Strategic Environmental Research and Development Program

Proceedings of the 2nd Annual Site Characterization and Analysis Penetrometer System (SCAPS) Sensor Development Workshop

29-30 August 1995,
Vicksburg, Mississippi

by Ernesto R. Cespedes, Diane M. Cargile

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Prepared for Headquarters, U.S. Army Corps of Engineers
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Preface

The 2nd Annual Site Characterization and Analysis Penetrometer System (SCAPS) Sensor Development Workshop was held at the U.S. Army Engineer Waterways Experiment Station (WES) on 29-30 August 1995. The workshop was sponsored by the Strategic Environmental Research and Development Program (SERDP), Washington, DC, under Project Number 94-729, "Accelerated Tri-Services SCAPS Sensor Development." Dr. John Harrison is Acting Executive Director, SERDP.

The workshop was organized and coordinated by Dr. Ernesto R. Cespedes, Environmental Engineering Division (EED), Environmental Laboratory (EL), WES, with the assistance of Ms. Diane M. Cargile, EED. This report on the proceedings of the workshop was compiled and prepared by Dr. Cespedes and Ms. Cargile.

This report was prepared under the general supervision of Mr. Norman R. Francingues, Chief, EED, and Dr. John W. Keeley, Director, EL.

At the time of publication of this report, Dr. Robert W. Whalin was Director of WES. COL Bruce K. Howard, EN, was Commander.

This report should be cited as follows:

1 Introduction

Background

The Site Characterization and Analysis Penetrometer System (SCAPS) is receiving wide acceptance as a versatile tool for rapid subsurface screening of contaminated sites. Since the fielding of the first SCAPS vehicle at the U.S. Army Engineers Waterways Experiment Station (WES) during 1990, the Tri-Service SCAPS fleet has grown to seven vehicles (four Army and three Navy). In addition, the Department of Energy operates two SCAPS vehicles, and private contractors, under licensing agreements, operate a number of SCAPS technologies that support DoD, DOE, and EPA site characterization efforts.

The SCAPS platform consists of a 20-ton truck equipped with vertical hydraulic rams capable of pushing a cone penetrometer into the ground at a speed of 2 cm/sec to depths of over 50 m in nominally consolidated, fine-grained soils. During a push, SCAPS is capable of collecting subsurface stratigraphy data with spatial resolutions of 2 cm, as well as chemical contaminant data by means of sensors and samplers incorporated into the penetrometer head. The primary application of SCAPS technology has been to characterize sites contaminated with heavy petroleum, oils, and lubricants (POLs) by means of a laser induced fluorescence (LIF) sensors (Lieberman et al. 1991). Successful fielding of the LIF technology led to increased interest in expanding SCAPS capabilities to address other contaminants (Cespedes et al. 1994)

In 1994 the Strategic Environmental Research and Development Program (SERDP) funded a Tri-Service effort to accelerate the development and testing of advanced sensors and sampling technologies for SCAPS to allow characterization of sites containing explosives, metals, volatile organic compounds (VOCs), light POLs, and radioactive wastes (SERDP 1995). During the 1994 SERDP Program Review, the Scientific Advisory Board requested that a peer review panel be set up to monitor the progress of the sensor development project. It was also requested that yearly meetings be held that included the peer review panel, the Tri-Service developers, and the SCAPS users. The first meeting was held during 16-17 August 1994 and was expanded to include DOE and EPA researchers and users. This report describes the second
meeting which was held during 29-30 August 1995 at the U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

Objective

The primary objective of this workshop was to have the Peer Review Panel evaluate the progress of the SCAPS sensor development project during the previous year and to have them recommend changes or re-directions of the research effort. In addition, the workshop provided an open forum for discussion of ongoing sensor development activities related to SCAPS within the Tri-Service, DOE, and EPA, with the goal of fostering partnering between agencies and reducing any duplication of effort. Lastly, the workshop provided an opportunity for SCAPS managers and users to evaluate ongoing research and to provide feedback to the sensor developers.
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4 Agenda

SCAPS Sensor Development Workshop
29-30 August 1995
USAE Waterways Experiment Station
3909 Halls Ferry Road
Vicksburg, Mississippi

Tuesday, 29 August 1995

0830 Welcome ................. COL Howard (WES Commander)
0835 Overview .................. Dr. Keeley (Env. Lab Director)
0845 Introduction of SERDP Panel Membership .... Dr. Cespedes (WES)
0900 Project Description/Status .................. Dr. Cespedes

0915 SERDP Program Research Areas .............. Dr. Cespedes

I. Laser Induced Breakdown Spectroscopy (LIBS) .... Dr. Cespedes
   Dr. Miziolek (ARL)
   Mr. Theriault (NRaD)

II. Laser Induced Fluorescence Sensors

   A. POL ................................ Dr. Lieberman (NRaD)
      Mr. Nielsen (USAF/AL)
   B. Explosives .......................... Dr. Cespedes
      Dr. Sausa (ARL)

1045 Break

1100 III. Fiber Optic Raman Sensors ............... Dr. Boss (NRaD)
         Mr. Nielsen
IV. Electrochemical Sensors
   A. Explosives ....................... Dr. Cespedes
   B. VOC ............................ Dr. Davis (WES)

V. Spectral Gamma Probe ................ Mr. Register (WES)

1230  Lunch

1315  VI. Sampling Technology ............ Dr. Brannon (WES)
       Dr. Davis
       Mr. Leavell (WES)

VII. Data Processing Methodologies .... Mr. Goodson (WES)
VIII. Technology Demonstration/Implementation .... Dr. Davis
      Mr. Drinkwine (MRK, COE)
      Dr. Lieberman

1500  Break

1515  User Needs ........................ SCAPS Managers & Operators
      (ARMY, Navy, DOE, EPA)

1630  Adjourn

Wednesday, 30 August 1995

0830  Conclusions and Recommendations ............ SERDP Panel

0915  DOE/EPA/DoD Related Research

   A. On-Line Organic Sampler ............. Dr. Doskey (ANL)
   B. Moisture and Pore Pressure Sensors .... Dr. Knowlton (SNL)
   C. Fiber Optic IR Sensor ............... Dr. Aggarwal (NRL)

1000  Break

1015  DOE/EPA/DoD Related Research (Continued)

   D. X-Ray Fluorescence Sensor .......... Dr. Elam (NRL)
   E. New Coring Device ................... Mr. Lien (EPA)
   F. Field Portable LIBS ................ Dr. Cremers (LANL)
   G. Direct Sparge Sampler ............... Dr. Davis
   H. Optical Sensors .................... Dr. Vo-Dinh (ORNL)

1130  DOE/DoD Coordination and Collaboration .......... All
1200  Lunch

1300  Tour of SCAPS Truck .................. Mr. Konecny (WES)
      3-D Visualization Demonstration .................. Mr. Goodson
      ITMS Demonstration ................................. Dr. Davis

1430  Adjourn
5 Abstracts, Papers and/or Presentation Materials

The following three chapters contain briefing materials submitted by the workshop presenters and are printed as submitted with no editing. Although varied in format, the materials in this section represent a good summary of the workshop. In addition to the presentations and discussions described in this report, the workshop included demonstrations of SCAPS prototype probes and samplers, of the SCAPS 3-D visualization software, and of the modified hydraulic equipment in the WES SCAPS truck.

### Conversion Factors,
Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

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<th>Multiply</th>
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<tr>
<td>feet</td>
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$^1$ To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use this following formula: $C = (5/9)(F - 32)$. To obtain kelvin (K) readings, use: $K = (5/9)(F - 32) + 273.15$. 
PROJECT DESCRIPTION

- SCAPS project is a fully coordinated Tri-Services effort to significantly accelerate the development, testing, and demonstration of sensor and sampler technologies to enhance the capabilities of SCAPS to detect and map subsurface contaminants in situ.

TECHNICAL OBJECTIVES

- Accelerate the development, testing, and demonstration of the following SCAPS technologies:
  1. LIBS - metals
  2. LIF - POLs, explosives
  3. FORS - VOCs
  4. Electrochemical sensors - VOCs, explosives
  5. Spectral Gamma Probe - radioactive wastes
  6. Sampling
  7. Data processing
SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM (SCAPS)

SCAPS Truck and Grout Trailer (Monitoring Well in Foreground)

Cone Penetrometer With Sensor Package

Grout Trailer

Data Acquisition/Processing Compartment

Hydraulic Operations Compartment

Three-Dimensional Contaminant Visualization
TECHNICAL APPROACH

- Select candidate sensing technologies
  - Appropriate for DoD, DOE, EPA contaminants of interest
  - Potential for rapid, in situ applications
  - Implementable in SCAPS
- Develop laboratory instrumentation to evaluate technology
  - Soil matrix effects
  - SCAPS implementation considerations
  - Detection limits
- Develop associated support technologies
  - Data acquisition hardware / software
  - Scientific visualization
  - Data analysis
- Develop prototype SCAPS sensor probe
- Conduct laboratory / field tests
- Conduct demonstration of new SCAPS sensor systems

TECHNICAL APPROACH

- Contaminants
  - Explosives
  - POLs
  - VOCs / Solvents
  - Heavy Metals
  - Radionuclides
- Sensor Technology
  - LIBS
  - LIF
  - Photofrag. / LIF
  - FORS
  - Electrochemical
  - Spectral Gamma
- Sampling Technology
  - Thermal Desorption
  - Multiport Sampler
- Data Processing

Demonstration ➔ Transition
TECHNICAL APPROACH

- Exploit technological advances
  - Fiber optics
  - Solid state tunable lasers
  - Diode lasers / arrays
  - Detector technologies
  - Computer hardware
  - Developments in the field or laser applications to chemical analysis

TECHNICAL RISKS

- Transition of laboratory methods to operational (field use) technology
- Performance variability of in situ sensors with site-specific conditions
  - Soil matrix
  - Interferences
  - Contaminant mix
  - Contaminant state
PERFORMERS

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- Technical POC - E. Cespedes
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  - North Dakota State University
  - University of South Carolina
  - University of Nebraska-Lincoln
  - Mississippi State University
  - University of Iowa
  - MIT/LL
  - Transducer Research, Inc.
  - Los Alamos National Laboratory
  - Naval Research Laboratory
  - Others TBD

Chapter 5  Abstracts, Papers and/or Presentation Materials
HIGHLIGHTS

- New prototype SCAPS probes
  - Explosives
  - Thermal desorption VOC sampler
  - Electrochemical VOC probe
  - FORS probe
- Demonstrated 3-D visualization in field
- Successful LIF demonstrations involving EPA, WGA

FIELD TESTS / DEMONSTRATIONS
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# RESEARCH AREA I

## LIBS SENSOR

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<td>Complete characterization of optical fiber</td>
<td>06/94</td>
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<td>Complete laboratory prototype F.O. LIBS system</td>
<td>09/94</td>
<td>10/94</td>
<td>10/94</td>
</tr>
<tr>
<td>Complete design of prototype LIBS probe</td>
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<tr>
<td>Complete LIBS software development</td>
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<tr>
<td>Complete fabrication of LIBS prototype probe</td>
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<tr>
<td>Complete field tests / demonstration of LIBS system</td>
<td>12/96</td>
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LIBS R&D TASKS

• Evaluate approaches for in situ plasma generation
  - WES
  - LANL
  - NRaD
  - UNL

• Design & characterize fiber optic delivery system
  - NRaD

• Evaluate alternate detection methods
  - ARL

• Develop software techniques for automatic multi-element detection/quantification
  - WES
  - NRaD
  - LANL
SCHEMATIC OF LIBS DIAGNOSTIC SYSTEM

COMPUTER

ICCD CONTROLLER

GATE PULSER

ND:YAG LASER

SPECTROMETER

ICCD

FIBER-OPTICS

Chapter 5  Abstracts, Papers and/or Presentation Materials
Time Resolved LIBS

25 Laser shots
21 mJ/pulse
100 ns Gate
Pure Pb
150 μm spot
5 ns pulsewidth
Spectra of Fisher Sea Sand and 214.438 nm Cadmium Line

Spectra of Fisher Sea Sand and 425.435 nm Chromium Line
Spectra of Yuma Sand and 405.785 nm Lead Line

Calibration Curve for Limit of Detection Limit Calculation
(Cadmium in Fisher Sea Sand at Laser Energy of 100 mJ)

LDL = 0.56 ppm

Chapter 5 Abstracts, Papers and/or Presentation Materials
Calibration Curve for Limit of Detection Calculation
(Lead in Yuma Sand at Laser Energy of 100 mJ)

LIBS Results Summary

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Spectral Line nm</th>
<th>Background Concentration ppm</th>
<th>LIBS Lower Detection Limit ppm</th>
<th>EPA Action Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>405.783</td>
<td>7.71</td>
<td>9.14</td>
<td>Water ppm</td>
</tr>
<tr>
<td>Pb</td>
<td>405.783</td>
<td>1.53</td>
<td>3.32</td>
<td>Soil ppm</td>
</tr>
<tr>
<td>Cr</td>
<td>425.435</td>
<td>1.80</td>
<td>1.62</td>
<td>5.0</td>
</tr>
<tr>
<td>Cd</td>
<td>214.438</td>
<td>&lt;0.02</td>
<td>0.56</td>
<td>1.0</td>
</tr>
<tr>
<td>Hg</td>
<td>435.835</td>
<td>0.30</td>
<td>3.77</td>
<td>2.0</td>
</tr>
<tr>
<td>Zn</td>
<td>202.548</td>
<td>1.30</td>
<td>0.99</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* Kentucky - Action level > background in soil (minimum 20 ppm)
Michigan - Action level 420 ppm in soil
Pennsylvania - Action level 200 ppm residential soil, and 600 ppm industrial soil
North Dakota - Action level 5 ppm in soil

