GE/Nomadics In-Well Monitoring System for Vertical Profiling of DNAPL
Contaminants

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Principal Author(s):

Ronald E. Shaffer, Radislav Potyrailo, Joseph Salvo, Timothy Sivavec,
Lloyd Salsman

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Submitted by:
GE Global Research Center
PO Box 8
Schenectady, NY 12301

Program Manager: Joseph J. Salvo
Phone Number: 518-387-6123
FAX Number: 518-387-7611

Principal Investigator: Ronald E. Shaffer
Phone Number: 518-387-4344
518-387-7611

Submitted To:

U.S. Department of Energy
National Energy Technology Laboratory
COR: Vijay Kothari

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ABSTRACT

This report describes the Phase I effort to develop an **Automated In Well Monitoring System (AIMS)** for *in situ* detection of chlorinated volatile organic compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE) in groundwater. AIMS is composed of 3 primary components: (a) sensor probe, (b) instrument delivery system, and (c) communication/recharging station. The sensor probe utilizes an array of thickness shear mode (TSM) sensors coated with chemically-sensitive polymer films provides a low-cost, highly sensitive microsensor platform for detection and quantification. The instrument delivery system is used to position the sensor probe in 2 inch or larger groundwater monitoring wells. A communication/recharging station provides wireless battery recharging and communication to enable a fully automated system. A calibration curve for TCE in water was built using data collected in the laboratory. The detection limit of the sensor probe was 6.7 ppb ($\mu\text{g/L}$) for TCE in water. A preliminary field test was conducted at a GE remediation location and a pilot field test was performed at the DOE Savannah River Site (SRS). The AIMS system was demonstrated in an uncontaminated (i.e., "clean") 2-inch well and in a 4-inch well containing 163.5 ppb of TCE. Repeat measurements at the two wells indicated excellent day-to-day reproducibility. Significant differences in the sensor responses were noted between the two types of wells but they did not closely match the laboratory calibration data. The robustness of the system presented numerous challenges for field work and limited the scope of the SRS pilot field test. However, the unique combination of trace detection (detection limits near the MCL, minimum concentration level) and size (operations in 2-inch or larger groundwater wells) is demonstration of the promise of this technology for long-term monitoring (LTM) applications or rapid site characterization. Using the lessons learned from the pilot field test, a number of design changes are proposed to increase the robustness of the system for extended field studies and commercialization.

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INTRODUCTION

Overview

This project addresses the problem of *in situ* detection of chlorinated hydrocarbons, such as trichloroethylene (TCE) and tetrachloroethylene (PCE), in difficult to access subsurface environments. GE Global Research and Nomadics, Inc. collaborated together to develop an in well monitoring system to provide a novel, cost-effective method for vertical and horizontal mapping of contaminant plumes in the vadose and saturated zones. The monitoring system takes advantage of low-cost chemical sensor array technology developed by GE for long-term monitoring and rapid characterization of environmental contaminants in groundwater wells.

This project was initiated in October 2001 and was designed for two phases. Phase I consists of project planning, test site selection, advanced engineering design work necessary to modify and integrate existing sensor technologies at GE and Nomadics, and a pilot field test at a selected DOE site. Phase II is optional and consists of activities leading to, and execution of, a large-scale demonstration at a selected DOE site.

The project has several overall objectives:

- Adapt GE's sensor array technology to meet DOE needs (Phase I)
- Integrate the sensor probe into an in-well monitoring system (Phase I)
- Demonstrate system capabilities during a pilot field test (Phase I)
- Perform a full-scale demonstration of the technology (optional Phase II)
- Develop a commercialization plan for the AIMS technology (optional Phase II)

The Phase I final report will discuss potential applications of the technology, describe the development of the primary subsystems of the in well monitoring system, describe laboratory testing of the sensor probe, and provide results from a pilot field study of the **Automated In Well Monitoring System (AIMS)** conducted at the DOE Savannah River Site.

Applications

At the end of the Phase II portion of the project, a commercial unit will have been developed that meets the needs of both DOE and industry end-users. The versatility of the AIMS technology will enable it to fulfill a number of DOE site technology need statements. The current baseline technology used across the DOE complex for characterization of chlorinated solvents in groundwater and soil gas is off-site laboratory analysis. The AIMS technology will provide on-site, in

situ, discrete sampling capability at lower cost, reduced operator risk, and faster turn-around time than the baseline method. To support site closure needs, this project has great potential to fulfill a number of unmet DOE needs for long-term monitoring [1]. Replacing off-site analysis with an in situ monitoring system such as AIMS will provide a step-change impact on EM cleanup schedule and cost. Table 1 contains a partial list of site-specific technology needs that the AIMS technology could potentially support.

Table 1. Representative DOE Site Technology Need Statements Requiring Long-term Monitoring or Rapid Characterization of Chlorinated Volatile Organic Compounds

Long Term Monitoring		Rapid Characterization	
Code	Need Title	Code	Need Title
AL-09-02-01	Long-term Site Monitoring System	ID-6.1.02	Real-time Field Instrumentation for Characterization and Monitoring Soils and Groundwater
OK01-31	Technology for In-Situ Long-Term Monitoring of Volatile Organic Compounds	ID-6.1.37	Real-Time Detection of Contaminant Using In-Situ Sensors
OK01-27	Long-Term Ground Water Monitoring	ID-S.1.04	Real-Time Field Instrumentation for Characterization and Monitoring Soils and Groundwater
CH-SS04-99	Long-Term Ground Water Monitoring	OK99-01	Characterization and Removal of DNAPLs and LNAPLs from Soil and Ground Water
ORHY-21	Real-time Performance Monitoring	RL-SS03	Improved, Real-Time Detection of Carbon Tetrachloride in Groundwater
SR00-3027	Long-term Monitoring Technologies	SR01-3031	Non-Invasive Characterization and Treatment Technologies for DNAPL
SR01-3029	Long-term Monitoring Technologies	RL-SS37-S	Monitoring of Contaminants - Chemical Sensor Principals

Note: Site Technology Need Statements taken from the Long-Term Monitoring Workshop Report [Appendix E and F].

