAL PERFORMANCE

The instrument is capable of preconcentrating, injecting and analyzing samples in less than 30 s. The system integrates efficiently to field conditions and does not require any special environmental requirements. It has been used from high humidity to high temperature desert conditions.

Table 6.3a shows selected compounds and their chemical properties (not inclusive of all of the substances eligible for analysis).

Four hours of basic training is sufficient to begin Model 4100 operations. As with any electronic test equipment, the user must exercise common sense and preventive maintenance. No special measures are required.

Cost. Table 6.3b shows base prices estimated for budget and planning purposes. Options are quoted based on the buyer's needs and specifications. Please contact George A. Pappas at (805) 495-9388 for a specific quotation. In addition, annual software maintenance fees are 9% of the price.

Table 6.3a. Detection limits for selected compounds.

Material Name	Minimum Detectable Vapor Concentration (ppb)
Trichloroethylene	40
Tetrachloroethylene	10
Carbon Tetrachloride	410
Chloroform	420
Dichloromethane	600
1,2-Dichloroethane	370
1,1,1-Trichloroethane	3,570
1,1-Dichloroethylene	1,110
1,1,2,2-Tetrachloroethane	3
Trichlorofluoromethane	25,640
Benzene	240
Toluene	19
Gasoline	10-100
Diesel Fuel	1

PROJECTED PERFORMANCE

The system is in portable briefcase size. Current R & D objectives are to miniaturize it to significantly smaller sizes.

APPLICABILITY

The technology can be applied to, but is not limited to, the following situations:

- EPA/ DOE environmental monitoring: Chemical processes, fugitive emissions, OSHA/ CAAA materials, environmental monitoring to include surface, subterranean and atmospheric monitoring of VOCs, organo phosphates, energetics, polychlorinated biphenyls, and dioxins.
- Industrial monitoring: stack emissions, dioxins, particle chemical processes, incineration, and continuous emission monitoring (CEM), toxic gas, combustibles, oxygen depletion.
- Law enforcement: military contraband, drugs, explosives, lethal chemicals, toxic gas warfare.

Table 6.3b. Base prices and availability.

Analyzers:	Base Price	Availability
Suitcase Model SAW/GC	$30K to $50K	Available for order
Laboratory Model SAW/GC	$30K to $50K	Available for order
Monitors:		
Industrial VOC Monitor		Available 1st Qtr 1996
Industrial HM Monitor		Available 1st Qtr 1996

STATUS

Prototype units are available for delivery in custom applications and research. Manufacturing began in March 1995. Full, high volume production units will be released by September 1995.

REGULATORY CONSIDERATIONS

The Model 4100 is considered intrinsically safe and no environmental impacts are anticipated from use of the technology.

POTENTIAL COMMERCIAL APPLICATIONS

The Model 4100 was demonstrated in drug and environmental areas. Other possible applications include food processing, chemical warfare, explosives, terrorist prevention, and specific vapor detection and monitoring. The industrial VOC and HM monitors will be available in early FY 1996.

BASELINE TECHNOLOGY

The baseline technology is the photo ionization detector (PID) or conventional gas chromatography equipped with an electron capture or electrolytic conductivity detector. The Model 4100 eliminates this process while decreasing reporting time to less than 10 s.

INTELLECTUAL PROPERTY

Patent: U.S. Patent No. 528915
The computer programs controlling the Model 4100 are proprietary and restricted. This includes all algorithms for peak detection and signal processing.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigators

Edward J. Staples
Amerasia Technology Inc.
2301 Townsgate Road
Westlake Village, CA 91359
(805) 495-9388; (805) 495-1550 FAX

Other Contacts

George A. Pappas and Teong Lim
Amerasia Technology Inc.
2301 Townsgate Road
Westlake Village, CA 91359
(805) 495-9388; (805) 495-1550 FAX

DOE Project Manager

C. Edward Christy
U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507-0880
(309) 291-4604; (309) 291-4469 FAX
Internet address: cchris@metc.doe.gov

REFERENCES

Amerasia Technology, Inc., will provide technical papers associated with this application upon request.

FIELD RAMAN SPECTROGRAPH FOR ENVIRONMENTAL ANALYSIS

DESCRIPTION

A field-hardened Raman spectrograph designed for use with fiber-optic probes has been fabricated. The instrument can be used for field screening and monitoring of a wide variety of wastes, pollutants, and corrosion products in storage tanks, soils, and ground and surface waters.

The spectrograph has no moving optical parts and employs fiber-optic sampling, a compact laser for Raman excitation, and a state-of-the-art charge coupled device (CCD) detector. The optical layout of the system, designed for far-visible and near-infrared operation, is shown in Figure 6.4. All components are positioned in the spectrograph on sturdy mounts that are secured firmly in position or on its side in a "tower" position. Realignment or wavelength calibration after changing positions is not necessary. Direct fiber coupling that is simple, more efficient, and more robust than optical slits was employed at the entrance.

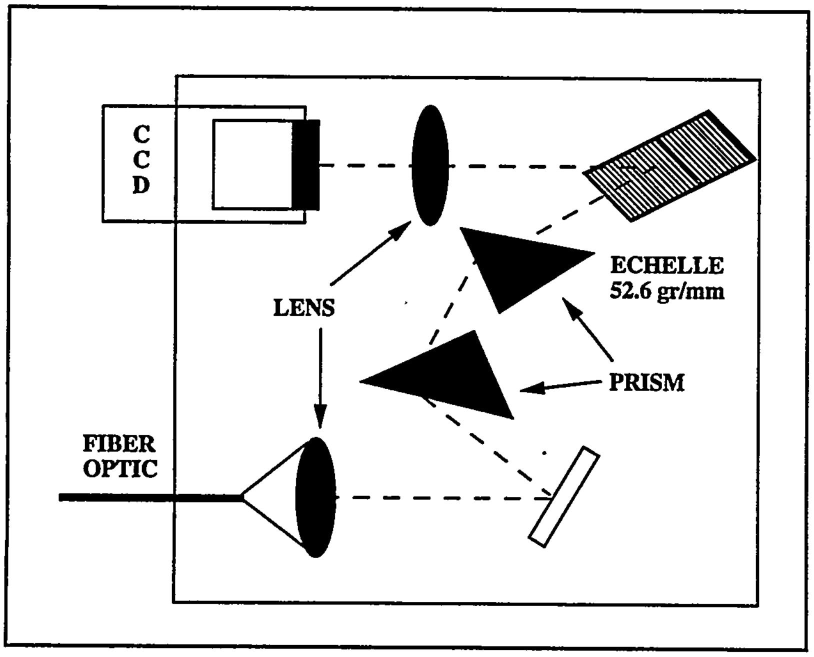


Figure 6.4. Optical layout of the near-infrared echelle spectrograph.

Spectrograph. In a direct coupled spectrograph, maximum throughput is achieved when the f-number (measure of optical throughput) matches that of the optical fiber (f/2). The echelle spectrograph was designed to be f/3, with low throughput losses. The optical components used were designed with antireflection coatings for maximum transmission of near-infrared light. The resulting spectrograph is better than conventional "fast" spectrographs which must sacrifice resolution and range to achieve high throughput.

The echelle spectrograph disperses the Raman spectrum in two-dimensions onto the CCD detector array, spreading the spectrum over about 10,000 detector elements. This allows a full Raman spectrum to be collected without repositioning the grating and with much better than 1 cm^{-1} resolution (about 0.3 cm^{-1}). With a conventional grating spectrograph using one-dimensional dispersion of the Raman spectrum and a typical 25 mm, 1,024-element detector array, the range is limited to 1,024 cm^{-1}. Because the complete Raman range is nearly 4,000 cm^{-1}, the grating must be moved at least three times to acquire a full spectrum.

The echelle spectrograph is compact, weighs approximately 60 lbs and is light enough for a person to carry short distances. The size of the spectrograph is 16 in (W) x 24 in (L) x 8 in (H) which allows it to be easily transported and operated in small trucks, vans, or automobiles.

Detectors. Three CCD detectors from Photometrics Ltd. were evaluated. The detectors differed in their mode of cooling and included liquid nitrogen, recirculating liquid, and air-cooled versions.

All three detectors performed well, with low dark currents (backgrounds) at integration periods up to 10 minutes. On the basis of convenience, size, and weight, the air-cooled version was recommended for future instruments unless a need arises for long (e.g., half-hour or more) integrations.

Lasers. Several solid-state and ion lasers were evaluated for field Raman applications. Solid-state lasers are better suited for field applications because of their potential for high output intensities in a compact unit. The diode-pumped, frequency doubled Nd:YAG laser available through Coherent Laser Group is the best example of a solid-state device with these features; however, the only drawback is its high price (about $30K). A flash lamp-pumped alexandrite laser being developed jointly by EIC Laboratories, Inc. and Big Sky Laser Technologies was selected to evaluate the echelle Raman system. Although, the prototype laser was the largest and heaviest tested, it provided the most output intensity (nearly 1 W at 752 nm). Full intensity could not be used when coupling to optical fibers because the high energy pulses being delivered damaged the fibers. One improvement being implemented is the reduction of pulse energy while maintaining average output intensity. The long-term objective is to produce a diode-pump laser similar to the Nd:YAG laser.

Fiber Optic Probes. Fiber-optic probes are a key component of any field Raman system, providing in situ detection capability at inaccessible locations such as hazardous waste tanks or subsurface soil and groundwater. Probes designed for use with 752 nm and 775 nm laser sources were fabricated, incorporating the following advanced features without altering the overall probe dimensions:

- An epoxy was used to seal the probe cover, viewing lens, set screws, fiber entry tubes, mirror holder, and internal components from water and water vapor.
- Moisture-resistant filters were employed in place of conventional filters that irreversibly lose optical transmission when exposed to water.
- Collection efficiency was improved by adding a fine adjustment capability to the collection fiber.
- Internal metal components were anodized black to absorb as much stray light as possible and spacial filtering (focused light collected from the sample through a pinhole aperture) was added to discriminate against stray laser light reflecting from odd angles through the probe.

The same features were incorporated in a "side-viewing" Raman probe. The side-viewing probe is well suited for direct Raman analysis when the probe is deployed through a medium such as soil or waste tank saltcake.

TECHNICAL PERFORMANCE

The capabilities of the fiber-optic Raman spectrograph were tested extensively using standard reference light sources and more than 70 DOE contaminants. Analytical parameters measured include: wavelength calibration (accuracy and stability), spectral resolution, and optical throughput determined as minimum detectable concentrations of analytes.

Wavelength Calibration. Calibration accuracy can be tested with chemical compounds for which Raman shifts have been well established. Raman shifts determined for solid naphthalene and a 50:50 (by volume) mixture of toluene and acetonitrile were compared using the echelle spectrograph (alexandrite laser excitation) with shifts established by ASTM. Overall, the values were in good agreement, matching to within 1 cm^{-1}. Long-term stability of the echelle's wavelength calibration was also excellent. The naphthalene calibration values were monitored during a several month period, and no shifts were observed.

It is important to note that qualitative identification of sample components can be achieved by spectral interpretation, but this process is slow and prone to error, particularly when complex sample mixtures are analyzed. In addition, few libraries have been developed for Raman spectroscopy and they do not include many of the contaminants of most interest to DOE. A catalog of intensity corrected, wavelength calibrated Raman spectra for more than 70 compounds found at various DOE sites has been compiled.

Resolution. Spectral resolution is most easily tested using narrow atomic emission lines from calibration lamps. A neon spectrum was acquired with the echelle spectrograph and compared to that acquired with a conventional Czerny-Turner imaging spectrograph (Model 270M from SPEX Industries) about the same size as the echelle. Closely spaced emission lines from the neon lamp were easily resolved with the echelle, even using a large, 100 μm core input fiber (resolution is optimum with a 25 μm core fiber). Resolution was noticeably poorer with the Czerny-Turner spectrograph which was operated under optimum resolution conditions (50 μm slits - narrower slits did not improve resolution). The Czerny-Turner spectrograph had a range limited to about 1,000 cm^{-1}.

Sensitivity. Sensitivity is an important parameter to consider for site characterization. Low sensitivity generally means that long, costly analysis times are required, and in the case of downhole sensors much of the in situ detection advantage is lost. In general, the sensitivity of the fiber-optic echelle Raman system compared favorably with conventional laboratory Raman instruments. With the echelle system, minimum detectable concentrations were in the range of 1-10 mM for both inorganic salts in aqueous solution and organic compounds in carbon tetrachloride. This level of sensitivity is suitable for in situ identification of major components in waste mixtures found in tanks or drums or nonaqueous phase liquids underground. The sensitivity is also better, by up to 10-fold, than can be achieved in the same analysis time using typical compact laboratory systems. Nearly all of the organic species could be readily detected at saturation levels in aqueous solution. The Raman intensity is linear with respect to concentration and is typical of what is observed for organic compounds in carbon tetrachloride or water and inorganic species in water. This is desirable for collecting semi-quantitative analytical data.

Hanford Waste Tanks. The Hanford Nuclear Reservation located in Richland, Washington, has 149 single-shell and 28 double-shell underground storage tanks that store highly radioactive, heat-producing wastes. The capabilities of the echelle Raman spectrograph were tested using three waste tank simulants provided from Hanford. The three samples represented different tanks and/or chemical processes. Aliquots were removed from each sample vial and placed on glass microscope slides for analysis. Using an end-viewing fiber-optic Raman probe and a krypton or alexandrite laser (100 mW of 725 nm excitation) with the echelle spectrograph, spectra were first collected for each sample wet and then after up to an hour of air drying. The sample position was not moved during the drying period. For comparison with the near-infrared echelle system, the Hanford samples were also analyzed with a visible Raman system consisting of an air-cooled argon laser operated at 514.5 nm and a SPEX 270 M spectrograph set at maximum resolution. The laser and spectrograph were connected to an EIC end-viewing fiber optic Raman probe. Again, 100 mW of laser excitation was delivered to the samples.

In summary, use of fiber-optic probes to safely collect high quality Raman spectra of Hanford tank samples remote from the spectrograph and operator has been demonstrated. The high-resolution of the echelle spectrograph is advantageous for this application because the samples contain multiple components of similar chemical structure. Spectral changes are also associated with the degree of sample wetness. Both visible and near-infrared Raman systems are needed for complementary characterization of tank samples -- with green excitation, fluorescence sometimes overwhelmed the Raman signal while dry samples often charred under the near-infrared.

Savannah River Site. The Savannah River Site (SRS) in Aiken, South Carolina, was the second location where the echelle Raman spectrograph was tested. Dense nonaqueous phase liquids (DNAPLs) such as trichloroethylene (TCE) and perchloroethylene (PCE) and light nonaqueous phase liquids (LNAPLs) such as gasoline have been found in SRS soils. A study of Raman detectability in soils from SRS at different excitation wavelengths was performed, to determine the best operating wavelength(s) for cone penetrometer deployment. Three soil samples were obtained from the M Area Basin of SRS where PCE and TCE DNAPLs were found at the bottom of a groundwater monitoring well. The soils were collected at depths of 23.8 ft, 105.2 ft, and 130.2 ft. Samples of each soil, alone and saturated with PCE, were excited with 35 mW laser power at 364 nm, 407 nm, 521 nm, 674 nm, and 752 nm, respectively.

In summary, the feasibility for detecting DNAPLs in SRS soils with a cone penetrometer Raman probe was demonstrated using near-infrared excitation. The lower visible wavelength excitation gave the best results overall. The study also showed that the optimum wavelength for Raman analysis is highly dependent on soil type.

Cost. The commercial price for a spectrograph (with detector, software, etc.) is estimated at $40K. This does not include the price of a laser which ranges from $10 to $40K; or fiber-optic probes ranging from $5 to $10K.

PROJECTED PERFORMANCE

Further evaluation and improvements include: (1) development of an enhanced instrument software package for improved data collection and signal processing, (2) expansion of the Raman spectral catalog and development of a computerized library format, (3) development and evaluation of advanced Raman probes for radioactive waste storage tank applications, (4) field evaluation of the cone penetrometer Raman system at SRS, and (5) preparation of an operation manual for the Raman spectrograph system.

APPLICABILITY

The Field Raman Spectrograph is applicable to field screening and monitoring of a wide variety of hazardous and radioactive wastes in storage tanks, soils, and ground and surface waters. Raman probes can be combined with the cone penetrometer for more rapid site mapping (than possible with drilled and excavated wells) and as a tool for searching for localized DNAPLs.

STATUS

The echelle Raman spectrograph is fully ready for evaluation at other DOE sites. An evaluation of the devices at the Savannah River site is planned. The technology is being commercialized by EIC Laboratories, Inc.

REGULATORY CONSIDERATIONS

The U.S. Environmental Protection Agency is aware of similar technologies being used with the cone penetrometer. Environmental impacts from the use of this technology are not anticipated.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is potentially applicable to a wide variety of sites where LNAPLs, DNAPLs, corrosion products in storage tanks, soils, and ground and surface waters may be present or hard to access.

BASELINE TECHNOLOGY

The baseline technology is the use of conventional Raman systems in the laboratory.

INTELLECTUAL PROPERTY

U.S. patent 5,112,127, "Apparatus for Measuring Raman Spectra Over Optical Fibers," Michael M. Carrabba and R. David Rauh, was issued on May 12, 1992.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Michael M. Carrabba
EIC Laboratories, Inc.
111 Downey Street
Norwood, MA
(617) 769-9450; (617) 769-2099 FAX

DOE Program Manager

Texas Chee
U.S. Department of Energy
19901 Germantown Road
Germantown, MD 20874
(301) 903-7926

REFERENCE

1. Rauh, R. D. and M. Carrabba, "Field Raman Spectrograph for Environmental Analysis," Phase I Topical Report prepared by EIC Laboratories, Inc., Norwood, MA, for the U.S. Department of Energy, Morgantown Energy Technology Center, Morgantown, WV, March 1995.

HALOSNIF FIBER-OPTIC SPECTROCHEMICAL SENSOR

DESCRIPTION

HaloSnif is a fiber-optic spectrochemical sensor capable of detecting any volatile chlorinated compound in air or gas. During operation, HaloSnif operating at subambient pressure (40 torr) continuously draws an air sample through a critical orifice into the plasma-excitation chamber where it is mixed with helium and excited with a radio-frequency signal inductively coupled to the plasma chamber. The plasma chamber is coupled via a fused silica optical fiber to the signal-processor unit. The optical emission of the plasma is filtered with a narrow-band-pass filter designed to monitor the 837.6 nm emission line from the excited chlorine atom. The intensity of the chlorine emission is directly proportional to the concentration of chlorine-containing species in the sample gas. The detection sensitivity for carbon tetrachloride is 5 ppmv. The response of the system is linear from the detection limit to 10,000 ppmv. The detection limit for other chlorine-containing compounds can be estimated by calculating the ratio of the percent of chlorine in the compound of interest to that of carbon tetrachloride.

Data acquisition is achieved using a LabView™ data acquisition software package mounted on a Macintosh computer system. The data-acquisition system is interfaced to the electro-optical signal-processing module via a 1 to 10 V analog output. Real-time concentrations of total chlorinated compounds are displayed on the monitor for observation by on-site personnel. All data are stored in computer memory for post-run processing and analysis.

TECHNICAL PERFORMANCE

HaloSnif's response to chlorinated species is linear from its lower detection limit of 1 to 5 ppmv (for most compounds) in air to approximately 10,000 ppmv. In addition, HaloSnif is not sensitive to moisture or other nonchlorinated compounds present in the sample gas. HaloSnif operates at 40 torr. Equilibration times are normally less than 1 min to reach 90% of full scale. The total weight of the HaloSnif system is 50 lb. HaloSnif also features real-time multipoint environmental field monitoring, small probe size, and the ability to use multiple probes with one central detection and data acquisition system. HaloSnif requires 5 A of 110 VAC power to operate.

HaloSnif can be reconfigured as an element-specific detector for gas chromatography effluents containing chlorine- and fluorine-containing

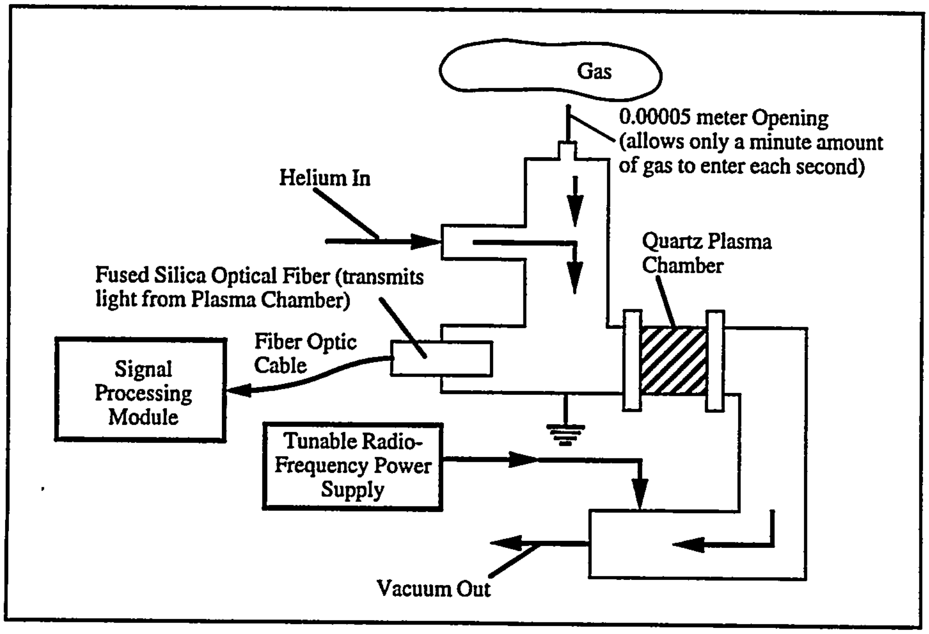


Figure 6.5. HaloSnif Fiber-Optic Sensor.

compounds. By simply replacing the critical orifice inlet with an open-face membrane material, HaloSnif is capable of measuring the concentration of total organic chlorine in water samples.

Cost. The unit is approximately $15K for the base system and approximately $250 per sensor assembly. Operations and maintenance costs are minimal. Contact Quanta Physik for details.

PROJECTED PERFORMANCE

HaloSnif has the potential to detect gas-phase compounds containing bromine, mercury, fluorine, and possibly phosphorus by simply modifying the analytical-emission wavelength monitored by the detector.

APPLICABILITY

HaloSnif is applicable to the detection of any volatile chlorine-containing compound including carbon tetrachloride, trichloroethylene, tetrachloroethylene, and chlorofluorocarbons in air or gases.

STATUS

All components of HaloSnif are commercially available through Quanta Physik, Palm Beach Gardens, Florida.

REGULATORY CONSIDERATIONS

HaloSnif is considered intrinsically safe, and no environmental impacts are anticipated.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications of HaloSnif include monitoring at waste sites, chemical storage areas, and process-based manufacturing plants using CFCs.

BASELINE TECHNOLOGY

The baseline technology is the photoionization detector (PID), or conventional gas chromatography equipped with an electron-capture or electrolytic-conductivity detector.

INTELLECTUAL PROPERTY

HaloSnif was developed at Pacific Northwest Laboratory (PNL). The patent has been assigned to PNL and the Department of Energy (DOE).

"Fiber Optics Spectrochemical Emission Sensors," Patent No. 5,085,499.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Khris Olsen
Pacific Northwest Laboratory
Battelle Boulevard
P.O. Box 999
Richland, WA 99352
(509) 376-4114

DOE Program Manager
Rashalee Levine
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7920

Industrial Partner
Quanta Physik
Palm Beach, FL
(407) 627-4525

REFERENCES

1. Anheier, N.C., K.B. Olsen, and J.W. Griffin, "Fiber-Optic Spectrochemical Emission Sensor: A Detector for Volatile Chlorinated Compounds," Sensors and Actuators, B, 11, 1993, pp. 447-453.1.

2. Griffin, J.W., K.B. Olsen, D.A. Nelson, B.S. Matson, and P.A. Eschbach, "Fiber Optic Spectrochemical Emission Sensors," Proceedings of the SPIE 1988 Symposium, Boston, MA, September 6-9, 1988.

3. Griffin, J.W., B.S. Matson, K.B. Olsen, T.C. Kiefer, and C.J. Flynn, "Fiber Optic Spectrochemical Emission Sensors: A Detector for Chlorinated and Fluorinated Compounds," Boston MA, Proceedings of the SPIE 1989 Symposium, September 5-8, 1989.

4. Olsen, K.B., J.W. Griffin, T.C. Kiefer, R.S. Matson, and C.J. Flynn, "A Fiber-Optic Spectrochemical Emission Sensor as a Detector for Volatile Chlorinated Compounds," ACS Symposium Series 479: Element Specific Chromatographic Detectors by Atomic Emission Spectroscopy, Ed. Peter C. Uden, 1992.

5. DOE-RL, "Technology Information Profile (Rev. 3), Technology Name: HaloSnif - Fiber Optic Spectrochemical Sensor," TTP Reference No. RL-8503-PT, March 29, 1993.

IN SITU MEASUREMENT OF VOLATILE AND SEMIVOLATILE ORGANIC COMPOUNDS IN THE SUBSURFACE

DESCRIPTION

Methods and a technology is being developed that will couple a cone penetrometer (CPT) with field-deployable gas chromatography/mass spectrometry (GC/MS) instrumentation to directly transfer volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) from subsurface material at depth to the analytical instrument in the field. Sampling, preconcentration, and analytical equipment will be directly coupled to the CPT to provide on-line, near-real-time analysis of VOCs (e.g., trichloroethylene, benzene) and SVOCs (e.g., polynuclear aromatic hydrocarbons, polychlorinated biphenyls) in subsurface materials. The VOC or SVOCs will be liberated from subsurface material and carried to the surface by an inert, heated transfer line, preconcentrated, and analyzed by thermal desorption GC/MS.

The in situ extraction and on-site analysis of VOCs and SVOCs will reduce waste generated as compared to conventional laboratory analysis.

TECHNICAL PERFORMANCE

Laboratory Experiments. Transfer efficiencies for VOCs through 15 m lengths (0.160 to 0.216 cm ID) of the tubings composed of Teflon® (Type PFA, PTFE, and FEP) were evaluated by using a dynamic system in which a certified gas standard containing chloroform, 1,1,1-trichloroethane, carbon tetrachloride, tetrachloroethylene, n-hexane, benzene, toluene, and o-xylene was mixed with air saturated with water at 25°C. The water content of the gas stream had an insignificant effect on the quantitative transfer of VOCs through Teflon® tubing but was critical to the efficient transfer of the compounds through metal tubing, particularly nickel. Transfer efficiencies for all eight analytes in moist gas streams through stainless steel tubing were greater than 95%. Toluene, tetrachloroethylene, and o-xylene were transferred with 93%, 81%, and 80% efficiency, respectively, when drawn through Teflon® PFA tubing at 25°C. The sorption of the VOCs by Teflon® tubing was reversible, and the transfer efficiencies improved to 94% when the tubing was flushed with 16 equivalent volumes of air. In general, the retention of the VOCs by Teflon® increased with decreasing aqueous solubility of the analyte. The outgassing of contaminants from Teflon® increased with increasing temperature. The efficiencies at which the VOCs were sparged for aqueous standards in Teflon® PFA, Type 304 stainless steel, and glass vessels were similar. In addition, the time required to sparge and transfer a sample to the surface in an in situ, on-line sparging system will be limited by the time required to flush the transfer line. [Air sparging is defined as the injection of air into saturated matrices to remove contaminants through volatilization.] The results from the evaluation of materials and testing of the laboratory-scale prototype provided the information needed to design a miniaturized version of the sparging vessel for the CPT.

Down-Hole Sparging Vessel. The design of an in situ, on-line sparging vessel incorporates the following features:

- A narrow stainless steel vessel with a 1:1 ratio of headspace to sample volume, in which the purge gas enters the base of the vessel through a stainless steel frit to optimize sparging efficiency by maximizing the contact between the purge gas and water.
- The ability to draw the sample into the vessel under a slight vacuum to facilitate sample collection.

- Control of the collection of a known volume of the sample and initiation of the purge cycle by a liquid level sensor electrically wired to two solenoid valves.
- A heated, stainless steel transfer line to efficiently transport the VOCs to the surface.
- Preconcentration of the VOCs at the surface on a mixed bed of porous and solid carbon sorbents.
- On-site desorption of the VOCs into an instrument for quantitative analysis.
- A back-flush cycle in which the transfer line is purged and the sparging vessel is drained in preparation for additional sample collection.

Figure 6.6a is a schematic of the down-hole sparging vessel.

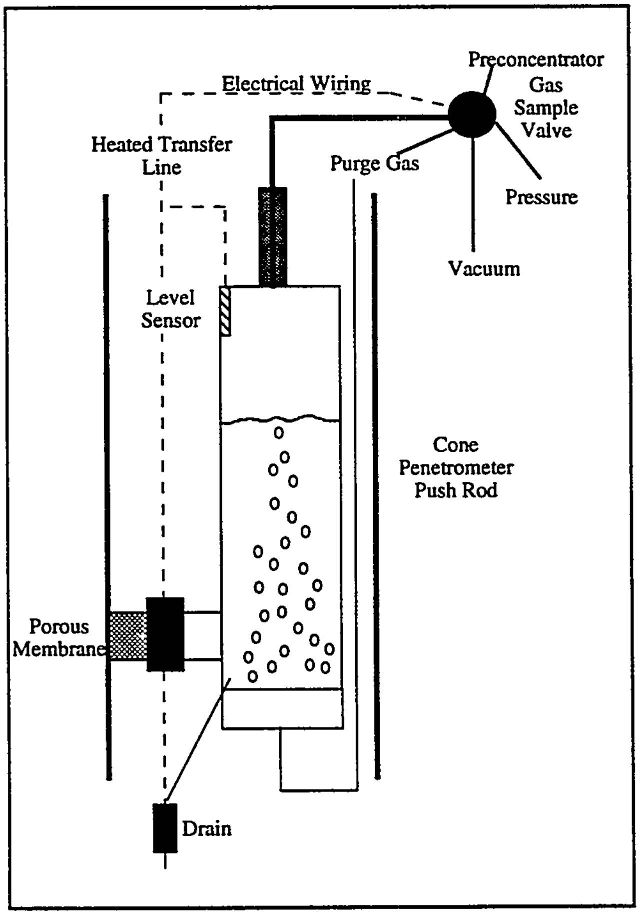


Figure 6.6a. Down-Hole Sparging Vessel.

Thermal Desorber. A thermal desorption device is incorporated into the CPT tip which heats the surrounding soil. The vaporized volatile and semivolatile organics (e.g., polynuclear hydrocarbons, petroleum products, PCBs) are swept into the device by an applied vacuum and transported to the surface in a gas stream through a heated transfer line. As with the purge device, the organics of interest are preconcentrated on the surface and then desorbed into a GC/MS or other instrument. Figure 6.6b shows is a schematic of the thermal desorption device.

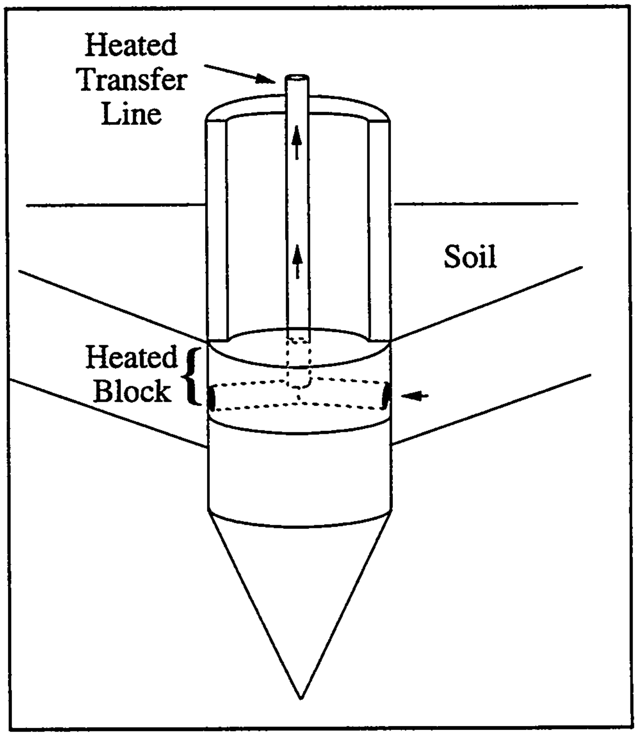


Figure 6.6b. Thermal Desorption Device.

Cost. A cost reduction of 90% has been estimated with use of the thermal desorption GC/MS for field analysis.

PROJECTED PERFORMANCE

The anticipated performance relative to the baseline technology includes:

- Quantitative -- defined volume, no losses during collection, transfer, shipment, storage, analysis.

- Acceptance -- conforms to 8240 and other EPA methods.

- Reliable -- depth profiling, faster data, cheaper (short wait to fill, less in/out).

- Disposal -- no sample brought to surface, therefore, no disposal costs.

APPLICABILITY

The technology is applicable to in situ characterization of VOCs and SVOCS in subsurface materials (e.g., groundwater and soil).

STATUS

The transfer line and the miniaturized version of the in situ purge device and the thermal desorption device were designed and fabricated. Testing of the in situ purge device and the thermal desorption device are expected to be completed in June 1995. A preliminary field demonstration is expected to be completed by the end of August 1995. Software development is planned for FY 1996.

REGULATORY CONSIDERATIONS

The two sample collection devices will remove only the vaporizable (i.e., organic) contaminants from the subsurface. These contaminants will be swept via a gas stream directly to an instrument and will be totally enclosed. Appropriate downstream trapping devices (e.g., a carbon trap) can be used for nondestructive detectors. There will be no hazardous or radioactive emissions.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be used for characterization of industrial waste facilities with organic chemical contamination, landfills, industrial process sewage leaks, storage tank leaks, etc.

BASELINE TECHNOLOGY

The baseline technology for collecting groundwater for analysis in the laboratory includes: (1) bailers which lose VOCs and are slow, (2) vacuum operated BAT sampler which generally does not work (needles clog), and (3) the hydropunch which is often clogged by silt, is slow, and is a "one shot" sample.

The baseline technology for thermal desorption/ screening is the Mostap core sampler and WES-modified Mostap which is mechanically complicated (no rocks), uses an unheated transfer line, and has limitations with mud and clay (vapor transfer out of bulk sample). Its efficiency depends on the permeability of the matrix.

As noted previously, the water sampler is technically equivalent to the EPA purge and trap technique (e.g. EPA Method 8260) and the soil sampler is functionally similar to the EPA thermal desorption technique (e.g. EPA Method 8275).

INTELLECTUAL PROPERTY

Patent disclosures have been filed.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Mitchell Erickson
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439-4843
(708) 252-7772; (708) 252-9594 FAX

DOE Projects Manager, CMST-CP

Eric Lightner
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7935

University Partner

Albert Robbat
Tufts University
Chemistry Department
62 Talbot Avenue
Medford, MA 02115
(617) 627-3474; (617) 627-3443 FAX

REFERENCES

1. Aldstadt, J.H., P.V. Doskey, J.M. Kuo, M.S. Constanza and M.D. Erickson, "In Situ Determination of Volatile Organic Compounds in Soil," 46th Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 1995.

2. Doskey, P.V., J.H. Aldstadt, M.S. Constanza, J. Kuo, and M.D. Erickson, "In-Situ Measurement of Volatile Organic Compounds in Groundwater by Methods Coupled to the Cone Penetrometer," Fourth International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, NV, February 1995.

3. Doskey, P.V., J.H. Aldstadt, M.D. Erickson, A. Robbat, and A. Gorshetyn, "In Situ Measurement of VOCs and SVOCs in the Subsurface: Development of Screening and Quantitative Field Methods Coupled to the Cone Penetrometer," Site Characterization and Analysis Penetrometer System Sensor Development Workshop, U.S. Army Corp of Engineers Waterways Experiment Station, Vicksburg, MS, August 17, 1994.

MINIATURE CHEMICAL FLOW PROBE SENSORS

DESCRIPTION

The objective of this project is to develop an in situ generic chemical speciating technology suitable for use in both: (a) field survey applications and (b) process control and monitoring applications. The technology to be implemented is a flowing reagent system in which analytes diffuse across a membrane into the reagent-containing volume. A chemical reaction between the reagent and the analyte then produces spectrally distinct products. The absorption characteristics of these products are measured by illuminating the reaction volume with broadband white light. This light is carried from a flash lamp into the reaction volume using optical fibers and then to a small, solid state spectrometer, again, using optical fibers. The generic nature of the instrument comes from the goal of designing a single probe body in which many different reagents and membranes could be used. The speciating characteristic is obtained from tailoring the reagent and membrane to the analytes and the matrix. The most general instrument would be one in which two or more reagents would be mixed at the reaction volume. Because of funding limitations, the current goal is to investigate only single reagent applications.

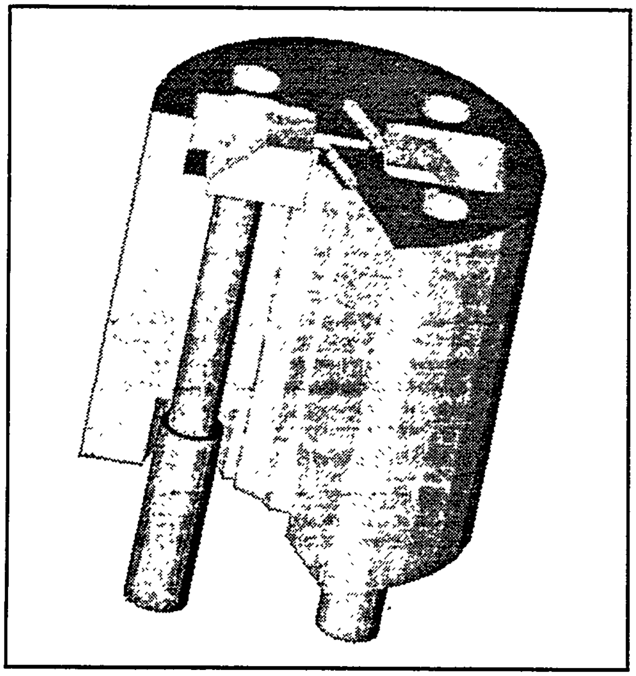


Figure 6.7a. Flow probe head.

The instrument can be used in situ at the point where chemical information is desired. The basic probe is a 0.5" diameter cylinder. Two different configurations are being designed: (a) an above-ground field or process monitoring instrument, and (b) a down-well unit suitable for 2" or larger well. Both configurations are designed for as many as 500 analyses before reagent replenishment is required.

The active element of the flow probe instrument is the probe head. This item is inserted in the environment of interest (see Figure 6.7a). The z-shaped element contains the reagent fluid and is the reaction volume. The center segment of the z-shaped region is illuminated with white light. The two prisms on either end of this reaction volume segment are used to turn light by 90 degrees. These prisms are made from sapphire. At the bottom of the prisms are the optical fibers that carry light from the flashlamps to the probe head and then into a spectrometer.

The flow probe instrument is suitable for measuring chemicals in the fluid state (both liquids and gases). The chemicals of interest must be able to diffuse across a thin membrane.

Three different contaminant environments are targeted: (a) metallic ions (specifically copper) in aqueous matrices, (b) volatile organic compounds (VOCs), specifically trichloroethylene (TCE), trichloroethane (TCA), and chloroform, in ambient air, and (c) VOCs in aqueous matrices. Field demonstrations will be performed in aqueous process streams, organic contaminated dry wells, and organic contaminated water containing wells.

TECHNICAL PERFORMANCE

The instrument is packaged into two suitcases. One suitcase (14" x 24" x 36") contains the electrical items (computer, flash lamps, power supplies, data acquisition units) and the other suitcase (10" x 24" x 23") contains the fluid handling items (reagent storage, valves, tubes, the probe umbilical). Electrical and optical cables interconnect the two suitcases for operation. The probe's point of insertion into the environment to be tested is 1 m from the fluid handling suitcase. Figure 6.7b shows the last of the laboratory configurations assembled. These items are then grouped into the two suitcases, which are not shown. Because this is the first development effort for this technology, we chose to require access to 110 VAC power.

A down-well unit is also being developed. This unit can be lowered into a well to a depth of 150 ft.

The software developed allows three different modes of operation: (a) manual operation mode in which an operator activates the data acquisition and control functions,(b) a semi-manual mode in which an operator initiates a predetermined sequence of data acquisition and control functions, and (c) an automatic mode in which the computer controls (without the need for any operator action) the activation of a number of predetermined sequences of data acquisition and control functions.

A typical sequence for an analysis consists of: (a) the reagent-controlling valve opening and then closing which allows fresh reagent fluid to flush the reaction volume clean of previous reaction products, (b) once the valve closes, the flashlamp pulses and the light carried by the optical fibers completely illuminates the reaction volume,(c) diffusion of fresh chemicals across the membrane is occurring and some reaction products are forming, (d) the absorption spectrum is measured by the spectrometer, (e) chemometric based analysis is performed, and (f) steps (b) to (e) are repeated at 1 min intervals. Some time between the 1 and 15 min is required for the algorithm to compute the concentrations of the analytes measured.

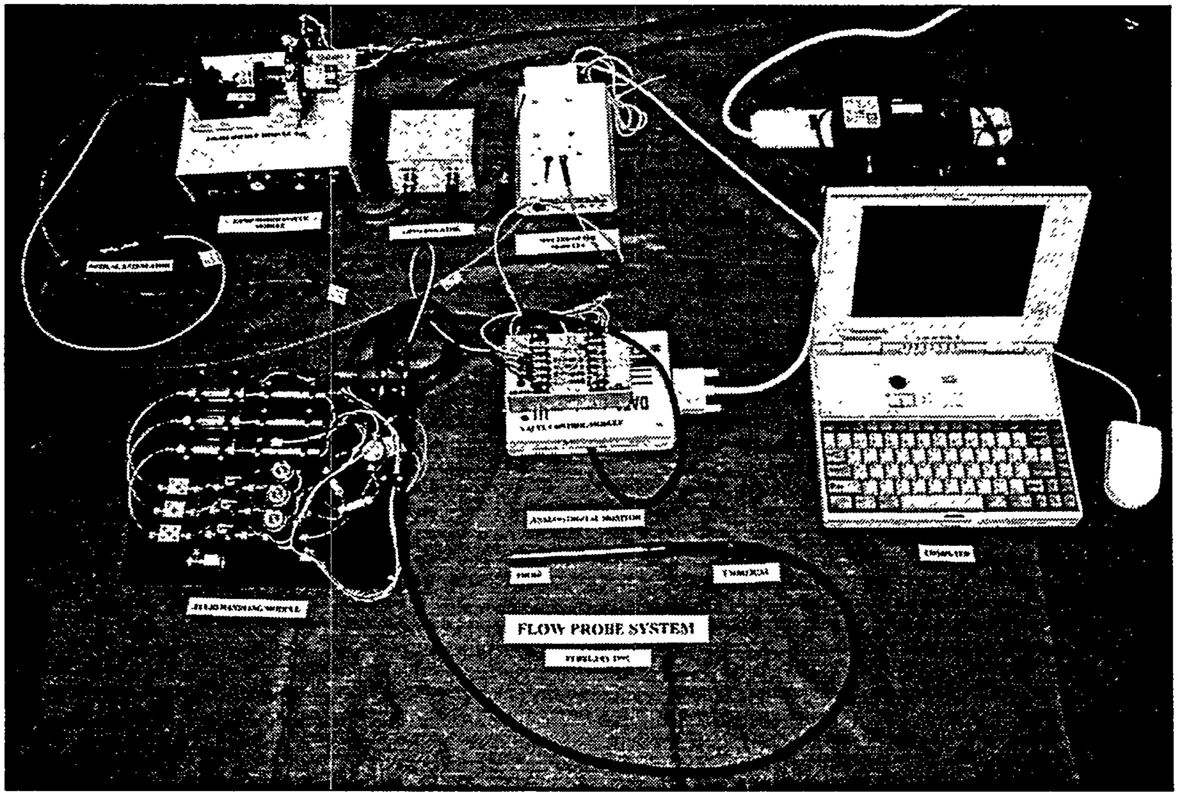


Figure 6.7b. Flow probe laboratory configuration.

Detection limits are similar to those in laboratory-based liquid reagent, absorption-based spectroscopy. These vary according to the analyte being measured. The VOCs being measured in the field trials can be analyzed down to 10s of ppb for TCE and chloroform and 1s of ppm for TCA in aqueous matrices. The copper ions in water can be measured in 10s of ppb.

Cost. The three field instruments that will be tested during summer 1995 cost approximately $17K. In production, this cost could come down to less than $10K. This is the fixed cost of an instrument. For a different set of analytes and matrices, only the probe and umbilical need be modified. These cost $700 for the field instruments and could be half that in production. The cost involved with development of reagents and membranes for different analytes and matrices is unknown. However, liquid reagent/absorption spectroscopy based analytical chemistry is a mature science, thus literature searches for specific applications followed by a calibration trial could be all that is required.

PROJECTED PERFORMANCE

Areas of further development include:

- Other probe head designs that lower the detection limits or make for easier probe head manufacturing -- for applications not limited in cross section.
- Membrane development -- while reagent chemistry is a mature science, membrane technology for diffusion applications is rather new.
- Multi-probe applications -- one controlling unit could obtain data from any number of probe/umbilical units.

APPLICABILITY

The flow probe technology is applicable for the measurement of volatile or dissolved materials capable of diffusion through thin membranes. This includes: (a) VOCs in air or other gases, and in liquids such as water, and (b) ionic or non-ionic materials that are dissolved in liquids such as water.

STATUS

The technology is in the bench scale or prototype stage. Two laboratory units are available and are in use for the calibration phase of the project. Three field units will be available the summer of 1995. Plans are to perform field demonstrations for a two-month period at two DOE production sites and four commercial industrial sites.

Commercialization activities are ongoing. A legal package including licensing, drawings, reports, and data results documentation is being assembled. A price for this package is being negotiated. The technology licensing will be transferred to one or more Center for Process Analytical Chemistry (CPAC) member companies.

REGULATORY CONSIDERATIONS

The technology essentially takes liquid reagent, absorption-based spectroscopy which can be and has been performed for nearly a century in test tubes in an analytic chemistry laboratory and packages the operation into a field instrument. The volumes of fluids used are considerably smaller (10 microliters per analysis). The total volume of liquid used for 500 analyses is 10 milliliters. This usage will create about the same volume of waste liquid that must be disposed of using approved methods. The reagents used for analysis depend upon the chemicals to be analyzed. Those currently used have pHs that range from 5 to 12; therefore, some care is needed in their handling and disposal. The worst case is a spill of up to 10 mil of fluid if the membrane were to burst and the liquid monitoring subroutines of the control system were to fail. Discussions with users and potential users have not raised any regulatory barriers to the use of the flow probe technology.

