

RECEIVED
AUG 10 8 1996
OSTI

GA--C22131(7/96)
GA-C22131

E-SMART SYSTEM FOR IN-SITU DETECTION OF ENVIRONMENTAL CONTAMINANTS

QUARTERLY TECHNICAL PROGRESS REPORT

**General Atomics
PO Box 85608
San Diego, California 92186-9784**

**Work Performed Under
DOE Cooperative Agreement DE-FC0795ID13352
U.S. Department of Energy
Idaho Operations Office
Idaho Falls, Idaho**

Effective Date of Contract:	March 20, 1995
Contract Expiration Date:	March 19, 1998
Reporting Period:	Q2CY96 (Apr-Jun 1996)

**GENERAL ATOMICS PROJECT 3719/4450
July 1996**

MASTER



DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *kg*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Contents

Abstract	1
Executive Summary	3
1. Work Conducted April - June, 1996.....	5
1.1 Multichannel Microsensor	5
1.2 Sawtek Integrated Modular Array Sensor (IMAS).....	17
1.3 Other Sensors and Actuators	17
1.4 E-SMART Network Management	17
1.5 Field Testing.....	18
1.6 Visualization.....	18
1.7 Program Management	21
1.8 Dual Use and Commercialization Planning	21
2. Problems.....	22
3. Plans for the Next Quarter	22
4. Milestones and Deliverables.....	22
5. Papers and Conferences	22
6. Financial Status Report.....	22

Abstract

General Atomics (GA) leads a team of industrial, academic, and government organizations to develop the Environmental Systems Management, Analysis and Reporting neTwork (E-SMART) for the Defense Advanced Research Project Agency (DARPA), by way of this Technology Reinvestment Project (TRP). E-SMART defines a standard by which networks of smart sensing, sampling, and control devices can interoperate. E-SMART is intended to be an open standard, available to any equipment manufacturer. The user will be provided a standard platform on which a site-specific monitoring plan can be implemented using sensors and actuators from various manufacturers and upgraded as new monitoring devices become commercially available. GA's team members include Isco, Inc., Photonic Sensor Systems (PSS), Georgia Tech Research Institute (GTRI), Science & Engineering Analysis Corporation (SECOR), and the U.S. Air Force Armstrong Laboratory Envirionics Directorate at Tyndall AFB(AL).

This DARPA TRP project will further develop and advance the E-SMART standardized network protocol to include new sensors, sampling systems, and graphical user interfaces. Specifically, the E-SMART team will develop the following three system elements:

- A new class of smart, highly sensitive, chemically-specific, in-situ, multichannel microsensors utilizing integrated optical interferometry technology,
- A set of additional E-SMART-compatible sensors and samplers adapted from commercial off-the-shelf technologies, and
- A Data Management and Analysis System (DMAS), including network management components and a user-friendly graphical user interface (GUI) for data evaluation and visualization.

In addition, the E-SMART TRP team has signed Articles of Collaboration with another DARPA TRP awardee, Sawtek, to develop an E-SMART-compatible Intelligent Modular Array System (IMAS) for monitoring volatile organic chemicals (VOC's) in the environment. This collaboration will simplify the network development required to field the IMAS sensor, and will encourage the adoption of the E-SMART standard by increasing the number of commercially available E-SMART sensors.

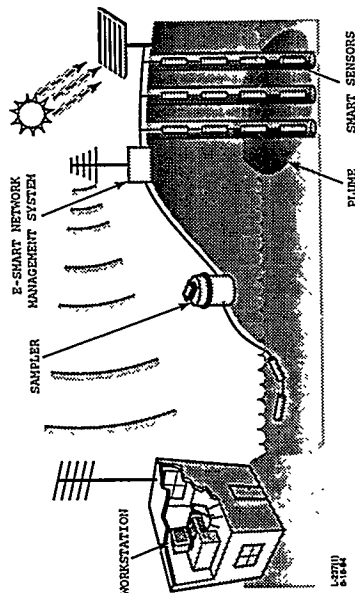
Figure 1 summarizes the vision and goals of the E-SMART TRP project.

E-SMART ARPA TRP

TEAM

General Atomics
Isco, Inc.
Photonic Sensor Systems, Inc.
Georgia Tech Research Institute
SECOR
EnviroNics Directorate, Tyndall AFB

VISION



OBJECTIVES

- Develop and promote E-SMART, an open standard for networking smart sensors at environmental sites. Prepare an initial set of E-SMART-compatible devices, including:
- A new class of smart, in situ, chemically-specific multichannel microsenors utilizing integrated optical interferometry technology.
 - Sensors and field measurement equipment, based upon commercial off-the-shelf technology, and adapted for E-SMART networks.
 - A data management and analysis system (DMAS), including a graphical user interface for data evaluation, data visualization, and network management.

SCHEDULE

ID	Task Name	1995	1996	1997	1998
1	100 DEVELOPMENT	Op 2 Op 3 Op 4	Op 1 Op 2 Op 3 Op 4	Op 1 Op 2 Op 3 Op 4	Op 1 Op 2 Op 3
2	100.100 Microsensors				
3	100.200 E-SMART Integration				
4	100.300 Visualization				
5	200 FIELD TESTING				
6	Preliminary Testing				
7	Integrated Testing				
8	300 PROJ MGMT				

Fig. 1. Quad Chart Summarizing the E-SMART Project

Executive Summary

- The E-SMART TRP team requested a one-year, no-cost extension to the TRP contract, that included some restructuring of scheduled activities to address technical issues related to the development of the multichannel microsensor technology. DOE-ID accepted this request and modified the TRP contract to reflect a 12 month, no-cost program extension. The new contract completion date is March 19, 1988. Each member of the E-SMART TRP team has prepared revised cost and schedule projections to accommodate the extension. These projections were provided to DOE-ID. Purchase order modifications reflecting scope changes for team members will be issued in July.
- A two-week environmental effects test was completed on an E-SMART sensor module-mockup at Tinker AFB in June. A sensor module was immersed for two weeks in a monitoring well to characterize degradation of sensor hardware. Although light fouling was observed for the Delrin housing and PVC cable coating, all seals and gaskets functioned properly. No major design changes for sensor hardware are anticipated as a result of the test.
- Much activity took place in preparation for the E-SMART field test at Tinker AFB, scheduled to begin on August 19th, and run for at least 2 months. The field test schedule is subject to change if support services at Tinker are not in place by middle of August. A white paper describing the field test was issued and transmitted to Tinker AFB staff. The white paper includes the test description and the general plan for the field test. In addition, an expanded Tinker AFB test plan is being drafted. Field test well locations, data quality objectives, and mobilization requirements were proposed by GA. Procurement of a trailer for the field test was initiated. Additional funding from Tinker AFB may extend the field test until December 1996 or longer.
- Microsensor development continued and focused on improvements to the fabrication process. Improvements for coupler fabrication were realized by using contact printing and reactive-ion etching.
- A test plan was written for development of microsensor coatings. The test plan includes a list of candidate polymers for final screening of BTEX-selective coating materials. The detailed screening process will take place next quarter. Initial tests with one polymer, polybutyl-isobutyl methacrylate (PBIBMA) produced sensitive, rapid, and fully reversible microsensor operation in the aqueous phase, coupled with highly distinctive response for BTEX compounds.
- The E-SMART team agreed upon a twelve compound background interferant test matrix for screening and characterization of microsensor selective coatings.
- A companion Small Business Technology Transfer (STTR) program is evaluating a preliminary version of the E-SMART microsensor in a cone penetrometer format.
- Improvements were made to designs for E-SMART-compatible interfaces for off-the-shelf pressure, oxygen, and volatile organic chemical (VOC) sensors. Seventy Delrin sensor-module housings were fabricated, and 5 complete sensor modules were assembled and readied for testing. Fabrication of circuit boards for the interfaces continued, as well as procurement of long-lead parts.