The DOE Savannah River Site (SRS) was chosen as the Phase I demonstration facility. Like a number of DOE and industrial remediation sites, SRS has numerous ground water monitoring wells requiring quarterly sampling and off-site laboratory analysis. According to the SRS site need statements SR00-3027, SR01-3029, and SR02-3029, long-term monitoring (LTM) of closed waste units will have significant future costs due to regulatory requirements for extended compliance monitoring. Using baseline technology, LTM will require expensive and time consuming field sampling and laboratory analysis. It was also noted that establishment of *in situ* remote monitoring methods will enable data to be collected more often and at substantial cost savings. In addition, SR00-3021 describes the need for alternative sample collection and well installation technology that eliminates or significantly reduces aqueous or non-aqueous investigative derived waste (IDW). It was noted that the ground water sampling program at SRS involves about 10,000 samples per year and that IDW management is a major task for the site.

One of the most prevalent classes of contaminants present in the ground water at SRS is dissolved volatile organic compounds (VOC). For a number of years, the waste handling practices at SRS often consisted of disposing of waste organic solvents directly into unlined pits and trenches, which resulted in extensive subsurface groundwater contamination. The two primary contaminants of concern are trichloroethylene (TCE) and tetrachloroethylene (PCE), which range in concentration across the site from a few ppb ($\mu\text{g/L}$) to the lower ppm (mg/L). Dissolved-phase DNAPLs such as TCE and PCE are also commonly encountered at DOD, NASA, and many of the nation's environmental superfund sites.

The need for LTM is becoming increasingly important because of the trend towards acceptance of monitored natural attenuation (MNA). MNA applies passive or natural remediation processes to an existing chlorinated VOC plume. The reductive dehalogenation process of chlorinated ethenes results in the breakdown of PCE and TCE into daughter products such as Cis 1,2, dichloroethylene (DCE) and vinyl chloride (VC). In a typical application, LTM is required for a minimum of 5 years, but is more likely to occur for 30 years or longer. A typical LTM program for MNA would be very expensive to operate using the baseline field sampling and off-site laboratory analysis. Traditional LTM techniques require semi-annual or quarterly sampling. The average cost for sampling and analysis has been estimated as approximately \$3000 per sample for a comprehensive suite of constituents (SR02-3029). Even for a smaller subset of analytes the analysis can run as much as \$500 per sample [1]. SRS has \$365M allocated for the 30-year LTM life-cycle. This cost can be significantly reduced using an *in situ* measurement system such as the one described in this report.

Chemical Sensor Technology

The development of a sensor platform for LTM or rapid site characterization is a challenging task. The baseline method for characterization of groundwater and vadose zone samples involves sample collection and off-site laboratory analysis. Sample collection can be performed by pumping the sample to the surface or lowering a sample collection system such as the Kabis™ sampler, or using a passive diffusion sampler bag. Laboratory analysis is conducted using gas chromatography with mass spectrometry (GC-MS) detection. The primary reason that *in situ* sensors are needed for this application is to reduce the overall cost burden sampling and off-site laboratory analysis. Ideally, a site manager could install a low-cost sensor system in each well and retrieve contaminant profiles instantaneously without collecting a sample.

The key requirements and desirable features for this application are summarized in Table 2. The first column in this table lists the specific requirements. The second column is a specification or further clarification of the requirement. The third column indicates how the baseline method fares against this requirement.

As shown in this table, the key problems associated with the baseline method are the high cost of analysis, turn-around-time, and generation of waste. The fourth column contains comments that allow us to group the individual requirements into different categories.

Certainly the most important requirement is cost. Regardless of how well a technology performs on the other 13 items, if the cost is not significantly reduced very few site managers will bear the risk of using a new technology. Requirements noted as differentiators indicate that the AIMS system has the potential to meet this requirement, while competitive *in situ* sensor technologies under development cannot. Other requirements are listed as a common advantage of *in situ* sensors. This means that the probe used in the AIMS product will have similar capabilities to other *in situ* technologies under development. Basic need requirements are those that are consistent across technologies. In other words, regardless of whether it is a sensor or an off-site analytical method it must be accurate and be able to perform quantitative analysis across several orders of magnitude. Other requirements are site specific and may change depending upon the customer (e.g., industrial site, DOE Savannah River, DOE Hanford).

There are no commercially available sensor systems (*ex situ* or *in situ*) available today to meet all of the requirements for LTM or rapid site characterization as described in the technology needs statements (Table 1). Numerous organizations within the DOE, EPA, and DOD have supported research and development towards alternative monitoring technologies for carbon tetrachloride, TCE, and chloroform in groundwater and the vadose zone.

Ho and coworkers at Sandia National Laboratory wrote a comprehensive review in 2001 describing the current technologies either commercialized or under development [2]. In this review, they broke down the types of sensors into four categories: optical, mass, electrochemical, and chromatography/spectroscopy. They concluded that electrochemical sensors offer the most potential because of their simplicity and robustness. They also noted fiber-optic and mass sensors (in particular acoustic wave devices) have many desirable characteristics for VOC analysis.

Since 1998, researchers at GE Global Research have been working on novel sensing technologies for environmental applications [3-5]. From the list of sensor modalities studied by the team, acoustic wave chemical sensors appeared to have the highest potential to provide the lowest detection limits for real-time measurements at low cost and in a portable configuration. When deployed in the headspace above water, acoustic wave sensors are capable of in-situ detection of organic solvents in groundwater at micrograms/L or parts-per-billion (ppb) levels. Detection of volatiles in the headspace provides several important advantages over a direct detection of these species in water. A crude separation of volatile organics can be easily achieved based on Henry's law. Also, surface

contamination, etching, and corrosion of the sensor by certain chemicals in water are greatly reduced, and sensor performance is not affected by variations in pH, ionic strength, viscosity, or density of water.