POTENTIAL COMMERCIAL APPLICATIONS

The applications for the flow probe technology are the same as for those which use reagent based, optical absorption spectroscopy. Those that have been discussed with the CPAC membership include: (a) waste water treatment monitoring, (b) process monitoring of a multitude of liquid-based processes including etching baths, and chemical inhibitor applications, (c) petrochemical process monitoring, (d) quick field monitoring of the near surface for volatile chemicals, and (e) long term monitoring of restoration projects in mining applications.

BASELINE TECHNOLOGY

The most commonly used technology is the taking of a grab sample in the field followed by transport to a remote general analytical location or facility for analysis. Issues relating to this process include: a) manpower intensive operation for field sampling, b) slow feedback that precludes smart sampling, c) high cost (about $200) per analysis, d) potential loss of volatile constituents from grab sample container resulting in sampling errors, and e) larger waste generation caused by the volumes of typical grab samples.

INTELLECTUAL PROPERTY

This project is a joint effort by Sandia National Laboratories (SNL) and CPAC. The intellectual property rights are being provided in a onetime fixed fee to various CPAC members. This arrangement between the SNL and CPAC is being undertaken to facilitate technology transfer in the quickest, and most efficient manner.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
George R. Laguna
Sandia National Laboratories
MS 0501
PO Box 5800
Albuquerque, NM 87185-0501
(505) 844-5273
email: grlagun@sandia.gov

DOE Program Manager
Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

Industrial Partner
Patrick L. Jones
Center for Process Analytical Chemistry
University of Washington, BG-10
Seattle, WA
(206) 685-2326
email: pljones@u.washington.edu

REFERENCES

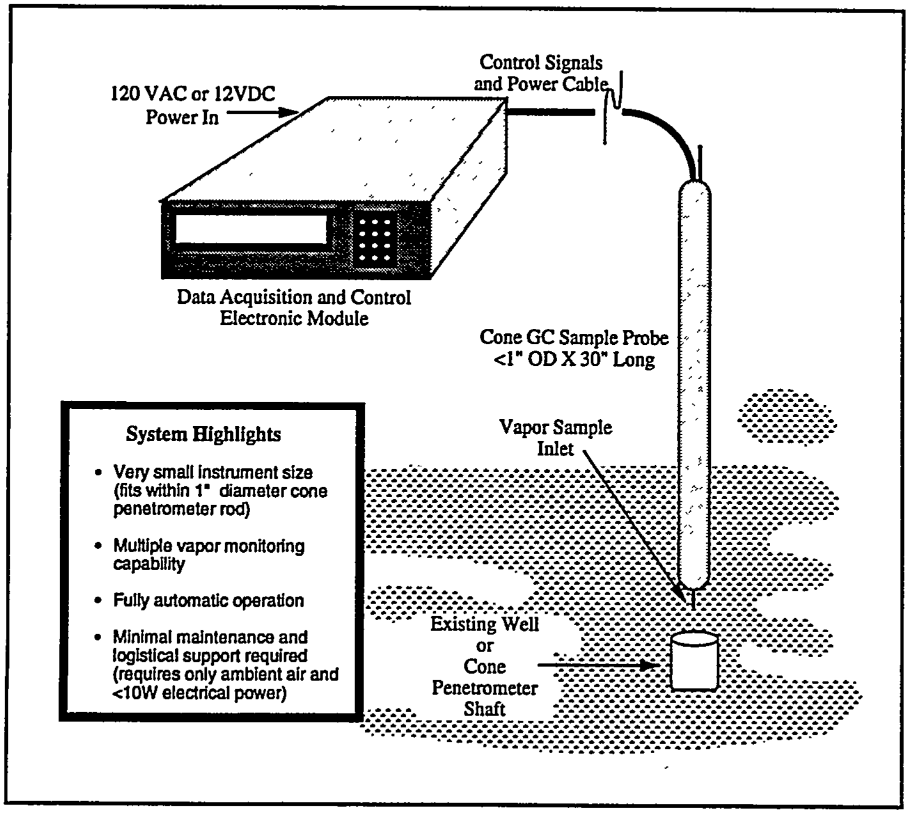
None.

MINIATURE GC FOR IN SITU MONITORING OF VOCS WITHIN A CONE PENETROMETER

DESCRIPTION

A high performance gas chromatograph that can be used with a cone penetrometer for accessing and quantifying organic contamination at DOE environmental clean-up sites is being developed. The Cone Penetrometer Gas Chromatograph (dubbed "Cone GC") is constructed in the shape of a cylinder whose maximum outside diameter is less than one inch, thereby allowing it to be incorporated as part of the piezocone assembly that is inserted into the soils. This instrument provides the capability for rapid assessment of vadose zone contamination allowing data to be collected directly at the emission source. By taking an in situ measurement, the Cone GC can establish a stratigraphic contamination emission profile with no sample handling. The Cone GC offers the unique capability of being able to go to the sample collection zone instead of the sample being collected and brought back to an instrument on the surface. This will avoid the need for long sample collection lines, and pumps and syringes, providing a convenient means for in situ measurements. An additional use of the Cone GC would be inserting the instrument at the perimeter of a hazardous waste area to gauge the potential migration of volatile organic contamination across the monitored zone.

The Cone Penetrometer Gas Chromatograph is rugged and unusually small. To fit within the cone penetrometer rod, the instrument must be less than 1 inch in diameter. The Cone GC is a completely self sufficient instrument requiring only electric power and a small amount of compressed air to operate. As Figure 6.8 illustrates, the Cone GC is split into two components: (1) the data acquisition control module located at the surface; and (2) the GC sample probe assembly that has a 1" diameter and is approximately 30" long. The cable connection between the GC piezocone and the data acquisition module provides instrument power, compressed air, and data transmission conduit.



System Highlights

- Very small instrument size (fits within 1" diameter cone penetrometer rod)
- Multiple vapor monitoring capability
- Fully automatic operation
- Minimal maintenance and logistical support required (requires only ambient air and <10W electrical power)

Figure 6.8. Cone Penetrometer GC concept sketch.

The Cone GC is designed to minimize the need for typical support overhead associated with gas chromatography. The instrument uses a miniature temperature controlled packed-column for sample analysis. Sample injection is performed by an electrically controlled gas sampling valve and the entire instrument operation is controlled by a microcomputer using a menu driven interface program. The Cone GC can be configured with different detector options that allow additional analysis flexibility and compound detection selectivity. There are two detector options. The first is a general hydrocarbon detector and the second is a halogen specific detector. These detectors in combination with the specific column selection offer ways to improve instrument selectivity. The Cone GC is designed to provide sub-ppm detection levels of multicomponent samples. The typical analysis time is usually less than 10 minutes. The instrument interface was designed so a field technician with limited background in the operation of a gas chromatograph could successfully operate the instrument.

Cost. The cost of the Cone GC probe assembly and the electronic controller module is anticipated to be about $10K. A replacement or an additional Cone GC probe assembly would be $4K. The costs do not include the price of the cone penetrometer and operational support requirements. These costs are only estimates based on current design objectives.

TECHNICAL PERFORMANCE

Technical performance data will be available in late 1995.

PROJECTED PERFORMANCE

The primary performance objective for the Cone GC is to be able to detect sub-ppm levels of chlorinated organics and hydrocarbons at DOE environmental clean up sites. This technology as part of a cone penetrometer will provide for contamination analysis data to be gathered in situ, establishing a depth emission profile. This will avoid the need for traditional headspace soil analysis and should allow a significant cost savings and faster data analysis.

APPLICABILITY

The Cone GC is capable of both general hydrocarbon analysis and chlorinated compound analysis. This instrument could be configured for a wide range of compounds depending on the scope of the application.

STATUS

This is an applied research project. The expected date for commercialization of the Cone GC is late 1996.

REGULATORY CONSIDERATIONS

The primary use of this technology will be in the area of field screening for hazardous waste site assessment. Gas chromatographic methods have been widely and successfully employed in this remediation assessment area. In general, regulations concerning subsurface access via well drilling will apply.

POTENTIAL COMMERCIAL APPLICATIONS

The Cone GC would offer an additional analysis tool for the environmental industry because cone penetrometer testing investigations provide a significant amount of physical data on soil conditions. Having an in situ gas chromatograph in conjunction with the cone penetrometer will provide additional analysis information on volatile organic emissions. Data provided by the Cone GC will allow contamination information to be gathered faster and at less cost than conventional methods.

BASELINE TECHNOLOGY

The baseline technology is laboratory characterization, which requires that the sample be collected and brought to a GC instrument on the surface.

INTELLECTUAL PROPERTY

Contact the Technical Coordinator for further information.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator

N. Lynn Jarvis
Microsensor Systems, Inc.
62 Corporate Court
Bowling Green, KY 42103
(502) 745-0099; (502) 745-0095 FAX

Technical Coordinator

Norman Davis, Jr.
62 Corporate Court
Microsensor Systems, Inc.
Bowling Green, KY 42103
(502) 745-0099; (502) 745-0095 FAX

DOE Project Manager

Carl E. Roosmagi
U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507-0880
(307) 721-7205

REFERENCES

None.

DESCRIPTION

Researchers have demonstrated applicability of a multianalyte single-fiber sensing technology for environmental monitoring. The sensing technology is based on the capability of placing multiple indicator chemistries which serve as discrete sensing sites at the distal end of a single imaging fiber. The indicators are sensitive to analyte concentration and exhibit changes in absorbance or luminescence, forming the basis of such sensors. An imaging fiber is typically 300 μm-400 μm in diameter, consisting of thousands of individual channels. The discrete sensing sites are a result of photopolymerizing different indicators in a polymer matrix on multiple regions of the fiber. By coupling the imaging fibers to a charge coupled device (CCD) detector, it is possible to spatially and spectrally discriminate the multiple sensing sites simultaneously and, hence, monitor analyte concentrations.

Indicator chemistry and immobilization procedures have been developed for pH, Al^{3+}, hydrocarbon, O_2, and CO_2 sensors.

TECHNICAL PERFORMANCE

The analyte-sensitive polymers can be placed at precise locations on the fiber surface. These reversible sensors are covalently bonded to the fiber so they are quite rugged. A portable, battery operated instrument was designed and built to demonstrate the applicability of multianalyte sensors for field measurements. The instrument is based on an imaging fluorimeter that provides filtered excitation light through the fiber to the sensors and interrogates the resulting fluorescence signal. The fluorescence from the sensor array is guided back through the imaging fiber and imaged onto the CCD. The CCD image is then used to calculate intensities for each of the spatially resolved sensors. These intensities can then be related to concentrations of a particular analyte.

Figure 6.9a shows a schematic of a pH/hydrocarbon array with seven analyte-sensitive polymer matrices. The sensor is comprised of three pH sensitive matrices containing eosin, two pH sensitive matrices containing fluorescein, and two hydrocarbon sensitive matrices of two photopolymerizable siloxanes.

Figure 6.9b shows the increase in fluorescence matrices 5 and 7 upon introduction of CH_2Cl_2 vapors and return to baseline fluorescence when pure N_2 was reintroduced. Panel A also shows that there is no significant fluorescence change of the other matrices upon introduction of CH_2Cl_2 vapors. Panel B shows the response of pH sensitive matrices. Between pH 2-6 the eosin-containing matrices show the maximum change in fluorescence, while the fluorescein-containing matrices are most sensitive to the pH range of 5-8.

PROJECTED PERFORMANCE

As a result of the initial success in measuring pH optically, an underground storage tank application is possible. A wide range of pH sensors could be placed to monitor for corrosive conditions, as well as a redundant number of individual sensors to mitigate the effects of a harsh environment.

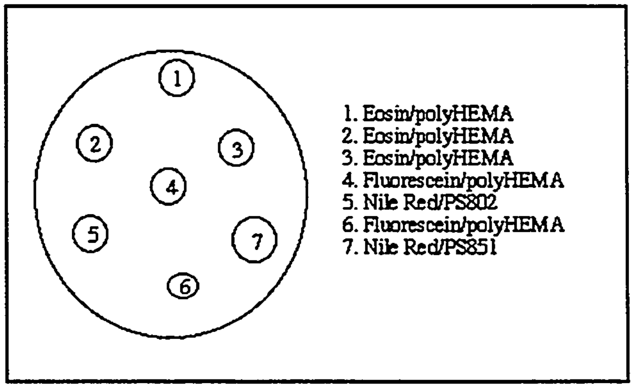


Figure 6.9a. Schematic of the pH/hydrocarbon array.

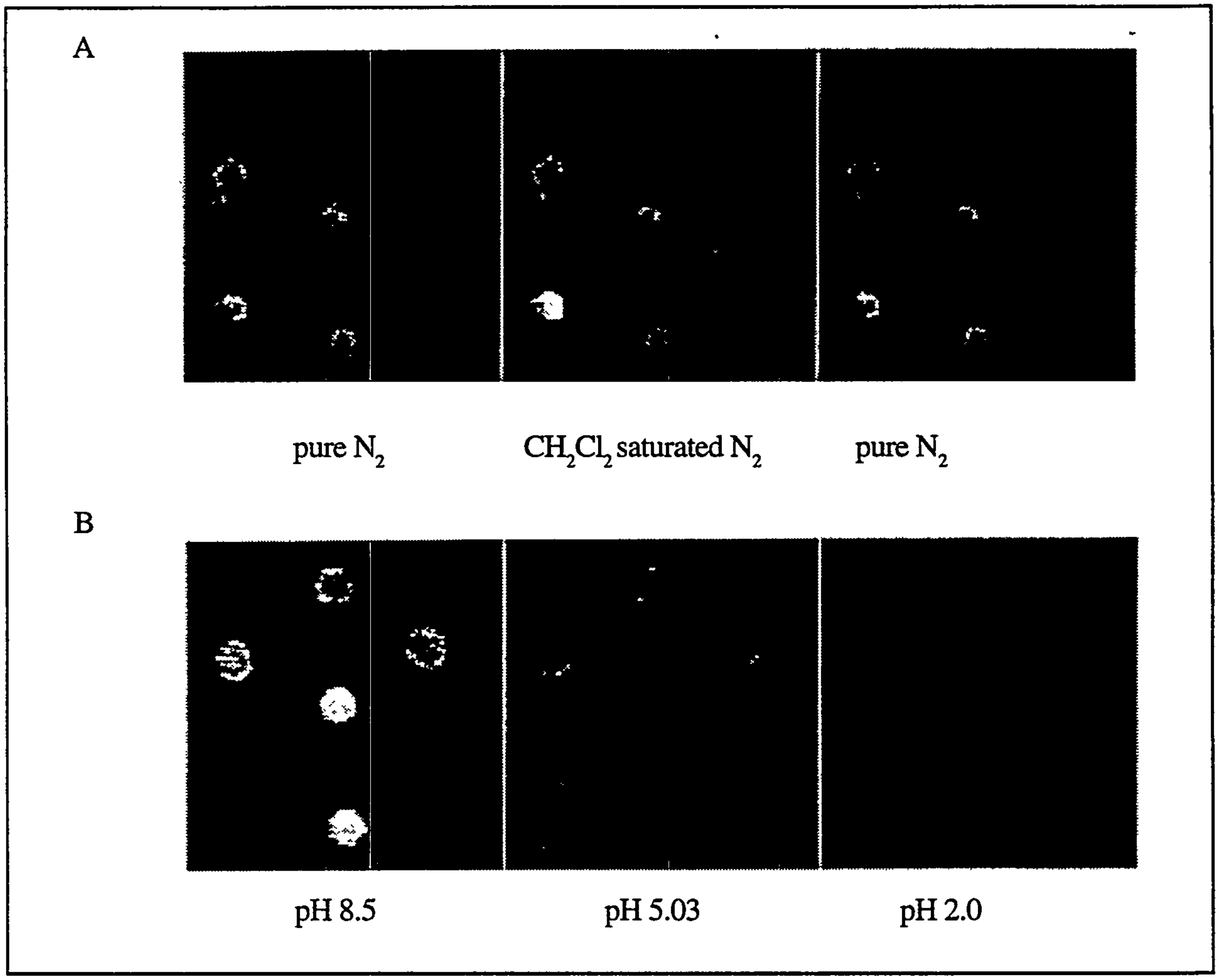


Figure 6.9b. Fluorescence images of a pH/hydrocarbon array. Panel A shows the response of the array to CH_2Cl_2 vapors. Panel B shows the response of the array to pH changes.

The O_2, CO_2, and pH sensors are being considered for deployment in bioremediation applications, including sites operating at elevated temperatures.

Lawrence Livermore National Laboratory (LLNL) plans to explore the potential application of a new concept recently demonstrated by Tufts University. The concept consists of a combination of slow release polymer technologies with fluoroimmunoanalysis that has the potential for a continuous reading antibody-based biosensor. Success would greatly increase the number of different analytes that could be measured with the multianalyte sensor.

APPLICABILITY

Multianalyte sensor arrays are applicable to the detection of pollutants in groundwater and waste water, as well as continuous monitoring of pollutants and respiration of biomass associated with bioremediation. The concept of multianalyte sensors is not limited to pH, Al^{3+}, O_2, CO_2, and hydrocarbons. As additional analyte-specific reagents and other transduction mechanisms are identified, these sensors will find greater scope of applicability.

STATUS

The capability of placing multiple indicator chemistries which serve as discrete sensing sites at the distal end of a single imaging fiber has been demonstrated. Indicator chemistries for a wide range of pH, Al^{3+}, O_2, CO_2, and hydrocarbons have been developed.

A small, low-cost, field portable instrument was designed, built, and successfully laboratory tested with prototype multianalyte sensors.

REGULATORY CONSIDERATIONS

The U.S. Environmental Protection Agency has no system for certifying sensor technologies.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include cost effective site characterization and monitoring of groundwater, and waste water, and bioremediation at industrial sites.

BASELINE TECHNOLOGY

Current methods for detecting nearly all priority contaminants require sampling and subsequent laboratory analysis.

INTELLECTUAL PROPERTY

The technology is being developed by LLNL in collaboration with Tufts University researchers. Tufts University has the following patents covering the core technology.

"Methods of making imaging fiber optic sensors to concurrently detect multiple analytes of interest in a fluid sample," Patent No. 5,250,264, issued October 5, 1993.

"Imaging fiber optic array sensors, apparatus, and methods for concurrently detecting multiple analytes of interest in fluid sample," Patent No. 5,244,636, issued September 14, 1993.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Fred Milanovich
Lawrence Livermore National Laboratory
P.O. Box 808, MS L-524
Livermore, CA 94551-0808
(510) 422-6838; (510) 422-8020 FAX

DOE Program Manager
Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

University Partner

Tufts University
Medford, MA

REFERENCES

1. Healey, B.G., S. Chadha, D.R. Walt, F.P. Milanovich, J. Richards, and S. Brown, "Development of Multianalyte Sensor Arrays for Continuous Monitoring of Pollutant," UCRL-JC-119797, Fourth International Symposium on Field Screening Methods, Las Vegas, NV, February 22-24, 1995.

2. Richards, J.B., S.B. Brown, F.P. Milanovich, B.G. Healy, S. Chadha, and D.R. Walt, Production and Preliminary Testing of Multianalyte Imaging Sensor Arrays, UCRL-ID-119706, Lawrence Livermore National Laboratory, Livermore, CA, November 1994.

PORTABLE ACOUSTIC WAVE SENSOR SYSTEMS

DESCRIPTION

The Portable Acoustic Wave Sensor (PAWS) system is designed to provide continuous, real-time monitoring of sites for levels of chlorinated hydrocarbons and other volatile organic compounds (VOCs). Prototypes have been developed for both above-ground and down-hole applications. Down-hole systems are being used with on-site monitoring wells. Present systems monitor vapor concentrations in air or from soil samples, while future systems will be configured to monitor groundwater.

The PAWS systems are built around surface acoustic wave (SAW) devices coated with visco-elastic polymers. Two independent responses of the SAW sensor (wave velocity and attenuation) are measured to provide information about the chemical species absorbed by the coating. The changes in the wave velocity and attenuation occur because the film coating the sensor softens and becomes heavier when it absorbs the contaminant. Sensing is rapid and reversible, and coatings can be optimized for particular chemical selectivity and sensitivity. The complete PAWS system consists of the following: (1) two SAW devices (a sensor and a reference); (2) RF oscillator electronics to drive the devices; (3) digital interface/communications electronics; (4) gas-handling hardware to sample the environment; and (5) a notebook computer to control the hardware and display responses in real-time. For down-hole applications, a portable tripod, a winch, and a braided cable are used to lower the sensor system into the well, while packers above and below the sensing section are used to isolate a region of the monitoring well. A purge pump can be added to extract the contaminant out of the soil for analysis. Figure 6.10a shows a schematic of PAWS.

TECHNICAL PERFORMANCE

The PAWS technology has capabilities for determining both molecular species and concentrations of isolated chemicals. Current minimum detection levels range from about 1 to 10 ppm for typical VOCs in a real-time mode. By incorporating an adsorbent preconcentrator, periodic (every few minutes) analysis down to the 10 to 100 ppb range, even in the presence of high concentrations of corrosive vapors, can be achieved. The systems have a wide dynamic range and can handle concentrations to near saturation (25,000 ppm observed in field and over 100,000 ppm in laboratory tests). The calibrations are stable, for example, in the last field demonstration, calibrations before and after the test were within 1.5%, even following the large amount of instrument handling experienced during the field demonstration.

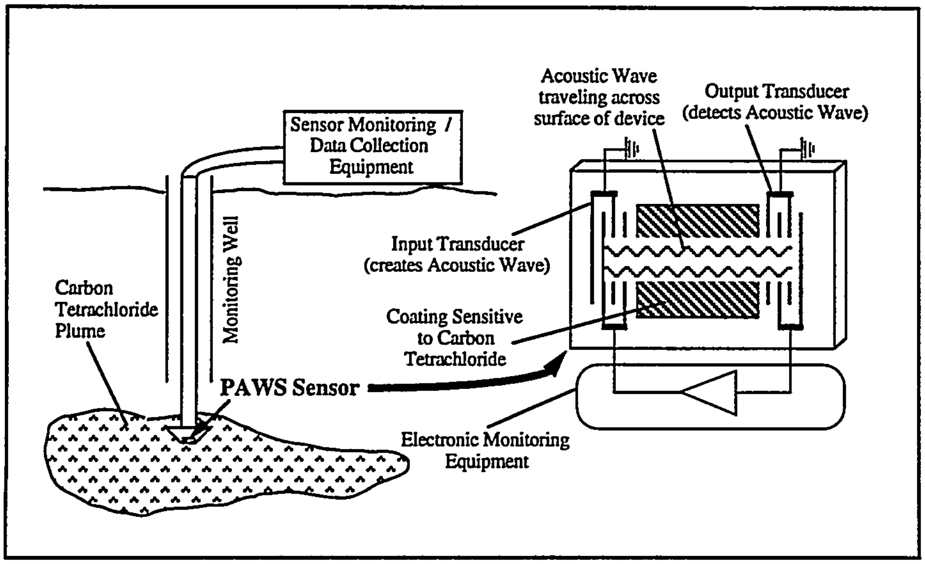


Figure 6.10a. Schematic of a Portable Acoustic Wave Sensor.

Above-Ground PAWS System. Various field demonstrations have been performed with the above-ground PAWS system. The PAWS system was used for real-time, on-line monitoring of VOC contamination in off-gas streams before any on-site treatment. The streams typically contained 100 to 1,000 ppm of one or two chlorinated hydrocarbons. The PAWS data showed good agreement (within 10%) with the on-site baseline analysis.

Another demonstration used the PAWS technology for real-time, on-line analysis of gas samples pulled to the surface during and after deployment of a cone penetrometer sampling probe. During cone penetrations, some concentration trends were observed; however, these concentrations were small compared with those for the stationary probes at the point of refusal. In general, the concentration was observed to rise with time until it reached a steady state value. For each of three nights where sampling was continued, a large drop (a factor of ten) in concentration was observed during the night followed by a rise the next morning.

Down-Hole Probe. Three demonstrations of the PAWS down-hole probes have been performed. The first used a fully integrated probe that only worked in 4 in diameter wells while the second two used a smaller, lighter-weight probe that had changeable packers for 4, 6, and 8 in diameter wells. In the latter two tests, gas samples were pumped to the surface using a long sample line and comparison analysis was performed using an above-ground PAWS system and a Brüel & Kjaer Model 1302 Photoacoustic IR system (B&K). Results are shown in Figures 6.10b and 6.10c.

Figure 6.10b shows analysis from a well with a very high concentration of carbon tetrachloride (CCl_4). Agreement between the above-ground PAWS and the commercial B&K instrument was within 2% from 100 ppm to over 20,000 ppm, demonstrating the accuracy of the PAWS system. However, differences were observed between the above-ground and down-hole systems. At high concentrations, the down-hole readings were higher (by about 20%), while at low concentrations in subsequent wells, the above-ground measurements were higher. These differences result from perturbations in the sample caused by the Teflon sampling line adsorbing and desorbing VOCs. These perturbations are not observed in tests where stainless steel tubing was used

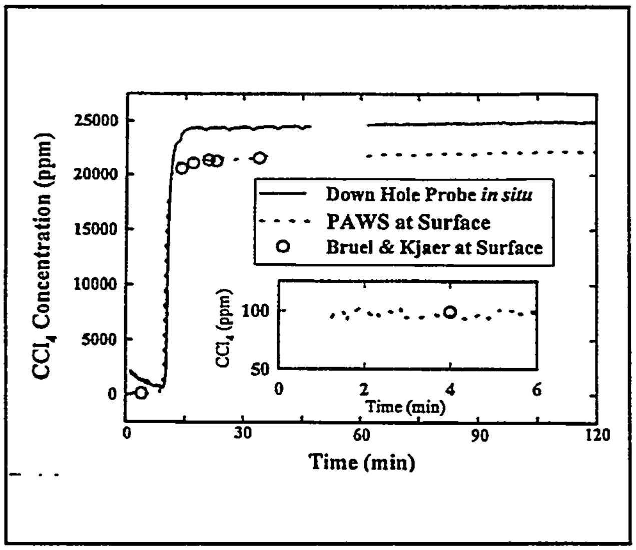


Figure 6.10b. In Situ PAWS analysis with above-ground comparison data from a separate PAWS System and a commercial IR system for CCl_4 in a high concentration vadose zone well at the DOE Hanford Site.

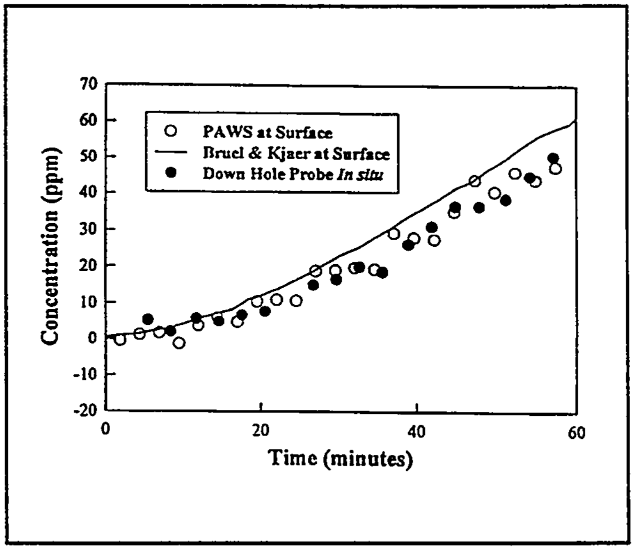


Figure 6.10c. In Situ PAWS analysis with above-ground comparison data from a separate PAWS System and a commercial IR system for CCl_4 in a low concentration vadose zone well at the DOE Hanford Site.

for the sample line; however, the tubing is expensive and difficult to deploy into the well.

Figure 6.10c shows data from a well with a low concentration of CCl_4. No detectable CCl_4 was observed by any of the instruments before turning on the purge pump. With the purge pump on, a slow rise in concentration was observed during the test. This rise was easily tracked by the PAWS system, even though it is small compared with the system's minimum detection level for CCl_4 of approximately 10 ppm. Again, good agreement was observed between the down-hole probe, the surface PAWS system, and the B&K instrument.

Cost. Expected cost of a single sensor system is $1K to $2K, while the cost for array systems for mixture analysis is expected to range from $3K to $5K. Operation of the unit requires about one hour per week, and anticipated maintenance is estimated to be less than one hour per month. Life-cycle costs will depend on use, frequency, and volume of data required.

PROJECTED PERFORMANCE

Future systems are being designed to have built-in preconcentration for trace detection, accessory modules for water and soil analysis, and an ability to provide molecular identification and quantitation of multiple VOCs in simple mixtures using arrays of SAW sensors.

APPLICABILITY

This field-monitoring system is applicable to the quantitative detection of a wide range of volatile organic compounds in soil, vapor, and water. Examples of targeted contaminants include CCl_4 and trichloroethylene (TCE).

STATUS

A collaborative industry/DOE team headed by Sawtek, Inc., will be involved in the commercialization of the PAWS system. PAWS prototypes for above-ground and in situ vadose zone for a single contaminant are available. Above-ground mixture analysis prototypes based on sensor arrays will be available in 1 to 2 years.

REGULATORY CONSIDERATIONS

The PAWS technology should provide an easy to use and low cost solution capable of meeting regulatory requirements for applications such as field screening, monitoring of remediation processes, continuous emissions monitoring, and workplace and personnel monitoring.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is potentially applicable to many industrial applications requiring real-time, on-line monitoring of exhaust stacks or workplace environments. Sensors can also be integrated into on-line process control systems to optimize process operations.

BASELINE TECHNOLOGY

Grab samples and subsequent laboratory or field analysis with a GC or IR analyzer are the baseline technologies.

INTELLECTUAL PROPERTY

Patent Ownership: DOE and Sandia National Laboratories

Patent Nos.: 5,076,094 and 5,224,972

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator

Greg Frye
Sandia National Laboratories
P.O. Box 5800, MS-1425
Albuquerque, NM 87185-1425
(505) 844-0787; (505) 844-1198 FAX

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

Participating DOE Laboratory

Pacific Northwest Laboratory
Richland, WA

REFERENCES

1. Frye, G.C., D.W. Gilbert, C. Colburn, R.W. Cernosek, and T.D. Steinfort, "Above-Ground and *In Situ* Field Screening of VOCs Using Portable Acoustic Wave Sensor (PAWS) System," to be published in: Proceedings Fourth International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Air and Waste Management, Pittsburgh, PA, 1994.

2. Cernosek, R.W. , G.C. Frye, and D.W. Gilbert, "Portable Acoustic Wave Sensor Systems for Real-Time Monitoring of Volatile Organic Compounds," Proceedings: Ideas in Science and Electronics, Inc., Albuquerque, NM, 1993, p. 44.

3. Frye, G.C., S.J. Martin, R.W. Cernosek, and K.B. Pfeifer, "Portable Acoustic Wave Sensor Systems for On-Line Monitoring of Volatile Organics," International Journal of Environmentally Conscious Manufacturing, Vol. 1, 37, 1992.

4. Frye, G.C., and S.J. Martin, "Velocity and Attenuation Effects in Acoustic Wave Chemical Sensors," Proceedings: 1993 Ultrasonics Symposium, IEEE, Piscataway, NJ, 1993, p. 379.

5. Frye, G.C. and S.J. Martin, "Utilization of Polymer Viscoelastic Properties to Enhance Acoustic Wave Sensor Performance," Proceedings: Symposium: Chemical Sensors II, Electrochemical Society, Pennington, NJ, 1993, p. 51.

6. Frye, G.C., S.J. Martin, R.W. Cernosek, K.B. Pfeifer, and J. S. Anderson, "Portable Acoustic Wave Sensor Systems," Proceedings: 1991 Ultrasonic Symposium, IEEE, Piscataway, NJ, 1991, p. 566.

7. Frye, G.C. and S.J. Martin, "On-Line Monitoring of Volatile Organic Species," Proceedings: First Annual International Workshop on Solvent Substitution, Weapons Complex Monitor Forums, Chicago, IL, 1991, p. 215.

8. Frye, G.C., R.W. Cernosek, and S.J. Martin, "Portable Acoustic Wave Sensors for Volatile Organic Compounds," Proceedings: Information Exchange Meetings on Characterization, Sensors, and Monitoring Technologies, Dallas, TX, 1992.

RCL MONITOR, A CHLORINATED ORGANIC VAPOR MONITOR

DESCRIPTION

The Transducer Research, Inc. (TRI), RCL Monitor is a handheld, battery-powered instrument for the detection and measurement of chlorinated hydrocarbon vapor in the field. The RCL Monitor contains the proprietary RCL Sensor which responds to carbon-chlorine vapors and will not respond to hydrocarbons or carbon-oxygen compounds. Because of the high selectivity for chlorinated organic compounds, this new sensor was called the RCL Sensor (where "R" refers to a generic organic molecule and "CL" refers to the presence of chlorine). The RCL Sensor exploits a high-temperature reaction between the analyte and a ceramic material which results in a transient change in electrical conductivity of the ceramic. The lower detection limit (LDL) for carbon tetrachloride is 0.2 ppmv; LDLs for other chlorinated compounds are less than 1 ppmv.

The conspicuous advantages of the RCL Monitor are:

- Handheld and completely portable
- Extremely selective for chlorinated vapors
- Highly sensitive

Accordingly it is useful as a survey instrument at sites where chlorinated or unknown solvent contamination is suspected. The sensitivity range is especially appropriate for carbon tetrachloride, one of the most difficult chlorinated solvents to measure, as well as one of the most toxic. Carbon tetrachloride has a Total Weighted Average (TWA) of 5 ppmv and an action level of 2 ppmv.

The RCL Monitor is also capable of repetitive analysis at programmed intervals, so that it can be used for workspace monitoring. About 500 data points can be logged for later transfer to a computer.

The RCL Monitor measures 6.5" W x 10.3" L x 6" H and weighs 12 pounds. It operates up to 6 hours on a fully-charged battery, and batteries can be changed in the field without loss of data. An AC adapter/charger is also supplied.

TECHNICAL PERFORMANCE

The RCL Monitor measures chlorinated hydrocarbons in 90 s, followed by a recovery period of 1 to 10 min. Although the readings will remain accurate in air temperatures from -10°C to 50°C, the interior temperature of the instrument should be kept between + 10°C and 40°C between readings. There is no humidity coefficient.

The RCL Monitor was designed to be easy to use. Control is via a touch panel and a four-line, backlighted display. The user selects HIGH or LOW concentration range, and one-shot SURVEY or repetitive MONITOR mode. An identification number is assigned to each measurement to aid in logging, although date and time are also logged. A simple procedure transfers the logged data to an external computer.

Limitations on the use of the technology are:

- The RCL Sensor is heated to about 800°C in use, and the instrument does not contain anti-explosion features. If high levels of combustible gases are possible, samples should be taken in one liter sample bags before measurement.

- The RCL Sensor should not be exposed to excessive concentrations of chlorinated hydrocarbons. Recovery can be extended for concentrations above 25 ppmv (low range) or 500 ppmv (high range).

- The material in the RCL Sensor is consumed with time. Under normal conditions, a sensor can be used for 350 to 1,000 measurements, but repeated exposures to high concentrations will disproportionately shorten its life.

- The RCL Monitor cannot distinguish among different chlorinated compounds. The specific responses among various chlorinated solvents vary over a twofold range, so the instrument must be calibrated for each analyte.

Field Tests. During development, the RCL Monitor was extensively field tested, and a large database on its capabilities exists. During these evaluations the instrument was operated during actual site activity, including well digging, routine surveys (well headspace, soil gas probe measurements, groundwater contamination levels), and other site restoration activities. On-site analysis were performed under battery power for up to 6 hours continuous operation. Because of its light weight (12 pounds), the instrument was conveniently transported for on-site analysis. The instrument was operated by both factory-trained personnel and by site personnel with less than 5 minutes of training. In addition, personnel in protective clothing, including chemical protection suits with supplied air, could easily operate the equipment.

Deployment of the RCL Monitor. Current efforts are focused on the deployment of the RCL Monitor in actual DOE operations and include:

- Routine Quarterly Monitoring (RQM) which is a routine site survey and characterization for subsurface chlorinated solvent contamination at the area around the radioactive waste management complex (RWMC) at the Idaho National Engineering Laboratory where both vapor and water analysis are required. The RCL Monitor was deployed as an auxiliary analytical tool in June 1994, and excellent agreement was obtained with the current method (gas chromatography). A significant time and cost saving is achieved with the RCL Monitor as illustrated in Table 6.11.

- Continuous monitoring of the a Soil Vapor Extraction System (VES) to assure compliance

Table 6.11. Cost benefit analysis for deploying the RCL MONITOR as the baseline analytical tool for vapor analysis in the RQM.

Vapor Samples	Gas Chromatography			RCL Analyzer		
SINGLE TIME EXPENSE						
Capital Equipment (analyzers)			$30,000.00			$17,500.00
Capital Equipment (pumps/sample)			$1,000.00			$5,000.00
TOTAL			$31,000.00			$22,500.00
MANPOWER REQUIREMENTS	man hours per RQM	cost per RQM	cost Annual	man hours per RQM	cost per RQM	cost Annual
Labor ($62.50/hr)	80	$5,000.00	$20,000.00	25	$1,562.50	$6,250.00
EQUIPMENT COST						
Annual Cap. Equipment Main.			$2,000.00			
Supplies per RQM		$100.00	$400.00		$200.00	$800.00
Equip Prep. Cost		$500.00	$2,000.00		$100.00	$400.00
Bags		$500.00	$2,000.00			
VEHICLE EXPENSE					$250.00	$1,000.00
est. daily fee ($50/day)		$400.00	$1,600.00		$100.00	$400.00
mileage (120 miles/day)		$288.00	$1,152.00		$72.00	$288.00
TOTAL		$6,788.00	$29,152.00		$2,284.50	$9,138.00

with emission standards. The VES is part of the expedited site response within the 200W area of the Hanford site. Initial deployment into the VES began in mid-December 1994.

- Continuous monitoring for temporal characterization of subsurface fluctuations at the 200W area at the Hanford site to provide the chemical database necessary to model the fluctuations and to exploit them as a cost effective complement to ongoing cleanup operations. Initial deployment to track well venting began in November 1994.
- Chemical monitoring of the 200W area at the Hanford site to verify that vapor levels in the work zone do not exceed regulator levels and to assure a safe work place environment for workers. The RCL Monitor is being used as a supplemental tool for photoionization detectors (PIDs).

Cost. The RCL Monitor is currently priced at $8.3K complete. In regular use, an instrument would use about 12 sensors per year at $200 each, and would require 100 liters of calibration gas at approximately $200.

PROJECTED PERFORMANCE

Technical performance of the RCL Monitor may improve within two years, as lifetime and recovery time of the sensor are improved, allowing more readings to be made more frequently between sensor changes.

APPLICABILITY

The RCL Monitor is applicable to the measurement of chlorinated hydrocarbon vapor in the field.

STATUS

The RCL Monitor is manufactured by TSI, Inc., the Minnesota based owner of Transducer Research. It has not yet been released for commercial sale. Scaleup of sensor production to meet expected demands of a commercial market is still in progress.

Prototype units are available for loan to DOE and contractors (until November 1995) provided that the borrower reports experiences with the instrument and supplies performance data for the final report and evaluation of the instrument.

REGULATORY CONSIDERATIONS

The RCL Monitor is being proposed to be the primary analytical tool for the vapor portion of RQM. Formal regulatory acceptance is pending.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include use by companies and government agencies that must monitor airborne concentrations of specific chlorinated hydrocarbons e.g., solvent recyclers, waste site cleanup operators, chemical production companies, and dry cleaners).

A water sampler that uses automated air-stripping to produce a vapor-phase sample is under development at Transducer Research, Inc. A major chemical manufacturer has been using an early version of the RCL Monitor with a homemade membrane sampler to continuously measure dichloromethane in waste water for several years.

BASELINE TECHNOLOGY

The baseline technology for measuring chlorinated hydrocarbons is capillary gas chromatography, which can identify individual compounds as well as measure them to within 3% (typically). The gas chromatograph requires an initial investment of about $50K for the instrument plus supporting equipment and supplies. A lab technician must normally be committed halftime or more for operation of the instrument.

INTELLECTUAL PROPERTY

The RCL Sensor is patented by Illinois Institute of Technology, Chicago, Illinois, and licensed exclusively to Transducer Research, Inc. No patent has been applied for on the RCL Monitor.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

William Buttner
Transducer Research, Inc.
999 Chicago Avenue
Naperville, IL 60540
(708) 357-0004; (708) 357-1055 FAX

DOE Project Manager

Rodney Geisbrecht
U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507-0880
(304) 285-4658

REFERENCES

1. Energetics, Inc. and Morgantown Energy Technology Center, "Evaluation of the Cost Benefit of the Rare Earth Semiconductor Technology for Field Detection of Chlorinated Hydrocarbons" prepared through DOE Contract No. DE-AC-21-92MC29231, in press, 1993.

2. Gossett, J.M., "Measurement of Henry's Law Constants for C_1 and C_2 Chlorinated Hydrocarbons," Environmental Science Technology, 21, 1987, pp. 202-208.

Mixed Waste

Section 7.0

CONTINUOUS EMISSIONS MONITOR FOR THERMAL TREATMENT SYSTEMS

DESCRIPTION

A continuous emission monitoring system for incinerators is undergoing evaluation to be accepted for measuring incinerator emissions by the U.S. Environmental Protection Agency (EPA).

The monitor is based on Fourier Transform Infrared (FTIR) spectroscopy. When a beam of infrared light is passed through stack gases, each compound in the gas absorbs specific light energies. The light absorption is detected and the instrument calculates which compounds are present. FTIR has the potential to detect and measure hundreds of chemical compounds at one time and is the only available technology that can continuously monitor many organic air toxics.

The instrumentation is relatively straightforward. The spectrometer contains an emission source, focusing optics, an interferometer, and a detector. The sample is contained in a heated long-path cell. Path lengths of 5-10 m are commonly used. These cells have a volume of approximately 2 L. A slip-stream of stack gas enters the cell at a rate of 1 L/min. Data collection takes less than one minute.

TECHNICAL PERFORMANCE

Laboratory Tests. The prototype FTIR spectrometer was tested on a laboratory incinerator constructed at Argonne National Laboratory (ANL). The burn conditions can be completely controlled by the operator who can set incinerator temperature, feed flow rate, air ratio, and supplementary feed flow rate. The objective of the test was to develop a system suitable for use in the field. In the laboratory tests the instrument gave readouts every six minutes and detected up to 10 pollutants at the parts per million level.

Field Tests. The prototype FTIR system was field-tested at the Toxic Substances Control Act (TSCA) incinerator at K-25 in Oak Ridge, Tennessee, in the Fall of 1993. The field test followed a standard operating procedure (SOP) developed for the test that was based on a proposed EPA Protocol for applying FTIR in emission testing. Ethylene was used as the calibration transfer standard (CTS) to ensure that spectral performance of the FTIR spectrometer in the field was consistent with that in the laboratory. Spike tests were regularly conducted with a known concentration of ethylene and a mixture of compounds to check the accuracy of the monitoring system. Sulfur hexafluoride was used as the internal standard. A nitrogen blank was proposed to obtain background spectra at an experimentally determined interval of four hours.

All measurements were made using a Mattson 7020 Infrared Spectrometer that contains a hot-wire source and a mercury cadmium telluride (MCT) detector. The instrument was connected to a personal computer (486DX50) through a serial port. Data were collected at 0.5 cm^{-1} resolution. Sixty-four scans were coadded and saved as a single interferogram file. The interferogram was Fourier-processed using a Beer-Norton medium apodization. A specially designed, heated, variable-path-length, long-path cell was interfaced to the interferometer.

The Toxic Emissions Air Monitor (TEAM) software developed for this project automatically collects data according to the quality control requirements of an EPA procedure. The software controls all switching valves, gas flows, pressures, and events automatically. The advanced data analysis software being developed provides unique analytical capabilities in addition to commercially available partial least square packages.

CTS tests were conducted before and after collecting reference spectra for the calibration training set. In the field, CTS tests were conducted every day that data were collected. The measured ethylene concentrations were always within 4% of the 121 ppm value of the CTS. The average measured concentration of ethylene was 120.0 ppm and the average percent deviation was 2%. This equivalence demonstrated that FTIR data collected during the field test was equivalent to the laboratory data. Thus, CTS data were within the acceptable limits required by the EPA protocol, and the calibration training set and the quantitative method based on the laboratory test can be used to analyze field test data.

The instrument response is measured by the signal-to-noise ratio (S/N) - the higher the S/N the more sensitive the instrument. The system was stable during the field test. The average throughput was 2.04 V and the variation was 3% of the average value. The throughput of the system did not change in seven days of continuous monitoring, indicating that the cells and mirrors were not contaminated by the flowing gas stream and the cell design is, therefore, adequate.

The matrix spike consisted of benzene, methane, chlorobenzene, trichloroethylene (TCE), toluene, and 1,1,1-trichloroethane. Except of methane, the detected concentrations of spiked compounds were close to the actual values. Concentrations for the September 1, 1993, run were excluded because the concentrations of water and carbon dioxide in the stack emission were not stable. The deviations of the detected values from the actual values were less than 25% for the remainder of the data. The methane analysis was complicated by the natural presence of methane and a high level of water (approximately 40% to 50%) in the stack gas. Table 7.1 shows the results of the matrix spike test.

Cost. The system will cost an estimated $50K.

PROJECTED PERFORMANCE

Data analysis is being enhanced with time and Fourier domain methods that mathematically, using peak width, separate components with overlapping bands. This combined approach will enhance the ability to detect substances that have overlapping absorbances and allow for the digital filtering of system noise.

Table 7.1. Results of the matrix spike test.

Analyte	Date	Time	File	Concentration (ppm) Calculated	Detected	%Error
Benzene	8/29	12:23	CH9121	14.1	16.8	19.1
	8/29	12:33	CH9122	14.7	17.5	19.0
	8/29	12:43	CH9123	15.4	17.2	11.7
	8/31	19:23	CH1171	13.0	12.6	3.1
	8/31	19:39	CH1172	13.0	12.6	3.1
TCE	8/29	12:23	CH9121	6.4	6.0	6.3
	8/29	12:33	CH9122	6.6	6.4	3.0
	8/29	12:43	CH9123	6.9	6.7	2.9
	8/31	19:23	CH1171	5.8	5.4	6.9
	8/31	19:39	CH1172	5.8	5.4	6.9
Methane	8/29	12:23	CH9121	14.5	20.2	39
	8/29	12:33	CH9122	14.5	21.7	50
	8/29	12:43	CH9123	14.4	22.2	54
	8/31	19:23	CH1171	16.8	17.5	4
	8/31	19:39	CH1172	16.8	17.3	3

APPLICABILITY

This technology is applicable to monitoring of organic and selected inorganics from incinerators, stacks and fugitive emissions.