- Echelon Corporation's Lonworks Network Services (LNS) has been successfully implemented, allowing E-SMART nodes to be installed on and to communicate data across the network. LNS is "Beta" software that is still under development. Bench-scale testing of the network using prototype E-SMART-compatible pressure sensors continued to evaluate network hardware and software.
- The internal structure of the hardware and software required for a device (e.g., sensor or actuator) to be compatible with an E-SMART network has been defined and has been documented in the preliminary release of the "E-SMART Node Specification," ES-TRP-GA-96-01. This document has been distributed to team members for review and comment. Some initial team member comments have been received. Portions of the Node Specification will be revised to address team member comments.
- Interactions continued between GA and Sawtek for developing an E-SMART-compatible IMAS later this year.

1. Work Conducted April - June, 1996

1.1 Multichannel Microsensor (PSS/GTRI)

During the quarter, microsensor development activities conducted by PSS/GTRI focused on (a) improvements to integrated sensor chip fabrication, (b) studies of polymeric coatings for discriminating and quantifying BTEX compounds in the aqueous phase, (c) understanding of polymer sensing mechanisms, and (d) evaluation of a preliminary version of the E-SMART microsensor in a cone penetrometer format.

1.1.1 Integrated Sensor Chip Fabrication

The integrated optic sensing chip currently being developed for the E-SMART microsensor relies on diffractive elements to couple light into and out of the waveguide device. These elements, commonly referred to as grating couplers, represent the most difficult and time consuming step in the fabrication process. In the previous quarterly report, progress on a photolithographic technique for coupler fabrication was noted. The approach relies on the fabrication of a metallized grating master (0.7 μm period, 0.35 μm line width) and copying or replicating the master grating. A master chrome oxide grating pattern was previously fabricated. During this reporting period, the master has been successfully replicated using contact printing, and gratings have been etched into substrates using reactive-ion etching (RIE). This technique is now being used for grating coupler fabrication. Note that contact printing places a premium on the use of optically flat substrates since two couplers separated by 18.5 mm are required for a device. Substrates flat to $1/10 \lambda$ are typically needed for satisfactory yields. Use of projection printing may ease this constraint.

1.1.2 Polymeric Coatings for BTEX Compound Detection

Initial emphasis for microsensor development will be discriminating and quantifying the BTEX compounds (i.e.; benzene, toluene, ethyl benzene and xylene). Similarly, the initial focus will be on aqueous phase measurements.

Demonstration of Reversible, Aqueous-Phase BTEX Detection: As reported in detail below, a number of polymers are being systematically screened as candidate coatings for detection of the BTEX compounds. Tests with polybutyl-isobutyl methacrylate (PBIBMA) illustrate the potential of this approach.

PBIBMA gives clear, fully reversible responses for each of the BTEX compounds (strongest for toluene and weakest for xylene). Figure 2 presents typical results when testing toluene/water mixtures. A PBIBMA-coated sensing chip is first exposed to pure water, followed by toluene in water at 20 ppm (starting at the time marked "on"), followed by a return to pure water (starting at the time marked "off"). Note that the system is allowed to reach equilibrium between each step. There is a $+7\pi$ radian phase shift as the toluene concentration goes from 0 to 20 ppm and a -7π radian phase shift as the toluene concentration returns to 0 ppm. Because of the mixing dynamics of the flow setup, it takes several minutes for the transition from 0 to 20 ppm of toluene and vice versa. Thus, the time response in Figure 2 is dominated by the flow dynamics, not the inherent sensor capabilities. The magnitude of the response extrapolates to being able to detect about 10

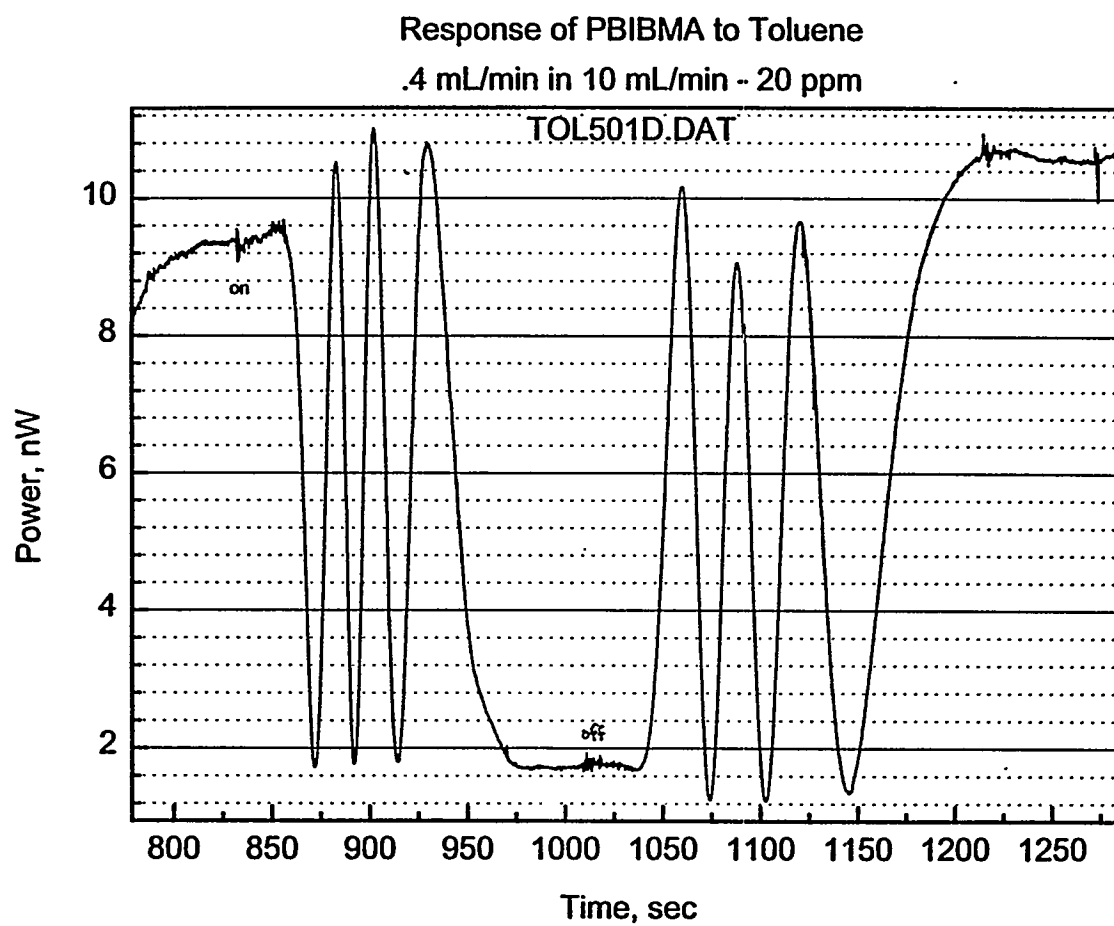


Fig. 2. Response of Polybutyl-isobutyl methacrylate (PBIBMA)
for Testing Toluene/Water Mixture.

ppb of toluene without additional optimization. Further, the PBIBMA responses to BTEX differ significantly from the responses for many other organic compounds. Figure 3 shows response curves for a variety of volatile organic/water mixtures up to their solubility limit (typically ≤ 250 ppm). The responses range from a relatively strong signal for toluene (0.378π radians/ppm) to a relatively weak signal for methylene chloride (0.016π radians/ppm). PBIBMA is essentially blind to a number of other organic compounds. For example, exposure to approximately 1000 ppm of acetone gives essentially no response. It should be noted that Figure 3 plots the absolute value of the sensor response. Several of the chlorinated solvents give responses *in the opposite direction* of the BTEX responses (i.e.; a positive phase shift for increasing BTEX concentrations versus a negative phase shift for increasing concentrations of the chlorinated solvents), providing a further means for discrimination.