The majority of the work done by the team has focused on 10 MHz thickness shear mode (TSM) crystals coated with a sorbent polymer film. These TSM devices are sometimes referred to as quartz crystal microbalances (QCM). The TSM sensors are mass sensitive devices. The polymer film acts as reversible sponge. As analyte vapors sorb into the polymer film the frequency of the TSM changes proportional to analyte concentration. The key innovation made by GE was discovery of a family of polymeric materials with high sensitivity toward chlorinated solvents and their daughter products. A calibration curve for one of the GE coatings is shown in Figure 1. For this coating, a detection limit of 54 parts-per-trillion for TCE in water and 4 parts-per-billion for vapor-phase TCE was found. The detection limit for TCE in water is calculated using Henry's law to concentrate the vapors in the headspace. For simplicity, the acronym ppbw is often used to signify part per billion in the aqueous phase (water). In addition to being highly sensitive, the sensor array can be used to differentiate among potential co-contaminants. Development of a series of laboratory and field prototypes demonstrated operation in the field, the capabilities for down-hole well monitoring, and the benefits of wireless data acquisition. These innovations form the basis of the AIMS sensor probe described in the report.

Figure 1. Univariate calibration curve for TCE using a 10 MHz TSM sensor coated with GE proprietary polymeric coating (Siltem). A vapor phase detection limit of 4ppb is shown and using Henry's law is estimated to be 54 ppt in water.

Table 2. In Situ Chemical Sensor Requirements for Long-term Monitoring and Rapid Site Characterization of Chlorinated Volatile Organic Compounds

Requirement	Description	Baseline Method	Comments
Cost	Must be step change (50% improvement)	\$500/sample	Cost drives end-user acceptance of new technology
Detection Limit	Quantify target analyte at MCL	Yes	Differentiator. Sensors with LOD above MCL of limited use
Speciation	Ability to quantify target analyte (51%) in presence of co-contaminants	Yes	Differentiator. Sensors with interference problems of limited value
Size	Capable of sampling a 2 inch well	Yes	Differentiator. Maximizes the number of wells that can be sampled
Turn-around-time	< 48 hours	2-14 days	Common advantage of <i>in situ</i> sensors
Minimize waste	No contaminants brought to surface	No	Common advantage of <i>in situ</i> sensors
Easy to use	Can be operated by field personnel with minimal training	Yes	Common advantage of <i>in situ</i> sensors
Sampling depth	0-110 m	Yes	Maximum sampling depth is site specific
Accuracy	Quantify +/- 20%	Yes	Basic need
Calibration range	MCL to 10 ppm for target analyte	Yes	Basic need
Reliable	Minimal down-time (2 year, stand-alone operating, including maintenance)	N/A	Basic need
Versatile	Detection of multiple chlorinated solvents in groundwater or vadose zone	Yes	Differentiator. Sensors that are specific will have limited access across sites
Spatial mapping	Capable of measurements at multiple depths at discrete points on scale of cm	No	Not required at every site

The two sensor technologies that are most similar to the type of sensor probe described in this project are the portable acoustic wave sensor (PAWS) and the chemiresistor microsensors. PAWS was developed at Sandia National Laboratory during the 1990's, while the chemiresistor microsensor is currently in development at Sandia. Without preconcentration, both methods are able to detect VOCs in the parts-per-million (mg/L) concentration range. PAWS consists of one or more surface acoustic wave (SAW) devices utilizing sorbent coatings to detect chlorinated hydrocarbons and other volatile organic compounds. PAWS was demonstrated at the DOE Savannah River Site for both above-ground and down-hole applications [6]. For *in situ* measurements in the vadose zone, a fully integrated probe was cable of operation inside 4-inch wells. Detection limits were 1-10 ppm, but this system was not capable of speciation since it only contained a single polymer-coated surface acoustic wave (SAW) device. The versatility of the PAWS system was also limited because it was unable to operate under water.

The chemiresistor technology currently under development by Cliff Ho and coworkers at Sandia National Laboratory is based on an array of polymer films containing conductive particles [7]. Vapor absorption causes reversible polymer swelling, changing the electrical resistance. The advantage of the chemiresistor technology is that it is extremely small (< 3cm diameter), has minimal power requirements, and can provide discrimination among common VOCs using multivariate pattern recognition software. A Gore-Tex ® membrane is used to protect the sensor from water and allows it to operate in either vapor or aqueous phase. The detection limit for aqueous phase TCE is approximately 1-10 ppm using Henry's law. The deepest the sensor has been tested is 60 feet below water.

The PAWS and the chemiresistor sensors share several similarities with the GE acoustic wave sensors. PAWS and the GE sensors are both mass sensitive devices utilizing polymer films, while the chemiresistor and the GE systems use a protective membrane to generate a headspace to allow aqueous measurements. Taking in account the vast improvements in the miniaturization of electronics and the sensitivity of the GE coatings, one can envision a sensor probe that can meet many of the requirements outlined in Table 2. One of the objectives of this project was to develop a prototype sensor probe that takes advantage of the lessons learned from the two Sandia prototypes and incorporates GE proprietary coatings to enable the smallest, most sensitive sensor probe tested to date.

EXPERIMENTAL

This section describes the overall concept of AIMS and the experiment work that led to the development of the prototype system.

AIMS Operational Concept

To meet the requirements listed in Table 2, a systems approach is necessary. The GE/Nomadics **A**utomated **I**n well **M**onitoring **S**ystem (AIMS) described in this report consists of 3 primary components: (a) sensor probe, (b) instrument delivery system, and (c) communication/recharging station. An overview of the operation of the system is shown in Figure 2. Using the instrument delivery system, the sensor probe is positioned to predetermined depths below the water table inside an existing groundwater monitoring well (2 inch diameter or larger). In Phase I testing, the sensor probe was positioned near the mid-point of the screened interval of the monitoring well. The distal end of the probe (bottom) contains a semi-permeable membrane. As organic vapors cross the membrane into the sensor headspace they are detected. The sensor data are stored on-board the probe and retrieved only during the data debriefing portion of the mission. Once the measurement(s) have been completed, the sensor probe will be returned to the surface for data debriefing and battery regeneration. The on-board data logging system can begin debriefing once it is within the range of the receiver located at the well cap. After data debriefing, the battery used to operate the sensor probe can be recharged wirelessly. While the recharging is being completed the sensor data is transferred from the probe to a laptop PC for detailed analysis and visualization.

Figure 2. Automated In-Well Monitoring System Concept

Advanced Engineering Developing using DFSS Tools

Tools and processes from Design for Six Sigma Methodology (DFSS) were used in the advanced engineering work to design, build, and test prototype AIMS. The DFSS process is a highly structured methodology that uses the techniques of predictive, statistical design. The DFSS process moves through a series of “tollgates”:

- Identification of critical customer needs and functions
- Definition of requirements and resources
- Conceptual, preliminary, and detailed design
- Production and design validation

The process employs a system of “scorecards” to predict subsystem variability and integrate the variability of each subsystem into a predicted system-level variability. Using the scorecards, the key problem areas quickly surface and are subjected to the statistical problem-solving tools of Six Sigma.