** North Dakota - Action level 5 ppm in soil
Remote *in situ* detection of heavy metal contamination in soils using a fiber optic laser induced breakdown spectroscopy (FOLIBS) system

Gregory A. Theriault

Stephen H. Lieberman

Naval Command, Control and Ocean Surveillance Center
San Diego, CA
Fiber-Optic Laser Induced Breakdown Spectroscopy

Traditional LIBS

Nd:YAG

Fiber-Optic LIBS

Nd:YAG

SILICA-CLAD
SILICA-CORE
LOW OH FIBER
ATTENUATION AT
1.06 μ ≥ 2 dB/km

INPUT POWER
DENSITY DAMAGE
THRESHOLD
>1 GW/cm²

INTERNAL POWER
DENSITY DAMAGE
THRESHOLD
>100 GW/cm²

SAMPLE

600-μ FIBER
IMAGES
TO ~200 μ
Desirable Features in a CPT Contaminant Probe

- Specific - Allows for Identification of Contaminant of Interest
- Simple - Requires Minimal Sample Preparation with only Optical Interrogation
- Rapid - Allows Site Characterization Decisions to be Made in Real Time
- Remote - Measurement to be Done Over Optical Fibers
- Inexpensive Probe
Spark Initiation Threshold on Soil

0.75 mJ, 9 ns Pulse, 150 μ Spot

\[ 0.75 \times 10^{-3} J \]

\[ (75 \times 10^{-4} \text{ cm})^2 \leq 0.5 \frac{\text{GW}}{\text{cm}^2} \]

Soils Tested:
- Guadalupe
- Coronado I, II
- Yuma
- Alameda
- Camp Pendleton
- Fisher Sea Sand

\[ 150 \mu \text{ DIAMETER SPOT SIZE} \]

Chapter 5  Abstracts, Papers and/or Presentation Materials
Deliverable Energy
(Single Fiber)

- >20 mJ Available from one fiber
- No Nonlinear Attenuation
- Data uncorrected for fiber input coupling
Laboratory Measurement of Soil Contamination Via LIBS

Diagram showing the setup for LIBS analysis, including components such as a Nd:YAG laser, beam splitter, optical multichannel analyzer, spectograph, and power meter.
Sample Spectra at Various Excitation Energies
100 ppm Lead on Sand

1000 SHOT AVG.
EXCITATION ENERGY
- 7.2 mJ
- 6.4 mJ
- 5.6 mJ
- 4.6 mJ
- 3.7 mJ
- 3.0 mJ
- 2.4 mJ

Fiber Optic LIBS
Pb and Fe Lines vs Laser Energy

![Graph showing the intensity of Pb and Fe lines vs laser energy. The graph includes data points for Fe 404.57 nm, Pb 405.75, Fe 406.32, and Fe 407.14 with corresponding intensity counts and laser energy (mJ).]
Pb Concentration Series
(Excitation 4.0 GW/cm², Normalized)
Pb on Sand
Detection Limit Calculation
(Data Normalized)

\[ y = 3.03x + 44.84 \]
\[ R^2 = 0.9995 \]
\[ 3\sigma/m = 6.4 +/- 1 \text{ ppm} \]
H₂O Dependence

1000 SHOT AVG.
PULSE ENERGY: 10 mJ

INTENSITY (counts above background)

PERCENT H₂O SATURATION

100
80
60
40
20
0

0
1E6
2E6
3E6
4E6
5E6

Fiber Optic LIBS
H₂O Dependence

Fiber Optic LIBS
Conclusions

- Detection capabilities on the order of ppm are possible with FOLIBS on sands and natural soils.
- Matrix effects due to $\text{H}_2\text{O}$ and finer grain size reduce sensor response.
- FOLIBS is possible over long lengths of fiber.
- The FOLIBS laser power delivery system is robust.
**SYSTEM COMPONENTS**

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser</td>
<td>KIGRE Nd:YAG Osc/Amp system &gt;80 mJ/pulse; 6 nsec pulsewidth; passively Q-switched; 1064 nm wavelength; 3-4 mm beam diam.; 1Hz rep. rate; passive air cooling; 24 meter cabling</td>
</tr>
<tr>
<td>Spectrograph</td>
<td>CHROMEX 250iS; 250 mm focal length; adjustable slits; 3600, 1200, and 600 l/mm gratings; all spectrograph functions are computer-controllable</td>
</tr>
<tr>
<td>Fiber Optics</td>
<td>Fused silica; 19 fiber bundle; circular-to-rectangular with CHROMEX mount; 24 meters long</td>
</tr>
<tr>
<td>Detector</td>
<td>ORIEL InstaSpec V; gated intensified CCD; 10 nsec minimum pulsewidth gate; 10 Hz data acquisition rate; 25 mm CCD; 18 mm diam. intensifier; 650 pixels active</td>
</tr>
<tr>
<td>Gate/Trig Pulse</td>
<td>Compact, LANL built</td>
</tr>
<tr>
<td>Generator</td>
<td>486 IBM Compatible</td>
</tr>
<tr>
<td>Computer</td>
<td>SPECTRA © -LANL developed spectral analysis software</td>
</tr>
</tbody>
</table>

**PRESENT STATUS OF PROJECT**

- Software completed
- CHROMEX, fiber optics, and computer on hand
- Delivery of laser by 31 August 95
- Detector delivery by 11 September 95 (use Insta Spec IV loaner in interim)
- System completed by 30 September 95
**ACOUSTO OPTIC TUNABLE FILTER**

**Serial No.: 9506-AO-960**

<table>
<thead>
<tr>
<th></th>
<th>SPECIFICATIONS</th>
<th>TEST DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wavelength Range</strong></td>
<td>380-600 nm</td>
<td>380-600 nm</td>
</tr>
<tr>
<td><strong>Spectral Resolution (Å)</strong></td>
<td>2 @ 380 nm</td>
<td>2 @ 380 nm</td>
</tr>
<tr>
<td></td>
<td>3 @ 600 nm</td>
<td>3 @ 600 nm</td>
</tr>
<tr>
<td><strong>Corresponding Drive Frequency</strong></td>
<td>200-350 MHz</td>
<td>218-434 MHz</td>
</tr>
<tr>
<td><strong>Input/Output Polarization</strong></td>
<td>Vertical</td>
<td>Vertical</td>
</tr>
<tr>
<td><strong>Drive Power</strong></td>
<td>1 Watt</td>
<td>1 Watt</td>
</tr>
<tr>
<td><strong>Time Delay</strong></td>
<td>10 μsec</td>
<td>10 μsec</td>
</tr>
<tr>
<td><strong>Rise Time</strong></td>
<td>30 μsec</td>
<td>30 μsec</td>
</tr>
<tr>
<td><strong>Package Type</strong></td>
<td>Air Cooled</td>
<td>Air Cooled</td>
</tr>
<tr>
<td><strong>RF Connector</strong></td>
<td>SMA</td>
<td>SMA</td>
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</table>

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e-mail: office@brimrose.com

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Chapter 5  Abstracts, Papers and/or Presentation Materials
**New Quartz AOTF**

- **Wavelength Ranges:** 200-400 nm
- **Spectral Resolution:**
  - 1\(\lambda\) @ 400 nm
  - 0.3\(\lambda\) @ 400 nm
- **Optical Aperture:** 10 x 10 nm
- **RF Frequency:** 95-200 MHZ
- **Driving Power:** 8 Watts
- **Input/Output Pol.:** Vertical/Horizontal
- **Diffraction Eff.:** > 50%
- **Time Delay:** 30 \(\mu\)s
- **Rise Time:** 30 \(\mu\)s
- **Package Type:** Air Cooled
- **RF Connector:** SMA

---

**PROGRESS**

Yet to be Accomplished

- Compare quality of LIBS spectra between OMA and AOTF e.g. for Pb lines around 400 nm.

- Establish whether single-photon counting using AOTF on and off resonance at 10+ microseconds yields advantageous S/N ratios.

- Time-resolved studies of plasma evolution.
Characteristics

- Solid State Device, Compact (cm$^3$) and Ruggedize Moving Parts
- Fast Tuning Speed (several $\mu$s to tens of $\mu$s)
- Random Wavelength Access/Hopping
- NO “dead spectral space” for KHz Rate LIBS
- Simultaneously Multiple Wavelength Measurement
- Spectral Imaging
- Built-in Solid State Chopper for Lock-in Amplification

PROGRESS
Equipment Acquired

- “Ultra-High Resolution” AOTF, State-of-the-Art commercial unit Spectral resolution ca. 0.3 nm

- Compact and portable Nd:YAG Laser (Big Sky Laser Model CFR 200-20 with mini CE portable power supply)

- 4-channel digital scope (LeCroy Model 9354TM-500MHz) with 500 Ms/s and 500K point record length/channel.
<table>
<thead>
<tr>
<th>Milestones</th>
<th>Schd</th>
<th>Reschd</th>
<th>Comp</th>
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<tr>
<td><strong>LIF POL Sensor</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Complete development of improved POL sensor</td>
<td>03/95</td>
<td></td>
<td>03/95</td>
</tr>
<tr>
<td>Complete field demonstrations of improved POL sensor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Photofragmentation/LIF Explosives Sensor</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Demonstrate feasibility of PF/LIF for in situ explosives sensor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complete prototype sensor</td>
<td>09/95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complete field tests of explosives sensor</td>
<td>12/96</td>
<td>06/97</td>
<td></td>
</tr>
</tbody>
</table>
XeCl Excimer Laser

- wavelength: 308 nm
- pulse energy: 2 mJ
- repetition rate: 100 Hz
- Gas: 99.7% He
  0.07% HCl
  0.2% Xe
- Laser pulses per fill: 3,000,000
  (8 hours or roughly 16 pushes)
- Fills per bottle of gas: ~100
The Model PSX-100 is an innovative multi-gas excimer laser which is both compact and portable and yet is capable of mJ pulse energies and, with a pulse duration of only 2.5 ns, peak powers in excess of 2 MW.

Both the laserhead and the power supply are incorporated in a single unit less than 1 ft. in length. The laser operates in a sealed-off mode and, despite its small gas volume, exhibits very respectable gas fill lifetimes even without the use of a gas processor.

The PSX-100 has been carefully engineered throughout, from its high-efficiency discharge circuit (with negligible reverse aftercurrent) to the use of high-quality, durable discharge circuit components and the careful selection of halogen compatible materials for the gas and discharge chamber.

Given its pulse energy and peak power capabilities, the PSX-100 represents a convenient and cost effective alternative to larger, much more costly lasers for many photoablation and micromachining applications. In addition, the laser's 2.5 ns pulse duration, unique among available excimer lasers, offers new possibilities in areas such as relaxation time studies and time resolved spectroscopy.

With its sealed-off mode of operation, air cooling and low power budget (100 W), the PSX-100 is also ideally suited for field use outside the laboratory.

**Features**
- Compact single unit construction
- Air cooled
- Short, high peak power pulses
- Efficient discharge circuit with negligible reverse aftercurrent
- Long thyatron life (> 3 x 10⁸ pulses)
- Halogen compatible construction for minimal repasivation
- Multi-gas optics (optional)
- Automatic gas refill (optional)

**Applications**
- Photoablation and micromachining
- Semiconductor processing
- Surface analysis
- Laser ionization mass spectroscopy
- Fluorescence spectroscopy
- Photochemistry
- Relaxation time studies
- Nonlinear optics
SCAPS using Excimer laser

- Advantages

  - Nitrogen laser can be directly replaced by excimer laser without changes to detection system/software

  - Less gas required compared to Nitrogen system

- Disadvantages

  - Added complexity working with toxic gases (small amount of HCl in excimer gas)
Detection of JP4

Dye Laser at 290nm - XeCl at 308nm
Excimer Laser Results

- integration into present SCAPS hardware straightforward

- laser very sensitive to gas contamination
  - operation ≤ 30 min per fill at present

Timetable for fielding

- lab evaluation: Underway
- field testing: First Quarter FY 96
Schematic of Downhole 266 nm Wavelength Microchip Laser

Laser Diode

\[ \lambda = 808 \text{ nm} \]

Lens

Fiber

Lens

808 nm

Nd:YAG

1064 nm

Quadrupling Crystal

266 nm

Microchip Laser

A0147-1.52mod
**Microchip Laser**

- wavelength: 266 nm
- power: 5 mW
- pump source: 1.2 W laser diode (located in truck)
- lifetime: 100,000 hours
- material: Nd:YAG (all solid state; no gas required)
- source: M.I.T. Lincoln Labs
Prototype Microchip Laser Probe

- Laser & collection fiber:
Microchip Laser Collaboration

• Partners: NRaD, San Diego
  MIT Lincoln Labs, Concord MA

• Lincoln Lab tasks
  – originally developed microchip laser (1064 nm)
  – frequency quadrupled output (266 nm)
  – frequency tripled output (355 nm)
  – designed mount for use in penetrometer

• NRaD tasks
  – integrate microchip laser into SCAPS
  – laboratory evaluation of LIF using 266 nm
  – field testing of SCAPS/microchip laser system

• Timetable
  – lab evaluation: Underway
  – field testing: Second Quarter FY 96
## Lasers for LIF Sensor

<table>
<thead>
<tr>
<th>Laser</th>
<th>Wavelength (nm)</th>
<th>Cost ($K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen</td>
<td>337</td>
<td>8</td>
</tr>
<tr>
<td>XeCl</td>
<td>308</td>
<td>12</td>
</tr>
<tr>
<td>Tuneable (ROST)</td>
<td>290 (variable)</td>
<td>100</td>
</tr>
<tr>
<td>Lipstick Nd:YAG</td>
<td>266</td>
<td>8</td>
</tr>
</tbody>
</table>
Accelerated Tri-Services SCAPS Sensor Development

Laser Induced Fluorescence and Fiber Optic Raman Sensors

Mr. Bruce J. Nielsen
Environics Directorate
Site Remediation Division
Laser Induced Fluorescence (LIF) and Fiber Optic Raman Sensors (FORS)

Objective: Perform Fluorescence and Raman Sensor R&D for SCAPS, Based on Tunable (ROST) Technology.