These are truly exciting results: sensitive, rapid and fully reversible operation in the aqueous phase, coupled with a highly distinctive response for the BTEX compounds versus many other organic compounds.

Interferant Test Matrix: On May 15th an E-SMART team conference call was held to identify the background interferant test matrix for use in laboratory screening and characterization of microsensor selective coatings. As a result of the conference call the E-SMART team has chosen the following twelve compounds for the background interferant test matrix.

- trichloroethylene
- methylene chloride
- ethylene glycol
- methyl ethyl ketone
- phenol
- humic acid
- 2,2,4-trimethylpentane
- naphthalene
- bis (2-ethylhexyl) phthalate
- sodium chloride
- nitrate
- sodium dodecyl sulfonate

An attempt was made to include a wide range of organic compound classes (e.g.; chlorinated hydrocarbons, alcohols, ketones, phenols, organic acids, aromatic hydrocarbons, ions and surfactants) and types (e.g.; polar, non-polar). Representative examples of these classes and types were picked from lists of compounds that occur frequently in groundwater and/or waste water settings. Inorganic compounds were excluded from consideration because they are unlikely to cause interference with the coatings materials under consideration.

Candidate coating materials will also be characterized against the BTEX compounds.

Systematic Screening of Polymer Coating Candidates: The following list of candidate polymers has been compiled for systematic evaluation. The list is based on laboratory experience at Georgia Tech as well as work by others studying polymer coatings on surface acoustic wave (SAW) devices in the vapor state (e.g.; Zellers and Grate). An attempt was made to include a broad range of organic functionalities (polar, non-polar, aromatic, hydrogen bonding, etc.), glass transition temperatures (T_g), molecular weights

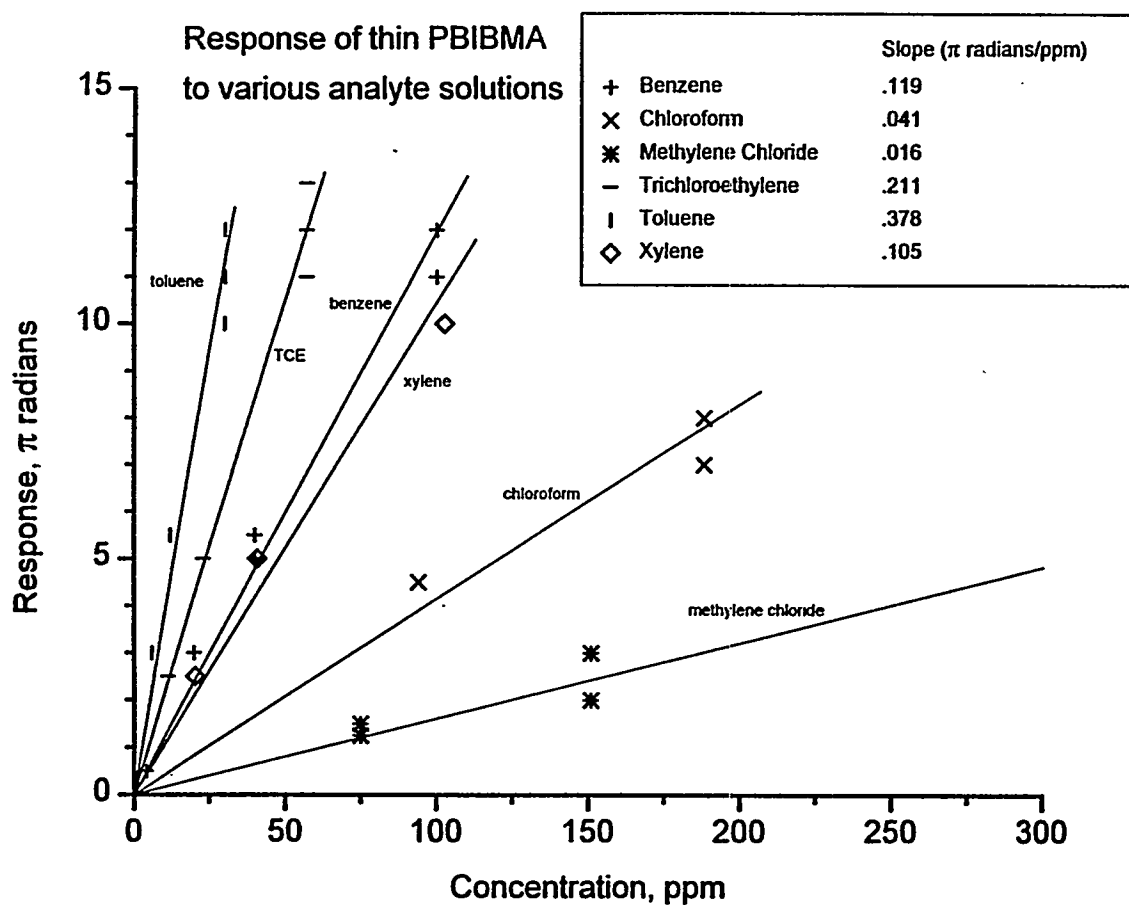


Fig. 3. PBIBMA Response Curves for a Variety of Volatile Organic/Water Mixtures up to their Solubility Limit.

(MW) and refractive indexes. Preliminary experiments have shown that liquid polymers are not suitable for aqueous phase devices, since they were deformed by the flow of the analyte solutions, so only solid polymers have been included. Only commercially available polymers have been included, removing the need for polymer synthesis.

Poly butyl-isobutyl methacrylate
styrene-allyl alcohol
caprolactone
a-methyl styrene
vinyl butyral
bisphenol A carbonate
styrene-acrylonitrile
sulfone
ethylene-maleic anhydride
vinyl acetate
N-vinyl pyrrolidone-vinyl acetate
styrene-butyl methacrylate
vinyl stearate
ethylene adipate
ethylene phthalate
isobutylene
acrylonitrile-butadiene
epichlorohydrin
hexyl acetate
methyl methacrylate
2-hydroxyethyl methacrylate
diallyl phthalate
1,2-butadiene
cyclohexyl methacrylate
2,3-dihydrofuran
diphenoxyl phosphazene
4,4'-dipropyl-2,2'-diphenylpropanefumarate
ethylene
isobornyl methacrylate
isopropyl methacrylate
methacrylonitrile
methylhexadecylsiloxane
methyloctadecylsiloxane
phenyl methacrylate
tetrahydrofurfuryl methacrylate
vinylidene fluoride
vinyl methyl ketone
vinyl naphthalene
ethyl cellulose
ethylene-acrylic acid
ethylene-vinyl acetate
acenaphthalene
amide
t-butyl methacrylate
t-butyl styrene
2,6-dimethyl-*p*-phenylene oxide
4-methoxystyrene

octadecyl acrylate
trimethylene adipate
vinyl chloride
vinyl ethyl ether
styrene-maleic anhydride
vinyl alcohol-vinyl butyral
Teflon AF
Nylon 6/10
Cellulose acetate

All screening and testing uses a standard integrated optic test chip consisting of a fused silica (SiO_2) substrate, a 140 nm silicon nitride (Si_3N_4) waveguide film, and a 40 nm fused silica overlayer. The 40 nm fused silica overlayer provides a convenient surface for attaching chemically active coating candidates. This test chip includes signal and reference regions and embedded gratings for input and output coupling of a Helium-Neon laser light source (633 nm). Beam combining and interference generation—which will be directly incorporated in the fully integrated microsensors—are accomplished via bulk optic elements. The reference region of the sensor chip is shielded from the environment with a 500 nm fused silica coating and the signal region is covered with a candidate polymer coating. For test measurements, water samples saturated with the organic species of interest are diluted to appropriate concentrations, and a flow cell arrangement is used to flow controlled analyte/water mixtures over the test chip surface. For direct comparison of relative sensitivity, the test chip response in π radians/ppm has been adopted as a standard figure of merit.

