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

QUARTERLY TECHNICAL PROGRESS REPORT

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

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Abstract

On this Technology Reinvestment Project (TRP) for the Advanced Research Project Agency (ARPA), General Atomics (GA) leads a team of industrial, academic, and Government organizations to develop the Environmental Systems Management, Analysis and Reporting neTwork (E-SMART). E-SMART is a comprehensive, fully-integrated approach to in-situ, real-time detection and monitoring of environmental contaminants. 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 Environics Directorate at Tyndall AFB(AL).

This ARPA 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 large, commercially viable set of E-SMART-compatible sensors, samplers, and network management components, and
- A user-friendly graphical user interface for data evaluation and visualization.

In addition, the E-SMART TRP team has signed Articles of Collaboration with another ARPA 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.

1. Work Conducted in Quarter 3, CY 1995

1.1 Multichannel Microsensor

Development efforts for the multichannel microsensor during the final quarter of 1996 focused on three sub-elements of the work breakdown structure:

- Develop Microsensor Requirements & Design Configuration -- The main work product in this area was the issuance of the first draft of the Microsensor Requirements Document. This document outlines the functionality, performance specifications, and physical configuration of the E-SMART-compatible microsensor to be developed during this project. A draft of the Microsensor Requirements Document was completed and will be distributed to E-SMART team members for review and comment. It is anticipated that this document will be refined and reissued based on feedback from the E-SMART team.

In addition, a tentative determination was made to develop two separate microsensors, each having identical electromechanical footprints. One microsensor will detect targeted volatile organics (BTEX chemicals, TCE and carbon tetrachloride) via an array of low-specificity polymers and pattern recognition, and the other microsensor will detect targeted metals (cadmium and chromium) using high-specificity complexing agents immobilized in a sol-gel matrix.

- Develop Coatings & Identify Interferants -- An initial screening of polymer coatings to determine their optical properties and their response to a wide range of volatile organic compounds was completed. From these tests, a list of candidate polymers that can be used to recognize and discriminate the BTEX chemicals, TCE and carbon tetrachloride, was developed. A first pass feasibility test for the candidate polymers was conducted by coating an optical chip with a copolymer which the screening tests had shown to be highly responsive to toluene. Soil was then placed in a small (~1 cm³), open cell on the surface of the optical chip, and a drop of water saturated with either toluene or gasoline was added to the soil. In both cases, there was a large, rapid optical response as the solution absorbed into the soil, and a slow reversal of the optical response as the organic compounds volatilized into the surrounding atmosphere. The magnitude of the

reversal was roughly equal to that of the initial response. This test confirmed that toluene can be rapidly and reversibly detected, and that the presence of interferants (i.e., the other gasoline constituents) does not necessarily mask detection. Also during this quarter, experimental work was begun to develop methods for on impregnating complexing agents for cadmium and chromium into thin films to be used on the microsensor. Progress in this area is further detailed in Sections 1.1.1 and 1.1.2 below.

- Build & Test Preliminary Microsensor Model -- A model of the basic integrated optical chip design proposed for the microsensors was completed. The design uses a waveguide on a glass substrate. In- and out-coupling diffraction gratings, reflective elements and beam splitters are incorporated into the waveguide layer and buried under a thick overlayer of silicon dioxide. This design allows compact integration of multiple sensing channels and has the advantage of isolating the optical elements from environmental effects or damage. A four-channel mockup of this design was fabricated and analyzed. Progress in this area is further detailed in Section 1.1.3 below.

1.1.1 Develop Coatings -- BETX/Chlorinated Hydrocarbon Detection

The chemical species selected from the BTEX group as target analytes include benzene, toluene, and xylene while the chlorinated species have been limited to TCE and carbon tetrachloride. Detection and monitoring capabilities depend on detection sensitivity and chemical specificity. The latter represents the most challenging problem because the organic species are small, simple molecules with similar chemical properties. The efforts in this program have focused on realizing useful detection sensitivity levels and evaluating relative sensitivity as a basis for specificity.