Approach:
- Provide for Refinement of Prototype Systems
- Test in Lab & Field Environments
- Determine Device Applicability

Payoff:
- Applicable to Site Characterization and Monitoring
- Accurate and Reliable Results
- In Situ, Real-Time Data
- Reduced Characterization and Monitoring Costs
- Remediation Process Control

Laser Induced Fluorescence Sensors

LIF POL Sensor
Principal Investigator: Dr Greg Gillispie
Dakota Technologies, Inc./North Dakota State University

Emphasizes Use of Tunable Dye Laser
- Study Soil Matrix Effects on Fluorescent Properties of Aromatic Hydrocarbons
- Oxygenated Versus Deoxygenanted Matrices
- Laboratory Testing Indicates Detection of #2 Diesel, DFM, Unleaded Gasoline, and JP-4 on Sand, Soil From China Lake, and Soil From Columbus AFB at 100 ppm or Lower Concentrations.
Laser Induced Fluorescence Sensors (cont.)

Research Questions:

- How Much Chemical Information Can Be Derived From Fluorescence Spectra?
- What Are the Detection Limits?
- How Linear Is the Calibration Curve?
- Deviations at Low and High Concentration Ends?
- Can Dissolved Phase Aromatic Hydrocarbons Be Detected?

Laser Induced Fluorescence Sensors (cont.)
Results:

- Developed Apparatus/Method for Spiking Soil Samples
  -- Teflon Containers/Paint Can Shaker
  -- Nonstick Surfaces/Good Mixing

- Five Soil Types Spiked With Diesel Fuel
  -- Sand Fluorescence Response 10X Silty Matrix
  -- Sand Fluorescence Response 100X Peat or Lean Clay Matrix

- Will Collaborate with WES Matrix Study
  -- Ten or More Soils
  -- Four Common Fuels
    --- Gasoline, Jet Fuel, Diesel #2, DFM
Laser Induced Fluorescence Sensors (cont.)

Tasks

(1) Pattern Recognition Techniques
   - Chemometrics (MATLAB Code to Analyze WTM Data)
   - Time Resolved Excitation Emission Matrices (TREEMs)

(2) Lower Detection Limits by Better Probe Design
   - The Probe Design Will Be Carefully Reassessed to Better Reject the Scattered Exciting Light, Especially With Regards to Tunable System.

(3) Lower Detection Limits, Improved Specificity by Time Gating
   - Characterize How Well a Gated-OMA Functions As Compared to an Emission Monochromator

Laser Induced Fluorescence Sensors (cont.)

Tasks

(4) Downhole Frequency Doubling
   - Use Powdered Doubling Crystals
   - Proof-of-Concept Performed
   - Characterize and Optimize Doubling Process

(5) Alternate Wavelength-Selectable Laser Sources
   - Raman Shifters
   - Optical Parametric Oscillators (OPOs)
   - Ti:Sapphire
1. Laser Photofragmentation

\[
\text{R-NO}_2 \xrightarrow{\text{hv}_1} \text{R} + \text{NO}_2
\]

2. Fragment Detection

\[
\text{NO}_2 \xleftarrow{\text{hv}_2} \text{NO}^+ + \text{O} \\
\text{NO}^+ + \text{O}
\]

where \(\text{hv}_1 = \text{hv}_2\)

---

SINGLE AND MULTIPHOTON EXCITED FLUORESCENCE

Laser

Fluo.

High Background

High Scatter

Laser

Fluo.

Low Background

No Scatter
Figure 4. Time-of-flight REMPI spectrum of NO generated from DMNA. Signal generated from 226nm excitation of DMNA (~100pJ).

Table 1
Limits of Detection for Various Compounds Studied Using the 226nm Laser Photofragmentation/REMPI Technique with NO Detection

<table>
<thead>
<tr>
<th>Compound</th>
<th>Limit of Detection (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>8</td>
</tr>
<tr>
<td>NO₂</td>
<td>240</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>1000</td>
</tr>
<tr>
<td>DMNA</td>
<td>450*</td>
</tr>
<tr>
<td>RDX</td>
<td>(2000)*</td>
</tr>
<tr>
<td>TNT</td>
<td>8</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>24</td>
</tr>
</tbody>
</table>

*Limit of detection obtained by laser-induced fluorescence of NO via its A²Σ⁺ → X²Σ⁻ transition.
Army Research Laboratory

SENSOR DEVELOPMENT WORKSHOP
29-30 August 1995
U.S. Army Corps of Engineers
Waterways Experiment Station

LASER-INDUCED FLUORESCENCE SENSORS

R.C Sausa
U.S. Army Research Laboratory
AMSRL-WT-PC
Aberdeen Proving Ground, MD 21005

Level of Support: FY94: 40K, FY95: 20K
OBJECTIVE

Develop and Deploy Advanced Optical Sensors Based on Laser Photofragmentation Laser-Induced Fluorescence for Rapid and Real-Time Site Characterization and Analysis
LASER PHOTOFragmentation/
LASer-INDuced Fluorescence

* Utilizes one laser to both fragment the target molecule and detect the characteristic fragments by laser-induced fluorescence.

* System utilizes an optical fiber to transmit the laser radiation and an interference filter/PMT combination or optical multichannel analyzer for detection.
TECHNICAL PROGRESS
(Accomplishments)

- Designed & constructed LP/LIF cell
- Performed literature search. Reviewed pertinent papers & started writing review article on laser-based techniques for detection of nitrocompounds including energetic materials (analytical chemistry)
- Determined LODs of various nitrocompounds using LP/one-photon LIF of NO (a-x)(0,0) band near 26 nm
- Determined LODs of NO & NO₂ by two-photon LIF of NO (a-x) transitions using laser radiation near 452 nm
- Wrote & tested multi-parameter computer program for spectral simulation of NO (a-x) band
- Initiated system design of prototypical system established contact with WES for field testing/use
- Three open literature
Nitroglycerine
Pentaerytritol tetranitrate
Nitromethane

RDX
HMX
DMNA

TNT
DATB
Nitrobenzene
APPROACH

1. Laser Photofragmentation

\[ \text{R-NO}_2 \xrightarrow{\text{hv}_1} \text{R} + \text{NO}_2 \]
\[ \text{NO}_2 \xrightarrow{\text{hv}_2} \text{NO} + \text{O} \]

2. Fragment LIF Detection

\[ \text{NO} \xrightarrow{\text{hv}_3} \text{NO}^* \]

where \( \text{hv}_1 = \text{hv}_2 = \text{hv}_3 \)
The diagram shows experimental and simulation spectra for two states: $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. The x-axis represents wavelength in Ångstroms (Å) ranging from 2255 to 2270 Å.
Limits of detection for various nitrocompounds studied using the technique of laser photofragmentation/ NO fragment detection by REMPI-TOF.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Limit of Detection (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>8, (1)\textsuperscript{a}</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>240, (22)\textsuperscript{a}</td>
</tr>
<tr>
<td>CH\textsubscript{3}NO\textsubscript{2}</td>
<td>1000, (220)\textsuperscript{a}</td>
</tr>
<tr>
<td>DMNA</td>
<td>450 (2000)\textsuperscript{b}</td>
</tr>
<tr>
<td>RDX</td>
<td>8</td>
</tr>
<tr>
<td>TNT</td>
<td>24</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>2400</td>
</tr>
</tbody>
</table>

\textsuperscript{a} LODs obtained by NO REMPI using a pair of miniature electrodes.
\textsuperscript{b} LOD obtained by LIF via the NO A\textsuperscript{2}Σ+-X\textsuperscript{2}Π (0,0) transition.
PROPOSED RESEARCH
FY96 - 130K
(Labor, 110K, ½ manyr + postdoc, Equipment, 20K)

- Designed and construct prototypical system to couple with penetrometer probe
- Laboratory test, evaluate, and optimize system using site samples
- Field test sensor at sites designated by WES
ACKNOWLEDGEMENT

* Dr. Robert Pastel, U.S. Army Research Laboratory Postdoctoral Fellow.

* Professor Josef Simeonsson of the University of Iowa, Department of Chemistry.

* Dr. Ernesto Cespedes of the U.S. Army Engineer Waterways Experiment Station.

* Strategic Environmental Research Development Program on Site Characterization and Analysis Penetrometer System.
RESEARCH AREA III
FOR SENSOR

Milestones

- Complete development of laboratory FORS system
- Complete characterization of detection capabilities
- Complete fabrcication of prototype FORS probe
- Complete design of resonance enhanced FORS probe
- Complete fabrcication of resonance enhanced FORS probe
- Complete FORS software development
- Complete field demonstration of resonance enhanced FORS probe
Advantages of Fiber Optic Raman Spectroscopy

1. Specificity
2. Simultaneous multicomponent analysis
3. Minimal Raman interferences from matrix
4. Remote
5. Real-Time
6. In-situ

Technical Challenges

1. Interferences due to Raman emissions in optical fibers
2. Fluorescence interferences from matrix
3. Low sensitivity
Reduction of Raman Emissions from the Optical Fibers
FFT Filtering

Unfiltered Raman Spectrum

\[ F \left( \right) \]

Fourier Transformed Spectrum

Filtered Raman Spectrum

\[ F^{-1} \left( \right) \]

Filtered Fourier Transformed Spectrum

High-Pass Filter

Spatial Frequency

Wavenumber (cm⁻¹)
Multiple Collection Fibers to Improve Collection Efficiency

- 6 CF AROUND 1 EF
- 1 EF, 6 CF
- 1 EF, 1 CF

Graph showing intensity vs. wavenumber (cm⁻¹) with different conditions.
Spectra Obtained at the Fuel Farm

depth = 12.6'

depth = 5'

depth = 15'
Former Liquid Waste Disposal Area
("Fiery Marsh")

EL 12 ft

Qaf1

RESIDUAL SOIL CONTAMINATION?

BL 5 ft

DWAPL TRANSPORT

B CLAY

GW

E0166-5.57
Naphthalene on Sand

- 100 ppt
- 10 ppt
- 50 ppt
- 5 ppt
Napthalene on Sand
Naphthalene on Site 9 Soil
Naphthalene on Site 9 Soil
Toluene on Sand

SATURATED

100 PPT

150 PPT

50 PPT
Toluene on Sand
(Subtract Fiber Background)
Toluene on Sand

![Graph showing intensity vs. wavenumber for toluene on sand at different concentrations, with a linear relationship graph showing concentration vs. intensity.]
FLUORESCENCE

1. Near IR Excitation
2. Pico-second Raman Spectroscopy
LOW SENSITIVITY

1. Resonance Raman Spectroscopy

2. Surface Enhanced Raman Spectroscopy (SERS)
SURFACE ENHANCED RAMAN SPECTROSCOPY

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method of Adsorption</th>
<th>Substrate</th>
<th>Excitation (nm)</th>
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<tbody>
<tr>
<td>benzene</td>
<td>electrochemical</td>
<td>Ag</td>
<td>488, 514.5, 670</td>
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<tr>
<td>toluene</td>
<td>electrochemical</td>
<td>Ag</td>
<td>514.5</td>
</tr>
<tr>
<td>nitrate</td>
<td>electrochemical</td>
<td>Ag</td>
<td>670</td>
</tr>
<tr>
<td>TCE</td>
<td>electrochemical</td>
<td>bi-phase Cu</td>
<td>647, 676</td>
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<tr>
<td>TCE</td>
<td>1-octadecanethiol</td>
<td>Ag</td>
<td>647</td>
</tr>
<tr>
<td>benzene</td>
<td>1-octadecanethiol</td>
<td>Ag</td>
<td>647</td>
</tr>
<tr>
<td>xylene</td>
<td>1-octadecanethiol</td>
<td>Ag</td>
<td>647</td>
</tr>
<tr>
<td>benzene</td>
<td>low temperature, 150K</td>
<td>Ag</td>
<td>488</td>
</tr>
</tbody>
</table>
Ultradimicroelectrodes (UME):

1. Diameters less than 20 microns
2. Fast response time
3. Diminished Ohmic losses
Fiber Optic Raman Sensors

FOR Solvent Sensor
Principal Investigator: Dr Greg Gillispie, Dakota Technologies, Inc./NDSU

Resonance Raman Approach
- Requires Tunable Laser or Multiple Wavelengths
- Proof-of-Concept Provided for TCE Detection

Raman Studies
- Use Nitrogen Laser With Subnanosecond Pulse
- Study Water Raman/Fluorescence Ratio

Raman Shifter Studies
- Vibrational and Rotational
  -- Function of Gas, Pressure, and Pump Energy
  -- Closely Spaced Output Lines in Ultraviolet
- Use of Solid State (Salt Crystal) Raman Shifter
- Using System With HPLC for Chemometric Studies
Fiber Optic Raman Sensors (cont.)