To evaluate the polymers, the following procedure is utilized. A polymer is dissolved into an appropriate organic solvent (generally toluene, methanol or chloroform) at a concentration of 50 to 150 mg/mL. The test chip is cleaned with hot chromic acid, and treated with hexamethyldisilazane for at least 30 min. This silation step is necessary to promote adhesion of the polymer film to the surface. The test chip is then spin-coated with the polymer solution, and the thickness measured by profilometry. This is repeated with different polymer solution concentrations until the resulting coating thickness is in the range of 700 to 1100 nm. Finally, the polymer film is annealed at 110 °C for about fifteen minutes. As previously noted, the test chip reference arm is buried under a thick (500 nm) layer of fused silica, so there is no need to physically remove a strip of polymer to create a reference.

The first step in the screening process is an evaluation of waveguiding properties of the polymer-coated test chip. If the light guides with minimal loss, a flow cell is attached to its surface. A carrier flow of deionized water is siphoned through the flow cell, and the flow rate is measured (generally about 10 mL/min). The test chip is exposed to benzene, toluene, xylene, trichloroethylene (a few points each at concentrations of 10 to 50 ppm) and methylene chloride (at concentrations of 100 to 500 ppm). If these tests give promising results (e.g.; relatively quick response, fairly strong signal), the test chip is next exposed to methyl ethyl ketone (at a concentration of about 1%), chloroform (at concentrations of 80 to 400 ppm) and hexane (at a concentration of approximately 30 ppm). In general, analytes are injected at a known rate with a syringe pump into the carrier water flow. Hexane is the exception. A saturated solution of hexane in water is diluted by a factor of three, and the carrier water stream is switched to this solution.

In instances where all of the above results are positive, similar polymers from the candidate list are considered for subsequent testing (based on MW, T_g , refractive index,

copolymers). In the case of negative results, the polymer is discarded, or an analog is chosen with lower T_g , different MW, or a copolymer that might provide a better response.

Results for some polymer films are shown below in Table 1. The numbers are in units of π radians/ppm. In general the response of the polymers proved to be fast, with response times of seconds to a minute. Those identified as slow exhibited responses on the order of many minutes, while very slow responses took over half an hour.

Table 1. Polymer Responses for Selected Analytes

	PBIBMA	PSMBA	PVAc	PIB	PMVK	PHEM
CH ₂ Cl ₂	.0035	.005	*	.0044	.0088	.0069
xylenes	.8, slow	very slow	*	.156	very slow	*
TCE	.03	.045	.06	.043	*	.017
toluene	.35, slow	.3	.047	.045	.15	0
benzene	.175	.25	.063	.022	.02	.021
acetone	.00005	.00015	*	0	.0017	*
hexane	.068, slow	.09, slow	*	.077	.013	.068, slow
CHCl ₃	*	.07	*	*	.018	.00875

PBIBMA = polybutyl-isobutyl methacrylate

PSMBA = polystyrene-butyl methacrylate

PVAc = polyvinyl acetate

PIB = polyisobutylene

PMVK = polymethyl vinyl ketone

PHEM = polyhydroxyethyl methacrylate

TCE = trichloroethylene

* = no data

A few other polymers have been tried with less success. Polydiallyl phthalate showed no response to methylene chloride, TCE, or benzene. Polyvinyl butyral and poly a-methylstyrene responded very slowly to most analytes. Polyvinyl acetate and polyethylene-vinyl acetate showed responses, but became extremely glossy very quickly. (It is surmised that these polymers are becoming detached from the waveguide with time.) In addition, some polymers have been easily discounted without much experimentation. For example, polycaprolactone is biodegradable, making it an inappropriate choice for groundwater monitoring. Polydiphenyl phosphazene turned out to be jet-black, which is not very good for an optical device. Polyvinyl stearate and polymethyloctadecylsiloxane give unsuitable films upon spin-coating excessive loss or scattering.

In general, results to date imply that amorphous polymers (e.g.; polyisobutylene) will respond faster than glassy polymers (e.g.; poly a-methylstyrene).

A subset of the candidate list will be chosen for more in-depth study, such as orthogonality of response and interferant effects. Work will also begin to developing methods of covalently bonding polymer layers to the waveguide surface, making the films more resistive to dissolution by pure solvent.

1.1.3 Polymer Sensing Mechanisms

It has been experimentally verified that there are at least three mechanisms contributing to the response of a given polymer coating to a given volatile organic in the aqueous phase: 1) polymer swelling (or shrinking), 2) displacement of water from cracks or fissures in the polymer, and 3) dissolution of the volatile organic into the polymer (based on the polymer/water partition coefficient for the volatile organic).

Polymer swelling causes a response because the polymer displaces water in the sensing region above the integrated optic sensing element (i.e.; the region probed by the evanescent wave) and, to the extent the polymer has a different refractive index than water, the displacement changes the effective refractive index of the sensing region. Swelling is eliminated as a sensing mechanism if the polymer coatings is thicker than the sensing region (≥ 500 nm). While swelling of the polymer will still occur, there will be no displacement of water from the sensing region. Using thick coatings has the advantage of shielding the sensing region from spurious environmental effects, such as dirt or air bubbles on the coating surface. Displacement of water from cracks or fissures also causes a response because the difference in refractive index of the polymer and the displaced water. As there is no reason to believe that this mechanism would be reproducible from sensor to sensor, controlled application or annealing of the polymer coatings will be used to reduce cracks and fissures to a negligible level. The remaining sensing mechanism—dissolution—causes a response because the refractive index of the polymer/analyte mixture is different from the refractive index of the pure polymer. Dissolution can be tailored to cause a positive response (analyte index > polymer index), a negative response (analyte index < polymer index), or even *no* response (analyte index = polymer index). This provides a powerful discriminator for pattern recognition. (Note that volatile organic compounds have refractive indexes that differ on the order of 10^{-2} . The Hartman interferometer is capable of discriminating refractive index differences as small as 10^{-6} .) Further, dissolution can be extremely sensitive because polymer/water partition coefficients can be strongly in favor of the polymer (up to 100,000 to 1).