In this project, the key components of the AIMS system (sensor probe, instrument deployment system, communication/recharging station, graphical user interface or GUI) were the first level subsystems as shown in Figure 3. The overall requirements of the system taken from Table 2 were “flowed down” to the subsystems. Each first level subsystem was further divided into a second level of subsystems. For example, the sensor probe consisted of the polymer coatings, sensor electronics, sampling system, system purge, power supply (battery pack), chemometrics, and packaging.

Figure 3. DFSS subsystem approach to the development of AIMS.

Using the last column of Table 2 as a guide, we selected detection limit, speciation, and size as our target requirements to focus on for Phase I. To enable us to understand how changes in the various subsystems impact our ability to meet the overall system requirements, a number of transfer functions were created. These transfer functions or models were used in the context of the subsystem flow-down design to “flow-up” the capabilities of the individual subsystems. The most critical of these was a transfer function to predict detection limit from the sensor noise, partition coefficients of the coatings, and maximum thickness of the coatings on the TSM sensors. The following sections describe the experimental work in each of the key first and second level subsystems, which are listed as subtasks in the statement of work. Subsystems that require construction of the sensor probe before testing, such as chemometrics, will be described in the results and discussion section. The

graphical user interface (GUI) does not have any requirements at the prototype stage, but will become important as this transitions to a commercial product.

Sensor Probe

Theory of Operation

The AIMS probe uses an array of thickness shear mode sensors with chemically sensitive polymer coatings to detect the presence and concentration of volatile organic compounds (VOCs). The probe uses a membrane to allow operation in either vapor or groundwater. The probe is completely self-contained. An induction link is used to communicate with the probe and to maintain the battery. A winch system provides the capability to position the probe in a monitoring well for multiple measurements.

The probe consists of a membrane, a TSM sensor array, a purification unit, an electronics module, and a power pack. Figure 4 shows the probe block diagram. Figure 5 is a photograph of the sensor probe (unassembled).

Figure 4. System block diagram

Figure 5. Photograph of probe and key subsystems

TSM Sensor Array

The TSM sensor array consists of eight crystal sensor channels (Figure 6). Each channel consists of a crystal sensor, an amplifier (used as an oscillator), and a gain control. The outputs of each oscillator feed into a common buffer amplifier. An onboard controller selects the active oscillator by reducing the gain on all oscillators except the active oscillator. With the gain below the oscillation level for the inactive oscillators, only the active oscillator will produce an output. The inactive oscillators will remain powered-up and at operating temperature until selected as the active oscillator.

The TSM array has one input connection and one output connection. The input connection receives a serial message from the controller. This message is interpreted to select an oscillator as the active output. It is possible to select no active oscillators. In this case, no output is provided. The output connection is designed for a 50-ohm load and is connected to the input of the frequency

multiplier unit. The active oscillator is directed to this output. Figure 7 is the oscillator block diagram. Power for the TSM sensor array is provided by the controller on the output connection. An “inductance isolated” dc supply is provided at the output.

Figure 6. Photograph of TSM sensor array

Figure 7. Oscillator Block Diagram

Frequency Measurement

The TSM sensor responds to a stimulus by a change in resonant frequency as shown in Figure 8. A frequency change of less than 1 hertz is significant. In order to package the sensor system for a 2-inch monitoring well, the volume and thermal load for the measurement electronics is limited. The available selection of small, low-power frequency references, normally required for frequency measurement, is small.

Figure 8. TSM Resonator Forward Transmission Characteristic (S21)

In the laboratory, a frequency counting technique is usually employed to measure the TSM frequency. A frequency reference is required to calibrate and stabilize the counting process. Counting times are long to reach high-resolution frequency measurements at low noise.

An alternative frequency measurement technique uses a time delay as a reference element as shown in Figures 9 and 10. The method compares the delayed versus the non-delayed input. The measurement is directly related to the input frequency and is available (virtually) immediately subject only to electronic delays. This method is generally referred to as "instantaneous frequency measurement" (IFM).

Figure 9. Block diagram of the IFM.

Figure 10. IFM Video Output

Efficient time delays can be implemented using surface acoustic wave (SAW) devices. To get a significant delay in a small size, the input frequency should be in the UHF (ultra high frequency) band. Operation at UHF allows off-the-shelf devices to be used.

A frequency multiplier is employed to raise the TSM input frequency (1 to 15 MHz) to the UHF range (855 MHz). A phase locked loop (PLL) circuit is used to control the frequency of a UHF oscillator in proportion to the input frequency (typically, the TSM output frequency). A frequency divider is used to lower the reference (TSM output) frequency to the “comparison” frequency. A voltage controlled UHF oscillator is input to a second frequency divider to produce the “comparison” frequency. A phase comparator compares the outputs of the two frequency dividers. The phase error is integrated by a servo to produce a frequency output adjustment signal. The frequency error is applied to the voltage controlled UHF oscillator to adjust its output frequency. The function of the PLL is to produce an output frequency (at UHF) that is proportional to the input frequency.

The bandwidth of the servo loop reduces the phase noise near the output frequency. The UHF output frequency is split into two input signals. One signal is delayed using the SAW delay line. The second signal is not delayed. A phase

comparator processes the delayed and non-delayed signals. The output of the phase comparator (effectively a complex multiplication of the two input signals) is related to the input frequency by $v = \cos(\omega d)$. Where v is the phase comparator output voltage (normalized), ω is the input frequency in radians/second, and d is the time delay in seconds.

The controller digitizes the phase comparator output voltage and records a block of samples. The samples are integrated by the controller and logged for later retrieval. The numerical conversion to frequency is performed offline on the downloaded data and will be described later in the results and discussion section.

Purification Unit

The purification unit consists of an absorber pack and a high volume pump. A photograph of the purification unit (unassembled) can be found in Figure 11. The headspace gas is removed and passed through the absorber to remove residual VOCs. The headspace gas is replaced by gas previously filtered by the absorber. A piston (or syringe) pump is used to exchange the maximum volume as quickly as possible.