Research Questions:

- Amount of Resonance Enhancement As Function of Excitation Wavelength?
  -- Use Raman Shifter

- Ability to Separate Raman From Background Fluorescence Signal?
  -- By Excitation Wavelength, Time Gating, and Data Processing

- Substances to Be Studied:
  -- BTEX, PCE, TCE, DCE, Carbon Tetrachloride, Chloroform, Hexane, Cyclohexane
Fiber Optic Raman Sensors (cont.)

Tasks

(1) Characterizing Fibers
   - Attenuation versus Wavelength
   - Interferences
   - Fiber Transmission Times

(2) Design Decision on Detector
   - PMT vs. CCD

(3) Characterizing Wavelength Dependence of the Resonance Enhancement
   - Determine Optimum Wavelengths
Fiber Optic Raman Sensors (cont.)

Tasks

(4) Suppressing Background Fluorescence
    With Time Shifting
    - Time Resolved Raman for Fluorescence Suppression
      -- The Raman Signal Is Coincident With the Laser Pulse

(5) Wavelength Shifting of the Raman Excitation Source
    - For Fluorescence Suppression

(6) Development of Data Analysis Methods For
    Real-Time Processing of Raman Spectral Data
RESERCH AREA IV
ELECTROCHEMICAL SENSOR

Milestones
- Complete fabrication of prototype VOC and explosives sensors
- Complete initial field test of first generation TNT sensors
- Complete demonstration of improved electrochemical sensor systems

Schd Reschd Compl
10/94 09/94 09/94
01/96
TECHNICAL DESCRIPTION

- SCAPS probe prototype that incorporates:
  - External heater to desorb and pyrolyze explosives contaminants in soils
  - Pneumatic system to transport pyrolysis vapors to internal sensors
  - Electrochemical sensor to detect vapors (selective to NO)
  - Signal conditioning electronics
  - Geophysical sensors (sleeve friction and tip resistance)
  - Grouting capability

- Probe collects soil classification data (site stratigraphy) continuously during push
- Probe collects contaminant data during retraction at discrete locations (approx. 1 minute required for each analysis)

ELECTROCHEMICAL SENSORS FOR SCAPS

- Low cost
- Small size
- Simple circuit requirements
- Low power requirements
- Powerful analytical properties

\[
\begin{align*}
\text{NO}_3 + \text{CH}_4 & \rightarrow \text{NO}_{2} + \text{O}_2 \\
& \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{CO} + \text{NO} + \text{NO}_2 \\
& \rightarrow \text{NO} + \text{H}_2\text{O} = \text{NO}_2 + 2\text{H}^+ + 2\text{e}^-
\end{align*}
\]
DATA ACQUISITION DISPLAY

FIELD TESTS

- Louisiana Army Ammunition Plant, LA, 12-16 Sep 1994
  - First prototype tested
  - Wet clay conditions
  - Heterogeneous TNT/RDX contamination
  - Improvements identified
- Pantex, TX (DOE), 6-10 Mar 1995
  - Modified probe tested
  - Dry sand / clay conditions
  - Heterogeneous RDX / HMX contamination
- Volunteer Army Ammunition Plant, TN, 3-7 Apr 1995
  - Improved pneumatic system
  - Improved data acquisition / display system
  - Moist clay conditions
  - Homogeneous (near surface) TNT contamination
Typical SCAPS Explosive Sensor Response For TNT And RDX Contaminants

LAAP, D-Line South
(1.6 foot depth)

Sensor response, mV

Time, seconds
Pantex
Soil Stratigraphy
# Laboratory Explosives Sensor Testing Device

**MICROMETER HEIGHT ADJUSTMENT FOR HEATER**

**CERAMIC HEATER WITH PLATINUM ELEMENT**

**UPPER HOUSING**

**SAMPLE CONTAINER**

**LOWER HOUSING**

**THERMOCOUPLE**

**GAS IN**

**GAS OUT**

**ANALYZER OUT**

**TO EXPLOSIVE SOURCE**

## Table: Sample Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Depth (ft BGS)</th>
<th>SCAPS Sensor Response (mV)</th>
<th>Field Screen TNT (mg/kg)</th>
<th>EPA 8330 TNT (mg/kg)</th>
<th>2,4-DNT (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS9</td>
<td>App. 1.5 ft N of 09-405</td>
<td>7.9-8.1</td>
<td>60</td>
<td>&lt;0.7</td>
<td>0.3</td>
<td>&lt;0.25</td>
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<tr>
<td>SS1</td>
<td>App. 3ft E of 06-404</td>
<td>0-0.33</td>
<td>69</td>
<td>0.7</td>
<td>0.4</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>SS6</td>
<td>App. 0.5 ft E of 04-404</td>
<td>0-0.25</td>
<td>156.7</td>
<td>12.1</td>
<td>3.6</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>SS13</td>
<td>App. 0.66ft W of 12-504</td>
<td>0-0.3</td>
<td>363.5</td>
<td>6.8</td>
<td>NP</td>
<td>NP</td>
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<tr>
<td>SS4</td>
<td>App. 0.66 ft S of 03-404</td>
<td>0.17-0.33</td>
<td>488</td>
<td>3.6</td>
<td>NP</td>
<td>NP</td>
</tr>
<tr>
<td>SS3</td>
<td>App. 0.33ft W of 03-404</td>
<td>0-0.2</td>
<td>590.5</td>
<td>377.5</td>
<td>413</td>
<td>2.1</td>
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<tr>
<td>SS10</td>
<td>Between 07&amp;08-404/5</td>
<td>0-0.2</td>
<td>811</td>
<td>89.1</td>
<td>4</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>SS11</td>
<td>Between 07&amp;08-404/5</td>
<td>0.25-0.4</td>
<td>1132</td>
<td>756</td>
<td>NP</td>
<td>NP</td>
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<tr>
<td>SS12</td>
<td>Between 07&amp;08-404/5</td>
<td>0.5-0.6 SAT.</td>
<td>601</td>
<td>105000</td>
<td>57.5</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** NP indicates that the sample was not analyzed in the laboratory by EPA method 8330. SAT. indicates that the sensor reached saturation (3142 mV).
SCAPS EXPLOSIVES SENSOR RESPONSE
(VAAP Test 03-06 Apr 1995)

Sample Analysis (Field Test Kits & EPA 8330)
- 3.8 ppm: 0.17-0.33 ft depth, 0.66 ft West of SCAPS push
- 413 ppm: 0.0-0.2 ft depth, 0.33 ft West of SCAPS push

Sample Analysis (EPA 8330)
- 10.5% TNT: 0.5-0.6 ft depth, 2 ft South of SCAPS push
EXPLOSIVES SENSOR DEVELOPMENT AND TESTING

- Accomplishments
  - Conducted extensive laboratory testing of electrochemical sensors
  - Completed three SCAPS field tests at explosives contaminated sites

- Planned
  - Complete laboratory characterization of pyrolysis products
  - Scheduled to conduct additional field tests at Longhorn Army Ammunition Plant, TX during Sep 95 and Camp Navajo, AZ during Oct 95
  - Field tests / demos at VAAP during 1996
CALIBRATION OF THE EXPLOSIVES SENSOR

10, 20, 50, 100, 250, 500 ppm-wt TNT

CALIBRATION OF EXPLOSIVES SENSOR

$r^2 = 0.997$
LDL = 0.05 ppm-wt
SCAPS ELECTROCHEMICAL VOC SENSOR

William M. Davis
Waterways Experiment Station

---

SCAPS Electrochemical VOC Sensor

- Based on Chlorine selective RCl sensor developed by Transducer Research, Inc.
- Plans to incorporate non-chlorinated VOC Sensor
- Soil vapor sensor, deployed in the probe housing designed for the Electrochemical Explosives sensor
- Field tested at Dover AFB, DE in May 1995
SCAPS Electrochemical VOC Sensor
(SCHEMATIC DIAGRAM)

Pull (from surface pump)
Push (from surface pump)
Dover Scaps/RCL Demonstration
Hole 21, Depth 8 feet

RCL COUNTS

TIME (seconds)
Dover Scaps/RCL Demonstration
Hole 22, Profile (Full Range)

Dover Scaps/RCL Demonstration
Hole 22, Profile (Low Range)
SCAPS
Electrochemical VOC Sensor

- Successfully field tested the RCI sensor alone
- Modify current probe design to include non-chlorinated VOC sensor
- Perform additional field test

SCAPS
Electrochemical VOC Sensor

- Performers:
  - WES: William M. Davis
    Ernesto Cespedes
  - TRI: William Buttnner
    Mel Findley
## RESEARCH AREA V
SPECTRAL GAMMA PROBE

### Milestones

<table>
<thead>
<tr>
<th>Description</th>
<th>Schd</th>
<th>Reschd</th>
<th>Comp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete improved SCAPS spectral gamma probe</td>
<td>03/95</td>
<td>10/95</td>
<td></td>
</tr>
<tr>
<td>Complete field testing / demonstration of improved gamma probe</td>
<td></td>
<td></td>
<td>02/96</td>
</tr>
</tbody>
</table>

## Spectral Gamma Probe Participants

- **Principal Investigator:** Ernesto R. Cespedes
- **Physicist:** Bobby E. Reed
- **Electrical Engineer:** Bryan A. Register
- **Physicist:** John C. Morgan
SPECTRAL GAMMA PROBE DIAGRAM

10 mA LOOP

GROUT TUBE

SENSOR CABLE

GROUTING MODULE

CRT DISPLAY

POWER SUPPLY

SIGNAL INTERFACE

TIMER 1/SEC

MEMORY 768 x 4

MEMORY CONTROL & CRT A/D

FRAME

HIGH VOLTAGE SUPPLY

PHP

SCINTILLATION DETECTOR

SLEEVE SENSOR

SOIL CLASSIFICATION MODULE

Chapter 5 Abstracts, Papers and/or Presentation Materials
CPT: SF11406A
STATE COORDINATES:
EASTING (ft.)  0
NORTHING (ft.)  0
ELEVATION (ft.)  0

Project: Fernald Demo

CPT based SOIL CLASSIFICATION

Cone Resistance
$Q_c$ (tons/ft$^2$)

Sleve Friction
$f_s$ (tons/ft$^2$)

SPECTRAL SUM

Gross Gamma Count

Depth (fet)
Spectral Gamma Probe Problems Encountered

Temperature Stability

Analysis Difficulty

Housing Attenuation

Spectral Gamma Probe Analysis Difficulties Encountered

High Thorium Background

Gain Shifts
Spectral Gamma Probe Improvements

- Standard Electronics
  - Custom electronics have been replaced with modular NIM rack mounted industry standards

- Improved Data Storage
  - Data is stored in small blocks allowing post processing methods

- Temperature Correction Algorithms
  - Gain shift and offset problems from temperature sensitive components can be corrected in post processing

- Fall-away Sleeve
  - Allows low energy portions of the spectrum to be observed, and reduces noise from scattered photons
## Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Sched</th>
<th>Rescd</th>
<th>Comp</th>
</tr>
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<tbody>
<tr>
<td>Complete initial testing of thermal desorption VOC sampler</td>
<td>05/95</td>
<td>05/95</td>
<td></td>
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<tr>
<td>Complete field evaluations of multiport VOC sampler</td>
<td>06/95</td>
<td>05/95</td>
<td></td>
</tr>
<tr>
<td>Complete laboratory testing of analyte behavior in soils</td>
<td>08/96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complete field tests of thermal desorption VOC sampler interfaced to analytical instr</td>
<td>10/96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complete description of analyte behavior in soils</td>
<td>12/96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complete evaluation of quantitative aspects of SCAPS samplers</td>
<td>12/96</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ANALYTE BEHAVIOR IN REGION OF SAMPLER
PROBLEM

- THE RELATIONSHIP BETWEEN SOIL CONTAMINANT CONCENTRATION AND THE CONCENTRATION MEASURED BY THE SAMPLER ARE UNKNOWN

APPROACH

- DEVELOP COMPUTATIONAL PROCEDURES VAPOR DRAWDOWN AND CONE OF INFLUENCE
- LABORATORY EVALUATION MIGRATION TO SAMPLING PORT GRADIENT CAUSED BY SAMPLING ACCURACY OF MEASUREMENT
- EVALUATE PROCEDURES DEVELOPED USING FIELD DATA
BENEFIT

MOVE FROM SCREEN TO SEMI-QUANTITATIVE WITH VAPOR SAMPLING DEVICES

IMPROVED VOC SAMPLER

US ARMY ENGINEER WATERWAYS EXPERIMENT STATION
3909 HALLS FERRY ROAD
VICKSBURG, MS 39180-6199
Thermal Desorption VOC Sampler
IMPROVEMENTS

- Expanded suite of compounds
- Soil vapor sampling
- Mechanical simplicity
- Improved gas manifold
- Direct analytical interface