It may seem counter-intuitive that aqueous phase dissolution of organic analytes into polymers is rapidly reversible. Most organic analytes of interest show limited solubility in water but have great solubility in polymers. When an organic analyte is introduced to an immiscible binary mixture of water and a polymer, most of the organic analyte prefers to dissolve into the polymer. Very little dissolves into the water. The magnitude of this preference is quantified by the partition coefficient, which is defined as the log of the concentration of the organic analyte in the polymer (usually determined using 1-octanol as the polymer) divided by its concentration in water. For example, toluene has a partition coefficient with most polymers of about 3. That is to say, for every molecule of toluene in the water layer, there are 1000 in the polymer layer. The amount of the analyte in either layer can increase until it reaches its solubility limit. In the case of the integrated optic sensing chip, a thin-film polymer coating of the chip surface serves as the polymer layer. When an aqueous solution of some organic analyte is introduced to the sensing chip surface, the analyte molecules begin to move into the polymer. This will continue until an equilibrium (dictated by the partition coefficient) is reached. If the aqueous solution contains 10 ppm of toluene, it is predicted that the polymer layer at equilibrium will contain

1000 times 10 ppm of toluene, or 10,000 ppm. This will remain steady unless the concentration in the aqueous solution changes. If the concentration of toluene in the aqueous solution decreases, toluene will come out of the polymer and into to water until a new equilibrium is reached. Obviously, if pure water were to flow over the polymer, all of the toluene would eventually come out. Although the tendency of the toluene to partition into the polymer is great, it can be overcome. The rate is a matter of volume and flow. Because the polymer film is extremely thin (≤ 750 nm), the volume of polymer on the integrated optic sensing chip surface is only about 5×10^{-6} mL. Allowing a polymer film with 10,000 ppm of toluene to equilibrate with an equal volume of pure water (5×10^{-6} mL) will result in the film losing 10 ppm of toluene to the water while retaining 9990 ppm of toluene. Removing this water and replenishing it with another equal volume of pure water will lower the toluene concentration another small increment. In this manner, the toluene can be extracted from the polymer in thousands of small steps. A flow of pure water over the sensing chip will continuously extract and remove the toluene. Since the volume of polymer on the sensing chip surface is so small, a flow of as little as 1 mL/min provides a change in water volume equal to the polymer volume tens of thousands of times per minute. Even though not all of the flowing water can interact with the polymer, it does not take long before there is no toluene left to partition between the polymer and the water. Given the overwhelming water/polymer volume ratio, the limiting factor in rapid reversibility is the diffusion time for toluene that may reside "deep" within the polymer. However, the fact that the polymer coatings are so thin minimizes the diffusion time needed to reach any new partition equilibrium. In any event, repeated aqueous phase experiments similar to those reported above have confirmed that a variety of thick, annealed polymers are not only sensitive (\leq part-per-billion range) but also quickly reversible (on a time scale much faster than the mixing dynamics of the test system).

1.1.4 Evaluation of Preliminary Microsensor Model

A companion Small Business Technology Transfer (STTR) program is evaluating a preliminary version of the E-SMART microsensor in a cone penetrometer format. This STTR program is part of the TRP matching funds. Early experiments using a BTEX-sensitive microsensor and a laboratory soil chamber have demonstrated the ability to track aqueous-phase benzene concentrations in a simulated subsurface environment down to at least the low parts-per-million level.

STTR Soil Chamber Tests: As illustrated in Figure 4, the laboratory soil chamber used for these experiments consists of a 5.5 inch outside diameter Pyrex glass cylinder 24 inches in length, with two, 8 inch diameter, stainless steel end platens (0.7 inches thick). All seals and fittings are constructed of either stainless steel or Viton, a BTEX-resistant material. The top and bottom platens are each equipped with two ports to allow control of the in-flow and out-flow of fluid to the chamber. A porous stone and a piece of filter paper were placed in the bottom of the chamber, and it was filled to approximately two-thirds height with Ottawa 20/30 sand placed at an intermediate relative density. Ottawa 20/30 is a relatively inert and pure silica sand, chosen to minimize interactions between the soil matrix and the test chemicals. The microsensor used for these experiments consists of a single-channel Hartman interferometer coated with polybutyl-isobutyl methacrylate (PBIBMA). As reported above, PBIBMA gives a strong, distinctive response for the BTEX chemicals. The integrated optic sensing chip was mounted in a bench-top configuration (as opposed to the eventual cone module packaging). A flow cell was fixed to the surface of the sensing chip, with small diameter (1 mm) source and exhaust tubes running in and out of the flow

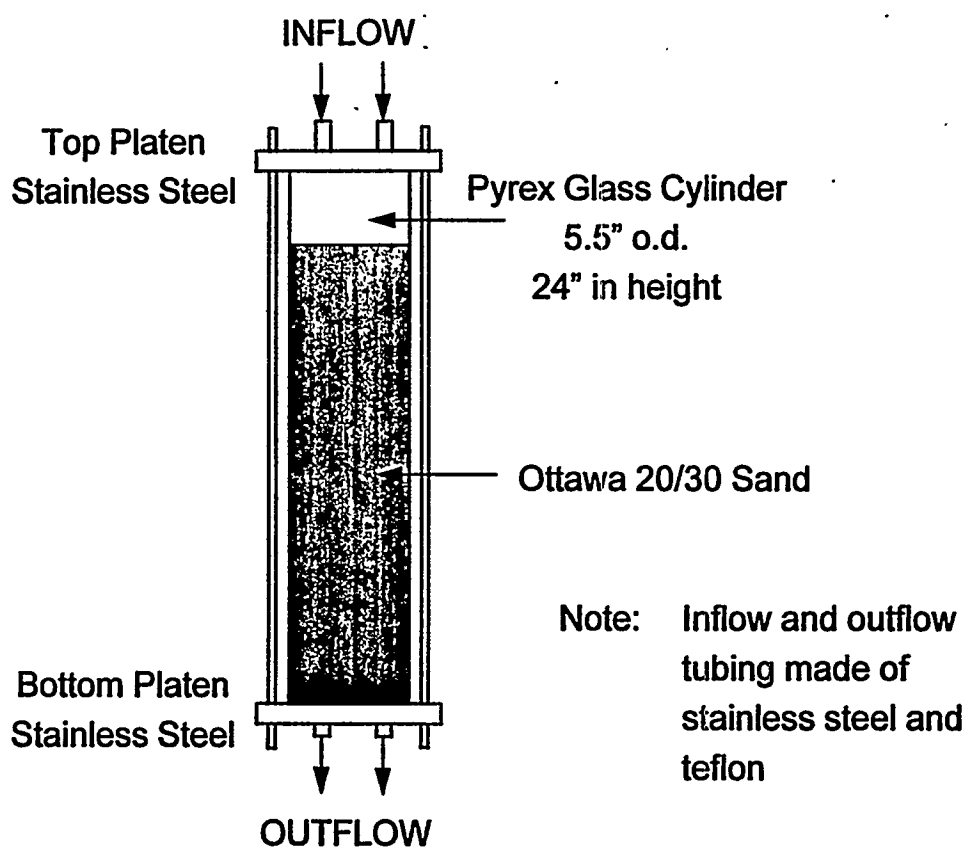


Fig. 4. Laboratory Soil Chamber used in Testing of Preliminary Microsensor Design.

cell. The open end of the source tube was buried several inches below the top of the soil column in the test chamber. The open end of the exhaust tube was placed in a bucket on the floor. Fluid was drawn from the test chamber across the sensing chip surface to the bucket by a gravity-driven siphon. The raw optical output of the sensor was collected by a photodetector and displayed on a personal computer. With this setup, the aqueous phase concentration of benzene at a point several inches below the soil surface could be continuously monitored.

As a benchmark test of this setup prior to measurements in soil, the laboratory soil chamber was replaced with a beaker of water, and the open end of the source tube was suspended below the surface of the water. Figure 5 shows a typical sensor response as the concentration of benzene in the beaker is varied. The beaker initially contained pure water. At roughly 560 seconds, a volume of water saturated with benzene was added to the beaker, causing a $+22\pi$ radian phase shift over about 40 seconds as the concentration of benzene in the beaker changed from 0 ppm to approximately 250 ppm. At roughly 950 seconds, the concentration of benzene was diluted by adding a volume of pure water to the beaker. This resulted in a -9π radian phase shift over about 100 seconds. The beaker was continuously stirred throughout this sequence. As would be expected, the reversal upon dilution with pure water is both smaller and slower than the initial response. (The initial addition is a larger change than the subsequent dilution.) Note that the time response in this experiment is dominated by the mixing dynamics in the beaker, not the inherent sensor capabilities.