Figure 11. Photograph of the purification unit.

A stepper motor drives the piston whose direction and speed can be controlled electrically. The absorber canister uses a kinematic seal to minimize friction during pumping. A section of the lower canister is closely machined and polished to match the cylinder bore. Kinematic viscosity of the air is used to develop a pressure drop across the seal in excess of the pressure drop through the absorber material. Residual VOCs in the headspace are removed and replaced with purified gas so that a baseline response may be established.

Environmental Sensors

The headspace environment is monitored for changes in temperature, relative humidity, and pressure. Figure 12 is a photograph of the environmental sensor subsystem. The headspace environment monitor was included so that equilibrium conditions could be identified and to provide some redundancy to the crystal temperature sensors. The state of the membrane could also be determined by monitoring pressure and comparing the descent position. The temperature sensor is an Analog Devices AD7417. The relative humidity sensor is a porous platinum conductivity sensor with a gel filling. The relative humidity sensor requires temperature correction of its output. The pressure sensor is a strain gauge mounted on a bellows arrangement. The pressure in a sealed vessel is compared to the internal pressure in the probe.

Figure 12. Photograph of environmental sensor section.

Controller

Control and communications is provided by an Atmel ATMEGA103L microcontroller. The controller includes internal program storage and both non-volatile and volatile data storage. Timing and communications functions are included. A separate flash memory unit (Dataflash) is included to perform data logging functions. The probe was used as a datalogging device to support field-testing. Figure 13 shows the controller block diagram.

The controller specifications are provided in the appendix. The controller selects the crystal measurement channel in the TSM sensor array, selects the frequency multiplication factor, digitizes the IFM output, integrates the IFM measurements, records environmental and sensor measurement data, operates the purification system pump, controls the power supply, sequences experiment operation, and communicates with the user. The controller is programmed entirely in C.

Figure 13. Controller block diagram.

Electronics

TSM Sensor

The TSM sensor consists of a 8mm quartz crystal resonator coated with a chemically sensitive polymer. The resonator is in a standard “HC50” mount. The HC50 mount has 0.050” diameter pins for connection to the oscillator circuit. The pin connections allow for replacement of individual sensors in the array. The pin receptacle is milled from a solid brass rod so that the connector becomes part of the seal between the headspace and the oscillator electronics. Coating thickness is gauged by the frequency offset between the uncoated and coated crystal. Practical offsets (thicknesses) are less than 150kHz (reduction in frequency).

Oscillator

In order to initiate and sustain an oscillation, a circuit must meet two criteria. The “loop gain” including the oscillator and the resonator must be equal to one. The phase shift around the loop must be 360° . The resonator phase shift crosses over from $+90^\circ$ to -90° at the series resonant peak response. This is also the point of maximum admittance for the crystal response (see Figure 8 TSM S21 response). It was found by experiment that the phase noise was reduced if the oscillator approached the series resonant frequency from above rather than below. The oscillator circuit employed uses this feature.

The amplifier used in the crystal oscillator has approximately 26 dB of excess gain to sustain oscillations. As the polymer coating responds, the electrical losses in the crystal increase. If the losses exceed the amplifier gain (26 dB – crystal insertion loss), the oscillator will stop.

The amplifier used in the oscillator has two buffered outputs. One output is used to complete the loop through the resonator to form the oscillator. The second output is the external output of the oscillator. The second output provides isolation from the oscillator load. This feature eliminates “pulling” of the oscillator by load changes. The amplifier outputs are amplitude limited so that excess gain does not affect the oscillator output.

The oscillator is turned on and off by controlling the amplifier gain. A switch is provided to reduce the amplifier gain below oscillation levels. By controlling the amplifier gain (rather than turning the amplifier power on and off), the amplifier is allowed to maintain a constant temperature.

Multiplexor

The oscillator outputs are selected one at a time to be routed to the frequency measurement electronics. The multiplexor consists of a small digital controller, a summing circuit, and a buffer amplifier.

The controller monitors a digital input for commands. The serial message is decoded to determine the selected oscillator. It is possible to select no output or to turn on all outputs. Raising the amplifier gain (by turning off the gain switch at the amplifier) to the oscillation level starts the selected oscillator. By controlling the gain (rather than powering the amplifier on and off), the amplifier temperature is maintained – minimizing “warm-up” delays.

Frequency Multiplier

The frequency multiplier consists of a phase locked loop (PLL), a loop filter, and a voltage controlled oscillator (VCO). The input signal from the TSM sensor array is limited and shaped to drive a frequency divider (reference input) in the

PLL integrated circuit. The frequency divider is programmable so that the multiplier can accommodate a range of input frequencies. The output of the reference frequency divider is called the “comparison frequency”. The frequency resolution of the PLL multiplier is determined by the selection of the comparison frequency (i.e., the multiplier output can only be adjusted in steps of “comparison frequency” size).

The output of the VCO is processed by a second frequency divider to obtain the comparison frequency. The outputs of both frequency dividers are input to the phase comparator. The phase error is integrated by the loop filter and applied to the VCO as a frequency error input. The VCO adjusts to match the input frequency times the ratio of the frequency dividers.

The current implementation uses a comparison frequency of 100 kHz. For a 10 MHz input signal, the frequency divider would be set to divide by 100. The delay line center frequency is 855 MHz. The VCO divider would be set to divide by 8550. The frequency multiplication achieved with these divider settings would be $8550/100$ or 85.50.

The design of the loop filter determines several operating characteristics of the PLL multiplier. A narrow bandwidth loop filter maintains tight frequency control but is slower to respond to changes in input frequency. A wide bandwidth filter is more responsive to input frequency changes but may have stability problems. The loop filter helps to suppress phase noise in the multiplier output. A wide bandwidth filter (20 kHz) was selected to minimize phase noise in the output.

Instantaneous Frequency Measurement

After frequency multiplication, the input frequency measurement is performed using a technique borrowed from electronic warfare technology. Measuring the carrier frequency of short pulse radars has long been a problem. As “short pulse” implies, the carrier is not available for a sufficiently long time to use frequency counting techniques to measure the carrier frequency.