APPROACH

- Extended range of compounds and provide for direct instrument interface
- Evaluation of improved sampler
- Field test in soil and vapor sampling modes
- Interface to analytical instrumentation
- Field test VOC sampler interfaced to analytical instrumentation
**ORIGINAL TARGET COMPOUNDS**

- *trans*-1,2-Dichloroethene
- Trichloroethene (TCE)
- Benzene
- Toluene
- Chlorobenzene
- Ethylbenzene
  
- *meta*-Xylene
- *para*-Xylene
- *ortho*-Xylene
- *meta*-Dichlorobenzene
- *para*-Dichlorobenzene
- *ortho*-Dichlorobenzene

**ADDED COMPOUNDS**

- 1,1-Dichloroethene
- *cis*-1,2-Dichloroethene
- Tetrachloroethene (PCE)
- Naphthalene
- 2-Methylnaphthalene
BENEFITS

- INCREASED NUMBER OF COMPOUNDS
- INCREASE SPEED OF ANALYSIS
- INCREASED VERSATILITY

MILESTONES

- 08/96: COMPLETE LABORATORY TESTING OF ANALYTE BEHAVIOR IN SOILS
- 10/96: COMPLETE DESCRIPTION OF ANALYTE BEHAVIOR IN SOILS
Demonstration of SCAPS In-Situ Thermal Volatile Organic Chemical Analysis System for Rapid Characterization of Solvent and POL Contaminated Sites

Lead Organization:
U.S. Army Environmental Center
Aberdeen Proving Grounds, MD 21010-5401

POC: Mr. George E. Robitalile
SFIM-AEC-ETP
Voice: 410-612-6865
FAX: 410-612-6836
TECHNICAL DESCRIPTION

- In-Situ Thermal Desorption of Soil VOC's
- Field Analysis of VOC's
  - Simple VOC Detectors
  - Gas Chromatograph or Ion-Trap
  - Mass Spectrophotometry
- Vadose Zone and Saturated Zone Sampling
- Vapor Sampling in Vadose Zone

VERIFICATION

- Laboratory Analysis of Verification Soil Samples
- Compare with VOC Analysis System Results
<table>
<thead>
<tr>
<th>SITE ID</th>
<th>SAMPLE ID</th>
<th>LOCATION</th>
<th>DEPTH</th>
<th>o-DCE</th>
<th>TCE</th>
<th>TOLUENE</th>
<th>PCE</th>
<th>T-XYLENES</th>
<th>GW DEPTH</th>
<th>FT BGS</th>
<th>ng/g</th>
<th>ng/g</th>
<th>ng/g</th>
<th>ng/g</th>
<th>FT BGS</th>
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<tr>
<td>APG 5234</td>
<td>HP18 S15 T26</td>
<td>HP18</td>
<td>15</td>
<td>ND</td>
<td>590</td>
<td>70</td>
<td>ND</td>
<td>90</td>
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<td>APG 5235</td>
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<td>16.5</td>
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<td>ND</td>
<td>77</td>
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<td></td>
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</tr>
</tbody>
</table>
THE
MULTIPORT
SAMPLER

OBJECTIVES

- Improve operational capabilities of Multiport Sampler
- Field Test the Multiport Sampler
- Model behavior of analyte in region of sampling port (in preparation of laboratory investigation)
ACCOMPLISHMENTS

- Modified the MPS to improve its operational capabilities:
  a) Eliminated the twelve screw attachment design (three dowel pins have replaced the screws).
  b) Fabricated new modules, ports, pistons, and adapters.
  c) Developed procedure for measuring volume drawn through the Contaminant Trap.
  d) Modified control panel to allow detection of port leakage.
  e) Fabricated two cone mandrels.

ACCOMPLISHMENTS (Cont’d)

- Field test at Dover AFB, Delaware.
- Initiated numerical analysis of analyte behavior in region surrounding sampling port.
FIELD TEST
DOVER AFB, DELAWARE
1-5 MAY 95

Multiport Sampler Direct Measurement and Contaminant Trap Field Data
Taken at Dover AFB, Delaware

<table>
<thead>
<tr>
<th>Hole</th>
<th>Data Type</th>
<th>Depth</th>
<th>1,1,1-TCA</th>
<th>TCE</th>
<th>Benzene</th>
<th>Toluene</th>
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<td>DVRMPS1</td>
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<td>1351</td>
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NUMERICAL MODELING OF ANALYTE IN REGION OF SAMPLING PORT

Modeling Parameters

- Permeability of moist sand to air
- Mass transfer rate of TCE from water to air
- Compressibility of air
- Maximum concentration of TCE in water
- Molecular diffusion of TCE in air
- Dispersivity (relative to flow direction)
- Effective porosity
- Maximum concentration of TCE in air
- Mesh dimensions
Research Area VII
Data Processing Methodologies

Milestones:
- Complete development of data processing methodology
- Complete development of enhanced data acquisition, analysis, and visualization software
- Complete testing and user review of enhanced software

Schd: 10/94
Reschd: 11/94
Comp: 03/96
06/96
SCAPS
DATA PROCESSING FRAMEWORK

• Objective
  – To develop acquisition, analysis, and visualization software to exploit the capabilities of emerging sensor and sampler technology

• Software Components
  – Acquisition and real-time display
  – Processing, analysis, and database management
  – 3D visualization

SCAPS
DATA PROCESSING FRAMEWORK

• Hardware Architecture
  – Acquisition - MS-DOS PC
  – Processing/Visualization - Unix workstation with 24-bit z-buffered graphics (may be ported to PC in the future)

• Approach
  – Develop a flexible software architecture that incorporates a graphical user interface and a well-defined database structure to facilitate incorporation of new sensors
SCAPS DATA PROCESSING FRAMEWORK

**Approach (cont.)**

- Continue development of the SCIRT (MSU) 3D visualization software
- Maintain links to Earthvision (DGI) software
- Incorporate new sensors
- Develop capability for storage/retrieval of SCAPS database on CD-ROM
- Investigate porting processing/visualization software to PC

ACCOMPLISHMENTS

- Completed initial version of software that incorporates a graphical user interface and database structure and provides an interface to SCIRT and Earthvision
- Demonstrated 3D visualization in the field
- **Modifications to SCIRT**
  - Improve interpolation algorithms
  - Display a site map on 3D plume
  - Conversion to open GL
3D Site Plot

Fluorescence Intensity
Aberdeen Proving Ground
Fluorescence Intensity
ACCOMPLISHMENTS

- Completed software to acquire and display data from explosives probe
- Procured and tested a CD-R system
- Investigated issues related to porting processing/visualization software to a PC

FUTURE WORK

- Complete SCIRT modifications and test
- Incorporate new sensors
- Make improvements to acquisition, processing, and database management software
- Evaluate the use of the groundwater modeling system (GMS) for SCAPS
- Documentation
- Port software to Windows NT-based PC
Technology Demonstration Implementation

- **OBJECTIVE:** To demonstrate SCAPS sensors, sampling hardware, and associated data processing technologies
- **APPROACH:** Conduct demonstrations with SCAPS, comparing SCAPS data with data obtained through traditional sampling and analysis methods

---

DoD/National Environmental Technology Demonstration Program

**SITE LOCATIONS**

- National Center for Integrated Bioremediation - Wurtsmith AFB
- McClellan AFB
- Mare Island Naval Shipyard
- USN Port Hueneme
- Volunteer Army Ammunition Plant

Chapter 5  Abstracts, Papers and/or Presentation Materials
Use of DoD NETDP Test Sites

- Groundwater Remediation Field Laboratory National Test Site (Dover AFB, DE) - LIF, VOC Probes
- Natural Attenuation Test Site (Columbia AFB, MS) - LIF
- Port Hueneme, CA - LIF
- Wurtsmith AFB, MI - LIF
- Volunteer Army Ammunition Plant - Explosives Sensors
- McClellan AFB, CA - LIF
- Others TDB

Field Testing & Demonstrations

- EPA SITE Demonstration of LIF POL Sensor
  Comp. 09/94
- Initial Field Testing of Explosives Sensor (LAAP)
  10/94
- Field Testing of Explosives Sensor (Pantex)
  03/95
- Field Testing / Demonstration of Explosives Sensor (VAAP)
  04/95
Field Testing & Demonstrations

- Conduct Columbus AFB Demonstration of POL Sensor 05/95
- Conduct Dover AFB Demonstration 05/95
- Complete Initial Field Evaluation of Thermal Desorption VOC Sampler 05/95
- Conduct Port Hueneme, CA Demonstration 06/95
- Conduct Wurtsmith AFB, MI Demonstration 07/95
- Conduct Field Test of Explosives Sensor (Camp Navajo, AZ) 08/95
- Complete Field Demonstration of Improved Multiport Sampler 10/95
(Continued)

Field Testing & Demonstrations

- Conduct Demonstration of SCAPS Electrochemical Probes with Associated Software 01/96
- Conduct Validated and Demonstrated Enhanced SCAPS LIF POL Sensor and Software 03/96
- Initiate Field Testing / Demonstrations of FORS System 04/96
- Complete Demonstrations of Improved Sampler Technologies 10/96
- Conduct Demonstrations of LIBS Sensor System 12/96
- Complete Demonstrations of FORS System 01/97
- Conduct Demonstration of PF / LIF Explosives Sensor System 06/97
TRANSITION PLAN

- R&D results will be documented in peer-reviewed journals, technical conference proceedings, and agency technical reports
- Yearly meetings of peer review panel, researchers, developers, and users will be conducted, and proceedings published
- Field demonstrations will be conducted and results will be documented in technical reports
- Validated sensors and supporting SCAPS technologies will be made available to Government SCAPS users, complete with documentation, O&M manuals, and onsite training
- Tri-Services will continue to aggressively pursue commercialization of SCAPS technology through licensing agreement, CRADA's, and TRP

EXPECTED PAYOFF

- Provide rapid, cost effective methods to characterize sites
- Significantly increase the number and types of contaminated sites that can be characterized by SCAPS
- Maximize cost savings by accelerating the fielding of new SCAPS technologies to support remediation efforts
- Increase acceptance of SCAPS as a rapid field screening tool by users, regulators, and public
Technology Demonstration/Implementation

Objective: Demonstrate SCAPS Sensors, Specifically Tunable LIF (ROST), Sampling Hardware, and Associated Data Processing Technologies With Respect to Jet Fuels and Gasolines Having Lighter Aromatic Compounds (BTEX).

Approach: Conduct SCAPS Demonstrations With Tunable LIF System, Comparing Data to that Obtained Through Traditional Sampling and Analyses Methods.

Payoff: Validation of SCAPS Performance and Cost Effectiveness for Site Characterization From a Users Perspective (KC CoE) and to Facilitate User and Regulatory Acceptance.

Technology Demonstration/Implementation Status

Making Use Of Kansas City CoE SCAPS
- Transitioned Laser - Sep 94
- Subcontract to DTI for Tunable Laser Support - May 95
- Hardware Upgrade - May 95
- Integrate Tunable Laser - June 95
- Provide Training, Including on the Job - May/June 95

Wurtsmith AFB National Test Site Demonstration Completed
- Firefighter Training Area Site Having Mixture of Contaminants
- Innovative Hollow Stem Auger/Split Barrel Sampler
  - Ensures What is Sensed is Sampled!
- Sample Analyses and Chemical Data Analysis Ongoing

Dover AFB National Test Site Demonstration Initiated
- Hydrant Fuel System Contamination Believed to be Just JP-4
- Site Also Has Sands/Gravels With Shallow Groundwater
Technology Demonstration/Implementation Status (cont.)

Columbus AFB, MS
- SERDP Funded Natural Attenuation Test Site (NATS)
- Primarily Sands/Gravels and No Contamination Until Release
- Demonstration Cancelled Due to Delayed Site Approvals

Port Hueneme, CA
- Also Primarily Sands
- Not Selected Due to Excellent Navy Sponsored Demonstration
  - Made Use of ROST System on Navy SCAPS

Site Needs
- Emphasize Demos at Sites Having Only Jet Fuel or Gasoline
  - Laser Wavelength at 290nm or Lower
- Heterogenety in Vadose Zone, Especially Fine Grained Soils
  - Sampling Below Water Table is Problematic

Technology Demonstration/Implementation Status (cont.)