Detection of the organic species of interest relies on absorption of target analytes into thin polymer coatings on the waveguide surface. The selected polymer coatings are designed to reversibly absorb the organic species to a greater or lesser extent, depending on the chemical nature of the polymer. The extent to which a particular organic species is absorbed by the coatings of each of the sensing channels and the magnitude of the polymer swelling, in combination with the refractive indices of the analyte molecules and the polymers, defines the magnitude of the index change resulting from the absorption process.

In practice, the effective index change can increase or decrease although the effective index is typically observed to increase as polymer swelling tends to dominate (due to displacement of air with an index on $n = 1.00$ by a polymer with an index of ≥ 1.45). A number of polymeric materials were evaluated as candidate coatings. The screening process compared the relative response of specific polymer coatings and characterized the actual response (signal versus concentration in ppmv) for selected coatings. The screening process not only identified suitable coatings based on detection sensitivity, but also provides the basis for selecting a combination of coatings (i.e. sensing channels) to provide enhanced specificity.

Vapor phase measurements were utilized since this approach offers the greatest flexibility where both soil and aqueous phase environments will be encountered. In the case of soils, the sensor can only detect the presence of trace vapors not bound to the soil particulates. In the case of aqueous environments, the relative solubility difference between water (very low) and the selective polymer layer (relatively high) limits the reversibility of the process. In practice, the dissolved organic species can come out of water and be absorbed by the selective polymer. The reverse process, however, is extremely slow or non-existent at low concentrations. For measurements in the aqueous phase, a separation membrane, a hydrophobic filter, is currently required. The separation membrane also provides other advantages as it serves to protect the waveguide sensing surface from mechanical abrasion and contamination.

1.1.1.1 Waveguide Sensor/Coating Response. For the test measurements, air saturated with the organic species of interest was mixed with flowing nitrogen to dilute the flow impinging on the polymer coated waveguide surface. The phase change was then detected and the relative response determined based on the known vapor pressures for the organic species of interest. The waveguide used for these experiments was a fused silica (SiO_2) substrate overcoated with a 110 nanometer (nm) silicon nitride (Si_3N_4) waveguide film and a 40 nm fused silica film. The 40 nm fused silica layer only serves to provide different chemistries for attaching chemically active films to the waveguide surface.

The relative response of various polymer films to different organic species (in the vapor phase) is illustrated in Table I. The results are normalized to take into account the

differing vapor pressures to permit a direct comparison of the relative sensitivities of the polymer films to a common species and the relative sensitivity to different species.

The larger numbers in Table I indicate higher sensitivity for the species tested. In particular Teflon AF (DuPont product and Trademark) exhibits good sensitivity to Toluene and Xylene. Conversely, poly(BIBMA) exhibits much better sensitivity to Xylene than to Toluene. Thus, while Teflon AF is an excellent candidate for sensitive detection of Toluene and Xylene, the addition of a second channel using poly(BIBMA) would provide a mechanism for discrimination between the two species.

TABLE I
RELATIVE SENSITIVITY OF POLYMER FILMS

^a Polymer Film Vapor Phase Species	Phase Shift (radians) ^d			
	Poly(vinyl acetate)	Poly(BIBMA) ^b	Poly(SBMA) ^c	Teflon AF
Toluene	2.0	2.5	1.0	6.0
Xylenes	4.5	6.1	1.25	6.25
Acetone	1.0	0.25	0.1	3.0
Methanol	3.0	0.3	<0.1	1.5
Water/Air	1.25	1.0	<0.5	<0.5
Methylene Chloride	3.5	0.25	0.2	1.25
Chloroform	2.5	0.5	0.7	7.5
Carbon Tetrachloride	2.0	0.5	0.35	2.0

a. Saturated vapor diluted into steam of nitrogen

b. poly(butyl-isobutyl methacrylate)

c. poly(styrene)-poly(butyl methacrylate) copolymer ([thick film])

d. normalized to 100 mm Hg vapor pressure of injected vapor

The results reported in Table I do not represent the optimum performance for this combination. In particular, the sensing polymer film thickness was kept very thin,

approximately 100 nm, and the total sensing pathlength was only 1.8 cm. With increasing pathlength, the sensitivity would increase linearly. Increasing the polymer film thickness offers the potential for significant increase in sensitivity.