The IFM technique uses a trigonometric identity introduced as a consequence of taking a product to measure frequency. The input signal to be measured is split into two signals. One signal is delayed in time. The phase error between the delayed and nondelayed signal is measured. The phase error is directly related to the cosine of the input frequency times the delay time. For values of the cosine function between 45° and 135° (or 225° and 315°), the function is nearly linear (see Figure 10). For frequencies in this range, the phase comparator output can be divided by the delay time to yield relative frequency (with corrections for the arccosine).

For the IFM used in the probe, a delay time of 2.5 microseconds was selected. This delay time corresponds to an ambiguous response interval of 400 kHz. The

“near linear” frequency ranges within this interval are 100 kHz. To provide continuous coverage of the frequency response, the 100 kHz intervals corresponding to 315° to 45° and 135° to 225° must be treated by a separate measurement illustrated in the following discussion.

The frequency multiplier can be adjusted in steps of 100 kHz (corresponding to the comparison frequency). To obtain coverage of the non-linear response areas, four measurements are made for each input. Each measurement is 100 kHz higher in frequency than the last. This procedure guarantees that at least two measurements will fall in a linear response region of the IFM and that the measurements will be complementary.

The time required to make a frequency measurement is limited only by the response of the frequency multiplier (a few microseconds) and the number of phase error samples that will be integrated (currently 500 samples at 1000 samples per second are being processed). A frequency measurement can be made in much less than one second.

The critical reference in the IFM is the stability of the time delay. The time delay used in the probe is a UHF SAW device. The time delay is temperature sensitive. To minimize temperature-dependent errors in the time delay, the device is packed in sand to increase its thermal time constant well beyond a typical measurement interval. The temperature of the delay is monitored using a temperature sensitive crystal attached to the delay.

Power Supply

The power supply for the probe consists of a rechargeable battery pack, consisting of ten 1.5 volt C cells. The coil for the induction link is located at the top of the probe assembly. The power supply regulators are located immediately below the link but above the battery. The induction link and power supply regulator electronics is sealed in a potted section of the probe. A cable from the induction link and power supply regulators extends to the base of the probe's battery section. The battery output is routed through a self-resetting overload device (polyfuse) and a magnetically de-activated reed switch. The reed switch is used to control the probe power supply by the application of an external magnet. Disconnecting the power supply, with the external magnet, forces a controller reset.

Testing/Studies

Several studies were completed to determine “design rules” for the TSM Sensor Array and the frequency measurement unit. These studies were to identify specific problem areas, to determine the severity level, and to assess methods to reduce or eliminate spurious effects.

Of particular concern was the ability to operate an array of crystal sensors without the sensors mutually interacting. A potential exists for crystal resonators, located in close mechanical proximity, to interact through either mechanical or electrical coupling. A test fixture was constructed so that a test crystal could be positioned with 0.020" of a reference crystal while operating. Crystals of nominally the same series resonant frequency were used. The method of coupling was assumed to be mutual capacitance between the rather large area crystal electrodes. Both oscillators were switched on and allowed to stabilize for 8 to 10 minutes. At the end of the stabilization period, one of the oscillators was turned off while the remaining oscillator was monitored for a frequency shift. If the devices were independent, no frequency change should occur.

The entire apparatus was enclosed in an insulated box to minimize external temperature influences. Initial test results showed a considerable frequency shift at the switchover point. A resistance load was added so that switching off the oscillator turned on an equivalent thermal load. Tests with this arrangement showed minimal frequency shift at the switchover point. The conclusion was drawn that thermal stability was a far greater concern than other coupling phenomena. As a result of these tests, the oscillator circuits were switched on and off using gain control rather than de-powering the amplifiers. The amplifiers were able to remain powered and at thermal equilibrium.

To study sensitivity toward volatile organic vapors, a test apparatus was constructed using two mass flow controllers (MFCs), a tank battery, a test chamber, and an environmental chamber. The MFCs were used to mix gas from the tank battery to form a programmable range of vapor concentrations for sensitivity testing. The test chamber contained an array of crystals (coated and uncoated). The gas mixture was provided to the test chamber through a length of stainless steel tubing. Both the tubing and the test chamber were contained in an environmental chamber to maintain isothermal conditions. Gas, flowing through the tube enclosed by the environmental chamber, was able to reach thermal equilibrium prior to being exposed to the sensor array in the test chamber. Under computer control, the gas mixtures could be changed while frequency data was recorded. Both an array of frequency counters (locked to a rubidium frequency standard) and a prototype IFM frequency measurement system were employed for testing. Testing revealed equivalent or better operation between the frequency counter and the IFM frequency measurement system. IFM operating characteristics were studied so that the thermal stability of the data collection process could be studied.

Four crystal frequencies were tested in selecting candidates for the TSM sensors. The coatings discovery work done in the high throughput screening setup used 13 mm crystals at 10 MHz. The requirement to operate in a 2" diameter well and to be capable of VOC speciation implied that smaller crystals operating in an array be used. Selection of a higher crystal resonance frequency had the potential to improve the sensitivity of the sensor. The 15 MHz crystals

have much higher phase noise in comparison to the 10 MHz crystals – an undesirable feature. The 15 MHz and 20 MHz crystals were much more fragile. Even with careful handling, the high frequency crystals were easily broken. The 10 MHz crystals were chosen for their reasonable sensitivity and more robust handling characteristics.

The physical dimensions of the crystals are also an important design criterion. To meet the desired size constraints 8 mm crystals in a standard HC50 package were selected. The package footprint allowed 8 crystals to be assembled in a radially distributed (i.e., each crystal lies along a radius) array in a 35 mm diameter. The HC50 package is mounted using a pair of 0.050" diameter mounting pins. By using the appropriate receptacle, the crystals in the array could be replaced by removing only the membrane holder and plugging in the replacement crystal set.

Purification Unit

The purification unit consists of a piston pump ("syringe"), an absorbent canister, and a motor operator. The motor operator is above a special seal. The remainder of the unit operates at headspace pressure. The motor operator consists of a "stepper" motor with magnetically activated limit switches indicating the piston travel extremes. The controller determines the pumping speed and duration under program control. The pump is capable of processing a gas volume at 42 ml/second.