Figure 6 shows a typical sensor response for experiments using the laboratory test chamber. As previously described, the open end of the source tube was buried several inches below the top of the soil column. The test chamber was then filled with water to a point above the top of the soil column. After several additions of water saturated with benzene and dilutions with pure water, the test chamber conditions were allowed to equilibrate. Paralleling the benchmark beaker-of-water-measurements described above, at roughly 6000 seconds a volume of water saturated with benzene was added through the in-flow ports at the top of the test chamber, causing a $+16\pi$ radian phase shift over about 1000 seconds (15 minutes). At roughly 9000 seconds, the concentration of benzene was diluted by adding a volume of pure water through the in-flow ports at the top of the test chamber and simultaneously draining contaminated water via the out-flow ports at the bottom of the test chamber. This resulted in a -18π radian phase shift over about 300 seconds. A second dilution/draining step was performed at roughly 9500 seconds, resulting in an additional -13π radian phase shift over the next 300 seconds. Absent an understanding of the contaminant transport characteristics of the soil column, the expected time behavior of the subsurface, aqueous-phase benzene concentration is pure speculation. Nevertheless, it is unlikely that the concentration varied much outside the range of 0 ppm to 250 ppm, and it is assumed that the cumulative reversal of nearly twice the initial rise somehow reflects benzene sorbed to the soil prior to 6000 seconds. The time scales to reach equilibrium in the soil column are clearly much slower than for the benchmark beaker-of-water-measurements. As might be expected, however, equilibrium was reached far more quickly when there was flow through the chamber (during the dilution steps).

Although the interpretation of these early soil chamber experiments is problematic, it is clear that—at least for a simplified high groundwater simulation—the sensor is capable of tracking variations in the subsurface, aqueous-phase benzene concentration.

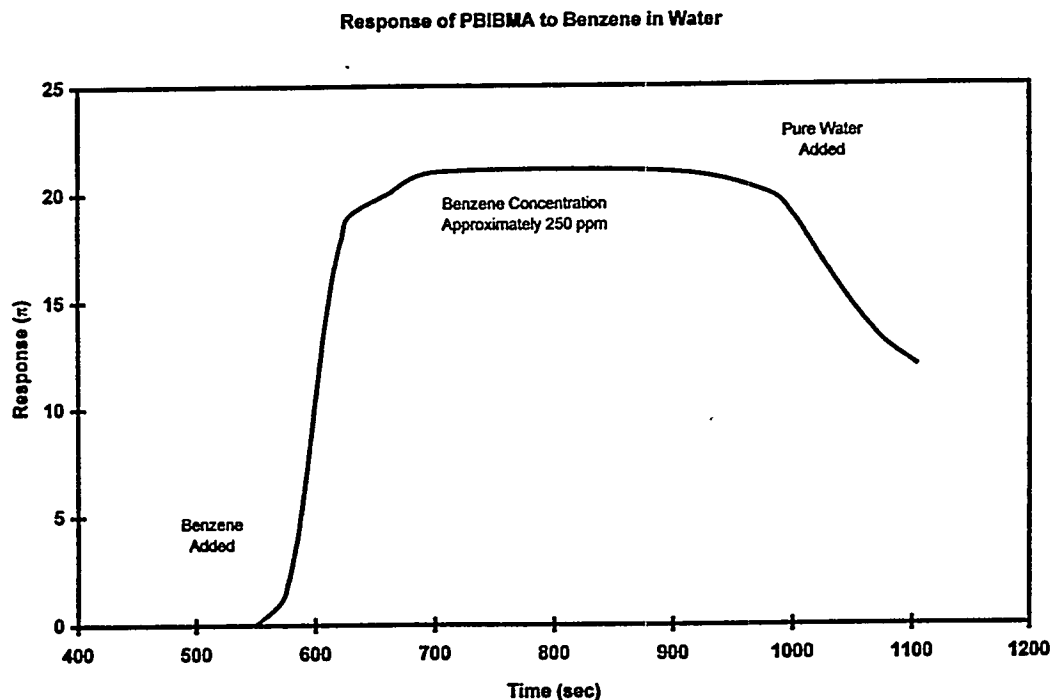


Fig. 5. Typical Sensor Response as a Function of Benzene Concentration in Water.

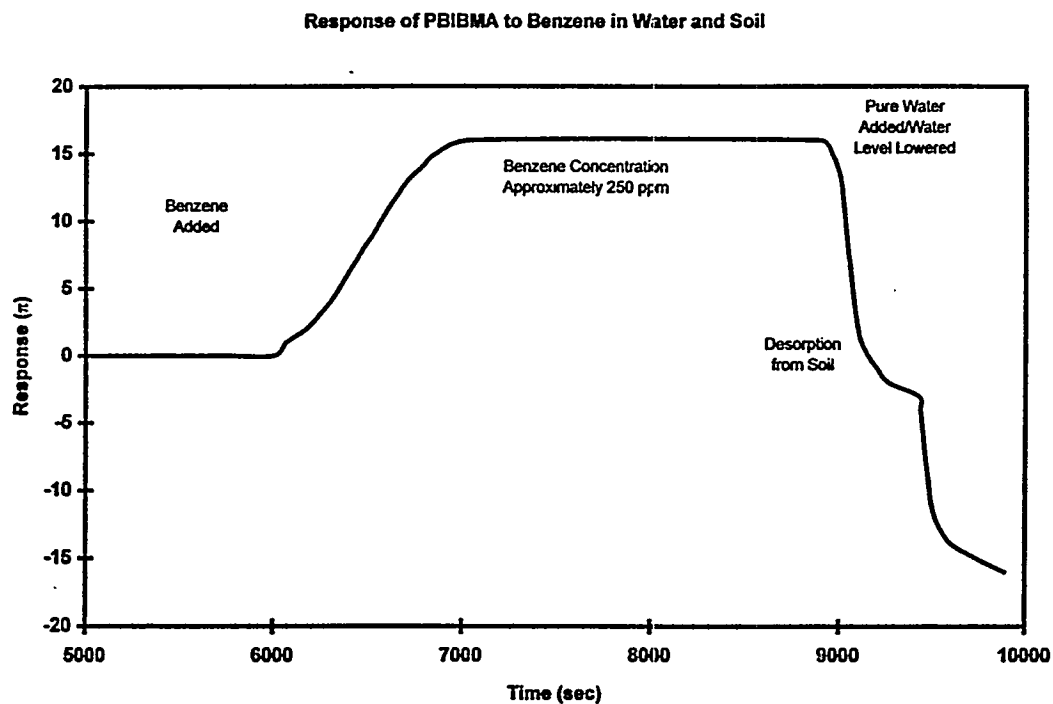


Fig. 6. Typical Sensor Response for Experiments using the Laboratory Test Chamber.

1.2 Sawtek Integrated Modular Array Sensor (IMAS)

Sawtek has informally proposed to GA that Perkin-Elmer be added to the IMAS TRP team as a commercialization partner. GA has furnished Sawtek with a copy of the preliminary E-SMART node specification. Brent Horine of Sawtek has reviewed this document. GA and Sawtek expect to begin developing an E-SMART compatible version of IMAS this Fall

1.3 Other Sensors and Actuators (GA)

Designs for E-SMART-compatible interfaces for off-the-shelf pressure, oxygen, and volatile organic chemical (VOC) sensors were updated. The E-SMART interfaces for these sensors provide signal conditioning and distribute intelligence to each sensor. Fabrication of circuit boards for the interfaces was completed. Procurement of most long-lead parts has also been completed.