STATUS

A Cooperative Research and Development Agreement (CRADA) with the Clean Air Engineering (CAE) and Martin Marietta Energy Systems (MMES) was established in October 1994. The CRADA, in combination with the EPA acceptance of the data validation, will make the system commercially available and facilitate public acceptance.

During FY 1995, the alpha unit will be constructed and tested under the CRADA. There will be at least two field tests of the new system, a long-term test at the K-25 TSCA incinerator and a short test at the Bureau of Mines vitrification facility at Albany, OR. Work will continue on advanced algorithms and validation of the EPA procedure.

REGULATORY CONSIDERATIONS

The benefit of the FTIR Continuous Emission Monitor is the near real-time determination of incinerator performance. On-stream analysis of the stack effluent would satisfy the requirements of the Clean Air Act Amendments of 1990.

The EPA issued a protocol for an FTIR continuous emission monitor. The protocol was adapted into a standard operating procedure that was tested at the K-25 (TSCA) incinerator. The objective is to meet all performance specifications required by the EPA so that the data will be considered compliant. The EPA is evaluating the data to verify compliance with the protocol.

ANL is also chairing the American Standard Testing Methods (ASTM) task committee to develop the FTIR continuous emission monitoring method.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is potentially applicable to more than 7,000 industrial (e.g., power plants, cement kilns, and industrial boilers) and municipal incinerators in the U.S. that burn hazardous and nonhazardous wastes.

BASELINE TECHNOLOGY

Monitoring of incinerator emissions is currently performed indirectly through the measurement of surrogates such as carbon monoxide and total hydrocarbons. Monitoring techniques currently used to characterize effluents include the volatile organic sampling train (VOST) followed by laboratory gas chromatography/mass spectroscopy (GC/MS). This method is required under current EPA procedures and provides a one-time analysis.

INTELLECTUAL PROPERTY

A patent application covering hardware and software is being prepared.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Jack Demirgian
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439-4835
(708) 252-6807; (708) 252-5655 FAX

DOE Project Manager

Al Tardiff
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7670

Industrial Partners

Clean Air Engineering

Martin Marietta Energy Systems

REFERENCES

1. Mao, Z., J.C. Demirgian, and G. Reedy, "Evaluation of a Fourier Transform Infrared Continuous Emission Monitor Field Test at a TSCA Incinerator," Proceedings of the 1994 Incineration Conference, May 1994.

2. Mao, Z., J.C. Demirgian, and E. Hwang, "On-Line Monitoring of Incinerator Emissions," Proceedings of the 1993 Incineration Conference, May 1993.

3. Mao, Z., M.J. McIntosh, and J.C. Demirgian, "On-Line Emission Monitoring of Chlorobenzene Incineration using Fourier Transform Infrared Spectroscopy," Proceedings of the 1992 Incineration Conference, Albuquerque, NM, May 1992.

FLOW-THROUGH ALPHA MONITOR

DESCRIPTION

The Flow-Through Alpha Monitor (FTAM) can monitor and measure the quantity of alpha emitting nuclides that may be present in a large volume of moving air. The FTAM is designed to quantitatively detect, in real-time, low concentrations (in the range of pCi/l) of alpha-emitting radioactive materials potentially present in an off-gas stream. The key obstacle to overcome in making this type of measurement is the short range of the alpha particles. For typical decay energies, alpha particles travel only a few centimeters in air, making their detection difficult. The FTAM detector overcomes this difficulty by using multiple, alpha-sensitive, scintillating plates spaced closely together, but covering a large volume. Figure 7.2 illustrates this approach. With this arrangement, approximately 75% of the alpha particles from radioactive decay in the active volume of the detector can reach a panel and generate a detectable light pulse. The light pulse is transmitted to a set of photomultiplier tubes by optical light guides.

A key feature of the FTAM detector is that the radioactive materials measured are not filtered, sampled, or otherwise removed from the primary gas stream for detection. The radioactive materials are detected directly when they emit an alpha particle. For most flow conditions, the entire gas stream, or a substantial fraction of the stream, can be monitored directly. The large active volume of the detector permits direct detection with high sensitivity without using concentration techniques (e.g., filtering) that require substantial collection times which limit the real-time capability of the system (without a filter, the maintenance requirements are greatly reduced). For response times of a few seconds, the detector has a sensitivity more than an order of magnitude higher than commercial systems. The detector's sensitive elements are easily cleaned and, with a modular design, can be easily replaced should they become damaged. The inherent redundancy of the multiple-plate design offers built-in fail safe operation.

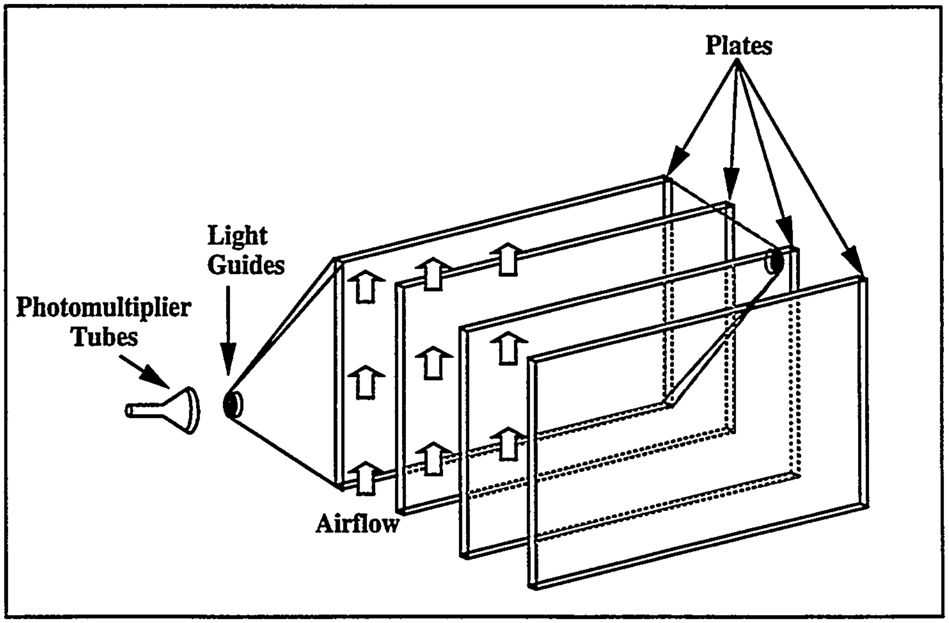


Figure 7.2. The FTAM multiple-scintillator panel approach.

TECHNICAL PERFORMANCE

Two versions of the detector were built and tested and a third is being built for field testing. The first version was a laboratory scale prototype unit designed to allow testing of the detector concept using a radioactive gas, on a scale large enough to be indicative of the design issues, but small enough to be easily fabricated, assembled and modified. This version used a stack of five scintillation plates, with a 2 cm inner-plate spacing, giving a total detector volume of 10,230 cm^3 (approximately 0.4 ft^3). A number of closed loop tests were conducted in which radon (^{220}Rn) from a thorium source was introduced into the detector box for a short time and then stopped. The radon concentration during these tests was typically less than 4 nCi/l. Air circulation continued in the box while the contained radon decayed, allowing confirmation of the radon half-life and the detector's long-term stability. During the tests the data acquisition system was typically set to integrate the detector count rate over 5 s intervals. This first series of tests resulted in three findings:

- The overall detector concept was sound and workable.
- The detector efficiency was 73%.
- The background in the detector was higher than expected based on earlier work.

The second version of the detector took the development to an intermediate step, beyond the laboratory scale prototype, but not as large as the unit to be used for the field test. The development and testing of this detector was focused on improving detection sensitivity by increasing the size of the detector and decreasing the background. In addition, engineering issues such as airflow were addressed. Table 7.2 compares the prototype, second generation, and field test systems.

As a result of adding a combination of passive and active shielding, the second generation systems showed a 37-fold reduction in the detector background. The passive shielding consists of a layer of steel and a layer of lead, which together reduce the background by a factor of 3. The balance of the reduction is attributed to the active shielding.

The second generation detector system was configured to monitor ambient levels of naturally occurring radon in room air pulled through the detector in a single pass. In a second set of tests, short bursts of ^{220}Rn injected into the single pass airstream just ahead of the detector were detected. Again, the data acquisition system was set to integrate the detector count rate over 5 s intervals. The system demonstrated real-time response to airborne activity in the tens of pCi/l range.

PROJECTED PERFORMANCE

Although designed for monitoring alpha radiation, experiments are being conducted to extend the detector into beta and gamma monitoring applications. While the ability of the detector to distinguish between alpha and some beta emitters may be poor, the detector should be able to provide alarming on total alpha and beta radiation. This "total radiation monitoring" feature is an attractive possibility, providing system operators comprehensive radiation alarming in a single device.

APPLICABILITY

The FTAM technology is being developed for on-line, real-time monitoring of off-gas stacks for low-levels of airborne alpha activity. Additional applications include monitoring gas/ventilation systems such as those on high-level radioactive waste storage tanks or other storage areas, and the monitoring of ventilation systems in buildings with combined labs and offices. FTAM offers the ability to monitor, in real-time, the very large (hundreds of

Table 7.2. Comparison of detector versions.

Detector:	Prototype	Second Generation	Field Test
Status:	Built 1993	Built 1994	In Design
Number of Plates:	5	10	16
Detector Volume (liters):	10.2	16.7	29.3
Background (cpm/cm^2):	2.6	0.07	<0.07
Guard Plates:	No	Yes (2)	Yes (2)

thousands of cubic feet per minute) volumes of air, needed to perform credible monitoring during large-scale site remediation and decommissioning.

STATUS

A full-scale prototype is being designed and will be tested at the STAR Center in Idaho. Testing will begin in July 1995 and will involve three phases. The first phase will be a functional test to verify the detector background and alpha detection performance under nominal conditions. The second phase will consist of a series of challenges such as temperature and humidity excursions. During this phase, one or more plates designed to fail at certain temperatures will be included to test the fail-safe operability. The final phase will consist of long-term exposure of the detector to the off-gas environment for life-cycle testing.

REGULATORY CONSIDERATIONS

This technology does not require any permits and will not impact the environment.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include some segments of the radon-monitoring market, including large facilities or a trailer-mounted mobile monitoring service. Another application in this general category is the monitoring of mines and mine shafts. Given the dynamic nature of mining operations, a single sampling-type monitoring system is insufficient. The FTAM could be used in the mine ventilation system; thus, monitoring much more effectively the worker's exposure. As a real-time monitor, this detector could be very effective in quickly shutting down dangerous operations (those that result in a high airborne alpha exposure).

BASELINE TECHNOLOGY

The baseline technology for alpha monitoring consists of extracting a sample of the gas being monitored and passing it through a filter placed close to a detector sensitive to alpha decay radiation. Particles bearing alpha emitting radionuclides are entrained on the filter and subsequent alpha decays are measured by the detection system. This approach has severe limitations in real-time applications. In addition, the small sample of gas extracted is assumed to be "representative" of the remainder of the stack. Sampling a small fraction of the total flow in the stack limits the useful sensitivity of the instrument.

INTELLECTUAL PROPERTY

Contact the prinicpal investigator for intellectual property information.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Russell Gritzo
Los Alamos National Laboratory
P.O. Box 1663, MS/J514
Los Alamos, NM 874545
(505) 667-0481; (505) 665-4955 FAX

Alternate Contact

Cheryl Royer
Los Alamos National Laboratory
P.O. Box 1663, MS/J514
Los Alamos, NM 874545
(505) 665-2154; (505) 665-4955 FAX

DOE Program Manager

Paul Hart

U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7456

Industrial Partner

EG&G Nuclear Instruments

REFERENCES

1. Gritzo, R., J. Wouters, and M. Fowler, An Innovative, Real-Time Monitor for Airborne Emissions, LA-UR-95-277, January 1995.

2. Gritzo, R.E., M.M. Fowler, and J.M. Wouters, Real-Time Monitoring of Alpha Emissions, Fiscal Year 1994 Final Report, LA-UR-94-4316, September 1994.

3. Gritzo, R., M. Fowler, and J. Wouters, "The Development of an Innovative, Real-Time Monitor for Airborne Alpha Emissions," Proceedings of the 1994 International Incineration Conference, Houston, TX, May 9-13, 1994.

LASER SPARK SPECTROSCOPY FOR CONTINUOUS METAL EMISSIONS MONITORING

DESCRIPTION

A new, efficient system for continuously monitoring the emissions of metals in hazardous waste treatment facilities is being developed. It is based on an advanced optical technique called laser spark spectroscopy (LASS), which has been used in the laboratory to determine the composition of coal particles. Figure 7.3 is a schematic of the LASS technique measuring atomic species.

In the LASS technique, a pulsed laser is used to rapidly heat either a single particle or an ensemble of particles, producing a plasma (or laser "spark") that contains excited-state ions. As the plasma cools, the excited-state species relax and emit optical energy at frequencies characteristic of the emitting elements. Spectrally resolved measurements of this emission can be used to identify and quantify the elements that are present. In addition, the technology simultaneously measures metals both in the vapor phase and in embedded aerosols, the latter of which account for most of the metals emitted from hazardous waste treatment processes.

TECHNICAL PERFORMANCE

A prototype portable continuous metal emissions monitor based on laser spark spectroscopy was designed and fabricated. The prototype and a data-acquisition system were demonstrated and evaluated in laboratory experiments. Experimental results of laboratory tests showed that the LASS technique can be used to measure the eleven metals regulated under the Clean Air Act Amendments of 1990. Measured detectability limits for these metals are shown in Table 7.3a. The first field test of a rugged prototype was conducted in cooperation with the joule-melter vitrification project at Clemson and Savannah River. Initial results from the field test follow.

Field Tests. The prototype fieldable metal-emissions monitor consists of: (1) an optical probe, which contains a pulsed Nd:YAG laser plus focusing and collection optics, (2) two rugged instrumentation racks that contain a spectrometer, detector, control instrumentation, and power supplies, and (3) a personal computer used for data acquisition and control.

In the field tests, emissions were measured in the effluent stream directly downstream from the joule melter as a steady state flow of surrogate waste-water-treatment sludge was introduced into the melter. Two mixtures were used as input

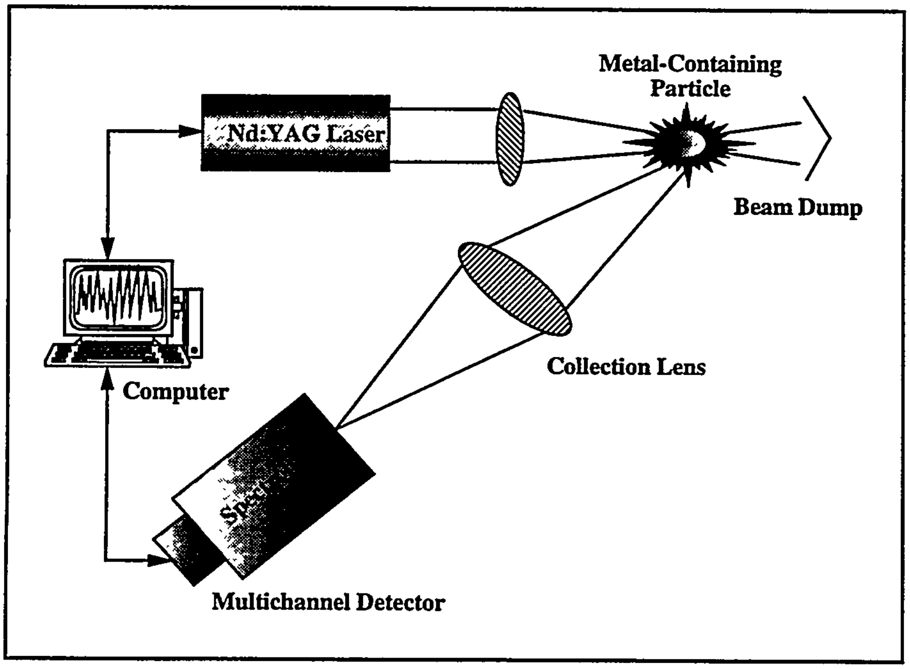


Figure 7.3. Schematic of the LASS measuring atomic species.

Table 7.3a. Minimum detectable concentrations of the Clean Air Act metals (as of April 1994).

Element	Minimum Detectability (µg/scm)
Beryllium	< 0.1
Manganese	0.25
Chromium	1
Cadmium	2
Cobalt	2
Arsenic	15
Mercury	15
Antimony	35
Nickel	40
Selenium	160
Lead	250

waste feeds. The first (base) waste feed contained metals expected from a silicate based mixture, such as calcium, aluminum, and silicon. The second mixture consisted of aliquots of the base input spiked with cadmium (Cd), lead (Pb), and manganese (Mn) salts so that the levels of Cd, Pb, and Mn in the waste ranged from 0.05 to 1.0% (wet). Iron was also added, in a few cases, to examine the severity of spectral interference from iron.

For experiments performed when the unspiked waste feed was running continuously, the metal emission monitor detected stack emissions of materials contained in the glass melt, including calcium, boron, and silicon. The response to these materials was very strong. When the spiked feed was introduced, Cd, Pb, and Mn were detected in the stack emissions at levels from 4 to 2,000 µg/scm. Signal-to-noise ratios were sufficient to detect cadmium and manganese at concentrations as low as 1 to 4 µg/scm.

The steady-state metal emissions were influenced by the rate at which the glass melt was stirred (higher stirring speeds appeared to result in lower metal emissions). In addition, inferred concentrations of Pb, Cd, and Mn in the effluent were not in the same proportions as the corresponding concentrations in the spiked feed, indicating that the fraction of the spiked feed that is emitted may be different for different metals. A greater fraction of the Pb and Cd in the spiked feed is emitted than is observed for Mn.

The interference of the iron spectrum with measurements of plasma emission from the regulated metals was not as severe as anticipated. The spectral features from the regulated metals could be measured in the presence of the relatively well isolated iron emission lines even when the iron concentration in the spiked feed was increased by a factor of 25 over its usual value.

The field test demonstrated that the prototype was easy to transport and setup. It took two days to install the probe, including uncrating the equipment, checking for damage, making electrical connections, performing minor realignment of the optical probe, and performing initial readiness tests. For comparison, it took two hours to uncrate the system and establish operations upon returning to Sandia National Laboratories (SNL), where electrical and water connections were already well defined.

Cost. Table 7.3b shows the approximate cost for the field prototype. An instrument manufacturer will optimize the cost, performance, and reliability.

Table 7.3b. Field prototype costs.

Component	Cost ($K)
Laser	35
Optics	10
Detector	40
Spectrometer	10
Computer	10
Packaging	20
Calibration Unit	15
Environmental Control	5
Total	145

PROJECTED PERFORMANCE

Continuing efforts on the development of a continuous emissions monitor for metals are directed toward two areas: (1) development of the integrated software and hardware necessary to determine metal concentrations in real-time and to control a process based on these measurements; and (2) hardware improvements to permit long-term automated operation in hostile environments.

In addition, SNL is pursuing ways to further reduce the minimum detectable concentrations by improving the signal-go-noise ratio for a given metal concentration. The signal level may be increased by increasing the laser pulse energy (increasing the size of the plasma cloud) or by improving the optical efficiency of the detection system. Noise can be reduced by eliminating systematic contributions to the apparent "noise" and by averaging a greater number of laser pulses.

APPLICABILITY

The LASS technique is applicable to the continuous monitoring of metal emissions from off gas thermal treatment units.

STATUS

On August 1994, the prototype was demonstrated at a DOE joule melter at Clemson University.

During FY 1995 several issues important to instrument commercialization will be addressed as follows:

- Calibration - in situ versus off-line and application- specific effects (phase, matrix, etc.).
- Practical issues for real applications - large-scale stacks, ruggedness/robustness, and environmental isolation.
- Collaboration with the U.S. Environmental Protection Agency (EPA) - Savannah River Continuous Emission Monitoring demonstration project at EPA Incineration Research Facility.

REGULATORY CONSIDERATIONS

No environmental impacts are anticipated from the use of this technology. In addition, the technology does not require regulatory permits for most applications including: (1) providing information for process control, system optimization, or (2) for engineering design. However, certification by regulators using the technology to assure environmental compliance of a system that is being monitored, may be required. Regulatory agencies are aware of the technology, and are interested in its capabilities as noted in the Status section of this profile.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is potentially applicable to industrial situations such as gaseous effluents monitoring, perimeter monitoring, and stack gas analysis where it is important to be able to identify and analyze small amounts of impurities. Munition deactivation furnaces, fossil power plants, industrial furnaces and boilers, and industrial processes, such as electroplating may potentially that may be monitored in the future by LASS.

BASELINE TECHNOLOGY

Current effluent measurement techniques are based on extractive samples followed by chemical analyses. In addition to being expensive and subject to human error, these methods provide no real-time data for operational feedback and turnaround times range from days to weeks.

INTELLECTUAL PROPERTY

A patent application has been filed for the laser-spark emissions monitor and some aspects of its design.

Licensing of the technology is possible and encouraged. Contact C.V. Subramanian, Licensing Manager, Sandia-California Technology Transfer Center, (510) 294-2311.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Bill Flower
Sandia National Laboratories
P.O. Box 969
MS 9103
Livermore, CA 94551-0969
(510) 294-2046; (510) 294-1377 FAX

DOE Program Manager
Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

Industrial Partner

ADA Technologies, Inc.

REFERENCES

1. Peng, L.W., W.L. Flower, K.R. Hencken, H.A. Johnsen, R.F. Renzi, and N.B. French, "A Laser-Based Technique for Continuously Monitoring Metal Emissions from Thermal Waste Treatment Units," prepared by Sandia National Laboratories, Livermore, CA, presented at the 1994 FACSS Symposium, St. Louis, MO, October 1994.

2. Flower, W.L., L.W. Peng, N.B. French, H.A. Johnsen, and D.K. Ottensen, "A Laser-Based Technique for Continuously Monitoring Metal Emissions from Thermal Treatment Units," 1994 International Incineration Conference, Houston, TX, May 1994.

3. Flower, W.L., L.W. Peng, M.P. Bonin, H.A. Johnsen, R.F. Renzi, D.K. Ottensen, L.V. Westbrook, and N.B. French, "A Technique to Continuously Monitor Metal Aerosol Emissions from Incinerators and Industrial Process Vents," 1993 International Incineration Conference, Knoxville, TN, May 1993.

4. Flower, W.L., L.W. Peng, M.P. Bonin, H.A. Johnsen, R.F. Renzi, D.K. Ottensen, L.V. Westbrook, and N.B. French, "A Laser-Based Technique to Continuously Monitor Metal Aerosol Emissions," EPRI/EPA Workshop on Trace Elements Transformations in Coal-Fired Power Systems, Scottsdale, AZ, April 1993.

TRANSIENT INFRARED SPECTROSCOPY

DESCRIPTION

Polyethylene encapsulation of low-level wastes is a promising waste immobilization technology being developed at the DOE Brookhaven National Laboratory, Rocky Flats Plant, and Hanford. In the encapsulation process, low-level radioactive salt waste is mixed with polyethylene pellets, heated, and extruded as a molten stream. Upon cooling, the mixture solidifies to form a stable waste form that is resilient to biodegradation and leaching. The salt to polymer ration is a critical parameter in the encapsulation process. An infrared-spectroscopy-based technique has been developed to monitor the encapsulation process and to provide quantitative information about the salt to polymer ratio. The ability to monitor the waste encapsulation process in real-time will provide the operators a means to guide the process so as to produce the most efficient, certifiable waste form possible.

Transient Infrared Spectroscopy (TIRS) is a mid-infrared-based technique that has been developed to obtain spectra of moving solids and viscous liquids. Figure 7.4 illustrates how the TIRS monitor operates. TIRS spectra are obtained from the generation of a thin, short lived temperature differential that is introduced by means of either a hot or cold jet of gas. When a hot jet is used, an emission spectrum is obtained from the thin, heated surface layer. This technique is known as transient infrared emission spectroscopy (TIRES). When a cold jet is used, the blackbody-like thermal emission from the bulk of the sample is selectively absorbed as it passes through the thin, cooled surface layer. The result is a transmission spectrum convoluted with the observed thermal spectroscopy. This method is known as transient infrared transmission spectroscopy (TIRTS). TIRS is ideally suited for on-line analysis because it is a single-ended technique that requires no sample preparation.

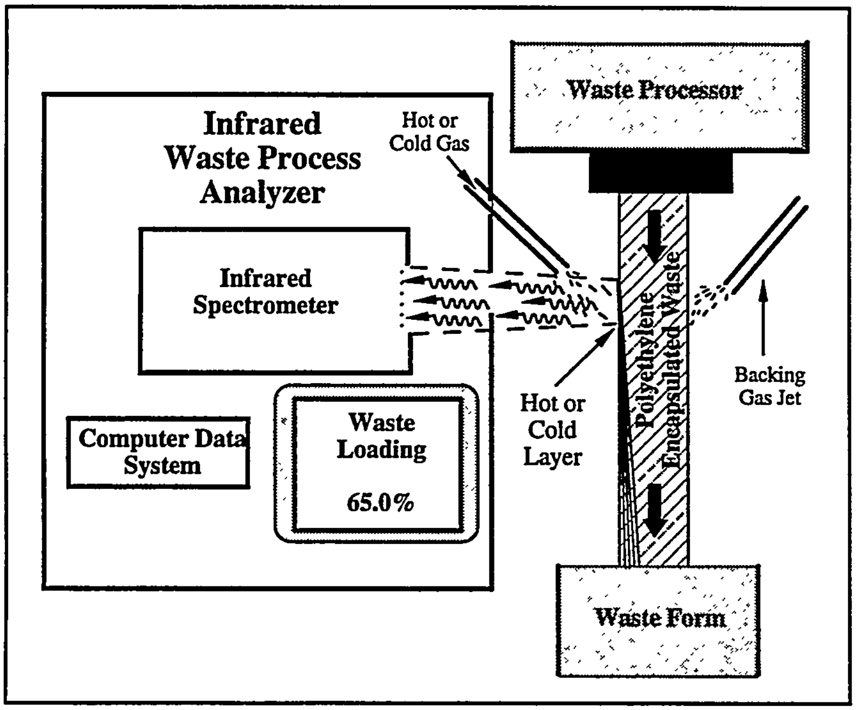


Figure 7.4. Schematic diagram of the Transient Infrared Analyzer monitoring the encapsulation process.

TECHNICAL PERFORMANCE

Laboratory Experiments. A bench-scale extruder with a 32 mm diameter screw was used as the encapsulating mixer. Two volumetric feeders were calibrated to deliver precise quantities of polyethylene and sodium nitrate. Sodium nitrate was used as the surrogate for the actual waste. Simulated waste streams were produced with nitrate loadings ranging from 0 to 67% by weight.

A Bomem model MB100 Fourier-transform infrared spectrometer equipped with an external focusing mirror and a wide-band liquid nitrogen cooled MCT detector was used to collect the spectral data. The spectrometer was operated with a mirror velocity of 0.75 cm/s and 8 cm^{-1} resolution. All spectra represent 100 coadded scans with an acquisition time of approximately 80 s. The hot jet of gas used for TIRES was produced by passing nitrogen through an electrically heated hot air gun controlled with a variable transformer. The cold jet of gas used for TIRTS was produced by passing helium through a copper coil immersed in liquid nitrogen. The jets were positioned approximately 3 cm downstream from the exit of the encapsulating mixer. This position was within the field of view of the spectrometer. A second jet was positioned directly behind the molten stream at the same level as the front jet. The function of this second jet was to compensate for the front jet's pressure on the stream and to help hold the stream in place. The production-scale process will have a stream that is much larger; therefore, the second jet will not be necessary.

Both TIRTS and TIRES data correlated well with the sodium nitrate concentration in the polymer melt stream. The TIRTS data had a root-mean-square error of 3.5% by weight while the TIRES data had a root-mean-square error of 5.4%. This data contributed to the proof-of-principle test.

A laboratory-scale demonstration at the Rocky Flats plant in May 1994 and a pilot-scale demonstration at Brookhaven in September 1994 on sodium nitrate waste surrogate was successful. The sodium nitrate loading in the molten process streams was measured to an accuracy of 0.7% by weight.

Cost. The TIRS analyzer instrument costs approximately $80K installed on a polyethylene encapsulation processing line.

PROJECTED PERFORMANCE

The monitoring system is being made more robust, so that it remains accurate when processing conditions change.

APPLICABILITY

The TIRS is a technique that can capture the real-time, mid-infrared spectra of moving, optically thick solids and viscous liquids. Data from the monitor can be used to guide processing, minimize waste volume, and certify the composition of the final waste form.

STATUS

TIRS was demonstrated at both Brookhaven and Rocky Flats. The principal component in a TIRS monitor is an infrared spectrometer. The project staff can provide TIRS systems built from commercial spectrometers to user sites. Iowa State University has patented TIRS and it is available for licensing.

More on-site demonstrations, including those involving low-level salt waste, are planned for FY 1995, as are tests on applying the monitor to low-level wastes other than salts.

REGULATORY CONSIDERATIONS

TIRS does not require any special permits.

POTENTIAL COMMERCIAL APPLICATIONS

TIRS can be used to monitor both production and feedstock streams at commercial waste processing facilities. TIRS monitors were demonstrated on the process and pilot lines of several manufacturers. TIRS was demonstrated in the laboratory for a wide range of solid and viscous liquid process stream properties, including chemical composition, cure level of paints and thermoset plastics, and oxidation level and mineral content of coal.

BASELINE TECHNOLOGY

There is no baseline technology with which to compare the TIRS technology. TIRS is the only technology available that can provide on-line, real-time monitoring of the molten process waste stream composition.

INTELLECTUAL PROPERTY

Iowa State University holds the patent on the TIRS technology.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

John McClelland
Ames Laboratory
B27 Spedding Hall
Iowa State University
Ames, IA 50011-3020
(515) 294-7948; (515) 294-3226 FAX

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

REFERENCES

1. Wright, S.L., R.W. Jones, J.F. McClelland, and P. Kalb, "Preliminary Tests of an Infrared Process Monitor for Polyethylene Encapsulation of Radioactive Waste," Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes, ASTM STP 1240, T. Michael Gilliam and Carlton C. Wiles, Eds., American Society for Testing and Materials, Philadelphia, 1994.

2. Jones, R.W., and J.F. McClelland, "On-Line Analysis of Solids and Viscous Liquids by Transient Infrared Spectroscopy," Process Control Qual., 4, 1993, pp. 253-260.

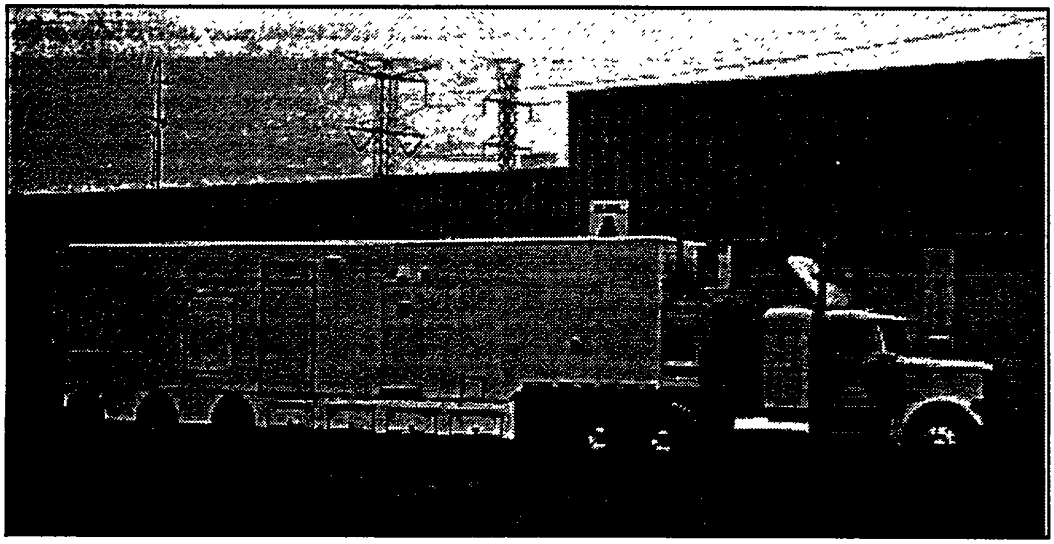
3. Jones, R.W., S. Ochiai, and J.F. McClelland, "On-Site Analyses for Complex Systems," Proceedings of the Information Exchange Meeting on Characterization, Sensors, and Monitoring Technologies, U.S. DOE Environmental Restoration and Waste Management Technology Development Program, Conference 920791, Dallas, TX, July 15-16, 1992.

WASTE INSPECTION TOMOGRAPHY

DESCRIPTION

The mobile Waste Inspection Tomography (WIT) system is designed for nondestructive evaluation (NDE) and nondestructive assay (NDA) of nuclear waste in drums up to 110 gal in volume and weighing up to 1,600 lbs each. WIT is a self sufficient 48 ft long mobile semitrailer, 13.5 ft tall, 8 ft wide, and weighs less than 100,000 lbs. The WIT trailer has an HVAC and an 80 kW generator that can be used when electrical power is not available (Figure 7.5a). WIT includes three noninvasive detection systems and six inspection methods using both x-ray and gamma-ray imaging approaches. The six inspection methods include:

- 2 MeV x-ray digital radiography (DR)
- 2 MeV x-ray transmission computer tomography (CT)
- Anger camera gamma-ray imaging
- Single photon gamma-ray emission CT (SPECT)
- Nuclear gamma-ray spectroscopy
- Active and passive gamma-ray CT (A&PCT) using a ^{166}Ho active source.



7.5a. Photograph of the WIT trailer.

The three detection systems include:

- An 896 channel array of 18-bit dynamic range solid-state, high-energy x-ray detectors. These are used for DR and CT with a 2 MeV x-ray source.
- Two Anger cameras, each with 55 photomultiplier tubes (PMTs) and a sodium iodide crystal with an active area of 14" x 17". These are used for area gamma-ray imaging for rapid location of gamma emission(s) within a drum.
- A single, high-efficiency, high-purity germanium detector (HPGe), used for both gamma-ray spectroscopy and A&PCT. The active source is 1.25 mCi of ^{166}Ho with a 25 mm x 25 mm aperture.

Data from the multiple methods of the WIT system can be fused into 2- and 3-D imaging formats for visualization of any gamma-ray source(s) within the waste drum. With gamma-ray spectroscopy and A&PCT, WIT can identify the gamma-ray emitting isotope(s) and measure external radioactivity. A&PCT enables the generation of energy-specific gamma-ray attenuation maps, and through their application, attenuation corrected determinations of the actual activities of gamma-ray sources within the waste.

WIT can also be used for quantitative analysis of drum content, including the measure of volumes of similar density materials (e.g., free liquids,), dimensional measurements (e.g., drum wall thickness), densities (e.g., specific gravity of heavy metals).

The WIT trailer is designed for the side loading and unloading of waste drums through two automated radiation-shielded doors (one on each side of the trailer). Site supplied forklifts or robotic automated handling system can be used for drum loading and unloading.

One drum at a time can be inspected. The six methods are applied sequentially. The throughput of each method is typically four drums per hour. The physics of the drum and the inspection protocol determine the throughput. As an example, the fastest throughput is for lightweight drums with high activity. The lighter the weight, the faster the NDE throughput.

Digital Radiography (DR). The 2 MeV x-ray source and a linear array of solid-state x-ray detectors is used for DR. DR produces a projection image of an entire drum with a 1024 x 1024 pixel image, where each pixel represents about 1 mm x 1 mm of the drum. The DR technique requires the drum to elevate past the stationary linear array of x-ray detectors with a single pass, as in an airport baggage inspection system. The resulting full drum image is analogous to a chest x-ray.

The WIT system has a true 18-bit dynamic range detector system, allowing for wide contrast imaging of a full drum in a single data set. Consequently, lightweight combustibles placed on top of a full 24" diameter of cement can be viewed in the same image data set with the cement through data windowing and level control for optimum gray scale presentation of the very different materials.

Viewing free liquid levels in containers such as aerosol cans, gallon pails, or plastic bottles is possible in a freeze frame format. The drum can be rotated for different DR viewing angles (e.g., 90° to the first DR or whatever is required). The speed of a single WIT DR scan of an entire 55 gal drum of cement is approximately 60 s, and the image can be viewed immediately. Faster DR scan times are sufficient for lighter weight waste drum matrices.

Computed Tomography (CT). During a CT scan, the drum rotates through a stationary fan beam of 2 MeV x-rays in a third-generation CT data collection mode using 896 channels of 18-bit x-ray detectors. Individual CT slices can vary between 2 mm and 10 mm thick.

The WIT CT scanner has a resolution of nearly 2 mm and a dimensional measurement capability with a sensitivity of nearly 0.25 mm. The drum elevates between slices in less than 2 s for adjacent slices. WIT CT slice scan times are in 4 s increments with the fastest scan time to date, of 8 s per slice for a combustible waste drum matrix. A cement matrix requires a 28 s scan time and a glass matrix requires a 10 min scan time per slice. The slower the WIT CT scan, the better the photon statistics and image quality.

The resulting WIT CT images can be 256 x 256, 512 x 512, or 1024 x 1024, pixel CT image reconstructions. If the operator chooses to save the raw data, any of the above mentioned CT image formats can be reconstructed at a later time. CT image processing can be concurrent with CT data collection. The DR scan can be used as a planning map for locating CT slices.

WIT features for CT image processing and analysis include Multiplanar Reconstruction (MPR), Volume Rendering (VR), dimensional analysis, volume analysis, density scaling, regions-of-interest (ROI) analysis, panning, zooming, window and level control, colorization, filtering, including edge enhancement, contrast stretching, statistics, histograms, cinematic presentation, and others.

An entire 55 gal drum can be CT scanned with 88 CT slices, each 10 mm thick. For combustible waste, this takes less than 15 min. MPR of an entire drum with interpolation of all 88 CT slices can be achieved in real-time, with concurrent image processing, providing four orthogonal drum views anywhere within a drum with nearly 1 mm cubic voxels. Paging through any orthogonal CT plane in an entire 55 gal drum from any direction is possible with about 1 mm interpolated positioning.

WIT can produce a single volume-rendered view of an entire drum or any volume within a drum with a light shaded cut-away plane. A 512 x 512 pixel presentation of a volume-rendered 55 gal drum can be achieved on WIT using 88 CT slices in less than 28 s. A 256 x 256 pixel volume-rendering of the entire drum can be viewed in less than 15 s.

Anger Camera Imaging. For rapid area localization of gamma-ray emissions with a resulting 2-D image planar projection, two Anger cameras are used. Each camera has 55 PMTs and a single sodium iodide crystal with a 14" x 17" active area. Compared to medical cameras, the WIT gamma cameras have scintillators with higher quantum efficiency, higher energy collimators, and a wider energy spectrum window (100 kV to 1.3 MeV).

One gamma camera views the top of the drum, while one looks at the bottom of the drum. The drum only needs to rotate for WIT gamma emission viewing. Thus far, the two WIT cameras have demonstrated sufficient sensitivity to image 9 μCi activity of ^{133}Ba on the surface of the drum with a scan time of nearly 10 s. Also, 250 μCi of ^{133}Ba activity is in the middle of a 55 gal drum with combustibles is demonstrable with 10 s data collection time. Typically, 60 s of data collection is used for each view to assure sufficient counting statistics. Anger camera images can be colorized, fused and registered with x-ray transmission image data.

Single Photon Emission Computed Tomography (SPECT). To locate the depth of gamma-ray emissions within a drum, Anger camera views can be used to provide a gamma-ray CT slice using the SPECT technique. The inherent gamma-ray emission from the waste is the radiation source for SPECT. Sixteen Anger camera views, each from (approximately 0.4 of drum rotation, are required to provide a coarse SPECT reconstruction for emission localization within a drum slice. WIT can reconstruct a 32 x 32, 64 x 64, and 128 x 128 pixel SPECT images across a drum diameter. WIT SPECT consists of parallel beam reconstructions with offset scanning. Thus, a full 360° of drum rotation is required for WIT SPECT.

Slices are coarse, consisting of 6 mm, 12 mm, and 25 mm thick scans with similar resolution. The SPECT slices can be volume-rendered, colorized, fused, and registered with x-ray transmission image data.

Gamma-ray Spectroscopy. WIT can identify gamma-emitting isotopes within the waste using a single high purity HPGe detector and spectroscopy analysis software from EG&G called Maestro. Maestro performs peak analysis and matches peaks to a software library of nuclear isotopic spectra. The Anger cameras lack the energy resolution for isotope identification, but they do allow for rapid localization of gamma emissions. Once the emission is located, the HPGe detector has an efficiency greater than 100% (with respect to sodium iodide), an energy resolution of less than 2 kV, and a square collimated aperture of 50 mm x 50 mm. The WIT HPGe detector can be elevated to nominal drum centered height and can be translated across and past the full diameter of the drum. The drum is elevated to achieve the precise height location of the emission at the hot spot(s).

Active and Passive CT (A&PCT). External measurements of gamma-ray emissions from waste drums can be deceiving because the waste matrix may be attenuating the emission. A&PCT provide an energy-specific attenuation map of the drum by utilizing an external transmission source with a gamma-ray energy similar to that of the waste. This waste enables calculation of attenuation-corrected activities.

WIT has an active source of ^{166}Ho with an activity of 1.25 mCi. Holmium has numerous gamma-ray energy peaks between 100 kV and 1.4 MeV, which makes it an ideal choice as an ACT source. Both A&PCT are performed on WIT in a first-generation

CT geometry with a single HPGe detector. The Holium source also translates across the diameter of the drum simultaneously with the HPGe detector for ACT. For PCT, only the HPGe detector translates. For both A&PCT , the drum elevates and rotates.

Typical WIT A&PCT data consists of 16 rays and 16 views with a resulting image of 14 x 14 pixels, where each pixel represents a 50 mm x 50 mm area of the drum. Depending on the waste, WIT can have ray integration times from seconds to tens of minutes, with resulting scan times from minutes to hours per slice, based on transuranic and low-level waste activity levels. The more active the gamma-emitting waste, the faster the A&PCT scan times and throughput.

TECHNICAL PERFORMANCE

The following WIT performance data are Phase I results from the WIT Program Research and Development (PRDA) contract acquired by Bio-Imaging Research, Inc., (BIR) between March and May 1995.

Experimental Study. The WIT phantom drum used to qualify each of the six WIT inspection methods during Phase I consists of a steel 55 gal drum with three ports of entry on top of the drum for the introduction of radioactive sources. The drum has three levels of waste matrices. The upper level has combustible materials consisting of mostly cloth and paper products and a plastic bottle with free liquid; the middle is a heterogeneous matrix consisting of mostly metals of steel and aluminum and aerosol cans with free liquid; the bottom layer is cement with embedded rods and tubes of plastics and metals.

Figures 7.5b through 7.5f are recent Phase I PRDA results acquired on the WIT trailer. The radioactive check source inserted into the combustible matrix of the WIT phantom drum consisted of a two ounce bottle containing liquid with a ^{133}Ba activity level of nearly 250μCi. Figures 7.5a, b, and c are superimposed images of fused transmission and emission images, indicating the ^{133}Ba gamma emission source in 2- and 3-D space. All three images indicate the

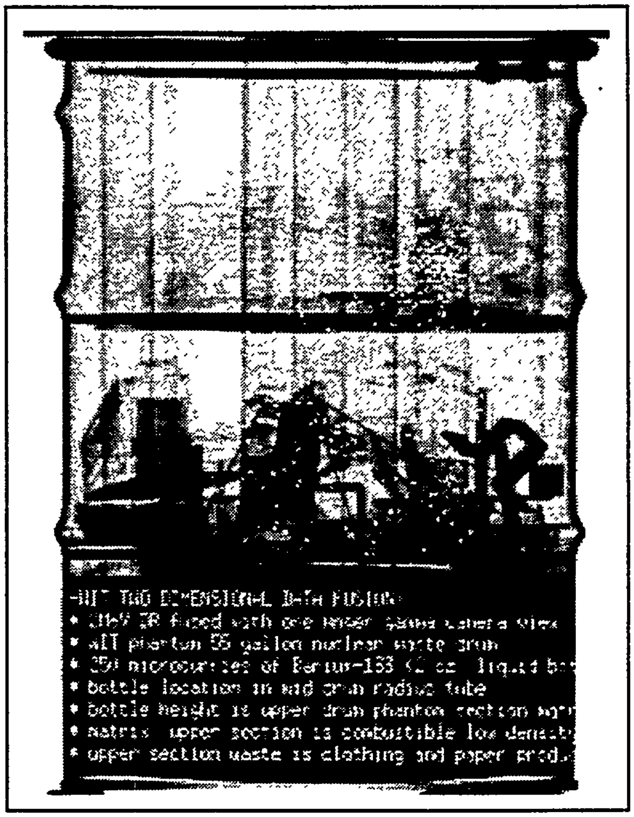


Figure 7.5b. 2 MeV DR of the WIT phantom drum fused with an Anger camera image of a ^{133}Ba gamma source located in a plastic tube in the combustible waste matrix.

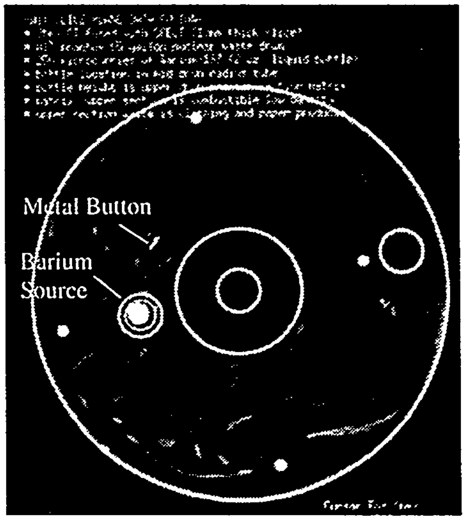


Figure 7.5c. 2 MeV x-ray CT of a 10 mm slice of the WIT phantom drum fused with a SPECT reconstruction of the ^{133}Ba source in the combustible matrix showing cloth and metal buttons.