Probe Package

The probe is constructed of 304 stainless steel. Probe sections above the purification unit are isolated from headspace pressure. The TSM sensor array and purification unit operate at headspace pressure. The probe consists of four independent components jointed by an exterior sheath. The sheath forms a mildly articulated structure for the probe components. The components (i.e., battery, electronics, purification unit, and TSM sensor array) are stacked on top of each other. Electrical connections pass between each component and are assembled from the membrane end toward the battery pack. Individual sheaths are joined at a "bulkhead" joint. The bulkhead joint consists of a solid stainless cylinder, grooved for o-ring seals at each end. The bulkhead is internally bored for cable passage through the center. The sheath slides over the bulkhead seal (from each end) and is secured by the heads (acting as pins) of three socket head machine screws evenly spaced about the periphery of the joint. The pinned joint allows for some articulation of the joint, minimizing the possibility of lodging the probe in the well. A bail (drawbar) is provided at the top of the probe for winch attachment. Completely assembled the probe is 5.5 feet long (1.68 m) with an outer diameter at the bottom of nominally 1.5 inches (3.8 cm).

Membrane Holder

The probe is exposed to the exterior through a polyester-backed Gore-Tex membrane. The membrane was furnished by the manufacturer (W. L. Gore, Co.) laser-cut to size and loaded with an adhesive ring applied to the Gore-Tex surface. To install a membrane, a thin stainless steel ring is applied to the adhesive surface. A “twenty four hour” cure must elapse before the membrane can be installed in the membrane holder.

A fully cured membrane attached to a support ring is placed over a perforated plate. The perforated plate (anvil) has an o-ring seal in a groove open on two sides. The seal operates against the wall of the membrane holder and against the polyester backing of the membrane. A special nut is screwed down over the membrane forcing the ring and the membrane against the o-ring seal.

Bulkhead Seals

A single o-ring seals each joint of the probe. The sheath passes over the o-ring and is secured by three socket head machine screws (functioning as pins). The machine screw heads prevent the sheath from sliding back over the o-ring while maintaining a flexible joint.

Bail

The probe is attached to the winch line by a “bail” formed from a stainless link. A pin secures the link to a special bulkhead joint. The bulkhead joint transfers mechanical force to the body of the probe through the sheath/pin junctions between each component.

Sheaths

Sheaths are formed from thin stainless tubing. The ends of the sheaths (except for the membrane holder) are drilled to accept the heads of three standard socket head machine screws, evenly spaced about the sheath periphery. Drawing force is transmitted by the sheath to the probe components only at the bulkhead joints by the pins.

Piston Seals

The purification pump uses three types of seals. The piston body is kinematically sealed by a polished surface section operating near the base of the piston and against the wall of the pump casing. A standing valve is located in the lower pump cap. A traveling valve is located in the bottom of the piston. The standing and traveling valves employ an o-ring seat for the valve operator. The piston is activated by a drawbar consisting of 0.060” diameter stainless rod. To minimize friction forces on the drawbar, a “lobed rectangular” cross section seal is used.

The seal friction force is adjusted by compression while monitoring motor current (torque/force).

Polymer Coatings Optimization and Selection

High Throughput Screening

Combinatorial and high-throughput screening (HTS) of combinatorial chemical libraries is a well-established discovery mode of new pharmaceutical compounds. Since 1995 these methods are also rapidly emerging into other materials areas for the discovery of inorganic and organic materials, polymers, and catalysts [8-9]. Development of new measurement tools with advanced capabilities makes possible discoveries in these areas.

Design of sensor materials with new functionality benefits strongly from the advances in combinatorial and high-throughput technologies. These benefits are provided by the capability of rapidly synthesizing diverse materials followed by materials evaluation using a variety of sensor transduction principles. The possibility of parallel synthesis of multiple materials opens up the opportunities to explore a dramatically expanded materials parameter space which was previously impossible to cover with conventional sequential evaluation methods.

Well recognized three critical aspects of sensor performance are (1) magnitude of sensor response to the parameter of interest; (2) sensor specificity against environmental interferences, and (3) long-term stability. This work addresses all three aspects in sensor development with a dedicated high-throughput screening approach. These attractive aspects in the design of sensor materials were achieved by combining three types of screening modes that included primary, secondary, and tertiary screening of materials (see Figure 14) using a recently designed and built 24-channel array of thickness shear mode (TSM) sensors [10]. Sensor materials were screened with the goal for the enhancement of selectivity of determinations of chlorinated organic solvents at part per billion levels in groundwater wells. The primary screen is the discovery screen where materials are exposed to a single analyte concentration. The secondary screen is the focused evaluation where the best subset of these materials is exposed to analytes and interferences. The tertiary screen involves evaluation of material performance under conditions mimicking the long-term application. As seen in Figure 14, screening started from six families of potential sensor materials and rapidly downselected the candidates by evaluating materials performance at different screening levels. Using this approach, one can efficiently design and screen sensor materials not only for their immediate performance but also for the long-term stability thus providing significant time savings in sensor design.

Figure 14. Strategy and materials spaces for screening of sensor materials for practical applications.

Details of the designed, built, and tested 24-channel TSM-sensor system are reported elsewhere [10]. For the application described here, the TSM resonators were the 10-MHz AT-cut piezoelectric quartz crystals with gold electrodes on the opposite sides of the crystal (International Crystal Manufactures, Oklahoma City, OK). The noise in the response of each sensor was about 0.1 Hz. Each crystal in the array was coated with a chemically sensitive material that was a derivative of polyimide-silicone hard-softblock polymeric sensor material (sometimes referred to as SILTEM) [5]. Sivavec and Potyrailo recently discovered that this polymer has a unique capacity for sorbing organic vapors at least 500 times higher than conventional sensor materials. Polymer derivatization was performed and involved six different types of chemical modifications of the polymer to induce diversity in the response of polymer derivatives when used in a sensor array (see Figure 14).