Improvements to sensor housing designs were made. Approximately 70 sensor housings made with Delrin® were fabricated this quarter. These housings are suitable for deployment in 2-in. diameter or larger monitoring wells. Five E-SMART sensor modules comprised of sensors, E-SMART interfaces, and Delrin housings were assembled and readied for testing.

Testing of off-the-shelf liquid level/barometric pressure sensors began this quarter, in preparation for the Tinker AFB field test. E-SMART liquid level/barometric pressure sensors utilize media-isolated, micromachined, silicon strain gauge transducers. The liquid level sensors will be required to resolve changes in liquid level equivalent to (or better than) 0.1 in. of H₂O. During extensive evaluation of the response of the silicon transducers, strong thermal dependencies were observed in the pressure output signal. A great deal of effort has gone into characterizing the thermal dependence of the sensor and developing mechanisms for minimizing and correcting for this effect. In addition, the sensor electronics also exhibited thermal dependencies which are being minimized and corrected for. These efforts will likely continue during the early phases of the Tinker AFB field test. As a result, sensor electronics and software will be regularly upgraded during the first 2 to 3 months of the field test.

1.4 E-SMART Network Management (GA)

Development of the E-SMART graphical user interface (GUI) continued. The Windows 95 GUI will allow users to install, configure, and access data from devices on the E-SMART network. Construction of the software objects comprising these GUI screens is continuing.

Incorporation of Echelon Corporation's new object-oriented approach to networking, the *LONWorks Network Services (LNS)* architecture, also continued. Thus far, the *Network Services Server (NSS)* has been successfully implemented, allowing E-SMART nodes to be installed on and to communicate data across the network. Bench-scale testing of the network using prototype E-SMART-compatible pressure sensors were conducted to evaluate network hardware and software, including network connections. These tests will continue throughout development of E-SMART network management.

E-SMART management software provides the ability to talk to nodes and to display data. The development of algorithms for characterizing each individual sensor for influence of temperature, pressure, and other environmental effects was initiated.

The internal structure of the hardware and software required for a device (e.g., sensor or actuator) to be compatible with an E-SMART network was defined and documented in the "E-SMART Node Specification," Preliminary Release, ES-TRP-GA-96-01, issued May 1996. This document has been distributed to team members for review and comment. Some initial team member reviews were received. Portions of the Node Specification have been revised to address team member comments.

1.5 Field Testing

A two-week environmental effects test was successfully completed on the E-SMART sensor module mockup at Tinker AFB in June. A sensor module was immersed for two weeks in a monitoring well to characterize degradation of sensor hardware. Although light fouling was observed after exposure on the Delrin housing and PVC cable coating, all seals and gaskets functioned properly. A mechanical connecting link did rust and will need to be replaced, but no major design changes for sensor hardware are anticipated as a result of the test. Figure 7 shows a field worker holding a sensor module over the well at Tinker AFB prior to the environmental effects test. Figure 8 shows the sensor secured in the well, and Figure 9 shows the sensor module and ballast during removal from the well after the two week immersion. Figure 10 shows details of the prototype E-SMART sensor module to be used in the Tinker AFB field test.

Preparation for the E-SMART field test at Tinker AFB in Oklahoma City, OK continued. The field test is scheduled to begin on August 19th, and run for at least 2 months. The field test schedule is subject to change if support services at Tinker are not in place by middle of August. Procurement of a trailer to serve as headquarters for the site field test was initiated.

GA held discussions with Tinker AFB staff regarding (1) well locations for the field test, (2) data quality objectives, and (3) mobilization requirements. An alternative under discussion is to establish a baseline E-SMART installation at Tinker AFB this summer, and to augment it over time as more E-SMART-compatible devices are ready for testing.

A white paper describing the field test was issued and transmitted to John Mills at Tinker. A copy of the white paper is provided in the Appendix of this quarterly report. The white paper includes the test description and the general plan for the Tinker AFB field test. Additional funding will be sought from Tinker AFB to extend the field test until December 1996 or longer.

1.6 Visualization

Investigation of mapping software extensions compatible with C++ and ArcView™ geographical information system (GIS) for use in E-SMART PC-based GUI was carried out. These extensions may be a lower cost alternative to 3-D visualization for the E-SMART workstation.

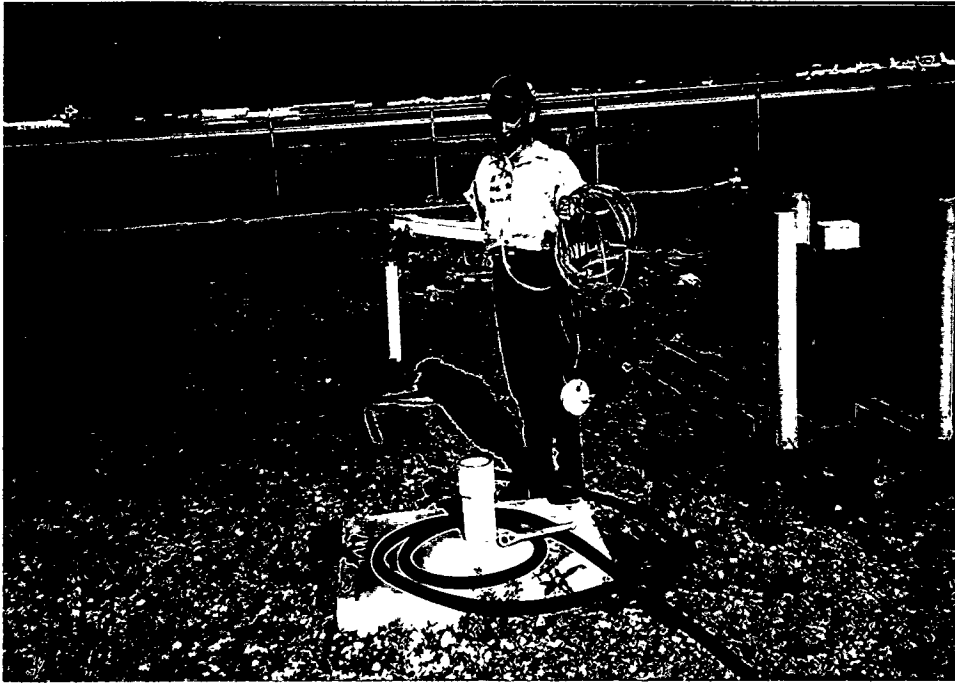


Fig. 7. Worker holding E-SMART Sensor Module and Ballast over Well at Tinker AFB.



Fig. 8. Sealed E-SMART Sensor with Well Cap Secured at Tinker AFB.

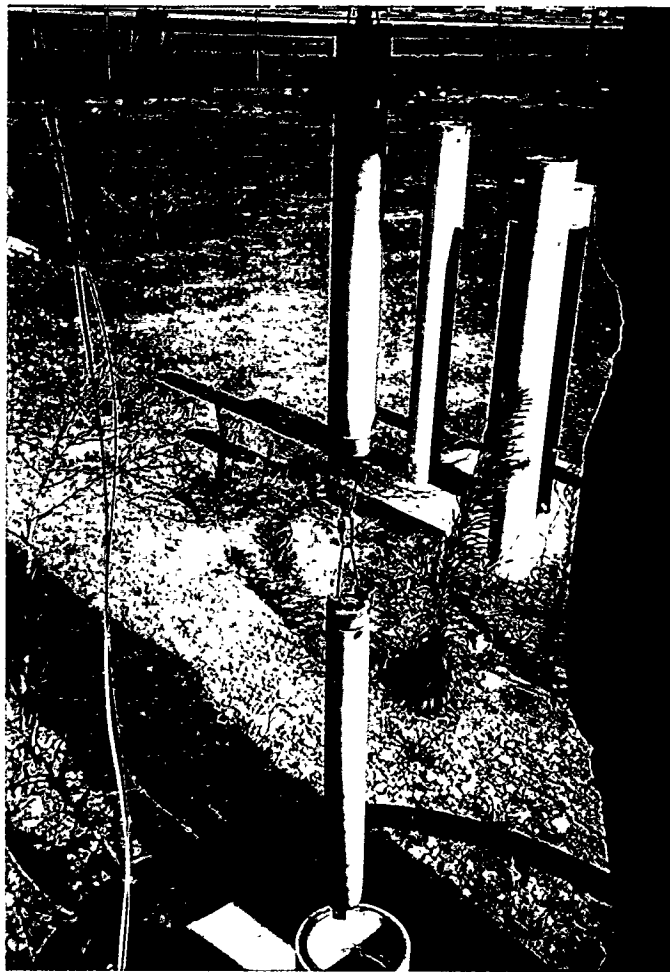


Fig. 9. E-SMART Sensor Module and Ballast after Two-Week Immersion in Well. Some surface fouling is observed.