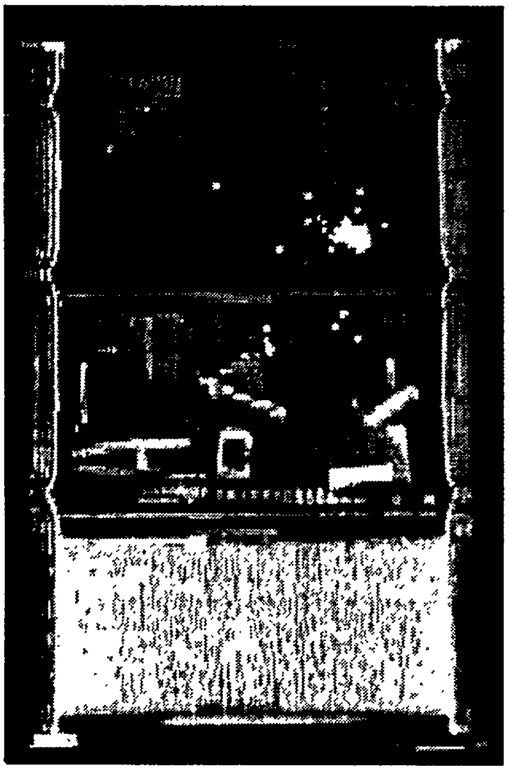


Figure 7.5d. Volume-rendered WIT phantom drum with cut-away wall showing drum content light shaded with transparent bottle with free liquid in the top layer fused to a SPECT reconstruction showing the ^{133}Ba source on the combustible matrix. The volume-rendered image was made from 88 CT slices, each 10 mm thick, with 256 x 256 image matrix. The volume rendering is a 512 x 512 pixel matrix.

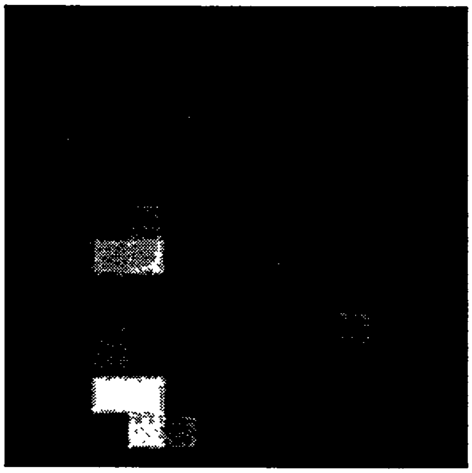


Figure 7.5e. Active CT image of the WIT phantom drum taken at the level of ^{133}Ba source using the ^{166}Ho active source. This active image is a coarse energy specific attenuation map for a gamma-ray energy similar to that of the ^{133}Ba source.

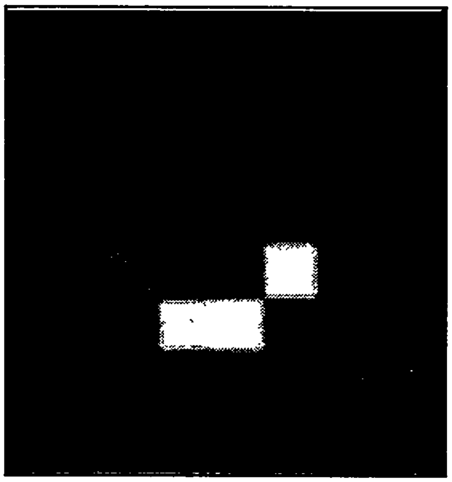


Figure 7.5f. Passive CT image of the WIT phantom drum showing the 133Ba gamma-ray emission inside the WIT phantom drum.

source of the emission relative to the waste matrix. Figure 7.5d and e are active and passive CT images of the ^{133}Ba source, respectively.

Cost. BIR plans to offer a mobile WIT service for noninvasive waste drum inspection and characterization. WIT is still in the development phase, and costs are continuously being ¡evaluated. However, projected costs range between $2M and $3M per WIT trailer. On a cost per drum basis, WIT inspections will be less than $1K per drum, with an average throughput of four drums per hour, per technique, with a cost per WIT day shift of nearly $20K. In comparison, invasive techniques may cost between $1K and $10K per drum.

PROJECTED PERFORMANCE

The nondestructive and noninvasive nature of WIT makes it a safer inspection method, as compared to invasive techniques. The four drums per hour projected throughput makes WIT compatible with other planned DOE production facilities, such as the Hanford Waste Receiving and Processing facility. The multi-method WIT approach provides both NDE and NDA characterization. The mobile capability allows WIT to be brought to the waste location, thus minimizing waste transportation. WIT eliminates the need to invest in permanent, more expensive facilities for waste drum characterization. Compared to invasive inspection techniques, WIT is projected to be more cost effective.

APPLICABILITY

WIT can be applied to a variety of wastes including combustibles, heterogeneous waste with metal components such as tools, cemented waste and other near-solid waste such as sand, earth, and sludges, compacted waste, and matrices as dense as glass logs. WIT accommodates any waste package smaller than a 110 gal drum, including waste bags, 1,5, 35, 55, 85, and 110 gal drums, drums with plastic or metal liners, and overpacks that are 110 gal or less in size or volume, and 1,600 lbs or less in weight. WIT can inspect low-level, transuranic, and mixed-waste drums. Typical DOE drums of 55 gal and weighing less than 800 lbs are ideal for the WIT system.

STATUS

The WIT system has been designed, built, and initially tested on phantom drums with check sources at the BIR facilities in Lincolnshire, Illinois. Further system integration and demonstration on actual nuclear waste drums will began in August 1995.

REGULATORY CONSIDERATIONS

Regulatory considerations for both operational safety and characterization performance are being incorporated into the design of WIT. Contact the principal investigator for additional information.

POTENTIAL COMMERCIAL APPLICATIONS

The WIT system is designed for nuclear waste inspection with commercial application, principally to DOE complex; however, it may be applicable to public utilities, processors, and other generators of nuclear waste (e.g., universities, hospitals, and private industry). Other applications include the nondestructive evaluation of potentially hazardous waste to identify the waste matrix and free liquids. A potential application for WIT CT is inspection of high value aerospace and aircraft engine castings for dimensional analysis and pattern development. The WIT mobile service is attractive to those WIT users who cannot afford a major capital investment.

BASELINE TECHNOLOGY

The baseline technologies include real-time radiography (RTR) and segmented gamma scanning (SGS). RTR provides 2-D transmission video images of waste and has a gray scale resolution of 4- to 12-bits, compared to 18-bits for WIT freeze frame DR and CT. WIT's greater dynamic range provides improved contrast and density resolution compared to that of RTR. Additionally, CT eliminates the superpositioning problems of RTR and DR with CT providing depth perception.

CT provides quantitative density and dimensional information in both 2- and 3-D space for waste matrix identification, all in a computerized digital format which is not available to RTR. RTR typically uses analog media, such as videotape. Achievable WIT media include CD-ROM, optical disks, DAT tape, magnetic hard drives, as well as videotape and hard copies.

Typically RTR in DOE applications uses 420 kV x-ray tubes for inspection of waste drums. The lower energy x-rays limit penetration capability for the larger and denser waste forms, such as drums of sludge and cement, which make up over half of the waste drums. WIT's 2 MeV source provides more rapid throughput with sufficient radiation penetration to inspect nearly all DOE drums on a mobile trailer.

WIT's Anger camera imaging provides rapid localization of gamma-ray emissions while allowing the high-efficiency and energy-sensitive nuclear spectroscopy instrumentation to be focused on the specific gamma emitting waste source(s) instead of searching a broader waste volume, as in SGS.

WIT's A&PCT provides energy-specific attenuation correction with smaller volume correction elements compared to SGS, thus providing WIT with a smaller error band for the calculation of internal gamma-ray activities from purely external measurements.

Finally, the fusion of emission and transmission images from WIT allows for the localization of the gamma-ray source(s) within the waste matrix. This is not available with the baseline technologies.

INTELLECTUAL PROPERTY

Intellectual property embodied in the software will be protected by copyright. Contact the principal investigator for additional intellectual property information.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Richard T. Bernardi
Bio-Imaging Research, Inc.
425 Barclay Boulevard
Lincolnshire, IL 60069
(708) 634-6425; FAX (708) 634-6440

DOE Project Manager
C. Edward Christy
U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507-0880
(304) 285-4469

REFERENCES

1. Waste Inspection Tomography (WIT), Technology Development Data Sheet (Brochure), Morgantown Energy Technology Center, DE-AC21-93MC30173, May 1994.
2. Waste Inspection Tomography (WIT), (Brochure), BIR, Inc.
3. Bernardi, R.T., and S.H. Kyung, "Nondestructive Evaluation and Assay of Nuclear Waste Drums with High Energy Transmission and Emission Computed Tomography," preprint from the Proceedings of the Waste Management '94 Symposia.
4. Bernardi, R.T., and R.E. Slocum, "Digital Radiography and Computed Tomography for Advanced Inspection of Solidified Nuclear Waste Containers," Review of Progress in Quantitative Nondestructive Evaluation, edited by D.O. Thomson and D.E. Chimenti, Plenum Press, New York; Vol 11, 1992, pp. 1893-1900.
5. Berardi, R.T., and H.E. Martz Jr., "X-Ray and Ultraviolet Sensors and Applications," Proceedings of the SPIE, Vol 2519, 1995.

Radioactive Contaminant Analysis

Section 8.0

AIR-QUALITY MONITORING FOR ALPHA CONTAMINATION LONG-RANGE ALPHA DETECTION

DESCRIPTION

Detectors for airborne alpha contamination are being developed based on Long-Range Alpha Detection (LRAD) technology. Using this technology, a gas/radon daughter detector is being developed.

Airflow detection of ionization caused by alpha particles is possible because an alpha particle deposits all of its energy to air in the form of ionization within a few centimeters of its source. Ionized electrons in air then quickly attach to other air molecules creating ion pairs. These ion pairs are transported to an electrode producing a current that can be measured. The integrated current measured, or the number of current pulses counted, is directly proportional to the concentration of alpha contamination in the detection volume.

The electrostatic filter is maintained at 600 V and is designed to filter out any ambient ionization that might otherwise be drawn into the sample chamber and bias the measurement.

Alpha decay rates can be measured in two distinct modes known as "single event" and "integrated current" modes. If the alpha decay rate is low enough to preclude pileup, current pulses produced by an individual alpha decay can be counted --single event measurement mode. If the alpha decay rate is too high to resolve individual current pulses, the integrated current at the ion collection electrode is measured. LRADs are unique in that the ionization produced from alpha decays in air is measured directly without the gas gain, special gases, thin windows, or other characteristic typical ionization detectors.

There are two classifications of LRAD detectors as follows:

- Electrostatic LRADs use an electric field to attract ions onto the electrode. This type of detector is used for monitoring flat surfaces such as concrete walls, floors, or for soil surface contamination measurements.

- Airflow LRADs use air currents to transport ions to the collection electrode. Detectors of this type are useful for monitoring irregular shaped or metal objects.

As illustrated in Figure 8.1a, the general design of an airflow LRAD consists of a box with a fan manifold to provide airflow and two ion grids. One grid acts as an electrostatic filter and the other acts as the ion-collection grid.

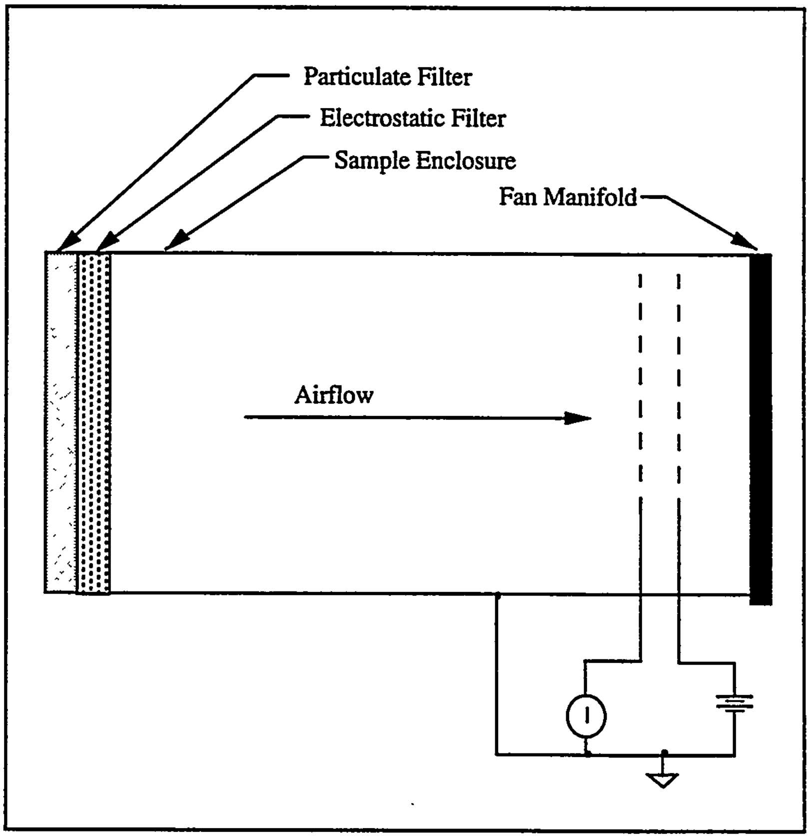


Figure 8.1a. Illustration of LRAD design.

TECHNICAL PERFORMANCE

LRAD Radon Monitor Prototypes. Several prototype detectors were tested both on the bench and in the Radon/Radon Daughter Environmental Chamber (RRDEC) operated by RUST Geotech at DOE's Grand Junction Projects Office located in Grand Junction, Colorado.

Initial RRDEC tests were conducted using two identical airflow LRADs originally designed as personnel Hand Monitors (HMs). HMs are rectangular detectors with a 23 L detection volume and a rubber iris valve on one side for inserting calibration sources or other objects (such as hands) into the detection volume. One HM was equipped with an efficient particulate filter and the second was equipped with only a light-duty furnace-type air filter.

The second set of RRDEC tests was conducted with a series of sub-elements made from 15 cm diameter tubing and originally designed as personnel Arm Monitors (AMs). The subassemblies can be attached to sample enclosures with detection volumes ranging from 2 to 20 L. Two identical AM detectors were configured with 6 L decay volume . One of the AM detectors was equipped with a high efficiency particulate air (HEPA) filter while the second had no filter. These detectors were used to investigate the speed of response to radon gas and the filtering of radon daughters attached to particles.

A Home Radon Monitor (HRM) prototype detector was also constructed to test the efficiency of electrostatic ion collection and the practicality of using current pulses from individual alpha decays to determine radon concentrations.

Linearity of Detector Response. Figure 8.1b shows detector response to radon concentrations ranging from 0.06 to 825 pCi/L. For each detector at each point, a 1-hour data set was taken after radioactive equilibrium was reached. The arithmetic means of these 1-hour data sets, minus a constant background caused by leakage currents and cosmic rays, are plotted against the mean radon concentration. The resulting plot shows that LRADs operating in an integrated current mode respond linearly with R²s of 0.999 or better, over the entire 4-decade radon concentration test range.

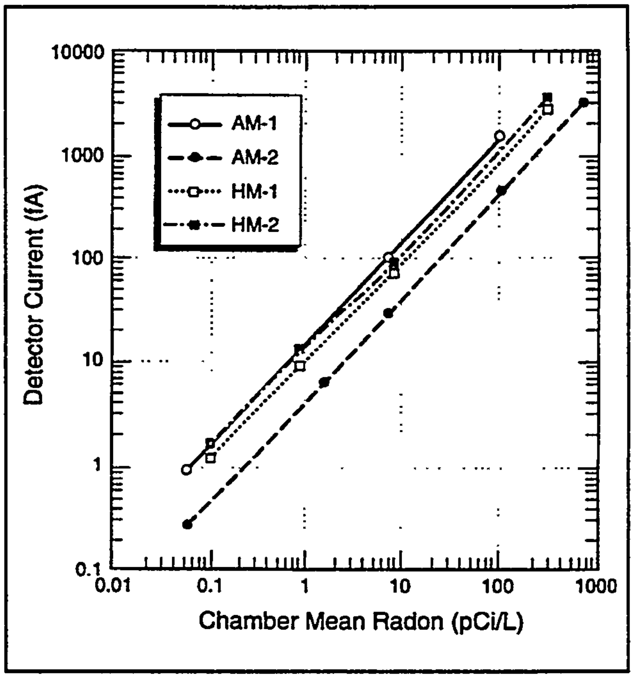


Figure 8.1b. Airflow LRAD ^{222}Rn response.

LRAD Electrometers. Measurement of small currents requires a very sensitive electrometer coupled to a detector designed and constructed to eliminate leakage currents. Initial tests were conducted using commercially available Keithley Model 617. To reduce cost, size, weight, and power requirements, several generations of LRAD-specific electrometers were developed. These electrometers are small, lightweight, battery powered, and provide temperature-compensated mV-level output signals with 0.01% full-scale resolution over jumper-selectable operating ranges from ±3 to ±300 pA. Table 8.1a lists relevant parameters for the electrometers.

Table 8.1a. LRAD-specific electrometers.

Generation	Size (cc)	Mass (g)	Battery Life	~Cost ($)
Keithley	10,000	3,600	AC	3,000
1st	300	342	8 weeks	500
2nd	200	320	2 years	300
3rd	25	16	6 years	200

Table 8.1b lists calibration coefficients and ion collection efficiencies extracted from the data plotted in Figure 8.1b. The improvements in ion efficiency of the AM detectors as compared to the HM detectors can be attributed to better airflow characteristics. Because the HM detectors have rectangular detection volumes, there are corners where the airflow forms eddy currents. Ions become trapped in these eddies and are eventually lost to the metal sides of the detector. The AM detectors have a smooth laminar airflow and, therefore, fewer ions are lost to the detector walls.

Table 8.1b. Airflow LRAD calibrations and efficiencies.

Detector	Volume (L)	Calibration (fA/pCi)	Efficiency (%)
HM-1	23	0.40	44
HM-2	23	0.50	54
AM-1	6	2.43	76
AM-2	6	0.71	77

Speed of Response. Figure 8.1c shows the speed of response of an airflow LRAD. The current output of an AM detector over a 2 min interval is shown. After 15 s, a constant amount of ^{220}Rn gas was injected into the airstream. Air flows through the detector at about 6 L/s, so the radon concentration went from near zero to approximately 80 pCi/L in about 1 s. Because the transit time for air through the detector is 1 s, each ^{220}Rn decay will be accompanied by a ^{216}Po decay (0.15-s half-life) for a total energy release of 13MeV. The AM detector responds to these changes in radon concentration in less than 5 s.

APPLICABILITY

The LRAD technology is applicable to the detection of airborne alpha contamination.

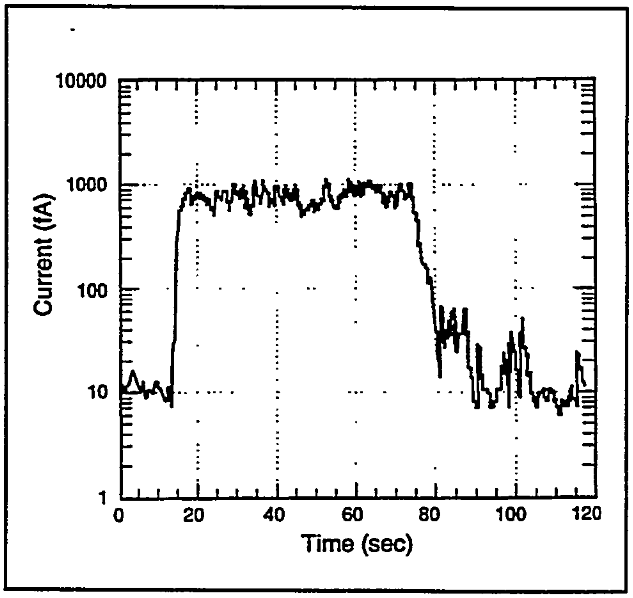


Figure 8.1c. AM speed of response to ^{220}Rn gas.

STATUS

Eberline Instruments the Los Alamos National Laboratory technology transfer partner, owns exclusive licenses to the technology and can either build detectors for users or sublicense the technology to other companies.

REGULATORY CONSIDERATIONS

The LRADs are passive, non-intrusive, and generate no waste or by-products.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is applicable to decontamination and decommissioning (D&D) of a variety of materials and equipment such as walls, concrete floors, pipes and equipment. During the D&D process, alpha contamination can become airborne. It is, therefore, important to monitor in near-real-time the alpha radiation levels present to protect workers. The LRAD technology is also applicable to the detection of radon in homes.

BASELINE TECHNOLOGY

Detection of alpha contamination in air samples is traditionally accomplished by use of continuous air monitor (CAM) detectors. CAM detectors must sample a given volume for several hours to achieve approximately 0.1 pCi/liter resolution.

INTELLECTUAL PROPERTY

A patent application for single event counting was submitted in November 1994.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Richard Bolton
Los Alamos National Laboratory
P.O. Box 1663, NIS-6/MS-J561
Los Alamos, NM 87545
(505) 667-8241; (505) 665-3657 FAX

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19910 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

REFERENCES

1. Bolton, R.D., J.P. Johnson, and G.J. Arnone, "Home Radon Monitor Modeled After the Common Smoke Detector," LA-UR-95-172, submitted to Waste Management 1995, Tucson, AZ, March 2, 1995.

2. Bolton, R.D., "Radon Monitoring Using Long-Range Alpha Detector-Based Technology," LA-UR-94-3637, submitted to Nuclear Science Symposium, Norfolk, VA, October 30 - November 4, 1994.

3. Johnson, J.P., R.D. Bolton, S.E. Garner, K.L. Benham and G.L. Langner, Jr., "LRAD Radon Test Results," LA-UR-94-186, submitted to Mid-Year Health Physics Society Meeting, Albany, NY, February 13-16, 1994.

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY FOR ANALYSIS OF MICROLITER SAMPLES AND SOLIDS

DESCRIPTION

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is already a highly sensitive and selective method for elemental and isotopic analysis. It is used widely in the nuclear industry for identification and quantification of stable elements and some radionuclides. In general, detection limits are approximately 1 ppt, accuracy and precision of several percent are possible, and as many as 70 elements can be determined in solution volumes as little as 100 µL. Despite these impressive capabilities, the absolute detection limits of ICP-MS are in need of substantial improvement. The most efficient quadrupole devices can detect about 10^6 atoms of an element in a plasma. However, the nebulizer efficiency is typically only 1%, so most of the sample merely dribbles down the drain of the spray chamber that houses the nebulizer. This is not much of a problem in most applications for stable elements, where plenty of sample solution is available. However, when radioactive samples are analyzed, the wasted solution in the nebulizer drain means secondary waste disposal (typically a mixed waste) and handling of larger sample volumes just to get enough atoms to the plasma for measurement.

For these reasons, there is a substantial need for nebulizers specially configured to handle small liquid samples of a few µL or less. This project will evaluate the analytical figures of merit of ICP-MS with a new type of sample introduction technology called monodisperse dried microparticulate injection (MDMI). A schematic diagram of MDMI is shown in Figure 8.2a. The MDMI uses a piezoelectrically-driven micropump to introduce all of a very small solution (1 µL or less) into the ICP, which improves detection limits and reduces contamination, containment, and waste disposal when analyzing radioactive solutions. The wet droplets from the micropump are all 57 ±3-µm in diameter, which is essentially monodisperse by the standards of conventional nebulizers. The droplets are then dried carefully in a laminar flow oven. The dried particles are kept in a straight line from the pump tip through the oven and into the plasma.

Because all the particles are localized along the central axis of the plasma, the sampling orifice of the ICP-MS can be positioned at just the right spot to draw in a large fraction of the ions produced. In contrast, even the best of the other nebulizers, such as the direct injection nebulizer (DIN), sprays droplets over a much wider volume of plasma, and much of the sample misses the sampling orifice. The MDMI is potentially more attractive than either the DIN or the electrothermal vaporizer for introduction of small, discrete samples into an ICP-MS device. Of course, the caveat to analysis of very small volumes is that a representative sample of the whole material must be analyzed. There are,

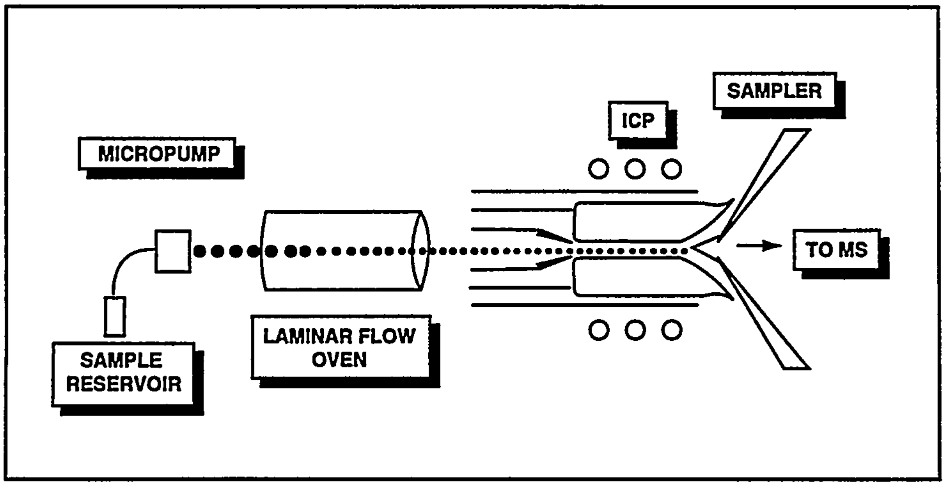


Figure 8.2a. Schematic diagram of MDMI and the ICP-MS components.

therefore, practical lower limits to the amount of solution necessary to provide valid analytical results. The MDMI can be used for sample volumes in the mL range, if desired; it is not limited to μL samples.

The MDMI will also be used to calibrate laser ablation ICP-MS for direct analysis of solids. This application will provide a general way to analyze solids accurately without calibration standards that closely match the composition of the solid, which has been a long-standing problem in analytical chemistry. Solid samples can be readily broken into small particulates with a focused laser. These particulates are then swept into an ICP, which produces atomic analyte ions for mass spectroscopic analysis. Qualitative and semi-quantitative characterization of solids is straightforward with this combined laser ablation-ICP-MS approach. Accurate quantification, however, is limited to those samples that are highly homogeneous and that closely match the composition of reference materials. Unfortunately, the production of particulates and the ablation efficiency depend on the sample matrix, so quantitative analysis of heterogeneous or unusual samples is difficult.

A second aspect of this project concerns developing a method of calibration using the MDMI for samples obtained by laser ablation. The MDMI will be used to deliver material from a standard reservoir that will be coupled with the laser ablated sample as shown in Figure 8.2b. Proper application will also include mass flow measurement of the laser ablation aerosol prior to mixing with the internal standard obtained by the peizoelectric micropump. In this way any variation in the laser power or sample matrix can be accounted for by the internal standard and mass flow measurements.

For a related discussion of standardization for the laser-ablation technique, see the technology profile titled, "Mobile Laboratory for Environmental Screening Technologies."

TECHNICAL PERFORMANCE

This is the first year of the project. The MDMI can be used for analysis of one sample per minute. It minimizes the radioactive waste that adheres to the ICP-MS device, which simplifies maintenance. Detection limits presently are approximately 1 femtogram (fg) for a variety of elements. The ruggedness of the MDMI and its susceptibility to interferences are being investigated. The device should be useful for any ICP-MS device.

Cost. As yet, a firm price for the MDMI is not available. The MDMI is on loan. A reasonable guess is $20K. Operating and maintenance costs are the same as with any other sample introduction device. An ICP-MS typically costs $180K.

PROJECTED PERFORMANCE

Because the project has just begun, information regarding projected performance is not available.

APPLICABILITY

This technology is applicable for the determination of radionuclides and stable trace elements in solutions, organic solvents, and, when combined with

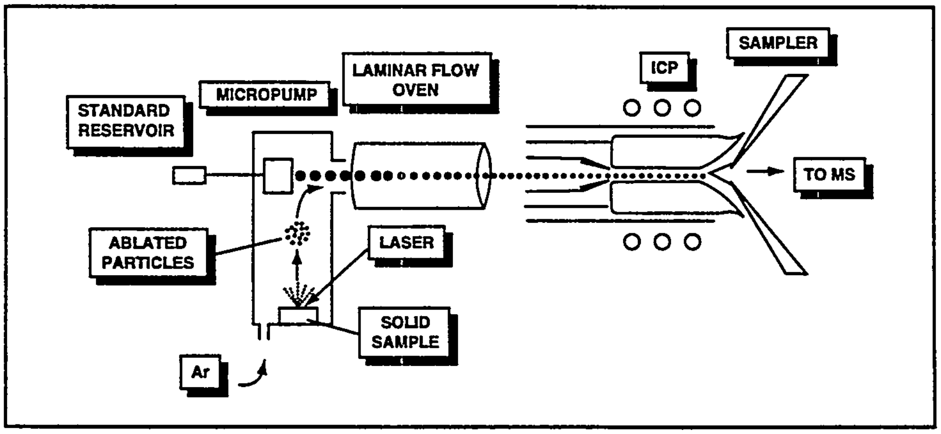


Figure 8.2b. Schematic diagram of laser ablation cell connected to MDMI for calibration.

laser ablation, for direct analysis of solids without dissolution. Sample matrices are widely varied and include groundwater, contaminated soil, and organic solutions from waste tanks, etc.

The MDMI technology should be suitable for use in either a laboratory or in a field-deployable instrument in a van.

STATUS

A second-generation MDMI was obtained from Perkin-Elmer SCIEX Inc. The device was delivered in April 1995. It was installed on a twin quadruple ICP-MS device and is working properly. Basic analytical figures of merit are being measured. The device is already a potential commercial product; there is not much to transfer to SCIEX Inc., other than the evaluation of its performance and possible areas of improvement.

REGULATORY CONSIDERATIONS

ICP-MS is widely used for regulatory purposes. None of the methods presently include MDMI, but they could be amended readily to do so if the device proves useful.

POTENTIAL COMMERCIAL APPLICATIONS

This device is potentially valuable in any application that requires analysis of very small solution volumes. These include semiconductor materials and biomedicine, in addition to the obvious uses in nuclear applications. It could be readily combined with chemical separation and preconcentration procedures used for isolating and quantifying radionuclides. The ability to analyze solids directly with reasonable accuracy using calibration with the MDMI will be invaluable in many applications.

BASELINE TECHNOLOGY

A variety of nebulizers are in use. These are all inefficient, and they all leave substantial amounts of waste solution behind. The direct injection nebulizer, developed at the Ames Laboratory, is an improved nebulizer technology in that it delivers the entire sample to the plasma, so there is no liquid waste; however, the aerosol from the DIN is polydisperse and is spread out over a substantial volume in the central axis of the plasma. Thus, much of the nebulized sample is not properly converted into atomic ions. Another state-of-the-art technology which the MDMI is intended to surpass in performance is the electrothermal furnace that has detection limits approaching a few fg, but has other problems. Namely, the signal is transient by nature, which limits the number of elements that can be measured during each firing of the furnace. Also, the precision is mediocre, i.e., 10% relative standard deviation (RSD) at best.

INTELLECTUAL PROPERTY

This is a potential commercial product of Perkin-Elmer SCIEX Inc. Information regarding intellectual property should be directed to Perkin-Elmer SCIEX Inc.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

R. S. Houk
Ames Laboratory
Iowa State University
Ames, IA 50011
(515) 294-9462; FAX 515-294-5233
rshouk@iastate.edu

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 10874-1290
(301) 903-7672

Industrial Partner

Ray Jong
Perkin-Elmer SCIEX Inc.
55 Glen Cameron Rd.
Thornhill, Ontario L3T 1P2
(416) 881-4646

REFERENCES

1. French, J.B., B. Etkin, R. Jong, "Monodisperse Dried Microparticulate Injector for Analytical Instrumentation," Anal. Chem., 66, 1994, pp. 685-691.

2. TTP CH1-5-30-03, "ICP-MS for Analysis of Microliter Samples and Solids," 1994.

IN SITU DETERMINATION OF RADIONUCLIDE CONTAMINANTS

DESCRIPTION

Traditional means of measuring radionuclide concentrations in soils over large areas are often time consuming, cumbersome, expensive, and nonrepresentative. The present technology is a method for real-time characterization of large-scale radionuclide contamination in soils. The objective of this technology is to provide real-time mapping of surface soils contaminated with radionuclides. In addition, the objective includes downhole applications for mapping axial and radial distributions of radionuclides in the subsurface using boreholes. It is noted that the boreholes should be installed with minimal disruption of the substrate to get an accurate distribution of contaminants.

The In Situ Determination of Radionuclide Contaminants (ISDRNC) technology largely eliminates the need for collecting a myriad of soil samples for subsequent laboratory analyses. ISDRNC provides a more representative soil map (more material analyzed) compared to discrete sampling and analysis. It may be considered to have a sample size of more than a ton compared to a single gram sample; therefore, sampling errors are reduced. ISDRNC provides results in real-time (i.e., minutes rather than months). Costs are on the order of $10/sample location analyzed in-situ compared to $1,000/ sample extracted and analyzed. ISDRNC is safer because sample handling by humans is not required, though some exposure may result from human presence on the site surface.

ISDRNC consists of a triad of original or adapted techniques including: (1) in-situ gamma-ray spectrometry (surface application with analytical depths to 15 cm below the soil's surface), (2) high energy beta scintillation sensor (for surface applications with analytical depths to 5 cm below the soil's surface), and (3) downwell gamma-ray spectrometry (subsurface application with penetration depths to about 15 cm radially from the edge of the borehole).

The targeted contaminants are all radionuclides which emit gamma rays, high-energy beta emitters, and other contaminants that must be quantified by indirect methods. Some radionuclides cannot be analyzed or are very difficult to analyze by nondestructive means (e.g., ^{3}H, ^{14}C, ^{63}Ni, ^{129}I, etc.) but their importance is often diminutive in terms of the objectives of this technology or their "known" absence because of provenance or historical analog analysis.

The physical basis of the technique is that many radionuclides are gamma-ray emitters (photon emission by radioactive decay), and these materials have characteristic emission energies. Therefore characterization is according to the observed emission energy; furthermore, location of the material and quantification is based on the observed intensities from several geometric positions in or above the matrix. Depth profiles based on gamma emission can be derived from observation of two or more gamma rays from the same isotope having different energy emissions (different energy photons undergo selective attenuation by the matrix). A key aspect of this advanced technology is the high-purity germanium (HPGe) diode detectors that are by far the most sensitive detectors available for gamma spectrometry. The first category of target contaminants that can be directly measured by in situ gamma ray spectroscopy (ISGRS) is that of gamma-emitting fission or activation products including but not limited to ^{60}Co, ^{137}Cs, and ^{154}Eu. In addition, the present technology can detect isotopes such as ^{90}Sr, which is not a gamma emitter; nevertheless, ^{90}Sr can be quantified, directly or indirectly, by detection of the high energy beta emission of its daughter product or by detection of the copious quantities of bremsstrahlung radiation generated by beta deceleration. Transuranic elements are a second type of detectable radionuclides and include plutonium, americium, neptunium, curium, and uranium. These transuranic elements all contain isotopes that emit sufficient quantities of characteristic gamma rays to identify and quantify their presence by ISGRS, but only in the absence of significant quantities of fission and/or activation products. Indeed, transuranic isotopes also generate neutron emissions, either from spontaneous fission or (α,n) reactions on light isotopes. Consequently, these neutrons can be useful for quantifying the transuranics when copious fission or activation products mask their gamma emissions by using a fiber-optic neutron detector similar to the beta scintillation detector.

The instrument is most effective when operated by a person skilled in electronic, computer, and data evaluation aspects of the technology. Although the system could be operated by a robot, the potential for quality data is greatly enhanced by a skillful operator. For example, a skilled operator will assure that the instrument is properly calibrated, in control, and acquiring data properly, and make adjustments as required to maintain quality data acquisition.

TECHNICAL PERFORMANCE

Current demonstration results indicate that the technology could be applied to completely characterize most sites in less than one week. The ground surface measurement techniques cover about 0.36 m^2/min (10 ft^2/min), but this rate depends on what is being measured, at what sensitivity, the desired confidence level, and the statistical sampling program desired. The downhole tool is different. Its rate depends on the isotope being looked for and how frequently measurements are desired (e.g., once every 5 min, etc.); however, a typical counting time is about 5 min. The sensitivity depends on the radionuclide, the direct or indirect physical phenomena associated with quantification, and the counting time. Detection of all the gamma-emitting radionuclides is the expected performance, including natural primordial activities, with a quantitative measure of their concentrations above a limit of about 1 pCi/g. Typical counting times are on the order of 5 to 15 min for most scenarios. Typical sensitivities for the gamma-emitting fission and activation products such as ^{60}Co and ^{137}Cs (determined by direct measurement) are 0.01 pCi/g, and for ^{90}Sr using the beta scintillation detector or the bremsstrahlung indirect measurement is 10 pCi/g. Typical transuranic sensitivities are 10,000 pCi/g when interfering fission and activation products are present (implies a neutron detection scenario may be preferred) but can be much lower if they are absent (then direct beta or gamma detection is possible).

In-situ Gamma-ray Spectrometry. The system is an extended surface-area gamma system that uses a collimated, down-looking, intrinsic HPGe detector/cryostat assembly with electronics packages similar to the downwell unit. When suspended one meter above the soil, this detector is sensitive to surface and shallow subsurface activity (e.g., to below surface depths approaching 20 cm for U) over many hundreds of square meters and effectively averages horizontal heterogeneities that may exist within its field of view. Empirical evidence indicates that approximately 80%-90% of the observed gamma fluence originates within a 10 m radius from the detector because of geometric factors and attenuation in the soil and air (for most gamma energies and soils).

Subsurface gamma spectrometer. This spectrometer consists of a highly sensitive gamma-ray detector (HPGe) adapted to fit in a borehole and is used to detect radionuclide activity concentrations down to background levels. The detector used for the Fernald Environmental Management Project (FEMP) measurements was a 108 cm3 coaxial HPGe spectrometer housed in a 7.30 cm O.D. (2.875 in) stainless steel canister that also contains the necessary signal processing electronics and a spill proof liquid nitrogen cryostat providing a 12 hour holding time. A new system is being constructed which resembles link sausage having 3 links with an O.D. of 4.84 cm (1.90 in). One link contains the HPGe detector, another contains the LN, and the third contains the necessary electronics. Future developments will include electrical cooling (if possible) to enable longer operation of the detector array. The new downhole detector system concept should allow application in 5.1 cm diameter (2.0 in) boreholes and small radius of curvature applications (6.5 cm in 7.6 cm diameter pipe). The present detector system will pass through any straight pipe or borehole larger than 7.30 cm in diameter, and will even pass through curved pipes as small as 10 cm in diameter. Axial and radial distributions of radioisotopes can be measured with the use of lead or tungsten collimators, which provide resolution of strata as thin as 1 cm or angular resolution as small as 0.1 steradians. The radial analytical depth is approximately 15 cm for U. The detector can be pushed into closed-end horizontal and lateral wells with rods and can also be pulled through daylight wells with cable. Concentrations of radioisotopes are generally reported at each measurement location along the pipe, assuming the radioactivity to be in a homogeneously distributed matrix with an infinite volume (approximately 1 m3) of sediments around the detector. This assumption is not restrictive, but is based on the calibration environment.

Beta Scintillation Sensor. This sensor is used to characterize potentially contaminated surface soils having beta emitting radionuclides or daughter products in the decay chain. The radiation sensitive portion of the sensor (1500 cm^2) is composed of multiple layers of 1.0 mm^2 plastic scintillation fibers that are particularly sensitive to energetic beta particles emitted from the ^{234m}Pa daughter product in the ^{238}U decay chain and that emit a 2.29 MeV (maximum) beta particle that can be selectively detected. The uranium concentration is calculated based on the secular equilibrium of ^{238}U with the given daughter product. Passage of the beta particles through the individual fibers causes ionizations and excitations of fluorescent dopants which subsequently deexcite via the emission of visible light. The resulting light pulses are then converted into electrical signals following their detection by photomultiplier tubes at the ends of the scintillating fibers. Although the beta scintillation fibers are somewhat sensitive to gamma emissions, the layered fiber design helps to maximize the signal to noise ratio, and therefore, discriminate between a beta emission event and other ubiquitous gamma phenomena. The viewing depth for this detector is 3-5 mm. The typical sensitivity is 10 pCi/g for ^{90}Sr and ^{238}U.

FEMP Demonstration. The technology was demonstrated at the Fernald Environmental Management Project (FEMP) in FY 1992. The FEMP former Drum Bailing Area (DBA) and a very large area outside the Sewage Treatment Incinerator (STI) were analyzed as part of this demonstration. The average uranium content was quantified in the upper 15 cm using the in-situ surface gamma ray spectrometry, and the upper 5 mm of soil was also analyzed using the beta scintillation sensor optimized for the high-energy beta decay associated with the ^{238}U decay chain. Eight boreholes were analyzed with the 7.30 cm downhole probe, and more than 175 individual sample sites covering nearly 53,000 m^2 (13 acres) in total were analyzed with the previously mentioned surface methods in 5 days. In this investigation, concentrations from <10 pCi/g to >3000 pCi/g were identified at the DBA and STI sites. The data were used to generate isopleth maps of the ^{238}U activity levels in support of the establishment of remedial protocols. Figures 8.3a and 8.3b are typical isopleths for the in-situ gamma-ray spectrometer and the surface beta scintillation sensor. The differences in the isopleth maps is largely caused by the difference in sampling depth of the direct gamma-ray spectrometry compared to the indirect beta scintillation method.

Similar results were reported for the Sandia National Laboratories (SNL) Chemical Waste Landfill demonstration in FY 1992 and also SNL's Mixed Waste Landfill demonstration in FY 1993. The technology was also demonstrated in a pipe inserted below the RB11 pit at Kirtland Air Force Base in FY 1992 with comparable results; although no man-made gamma-radiation was detected below the pit. The next scheduled demonstration is planned at the Hanford site in Richland, Washington.

Cost. A complete system could be obtained for less than $100K. Operations and maintenance costs are

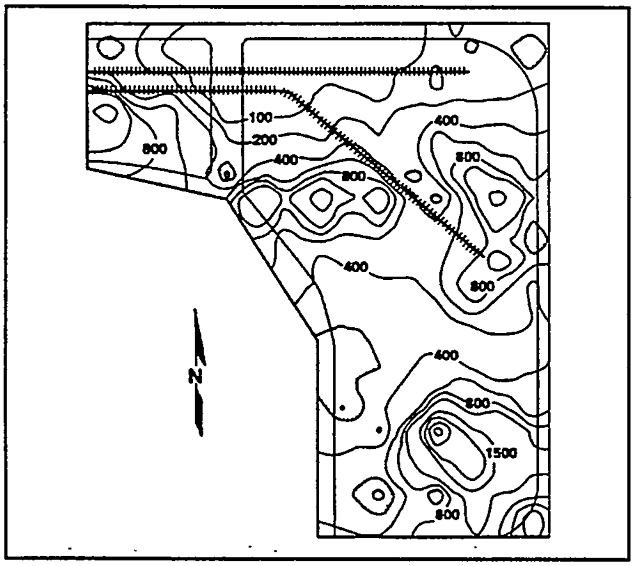


Figure 8.3a. Contour plot of activities at the DBA based on the beta sensor. Contour intervals, excluding the 100 pCi/g delineation, are 200 pCi/g when ≤ 1,000 pCi/g and 500 pCi/g when ≥ 1,000 pCi/g.

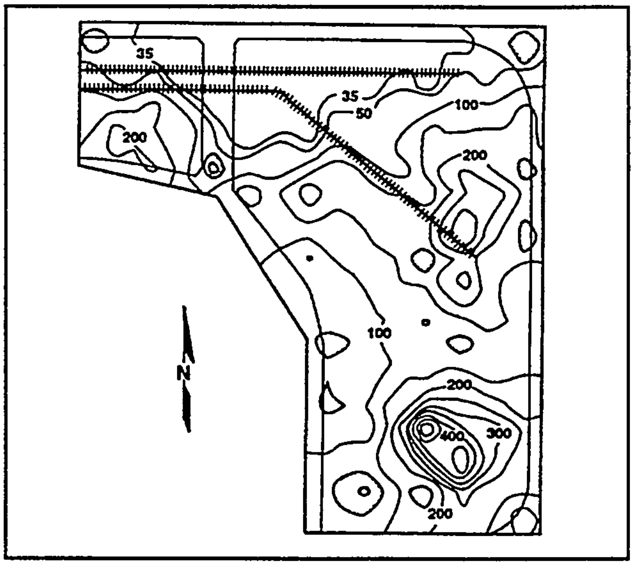


Figure 8.3b. Contour plot of activities at the DBA based on the in situ gamma-ray spectrometer. Contour intervals, excluding the 35 pCi/g delineation, are 50 pCi/g.

associated with one person for operation and a few liters of liquid nitrogen each day. Operation of the equipment requires a single standard 115 volt AC circuit, or in remote locations, a portable generator. Electrical energy usage is at a rate of 1 kW. Characterization of the RB11 pit was accomplished with 21 individual measurements made in a day and a half. Each measurement resulted in a concentration limit for 23 different radionuclides (more radionuclides could have been included in the library if desired). Therefore, 483 individual concentration measurements were made at a unit quantitative analytical cost of $3/sample. The alternative approach (baseline) would have a cost in the range $100 to $1,000/sample.

PROJECTED PERFORMANCE

The ISDRNC technology has a sensitivity of 0.01 pCi/g for fission and activation products that emit gamma radiation. The beta scintillation detector is projected to have performance as described above as no modifications have been indicated for the near future. Finally, the major improvements to the technology are related to the downhole probe with respect to size reduction. A next generation downhole gamma-ray spectrometry probe is being constructed (available September 1995) that will have an O.D. less than 4.84 cm (approximately 1.90 in), and will be able to pass around curves as tight as a trap in a 3 in drain line. The technology is expected to be able to fully characterize most sites with installed monitoring wells in less than a week.

APPLICABILITY

The technology is applicable to radionuclide contaminants in soils over large areas.

STATUS

The technology was demonstrated at the aforementioned sites and improvements are ongoing. The next generation of the downhole gamma-ray spectrometer probe is scheduled for completion in September 1995. All other technologies are available for demonstration.

REGULATORY CONSIDERATIONS

This technology is likely to exceed any regulatory requirements for detection limits. This equipment is sensitive enough to measure the natural background radioactivity in the ground, and in fact will measure lower levels of radioactivity when going deeper into a hole because of the increased shielding from cosmic radiation. Regulatory compliance limits have not been formally set for remediation of radiologically contaminated sites. Reasonable limits should not be less than the background levels.

POTENTIAL COMMERCIAL APPLICATIONS

The technology is potentially applicable at nuclear fuel production and also nuclear power facilities both domestically and abroad for the rapid characterization of surface contamination by radionuclides.

BASELINE TECHNOLOGY

The baseline technology is analog site characterization and consists of discrete sample collection and off-site analysis.