Propose Eaker AFB, AR as Demonstration Site
- Excellent Data Set From AFCEE SCAPS Project
  - Used N, Laser
- Gasoline Contamination (Dover Provide JP-4 Site)
- Heterogeneous Soils
  - From Fine Grained (Silt/Clays) to Sands
- Contamination in Vadose Zone Above Water Table

Project Schedule
- National Test Sites
  - Wurtsmith AFB, MI - Jun/Jul 95
  - Dover AFB, DE - Jul/Aug 95
- Eaker AFB, AR - Sep 95
- Complete Laboratory Analyses & Reporting - Sep 95
- Complete Draft Report Delivered - Oct 95
- Project Outbrief To Armstrong Lab & Tri-Services - Nov 95
- Final Technical Report and Project Completion - 31 Dec 95
IMPLEMENTATION:
NAVY SCAPS-LIF PROGRAM

- JUNE 1993 - HQ/NAVFAC INITIATED PROGRAM
- PROGRAM ELEMENTS (TRI-SERVICE COORDINATED)
  ▶ EXPEDITED DUAL-USE OF R&D SYSTEM (EDM-1)
    - SITE WORK (NAVY)
    - REGULATORY ACCEPTANCE (TRI-SERVICES)
  ▶ EXPEDITED TECH TRANSFER
    - LIMITED NAVY ACQUISITION (2 EDMs)
    - COMMERCIALIZATION (CRADA, ET AL)
  ▶ PRE-PLANNED PRODUCT IMPROVEMENTS
    - UPGRADED SYSTEMS/PROCESSES
    - NEW SENSORS
NAVY PROGRAM ELEMENTS:
EXPEDITED DUAL-USE OF RESEARCH SYSTEM

• NAVY SITE WORK
  > HIGH PRIORITY IR SITES WITH DISTINCT
    SCAPS-LIF VARIABLES
  > 14 SITES
    > PRODUCTS: KNOWN/UNKNOWN POLs-FRESH/AGED,
      SEPARATE/MIXED, ABOVE/BELOW WATER
    > SOILS: CLAYS-SANDS-COBBLERS, LAYERED MATRICES,
      DRY-VADOSE-SATURATED ZONES
    > SITES: COASTAL/DESERT, URBAN/REMOTE,
      SHALLOW/DEEP WATER
    > REGULATORS: LOCAL, STATE, REGIONAL, FEDERAL
    > EXAMPLES: 100 YR OLD REFINERY, ACTIVE/INACTIVE
      FUEL FARMS, ABANDONED OIL FIELD, FIRE FIGHTER
      TRAINING SITES, GAS STATIONS, USTs
NAVY PROGRAM ELEMENTS:
EXPEDITED DUAL-USE OF RESEARCH SYSTEM
(CONTINUED)

• TRI-SERVICE REGULATORY ACCEPTANCE
  ▶ ESTABLISH HIGH QUALITY VALIDATION DATABASE CONCURRENT WITH FIELD OPS
    ▶ USE/COMPARE TRADITIONAL VS SCAPS-LIF
    ▶ WORK CLOSELY WITH REGULATORS
  ▶ LIF DEMO: THREE INTERLINKED PROGRAMS
    ▶ CAL EPA "CERT" PROGRAM (STATE)
    ▶ WGA/DOIT DEMONSTRATION (REGIONAL)
    ▶ US EPA CONSORTIUM DEMONSTRATION (NATIONAL)
  ▶ EAST COAST REGULATORY ACCEPTANCE
    ▶ REPLICATE/EXTEND VALIDATION PHASE (ESTCP)
    ▶ WORK WITH RPMs AND LOCAL/STATE/REGIONAL REGULATORS
    ▶ INTEGRATE WITH WESTERN RESULTS
NAVY Validation Sites

- NAS North Island, Fuel Farm
- NS San Diego, FFTF
- NAB Coronado, abandoned fuel farm
- MCAS Yuma
- NAS Alameda, old refinery site
- Camp Pendelton, UST
- NAS North Island, expedited tank yank
- Guadalupe Oil Field
- NTC San Diego, gas station
- NTC San Diego, auto hobby shop
Scatter Plot/Contingency Plot of TPH vs TRPH
Normalized Data for Ten Sites

Y MCAS Yuma
C NAB Coronado
F NS 32nd St
A NAS Alameda
P MCB Camp Pendleton
G Guadalupe
H NTC Hobby Shop
I NASNI Fuel Depot
U NASNI UST
X NTC Gas Station
## Cumulative Contingency Analysis Summary for 10 Sites (n=219)

<table>
<thead>
<tr>
<th>Method</th>
<th>% Correct</th>
<th>% False Pos</th>
<th>% False Neg</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIF vs. TRPH</td>
<td>83</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>LIF vs. TPH</td>
<td>84</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>TPH vs. TRPH</td>
<td>93</td>
<td>2</td>
<td>5</td>
</tr>
</tbody>
</table>
Port Hueneme
National Test Site Demo
Depth vs Fluorescent Intensity
Demonstration of Direct Sparge Volatile Organic Carbon Sampler with Hydropunch Direct Push Groundwater Sampler with the Site Characterization and Analysis Penetrometer System

Lead Organization:
U.S. Army Environmental Center
Aberdeen Proving Grounds, MD 21010-5401

POC: Mr. George Robiale
SFMA-CE-ETP
Voice: 410-862-9855
FAX: 410-862-6836

TECHNICAL DESCRIPTION

- Hydropunch commercially available direct push groundwater sampler to access groundwater

- Direct sparge sampler strips VOCs from groundwater in-situ and transports analytes to surface

- Analytes identified and quantified using Teledyne field portable ITMS
METHOD FOR 
VERIFYING TECHNOLOGY

- Obtain groundwater samples from each Hydropunch/direct sparge/ITMS experiment for laboratory analysis by EPA Method 8260
- Compare Hydropunch/direct sparge/ITMS results with data obtained from conventional monitoring wells at each site
- Low flow pumping in place of bailers for collection of samples

PERFORMERS

- AEC, Mr. George Robitaille, SFIM-AEC-ETP, Aberdeen Proving Grounds, MD; Project management, coordination with users and regulators
- WES, Dr. William M. Davis, CEWES-ES-P, 3909 Halls Ferry Road, Vicksburg, MS; conduct field demonstration/validation, laboratory analysis/data reduction, document results in guidance documents
- ORNL, Dr. Mark Wise, Martin Marietta Energy Systems, Inc., ORNL, P.O. Box 2008, Building 4500-S, Oak Ridge, TN; provide support and assistance with field demonstration/validation, data reduction and documentation
SCAPS Hydropunch/Direct Sparge/ITMS Study, WP21 Dover AFB

\[ DS = (0.86 \times \text{EPA 8260}) + 155, \quad r^2 = 0.86 \]
SCAPS Hydropunch/Direct Sparge/ITMS Study, Bldg 525 Aberdeen Proving GRD

\[ \text{EPA} = 0.574 \times \text{HP/DS/ITMS} + 1, \quad r^2 = 0.92 \]
6 SERDP Peer Review Panel
Conclusions and
Recommendations

The SERDP funded Tri-Service Accelerated SCAPS Sensor Development Project is composed of seven research areas as follows:

I. Laser Induced Breakdown Spectroscopy (LIBS) sensor development for detecting metals in soils.

II. Laser Induced Fluorescence (LIF) sensor development for detecting
   a. POL contaminants
   b. Explosive contaminantants

III. Fiber Optic Raman Sensor (FORS) development for detecting VOCs (LNAPLS and DNAPLS).

IV. Electrochemical sensors for detecting
   a. Explosive contaminants
   b. VOCs

V. Spectral Gamma probe for detecting radioactive wastes

VI. SCAPS sampler development
   a. Thermal desorption VOC sampler
   b. Multiport sampler

VII. Data processing methodologies to provide on site 3-D visualization
     and to interface emerging sensors into the SCAPS data acquisition,
     processing, and visualization systems

The SERDP project briefings were arranged in the order listed above and the briefing materials are included in this chapter. Since some of the research areas are being pursued by multiple Tri-Service partners, some of the research areas contain more than one set of briefing materials.
7 User Needs

SCAPS users from the Army Corps of Engineers Districts, the EPA, and DOE were invited to attend and to participate in the presentations and discussions. Mr. Arbor Drinkwine of the Kansas City District of the Corps of Engineers presented a video describing their innovative over coring technique used to verify SCAPS LIF sensor responses. This technique has been very useful in reducing the effects of soil/contaminant heterogeneities, and for comparing LIF sensor results with EPA approved methods in order to obtain regulatory acceptance of SCAPS technologies. Mr. Bob Lien of the Environmental Protection Agency, Ada OK, presented a slide briefing of a different coring technique that is also applicable to the verification of SCAPS sensor responses. Due to the format of these presentations, no hardcopy materials were available for inclusion in this report.
A number of DOE and EPA researchers were invited to attend the workshop and to make presentations on their ongoing research that is relevant to the SCAPS sensor development effort. This chapter contains the unedited briefing materials submitted for this portion of the workshop.
On-Line Organic Samplers for the Cone Penetrometer

P.V. Doskey, J.H. Aldstadt, and M.D. Erickson

Environmental Research Division
Argonne National Laboratory

A. Robbat

Chemistry Department
Tufts University
Outline

- Objective
- Approach
- Results
- In Situ Purge Device
- Thermal Desorption Device
- Transfer Line
- Conclusions
- FY 96 Plans
Objective

To provide *in situ*, on-line analyses for VOCs and SVOCs in subsurface materials.

- Maintain sample integrity
- Eliminate sample manipulation
- Increase speed of data acquisition
- Decrease the cost of site characterizations
Approach

*In Situ* Purging

*In Situ* Thermal Desorption

Transfer Line

Prescreening with non-destructive detector

Preconcentration

Detection and Quantitation - GC/MS
In Situ Purge Device Materials

- Type 304 Stainless Steel
- 75 mL Gas Sampling Cylinder
- Teflon® PFA
- 2.667 cm OD Pipe
Laboratory ISPD (2:1)

- Gas Input
- Sample source Input
- Septum
- Collection Vessel
- Heated Transfer Line
- Level Sensor
- Manual Valve
- Air Activated Valve
- Drain
Comparison of Different ISPD Headspace : Sample Volume Ratios
Conclusions

In Situ Purge Device

Sparging efficiencies for vessels made of glass, Teflon®, and stainless steel are similar.

The optimum headspace to sample volume ratio for a purge vessel is 2:1.

A stainless steel ISPD has been integrated within a CPT push rod that employs microvalve technology and a conductivity level sensor to accurately purge a 5 mL groundwater sample as described in EPA Method 624.
## Material Balance for Standard Addition to Dry Sand

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Transferred (%)</th>
<th>Residual in Soil (%)</th>
<th>Residual in Transfer Line (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250°C</td>
<td>300°C</td>
<td>250°C</td>
</tr>
<tr>
<td>Aroclor 1248</td>
<td>92.4</td>
<td>95.2</td>
<td>5.03</td>
</tr>
<tr>
<td>BHC</td>
<td>87.1</td>
<td>91.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>73.1</td>
<td>66.0</td>
<td>26.0</td>
</tr>
<tr>
<td>4,4'-DDT</td>
<td>67.3</td>
<td>72.3</td>
<td>19.1</td>
</tr>
<tr>
<td>Fluorene</td>
<td>71.5</td>
<td>75.4</td>
<td>0.00</td>
</tr>
<tr>
<td>Fluoranthenene</td>
<td>79.0</td>
<td>80.2</td>
<td>4.50</td>
</tr>
<tr>
<td>Pyrene</td>
<td>86.3</td>
<td>82.9</td>
<td>9.00</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>64.5</td>
<td>65.4</td>
<td>31.0</td>
</tr>
</tbody>
</table>

28 ppm
12 ppm
15 ppm
## Instrument Calibration

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Dynamic Range (ng)</th>
<th>Detection Limit (ng)</th>
<th>RSTD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-BHC</td>
<td>0.5 - 1000</td>
<td>0.5</td>
<td>6</td>
</tr>
<tr>
<td>PCB (Cl-4)</td>
<td>3.7 - 950</td>
<td>4.0</td>
<td>8</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.5 - 1000</td>
<td>0.7</td>
<td>18</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.5 - 1000</td>
<td>1.3</td>
<td>25</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.5 - 1000</td>
<td>0.7</td>
<td>13</td>
</tr>
<tr>
<td>4,4'-DDT</td>
<td>0.5 - 1000</td>
<td>0.5</td>
<td>11</td>
</tr>
<tr>
<td>Dibenz[a,h]anthracene</td>
<td>0.5 - 1000</td>
<td>0.6</td>
<td>14</td>
</tr>
</tbody>
</table>
Conclusions

In Situ Thermal Desorption Device

A temperature of 250°C is sufficient to thermally desorb PCBs, PAHs, and pesticides from a dry sample matrix with 50-95% efficiency.

Volumetric flow rates of 15 - 60 mL min⁻¹ and purge volumes exceeding at least 30 volumes of the thermal desorption system are necessary to efficiently transfer the desorbed analytes and preconcentrate them on glass wool at -60°C.

The thermal desorption efficiency decreases with increasing water content of the matrix.
Transfer Line Materials

(15 m x 0.318 cm OD x 0.160-0.216 cm ID)

Stainless Steel (Type 304 and Type 316)
Nickel (Type 200)
Aluminum
Teflon® (Type PTFE, FEP, PFA)
Dynamic Dilution System
Conclusions

Transfer Line

Stainless steel is superior to Teflon® as a transfer line material.

Gentle heating to prevent condensation of water in the transfer line will be necessary for efficient VOC transfer.

Glass-Lined or passivated stainless steel tubing may be necessary to efficiently transfer SVOCs from the thermal desorption device.
FY 96 Plans

Field test of on-line organic samplers at ANL.

10/95 - 11/95
12/95 - 2/96
3/96 - 8/96

Laboratory Test of Thermal Desorption Device for VOCs.
Modify samplers.