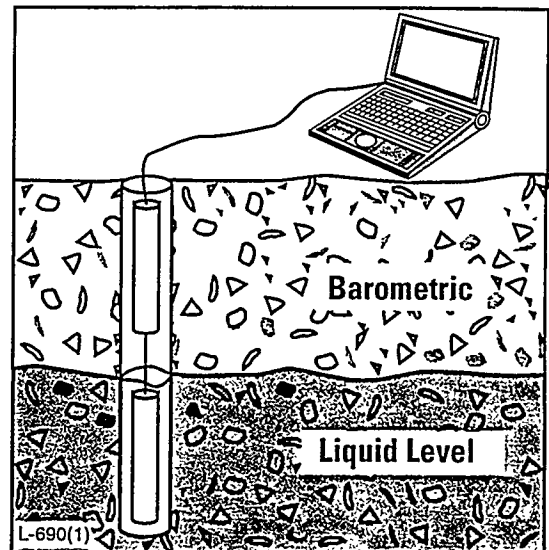
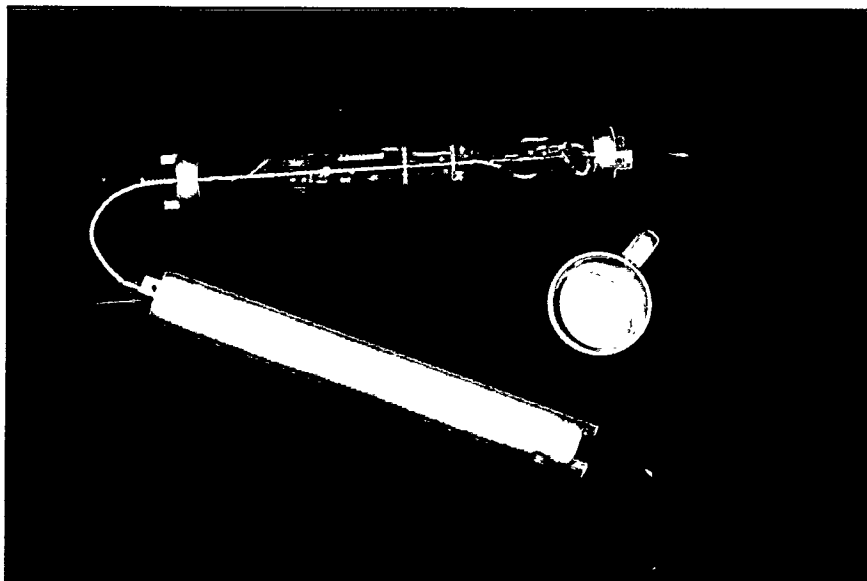


Fig. 10. Prototype E-SMART Sensor Module to be used in Tinker AFB Field Test.

1.7 Program Management

A one-year, no-cost extension to the Isco and PSS/GTRI TRP subcontracts was granted. This extension will produce some restructuring of the Isco and PSS/GTRI scheduled activities. The purpose of the restructuring is to allow these team members to address technical issues related to the development of the multichannel microsensor technology. Scope of work modifications for each team member resulting from the one-year extension are summarized below.

General Atomics

- Develop additional E-Smart-compatible sensors and software(to be performed either by GA and/or new team members.)
- Extend program management for one year.

Isco

- Increase support to PSS/GTRI for development of robust and reliable optics and optoelectronics for the microsensor.
- Defer adaptation of existing Isco samplers, flowmeters, rain gauges, and software to E-SMART networks (This work will be performed (1) after completion of this contract with Isco funds or (2) during the option period of this contract.)

PSS/GTRI

- Increase scope to optimize pattern recognition, improve waveguide quality, and develop improved fabrication techniques.
- Increase coating chemistry development scope for the microsensor. Focus initial chemistry development to target the detection of a single set of analytes (BTEx, VOCs, or metals), followed by additional sets of analytes.

SECOR

- Increase workscope to provide additional field support and environmental requirements support.
- Develop additional E-SMART-compatible software such as a report generator module for the Data Management and Analysis System.

Each member of the E-SMART TRP team has prepared revised cost and schedule projections to accommodate the proposed one-year, no-cost extension. GA has agreed with the subcontractors on the new scope and schedule. DOE-ID has concurred. Modified team member subcontracts should be in effect by early August.

1.8 Dual Use and Commercialization Planning

Interactions with Biode, Inc. were initiated for development of an E-SMART compatible Hg sensor. This is a SBIR project that currently has DOE funding.

GA staff visited the guided missile destroyer Harry W. Hill, which has been designated as the USN West Coast "Smart Ship" to discuss E-SMART applications in the Smart Ship Program. GA staff inspected the control systems and the Damage Control Center.

Briefings were given to Capt. Robert Lowell, USN, and Stan Seigel, DARPA Tactical Technology Office on application of E-SMART systems for the Smart Ship Program.

2. Problems

Schedule changes produced by the one-year extension of the TRP contract were resolved. GA has submitted a formal request for contract amendment to DOE-ID for the proposed project restructuring which was agreed to by DOE-ID. Modifications to team member subcontract are being issued.

3. Plans for the Next Quarter

Optimization of pattern recognition and improvements to waveguide quality and fabrication techniques for microsensors will continue.

Microsensor coating chemistry development will continue, focusing on screening of BTEX-selective coating materials.

Advances in E-SMART network management, data management, and visualization will continue, including continuation of the system upgrades to incorporate the Echelon LNS architecture.

The Tinker AFB field test will begin August 19th. A DOE/DARPA meeting at the field test site will be planned for mid-September.

A meeting will be scheduled in early September with Sawtek and Perkin-Elmer to discuss their TRP project.

The E-SMART Node Specification will be revised and reissued after incorporation of comments from team member reviewers.

4. Milestones and Deliverables

E-SMART System for In-situ Detection of Environmental Contaminants - Quarterly Technical Progress Report, Quarter 1, Calendar Year 1996 - completed and delivered per contract requirements.

Financial Status Report-Standard Form 269A, Reporting Period 1/1/96 - 3/31/96 - completed and delivered per contract requirements.

5. Papers and Conferences

Attended "1996 Spring LonUsers International Conference," sponsored by Echelon Corporation, May 21-22, 1996, Santa Clara, CA. Presented paper "Initial Experiences Building an E-SMART Network Using LNS."

6. Financial Status Report

Per contractual direction, DOE form SF-269A, "Financial Status Report", has been completed by GA for this quarter and has been distributed to the following individuals at DOE-Idaho:

- Patrick Trudel, Program Manager
- Chief Financial Officer, Financial Management Division
- Rebecca Rich, Accounting, Financial Management Division
- Wade Hillebrant, Contract Specialist