INTELLECTUAL PROPERTY

A patent is being issued for the beta scintillation detector. Contact the principal investigator for additional information.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Ron L. Brodzinski
Battelle
Pacific Northwest Laboratories
P.O. Box 999, MS P8-01
Richland, WA 99352
(509) 376-3529; (509) 372-0672 FAX

DOE Program Manager

Skip Chamberlain
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

REFERENCES

1. Abel, K.H., R.J. Arthur, M. Bliss, D.W. Brite, R.L. Brodzinski, R. A. Craig, B.D. Geelhood, D.S. Goldman, J.W. Griffin, R.W. Perkins, P.L. Reeder, W.R. Richey, K.A. Stahl, D.S. Sunberg, R.A. Warren, N.A. Wogman, and M.J. Weber, "Scintillating-Glass-Fiber Neutron Sensors," Nucl. Instrm. Methods Phys. Res. A 353, 114, 1995.

2. Schilk, A.J., R.W. Perkins, K.H. Abel, R.L. Brodzinski, D.P. Brown, R.C. Thompson, and M.A. Knopf, "Quantitative In-Situ Uranium Contaminant Mapping Using High-Resolution Gamma-Ray Spectrometry and Beta Scintillation Counting," Proceedings of ER'93: Meeting the Challenge, Augusta, GA, Oct. 24-28, 1993.

3. Schilk, A.J., R.W. Perkins, D.E. Robertson, and R.L. Brodzinski, "In-Situ Mapping of Radionuclides in Subsurface and Surface Soils," Proceedings of the Information Exchange Meeting on Characterization, Sensors, and Monitoring Technologies, Dallas, CONF-920791, July 15-16, 1992.

4. Nielson, K.K., C.W. Thomas, N.A. Wogman, and R.L. Brodzinski, "Development of a Plutonium-Americium Monitor for In Situ Soil Surface and Pond Bottom Assay," Nucl. Instrm. Methods 138, 227, 1976.

5. Nielson, H.L., N.A. Wogman, and R.L. Brodzinski, "In Situ Subterranean Gamma-Ray Spectroscopy," Nuclear Instrm. Methods 143, 385, 1977.

6. Brodzinski, R.L., and H.L. Nielson, "A Well Logging Technique for the In Situ Determination of ^{90}Sr, " Nucl. Instrm. Methods 173, 299, 1980.

7. Brodzinski, R.L., "In-Situ Determination of Actinides by High Resolution Gamma-Ray Spectrometry, Methods of Low-Level Counting and Spectrometry," Proceedings of a Symposium, Berlin, Germany, IAEA-SM-252/18, April 6-10, 1981.

8. Brodzinski, R.L., "Portable Instrumentation for Quantitatively Measuring Radioactive Surface Contaminations, Including ^{90}Sr," IEEE Transactions on Nuclear Science, Vol. NS-31, 686, 1984.

LONG-TERM, POST-CLOSURE RADIATION MONITORING SYSTEM

DESCRIPTION

A Long-Term Post-Closure Radiation Monitor is being developed. The concept employs a passive in-ground measurement probe which contains a scintillator coupled to an optical lightguide. Gamma radiation absorbed by the in-ground scintillator generates optical photons which are coupled into the lightguide, conveyed to the surface and detected as an indication of the instantaneous subsurface radiation level. The in-ground probes will be configured to geometrically resemble cone penetrometers or penetrometer-based sampling tools and, thus, can be installed to depths of 50 meters using conventional CPT trucks and methods (see profile featuring the Heavy Weight Cone Penetrometer). A large number of in-ground passive probes can be multiplexed to a single, above-ground opto-electronics unit to provide for detection and readout of any long-term changes in the distribution of the radionuclides in the vadose zone. Figure 8.4 shows a conceptual drawing of an installed radiation monitoring system.

Phase I of a three phase development program consisted of selecting the most appropriate components to maximize the signal reaching the detectors and thereby minimizing the integration time required to obtain a reliable measure of radiation. Phase I ended with the design of a prototype radiation probe. Phase II encompassed the fabrication and testing of the integrated unit at DOE's Fernald Environmental Management Project (FEMP) in southwestern Ohio.

TECHNICAL PERFORMANCE

FEMP Tests. Two locations at FEMP were sampled and analyzed for uranium contamination versus depth; gamma activities with depth at these locations were

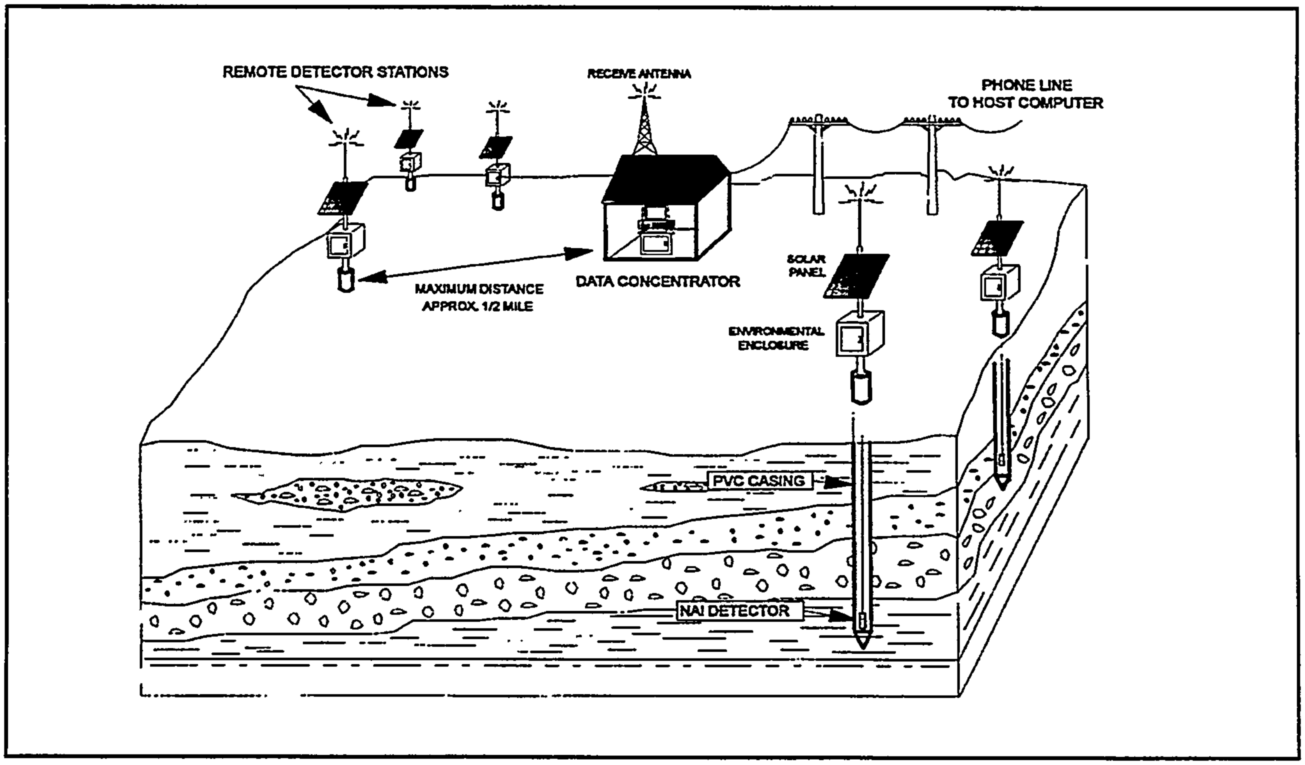


Figure 8.4. Conceptual drawing of an installed radiation monitoring system.

also measured with a commercial gamma probe. The bores at these locations were then cased with 1.5 " PVC casing for later measurement. The B&W Survey Tool Program provided a gamma measuring tool with a butt coupled iodide scintillator which was used to generate comparison data for each of the tests performed. Data for both probes was acquired with B&W's laboratory two channel gamma spectrometer.

Four weeks of tests (October - November 1994) included measurements in drums of contaminated soil (at natural moisture and saturation) with known contaminant levels, in situ tests near grade in an existing monitoring well, in situ tests in two temporary PVC borings at depths up to 3 meters, and measurements of drums of contaminated water, both with and without a sand matrix.

Tests showed that the methods used in designing and analyzing the probe were adequate for calculating gamma flux, soil and water adsorption, window absorption, absorption rates by the scintillator, scintillation efficiency, optical losses, resolution, and count rates.

Cost. Cost information was not available at this writing.

PROJECTED PERFORMANCE

During Phase III, a prototype system consisting of several probes multiplexed to a single data concentrator will be fabricated and subjected to a year-long field test at the Fernald site. The test experience will be used to develop a final commercial design for the radiation monitoring system.

APPLICABILITY

This technology is applicable to long-term monitoring of hazardous waste sites for migration of radionuclides.

STATUS

Phases I and II have been completed. Phase III is underway. Final activities include the design of a production system and the selection of vendors to produce the system.

REGULATORY CONSIDERATIONS

Contact the principal investigator for regulatory information.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is potentially applicable to may commercial hazardous waste sites throughout the country to monitor migration of radionuclides in the subsurface.

BASELINE TECHNOLOGY

The baseline technology includes sensors which can be lowered into boreholes to make radiation measurements; however, the sensors are relatively complex and expensive and may not be suitable for long-term monitoring.

INTELLECTUAL PROPERTY

None.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Stu Reed
Babcock & Wilcox
1562 Beeson Street
Alliance, OH 44601
(216) 821-9110; (216) 823-0639 FAX

DOE Program Manager

Texas Chee
U.S. Department of Energy
19901 Germantown Road
Germantown, MD 20874
(301) 903-7926

REFERENCES

None.

PORTABLE HIGH-ENERGY BETA DETECTOR

DESCRIPTION

A novel scintillating-fiber sensor for detecting high-energy beta particles to characterize ^{238}U and ^{90}Sr in surface soils is being developed. The sensor employs a vertically stacked configuration of fiber ribbons that allows discrimination between unattenuated beta particles from ^{90}Y or ^{234m}Pa (decay daughters of ^{90}Sr and ^{238}U, respectively), and lower-energy beta particles typically arising from natural sources (i.e., other ^{238}U daughters, ^{232}Th and its daughters, and ^{40}K). The sensor indirectly detects uranium and strontium activity based on the assumption that secular equilibrium exists between the parent radionuclide and its daughter. The multilayer design affords some discrimination against gamma rays and cosmic-induced species (protons, muons, etc.) by observing and partially canceling the contributions from these ubiquitous phenomena.

Figure 8.5 illustrates the current sensor design. The sensor has a larger active region (30 cm x 60 cm) and incorporates improvements that decrease the inherent background signal observed in an earlier proof-of-principle detector. The result is an enhanced overall signal-to-noise ratio. For example, cosmic influences are minimized by incorporating an overlying anti-coincidence ribbon that detects energetic charged particles originating above the sensor and rejects their contribution. A 6 mm thick acrylic absorber separates the cosmic anti-coincidence layer from the underlying sensitive region and precludes any charged particles originating below the sensor from reaching the top layer. Gamma-ray-induced signals are reduced by placing thinner scintillating fibers in the layer closest to the soil, which decreases the probability of generating Compton electrons in this layer. These electrons (denoted as e⁻ in Figure 8.5) are indistinguishable from beta particles. Significant improvements in the electronic components and circuitry have allowed the establishment of a much narrower coincidence window (on the order of 10 to 20 ns), further decreasing the background generated by coincident thermionic emissions from multiple photomultiplier tubes.

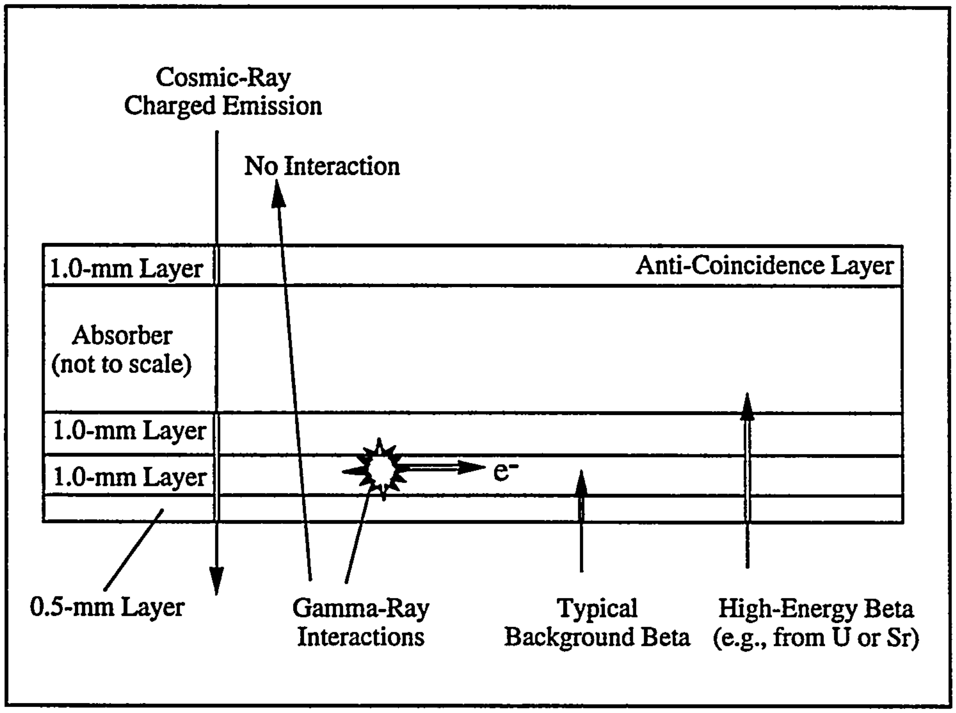


Figure 8.5. Schematic representation of the current sensor design highlighting potential interactions. Double lines denote particle tracks that lead directly to excitations/ionizations and consequent scintillations.

TECHNICAL PERFORMANCE

The prototype high-energy beta scintillation sensor was successfully demonstrated and evaluated in various laboratory and field scenarios.

Fernald Soil Decontamination Pilot Plant. The beta scintillation sensor was evaluated at the Soil Decontamination Pilot Plant (SDPP) at the Fernald Environmental Management Project (FEMP) located near Fernald, Ohio, to establish the utility of the detector for the measurement of uranium-contaminated soils from various stages of a soil washing process stream in a relative-motion (i.e., conveyor-belt) scenario.

Measuring uranium indirectly via its daughter activity does not preclude effective use of the beta sensor for such a scenario, but necessitates a thorough understanding of: (1) the ^{238}U-^{234}Th decontamination ratios (i.e., the degree of uranium and thorium stripping as a function of the washing process) and (2) the temporal relationship between the U-Th removal stage and the monitoring stage. Because moisture content can affect sensor response, moisture content is a critical parameter and must be well characterized before the sensor is used to quantify radionuclide activities.

Calibration of the sensor was performed by characterizing three sand samples that were spiked with a solution of $^{238}UO_2(NO_3)_2$ to levels of 5, 15, and 35 pCi of ^{238}U(^{234}Th, ^{234m}Pa) per gram of soil. The sources were first characterized in the laboratory and followed by a calibration performed at the SDPP (although in this case the width of the soil was restricted to match the conveyor-belt dimensions). The SDPP calibration corroborated the laboratory data.

The inherent stability of the sensor was determined by taking one-hour background counts at various times during the evaluation process while the sensor was maintained in a standardized configuration (1 to 2 cm above the sample surface and centered on the conveyor-belt width). The average background count rate within the SDPP facility was found to be comparable to that observed during previous laboratory conditions, with a triple-coincidence rate of approximately 7 counts per second.

The effectiveness of the sensor for analyzing soils on a moving belt was evaluated. The sand standards were passed 1 to 2 cm below the sensor at various speeds (approximately 1, 5, and 15 ft/min) to establish dynamic calibrations as a function of relative speed. Calibrations were based on the net cumulative counts obtained during each traverse of a 20 cm x 60 cm x 1 cm soil standard. Damp soil samples were then monitored under equivalent conditions and net counts were determined. The resulting data indicated that the sensor response was consistent for multiple belt speeds and that static and dynamic results were mutually supportive.

Fernald Incinerator Site. The high-energy beta sensor was used to acquire information about the distribution of uranium contamination in surface soils at a large field north of the FEMP incinerator site. The surface of the field was contaminated by fallout from stack emissions from the incineration of uranium-contaminated combustibles; the emissions were carried in that direction by the prevailing southwesterly winds.

Calibration standards were prepared and two calibrations on two separate days were performed with the beta sensor. The results for both days were very similar, generating a near-ideal calibration function (i.e., linear plot with an intercept near zero). During the field-analysis phase, the sensor was placed directly on the soil surface (vegetation was cropped to within 5 cm) and counts were performed for 10 to 15 min at each sample location. Sensor reproducibility was investigated by revisiting two specific field locations throughout the demonstration to compare detector output as a function of time and environmental conditions (e.g., intermittent rain). This allowed investigators to scale the beta sensor response to other field locations monitored throughout the day and to give results based on dry soil conditions.

Scaled measurements from these demonstrations were modelled with a commercial geostatistical software package, and a two-dimensional surface activity contour map was generated. The map was consistent with site historical information indicating that contaminated particles originating from the incinerator stack were transported to the north and east, across the field site, and uranium activity levels were observed to decrease as a function of distance from the incinerator. Further support for the beta sensor results was provided by concurrent in situ gamma-ray spectrometry measurements and surface soil analysis, both of which generated similar contour maps.

PROJECTED PERFORMANCE

Current and projected efforts will concentrate on further miniaturization of the custom electronic package, improvement in the unit's minimum detectable activity level, and modularization of the sensor package.

APPLICABILITY

The high-energy beta scintillation sensor is applicable to detection and quantification of uranium and strontium contamination on surfaces, in surface soils, and in other similar materials.

STATUS

Planned demonstrations at the time of this writing include the characterization of ^{90}Sr contamination in soils and soil cores at the Inhalation Toxicology Research Institute in Albuquerque, New Mexico and on conveyor-transported soils at the Savannah River Site in Aiken, South Carolina. The high-energy beta scintillation sensor will also be demonstrated at the International Atomic Energy Agency headquarters, Vienna, Austria, for the detection of ^{238}U in soils for nuclear nonproliferation monitoring.

REGULATORY CONSIDERATIONS

No environmental impacts are associated with the use of this technology and no regulatory barriers to its widespread use are anticipated.

POTENTIAL COMMERCIAL APPLICATIONS

As a means of establishing remedial protocols, verifying cleanup operations, and identifying nuclear proliferation activities; this technology is directly applicable to many existing nuclear waste and soil contamination problems throughout the world.

BASELINE TECHNOLOGY

Traditional methodologies for quantitative characterization of radionuclide-contaminated soils over extended areas are often tedious, costly, and yield nonrepresentative results. Such means include ground-deployable gamma-ray-measurement techniques (e.g., in situ gamma-ray spectrometry), and aerial surveys using NaI(T1) or HPGe gamma-ray sensors for uranium detection, and hand sampling followed by gamma-ray counting (for uranium) or extensive radiochemistry and subsequent beta-particle counting (for both strontium and uranium).

INTELLECTUAL PROPERTY

A U.S. government patent was issued for this technology in August 1995. A licensing agreement with Quantrad Sensor of San Jose, California, is anticipated to be signed in October 1995. Commercialization and mass production of this technology is expected by 1996 or 1997.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator

Alan J. Schilk
Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352
(509) 376-9510; (509) 376-3868 FAX
Internet: aj_schilk@pnl.gov

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19910 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

REFERENCES

1. Schilk, A.J., K.H. Abel, and R.W. Perkins, "Characterization of Uranium Contamination in Surface Soils," Journal of Environmental Radioactivity, 26, 1995, pp. 147-156.

2. Schilk, A.J., C.W. Hubbard, M.A. Knopf, and R.C. Thompson, "Direct Measurement of Sr-90 and U-238 in Soils on a Real-Time Basis: 1994 Summary Report," PNL-10483, Pacific Northwest Laboratory, Richland, WA, 1995.

3. Schilk, A.J., and M.A. Knopf, "Results from the Preliminary Conveyor Evaluation of the High-Energy Beta Scintillation Sensor at the Fernald Soil Decontamination Pilot Plant," PNL-9986, Pacific Northwest Laboratory, Richland, WA, 1994.

4. Schilk, A.J., M.A. Knopf, R.C. Thompson, C.W. Hubbard, K.H. Abel, D.R. Edwards, and J.R. Abraham, "Real-Time, In Situ Detection of Sr-90 and U-238 in Soils via Scintillating-Fiber-Sensor Technology," Nuclear Instruments and Methods in Physics Research, A353, 1994, pp. 477-481 .

5. Schilk, A.J., K.H. Abel, D.P. Brown, R.C. Thompson, M.A. Knopf, and C.W. Hubbard, "Selective, High-Energy Beta Scintillation Sensor for Real-Time, In Situ Characterization of Uranium-238 and Strontium-90," Journal of Radioanalytical and Nuclear Chemistry, Vol. 193 (1),1995, pp. 107-111.

Remote Sensing

Section 9.0

DESCRIPTION

Remote sensing techniques such as aerial photography, multispectral scanning, and airborne geophysics are of unquestioned value for hazardous waste site characterization, facility monitoring, and cleanup verification. However, remote sensing is often dismissed as too expensive when planning remediation activities at small sites. For example, when new buildings or roads are constructed at an active disposal area, the facility manager's existing aerial photographs become out of date, which hinders future planning. Using a small, radio-controlled airplane, equipped with an ordinary 35 mm camera, a new aerial photograph can be taken of the site. The cost and inconvenience of hiring a helicopter or fixed-wing aircraft can be avoided.

Efforts underway are not limited to photography. A new generation of lightweight, low-power sensors that offer new applications for airborne miniature platforms, are being developed by the DOE Office of Technology Development. Model airplanes and helicopters can be flown by any radio-control hobbyist and can carry a 5 to 10 lb sensor payload.

Two planes in use at the Oak Ridge Reservation in Oak Ridge, Tennessee, were designed by Jim Walker of Brigham Young University. These "Droop Snoops" are modified "Senior Telemasters" (model kit). Modifications include a wider fuselage to accommodate a 35 mm camera, a "butterfly" wing, and the addition of carbon fiber to minimize vibration in the camera compartment (see Figure 9.1).

The Droop Snoop can fly as slow as 15 to 20 mph. At a speed of 15 mph the plane travels 0.26 inches in 1/1,000 of a second, so the image quality is excellent. A typical flight lasts 20 to 30 min, and consists of hand launching the airplane, flying it to an altitude of 500 ft, making several passes over the target area usually shooting a full 36-exposure roll of film to ensure coverage, and landing the plane in the nearest available clearing. A crew of two generally suffices (a pilot to fly the plane and trigger the camera, and a spotter to launch the plane and notify the pilot when the plane is over the target). Range is limited by the need for the pilot to be able to maintain eye contact (not radio power) with the plane.

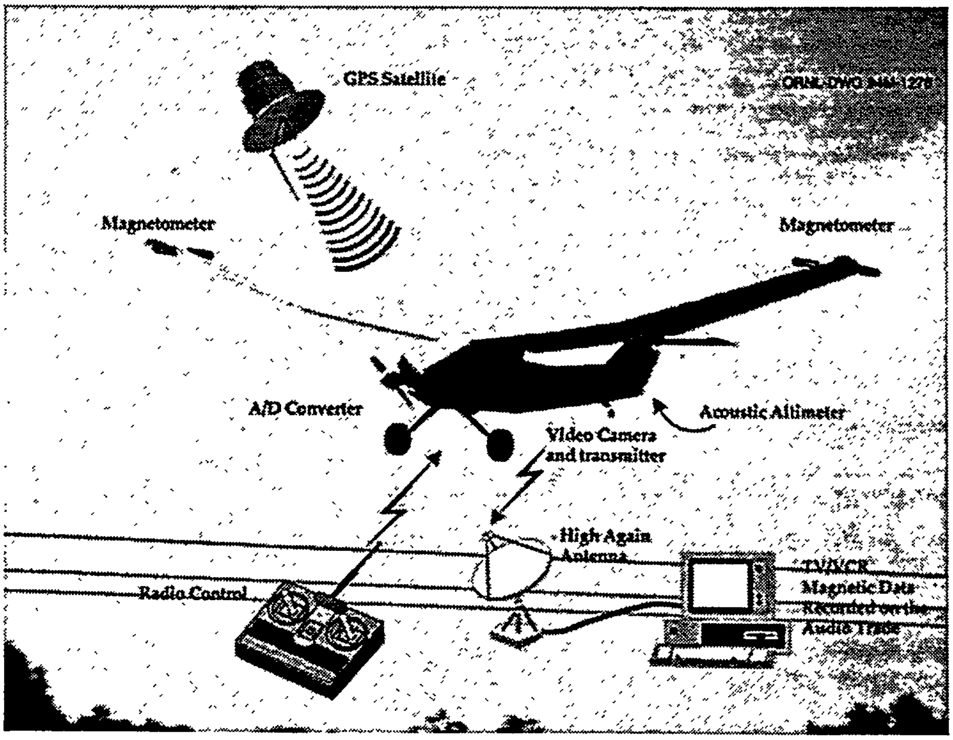


Figure 9.1. A model airplane: The Droop Snoop.

TECHNICAL PERFORMANCE

Aerial photography with the Droop Snoop has been successfully used at the Solid Waste Storage Area 5 and the Hydrofracture Deep Waste Injection Facility located on the Oak Ridge Reservation.

Solid Waste Storage Area 5. This storage area is a burial ground that was used to dispose of low-level radioactive waste. Much of the waste was buried in unlined trenches reported to be 10 to 15 ft deep, 10 to 12 ft wide and 40 to 500 ft long. The precise location of the trenches was unknown. Photographs taken clearly showed the outline of several trenches. Apparently, as the trench fill settled, a small depression formed over the trench that both acts as a rain water catchment and prevents the mower blades from cutting as close to the ground. The result is greener grass over the trenches. This disturbed vegetation pattern is difficult to see in ground-based photographs because of the mowing patterns and because one is simply too close to get a proper perspective.

Hydrofracture Deep Waste Injection Facility. At this facility, low-level waste was mixed in a concrete grout and injected under pressure deep into bedrock. Because the grout did not settle properly, radionuclides are leaching away from the site as confirmed by groundwater samples. Seismic and borehole geophysical investigations are planned for the site. An aerial photograph taken with the Droop Snoop shows the size of the facility, the layout of the roads and buildings, and the deteriorating condition of some of the old storage tanks. The image quality is excellent; drainage ditches, mowing patterns, even individual power lines can be seen on the original photograph.

Cost. For an experienced builder, a Droop Snoop can be constructed in about 40 hours at a cost of $500-$1,000 for the complete system including wood, epoxy, servos, engine, radio controller, flight box, and camera.

PROJECTED PERFORMANCE

Aerial photography is only one of many possibilities of radio-controlled aircraft. A model plane is being designed that will carry a three-component flux-gate magnetometer, a global positioning system (GPS), an altimeter, and data telemetry. Radiation sensors and very low frequency monitors are examples of sensors that may be added in the future.

APPLICABILITY

Remote sensing techniques such as aerial photography, mutispectral scanning, and airborne geophysics are applicable to hazardous waste characterization, facility monitoring, and cleanup verification. Remote sensing of small sites with a radio controlled-aircraft or helicopter to collect high-quality data, quickly and at a low cost, is now possible.

Aerial photography can be used: (1) to show changes over time by flying repeated missions over the same site, (2) to capture leaf-out in the spring, (3) to detect changes in sediment transport patterns after storms, or (4) to document changes at a waste site undergoing remediation.

STATUS

As stated previously, current efforts are focused on equipping a model plane with a miniature three-component magnetometer similar to those used by geophysicists in land-based surveys to look for buried drums and waste trenches. The first demonstration is expected to take place in September 1995 at the Y-12 Plant burial grounds.

REGULATORY CONSIDERATIONS

This technology is non-intrusive and passive and is not expected to impact the environment.

POTENTIAL COMMERCIAL APPLICATIONS

This technology has very wide commercial application potential at waste sites, and burial sites, and for facility monitoring and cleanup verification. It is limited only by the sensors and other equipment placed on the aircraft.

BASELINE TECHNOLOGY

For large sites the baseline technology for aerial photography is the use of a helicopter or fixed-wing aircraft, which is much more expensive than using model aircraft to take photographs. For small sites there is no baseline technology with which to compare.

INTELLECTUAL PROPERTY

None.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Jonathan E. Nyquist
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6317
(615) 574-4646; (615) 574-7420 FAX
email: nyq@ornl.gov

DOE Program Manager
Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

REFERENCE

1. Nyquist, J.E., "A "Model" Geophysics Program," Proceedings from the Symposium for Applications of Geophysics to Engineering and Environmental Problems, Engineering and Environmental Geophysics Society, 1994, pp. 817-824.

Sampling and Drilling

Section 10.0

DIRECTIONAL DRILLING POSITION AND LOCATING DEVICE

DESCRIPTION

A new directional drilling guidance and borehole mapping system was developed to fill a need in the penetrometer, lysimeter, and directional drilling industries. This device gives accurate position and location of the head of a sampling or drilling rod without interference from subsurface magnetic materials or depth limitations. The Position Location (POLO) technology is most highly developed for application in subsurface geologies while inserting cone-penetrometer devices. It can also be used to give a 3-D map of an existing borehole. It is not generally limited by depth. Other POLO applications outside the penetrometer field are also being pursued.

POLO operation is based on measurement of bending strains along the POLO module and relating them to the radius of curvature of the module as it is pushed through the ground. The POLO technique is analogous to navigation by dead reckoning where the course record is determined by 3-D deflection measurements combined with the known drill string length. POLO consists of a pipe section with strain dependent resistors that are connected in an initially balanced bridge circuit which produces an output voltage proportional to the strain. When the strain gages are located along the axis of a penetrometer pipe section as shown in Figure 10.1a, information on the deflection angle and radius of curvature at each push of the penetrometer pipe can be measured. As each 1 meter penetrometer pipe section is pushed into the ground, the axial strain gage array provides sufficient information to calculate the angle of deflection and radius of curvature with respect to the neutral strain axis, Figure 10.1b. This information is only sufficient to describe a 2-D position-location. The complete description of a 3-D deflection is determined by an additional circumferential strain gage array located at 60° intervals about the POLO module (Figure 10.1c). The planar deflection data is combined with the azimuthal orientation to give a 3-D position-location of the penetrometer head. The initial location and position of the penetrometer head before insertion is required and is achieved by a specially

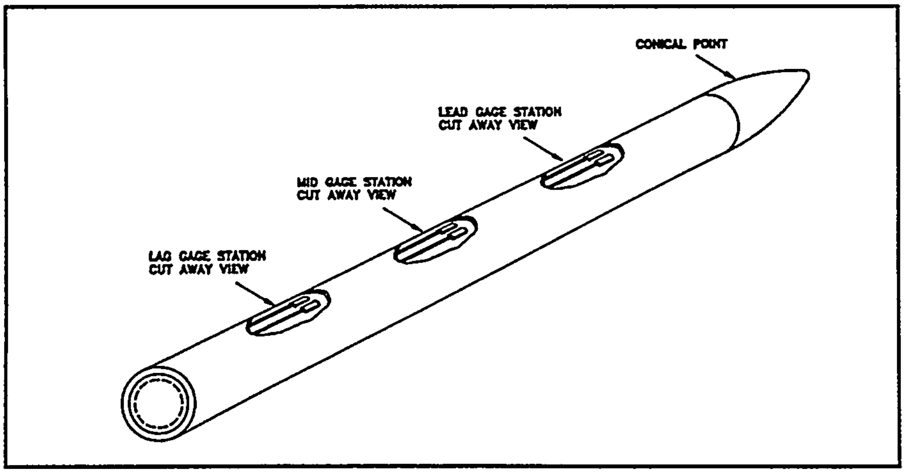


Figure 10.1a. POLO module design.

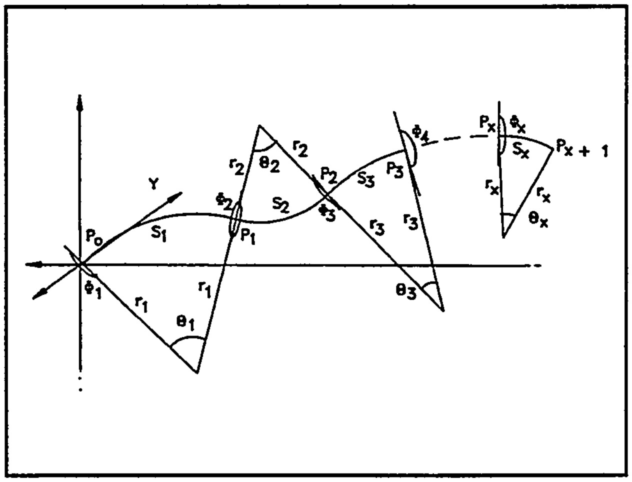


Figure 10.1b. POLO tracking algorithm.

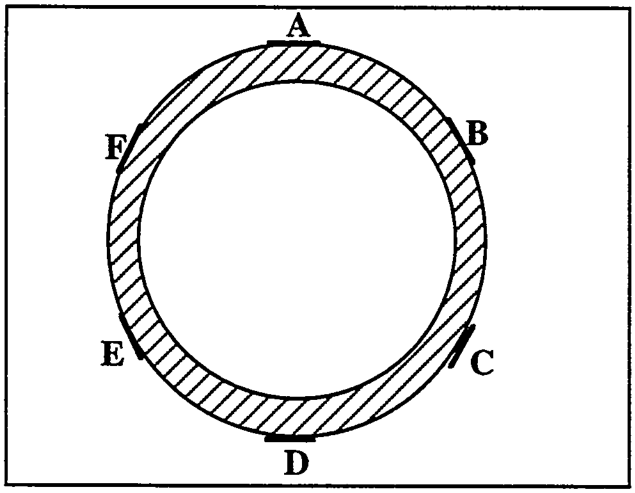


Figure 10.1c. Azimuth distribution.

designed "initializer" that provides the necessary reference frame for all POLO calculations.

In a penetrometer system, the MODULE (strain gaged rod or pipe) has several important capabilities. It: (1) maintains a uniform section modulus that approximates the stiffness of the penetrometer sections to ensure uniform bending, (2) protects the strain gages and their circuits from the environment, (3) survives in what is often a hostile environment, (4) measures the strain at several points along its axis to verify that it is bending in a true circular configuration (or some other well defined configuration), (5) is hollow so that umbilicals from sampling cones being used with POLO can pass through its center, and (6) has temperature compensated strain gages that are wired in a bridge circuit which will measure bending strain differences while remaining unaffected by axial or torsional loads.

TECHNICAL PERFORMANCE

The present POLO module has a 1.75" O.D. and a 1.0" I.D. and is instrumented with lag and lead strain gage stations, each of which employs 6 strain gages. The POLO module is capable of use in large and small diameter sizes and always has an axial hole available for umbilicals, fluid flows, or other requirements.

Experimental Verification. Field tests were conducted in two stages. The first stage was conducted in June 1994 in test areas near the home office of UTD, Inc., in northern VA. The initial field test was used to debug and refine individual components of the integrated POLO system. The second stage of field testing was conducted in July 1994 at an uncontaminated location on the Savannah River Complex (SRC) in Aiken, SC. At the field test, a series of horizontal penetrometer holes was created near the

Table 10.1a. Field test results from Virginia.

Test No.	Total Distance inches	Survey Coordinates			System Error %
		X	Y	Z	
1	276	-11.9"	272.0"	-33.8"	0.22
2	552	-85.7	529.3	-98.5	0.25
3	413	-43.9	401.3	-72.6	0.13
4	394	-20.3	386.5	-66.3	0.48(1)

(1) Survey coordinates are estimated to have errors of ± 1.0 inches based on an independent check.

Table 10.1b. Field test results from South Carolina.

Test No.	Total Distance inches	Survey Coordinates			System Error %
		X	Y	Z	
1	589.0 est	3.4"	588.0"	1.2"	0.45
2	616.2	33.9	608.4	-5.6	0.46
3	557.6	-39.3	553.2	-18.6	0.48
4	413.7	5.7	412.9	-23.7	0.36(1)

(1) Based on Savannah River Complex survey data.

surface up to 51 ft in length. An independent SRC survey crew located the penetrometer head in the ground after it reappeared at the surface. The predicted location was compared with the survey coordinates to obtain the system error. Tables 10.1a and 10.1b give representative results of the field tests in VA and SC, respectively.

Cost Data. The UTD, Inc., target selling price for a complete POLO system is $15K. Finalization of the manufacturing costs is in progress; the final selling price may change depending on the results of cost containment studies.

PROJECTED PERFORMANCE

The key near-term improvement to the technology will be to develop a user interface with graphical images of the drill path. Another key feature for future application is the development of a feedback system for guidance during complex penetrometer procedures where there are small radii or when avoidance of subsurface objects is required. Other improvements include adapting the POLO module to other directional drilling applications. The topic of a guided drill string is more complicated because POLO must be incorporated in such a way that it will permit torque and thrust to be transmitted. To do this, the module must be rugged, and the installed electronics, including umbilical cord, if used, must be capable of withstanding the shock and vibration environment of this type of drilling.

APPLICABILITY

The POLO concept was developed by UTD, Inc. as an instrument system that could accurately locate the tip of a penetrometer or the bit on a drill string. To date the emphasis has been placed on penetrometer applications. The POLO bend sensor is applicable to mapping a borehole during or after drilling using either a cone penetrometer device or some other directional drilling device. Modifications to the design may also make it applicable as a pre-failure, critical bend indicator for penetrometer rods.

STATUS

POLO development for cone penetrometer applications is nearly complete; field-scale testing was completed in July 1994. Refinements to the computer and graphical interface are being developed.

REGULATORY CONSIDERATIONS

There are no environmental impacts anticipated as a result of using the POLO technology, and the U.S. Environmental Protection Agency is aware of similar technologies. A potential regulatory barrier is the use of POLO close to structures such as underground storage tanks. Regulatory agencies may want to be involved in addressing how close POLO should be allowed to a structure. Any other regulatory considerations would be similar to those related to using penetration systems.

POTENTIAL COMMERCIAL APPLICATIONS

POLO is applicable to post-drill well mapping as well as concurrent mapping of penetrometer installed wells. The system could also be sold as a feedback system to guide well installation to a desired location. The feedback information can also provide information with respect to critical penetrometer bending for failure protection. The utility contractor directional drilling industry is another key commercial market where jobs involve both the installation of cables and pipelines, and environmental issues, all with a need for a non-depth dependent, non-magnetically influenced position location tool such as POLO. To date, however, the development of POLO for such markets is not complete. If future developments are successful, POLO can potentially be used in oil and gas exploration, geothermal drilling, installation of utility lines in residential areas, and in environmental assessment and remediation in larger wells that employ steam injection or extraction.

BASELINE TECHNOLOGY

The two general types of horizontal directional drilling guidance systems used to date are magnetometer-gyroscopic accelerometer and radio beacon systems (Sonde based locators used in the utility industry). The disadvantages of the magnetometer-accelerometer systems are that they are costly, are influenced by subsurface magnetic materials, and have excessive length which prohibits them from being used in a well-bore with a small radius of curvature. The unique advantage of the POLO technique is that it is unaffected by magnetic materials in the subsurface. POLO can be used at great depths since it does not require a constant radio link. Given POLO's size, range, immunity to electromagnetic interference, competitive price, and ease of use, POLO is more suited to rapid characterization at environmental sites where: (1) characterization is performed simultaneously with penetration, and (2) characterization adjacent to buried ferro-magnetic materials is needed.

INTELLECTUAL PROPERTY

The POLO system has been patented in the United States and foreign patents are pending. Patent Owner: UTD, Inc.; U.S. Patent No.: 5,193,628, March 16, 1993.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Eugene L. Foster
UTD, Incorporated
8560 Cinderbed Rd., Ste. 1300
Newington, VA 22122
(703)339-0800

Other Contacts at UTD, Inc.

William J. Hutzel and John Hill
UTD, Incorporated
8560 Cinderbed Rd., Ste. 1300
Newington, VA 22122
(703)339-0800

DOE Project Manager
Robert C. Bedick

Morgantown Energy Technology Center
3610 Collins Ferry Rd.
Morgantown, WV 26505
(304) 285-4505

REFERENCES

1. "Directional Drilling Guidance Systems," Horizontal News, published by Colorado Center for Environmental Management for the Department of Energy Office of Technology Development, Vol. 1, No. 1, Winter 1995.

2. Hill, J.L. III, Hutzel, W.J., and Foster, E.L., "POLO, An Entirely New System for Directional Boring Tracking," Proceedings: NASTT NO-DIG '94, North American Society for Trenchless Technology, 1994, pp. L1:2-6.

3. Hutzel, W.J., Amini, A., Foster, E.L., Nelkin, G.A., "Innovative Directional and Position Specific Sampling Technique," Proceedings of Opportunity '95-Environmental Technology Through Small Business, Sponsored by the US-DOE, METC, 1994, pp. 134-141.

4. UTD, Inc., "The UTD POLO System," Bulletin POLO-4B, September 27, 1994.

DESCRIPTION

The cone penetrometer (CPT) is a truck-mounted device that rapidly penetrates the ground to collect site data. It has been used for approximately 50 years for geotechnical applications, but its use in environmental restoration is relatively new. The cone penetrometer rod has a conical tip of up to 2" diameter. It is pushed hydraulically into the ground with a maximum pressure of 80,000 lb. The hole generated by the cone penetrometer retains the outside diameter of the rod and can be grouted as the probe is withdrawn to seal the hole and prevent groundwater contamination. As the rod progresses into the ground, a computer reads data from sensors located in both the tip and the side of the probe (for soil characterization). The cone penetrometer can monitor for contaminants as the probe is advanced or can leave monitoring points in place as the rod is withdrawn. It can advance through coarse-grained soils at a rate of 40 to 50 ft/h. The cone penetrometer is used to install characterization and monitoring points and may be able to provide chemical and radiological readings from the subsurface. Successful development, demonstration, and deployment of the system as a source-detection tool will provide more cost-effective site characterization and remediation by reducing the number of drill holes required, minimizing secondary waste, and reducing potential worker exposure to contaminated materials. Figure 10.2 is a schematic of source detection screening using the CPT.

TECHNICAL PERFORMANCE

The system requires a high level of understanding of soil and hydraulics. The cone penetrometer system functions well in a wide range of soils. It can advance through coarse-grained soil at a rate of 40 to 50 ft/h.

Demonstration. The CPT was tested at the Hanford site, Washington, from July 16 through August 6, 1992, to demonstrate the effectiveness of the CPT system in gravelly-cobblely materials while addressing the site's characterization needs. The CPT was successful in penetrating the Hanford soils. Depths ranged from 40 to 147 ft. Additional information acquired included measurement of radiation contamination and soil gas organic-vapor concentrations.

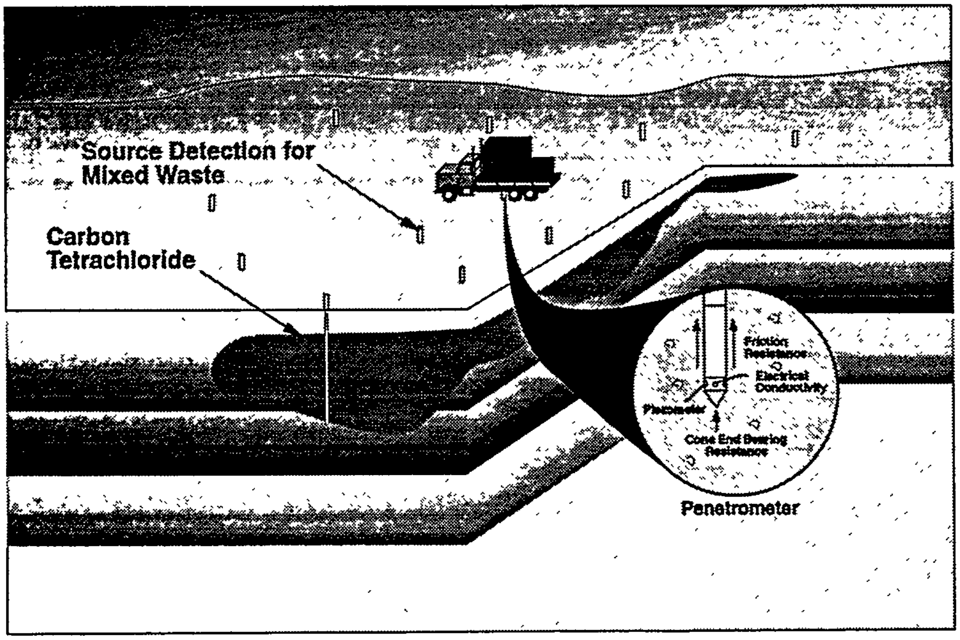


Figure 10.2. Source detection screening using the Cone Penetrometer.

The reliability of the CPT varies with soil type. When used in gravel, the CPT maintains approximately 100% reliability (minimal refusal) with two attempts in gravels to depths of 50 ft. In gravels to 100 ft the reliability drops to approximately 50 to 75%. In soft soil the CPT maintains nearly 100% reliability.

Cost. Start-up costs are $500K, operations and maintenance costs are $3K/day, and life-cycle depreciation is approximately 10 years.

PROJECTED PERFORMANCE

The cone penetrometer was adapted for full use in the gravel/cobble subsurface common to arid sites. This required increasing the weight capacity of the truck, reinforcing tools associated with the penetrometer to withstand the additional force, and evaluating the use of vibration to facilitate penetration through gravel.

APPLICABILITY

This technology is applicable at hazardous waste sites to evaluate the extent of groundwater and soil contamination. Cone penetrometers may be used to deploy many different state-of-the art line sampling and instrument devices. The CPT may be more acceptable at sites where the generation of airborne contaminants are a problem.

STATUS

CPT services are available at the DOE Hanford Site and Savannah River Site, and have been demonstrated at several other DOE sites. CPT services are also being procured by a variety of commercial clients and the U.S. Department of Defense. In addition to the specialty probes being developed and tested, research continues on the use of vibrational assistance to facilitate penetration through gravel. The status of several cone penetrometer sensors is shown in Tables 10.2a and 10.2b.

REGULATORY CONSIDERATIONS

Regulatory issues vary depending on the type of waste to be characterized. In general, regulations concerning subsurface access characterization well drilling will apply. Ecological impacts are minimal.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is very applicable for any commercial environmental characterization need. Industries such as power, fuel storage and distribution, chemical, refineries, and many others that may have soil or groundwater contamination could benefit by this rapid, extensive, and visually and economically attractive contamination site characterization technology.

Table 10.2a. Standard penetrometer probe.