Field tests of on-line organic samplers at additional sites.
Acknowledgment

Charles H. Batson
Molly S. Costanza
Aleksandr Gorshteyn
Tammi R. James
Jacqueline M. Kuo
Alice F. Martin

U.S. Department of Energy
Characterization, Monitoring, and Sensor Technology Integrated Program
Office of Technology Development

Manager: Caroline Purdy
Manager: Eric Lightner
presentation for the
SCAPS Sensor Development Workshop
August 29-30, 1995

Bob Knowlton
Sandia National Laboratories
Albuquerque, New Mexico
(505) 844-8533

Sponsors

US Department of Energy
Office of Science and Technology Development (EM-50)
Commercial Partners

- GEOCENTERS, Inc., Boston, Mass. USA
  - Contributed the fiber optic pore pressure sensor
  - Fabricated and field tested the Sandia probes

Topics to Cover

- Objective and needs of research
- Design and testing specifications for moisture probe
- Design and testing specifications for capillary pore pressure probe
- Field testing results
Objective:

To design, fabricate, test & evaluate a new cone penetrometer application for characterizing hydrogeologic parameters (with a Time Domain Reflectometry [TDR] sensor and fiber optic probe)

Data Needs:

- Hydrologic characterization
  - Moisture content and pore pressure are critical parameters for flow & transport modeling (used in risk assessments)
  - Moisture content and pore pressure can be used with stratigraphic info to correlate geologic units
- Remediation
  - Moisture content is important data for optimizing soil vapor extraction options, because volatiles flow readily through low-moisture content, high permeability zones, and not through high-moisture content, low permeability zones
  - Moisture content is important data for optimizing/monitoring bioremediation projects
TDR Probe

Strong contrast between dielectric of soil (2 to 4) and water (80). Calculate the dielectric constant of a porous media, $K_a$:

$$K_a = \left( \frac{l}{l^* v_p} \right)^2$$

where:
- $l = \text{actual probe rod length [L]}
- l^* = \text{apparent length of the probe rod as determined from the TDR trace [L]}
- v_p = \text{propagation velocity of the signal [L/T]}

and moisture content is calculated as:

$$\theta = -0.053 + (0.0292)K_a - (5.5 \times 10^{-1})K_a^2 + (4.3 \times 10^{-6})K_a^3$$

TDR Probe (continued)

- For good accuracy, recommend calibrating to the soils at the site
- For precision, expect ± 1% moisture by volume (if calibrated)
- The probe configuration will be of use in two applications:
  - As part of a cone penetrometer sensor system
  - As a down-hole logging device for characterization and post-closure monitoring (a side benefit of this research)
Cone Penetrometer through Subsurface Geology

Subsurface Contamination

Cone Penetrometer Sensors

Sandia National Laboratories
Albuquerque, New Mexico USA
Radius of Influence Experiment
Relative Contributions of Inner and Outer Regions to TDR Measured Dielectric
Dry Bulk Density vs. Distance from Edge of Cone
Fiber Optic Capillary Pore Pressure Sensor

- Optical chemical indicator sensor with a porous polymer substrate (patented proprietary product by GEOCENTERS, Inc.),
  LED dual wavelength optical signal, and a photo-diode/timing circuit to read results.

- The polymer matrix is based on a mixture of:
  - cobalt chloride hexahydrate, and
  - poly-methyl methacrylate (PMMA)

- Measures relative humidity in soil gas, from which capillary pore pressure is calculated: 
  \[ P_e = \frac{(RT/M)}{\ln(p_r)} = \frac{(RT/M)}{\ln(R.H.)} \]

Hydrophobic porous polymer R.H. measurements

![Graph showing the relationship between Red Light Intensity and Relative Humidity at 22°C](image)

Chapter 8  DOE Related Research  251
Results of Cone Penetrometer Testing of Sandia's TDR Moisture Probe
Area 1 Cone Penetrometer Push Locations
Area 1 Subsurface Geology and Moisture Content
Other Work

- Technology transfer initiative with the Navy and the AEC for the TDR probe
- Technology transfer initiative with ARA for commercialization
Field Testing at Two Sites

- South Royalton, VT at ARA facilities, 10/94
- Albuquerque, NM at Sandia National Laboratories, 11/94

Conclusions

- TDR probe met or exceeded expectations for a real-time moisture content sensor
- Fiber optic capillary pore pressure sensor was successful in accuracy and precision, but less than desirable on equilibration time
  - Recommend for use in long-term spot measurements or as a monitoring device
Fiber Optic IR Cone Penetrometer for Site Characterization

A research and development program funded by the U.S. Army Environmental Center

Sponsor: Mr. George Robitaille, AEC

Participants:
Naval Research Laboratory - Washington
  - Dr. Ish Aggarwal (PM)
  - Dr. Frank Bucholtz (PI)
US Geological Survey
Army Waterways Experiment Station

OBJECTIVES
- Develop fiber optic sensors to provide remote, in-situ detection of hydrocarbon contamination in soil for screening and characterization of environmental sites.
- Perform field tests in conjunction with SCAPS.

APPROACH
- Integrate infrared optics, FTIR spectroscopy and newly-developed IR transmitting chalcogenide fibers to produce a field-ruggedized sensor system.

DELIVERABLE
- IR fiber optic sensor system for in-situ detection of hydrocarbon contaminants in soils.

Naval Research Laboratory
Fiber Optic IR Cone Penetrometer

Laboratory Measurements

Normalized Diffuse Reflectance (%)

Wavelength (µm)

TCE on Sea Sand

DFM on Sea Sand

NRL/WES/USGS
## SUMMARY

**Pre-Dover Laboratory Results on Cone Penetrometer System**

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Conditions</th>
<th>Detection Limit (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFM</td>
<td>SAND, Large Sample, No fiber</td>
<td>50</td>
</tr>
<tr>
<td>DFM</td>
<td>SAND, Penetrometer, Cabled fiber</td>
<td>200</td>
</tr>
<tr>
<td>TCE</td>
<td>SAND, Large Sample, Cabled fiber</td>
<td>200</td>
</tr>
</tbody>
</table>
TECHNICAL ISSUES
Pre-Fabrication Stage (Fall '94)

1. Miniaturization of optics
   - Reduction in optical throughput
   - Custom fabrication

2. Robustness of chalcogenide fiber cabled to useful lengths

3. Ruggedness and modularity of system (downhole optical rail, topside spectrometer)

4. Suitability of downhole source
   - Reliability
   - Effect of increased temperature on fiber, optics
NRL Fiber Optic IR Cone Penetrometer

Initial Design

Prototype Design
- Reduction in downhole components
- Source flexibility
- Robust

Naval Research Laboratory
Fiber Optic IR Cone Penetrometer

**Hardware and Performance**

*Summary: Bover AFB Field Test, May 1995*

- Quick set-up (<1 hr)
- All hardware performed properly
- No failure/breakage in IR fiber cable during normal handling and operation in SCAPS

*Performance of cabled IR fiber*

Wavelength range of operation: 1.5 - 5.5 μm*

Total Optical Throughput (all wavelengths)
Field vs Lab: > 90%

* Limited by bulk optical components. Fiber itself extends to ≥ 10 μm.

NRL/WES/USGS
Fiber Optic IR Cone Penetrometer

Field Result: Observation of Kaolinite (Clay) Absorption Band

NRL/WES/USGS
USGS COMPARISON OF SPECTRA FROM DAFB WITH TWO LABORATORY STANDARDS OF KAOLINITE.

type a to Change SCALE, e to ERASE, x to EXIT, or return to continue

[Graph showing spectra with labels]

DAFB SPECTRA OF KAOLINITE

LABORATORY STANDARDS - KAOLINITE
SUMMARY of TEST RESULTS
DAFB Field Test, May 1995

Demonstrated rugged sensor system comprising IR-transmitting fiber cable, cone penetrometer optics, and spectrometer.

- Quick set-up (< 1 hr)
- Hardware functioned properly
- No special cable handling required
- Optics continued functioning after penetrometer tube was bent

Successfully observed kaolinite (clay) absorption spectra & variation of absorption band with depth & location

Hydrocarbon bands not observed due to combination of low/unknown concentration levels and remaining technical issues:

- Low soil albedo compared to background
- Competing absorption bands in soil, optics (H2O, HS)
- Interfering hydrocarbon bands
### PROPOSED SYSTEM IMPROVEMENTS
(Based on Dover AFB Field Test Results)

<table>
<thead>
<tr>
<th>Technical Issue</th>
<th>Solution</th>
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<tr>
<td>Low soil albedo compared to background</td>
<td>Improve optical throughput (x 25 expected)</td>
</tr>
<tr>
<td>Competing absorption bands</td>
<td>7-Fiber bundle</td>
</tr>
<tr>
<td></td>
<td>CPC collector mirror</td>
</tr>
<tr>
<td></td>
<td>Paraboloidal exit mirror</td>
</tr>
<tr>
<td></td>
<td>AR coating</td>
</tr>
<tr>
<td>Interfering hydrocarbon bands</td>
<td>Replace KBr optics with CaF2, ZnSe optics</td>
</tr>
<tr>
<td></td>
<td>Improve fiber materials</td>
</tr>
<tr>
<td></td>
<td>Improve purge system</td>
</tr>
<tr>
<td></td>
<td>Reduce CH contamination in fiber &amp; optical system</td>
</tr>
</tbody>
</table>

*950707 improv*
IR PROBE COLLECTION OPTICS ENHANCEMENT

COMPOUND PARABOLIC CONCENTRATOR (CPC)

TRADE AREA FOR NA

ALLOWS FOR CLOSE TO THEORETICAL MAXIMUM
CONCENTRATION OF INCOMING RADIATION (NA OUT =1)
C_{max} = (1/\sin(\Theta_{in}))^2

CPC OPERATION

NEW COLLECTION SYSTEM

Fiber Bundle
OPTICAL THROUGHPUT IMPROVEMENTS

CURRENT SYSTEM

- OPTICAL FIBER BUNDLE
- F#1 CsF LENS
- COLLIMATION MIRROR
- FTIR ENTRANCE PORT

IMPROVED SYSTEM

- FIBER BUNDLE
- CPC CONE
- PARABALOID
- BUNDLE FACE AT PARABALOID FOCUS
- FTIR ENTRANCE PORT

REASONING

- ACCEPTANCE ANGLE OF TEFNON CLAD CHALCOGENIDE FIBER = OUTPUT ANGLE CPC
- CHALCOGENIDE FIBER
- OUTPUT ANGLE OF IMAGING OPTICS

IMPROVEMENT

- SINGLE FIBER
- 7 FIBER BUNDLE
- CURRENT FOCUS SIZE
- CPC IMPROVED FOCUS SIZE
Comparison of Optical Power Spectra
Dover AFB May 95 (Hole 10)

![Graph showing diffuse reflectance spectrum (arb) compared to different materials: Max Throughput, Sand (Laboratory), Clay, and Background. The x-axis represents wavelength (µm) ranging from 2 to 3.5, and the y-axis represents diffuse reflectance spectrum (arb) ranging from 0.1 to 10^4.]
Metals Detection with an XRF Sensor for the Cone Penetrometer

W. T. Elam
Naval Research Laboratory
Code 6685
Washington, DC 20375-5345

30 August 1995
XRF Sensor for the Cone Penetrometer Concept

Code 6680, Naval Research Laboratory
XRF Sensor for the Cone Penetrometer

Requirements

must fit penetrometer geometry
small diameter (max. 2 inch O. D.)
rugged construction
strong x-ray window

detect all metals Z>20 (scandium)

Detection limits well below 100 ppm
(field screening)

100 or less second data collection times
(approx. time required for penetrometer ram retraction)
# XRF Sensor for the Cone Penetrometer

## Sub-Systems

<table>
<thead>
<tr>
<th>Below Ground</th>
<th>Cables</th>
<th>Above Ground</th>
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<tbody>
<tr>
<td>X-ray Source</td>
<td>High Voltage</td>
<td>X-ray Source Power Supply</td>
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<tr>
<td>Collimators</td>
<td>Signal</td>
<td>Detector Amplifier and Pulse Shaping</td>
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<tr>
<td>Window</td>
<td>Power</td>
<td>Interlocks</td>
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<tr>
<td>X-ray Detector</td>
<td>Shields and Grounds</td>
<td>Multi-Channel Analyzer</td>
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<tr>
<td>Preamp</td>
<td></td>
<td>Data Reduction</td>
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<td>Mounting Platform</td>
<td></td>
<td>Display</td>
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<tr>
<td>Heat Dissipation</td>
<td></td>
<td>Interface to Penetrometer Truck</td>
</tr>
</tbody>
</table>
XRF Sensor for the Cone Penetrometer

X-ray Optics Layout

- Soil
- Incident beam path
- Boron Carbide Window (1 mm)
- Mo filter (0.05 mm)
- Fluorescent beam path
- Aperature
- X-ray tube (Mo anode)
- Detector
XRF Sensor for the Cone Penetrometer

Engineering Layout

HV connector

boron carbide window

window holder

collimator and shield assy (details omitted for clarity)

HV cable assy

detector preamp

rail

penetrometer pipe

detector cable

X-ray tube

incident beam path

fluorescence beam path

detector
SRM 2710 with Amptek XR-100T miniature X-ray Detector
Montana Soil with Highly Elevated Heavy Metal Contamination

Counts in 100 sec.