1.1.1.2 Sensor Response in Soil Samples. To test the sensor response using a separation membrane, the configuration illustrated in Figure 1 was used. The waveguide was identical to that described previously while the polymer film used was poly(SBMA) described in Table I. For test purposes, the soil sample was contaminated with small sample volumes toluene. The response of the sensor was recorded as function of time. The time dependent response is strictly defined by the diffusion of the specimen through the thickness of the soil layer which was 1 cm. The specimen, having a volume of approximately 1 microliter, was placed directly on the top surface of the soil for these test. A response typical of that presented in Figure 2 was observed indicating the presence of toluene. Note the detected signal is extremely large in comparison with the minimum detectable signal of 0.01 radians. The slow recovery time (full recovery required 30 minutes) occurs because the test species as released from the selective polymer film was entrapped.

Figure 1. Laboratory test bed for soil testing.

Figure 2. Sensor response to the introduction of toluene into soil samples.

1.1.1.3 Waveguide Surface Protection. Because the waveguide surface is sensitive to mechanical abrasion and its throughput can be attenuated by opaque residue deposited directly on the waveguide surface, the sensing surface must be protected. As noted previously, a separation membrane has been used as a means of overcoming the lack of reversible absorption observed in an aqueous media. The membrane offers further advantage in that it aids in the protection of the surface. To further enhance protection, the entire waveguide surface was fluorinated. The latter creates a hydrophobic surface which tends to reduce binding of residue to the waveguide surface.

1.1.2 Develop Coatings--Metal Ion Detection

The strategy for detecting chromium (III) and cadmium (II) in solution with the waveguide interferometer is basically the same for both ions. A complexing agent for the metal ion can be confined at the waveguide surface; a phase change would result when the ligand complexes with the metal ion. The complexing agent can be covalently bound to the waveguide surface using silylating chemistry and a derivatized complexing agent; however, this requires synthesis of the ligands to react with the silylating agent. Also, the resulting monolayer of complexing chemistry formed this way might limit the dynamic range and sensitivity of the interferometer for these ions. We feel that a thicker sensing layer will give us more sensing capability by using a three dimensional sensing volume versus a two dimensional monolayer. To achieve this, we are pursuing the incorporation of the sensing moiety into a relatively thick layer (hundreds to thousands of angstroms) that would allow passage of these ions into and out of the layer. The complexing agent may either be

trapped physically in the layer or covalently bound in the matrix. Initially we are planning to use a sol-gel of an organically derivatized silicon dioxide as the matrix to contain the complexing agent. The sol-gel solution is created by acid hydrolysis of a methyl-triethoxysilane/ ethanol solution and can either be spin-coated or dip-coated onto the waveguide to form the sensing layer. Initial results show that dip-coating gives a superior coating. Dip-coating with this sol-gel solution onto BK-7 ion exchange waveguide yielded a fairly uniform film approximately 3000 Å with minimal effort. Light easily propagates under this film with little loss over 1.5 cm of travel.

Recent efforts have been directed to mixing the complexing agent with the sol-gel solution before dipping. After dip-coating and drying, the complexing agent will be physically entrained in the sol-gel layer. If we find that the complexing ligand leaches out of the matrix in aqueous solution, it will be covalently linked to the sol-gel matrix, or the leaching can be prevented by modifying the ligand so that the ligand could be rendered less water-soluble by attaching a long hydrocarbon tail.

We are also considering incorporating functional silanes into the sol-gel, adding the metal ion we seek to detect to the sol-gel solution, then applying the entire mixture to the waveguide surface. Upon dip-coating and drying, the functional ligands on the silane could complex to the metal ions and form sites in the matrix approximately the size and orbital configuration of the metal ion. Then the metal ion is removed either by leaching it out or by a redox reaction. A sensing film ideally suited for a particular metal ion would result.