1-40,000 lb Tip Load Cell	AV
0-20,000 lb Sleeve Load Cell	AV
0-500 psi Pore Pressure Transducer	AV
Equal-End-Area Friction Sleeve	AV
Pore Pressure Sensed Behind Tip	AV
Pore Pressure Sensed on Surface of Tip	AV
Two-Axis Tilt Sensor (± 15°)	AV
Calibrated Seismic Transducers in Triaxial Configuration	AV

Table 10.2b. Specialty penetrometer probe.

Electric Resistivity	AV
Soil, Water, Soil Vapor Samplers	AV
Ground Penetrating Radar (10-ft range)	PT
Active Hydrolic Conductivity	PT
Grouting Capability After Probe Withdrawl	AV
Gamma Radiation Detector	AV
Temperature Measurements	AV
In Situ Soil Density	CD
Self-Grouting	AV
Downhole Laser Induced Fluorescence	AV

AV = Available
PT = Prototype Tested
CD = Conceptual Design

BASELINE TECHNOLOGY

The baseline technology for site characterization is conventional drilling (auger or mud rotary) and laboratory characterization. The traditional approach lacks detail and precision, is slow because it requires laboratory analysis, risks cross-contamination, and is potentially hazardous (drilling in the waste site). The CPT integrated technique for site characterization: (1) is faster, using less costly procedures, (2) has minimum invasiveness, reducing cross-contamination risk, (3) gives greater detail information, except in geophysical logging, and (4) has field analytical ability and real-time data processing.

INTELLECTUAL PROPERTY

There is no patent on this technology, which has been used for geotechnical applications for the past 50 years.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Bruce R. Cassem
Westinghouse Hanford Company
MSIN N3-05
P.O. Box 1970
Richland, WA 99352
(509) 376-1007

DOE Program Manager

Rashalee Levine
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7920

Industrial Partner

Wes Bratton
Applied Research Associates, Inc.
Box 120A, Waterman Road RR1
South Royalton, VT 05068
(802) 763-8348; FAX (802) 763-8283

REFERENCES

1. Applied Research Associates, Inc., "CPT-LIF Investigation of LUST Contamination at Tinker AFB, Oklahoma," Unpublished ARA Report, 1993.

2. Applied Research Associates, Inc., "Synergistic 3-D Site Characterization," collection of presentation graphics, Unpublished ARA Report, 1993.

3. Applied Research Association, Inc., "ARA Southwest Division, Environmental Capabilities," Unpublished ARA Report, 1993.

4. DOE-RL, "Technology Information Profile (Rev. 3), Technical Name: Cone Penetrometer," DOE ProTech Database, TTP Reference Number: 421103, March 29, 1993.

DESCRIPTION

The Hybrid Directional Boring and Logging (HDBL) system was developed for cost-effective, high-quality access to an otherwise inaccessible contaminated subsurface for site characterization and sensor emplacement. Figure 10.3a illustrates the horizontal/directional drilling concept. The directional boring technology is an adaptation of existing hardware from various underground industries, primarily from the underground utilities industry.

Hardware integrated for the directional-boring facet of this technology includes wireline coring rigs, hydraulic thrust systems, electric cone penetrometers, steering-tracking hardware, and push-coring systems. Hydraulically activated thrust equipment capable of exerting more than 40 tons of thrust is used to push the directional boring heads into the earth. Directional control is obtained by proper positioning of the face of the nonsymmetric boring head. Slow rotation of the boring head will cut and compact the geologic material into the borehole wall. Thrusting a boring head that is not rotating will cause a directional change. The machinery is capable of initiating a borehole, steering down to a desired horizontal depth, continuing at that depth, and then steering back to the surface at a down-range location. This directional boring technology is desirable for environmental applications because the access method requires very minimal addition of fluids and very little soil removal during the drilling process.

Various logging and sampling technologies could be adapted, such as gamma and spectral gamma sensors, resistivity, mass spectrometry, fiber-optic fluorescence, pore pressure, soil moisture, temperature, volatiles sampling (contaminant vapors), and a sidewall coring/soil sampling apparatus (second generation). In addition, various methods to emplace monitoring equipment could be developed including a pneumatic hammer technology for sleeve emplacement. A key function of the sampling hybrid concept is to provide multiple discrete samples per run. It has the potential to recover pristine samples; moreover, it can be used to develop an inexpensive grid of horizontal wells in an otherwise inaccessible subsurface for contamination characterization, plume monitoring, and remediation verification.

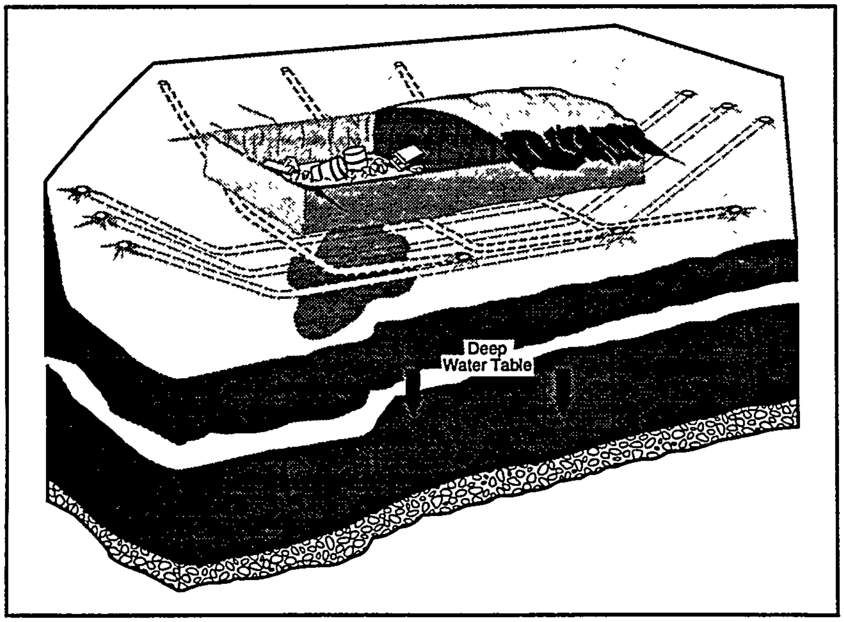


Figure 10.3a. Horizontal/Directional Drilling concept.

The following are important technical issues that must be considered by potential users of the technology.

Geology Dependency. Equipment that cuts and compacts the cuttings works best in soils that are homogeneous without rocks and cobbles. These soils are typically clays and cemented sand/gravel formations. Formations containing very wet sands or fine dry non-cemented sands are easy to penetrate, but provide very little wall stability for buttressing steering control forces. These formations tend to collapse on the drill string preventing any forward or rearward movement. Widely heterogeneous formations such as alluvial fills with caliche, sand, gravel, cobbles, and boulders are very difficult to penetrate/cut and to control steering. Wall stability, either naturally occurring or resulting from compaction by the boring head, plays a large role in the success or failure of a boring operation.

Onboard Position Tracking. A low-cost ($12K) 2-axis magnetometer-accelerometer type wireline guidance package used in the river-crossing industry was used. This equipment is less sophisticated than systems used on larger rigs, but was adequate for development testing. The guidance system used was subjected to the severe environments of frictional and torsional/longitudinal vibration caused by the drilling process. Charles Machine Works Inc. (CMW), in partnership with a major manufacturer of steering tools, has developed a more sophisticated steering tool package that will be tailored to the shallow boring market.

Bits and Steering Faces. Cutting and successful compaction of the cuttings occurs over a short horizontal distance, and mechanical wear is severe. A key improvement in cutting, compacting, steering, and borehole stability was attained when a small amount of water (2 to 5 gal/min) was added to cool and lubricate the bit/drill string, cool the locating electronics, and aid in compaction of the cuttings on the borehole wall.

Wellbore Completion Hardware. After the wellbore is drilled at some nominal diameter (3 to 5 in), the wellbore is typically reamed to a larger diameter (6 in) to accommodate the pullback of a 4.5 inch diameter casing/screen string. Each reaming pass from the exit portal to entry portal can take as long as the original boring operation. The reamers must enlarge the borehole diameter, then compact and stabilize the cuttings in the borehole wall. This operation may require as much as 10 gpm (typically 5 gpm) of potable water. Several reamer passes may be required in alluvial type soils. After the reaming is complete, a pullback hardware string is assembled for the casing pull. This hardware string is typically composed of the reamer in front, followed by a swivel, a slip link, a pulling plug, and the casing. This is a very critical part of the well emplacement, fraught with potential problems.

Casing Materials. Casing/screen materials are commercially available for vertical environmental wells. When this material is used in directional wells, the combined vertical stresses, mechanical loading, and abrasive environment that affect it are much different and more severe than those encountered in vertical wells. Materials being considered for casing in horizontal boreholes comprise a cost spectrum from $4/ft of HDPE utility conduit to $20/ft of high-strength fiberglass tubing. Screen materials can be more expensive because of the slots, perforations, or gravel packs that may be required. The material choice can be critical to installation success or failure. Site geology is a controlling factor. Higher-strength fiberglass casing was used successfully in this project.

TECHNICAL PERFORMANCE

Two major successful tests at the Savannah River Site (SRS) in South Carolina and at the Sandia National Laboratories (SNL) RB-11 site located at the Kirtland Air Force Base in New Mexico, which have different geologies, demonstrated that this hybrid technology adapted from the underground utilities industry has many potential cost-effective applications for environmental work. A major test at the Hanford site in Washington had limited success and demonstrated that the technology will not be applicable to all geologies.

SRS Field Tests. The first test of the X-810 boring machine was performed at the SRS M-Area. Testing of directional boring for monitoring-equipment installation was performed at the Savannah River Site (SRS) in an actual contamination zone during the summer of 1992. This test used onboard electronics from the river-crossing industry, new-generation bits/reamers/casing pulling plugs, and several new types of environmental casing/screening materials, and was highly successful. The test provided preliminary data, hardware confirmation, and a 570 ft long, 40 ft deep, 3 in diameter (see Figure 10.3b), fiberglass-cased environmental well for Savannah River Radio Frequency soil heating tests. The soils at the site are coastal-plain sediments consisting mostly of dense clays and sands.

Hanford Tests. The limits of the X-810 boring machine were tested at the Hanford site in Washington during March 1993. This test provided additional thrust data and evaluated steering control in loose cobbles and gravels of the glacial till. The glacial till was the most difficult formation encountered during development testing and limited the success in cutting, compaction, steering, and casing emplacement. Additional testing at another Hanford location using the standard P-80™ rod pusher with soil samples was successful from the standpoint of steering control and the ability to collect interstitial uncemented sand samples. A Pierce-Airrow™ 4 in diameter pneumatic piercing tool was also relatively successful in penetrating the Hanford formation in a very qualitative test.

RB-11 Tests. The prototype was again used in FY 1993 to emplace a 410 ft well at a depth of 33 ft at SNL. The RB-11 operation helped to define acceptable, but not optimal, reamer designs for shallow directional boring. Several iterations caused by reamer hardware wear and breakage allowed researchers to try new geometries and materials that ultimately proved successful. The test provided additional data on machinery capabilities and hardware designs.

Costs. Drilling costs in the range of $25 to $75/ft (excluding the cost of casing/screen materials) were experienced during developmental testing. Cost effectiveness encompasses many variables: (1) time necessary to drill and complete a borehole with appropriate casing/screen, (2) the crew size necessary to operate the rig effectively and safely, (3) transportation costs of the machinery to the site, (4) the field support needed by cranes, excavators, backhoes, welders, etc., (5) completed borehole dimensions (length, depth, diameter), (6) the type of casing/screening required for completion, and (7) the sophistication/cost of steering tools.

PROJECTED PERFORMANCE

CMW is continuing with design work, testing, and evaluation of the wellbore completion hardware. Other goals are to log multiple discrete soil samples per run and to integrate various instrumentation and sensing packages into the boring hardware.

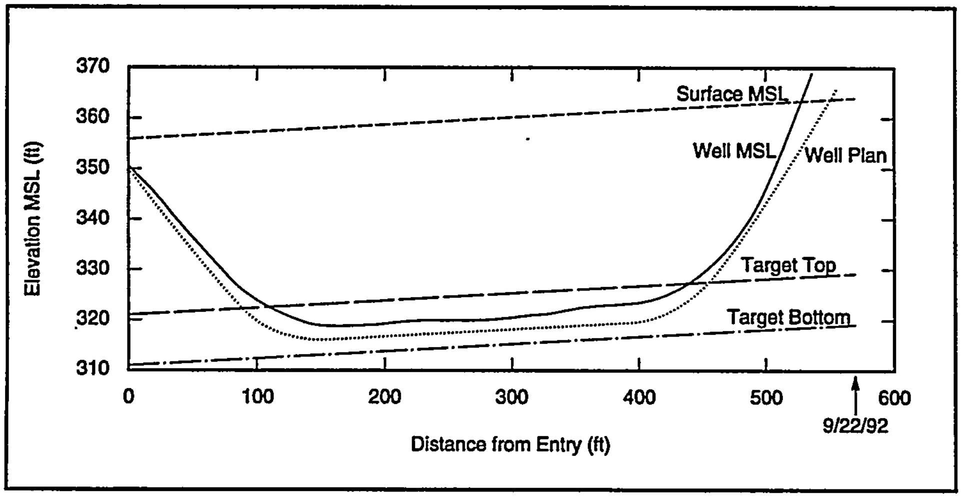


Figure 10.3b. Savannah River Site M-Area. Elevations are given with respect to mean sea level (MSL).

APPLICABILITY

The HDBL technology provides access to the subsurface for characterization and monitoring activities in a wide variety of geologies.

STATUS

The project is being completed in FY 1995; however, there are tasks in sampler development that have not been completed. CMW is developing the technology to a commercial product level with private capital and has formally entered the environmental boring machinery market.

A recent partnership with SNL and CERL Inc., an environmental engineering firm in Santa Fe, NM, was established to evaluate shallow directional drilling as a remediation technology for radon in public buildings.

REGULATORY CONSIDERATIONS

The secondary process waste of this drilling technology is kept to a minimum by using only a small amount of water for drilling and electronics cooling. Cuttings are compacted into the formation with very little returned to the surface. Various drilling and safety regulations apply, depending on the type of contaminant in the soil.

Current regulations do not cover directional work; however, work plans submitted to a state regulatory agency may require a discussion of the differences between the directional drilling versus vertical drilling to assure that groundwater is protected and that well completions would be constructed in such a way as to protect against surface water infiltration around the casing. Ultimately, changing or adding to the current drilling regulations to recognize and allow directional boring as an optimal technology for environmental site characterization, monitoring, and remediation will be required.

POTENTIAL COMMERCIAL APPLICATIONS

The environmental monitoring, sensing, and characterization applications are useful to many industries (i.e., steel, aluminum, petrochemical refining, fertilizer, plastics, heavy and light manufacturing, etc.) that may have a shallow contaminant plume. Fuel storage and small fuel distribution sites such as local gas stations may also find the technology more cost effective for in situ sampling and monitoring than current methods. The hybrid technology can be used economically by many industries to characterize, remediate, or monitor contamination. In addition, the parent underground utilities installation industry can benefit from this development work by the future availability of machinery with enhanced capabilities.

This technology could contribute to cost-effective characterization and remediation/ventilation beneath occupied buildings in regions where natural radon gas infiltration has occurred.

BASELINE TECHNOLOGY

A baseline technology might be any larger directional-boring and drilling rigs adapted from the oil, gas, and river-crossing industries. The larger-equipment technologies are much more expensive ($300/ft of well bore compared to $20 to $75/ft with HDBL) for directional drilling applications and may not be appropriate for use at shallow depths.

INTELLECTUAL PROPERTY

Several patent disclosures have been made as follows:

SNL: "Sampler Latch Mechanism," R.D. Meyer, 1992; and, "Multi-Sample Sampler," R. P. Wemple and R.D. Striker, 1992.

CMW: " Bit and Reamer Designs," (a total of three applied for in FY 1992 and FY 1993).

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator

Robert P. Wemple
Sandia National Laboratories
Department 6111, MS 1033
P.O. Box 5800
Albuquerque, NM 87185-1033
(505) 844-2230; FAX (505) 844-3952

DOE Program Manager

Skip Chamberlain
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

Industrial Partner

R. R. Layne
New Product Research and Development
Charles Machine Works Inc. (TM-Ditch Witch)
P.O. Box 66
Perry, OK 73077-006
(405) 336-3591; FAX (405) 336-5452

REFERENCES

1. Wemple, R.P., R.D. Meyer, G.E. Staller, and R.R. Layne, Final Report for SNL/NM Environmental Drilling Project, Sandia National Laboratories, NM, SAND94-2388, November 1994.

2. Wemple, R.P., R.D. Meyer, and R.R. Layne, Interim Report for SNL/NM Environmental Drilling Project, Sandia National Laboratories, NM, SAND93-3884, March 1994.

3. Staller, G.E., R.P. Wemple, and R.R. Layne, Casing Pull Tests for Directionally Drilled Environmental Wells, Sandia National Laboratories, NM, SAND94-2387, 1994.

4. Westmoreland, J., Evaluation of an Air Drilling Cuttings Containment System, Sandia National Laboratories, NM, SAND94-0214, 1994.

5. Wemple, R.P., R.D. Meyer, R.D. Jacobson, R.R. Layne, "Continued Development of Hybrid Directional Boring Technology and New Horizontal Logging Development for Characterization, Monitoring and Instrument Emplacement at Environmental Sites," 7th Annual DOE Model Conference on Waste Management and Environmental Restoration, Oak Ridge, TN, October 1991.

MINIATURE PUMPS FOR THE CONE PENETROMETER

DESCRIPTION

Miniature pumps are being developed by the Savannah River Technology Center (SRTC) for use with Cone Penetrometer Technology (CPT) probes to obtain groundwater samples. At present, available commercial samplers for use with CPT are cumbersome and subject to routine operational failures. Use of these samplers requires removal of all cone penetrometer push rods from the ground to deploy the bailer type of sampler. Depending on the depth of investigation, this process can take several hours, and each sample requires that the sampler be deployed to depth and be retrieved for sample collection at the surface. The miniature pumps being developed eliminate most of the problems associated with water sampling by the Cone Penetrometer.

Miniature pumps installed at the tip of a cone penetrometer allow depth discrete semicontinuous sampling of groundwater during a cone penetrometer push. By installing these pumps in the cone penetrometer, the need to exit and reenter the hole is eliminated resulting in a significant time savings (30 to 60 min) for each sample collected. Two types of miniature pumps are being developed and tested (see Figure 10.4). The first is a gas lift pump called the Cone Sipper™ that uses alternating vacuum/pressure and miniature valves to move liquid or gas samples. The second design is a miniature positive displacement pump that uses water as a hydraulic fluid to actuate the piston. Use of these pumps will allow collection of representative groundwater samples required by environmental regulations without requiring installation of monitoring wells. Because samples can be collected without having to remove the penetrometer, the number of samples can be increased. As a result, the accuracy of a site's subsurface conceptual model of contaminant distribution will improve significantly.

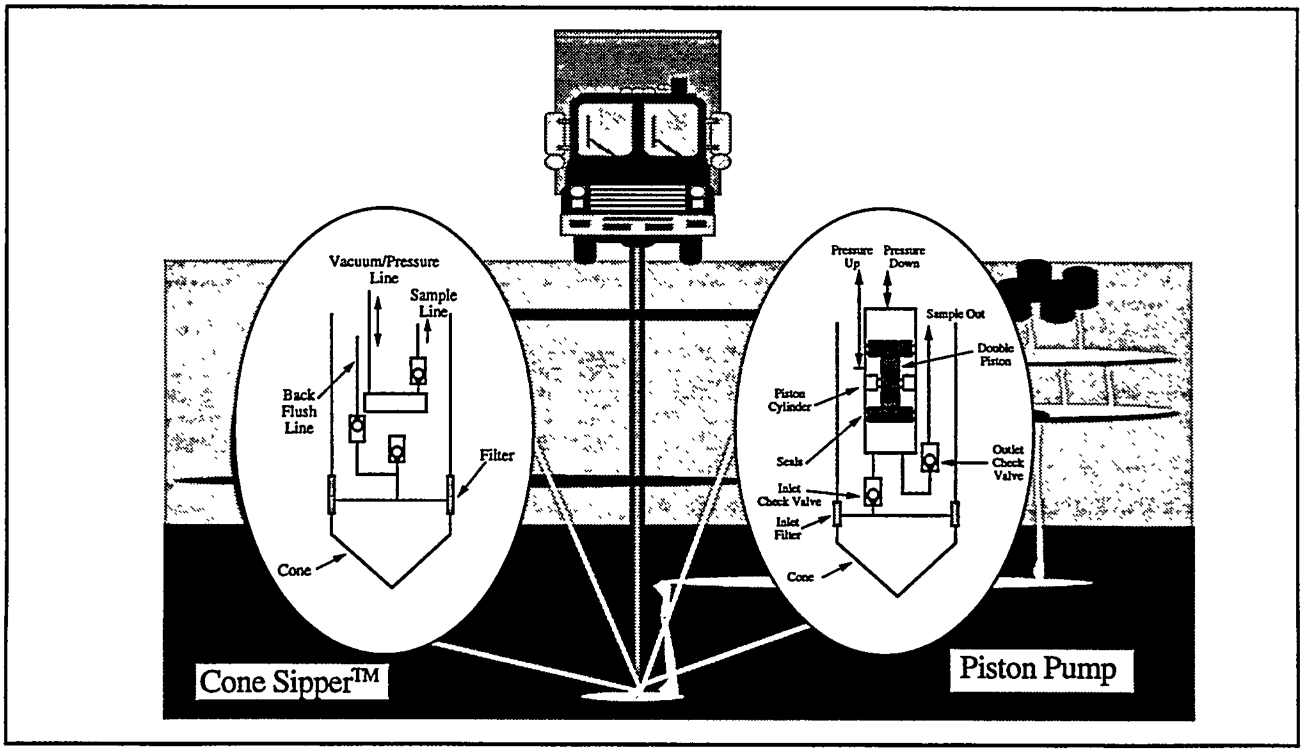


Figure 10.4. Miniature Sampling Pumps for the Cone Penetrometer.

Gas Lift Pump-Cone Sipper™. The Environmental Sciences section of SRTC has patented a design for a miniature sample pump based on a gas lift principal. The first version of this pump (not shown) incorporated a single electrically operated valve on the sample inlet line. This design was shown to be capable of delivering a sample from a depth of 180 ft below ground surface when it was tested in a hollow penetrometer body at Savannah Rivers Site (SRS). The initial results indicated that design changes could be made to improve the reliability and sample integrity. Subsequently, a second version was developed (shown in Figure 10.4) which functions by pulling a slight vacuum on the vacuum/pressure line that will draw the groundwater in through the filter on the outer edge of the penetrometer body. The vacuum is held until the chamber is full. The vacuum is replaced by pressure, usually nitrogen or air, and the sample trapped in the chamber is gently blown to the surface through the sample line. After the desired sample is obtained, the sampling system and associated tubing can be flushed by using pure water and/or gases pushed down through the backflush line. The check valve in the back flush line has a high cracking pressure compared to the sample inlet and outlet check valves so it stays closed during normal sampling operations.

Miniature Piston Pump. The Sensor and Analyzer Technology Group of SRTC has patented a second design of a miniature pump based on a small, double acting piston. The initial tests of this concept were conducted with a single piston design, and a spring was used for the return power stroke. The pump was tested at the SRS in existing wells at depths up to 40 ft, but further developments showed that the spring pressure method was not the most reliable way to provide return action for the piston. Design enhancements resulted in the double acting piston arrangement as shown in Figure 10.4. The pump operates from hydraulic pressures supplied by either a hand pump using pure water or a motor driven positive displacement pump with appropriate valving. Alternating hydraulic pressure is used to force the piston up and down while the sample is drawn in through the outlet tubing and brought to the surface. The sample outlet check valve prevents the sample from back flowing into the piston chamber. This design has been operated at SRS in existing wells at depths up to 130 ft.

TECHNICAL PERFORMANCE

The second Gas-Lift Cone Sipper™ design was turned over to a commercial partner, Applied Research Associates, Inc., for their design evaluation. ARA's interest in the pump resulted in their own design modifications to the Cone Sipper™ built into a penetrometer tip section and tested at their Vermont home office. Since their initial redesign and test, they have developed two more modified designs with one being used while performing work for Argonne National Labs at a test site in West Virginia.

Both pumps were evaluated in 500 ft deep existing wells at SRS that provided various levels of volatile organics (see Table 10.4).

The initial results from these tests indicated that operating parameters for flushing and cleaning the sample lines and chamber need to be refined. The volume of clean water required to wash the cell and tubing is estimated to be greater than or equal to 3 times the 80 ml cell volume. These operating changes were made and further tests were conducted in late April 1995.

Cost. As design modifications are ongoing, cost estimates were not available for this writing.

PROJECTED PERFORMANCE

Future work for both pumping concepts includes the establishment of operating parameters. There is a limit on the level of vacuum that can be pulled on the sample chamber for the Cone Sipper™ as well as the upper pressure for blowing the sample to the surface without affecting the sample integrity (chemistry). In addition, the choice of tubing materials is critical to maintaining sample integrity. Similar perfor-

Table 10.4. Preliminary data from wells.

Well ID; Contaminant	**Bailer Conc. (mg/L)**	**Sipper Conc. (mg/L)**	**Bailer Conc. (mg/L)**	**Piston Conc. (mg/L)**
MHT 1D; PCE	0.07	0.07	0.05	0.03
MHT 1D; TCE	0.27	0.25	0.17	0.15
MHT 4D; PCE	0.51	0.40	0.34	0.18
MHT 4D; TCE	2.67	2.08	1.51	1.00
MHT 6D; PCE	0.01	0.01	0.01	0.01
MHT 6D; TCE	0.34	0.31	0.19	0.18
MHT 8D; PCE	0.15	0.10	0.10	0.07
MHT 8D; TCE	0.55	0.47	0.34	0.30

mance criteria will exist for the piston pump. A series of tests are being planned to establish this data by using standard samples and elevated towers to simulate well depths.

APPLICABILITY

The two concepts for miniature pumps are intended for use with a Cone Penetrometer device. Groundwater sampling is the application. The intent is to be able to take multiple samples during subsurface investigations using a Cone Penetrometer (CP) as well as to allow monitoring once the well is in place. Samples are acquired without removing the CP rods.

STATUS

This technology is in the laboratory/field scale prototype design iteration phase of development. Prototype versions of both pump designs are assembled and have demonstrated proof of concept. Future work will be focused on improving pump designs and testing for field application. Pump performance under various conditions, like water depth, particulate loading, and solvent contamination, will be evaluated to identify design improvement needs.

REGULATORY CONSIDERATIONS

Tests are also being planned to demonstrate the pumps' ability to provide representative samples of regulated contaminants in groundwater.

Local regulators are aware of this technology and are awaiting field test results and methods development.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is applicable to many commercial environmental characterization needs. Industries such as power, fuel storage and distribution, chemical, refineries, and many other that may have soil or groundwater contamination could benefit from it.

BASELINE TECHNOLOGY

The baseline technology for groundwater sampling is to install monitoring wells and obtain groundwater samples using a bailing device.

INTELLECTUAL PROPERTY

Patents are applied for, but the process is not complete.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigators

Jerry McCarty (Piston Pump)
Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, SC 29808
(803) 725-4650

Joe Rossabi and Brad Pemberton (Cone Sipper™)
Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, SC 29808
(803) 725-5220 and (803) 725-5182

DOE Projects Manager, CMST-CP

Eric Lightner
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7935

Industrial Partner

Wes Bratton
Applied Research Associates, Inc.
Box 120A, Waterman Road RR1
South Royalton, VT 05068
(802) 763-8348; FAX (802) 763-8283

REFERENCES

None.

RESONANTSONIC^{SM} DRILLING

DESCRIPTION

ResonantSonic^{SM} drilling is being used in the environmental industry to drill faster, cheaper, and more safely than conventional drilling methodologies. ResonantSonic^{SM} is a registered service mark of the Water Development Corporation (WDC), Woodland, California. The ResonantSonic^{SM} drilling method commonly requires no drilling mud, air, or water for rapid penetration through geologic materials ranging from clay to sand and boulders.

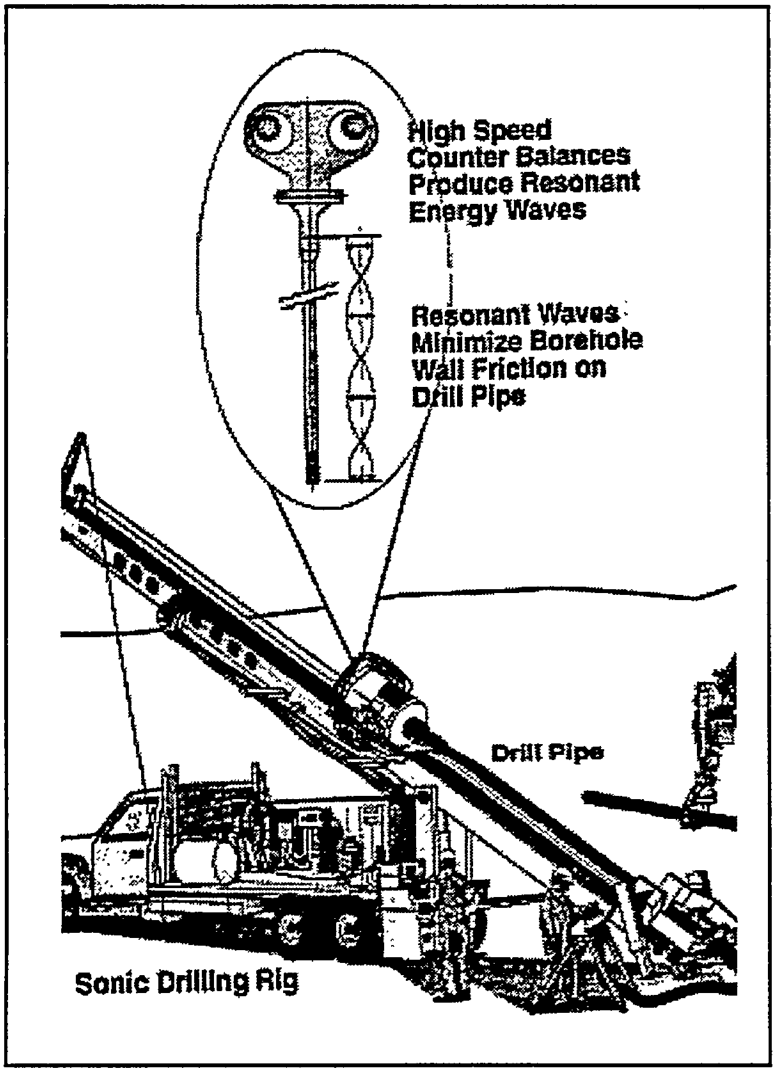


Figure 10.5a. Schematic of ResonantSonic^{SM} Drilling.

The ResonantSonic^{SM} drilling system (Figure 10.5a) uses a combination of mechanically generated vibrations and rotary power to penetrate the soil. The oscillator, or drill head, consists of two counter-rotating rollers that cause the drill pipe to vibrate. The rollers are synchronized to ensure that the vertical force component is transmitted downward through the drill pipe or core barrel (Figure 10.5b). The vibrations are isolated from the rig structure by an air spring. When the drill pipe is in resonance, the maximum displacement of the pipe (a function of its elasticity) is occurring. Resonance is the term used to describe the condition when the frequency of the vibrations is equal to the natural frequency of the drill pipe.

The vibration of the drill pipe coupled with the weight of the drill pipe and downward thrust of the drill head, allows for penetration of the formation. Concurrent with the resonant energy, the drill head can be rotated to assist in formation penetration and to ensure that the formation is always adjacent to the cutting surfaces of the drill bit. The vibrations generated in the drill string by the sonic drill range from 0 to 150 Hz and create up to 91,000 kg (200,000 lb) of force depending on the size of the drill head and power to the unit.

As the rotation and vibrational energy is generated, the drill pipe advances into the ground because the vibrational component literally causes the formation to yield beneath the drill bit. The drill string advances using minimal force that is applied hydraulically with the drill head. The drill rig can generate a maximum of 4,500 kg (10,000 lbs) of thrust; however, rapid penetration rates are commonly achieved with less than 450 kg (1,000 lbs)

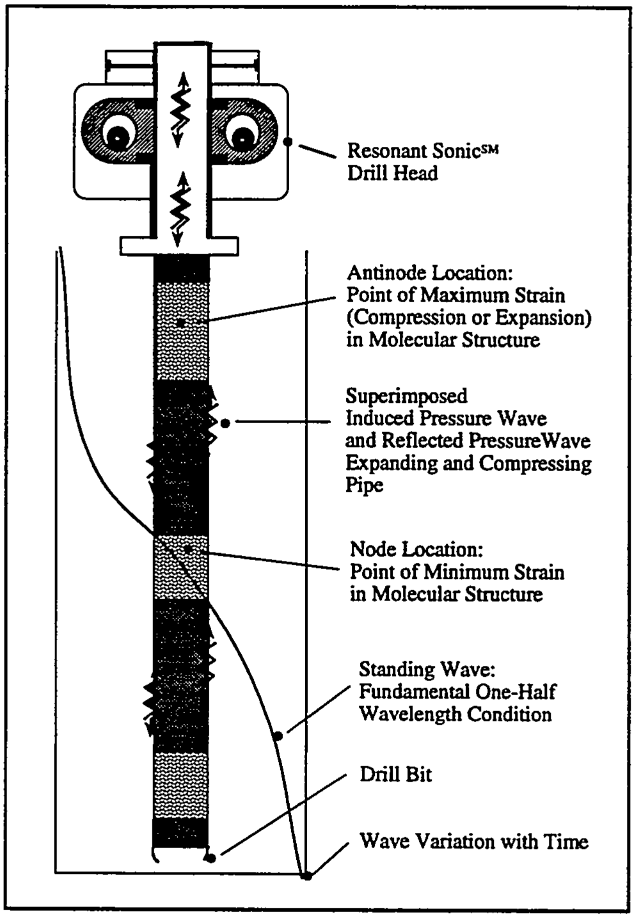


Figure 10.5b. ResonantSonic^{SM} energy.

of downward thrust. The resonant energy emitted along the length of the drill pipe substantially reduces the amount of friction between the drill pipe and the borehole wall.

As the hole is advanced, additional sections of the drill pipe (typically 5 to 10 ft lengths) are added and drilling continues. The soil enters the drill string through an open-face (core-type) drill bit and is contained in an inner core tube. Larger diameter casing is advanced sequentially (commonly every 10 ft) with the drill pipe.

A continuous core of the formation is commonly obtained without the use of a circulation media (e.g., fluid or air). As is common with a core drilling process, the length of the core retrieved each time is dependent on the stability of the formations encountered. Using the ResonantSonic^{SM} method, the length of the core retrieved is frequently greater (core growth) than the distance drilled, because of the displacement of the soil to the path of least resistance. Borehole integrity is maintained by the drill casing that remains in the ground while the coring string is removed.

Because of the high forces developed by the resonant drill head and the external flush nature of the drill pipe, formation material displaced by the cutting face of the bit is forced either into the borehole wall or into the core barrel. Thus, no cuttings are generated in the drilling process. In order to enhance core quality, little, if any, rotation of the drill rods is used in this method.

TECHNICAL PERFORMANCE

Sonic drilling generally produces only the cored sample, and holes are drilled at double the baseline rate.

This technology was successfully applied to continuous coring, monitoring well construction, and horizontal drilling activities. A demonstration of the improved system, with a feedback control system to help mitigate pipe failure and component redesign for improved reliability and more rapid access, is planned.

Drill Head. Depending on the size of the sonic head, dynamic force output is 30,000 lb at 120 Hz. Power input ranges from 150 to 800 HP. Rotational torque ranges from 25,500 to 40,000 in-lb. Rotational speed is variable from 0 to 60 rpm.

Drill Rig. Vertical (90°) to horizontal (0°) drilling capabilities are available.

Speed of Drilling. The penetration rate of the sonic drill varies depending on the type of formation being cut. Speeds from 1 ft/s to 0.5 ft/min are encountered when drilling loose to compact formations.

Formations. It drills any type of formation: alluvium, sands, clays, cobbles, boulders, bedrock, permafrost, caliche, and other types of formations, including landfills. It is able to drill through metals, garbage, tires, wood, and concrete.

Cost/Benefits. A recent cost study revealed a 30% - 50% reduction in cost as compared to cable tool drilling.

A cost comparison was conducted between the cable tool and ResonantSonic^{SM} methods. Because of variability in geology and sampling requirements on individual holes, an exact comparison was not feasible. To provide a fair comparison, cable tool costs presented are established baseline costs from numerous holes using this drilling method. Cable tool drilling costs at the Hanford Site, as a typical hazardous waste site, was $441/ft (Booth and Masten, 1994).

WDC's multipurpose environmental drill (XT-70E) was used to install the ResonantSonic^{SM} drilled wells. The ResonantSonic^{SM} method, used in conjunction with the Guzzler^{TM} Containment System, drilled three 28 cm (11 in) diameter holes in excess of 91 m (300 ft). These tests were conducted at the In-Situ Bioremediation Demonstration Site located in the 200 West Area of the Hanford Site in Richland, Washington.

Well installation costs at the Bioremediation Site using the ResonantSonic^{SM} method were $253/ft, resulting in a cost savings of $188/ft (42%). This reduces drilling and direct labor costs by over $58,000 for a standard 300 ft deep well installation. In addition, time savings were also possible. Drilling and well completion with the multipurpose ResonantSonic^{SM} drill rig averaged 12 days (10 days drilling, 2 days for well completion) on the final two wells compared to 32 days (20 days drilling, 12 days for well completion) for cable tool (baseline) drilling rates.

PROJECTED PERFORMANCE

With the refinement of the sonic head, drill pipe, sampling tools, and core catchers, it is projected that the downtime can be reduced to less than 10%, which results in a substantial reduction in drilling costs.

APPLICABILITY

This technology is applicable for monitoring wells, vadose-zone soil-gas sampling, neutron-probe pipe installation, core sampling, and injection and extraction wells for bioremediation and/or air stripping/ vacuum extraction remediation projects. Additionally, in most conditions, closed-end tubes can be resonated into the ground to significant depths to yield no cuttings or core and to take discrete water samples or in situ cores.

STATUS

The ResonantSonic^{SM} method has been used for projects ranging from pile driving to horizontal drilling. Current programs are using the technique as a valuable tool for obtaining in situ, pristine environmental samples. In the future, this drilling technology could be used for remote, automated sampling at hazardous waste sites.

The ResonantSonic^{SM} technology was first developed in the 1950s by Albert Bodine, Jr. Mr. Bodine discovered how to design and build a machine that would generate high-frequency vibrations with very high-force output that would not self-destruct while passing the vibrations on to the object being resonated. In the 1970s and 1980s, Hawker Siddeley, Ltd., in Canada, made further advances to the patented drilling head and built several rigs for field application. In the 40 years since its invention, traditional sonic drilling equipment has been underused, suffered reliability problems as a system, and had difficulty being accepted in the marketplace.

The Department of Energy (DOE) Office of Science and Technology, and its contractors Westinghouse Hanford Company (Westinghouse Hanford), PNL, and industry partner WDC, through a CRADA, are developing improvements to the ResonantSonic^{SM} drilling technology to enhance environmental cleanup efforts at DOE sites.

REGULATORY CONSIDERATIONS

Drilling and subsurface access regulations may vary, depending on waste-site characteristics. Ecological impacts are minimized or eliminated by the absence of secondary waste streams. Occupational Safety and Health Administration (OSHA) regulations apply for drilling equipment operation, high noise levels, and potential contaminant exposure.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be applied to environmental drilling, natural-gas wells, geothermal wells, and oil well drilling. It is also useful to industries that may have soil or groundwater contamination problems. Rapid access to the subsurface, without excess soil removal or secondary waste streams, is economically desirable for such industries to determine the scope of the problem and to remediate the contamination. This method of continuous core removal is useful for other geologic studies and to the mining industry.

BASELINE TECHNOLOGY

Baseline drilling methods include hollow-stem auger and cable-tool methods that are commonly used for environmental characterization at Hanford. Results indicate a 3-fold increase in penetration rates.

INTELLECTUAL PROPERTY

U.S. patents for ResonantSonic^{SM} Drilling technologies are held by the WDC. Patent numbers are available from the technology developer, WDC.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Greg W. McLellan
Westinghouse Hanford Company
MSIN N3-05
P.O. Box 1970
Richland, WA 99352
(509) 373-7539

DOE Program Manager
Rashalee Levine
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7920

Industrial Partner
Jeffrey Barrow
Water Development Corporation
1202 Kentucky Avenue
Woodland, CA 95776
(916) 662-2829

REFERENCE

1. Volk, B.W., G.W. McLellan, D.J. Moak, R.E. Lerch, K.M. Thompson, and J.C. Barrow, ResonantSonic Drilling: History, Progress and Advances in Environmental Restoration Programs, WHC-SA-1949-FP, Westinghouse Hanford Company, Richland, WA, September 1993.

SEAMIST™ BOREHOLE INSTRUMENTATION AND FLUID SAMPLING SYSTEM

DESCRIPTION

SEAMIST™ is an instrumentation and fluid sampler emplacement technique designed for in situ characterization and monitoring. It uses an inverting, pneumatically deployed tubular membrane (impermeable material) to install sampling devices and instruments in boreholes (see Figure 10.6).

The membrane is forced into a drilled or punched well by air pressure. The membrane descends, inverts, and presses against the hole wall, providing wall support and the effect of a continuous packer. After emplacement, the entire hole wall is sealed, thus preventing ventilation of the pore space or circulation of pore water in the well. The membrane can be retrieved from the hole.

Monitoring instruments and pore fluid sampling devices are placed on the outer surface of the membrane, where they will be in contact with the hole wall. The membrane isolates each measurement location. Emplacement has been demonstrated for vertical, horizontal, and crooked or partially obstructed holes. Instruments or samplers are not dragged along the hole wall at any time.

Permanent installation of the membrane is possible by filling the membrane with grout after emplacement. Semi-permanent installation can be accomplished by filling the membrane with sand after emplacement.

The membrane can be applied to perform vadose-zone pore and fracture liquid sampling through the use of absorbent pads. Electrical resistance measurements inside the pads indicate moisture uptake. By attaching an array of absorbent pads to the membrane, high spatial resolution of the contaminant distribution is possible.

Extraction of soil-gas samples from a hole can be accomplished via tubes to surface sample collectors or Getters (such as activated-charcoal absorbers) can be attached to the membrane surface to absorb contaminants. A hybrid concept is to pull a gas sample through a charcoal filter positioned at the sampling point.

Air-permeability distribution within a soil matrix can be measured by emplacement of a membrane with several gas-sampling ports. As the gas is pulled from one port to the surface, its flow rate and measured pressure response at the adjacent ports imply a local permeability distribution.

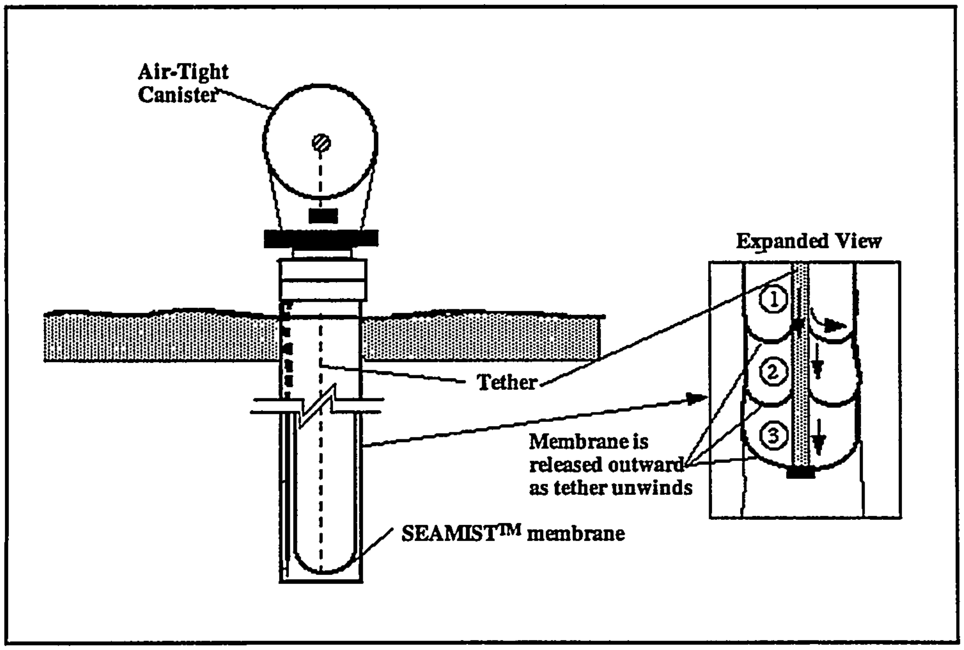


Figure 10.6. SEAMIST™ Emplacement System.

Additional instruments can be applied, including temperature sensors, thermocouple psychrometers, and fiber-optic sensors. Colorimetric materials can be used for visual indications of contaminant distribution.

TECHNICAL PERFORMANCE

Tritium Plume Monitoring. Two systems installed at Lawrence Livermore National Laboratory (LLNL) in 1991 are tracking the movement/concentrations of a tritiated water plume (vapor and liquid-water sampling) to 40 ft depths.

Carbon Tetrachloride Monitoring. Two emplacement systems with disposable membrane liners are in use at Hanford for carbon tetrachloride plume monitoring.

Fracture Flow Mapping and Rate Measurement. Membranes coated with liquid-indicating and wicking layers were used to map and measure brine flows underground at the Waste Isolation Pilot Plant (WIPP).

Tritium and VOC Sampling. The SEAMIST™ system transported vapor-sampling tubes and absorbent collectors 230 ft horizontally beneath an old radioactive-waste landfill at Los Alamos National Laboratory (LANL).

SNL Chemical Waste Landfill (CWL). The SEAMIST™ system transported logging tools and cameras in horizontal boreholes of up to 230 ft length and 1.75 to 4.0 in. diameters. It performed gas-sampling and permeability measurements in two boreholes of 11.5 in. diameter and 110 ft depth immediately after augering in SNL's CWL. It installed three borehole liners 110 ft long for continuous soil-gas pressure monitoring.

Vapor Sampling/Permeability Measurements. Three membranes were instrumented and installed at SRS in July 1992 for soil-vapor, vapor-pressure, and permeability measurements. Maximum depth was 130 ft, with ten sampling elevations per membrane.

Neutron Logging Tool Transport. The membrane towed a 3 lb neutron moisture-logging tool in horizontal boreholes at Los Alamos, New Mexico. Typically, four 4.5 in. diameter holes (200-250 ft) were logged in one day, with data taken every 2 ft.