Fe Kα
Cu Kα
Zn Kα
Pb Lα
Pb Lβ
Sr Kα
Y Kα

Mo Kα Excitation
(Compton and Rayleigh scattered peaks)

Energy (keV)
XRF Sensor for the Cone Penetrometer

X-ray Tube Requirements

Critical requirements:
- Molybdenum anode
- Maximum operating voltage 35 kV (continuous)
- Maximum operating current 0.5 ma (continuous)
- Maximum operating power 18 watts (continuous)
- Cooling via contact with housing
- Maximum length 6 inches
- Focal spot approximately 0.080 inch (2 mm) diameter or less
- Maximum diameter 0.625 inches (15 mm) at any point on length
Prototype Development Timeline

XRF Sensor for the Cone Penetrometer

- Assemble Sensor
- Obtain Performance Data (especially detection limits)
- Field Test of Sensor

- October 1995
- March 1996
- Summer 1996
XRF Sensor for the Cone Penetrometer

Requirements and Status

(as of August 1995)

Detector
Re-mounted preamp
Boron Carbide Windows
Mounting rail
X-ray tube
Structural Components
    Collimators
    Window holder
    Pipe section

On hand, tested
In progress
Received and mounted, testing in progress
On hand
Vendor selected, order in progress
Final design waiting on x-ray tube design
9 SERDP Peer Review Panel Conclusions and Recommendations

The peer review panel members raised questions and made comments throughout this workshop. The panel members were asked to submit their written comments to the workshop coordinator to be included in these proceedings. The following comments were submitted in memorandum form and have not been altered.

MEMORANDUM FOR THE RECORD

SUBJECT: Second Annual SCAPS Sensor Development Workshop

FROM: Jeff Marquesee

DATE: August 31, 1995

The annual Tri-Service SERDP SCAPS program review was held at Waterways Experiment Station August 29 and 30. The SCAPS Tri-Service funding profile from SERDP and other DoD sources is shown below.

<table>
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<td>2,580</td>
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<td>350</td>
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<tr>
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<td>6,016</td>
<td>3,640</td>
<td>2,640</td>
<td>2,700</td>
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In addition to these funds, ESTCP and Navy DERA have provided funding for the demonstration and validation of SCAPS technology.
The SERDP Science Advisory Board requested that the program be reviewed by an independent peer review group every year. The review committee consisted of:

Dr. Jeffrey Marquesee, DoD  
Mr. Eric Lightner, DOE  
Dr. Greg Rosasco, NIST  
Dr. Carl Enfield, EPA

The review covered the seven areas currently receiving SERDP funding. They are:

1. Laser Induced Breakdown Spectroscopy  
2. Laser Induced Fluorescence Sensors: POL and Explosives  
3. Fiber Optic Raman Sensors  
4. Electrochemical Sensors: Explosives and VOCs  
5. Spectral Gamma Probe  
6. Sampling Technology  
7. Data Processing Methodologies  
8. Technology Demonstration

Details on these seven topics are available.

Attached are my comments and recommendations provided to the program manager regarding the ongoing SERDP funding work.

Comments on SERDP Funded SCAPS Development

General

• Overall, the work is important to the DoD and addresses real user needs. The quality is high and support should be maintained.

• For successful execution, tri-service participation is essential. Although the SCAPS program’s level of tri-service cooperation is far beyond other environmental programs, improvements in coordination are still needed. In particular, the work being performed by the Air Force is not being coordinated sufficiently with the ongoing Army and Navy work.

• SCAPS clearly addresses a specific user defined requirement. The earlier development of the POL LIF sensor had close interaction with the user community. The current sensor development needs to maintain a high level of user interaction to assure that these sensors will provide operational capabilities needed by the DoD cleanup community. It is recommended that on a sensor/contaminant basis the developers meet with members of the user community and obtain appropriate feedback.
• The current review was limited to government participants. It is recommended that in the future the non-government groups involved in the SERDP funded R&D be invited.

• It is recommended that the program maintain its short term focus on providing the user community with near term technologies that can be used for screening the condition of a contaminated site. The current approach of simultaneously looking at multiple technical approaches to address a single problem should be maintained in order to move the technology to the field rapidly. While maintaining this near term focus, SERDP should also consider supplementary efforts to exploit the potentially more quantitative nature of these sensors. In the out years, the user community will have an increasing need for characterization tools that can monitor the progress of ongoing remediation activities. The value of a quantitative measurement of the ratio of various aromatic compounds by LIF would be high, even if the absolute scale for an individual compound cannot be determined.

• The role of field testing and demonstrations is important. The ongoing work under SERDP funding appears to be of mixed quality and at times unfocused. With increased support planned for these activities in FY96, it is important that the objectives of the various field tests be clearly defined.

Below are additional comments on the specific areas briefed.

**Laser Induced Breakdown Spectroscopy**

The work in this area has a great potential payoff and support should be maintained at a high level to assure a rapid transition to the field user.

**Laser Induced Fluorescence Sensors**

**POL**

• The ongoing work at NRaD is of high quality with an excellent short term focus on providing opportunities for technology insertion into existing systems.

• The lasers being provided by MIT/LL offer a great potential and should be fully exploited to determine their value.

• The work described by the Air Force and Navy appears uncoordinated and potentially duplicative. A coordinated program needs to be constructed.

• The Air Force work appears to be supporting one commercialized approach and overlaps the TRP funded work in this area.
Explosives

- There is great need for a sensor which could cost effectively and rapidly map out explosive contaminants in groundwater. This sensor is advertised as having that potential.

- The current effort appears to be funded at such a low level that it is below the critical mass needed to really advance the technology. The measurement approach needs to be pushed in the lab to answer the basic questions on feasibility followed by a decision to either drop support or significantly increase support.

- It is recommended that in the near term, lab experiments be performed to determine if this technology can detect explosives in the soil, then the focus must move to determine if there is a potential to differentiate between NO from explosives vs. NO from fertilizer sources that widely contaminant groundwater in the U.S. If there is no potential for differentiating these two sources then the user community in the Army needs to be queried on the potential value of such a sensor.

Fiber Optic Raman Sensors

- The Navy work briefed clearly showed the shortcomings of this approach. The work was high quality even if the resulting answer is a disappointment.

- The Navy is currently altering their work to look at surface enhanced Raman for a detector of DNAPL. Before proceeding with this project, it is recommended that the Navy assess whether such a technically sophisticated sensor is really the best approach if it will only be able to detect free product and if the market will support such a sensor.

- Given the recent results of the Navy, the current Air Force plans are not well justified. The work proposed is not clearly leading to an advancement, which will provide a new operational capability.

Electrochemical Sensors: Explosives and VOCs

- These sensors represent good near term products that should be transitioned to the user rapidly.

Spectral Gamma Probe

- This work does not address a DoD requirement. It is recommended that SERDP support for this work be discontinued.

Sampling Technology
• The thermal desorption sampling is an excellent tool that should be transitioned rapidly. The future SERDP work should focus on questions associated with its operational use; i.e., developing an appropriate protocol for field use to assure an accurate sample is collected.

• The multi-port sampler results were inconsistent. The modeling proposed to understand the results will not fully address the important questions. It is recommended that additional experimental work be performed to identify the cause of the anomalous results.

Data Processing Methodologies

• It is recommended that this effort be decreased in the out years. The work presented appeared to be of good quality, but SCAPS should exploit and rely on existing commercial software to the maximum extent possible.

Technology Demonstration

• The planned demonstrations conducted by the Services require greater coordination.

• The value and expended product for each field test should be explicitly defined prior to initiating any extensive field activities.
General comment:

As discussed at the time of the meeting, it would be most helpful for the purposes of such a review to provide an overall roadmap which provides the rationale for the technical program for each of the technologies presently encompassed by the SERDP sensor acceleration funding. This roadmap would provide a brief description of the measurement problem, e.g., POL contamination characterization, the critical requirements of the measurement system, e.g., detection and relative quantitation at the sub 400 ppm level in the vadose or water table level for the following compounds in an asserted priority order. The problem definition should give some sense of user priority and critical measurement needs, both within an area, e.g., energetic compound detection, and between areas, e.g., relative importance of heavy metal detection vs. POLs or explosives. The problem definition would be followed by a brief assessment of the current state-of-the-art in sensor technology to address this problem, this should logically set the rationale for the SERDP funded effort. Within each technology selected for acceleration, critical decision points, accomplishment and time schedules, should be identified to understand the decisions as to continuation, expansion, cessation, incorporation in penetrometer test, etc. The comments with regard to “not understanding how the AF portion of the effort fit into the overall strategy” I think were engendered by this lack of clear understanding of the bigger picture. This not to say that such a roadmap or plan doesn’t exit, but rather that the review team could not discern the plan in the time allowed for the review.

Individual program areas:

LIBS: An innovative, highly promising approach which, if rapidly incorporated in survey studies, could greatly add to the understanding of heavy metal contamination, transport, and remediation. Since the fiber optic transmission of the receiver is better than 20 percent for wavelengths above 330 nm, some evaluation of the ability to detect Cd and Zn for longer wavelengths should be tested in the lab. The likelihood that the AOTF-PMT down-hole detector approach will provide analytically significant data (in the 220 nm region or any other spectral region) in time to incorporate the technology into the SCAPS system does not appear to be high. The inherent irreproducibility of the spectrum on a shot-to-shot basis suggests that the only useful normalization will come from simultaneous multielement comparisons available from the currently practiced multichannel spectroscopy approach. The downhole, high energy Nd:YAG system seems ideal (even if the rep rate is low). Some focus adjustment may be required to optimize plasma generation depending on soil type; as an alternative to the current design for the probe, one could imagine a small, 250 micrometer port which would allow access to the soil with a purge and dump area below it to allow any material that entered through the port to be expelled. The system seems very close to ready for field tests. Good work.
LIF for POL: Outstanding results, especially those related by Dr. Lieberman in his review of the Navy demonstrations in CA. The potentialities of the diode laser pumped downhole Nd:YAG laser are outstanding. If the system could be configured to allow wavelength selection, the range of excitation wavelengths would be remarkable, and thereby allow a tremendous number of tests, including wavelength optimization for Raman spectroscopy, which is after all, at least operationally, just off resonance fluorescence. The wavelength selection could include 808 nm from the diode, 1060 nm from the YAG, either of which might reduce fluorescence for Raman, (unfortunately one would have to use FT Raman analysis for the 1060 excitation). The 532 nm power would be useful for Raman excitation and would eliminate the current problems with the interfering silica Raman spectrum coming from the input excitation fiber in the current FORS system, this may allow mineral characterization and perhaps water content measurements, a subject of interest in general. The ability to switch to short wavelength excitation of the POLs may add the ability to do some relative quantitation of heavy and light fractions or aging, as discussed in the meeting. This is a first rate opportunity and should be pushed hard. No similar justification has been advanced for the dye system, the OPO, the powdered doubler or the Ti:Sapphire work. The explosives detection effort of Sausa should be funded at a sufficient level to allow a critical test of the possibilities of detection of the compounds of interest in the matrix of interest in the presence of the user identified interferants. No spectroscopy, simply see if a one photon, deep UV or a two photon, excitation detection scheme will give qualitative, analytically useful (perhaps for screening purposes) indication of the presence of the explosives.

FORS: The work to date is first rate, a sensible, “utilize the state-of-the-art approach” has been followed. Other than the suggestions above with regard to the potential of a downhole multiwavelength source, the near term utility of this system seems to have been evaluated. It is unfortunate that no data appear to have been taken in any part of the push, prior to failure in the one field test that was reported. There is still the question as to the utility of Raman spectroscopy to help distinguish the nature of the geological layer that the probe is passing through, as a supplement to the other, admittedly crude, characterizations available from the geotechnical stress/friction data. Although I am vaguely familiar with a SERS based enhancement of sensitivity for Raman spectroscopy, I think there are other extractive, trapping technologies available and better suited to the needs of SCAPS.

Electrochemical sensors: Ready for incorporation in the SCAPS system and should be subjected to complete validation tests in parallel with other such tests. Good work.

Spectral gamma: Subcritical effort, no further comment.

Sampling technology: This catalytically enhanced thermal desorption technique appears ready for field validation and deployment. Good work. The multiport sampler needs some more thought as to how to perform the validation studies, but it appears otherwise a mature technology for soil gas
sampling. I am not sure why one needs both the thermal desorption and the multiport to get soil gas, one could just turn off the heater in the retracted cone version of the thermal desorption sampler and have a means to sample a controlled volume for soil gas. This multiport sampler is mature, it does not need more SERDP acceleration funding.

Data processing methodologies: Should be incorporated as required in the transitioning of each technology into the SCAPS. It should not be a research area in itself.

Field Demonstrations: Some are just field tests, and these should be differentiated and included in the process of transitioning the technology into the SCAPS. The demonstrations at Dover and those conducted at Port Hueneme and North Island jointly with CAL EPA and the Western Governors Association were outstanding examples of what to do in a field demonstration. More sensors and more data should be obtained in such tests, since so much expense goes into the testing and supportive extractive analyses.

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References


**REPORT DOCUMENTATION PAGE**

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<th>1. AGENCY USE ONLY (Leave blank)</th>
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| The Second Annual Site Characterization and Analysis Penetrometer System (SCAPS) Sensor Development Workshop was held at the U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, during August 29 and 30, 1996. In attendance were researchers, managers, and SCAPS users representing the Army, Navy, Air Force, the Department of Defense, the Department of Energy, the Environmental Protection Agency, and the National Institute of Standards and Technology. Workshop participants presented briefings on the status of their SCAPS-related sensor research, development, and demonstration efforts. Managers and users of SCAPS technologies participated in the briefings and discussions and described the needs and concerns from the users' perspective. The Peer Review Panel evaluated the progress of the Tri-Service SCAPS sensor development project and presented recommendations for future work. | Chemical sensors
Cone penetrometer
Environmental sensors | In situ sensors
Monitoring
Site characterization | 299 | |

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