1.1.3 Waveguide/Sensor Head Development

To demonstrate the integrated optic (IO) interferometric sensing configuration, a four channel IO interferometer has been designed for testing purposes. The IO sensor relies on single mode waveguide operation. The advantage of this design focuses on the ability further subdivide each IO channel into additional sensing channels with only minor variations in the fabrication process. It is anticipated that the current channel width of 500 micrometers can be subdivided into five 100 micrometer channels and possibly ten 50 micrometer channels making available a total of either 20 or 40 sensing channels with the current design. The degree of subdivision will depend on the quality of the waveguides and the beam splitting and or combining elements.

Operation of a fully integrated four channel interferometer device has been demonstrated using a lab bench setup. The results, however, demonstrate the waveguide quality must be improved. Phase errors and noise were observed due to scattering within the waveguide and also due to roughness associated with the faces of the reactively ion etched (RIE) total internal reflection (TIR) mirror and beam splitter elements. These results were observed on silicon nitride (Si_3N_4) waveguides deposited on both fused silica and BK-7 glass. The columnar growth of the Si_3N_4 introduces a granular structure to the waveguide film causing scattering of a guided wave and contributing to roughness of the RIE etched faces on the thin film elements. The latter represents a serious source of signal attenuation and phase errors or noise. To overcome these difficulties, a low pressure chemical vapor deposition (LPCVD) system has been purchased by GTRI through equipment funding completely independent of this ARPA TRP program. LPCVD has been shown to be capable of producing waveguide films with properties that are at least an order of magnitude better than the plasma enhanced chemical vapor deposition system (PECVD) currently being utilized. It is expected this system will fully operational around the May or June time frame.

In addition to alternate Si_3N_4 waveguide films, different waveguide material systems may be utilized. The evaluation of a fully integrated design has shown a dramatic improvement in the signal-to-noise ratio. Thus, waveguide material systems may be utilized that offer lower sensitivity with the signal loss reclaimed by amplification of the low noise signal. This approach is also being investigated concurrently using ion-exchange waveguides. The experimental results from these concurrent approaches will be compared to evaluate overall sensitivity.

1.2 Sawtek Integrated Modular Array Sensor (IMAS)

General Atomics met with members of the IMAS TRP team at the Sawtek headquarters in Orlando, Florida, twice during this quarter. The first meeting was held on November 21 and focused on the IMAS architecture, system specification, and commercialization plan, including the requirements for E-SMART compatibility. The second meeting, held December 11, was the formal kick-off for the IMAS project. It was attended by Sawtek TRP members, General Atomics, and representatives from ARPA and DOE.

1.3 Other Sensors and Actuators

An evaluation of commercially available chemical electrode sensors and their applicability to E-SMART networking was conducted. This evaluation applied to pH, ion-selective, and redox (ORP) electrodes.

After initial review of the electrode sensors currently available, a preliminary specification was prepared which outlined the electronics and signal conditioning necessary to make these sensors E-SMART-compatible. This specification was followed by a list of the key technical challenges requiring additional evaluation prior to sensor development.

1.4 E-SMART Network Management

Several upgrades and improvements were made to the E-SMART network management system. The graphical user interface (GUI), which had previously been developed with Microsoft's Visual Basic software running on Windows 3.1, will now be upgraded using Visual C++ running in Windows 95. This change will allow for a more streamlined approach to GUI development, increasing the speed, performance, and reliability of the system. These software packages were procured and installed on E-SMART computers, and GUI upgrade was begun.

In addition, Echelon Corporation has released a new object-oriented approach to networking with LONWorks referred to as the *LONWorks Network Services (LNS)* architecture. The LNS is a comprehensive set of hardware and software improvements that will enhance the functionality of the E-SMART network management system. General Atomics is participating with Echelon in adopting this architecture via Echelon's *LNS Early Access Program*. The initial components of the LNS have been received and installed, and will be evaluated and integrated into the E-SMART architecture as new components are released by Echelon during the upcoming year. The approach to E-SMART networking outlined in the E-SMART standard is being revised to incorporate this change in system architecture. A preliminary object-oriented standard for E-SMART devices (sensors, actuators, and controllers) is under development and will be completed in the first quarter of 1996.

1.5 Field Testing

No field test activities were conducted during this quarter.