Vapor Sampling. A vapor-sampling system was installed to 90 ft depth for long-term monitoring at a commercial site in Tucson, Arizona.

Vapor Sampling in Long Horizontal Well. A SEAMIST™ membrane was installed in a 450 ft long, 4 in diameter screened well emplaced under a radiological/biological area. Seven soil-gas monitoring points were used to sense the presence of organic vapors.

Sensor Integration. Two SEAMIST™ membranes were integrated with a variety of chemical, temperature, pressure, and hydrologic sensors in a demonstration at the Chemical Waste Landfill.

Contaminant Transport Monitoring. Three SEAMIST™ membranes with vapor-sampling ports were used with an automated soil gas pressure and vapor-analysis system to monitor contaminant and tracer plume movement in the Chemical Waste Landfill. Both diffusion and barometric transport mechanisms were monitored.

Vapor Monitoring near Radioactive Waste Landfill (Los Alamos). Five vapor-sampling SEAMIST™ membranes were installed in 8 in diameter boreholes, 250 to 310 ft deep. These will provide continuous monitoring of VOCs and soil-matrix potential at twelve discrete elevations per membrane.

Cost. Membrane - \$500 to \$10K, depending on complexity; emplacement canisters and support systems - \$1K to \$5K.

PROJECTED PERFORMANCE

Key performance parameters are listed in Table 10.6, including projections of near-term (1-3 yrs) performance.

APPLICABILITY

This technology is applicable for measurement/monitoring of soils contaminated with tritium, carbon tetrachloride, and volatile organic compounds (VOCs).

STATUS

- Demonstrated capability to tow logging devices and cameras up to 250 ft in horizontal boreholes.
- Performed depth-discrete soil-gas sampling with up to 12 measurement ports, down to 310 ft.
- Blank membranes up to 500 ft long have been employed to seal and stabilize boreholes.
- Membranes have served as vehicles for a variety of chemical, temperature, matrix-potential, and pressure sensors.

REGULATORY CONSIDERATIONS

Regulatory considerations depend on where the technology will be used, the nature of contamination, and the intended application of the technology.

POTENTIAL COMMERCIAL APPLICATIONS

SEAMIST™ is commercially available for borehole lining, liquid/vapor sampling, and permeability measurements. Potential near-term applications include water sampling below the water table and large-scale vapor-plume movement experiments/monitoring. These applications would be useful to: the chemical, mining, oil, and natural gas industries; Environmental Protection Agency (EPA) and Department of Defense (DoD) cleanup operations; and various federal programs.

BASELINE TECHNOLOGY

SEAMIST™ is a new technology. It replaces the need for ex situ soil-sample analysis and multipoint, permanently installed vapor-sampling wells. The membrane minimizes the likelihood of contamination release from sampling and monitoring boreholes.

INTELLECTUAL PROPERTY

Patent and Trademark Ownership: Eastman Cherrington Environmental, Houston, TX; Patent No. 5176207.

Table 10.6. Key Performance Parameters for SEAMIST™.

Performance Parameter	Demonstrated	Projected
Hole Diameter (in)	1.75 - 11.5	1.0
Hole Vertical Depth (ft)	310	>300
Hole Horizontal Length (ft)	450	>300
Vertical Deployment Speed (ft/min)	30	30
Horizontal Deployment Speed (ft/min)	30	30
No. Vapor Sampling Points/Membrane	12	30

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Cecilia Williams
Sandia National Laboratories
P.O. Box 5800, Org. 6621
Albuquerque, NM 87185-5800
(505) 844-5722

DOE Program Manager
Skip Chamberlain
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

Industrial Partner
Bill Lowry
Science & Engineering Associates, Inc.
1500 Pacheco St., Suite D-1
Santa Fe, NM 87505
(505) 983-6698; FAX (505) 983-5868

For Purchase/Service:
Carl Keller
Eastman Cherrington Environmental
(505) 983-3199

REFERENCES

1. "SEAMIST™ an In-Situ Instrumentation and Vapor Sampling System Applications in the Sandia Mixed Waste Landfill Integrated Demonstration Program," ER'93 Conference Proceedings, Augusta, Georgia, October 1993.

2. "Development of the SEAMIST™ Concept for Site Characterization and Monitoring," DOE/CH-9213, November 1993.

3. "High Resolution Gas Permeability Measurements with the SEAMIST™ System," Proceedings of the 5th National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring, and Geophysical Methods, Las Vegas, NV, May 1991.

4. "A New Vadose Zone Fluid Sampling System for Uncased Holes," Proceedings of the 4th National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring, and Geophysical Methods, Las Vegas, NV, May 1990.

ZERO-TENSION LYSIMETERS TO MONITOR COLLOID TRANSPORT IN THE VADOSE ZONE

DESCRIPTION

There is increasing evidence that mobile colloids facilitate the long-distance transport of some kinds of contaminants. The mobility of fine particles and organic macromolecules has been linked to the movement of actinides, organic contaminants, and heavy metals through soil. The potential for colloid-facilitated transport of contaminants from hazardous-waste sites requires adequate monitoring before, during, and after *in-situ* remediation treatments.

A lysimeter is a device permanently installed in the soil to sample water periodically. Zero-tension lysimeters (ZTLs) are especially appropriate for sampling water as it moves through saturated soil, although some unsaturated flow events may be sampled as well. Because no ceramic barrier or fiberglass wick is involved to maintain tension on the water (as is the case with tension lysimeters), particles suspended in the water as well as dissolved species may be sampled with ZTLs. The lysimeter described here may be especially useful to monitor colloid mobilization and transport during *in-situ* remediation treatments that require long periods of saturation and significant fluid flux.

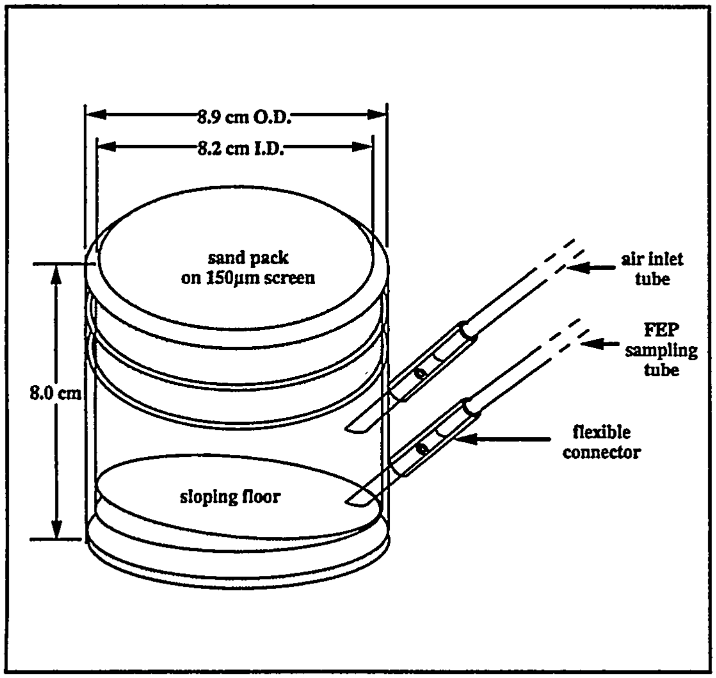


Figure 10.7a. Design of the Zero-Tension Lysimeter.

ZTLs can be used to capture samples of suspended colloids as they move in the vadose zone. The specific benefits of the new design are related to the simplicity of installation (minimizing soil disturbance) and the concomitant improvement in the accuracy of monitoring. Because more ZTLs can be installed to assess site spatial variability (compared to conventional ZTL designs), more accurate monitoring of contaminant transport before, during, and after remediation will be achieved. In addition, because of the improved spatial resolution in sampling and monitoring, if contaminants are indeed mobilized during *in situ* remediation treatment or natural rainfall, their source can be more easily identified than with piezometer-based monitoring methods.

The improved ZTL consists of a cylinder made of polycarbonate or polytetrafluoroethylene (PTFE) that is placed in the soil. Both materials were used in the construction of prototypes. Both materials minimize the sorption of contaminants and natural, suspended colloids by the device itself. PTFE also has excellent resistance to a very large number of chemicals and pH ranges. In many soils, a hydraulically powered sampling tube may be used to extract an undisturbed core of soil, enabling placement of a lysimeter. The lysimeter cylinder dimensions are shown in Figure 10.7a. The lysimeter outside diameter is 1.3 cm smaller than the 10.2 cm diameter sampling tube of a Giddings hydraulic soil coring and sampling machine. This is the largest practical size for most soils. The cylinder is sealed to a base which has a sloping floor, also made of PTFE (or polycarbonate). The upper 1 cm of the cylinder is indented by 2 mm so that an 8.3 cm ID ring can fit at the top. A polyester screen with 150 μm openings is placed between the cylinder and the ring and is bonded into place. The ring edge is beveled at a 35° angle to penetrate unconsolidated soil material that overlies the lysimeter upon installation in the soil core. Before placing the lysimeter into the ground, a layer of acid-washed silica sand, sieved to 1-2 mm, is placed onto the screen at the top of the cylinder to fill the cavity and to provide hydraulic contact with the overlying soil. After placing the lysimeter in the ground at the base of the hole, it is surrounded with sand for stability. For monitoring contaminants near the soil surface, a placement depth of about 50 cm is typical. Increased depth is possible, but soil core removal and replacement in an undisturbed form is an engineering problem.

Samples of soil solution or suspension are removed from the lysimeter by applying suction to the sampling tube with a hand pump or a peristaltic pump. An air-inlet tube is included in the design to provide make-up air and exhaust air when pumping or filling the lysimeter, respectively (Figure 10.7b). Normally, sampling takes place shortly after it is believed that saturated flow has occurred in the soil, e.g., following spring snow melt, long periods of rain, heavy rainstorms, etc., or during *in situ* remediation treatments that require long periods of saturation and significant fluid flux. The sampling interval depends on depth of the lysimeter placement as well as soil water content. In samples collected from lysimeters, suspended colloid concentrations, heavy metals, dissolved organic carbon, electrical conductivity, and pH are typically determined. Cleaning the lysimeter is accomplished by introducing a chemically neutral soap solution followed by quantitative rinsing with distilled water.

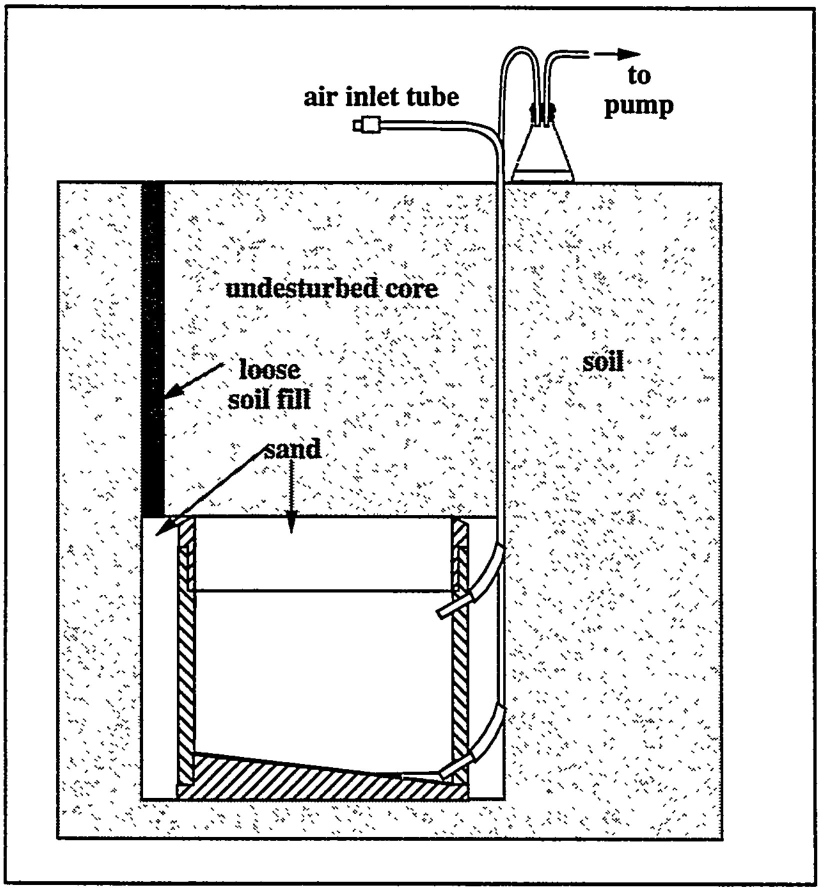


Figure 10.7b. Sampling and maintenance of the Zero-Tension Lysimeter.

TECHNICAL PERFORMANCE

The improved zero-tension lysimeters were installed at five sites contaminated with americium and plutonium at the Rocky Flats Plant in Golden, Colorado. Rainfall simulation experiments were performed to test the ability of the improved ZTLs to intercept mobile colloids and actinides and to compare their behavior with that of conventional ZTLs. The improved ZTLs were also been installed near Ames, Iowa, where colloid-facilitated transport of heavy metals (copper, nickel, cadmium, and zinc) in municipal sewage sludge amendments is currently monitored. Rainfall simulation experiments, designed to approximate the intensity of typical summer storms, were performed.

Ames, IA, Field Investigation. Zero-tension lysimeters were installed at the Ames Water Pollution Control Facility (WPCF) near Ames, Iowa, to monitor colloid transport in the soil during amendments with treated municipal biosolids. Twenty-four lysimeters were placed in plots associated with three levels of biosolids treatment (application of about 0, 2, and 5 dry tons per hectare) and two vegetation treatments (switchgrass and hybrid poplar). Half of the ZTLs were installed in the fall of 1991, and half were installed in the spring of 1992. The lysimeters were placed at a depth of 50 cm. The soil consists of a fine-loamy, mixed, mesic Endoaquic Hapludoll. To a depth of about 1 m the soil is a clay loam (about 380 g clay per kg soil). The surface horizon is massive in the upper 15 cm, and from 15 cm to about 60 cm structure is moderate, fine and medium, subangular blocky. There was considerable variability in the volume of water collected by the lysimeters; but the mean volume collected (about 175 mL) did not vary much with precipitation. The volumes collected were less variable when the precipitation exceeded 60 mm. Turbidity as well as concentrations of dissolved organic carbon and heavy metals were determined on the collected water samples. The variability of turbidity in suspensions collected by replicate ZTLs was large, with coefficients of variation ranging from 26 to 128%. The foregoing observations of the volume and turbidity of water collected by the ZTLs confirm the significance of the spatial variability of water flow and colloidal transport, supporting the use of ZTLs that can be installed quickly and cheaply in large numbers at a study site. Similarly, differences in dissolved organic carbon levels in mobile soil water associated with the two vegetation treatments were documented (Figure 10.7c).

Rocky Flats Field Investigations. Soils near the 903 Pad at the Rocky Flats Plant (RFP) were contaminated as a result of leaking barrels of plutonium-contaminated oil. Surficial soil horizons within 1 km of the pad were subsequently contaminated by wind dispersal of plutonium oxide particles during cleanup operations. Aerial and vertical surveys indicate that approximately 90% of the plutonium contamination

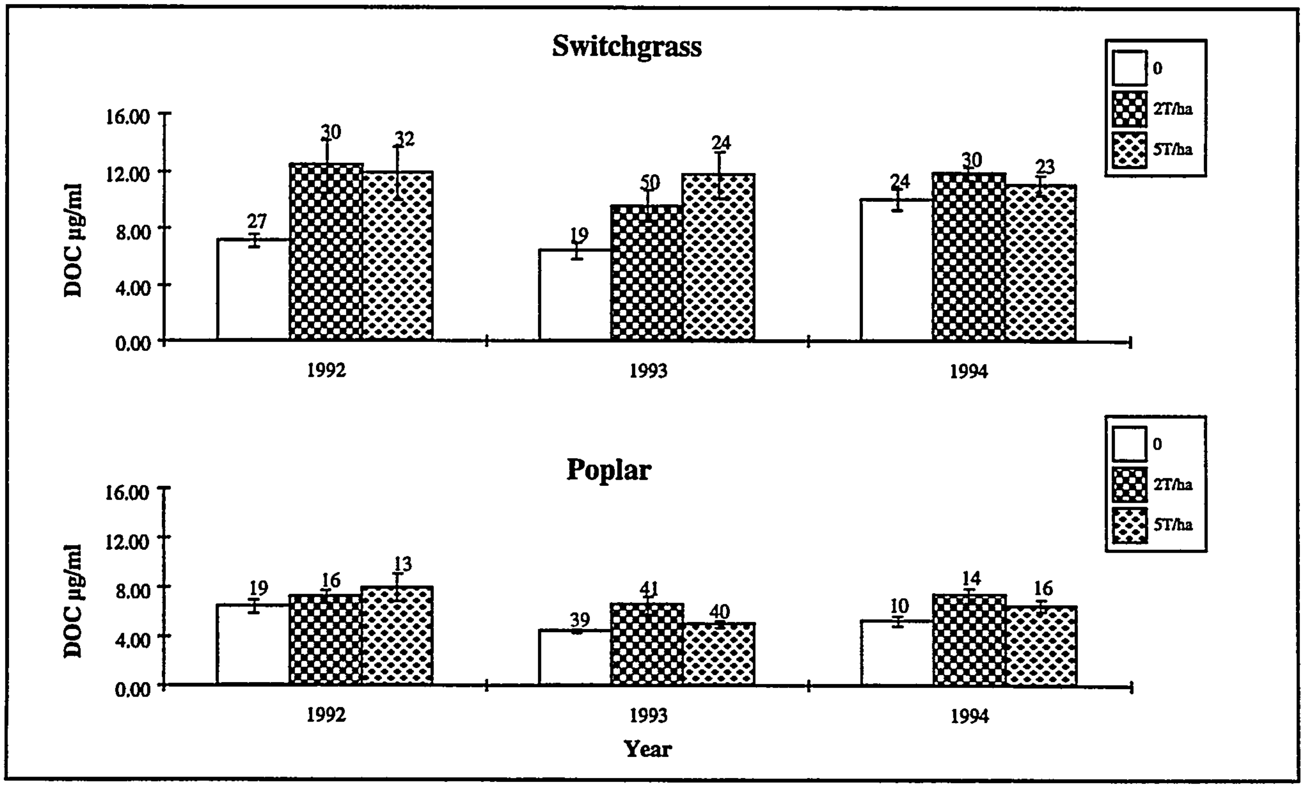


Figure 10.7c. Mean dissolved organic concentrations in mobile soil water. Numbers above the error bars indicate the number of samples averaged for each bar.

is in the top 10 cm of soil, but as much as 10% of the contamination may have migrated deeper.

In 1994, five ZTLs were installed at the Rocky Flats research site in vertical holes with replaced undisturbed cores. Undisturbed cores as long as 50 cm were collected by using a Giddings hydraulic soil probe. These cores provided excellent morphological documentation concerning the likelihood of preferential flow of water in soil macropores. Both simulated and natural precipitation data indicated that the lysimeters installed using the Giddings soil probe functioned well to capture mobile soil water. *Cost.* A ZTL constructed of polycarbonate costs approximately $60 for labor and materials. A ZTL constructed of PTFE costs approximately $200 for labor and materials. The cost of ZTL installation at a site includes both labor and access to a Giddings soil probe. Once experience has been gained at installation procedures, each installation (at a 50 cm depth in unconsolidated soil) takes two people about 45 min. A trailer-mounted Giddings soil probe costs about $20K.

PROJECTED PERFORMANCE

Future improvements will include automation of ZTL sampling. Design work for automation was completed in September 1994, and portions of a prototype automated-sampling ZTL system have been fabricated.

The automated design is briefly described here. Sensing probes are placed through the side of the ZTL to determine the presence of a chosen level of leachate (e.g., 20 mL). The probes are connected to a monitor box in which a light, buzzer, and microprocessor are located. When water is present to the level of the indicator sensor, the light will flash and the buzzer will sound. When leachate rises to the level of the pump sensor, a pump will be automatically activated to empty the lysimeter into an aboveground container that can be retrieved by personnel later. The microprocessor controls the pumping according to the water levels detected.

APPLICABILITY

This ZTL is applicable to monitoring colloid mobilization and transport in the vadose zone during rainfall events and during *in-situ* remediation treatments that require long periods of saturation and significant fluid flux. A series of installed ZTLs could be used to document preferential flow paths or significant contaminant migration. Key measurements might include: (1) collected water volume (i.e., flux of water in the soil), (2) turbidity (as an indicator of colloidal concentration), (3) solution pH, (4) heavy metal concentrations, and (5) dissolved organic carbon concentration.

STATUS

The new type of ZTLs presented here, namely, those installed in vertical holes with replaced undisturbed cores, as described above, was field tested. A prototype of an automated version has been constructed.

REGULATORY CONSIDERATIONS

There are no known regulatory barriers to using this technology. Regulatory agencies are familiar with conventional designs of zero-tension lysimeters. Because this design requires less site disturbance during installation, regulatory agencies would be expected to favor its use. Site excavation permits are likely to be required for installation.

POTENTIAL COMMERCIAL APPLICATIONS

This ZTL is applicable to monitoring colloid mobilization and solute transport in the vadose zone during rainfall events and during *in situ* remediation treatments that require long periods of saturation and significant fluid flux. A series of installed ZTLs could be used to document preferential flow paths or significant contaminant migration.

BASELINE TECHNOLOGY

The baseline technologies include alternative approaches such as ZTLs of conventional design (i.e., lateral installation) and piezometers. The disadvantages of conventional ZTLs are related to the possibility of site disturbance during installation and also the higher costs associated with opening a large pit, so the device can be installed. The advantage of the newly designed ZTL is that more devices can be installed in a given amount of time for less cost with minimal ground disturbance. Such installations would make feasible more reliable assessments of the spatial variability of colloid-facilitated transport of contaminants.

Piezometers have been used to sample groundwater for mobilized colloids, but serious questions have been raised about disturbances of fine-grained aquifer material during purging and sampling of wells. To prevent disturbance of normally immobile colloidal materials may require extremely slow pumping rates that are not cost effective.

INTELLECTUAL PROPERTY

This work was conducted at Ames Laboratory and Iowa State University with funds provided by the Characterization, Monitoring, and Sensor Technology Crosscutting Program of the Office of Technology Development, U. S. Department of Energy.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Michael L. Thompson
Agronomy Department
Iowa State University
Ames, IA 50011
(515) 294-2415
e-mail: thompsonm@ameslab.gov

DOE Program Manager

Caroline Purdy
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7672

REFERENCES

1. Thompson, M.L. and R.L. Scharf, "An Improved Zero-Tension Lysimeter to Monitor Colloid Transport in Soils," Journal of Environmental Quality, Vol. 23, 1994, pp. 378-383.

2. Ames Laboratory, Zero-Tension Lysimeters: An Improved Design to Monitor Colloid-Facilitated Contaminant Transport in the Vadose Zone, prepared for the Characterization, Monitoring, & Sensor Technology Crosscutting Program, IS-5117 UC-600, Iowa State University, Ames, IA, 1995.

Statistically Guided Sampling

Section 11.0

DESCRIPTION

Site characterization has traditionally been a very expensive process. Sampling programs to identify the presence and extent of contamination were built around pre-planned sampling grids and off-site analyses of samples. The result was an expensive and time-consuming process, with significant pressures to over-sample a site and the need for frequent return site visits to clarify unexpected findings. Recent advances in field-screening technologies that can provide "real time" results for a variety of contaminants allow the application of adaptive sampling programs for site characterization. Adaptive sampling programs change, adjusting to new information as it is generated in the field. Effective implementation of adaptive sampling programs requires: (1) a means for integrating, managing, and visualizing site data in the field, (2) determining new sampling locations that provide the most information, and (3) constructing estimates of contaminant extent based on available data.

Two technologies were developed to address the particular demands of adaptive sampling programs (see Figure 11.1). The first called SitePlanner™, provides qualitative support for adaptive sampling programs. SitePlanner™ is a graphical, object-oriented database designed to support environmental site assessment work. SitePlanner™ organizes its data by object (such as monitoring wells, soil bores, landfills, etc.), not by table. Data objects are displayed visually as icons in a variety of graphics, including plan views, profile views, fence diagrams, and bore logs. All SitePlanner™ graphics are dynamically tied to the data for a site and can be retrieved interactively. SitePlanner™ is built around OpenWindows and is a completely mouse- and menu-driven package that is relatively easy to learn and use. In the context of adaptive sampling programs, SitePlanner™ provides a rapid and simple means of integrating, managing, and visualizing site data as they are being generated. SitePlanner™ provides field staff with the ability to understand their data as quickly and efficiently as possible.

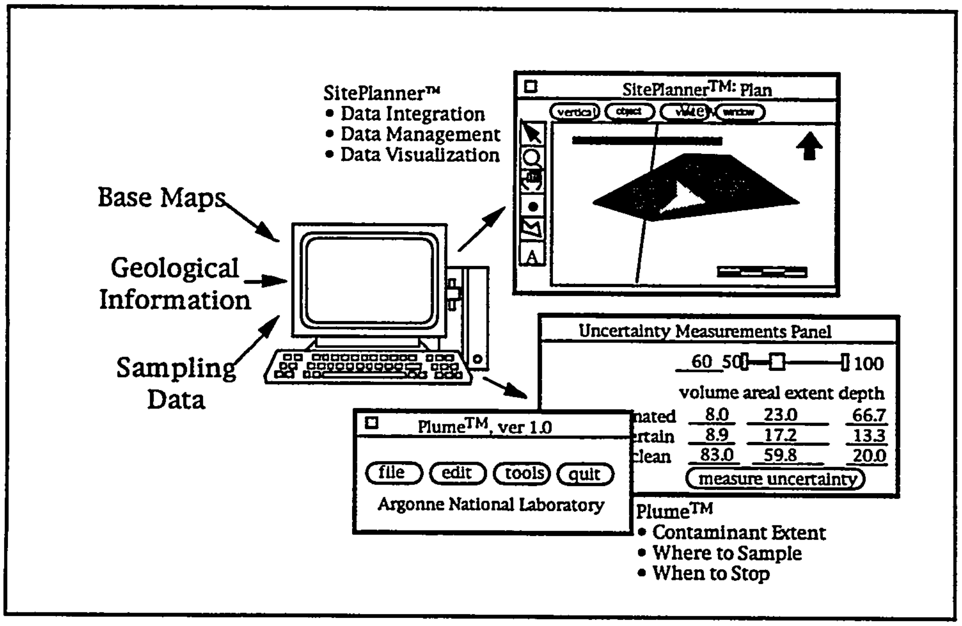


Figure 11.1. Adaptive Sampling Programs.

The second technology, PLUME™, provides quantitative support for adaptive sampling programs. It allows the integration of "soft" information regarding contaminant location with hard sampling data to form a conceptual image of contamination extent. Based on this conceptual image, PLUME™ uses a combination of Bayesian and spatial statistics to measure the potential impact of additional sampling points and to search for the next set of sampling points that would contribute most to the delineation of contamination. PLUME™ provides statistical estimates of contaminant extent, such as estimates of volumetric contamination and lateral extent, and measures the uncertainty associated with these estimates. Its approach to uncertainty is consistent with the Environmental Protection Agency Data Quality Objectives process. PLUME™ can be used to target new vertically and/or directionally drilled borings that would have the greatest impact on the uncertainty associated with estimation of contaminant extent. PLUME™ can estimate the value additional sampling data may provide, allowing staff to weigh the benefits of collecting more samples against the additional sampling and analysis costs. PLUME™ can be connected with SitePlanner™, allowing the use of SitePlanner™ for data management, and for visualization of PLUME™ results.

TECHNICAL PERFORMANCE

SitePlanner™ and PLUME™ were demonstrated at Sandia National Laboratories (SNL), at the Kirtland Air Force Base RB-11 site, and at Argonne National Laboratory (ANL).

SNL Demonstration. At SNL, activities focused on delineating subsurface chromic acid contamination beneath the unlined chromic acid pit and the 60s pits within the Chemical Waste Landfill. Retrospective studies of the characterization efforts for those sites indicated savings of more than 50% could have been realized if an adaptive sampling program including field screening technologies, SitePlanner™, and PLUME™ had been used from the outset.

RB-11 Demonstration. At the RB-11 site, SitePlanner™ and PLUME™ were used to design and implement an adaptive sampling program to characterize contaminant migration from a series of trenches containing mixed wastes. Here with only 78% of the bores and 50% of the samples employed by a concurrently conducted conventional sampling program, the adaptive sampling program provided equal quality of characterization.

ANL Demonstration. At an ANL site known as the 317 area, SitePlanner™ and PLUME™ were used to support an adaptive sampling program that delineated volatile organic compound (VOC) contamination in near surface soils. The original sampling program proposed by the contractor included the collection of 600 split-spoon samples on a regular grid. By adapting the sampling program based on field screening results and by optimizing subsequent sampling locations with SitePlanner™ and PLUME™, only 150 samples were required to complete the characterization task.

Costs. Commercial implementation of SitePlanner™ and PLUME™ for adaptive sampling program support requires computer hardware that currently costs about $6K and associated software that currently costs about $4,5K. Computer hardware and software costs, however, have been falling dramatically.

PROJECTED PERFORMANCE

ANL is working with Consolve, Inc., to provide a Microsoft Windows-compatible version of PLUME™. When available, PLUME™ will no longer require the use of a UNIX workstations.

WASTE APPLICABILITY

The adaptive sampling approach embodied in SitePlanner™ and PLUME™ is designed specifically for characterizing the presence and extent of contamination in groundwater and surface and subsurface soils.

STATUS

Both SitePlanner™ and PLUME™ are commercially available products. Both are available on Sun Sparcstations with Sun OS 4.1.x and OpenWindows, and on PC compatibles with SCO Unix. Minimum hardware requirements are 32 Mbytes of RAM, and 75 Mbytes of swap space. Microsoft Windows-based versions are being developed.

REGULATORY CONSIDERATIONS

There are no regulatory considerations directly associated with this technology.

POTENTIAL COMMERCIAL APPLICATIONS

Recent advances are providing a growing array of field-screening analytical technologies applicable to different types of contaminants and media. The availability of these technologies enables the application of adaptive sampling programs to the problem of identifying the presence and extent of contamination at hazardous waste sites. SitePlanner™ and PLUME™ together provide a cost-effective approach to supporting adaptive sampling programs in the field. For SitePlanner™, this includes field-level data integration, data management, and data visualization. For PLUME™, this means directing the progress of the sampling program and providing estimates of contaminated volumes. Cost savings are realized by reducing the cost per sample analyzed, the number of samples taken, and the number of trips to the field required to bring characterization activities to closure. Given the large number of federal and private installations awaiting site characterization activity, the overall potential for cost savings is enormous.

BASELINE TECHNOLOGY

The alternative to adaptive sampling programs is a standard, pre-planned sampling program approach. These types of programs are typically based on a set grid superimposed over the area of concern. Samples are collected from the grid and sent to off-site laboratories for analysis. The time required for off-site sample analyses precludes the use of data within the sampling program. Data from these programs ultimately reside in centralized data archiving systems and/or standard geographical information system (GIS) packages. The results are pressure to oversample initially, frequent return visits to the field to clarify the unexpected sample values, and long lag times before data become available to program managers.

INTELLECTUAL PROPERTY

Patents:	None.
Copyrights:	SitePlanner™—ConSolve, Inc. PLUME™—University of Chicago
Trademarks:	SitePlanner™—ConSolve, Inc. PLUME™—University of Chicago

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Robert Johnson
Argonne National Laboratory
EAD/900
9700 South Cass Avenue
Argonne, IL 60439
(708) 252-7004; FAX (708) 252-3611

DOE Program Manager
Skip Chamberlain
U. S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7248

Industrial Partner
Gregory Baecher
ConSolve, Inc.
297 Boston Post Road, Suite 203
Wayland, MA 01778
(508) 358-8061; (508) 358-8065 FAX

REFERENCES

1. Johnson, R., "A Bayesian/Geostatistical Approach to the Design of Adaptive Sampling Programs," Geostatistics for Environmental and Geotechnical Applications, ASTM STP 1283, R. Mohan Srivastava, Shahrokh Rouhani, Marc V. Cromer, A. Ivan Johnson, Ed., American Society for Testing and Materials (in press).

2. Johnson, R., "Extent of Chromium Contamination Beneath the 60s Pits in the Chemical Waste Landfill at Sandia National Laboratories, Albuquerque, New Mexico," Argonne National Laboratory Technical Memorandum, ANL/EAD/TM-19, 1994.

3. Johnson, R., "Adaptive Sampling Program Support for Expedited Site Characterization," ER'93 Environmental Remediation Conference Proceedings, Augusta, GA, Oct. 24-28, 1993.

4. Johnson, R., "Adaptive Sampling Strategy Support for the Unlined Chromic Acid Pit, Chemical Waste Landfill, Sandia National Laboratory, Albuquerque, New Mexico," Argonne National Laboratory Technical Memorandum, ANL-EAD/TM-2, 1993.

5. Johnson, R., "A Bayesian Approach to Contaminant Delineation," Proceedings of the Groundwater Modeling Conference, Golden, CO, E. Peter, S. Ashock, and J. Proud, eds. Colorado School of Mines, Golden, Colorado, June 9-12, 1993, pp. 87-95.

Tank Waste

Section 12.0

ACOUSTIC CHARACTERIZATION OF WASTES IN DOUBLE-SHELLED UNDERGROUND STORAGE TANKS

DESCRIPTION

This project is adapting commercially available acoustic (sonar) devices to meet specific needs in the mitigation and characterization of high- and low-level waste being stored in underground storage tanks (USTs) at the Hanford Nuclear Reservation in eastern Washington. Two sensors are being developed to comprise a monitoring system (an echo sounder for locating interfaces and tank obstructions, and a density monitor for reporting changes in mixed fluid density during waste mobilization procedures). With each device, acoustic pulses of a specific frequency are generated and sent into the tank, either to be bounced off interfaces and objects in the tanks, as with the echo sounders; or to be received by a separate transducer, as with the density monitor. In each case the received signals can be analyzed to determine some of the properties of the materials with which the sound pulses have interacted.

In the planned effort to pump the waste out of double shelled tanks (DSTs) and vitrify it for permanent disposal and then transfer single-shell tank (SST) waste to the DSTs for interim storage, process monitoring will be very important. Critical data will include, but not be limited to, radius of cleaning from the mixer/transfer pump, locations of submerged objects, and density of waste mixtures. The absence of such data could compromise: (1) adequately designing a pump, (2) predicting the effectiveness of transfer through lines without plugging, (3) determining how completely a tank has been cleaned, and (4) determining whether obstructions or debris in the tank will interfere with pumping. An acoustic method, such as is being addressed in the current work, shows considerable promise of meeting these data needs.

The echo sounders are transducers which are produced for commercial and sport fishing use, but have been adapted to tolerate the high pH, high temperature, and radiologically hot environment in DSTs. A signal source for making the sonar measurement has been obtained commercially and is currently being adapted to meet the smaller scale and more attenuative environment than its 'designed for' sea water conditions. Time of flight and attenuation measurements on the original and return signals provide information on object locations and the amount of mixing being done in the tank.

The density monitor is being developed using the adapted transducers along with standard laboratory signal sources and data acquisition equipment. Two transducers, a transmitter and a receiver, are used to send and receive, respectively, the acoustic pulses. Changes in the phase of the signal are used to determine changes in the density of the fluid between the sensors.

Currently, information about material properties in USTs is provided by intrusive methods such as core sampling, buoyancy-based density measurements, level tapes, and video cameras. None of these methods are effective in determining the distribution of waste types and submerged objects beneath the surface of the waste. The acoustic methods being developed allow near real-time, remote analysis of the waste in the tanks with little or no human contact with the tanks or the waste mixtures. The sensors also provide a means for locating interfaces and object locations, a capability that is currently unavailable. Additionally, the cost is low for in-tank assessment capability because the costliest equipment is reused and not contaminated.

Most of the waste in the tanks is in the form of sludge, saltcake, and pumpable and nonpumpable liquids. The sludge consists of the solids (hydrous metal oxides) precipitated from the neutralization of acid wastes. Saltcake is made up of various salts formed by crystallization and precipitation after concentration of liquid wastes.

TECHNICAL PERFORMANCE

The echo sounders and density monitors are shielded in mild steel housings to protect them from the intensely radioactive and caustic in-tank environment. Data taken with devices left in tank SY-101 for more than a year have shown little effect from continuous exposure to the environment. Laboratory tests to determine the effect of temperature on the optimum operating frequency showed that temperature has a very small effect on the performance of the transducers.

The absolute detection limits of the echo sounders in actual tanks have not been experimentally determined because tank entries were delayed. Tests done in a 12 ft test tank yielded three round trip return signals, implying a signal pulse strong enough to penetrate more than 36 ft in a full sized tank. The penetration will depend upon the acoustic characteristics of the waste, which will be evaluated at upcoming in-tank tests at tank AN-107 at Hanford. Acoustic impedance mismatch is the key parameter that determines reflectance from a sludge-fluid interface, and test tank results have given interface detection for a mismatch of a few percent. The minimum detection distance is approximately one meter, a distance controlled by the length of the acoustic pulse, which in the current prototype is a meter. We can currently discern a layer interface from the bottom reflection for layer thicknesses of one foot or greater.

The density monitor is designed to detect sound speed changes that correspond to density changes of approximately 1% of initial density. Testing with some simulated environments shows promise in achieving this limit; however, factors such as vibration and fluid motion between the sensors are still being evaluated in the laboratory.

Because the acoustic sensors are very sensitive to the presence of small bubbles trapped in the fluid, the system may become less functional during the mixing process, as the pump introduces bubbles into the mixture. Performance may also be affected by monitoring solid materials that have a very small acoustic impedance mismatch with the supernatant. The closer the acoustic impedances of a sludge layer are to the supernatant, the less likely it is that there will be a return from that particular interface. Experiments at Iowa State in the 5,000 gallon test tank have also shown that the sensors do not work well when the sludge layer is thin (less than 1 m thick) or when objects are closer to the sensor than 1 m. At these distances the return signals get lost in the bottom return or the initial pulse, respectively.

The commercially obtained signal source (a JFV-120 from Raytheon) requires a 24 V DC power source that can be supplied by a commercially available AC to DC converter. All other equipment can be operated using standard 120 V AC power. No special personnel requirements will be necessary with the final prototype system. Personnel must be familiar with computers and data acquisition equipment, including oscilloscopes and frequency generators.

The majority of tests were conducted at Iowa State University in a 12 ft high, 5,000 gallon tank containing water and a sludge layer of calcium carbonate. Also, limited testing was performed in a swimming pool containing chlorinated water when the 5,000 gallon tank was not large enough. Tests were conducted to: (1) determine speed of sound in the supernatant (water) and sludge (calcium hydroxide) layers, (2) determine interface locations, and (3) detect and determine the distance to submerged objects. Experiments were also conducted with the density monitor to relate a change in the phase of the transducer signal to the change in density of two different test solutions, a sodium chloride solution and a mixture of water and silica flour.

Tests in the 5,000 gallon test tank have shown that an interface is detectable using the echo sounders even with a very small impedance mismatch between the sludge and the supernatant liquid. The ability to detect an interface between simulant sludge and water was demonstrated at distances from 1 to 3 m directly, and to approximately 10 m indirectly. Submerged objects were similarly detected up to distances of 12 m. Because the simulants used to create interfaces have small acoustic impedance mismatches compared to what is expected for in-tank wastes, the probability of successful application of the interface detector is high.

Cost. Costs are not available.

PROJECTED PERFORMANCE

A density monitor and echo rangers were delivered to the Hanford site and will be mounted on a mixer pump to be used in DST-AN-107 for a caustic addition late in FY 1995. Preliminary evaluation of the sensors to measure sludge layer depth, dispersion of the sludge under stirring, changes in supernatant density, effective cleaning radius, and location of in-tank structures is scheduled to occur in the third quarter of FY 1995. The prototype monitoring system will be used by Hanford with Ames Laboratory support during the development period. A more automated monitoring system based on FY 1995 results is scheduled to be evaluated during the final test/demonstration period planned to occur in DST-AZ-101 in April 1996.

Performance goals in FY1995 will be to demonstrate that the density and interface detection measurements provide the desired data for monitoring mixing. Sound speed, density and interface/object location accuracy of better than 5% is optimal. Meeting performance goals under tank mixing conditions, as well as quiescent conditions, is intended for FY 1995 in AN-107; but doing so depends on Hanford's schedule for the pumping to occur during the caustic addition tests. Based on results in FY 1995, improvements and demonstrations in DST-AZ-107 will be performed and a final prototype will be constructed in FY 1996.

APPLICABILITY

The acoustic sensors were designed to operate in a harsh caustic and radioactive environment with liquid/sludge materials. The sensors are not designed to detect or monitor any particular type of waste (e.g., radionuclides, inorganic compounds) and could potentially be used in any tank environment that would not adversely affect either the mild steel casing, such as an acidic environment, or the cables used to connect the sensors to data acquisition equipment. The acoustic sensors promise to be applicable to any fluid filled tanks, and as more systems are operational in actual tanks, additional acoustic characterization of wastes will allow the technology to be fine-tuned for use in a range of waste types.

STATUS

Initial bench-top tests were conducted in a small 25 gallon aquarium using several high frequency transducers (500 kHz) with a mixture of water and calcium carbonate. Similar small scale tests were also conducted with the high frequency transducers in a water tank with a sludge layer composed of denser metal oxides. Larger pilot-scale tests were conducted using the actual dual frequency (28/50 kHz) Airmar sensors in the 5,000 gallon tank containing water and calcium carbonate. The most recent work has continued in the large tank focusing on detecting sludge interfaces and locating objects either suspended in the tank or buried within the sludge layer. Currently the visual observation of waveforms on an oscilloscope gives somewhat better precision than the display of the commercial echo sounding pulser (the JFV-120). The pulser CRT display provides the advantage, however; of giving a quick, easily read idea of the hardness of and distance to targets in the sensor beam.

The project is scheduled to conclude following FY 1996 with the delivery of a prototype automated system capable of monitoring the degree of mobilization during waste mixing and transfer. Completion of the prototype will include design and fabrication of the sensors, mounting of sensors on a mixer pump, assembly of the out-of-tank instruments, development of basic instrumentation control codes, and drafting a system manual.

REGULATORY CONSIDERATIONS

While no permits are required to use the sensors, each transducer and the system as a whole must pass a safety inspection before activation in the tank environment to insure that all leads have been grounded and there is no danger of sparking, shorting, or explosion in those tanks that contain combustible gases.

Because several tanks contain potentially explosive amounts of hydrogen and nitrous oxide gases, care must be taken when installing instruments such as mixer pumps, which must go through one of the large risers, and that would react badly to friction sparks. The standard safety assessment for installing pumps in such an environment addresses all needed issues for installation of the acoustic sensors. A safety assessment performed for these sensors for tank 241-SY-101 covered issues for the use of this technology, which is not considered potentially hazardous.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include dredging small bodies of water, and monitoring waste and drinking water treatment plants. Note that this work started with a fairly mature technology and so has already been commercially applied.

BASELINE TECHNOLOGY

Currently information about material properties in USTs is provided by intrusive methods such as core sampling, buoyancy-based density measurements, level tapes, and video cameras. None of these methods effectively determines the distribution of waste types and submerged objects beneath the surface of the waste.

INTELLECTUAL PROPERTY

There are no pending or existing patents.

The Westinghouse Hanford Company is scheduled to take possession of the final prototype system at the conclusion of the project. It is believed that they will also be the group to license the technology.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

M. Amanda Clark
Iowa State University
Ames Laboratory & The Center for NDE
ASC-II, Rm. 251B
Ames, IA 50011
(515) 294-6695; FAX (515)294-6368
email: amanda@cnde.iastate.edu

DOE Project Manager

Al Tardiff
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7670

Industrial Partners

Airmar Technology
Raytheon
Westinghouse Hanford Company

REFERENCES

1. Clark, M.A., and D.M. Martin, "Acoustic Properties of Underground Storage Tank Simulant Wastes," Review of Progress in Quantitative Nondestructive Evaluation, Vol. 13, Plenum Press, NY, 1994, pp. 1075-1081.

2. Jeong, P., D. Martin, and R. Roberts, "Ultrasonic Characterization of the Contents of Underground Storage Tanks: The Status of Current Research Efforts," Review of Progress in Quantitative Nondestructive Evaluation, Vol. 12, Plenum Press, NY, 1993, pp. 2281-2287.

ACOUSTIC WAVE SENSOR FOR IN SITU MONITORING OF HEADSPACE GASES IN UNDERGROUND STORAGE TANKS

DESCRIPTION

A gas sensor system based on thin film resonator technology which could be field deployable and applicable to monitoring headspace gases in underground storage tanks (USTs) and remediation sites is being developed. The headspaces of USTs often contain explosive and toxic gases including hydrogen (H_2), nitrous oxide (N_2O), ammonia (NH_3), and various hydrocarbons. These gases are released from high-level tank wastes, inducing transient and potentially hazardous increases in local concentrations. Methods are needed to characterize the release and movement of these gases with minimal maintenance. The appropriate method would monitor quantitatively the concentrations of these gases during extended periods of time at several locations in each tank, and at several tanks. In view of the explosive potential of these headspace gases, it is also important that the sensors not pose a spark hazard. The thin film resonator (TFR) technology for gas characterization and monitoring meets these needs because since quantization can be achieved for different gases in a mixture with low maintenance, low cost and minimal spark hazard. The gas sensors use bulk acoustic wave piezoelectric mass sensors coated with materials that selectively sorb the target gases.

The sensor is a TFR constructed from thin piezoelectric aluminum nitride (AlN) membranes shaped in 150 mm squares supported by a silicon substrate (Figure 12.2a). When subjected to an alternating potential, a piezoelectric material such as AlN will vibrate at a frequency that is characteristic of the thickness and density of the material. Because of the small thickness of the AlN piezoelectric film used in this application, the frequency is in the GHz range. The frequency decreases with increasing mass of gas molecules adsorbed on the piezoelectric interface. This is because the thickness and density parameters of the piezoelectric film are altered by the adsorbed gas molecules. To make a selective sensor, the resonator is modified by adding a chemically selective membrane film on the side exposed to the gas. Details of the membrane coated piezoelectric gas sensing system are illustrated schematically in Figure 12.2b.

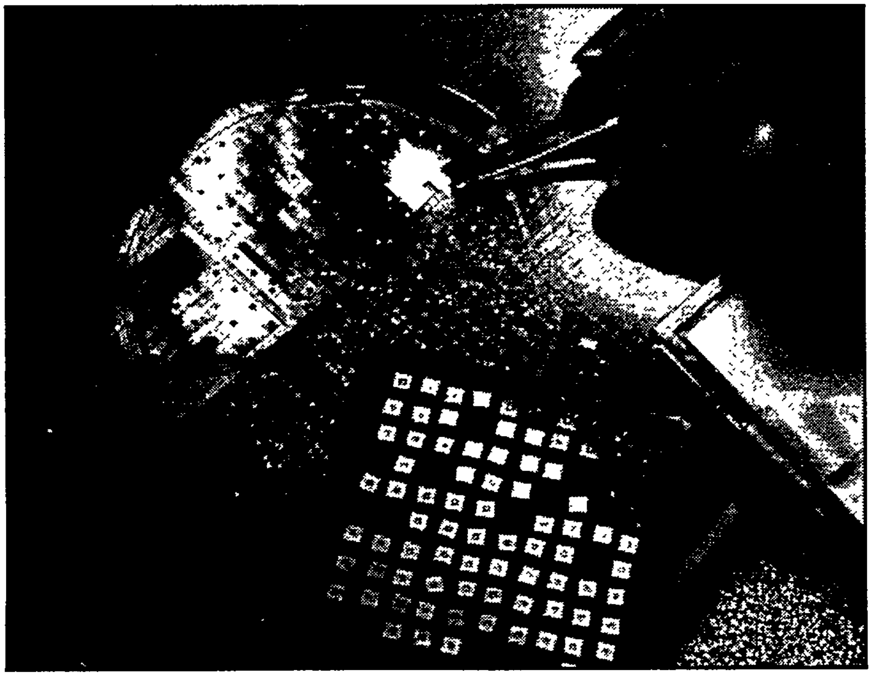


Figure 12.2a. A wafer of TFRs after processing and prior to packaging and incorporation into an array.

The TFRs are made with micorlithographic techniques well known in the microelectronics industry. A coating of AlN is deposited as a thin film layer (5 mm thickness) on a silicon wafer support. The AlN layer is then coated on one side with a chemically selective coating or a gas-specific permeable membrane layer. The opposite side of the silicon wafer is then etched to the AlN layer and subsequently coated with a conductive metal such as gold. The other side is coated similarly with conductive metal to provide a small area electrode. Palladium-based coatings are being used for H_2 detection. Other coating materials, including soluble polyelectrolytes such as poly(vinyl-benzyl-trimethyl ammonium chloride) and polyvinylpyrrolidone, are being tested for the detection of nitrous oxide.

The sensor system uses reference-indicator TFR pairs. The reference TFR is coated with a passive material and the indicator TFR has a chemically sensitive coating. The two TFRs are used as the frequency-control elements in separate oscillator circuits. The signals from the oscillator with the reference TFR and the oscillator with the analyte-sensitized TFR are mixed to obtain a difference frequency. The difference frequency reflects the change effected by the mass of the selectively adsorbed gas. Such comparison of the reference and indictor frequencies largely eliminates the effects of chemically nonspecific influences such as temperature, and provides a low-frequency output.

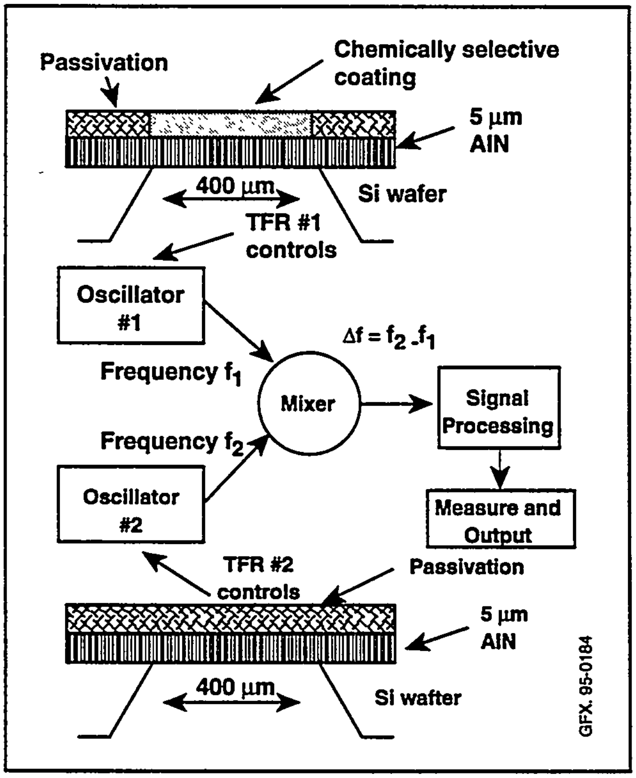


Figure 12.2b. Thin film resonator sensors.

The ultimate gas sensor system will be composed of arrays of piezoelectric mass sensors (TFRs) and electronic readout instrumentation for determination of the concentrations of several hazardous gases in the hostile environment of USTs (e.g., H_2, N_2O, NH_3). Using integrated circuit technology and specially synthesized surface coatings, small, low cost sensor systems capable of long term, low maintenance operation are being fabricated as field deployable prototypes. These sensors can detect mass loading at extremely low levels (i.e., 2 ng/cm^2), which is well below the mass loading corresponding to the adsorption of a single molecular layer of the target gases.

TECHNICAL PERFORMANCE

Prototype hydrogen sensors have been created by depositing a variety of doped and alloyed palladium films described in the literature to the surfaces of quartz crystal microbalances (QCMs). The general development approach was to first test coatings on QCMs and then on TFRs. Linear responses over two orders of magnitude were obtained with a detection limit of a few ppm. An example set of results is illustrated in Figure 12.2c.

Importantly, the response of these PdNi coatings to H_2 is the result of dissociation and subsequent uptake of the analyte into the bulk of the coating, whereas the response to interferences is confirmed to be a surface adsorption process. Thus, an analysis of the responses from an array of these sensors with varied coating thicknesses provides a basis to account quantitatively for the effects of interferences.

PROJECTED PERFORMANCE

It is projected that the TFR mass sensor arrays will be able to accurately and reliably detect specific gases including H_2, N_2O, and NH_3. The goal is detection sensitivities at the ppm level so that accurate monitoring at 15 to 20 ppm is viable with response times on the order of 30 s. The design is intended to account for various interferences by using sensor arrays with different thicknesses and different coating materials.

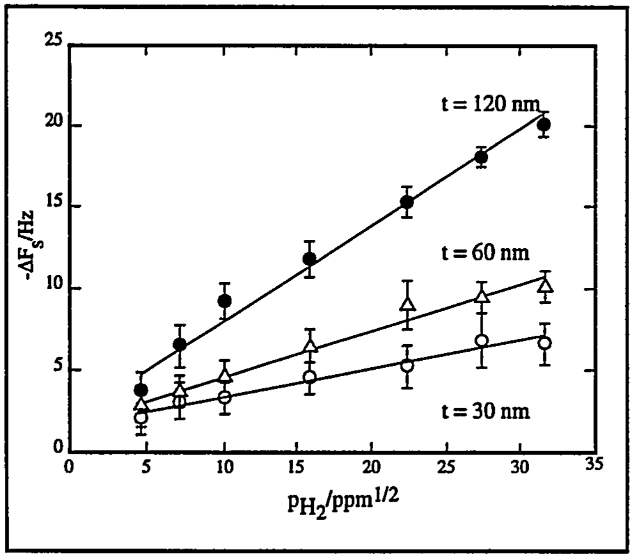


Figure 12.2c. Responses of QCM/PdNi to H_2 as a function of film thickness.

A key challenge is to develop a method to account for variable temperature effects.

APPLICABILITY

The thin film resonator technology for gas detection is applicable to the detection of specific gases in a gas mixture. In principle, wherever known chemistry suggests a chemically selective coating material for a given gas, then that gas can be detected selectively. The gases for which chemically selective coatings are currently being developed are H_2, N_2O, and NH_3.

STATUS

This technology is in the laboratory developmental stage with first field testing planned near the end of 1995. The construction of a laboratory demonstration system is complete and it is being used in technology transfer demonstrations.

REGULATORY CONSIDERATIONS

The baseline technology has been in use for target applications. Therefore, extensive regulatory complications are not anticipated.

POTENTIAL COMMERCIAL APPLICATIONS

The technology is applicable to field deployable monitors and for flammable gases and priority pollutants.

BASELINE TECHNOLOGY

The baseline technology tested at the Hanford facility, only partially solves the monitoring needs at the USTs. Whitaker cells (the baseline) exhibit the requisite selectively for H_2 monitoring. The performance of the Whitaker cells is not sufficient; however, to monitor accurately at the 15 to 20 ppm levels required for compliance monitoring, and the response times (approximately 2 min) are about four times longer than those needed for reliable assessment of the waste outgassing dynamics. Similar limitations exist for the monitoring of NH_3, where a photoacoustic cell has been coupled with an infrared spectrometer. Other conventional approaches have also been suggested, such as miniaturized gas chromatography. This latter approach has prohibitively high development and operational costs.

INTELLECTUAL PROPERTY

The basic TFR device is covered by U.S. Patent Number 4,502,932. Several other patent applications have been filed. Licensing arrangements can be made through the Center for Advanced Technology Development, Iowa State University. The contact person is Kannah Grant, (515) 294-5702.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator

Marc D. Porter
U.S. Department of Energy
Ames Laboratory
Ames, IA 50010
(515) 294-6433; (515) 294-3254 FAX

DOE Project Manager, CMST-CP

Al Tardiff
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7670

REFERENCE

1. O'Toole, R.P., S.G. Burns, G.J. Bastiaans, M.D. Porter, "Thin Aluminum Nitride Film Resonators: Miniaturized High Sensitivity Mass Sensors," Analytical Chemistry, 64, 1992, pp. 1289-1294.

FOURIER-TRANSFORM INFRARED PHOTOACOUSTIC SPECTROSCOPY

DESCRIPTION

Fourier-transform infrared photoacoustic spectroscopy (FTIR-PAS) is being employed for the quantitative determination of infrared active species in underground storage tank (UST) wastes at the DOE Hanford site in Richland, Washington. FTIR-PAS provides quantitative compositional analysis of the multiatomic ions and molecular species which are chemically active components in sludges and solids. The advantages of FTIR-PAS are that small samples (milligram size) and little sample preparation are needed. Thinning or diluting the sample is not required as in other conventional spectroscopic methods.

Signal generation in FTIR-PAS results from the absorbed infrared radiation being converted into heat. The heat produces a thermal wave within the sample which travels to the surface and transfers to the surrounding gas in the PAS cell. Thermal expansion of the gas then results in an acoustic wave that is picked up by a microphone in the PAS cell. Because the photoacoustic signal is largely dependent on the absorption coefficient and thermal properties of the sample, all that is required to perform quantitative analysis is a sampling geometry that results in samples of constant volume and uniform composition. Uniform samples for analysis have been produced by freeze drying to remove interfering water and prevent the soluble components in the simulants from migrating.

Cost. The cost of the FTIR-PAS analysis instrument is approximately $26K.

TECHNICAL PERFORMANCE

The FTIR-PAS method was developed with UST simulants prepared by the Westinghouse Hanford Company. Emphasis was placed on analysis of disodium nickel ferrocyanide, sodium nitrate and sodium nitrite because of the concern for the potential exothermic reactions occurring between oxidizers and ferrocyanide containing compounds present in the tanks. PAS was used as a direct analysis method for tank wastes because of its capability to optically interrogate small amounts of intractable materials which are fairly opaque.

Laboratory Experiments. Samples for analysis were prepared by applying a small amount (approximately 1 mg) of tank waste simulant to a specially designed sample disk which had a small cavity allowing a small, reproducible volume of sample to be acquired. The sample was then freeze dried. After freeze drying the sample was brought to room temperature, removed, and placed in a desiccator for analysis.

All data was collected on a Bio-Rad Digilab FTS-60 FTIR spectrometer equipped with a MTEC Model 200 photoacoustic cell. Helium was used as the purge gas in the photoacoustic cell. Two-hundred fifty-six scans were accumulated at 2.5 kHz at 8 cm^{-1} resolution. Sludge spectra were normalized against carbon black to account for spectral variations caused by the infrared source and spectrometer.

Step-scan phase modulation studies were also performed on the FTS-60A. Data were collected at a mirror velocity of 25 Hz, phase-modulation frequency of 400 Hz, and phase-modulation amplitude of 2 laser fringes. A simple sample preparation protocol was then followed and spectra obtained.

Figure 12.3a shows typical photoacoustic spectra of several tank waste simulants that were obtained. Sharp absorption bands are observed that can be used for both qualitative and quantitative analysis. The

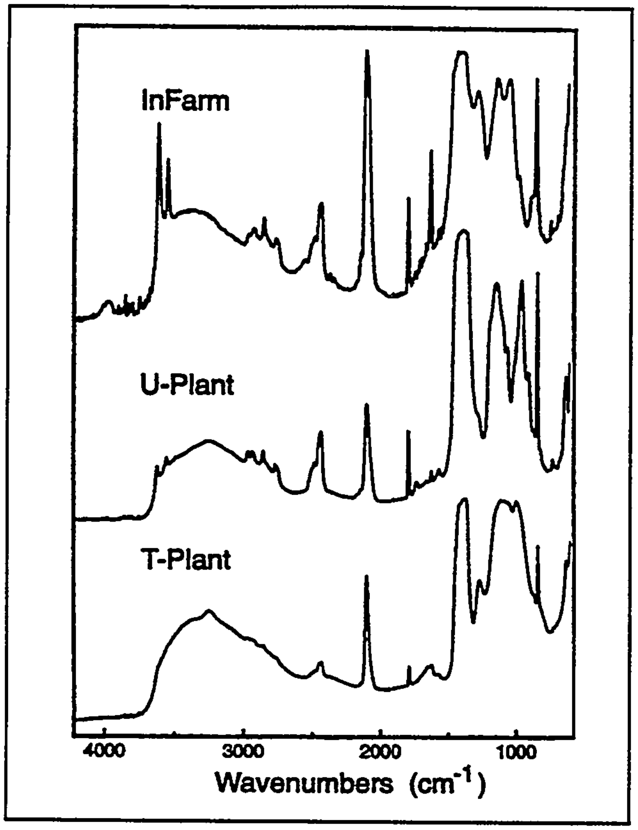


Figure 12.3a. Photoacoustic spectra of different UST waste simulants.

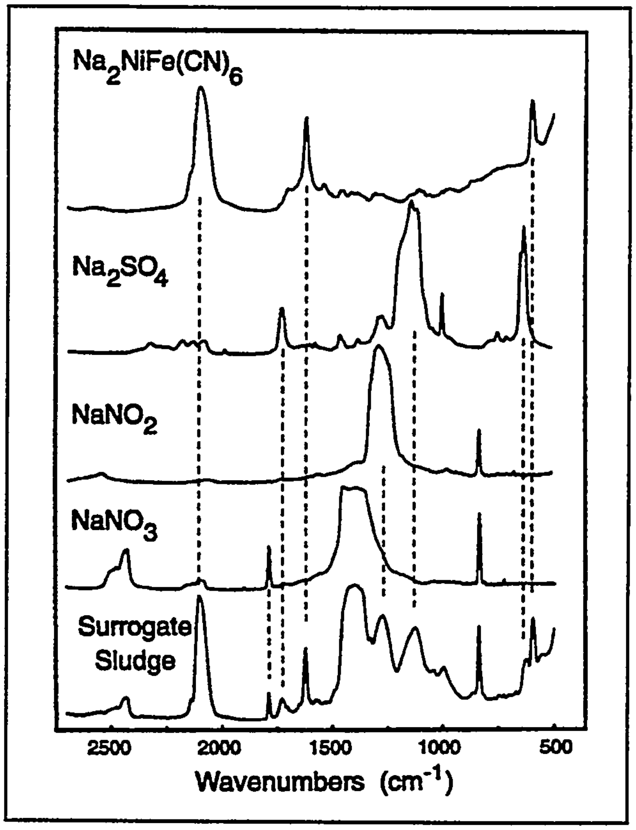


Figure 12.3b. Photoacoustic Spectra of a tank waste surrogate and several pure components which are present in the surrogate.

three formulations (indicated by InFarm, U-Plant, and T-Plant) differ by the amount of certain components as exhibited by the varying intensities of several absorption bands in the photoacoustic spectra. Compositional analysis of the tank waste surrogates was performed by comparing the absorption bands of a simulant with those of pure compounds. The spectra are shown in Figure 12.3b.

The FTIR-PAS was shown to be viable for analysis of UST waste surrogates for nitrate and nickel ferrocyanide within the concentration range of interest.

PROJECTED PERFORMANCE

Not applicable.

APPLICABILITY

FTIR-PAS is applicable to physically and chemically heterogeneous, chemically active, and radioactive sludges and solids.

STATUS

The photoacoustic detectors used in FTIR-PAS were been commercialized by MTEC Photoacoustics, Inc.

REGULATORY CONSIDERATIONS

This technology does not require any special permits.

POTENTIAL COMMERCIAL APPLICATIONS

FTIR-PAS can be used in industrial applications for solid-sample analysis, and depth-specific PAS could also be developed as a new method for gas chromatography detection of compounds that absorb very weakly in the IR region of the spectrum.

BASELINE TECHNOLOGY

The baseline analytical methods include IR transmission spectroscopy methods such as specular reflectance, diffuse reflectance (DRIFTS), and attenuated total reflectance (ATR) methods. These methods typically require extensive sample handling procedures to either thin the sample or to separate components before analysis.

INTELLECTUAL PROPERTY

FTIR-PAS was commercialized by MTEC Photoacoustics, Inc.- the principal producer of photoacoustic detectors worldwide.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
John McClelland
Ames Laboratory
B27 Spedding Hall
Iowa State University
Ames, IA 50011-3020
(515) 294-7948; (515) 294-3226 FAX

DOE Project Manager
Al Tardiff
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7670

Industrial Partner

MTEC Photoacoustics, Inc.
P.O. Box 1095
Ames, IA 50014
(515) 292-7974

REFERENCES

1. Bajic, S.J., S. Luo, R.W. Jones, and J.F. McClelland, "Analysis of Underground Storage Tank Waste Simulants by Fourier Transform Infrared Photoacoustic Spectroscopy," Applied Spectroscopy, July 1995.

2. Nobel, D., "FT-IR PAS Steps Up to Depth Profiling," Analytical Chemistry, Vol.66, No. 14, July 15, 1994, pp. 757A-760A.

IMAGING THROUGH OBSCURATIONS DURING SLUICING OPERATIONS

DESCRIPTION

Three candidate methods for viewing through obscurations such as fog and water droplets that can occur during waste tank remediation efforts were evaluated. Workspace images guide the movement of remediation equipment, creating a need for rapidly updated imaging capability, in near real-time. Optical, acoustic, and radar imaging techniques that provide high-resolution, three-dimensional images were evaluated.

The waste tank remediation work being conducted at the DOE Hanford site in Richland, Washington, was used as a model for the requirements of a viewing system. A test chamber was fabricated to test the candidate methods. The chamber consisted of four sections of fiberglass tube, 3 ft in diameter and 10 ft long. The adjacent tube sections were attached to each other using a rubber clamp and a sheet metal clamp. Thus, the test chamber was 40 ft long with open ends so the instruments and target could be mounted without getting wet. A pump and an air compressor fed water and air through piping at the top of the test chamber to spray nozzles within the chamber. Three sets of changeable nozzles were used for the tests: one set of nozzles produced 25 micron size particles (fog) at a flow rate of 0.05 gal/min, a second set of nozzles produced 700 micron size particles (water droplets) at a flow rate of 0.5 gal/min, and a third set of nozzles produced 1,100 micron size particles at a flow rate of 1.7 gal/min.

TECHNICAL PERFORMANCE

Of the three imaging techniques tested, the sensors operating with millimeter waves (94 GHz) were best able to penetrate the fog/water droplets. Signal loss ranged from 0.015 db/ft in 25 micron diameter fog to 0.110 db/ft for 1,100 micron diameter water particles. Signals were measured 30 db - 40 db above noise, using a high-reflecting target. In addition, the millimeter wave sensor was not affected by increasing the conductivity of the fog/water droplets. The antenna used for these tests was small (1" W x 1" H x 3" L) and could be placed on a scanner to obtain the desired images.

Video imaging was not able to penetrate the thickest fog/water droplets; however, it is the least expensive, would require the least amount of technical development, and can be used when the fog/water droplets are not as dense.

Laser range gating was successfully used for imaging through murky water; however, no system is commercially available system that is able to operate at the short target distances that will occur in a waste tank.

Infrared optical techniques do not appear viable for viewing through obscurants during a sluicing operation. Although infrared detectors did operate in thicker fog than visible techniques, they exhibited higher attenuation in water droplets.

The selection of the best method for viewing through fog/water droplets in a waste tank depends on the specific waste tank conditions such as the density of the fog/water droplets.

Acoustic sensors would need to be operated at higher power to be used for this application. At 215 kHz, 75% of the power of the beam would be lost in the fog in the round-trip travel to a target 80 ft away.

Table 12.4 summarizes the results of the study. The results are stated in terms of a "figure of merit," which is the ratio of the distance to the target where the target is just visible using the stated detection/illumination method to the distance at which the target is barely able to be seen by the naked eye. If the figure of merit is greater than unity, then the target can be

Table 12.4. Comparison of test results with different sensors.

Sensor	**Wavelength (Microns)**	**Figure of Merit**						**Notes**
		40 ft Target Distance Particle Size (micron)			80 ft Target Distance Particle Size (micron)			
		25	700	1,100	25	700	1,100	
Optical Sensors								
CCD	0.4-1.1							
Backlighted		0.67	0.59	0.39	—	—	—	1,2
Frontlighted		1.00	>0.67	>0.50	1.01	0.55	0.49	1,3
CID	0.4-1.1							
Backlighted		0.68	0.51	0.39	—	—	—	1,2
Frontlighted		—	0.51	0.46	—	—	—	1,3
Image Intensified	0.4-1.1	—	—	—	—	—	—	1,4
Contrast Enhanced	0.4-1.1							
Backlighted		0.82	>0.67	>0.50	—	—	—	1,2
Frontlighted		1.29	>0.67	>0.50	1.29	0.93	0.78	1,3
Laser Rangefinder	0.83	0.73	0.33	0.30	—	—	—	5
Photoconductive	0.4-2.2	0.56	0.51	—	—	—	—	1,6
In-Sb	2.0-5.6	1.18	0.30	0.30	0.85	0.31	0.21	7,9
Hg-Cd-Te	3.2-5.6	0.75	0.19	0.24	0.50	0.12	0.07	8
Hg-Cd-Te	8-12	1.43	0.23	0.14	2.00	0.24	0.15	7,9
Acoustic Sensors								
Electrostatic	6,600 (50 kHz)	—	—	—	—	—	—	10
Piezoelectric	6,600 (50 kHz)	—	—	—	—	—	—	10
Piezoelectric	1,500 (215 kHz)	—	—	—	—	—	—	11
Millimeter Wave Sensors								
94 GHz	3,190	>2.67	>0.67	>0.50	—	—	—	12

Notes

1. The target for the tests in the visible region was an oxidized steel plate with a reflectivity of 25% and illuminated with 38 ft-c.
2. Backlighting at 80 ft could not be accomplished with the test set-up.
3. The visual range with frontlighting will decrease as the intensity of the light source increases.
4. Image blooming occurred with the image intensified camera.
5. Backscatter from the fog/water droplets resulted in the loss of range data but images were obtained providing water droplets were at least 16 ft from the rangefinder.
6. An arc lamp was used as the light source in testing this camera. There was no change in the visibility range of the fog/water droplets when the image was viewed in the near infrared.
7. Detector is cooled with liquid nitrogen.
8. Detector is thermoelectrically cooled.
9. This is with target at 10°F above ambient. The target will be visible through denser fog/water droplets as the target temperature increases.
10. The 50 kHz acoustic sensor is affected by noise of air/water movement.
11. The commercial acoustic sensor that was tested did not have enough power to penetrate the fog. Tests indicate that this acoustic sensor would lose 75% of its power traveling to and from a target at 80 ft.
12. The mm-wave sensor was able to penetrate the thickest fog/water droplets produced by the test chamber. Attenuation was measured to be 1-8 db for a target at 40 ft.

detected at a greater distance than it can be seen visually. The higher the figure of merit, the better the method is for imaging through fog/water droplets.

Cost. It is estimated that the hardware to develop a millimeter wave system to be placed in a waste tank would cost (unburdened) approximately $100K-$125K. Additional costs include the deployment system, and labor for assembling, testing, and deploying the system.

PROJECTED PERFORMANCE

In FY 1995, a millimeter wave imaging system will be developed to provide a system that may be used by tank operations. The millimeter wave imaging system is expected save a substantial amount of time and money for remediation of tank wastes.

APPLICABILITY

The viewing systems tested are applicable to viewing through obscurations such as fog and water droplets that can occur during waste tank remediation efforts.

STATUS

Test results from the experiments performed will provide the basis to determine the best method to view through fog/water droplets in a waste tank during a sluicing operation.

REGULATORY CONSIDERATIONS

The technology does not require any permits.

POTENTIAL COMMERCIAL APPLICATIONS

This technology has potential commercial applications in surveillance (e.g., police, border patrol), collision avoidance (e.g., robots, vehicles), and remote detection of objects.

BASELINE TECHNOLOGY

There is no baseline technology with which to compare. At present, because of the closed environment in which the tank waste remediation effort is conducted, a substantial amount of time is needed to clear the atmosphere so that the effect of the remediation effort can be determined. During this time, labor costs continue and equipment is being exposed to the hazardous environment. In addition, safety can be jeopardized because the remediation operation is not being viewed in near real-time.

INTELLECTUAL PROPERTY

None.

For more information, please contact:

Center for Environmental Management Information
1-800-736-3282

Principal Investigator
Douglas McMakin
Pacific Northwest Laboratory
P.O. Box 999, MS K5-25
Richland, WA 99352
(509) 375-2206

DOE Project Manager
Al Tardiff
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7670

REFERENCE

1. Peters, T.J., D.L. McMakin, D.M. Sheen, and M.A. Chieda, Imaging Through Obscurations for Sluicing Operations in the Waste Storage Tanks, Pacific Northwest Laboratory, Richland, WA, PNL-9998, August 1994.

IN-TANK INTERFACE DETECTION USING TIME DOMAIN REFLECTOMETRY

DESCRIPTION

Time Domain Reflectometry (TDR) is a cost-effective means of monitoring liquids in waste tanks at the DOE Hanford Site located in Richland, Washington. Of the 150 underground storage, single shell tanks (SSTs) at the Hanford Site, at least half are assumed or known leakers with no sufficient level detection being employed. After stabilization by removing the free liquid volume, the interstitial liquid in the remnant salt cake is a persisting potential for leakage, moreover, current level detection methods for the remnant pore volume liquid are not viable. Successful application of TDR level detection to this situation would be a significant accomplishment.

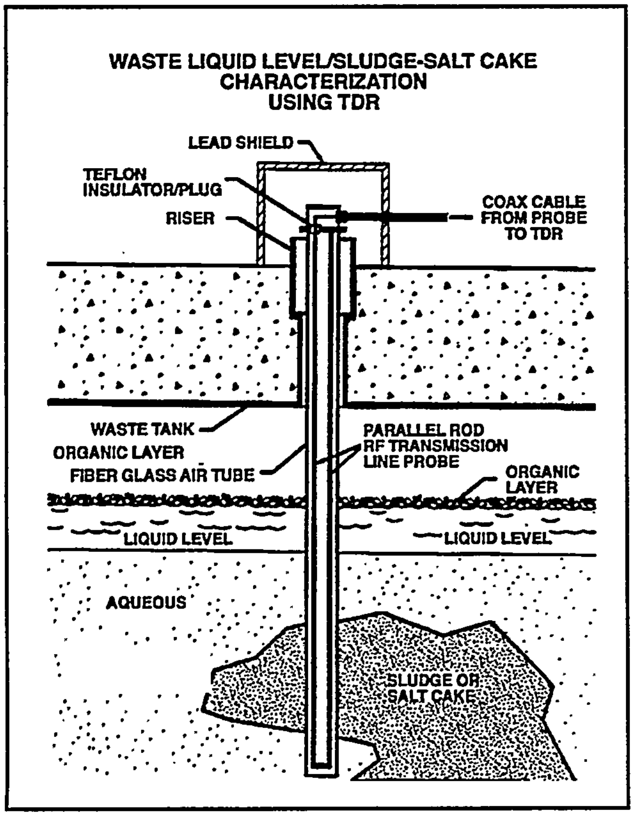


Figure 12.5a. Waste liquid level/sludge-salt cake characterization using Time Domain Reflectometry.

Computer controlled TDR is the most advanced and safest method of liquid level detection for hazardous, high value, or highly sensitive liquids. TDR is an internal radar system using radio frequency (RF) cable. Impedance dicontinuities such as an air/liquid interface, cause reflections of the interrogation signal. A receiver detects the small signals created by the reflections and measures travel times. Both the interrogation signal travel time and the reflection "flight time" are measured. The total signal "flight time" is proportional to distance and this distance can be translated to a measurement of the liquid level.

The receiver is a digital oscilloscope and, therefore, has the capability of measuring precise times. Any spurious reflection noise will not affect the application because a threshold amplitude can be preset such that only signals above this level will be considered for travel time measurements. This adjustable parameter enables the system to also distinguish between different impedance discontinuities and therefore separates reflections caused by calibration targets and other interfaces from the desired liquid/air interface. The digital oscilloscope is computer controlled via the IEEE 488bus. The computer converts the oscilloscope readings to liquid level.

Figure 12.5a shows how the TDR is applied through a tank riser to measure the liquid level. The probe consists of a stainless steel (SS) rod inside a perforated SS pipe. The rod is welded to the bottom of the pipe and extends through a gas tight insulating bushing at the top and terminates in a standard type "N" RF connector. An RF transmission line connects the probe to the TDR electronics.

Any problem with the interconnecting coax can be determined (shorts, opens and their position). Software development has integrated computer controlled microwave coaxial switches into the existing equipment. This allows the multiplexing of several probes to one system of TDR electronics. A failure of the TDR will be instantly sensed by the computer, as well as any drift that causes an out of tolerance reading of the distance between the calibration targets. The computer can also periodically scan the length of the coax for any indications of cable damage or degradation.

The system is self calibrating and not subject to unknown or slow drift. No flowing gas is required; therefore, accuracy is not affected by changes in headspace pressure, liquid density or conductivity, barometric pressure, temperature, contaminants in the liquid, radiation levels, or by corrosiveness or reactivity in the liquid.

TECHNICAL PERFORMANCE

The TDR is unaffected by radiation, temperature, pressure or liquid composition. The probe can function in the liquid or possibly inside the liquid observation wells (LOWs) present in the Handford tanks. Tests with a laboratory twin lead probe in a LOW mock up showed that the configuration can detect liquid outside the LOW with surprising accuracy (see Figure 12.5b). For static or slowly changing levels, accuracy approaching 0.01" is achievable. This finding is very encouraging because of the possibility that interstitial water in salt cake can be monitored in the Hanford tanks using their LOWs.

1994 Accomplishments. Several probe configurations were designed and tested. These included both coaxial and twin lead probes with calibration discontinuities. An improved constant impedance connector was also fabricated. A microwave coaxial relay was integrated into the system along with the controlling software permitting multiplexing up to six probes to a single TDR electronics system. The Savannah River TNX single probe system was upgraded using the improved connector design with two additional probes for a system total of three. Two organic/aqueous decanters and one organic hold tank are continuously monitored at present by the TNX probe. Now that the aqueous level has been determined, the organic thickness can also be determined based on the aqueous information not previously available. The TDR information is the controlling factor in the process. The probe tests determined that a twin lead probe was best suited for use in Hanford SSTs.

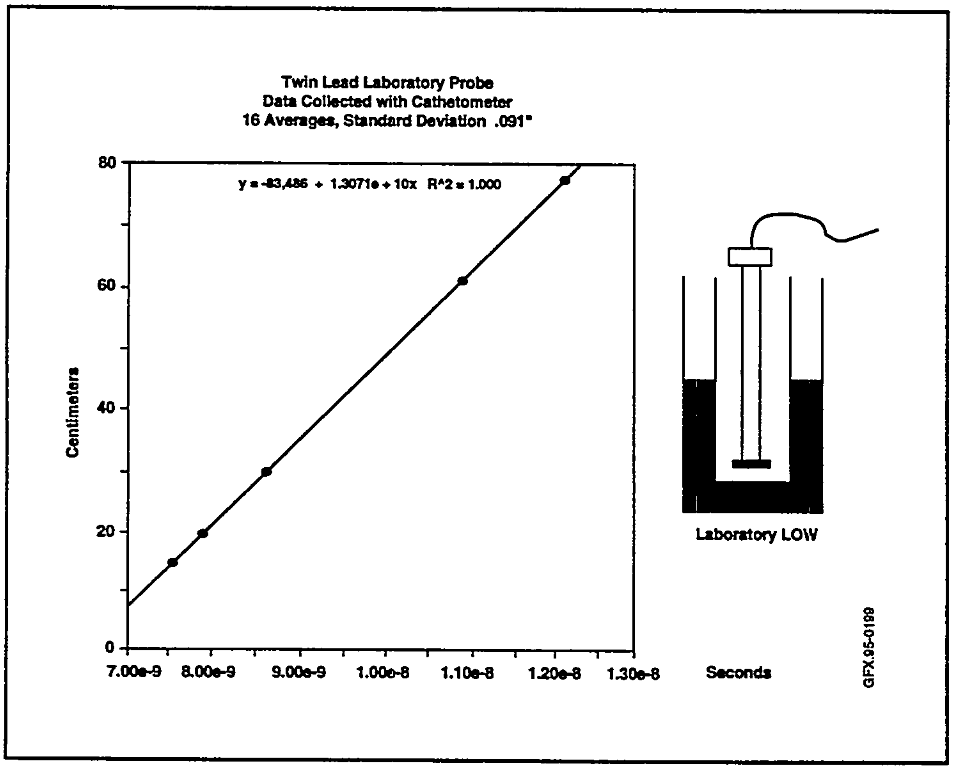


Figure 12.5b. Twin lead laboratory probe data collected with cathetometer.

Cost. Cost estimates were not available at this writing.

PROJECTED PERFORMANCE

Tests will be performed with waste simulants (with different moisture contents) in a Hanford waste tank mockup. Tests with neutron and electromagnetic (eddy current) moisture measurement devices will also be performed under the same conditions by Hanford personnel so the results can be directly compared.

APPLICABILITY

This technology is applicable to the measurement of liquid levels (and presumably solids levels) in any tank, above ground or underground by measuring the location of a microwave impedance discontinuity. An impedance discontinuity can result from a liquid/air interface or a liquid interface if the densities are significantly different. The TDR probe is unaffected by radiation, temperature, pressure, or liquid composition. The TDRs can also be applied to measure the liquid level of pores in the solid phase.

STATUS

This technology has been prototyped in as much as it was used at the Savannah River Site in the K reactor before its shut down. For simple liquid-in-tank applications, the technology is available; however, for more complex applications such as the Hanford application (liquid level in porous material with limited access to storage tanks), TDRs have only been tested at the laboratory scale.

REGULATORY CONSIDERATIONS

Contact the principal investigator for regulatory information.

POTENTIAL COMMERCIAL APPLICATIONS

This technology could potentially be used in the chemical and petrochemical industries to measure and monitor liquid levels, especially in critical safety or highly valued chemical applications. It could also be applied in boiling water nuclear reactor applications or other critical coolant applications in the nuclear industry.

BASELINE TECHNOLOGY

There is no baseline technology for the monitoring of liquid levels in the pores of salt cake.

INTELLECTUAL PROPERTY

Contact the principal investigator for intellectual property information.

For more information, please contact:

Center for Environmental Management Information

1-800-736-3282

Principal Investigator

Hilton R. Tilley, Sr.
Westinghouse Savannah River Company
Aiken, SC 29808
(803) 725-1876

DOE Project Manager

Al Tardiff
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-7670

REFERENCES

None.

Additional Technology Information

Section 13.0

13.0 ADDITIONAL TECHNOLOGY INFORMATION

The DOE Center for Environmental Management Information

The DOE Center for Environmental Management Information provides environmental restoration and waste management information through a variety of electronic sources and through technical and nontechnical documents, visuals, videos, periodicals and news articles. By dialing one of the numbers listed below, a caller can obtain facts and details related to DOE Environmental Management programs.

Toll-Free Number:	1-800-7-EM DATA (1-800-736-3282)	Monday - Friday 9 a.m. - 7 p.m. Eastern Time
In Washington, DC:	202-863-5084	

The DOE EnviroTRADE® Information System

EnviroTRADE® (**Environmental** Technologies **R**emedial **A**ctions **D**ata **E**xchange) is an international environmental information system that matches environmental needs with potential technological solutions (and vice versa) by combining state-of-the-art information management techniques, graphical user interfaces, and geographical informations system (GIS) capabilities. The EnviroTRADE® information system contains profiles on domestic and foreign environmental restoration and waste management technologies. EnviroTRADE® may be accessed via the Internet at th283e URL: http://ramah.geoid.sandia.gov

The CMST Catalogue Internet Homepage

Information about the DOE Office of Science and Technology Characterization, Monitoring, and Sensor Technology Crosscutting Program is available on the Internet at the URL address: http://cmst.ameslab.gov/cmst/homepage.html. The CMST Catalogue can be accessed under the "Reports and Publications" heading on the homepage.

List of Acronyms

Section 14.0

14.0 ACRONYMS AND INITIALISMS

3D-ICAS	Three-Dimensional Integrated Characterization Archiving System
A&PCT	Active and Passive Gamma-ray Computer Tomography
AA	Atomic Adsorption
AIM	Acquisition Interface Module
AMs	Arm Monitors
ANET	Active Nitrogen Energy Transfer
API	Associated Particle Imaging
ARA	Applied Research Associates, Inc.
ASTM	American Standard Testing Methods
ATR	Attenuated Total Reflectance
B&W	Babcock & Wilcox
BAT	Best Available Technology
BIR	Bio-Imaging Research, Inc.
CAAA	Clean Air Act Amendments
CAMs	Continuous Air Monitors
CCD	Charge Coupled Device
CDIF	Component Development Integration Facility
CEM	Continuous Emission Monitoring
CFCs	Chlorofluorocarbons
CLP	Certified Laboratory Procedure
CLR	Coherent Laser Radar
CLVS	Coherent Laser Vision System
CMW	Charles Machine Works Inc.
CP	Cone Penetrometer
CPAC	Center for Process Analytical Chemistry
CPT	Cone Penetrometer Technology
CRADA	Cooperative Research and Development Agreement
CRC	Coleman Research Corporation
CT	Computer Tomography
CTP	Cold Test Pit
CTS	Calibration Transfer Standard
CW	Chemical Weapons
CW	Continuous Wave
CWL	Chemical Waste Landfill
D&D	Decontamination and Decommissioning
D-B	Dielectric Barrier
DAC	Derived Air Concentration
DAS	Diode Array Spectrophotometer
DCBF	Dichlorodibenzofuran
DIN	Direct Injection Nebulizer
DNA	Deoxyribo Nucleic Acid
DNAPLs	Dense Nonaqueous Phase Liquids

DoD	Department of Defense
DOE	Department of Energy
DOF	Degrees of Freedom
DR	Digital Radiography
DSITMS	Direct Sampling Ion Trap Mass Spectrometry
DST	Doubled-Shell Tank
EDTA	Ethylenediamine Tetraacetate
EM	Electromagnetic
EnviroTRADE	Environmental Technologies Remedial Actions Data Exchange
EPA	Environmental Protection Agency
ERT	Electrical Resistance Tomography
FEMP	Fernald Environmental Management Project
FTAM	Flow-Through Alpha Monitor
FTIR	Fourier Transform Infrared
FTIR-PAS	Fourier-Transform Infrared Photoacoustic Spectroscopy
FUSRAP	Formerly Utilized Sites Remedial Action Program
GC	Gas Chromatograph
GC/MS	Gas Chromatography/Mass Spectrometry
GIS	Graphical Information System
GPER	Geophysics Performance Evaluation Range
GPS	Global Positioning System
GRASS	Geographical Resource Analysis Software System
GROs	Gasoline Range Organics
HDBL	Hybrid Directional Boring and Logging
HEPA	High Efficiency Particulate Air
HMs	Hand Monitors
HPGe	High Purity Germanium
HRM	Home Radon Monitor
HVAC	Heating, Ventilating and Air Conditioning
ICAP	Inductively Coupled Argon Plasma
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICPP	Idaho Chemical Processing Plant
INEL	Idaho National Engineering Laboratory
ISDRNC	In Situ Determination of Radionuclide Contaminants
ISGRS	In Situ Gamma-Ray Spectroscopy
ISURF	Iowa State University Research Foundation
ITMS	Ion Trap Mass Spectrometer
LA-ICP-AES/MS	Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectrometry/Mass Spectrometry
LASS	Laser Spark Spectroscopy
LDPE	Low-density Polyethylene
LIBS	Laser-Induced Breakdown Spectroscopy
LLD	Lower Level of Detection
LLNL	Lawrence Livermore National Laboratory
LNAPLs	Light Nonaqueous Phase Liquids
LOWs	Liquid Observation Wells
LRAD	Long-Range Alpha Detection

MCT	Mercury Cadmium Telluride
MDL	Method Detection Limit
MDLEST	Mobile Demonstration Laboratory for Environmental Screening Technologies
MDMI	Monodisperse Dried Microparticulate Injection
MIR	Mid-Infrared Reflectance
MMES	Martin Marietta Energy Systems
MPA	Most Probable Number
MSL	Mean Sea Level
MTA	Magnetometer Towed Array
MVS	Molecular Vibrational Spectroscopic
NDA	Nondestructive Assay
NDE	Nondestructive Evaluation
NIR	Near-Infrared Raman
NIST	National Institute of Standards and Testing
OFFE	Office of Federal Facility Enforcement
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
PAS	Photoacoustic Spectroscopy
PAWS	Portable Acoustic Wave Sensor
PCBs	Polychlorinated Biphenyls
PCDF	Polychlorinated Dibenzofuran
PCE	Tetrachloroethylene
PCM	Post-Closure Monitoring
PGNAA	Prompt Gamma Neutron Activation Analysis
PID	Photoionization Detector
PLFA	Phospholipid Fatty Acid
PMT	Photomultiplier Tube
PNL	Pacific Northwest Laboratories
POLO	Position Location
PRDA	Program Research and Development Agreement
PSI	Physical Sciences, Inc.
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
RCRA	Resource Conservation and Recovery Act
RF	Radio Frequency
RFP	Rocky Flats Plant
RGS	Rapid Geophysical Surveyor
RH	Relative Humidity
RQM	Routine Quarterly Monitoring
RRDEC	Radon/Radon Daughter Environmental Chamber
RSD	Relative Standard Deviation
RSSAR	Rapid Surface Sampling and Archival Record
RTML	Rapid Transuranic Monitoring Laboratory
RTR	Real-Time Radiography
RWMC	Radioactive Waste Management Complex
S/N	Signal/Noise

SA	Stripping Analysis
SAW	Surface Acoustic Wave
SDA	Surface Disposal Area
SDPP	Soil Decontamination Pilot Plant
SEA	Science and Engineering Associates, Inc.
SEG	Scientific Ecology Group, Inc.
SERS	Surface Enhanced Raman Spectroscopy
SGI	Sol-gel Indicator
SGS	Segmented Gamma Scanning
SNL	Sandia National Laboratories
SOP	Standard Operating Procedure
SPECT	Single Photon Gamma-ray Emission Computer Tomography
SRS	Savannah River Site
SRTC	Savannah River Technology Center
SS	Stainless Steel
SST	Single-Shell Tank
STI	Sewage Treatment Incinerator
STNG	Sealed Tube Neutron Generator
SVOC	Semivolatile Organic Compound
TCA	Trichloroethane
TCE	Trichloroethylene
TCL	Target Compound List
TD	Thermedics Detection
TDR	Time Domain Reflectometry
TEAM	Toxic Emission Air Monitor
TFR	Thin Film Resonator
TIP	Technical Integration Program
TIRES	Transient Infrared Emission Spectroscopy
TIRTS	Transient Infrared Transmission Spectroscopy
TRU	Transuranic
TSCA	Toxic Substances Control Act
TWA	Total Weighted Average
UCAP	Unlined Chromic Acid Pit
UFA	Unsaturated Flow Apparatus
UST	Underground Storage Tank
VES	Vapor Extraction System
VOC	Volatile Organic Compound
VOST	Volatile Organic Sampling Train
WDC	Water Development Corporation
WIT	Waste Inspection Tomography
WPCF	Water Pollution Control Facility
XRF	X-Ray Fluorescence
ZTL	Zero-Tension Lysimeter

Distribution List for the SAND Report - CMST Catalogue

3 Joseph Paladino
Program Manager
EM 52.1
U.S. Department of Energy
Cloverleaf Building
19901 Germantown Road
Germantown, MD 20874-1290

1 Paul Wang
Ames Laboratory
125 Spedding Hall
Iowa State University
Ames, IA 50011-3020

5 Jeff Lenhert
U.S. Department of Energy
Albuquerque Operations Office
Office of Energy and Science Technology
P.O. Box 5400
Albuquerque, NM 87185-5400

6 Dan Krivitsky
U.S. Department of Energy
Albuquerque Operations Office
P.O. Box 5400
Albuquerque, NM 87185-5400

5 Richard Jimenez President
Applied Sciences Laboratory, Inc.
P.O. Box 21158
Albuquerque, NM 87154

SNL PRINCIPAL INVESTIGATORS

1 MS 1326 John Cochran, 6851

1 MS 0720 Robert Knowlton, 6626

1 MS 9103 William Flower, 8111

1 MS 0750 David Borns, 6116

1 MS 1033 Robert Wemple, 6111

1 MS 0503 George Laguna, 2337

1	MS 0351Greg Frye, 1315
1	MS 0750 Sanford Ballard, 6116

SNL INTERNAL

1	MS 0724 Joan Woodard, 6000
1	MS 0726 James Rice, 6600
1	MS 0727 Tom Sanders, 6404
1	MS 0756 George Allen, 6610
1	MS 0756 Reeta Garber, 6610
1	MS 0746 Charlene Harlan, 6613
1	MS 0722 Mark Harrington, 6614
1	MS 0719 Thomas Burford, 6621
1	MS 0719 Jennifer Nelson, 6621
1	MS 1335 Margaret S.Y. Chu, 6622
1	MS 0719 Cecilia Williams, 6621
1	MS 9018 Central Tech Files, 8523-2
5	MS 0899 Tech Library, 4414
1	MS 0619 Print Media, 12615
2	MS 0100, Document Processing, 7613-2 For DOE/OSTI
25	MS 0761 R.V. Matalucci, 5822