1.6 Visualization

An evaluation copy of *Sammi*, a graphical user interface (GUI) development program, was obtained from Kinesix, a division of Scientific Software. This evaluation will be targeted at determining whether Sammi is well suited to generating GUI's for the E-SMART application modules to be housed in the E-SMART workstation platform.

Test cases of three-dimensional grid files were created with earthVision™, the subsurface visualization software chosen for the E-SMART workstation, to determine the ease of grid file export for use in subsequent analysis by predictive fate & transport analytical models. These files were found to be easily written into formats consistent with the most commonly used software packages.

1.7 Program Management

A formal E-SMART TRP Kick-Off meeting was held in San Diego, CA, on October 18th. The meeting was attended by representatives from the E-SMART TRP team, ARPA, DOE EM-50, and DOE/Idaho. The purpose of the meeting was to discuss the status of the project and plans for future development, including issues relating to subcontracting and schedule. A primary issue was a request from Isco, Inc., to delay their participation in the E-SMART TRP project pending the successful completion of a separate Isco/PSS/GTRI project which uses a technology related to the microsensor under development in this E-SMART TRP. This delay may require a one-year, no-cost extension to the TRP contract, or it may result in a restructuring of Isco's schedule and scope-of-work. These issues were discussed at length at the E-SMART TRP Kick-Off meeting, and were also subsequently discussed with ARPA and DOE representatives to explore the options for contract extension.

Based upon these discussions, subcontract negotiations with Isco were completed and their subcontract was signed on November 28th. The remaining commercial team member, SECOR, signed their subcontract on November 8th, thereby completing the formal subcontracting to the commercial members of the E-SMART TRP team.

1.8 Dual Use and Commercialization Planning

General Atomics represented the E-SMART TRP project at the ARPA Dual Use Conference in Washington DC on October 12-13, 1995. For this conference, General Atomics prepared a display booth and literature which summarized the E-SMART TRP goals, team, and technical status.

2. Problems Encountered

Isco has requested schedule changes, including a possible no-cost extension to the TRP contract, to provide more time to assess the results of an independently funded, ongoing effort with PSS and GTRI to implement a sensor utilizing the Hartman Interferometer technology which underlies the proposed multichannel microsensor. In addition to possible schedule changes, Isco may also choose to restructure the scope of their efforts on this project. These issues are expected to be resolved in the first quarter of next year, when Isco will have sufficient technical information to clearly define their extent of TRP participation.

3. Plans for Quarter 1, CY 1996

During the next quarter, we plan to continue the efforts to improve the four channel sensor performance. The investigation of selective polymer coatings will continue with emphasis on testing a variety of the coatings developed for surface acoustic wave (SAW) devices. Also during the next quarter we will look into complexing agents for the cadmium (II) and chromium (III) ion and incorporate these into the sol-gel system. More work will be done to maximize the uniformity of the sol-gel layer by mechanizing the dip process so that withdrawal of the waveguide is at a controlled rate. In addition, we hope to investigate the idea of metal ion imprinting of the sol-gel matrix using commercially available silane reagents

with complexing capabilities for chromium or cadmium ions. Approaches to incorporating an integral permeable membrane, a membrane in the form of a thick film attached to the waveguide surface, will also be investigated. Advances in E-SMART network management, data management, and visualization will continue, including continuing the upgrade to the Echelon LNS architecture.

4. Milestones and Deliverables

- *E-SMART System for In-situ Detection of Environmental Contaminants - Quarterly Technical Progress Report, Quarter 3, Calendar Year 1995* - completed and delivered per contract requirements.
- *Financial Status Report-Standard Form 269A, Reporting Period 7/1/95 - 9/30/95* - completed and delivered per contract requirements.

5. Papers and Conferences

Nielsen, Bruce (AL/EQW-OL), and Steve Leffler and Denise Osborne (General Atomics), "*Environmental Systems Management, Analysis, and Reporting Network (E-SMARTTM) - A Defense/Industry Technology Partnership*," presented at the NASA Technology 2005 Conference & Exposition, Chicago, IL, October 24, 1995.

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