The primary and secondary screens were performed with the system shown in Figure 15. The array of coated sensors including two sealed crystals used as reference was arranged in a gas flow-through cell. The whole arrangement was kept in an environmental chamber that provided an adequate (0.1 °C) temperature control (see Figure 15A). Gases were introduced into the gas cell with a four-channel computer-controlled gas flow system (nitrogen, vapor 1, vapor 2, and vapor 3) as shown in Figure 15B. The gas flow system was operated by a digital four-channel readout unit (model 247C, MKS Instruments, Andover, MA) connected to four mass-flow controllers (model 1179A, MKS Instruments). Three vapors 1 – 3 were introduced in sequence with no blank gas

(nitrogen) in between. Experiments were performed using six vapors where three vapors were used as analytes and three were used as interferences. Analyte vapors were tetrachloroethylene (PCE), trichloroethylene (TCE), and cis-dichloroethylene (cis-DCE). Interference vapors were carbon tetrachloride, toluene, and chloroform. The nature of analyte and interference vapors was determined from the detailed analysis of the historic data on the planned analyzed groundwater wells. Gases were in a dry air (water level less than 15 ppm) and were purchased from Airgas (Radnor, PA) and Air Products (Glenmont, NY). Details are provided in Table 3. Blank gas was introduced between three replicates of three-gas exposures. Typical exposure time per vapor was 200 data points (~80 min). Data analysis was performed using KaleidaGraph software (Synergy Software, Reading, PA) and PLS_Toolbox software (Eigenvector Research, Inc., Manson, WA) operated with Matlab software (The Mathworks Inc., Natick, MA).

Figure 15. Operation of the HT system for primary and secondary screens. A, system components positioned in a temperature controlled environment. B, Computer control and vapor-delivery system components.

Table 3. Analyte and interference vapors used in these studies.

Analyte vapors		Interference vapors	
Vapor type	Concentration (ppm)	Vapor type	Concentration (ppm)
perchloroethylene (PCE)	12	carbon tetrachloride	10
trichloroethylene (TCE)	9.95	toluene	10.5
cis-dichloroethylene (cis-DCE)	12	chloroform	10.1

Chlorinated solvents and their transformation products are regulated under the 1986 Safe Drinking Water Act Amendments because they pose a threat to public health being toxic and carcinogenic. It is therefore critically important that any new type of instrumentation developed for real-time groundwater monitoring of chlorinated solvents be able to detect and even distinguish PCE, TCE, and cis-DCE at trace levels. In the past, we performed these determinations for the concentrations of volatiles at the part-per-million range. Selective determinations at part-per-billion levels were impossible because of the lack of chemically sensitive materials with high enough partition coefficients. Thus, the focus of our combinatorial developments in this area was to find materials with improved diversity in response to the chlorinated organic solvent vapors. For materials screening, we produced diverse materials families with potential diversity in sensor response.

For development of materials for ppb detection of chlorinated solvent vapors, we identified and made six families of materials based on the best material that we discovered earlier. This material had a partition coefficient of at least 500 times higher than that of conventional materials (e.g. polyisobutylene). However, our base material alone did not provide the required discrimination in detection of different analytes and interfering species such as chloroform, toluene, and carbon tetrachloride. Thus, new families of materials were developed in order to induce diversity in sensor response.

Our strategy for screening of sensor materials for practical applications is presented in Figure 14. It included three levels of screening. The primary screen was the discovery screen where materials were exposed to a single analyte concentration. The secondary screen was the focused evaluation where the best subset of these materials was exposed to analytes and interferences. Finally, the tertiary screen involved evaluation of material performance under conditions mimicking the long-term application.

The data processing steps in the primary screen are summarized in Figure 16. The steps included visualization of individual responses for their reversibility and determination of the relative sensitivity of each material with respect to one of three vapors. Such analysis compensated for any variability in the absolute response of the replicates of the material due to thickness differences, yet demonstrated the reproducibility of the sensor response and the sensitivity pattern. As a result of the primary screen, materials with good reproducibility and statistically different responses to vapors 1 – 3 were passed onto the secondary screen.

Figure 16. The data processing steps in the primary screen.

Results of the primary screening of several families of these materials are presented in Figure 17. The 6 x 4 array of sensors was comprised of diverse materials that were deposited as films of different thickness. Also, two reference sealed crystals were used (channels 18 and 19 in Figure 17A). As shown in

Figure 17A, responses of all sensor materials were reversible on the time scale of testing. Results of the evaluation of the response pattern upon exposure to three analyte vapors are depicted in Figure 17B. These analyte vapors were PCE, TCE, and cis-DCE, all at about 10 ppm (see Table 3). This data showed two important aspects of the primary screening. First, reproducibility of responses was easily quantified by the magnitude of the variation between replicate material films and variation between replicate measurements in individual films. For example, material B showed poor run-to-run ($n = 3$) and film-to-film ($n = 2$) reproducibility, while material E demonstrated a good reproducibility for both types of measurements as indicated by the small run-to-run error bars for each material ($n=3$) and similar relative sensitivity for replicate films with material E ($n=3$).

The diversity in material response to three analyte vapors was evaluated by plotting the sensor responses relative to the response of sensors to TCE. The information of interest here was the combination of the individual responses of materials. For example, materials C and E had the same relative response to cis-DCE while material C had significantly larger relative response to PCE than material E (see Figure 17B).

A

B

Figure 17. Results of the primary screening of several families of sensor materials. A, visualization results of the baseline stability and reversibility of sensor response. B, Results of the evaluation of the response pattern upon exposure to three analyte vapors PCE, TCE, and cis-DCE, all at about 10 ppm.

The data processing steps in the secondary screen are summarized in Figure 18. The steps included visualization of individual responses and the determination of partition coefficients of the materials with respect to analyte and interference vapors. Calculated partition coefficients were displayed for comparison. Such comparison was performed using bar-graphs and multivariate statistical tools. As a result of the secondary screen, materials with different responses to analytes and interferences were passed onto the tertiary screen.

Figure 18. The data processing steps in the secondary screen

Figure 19. Results of the calculation of partition coefficients of the materials during different days of experiments. Error bars of each column, $n=3$) and day-to-day reproducibility (different columns of the same color).

In the secondary screen, experiments were done repetitively over several days. The calculated partition coefficients for the materials from different days are presented in Figure 19. The acceptable run-to-run reproducibility (error bars of each column, $n=3$) and day-to-day reproducibility (different columns of the same color) were observed as shown in the inset of Figure 19. As a result of our screening efforts, we have identified materials with improved partition coefficients (e.g. materials Q, R, and T) and with diverse responses to analytes.

Results of material performance with respect to the differences in partition coefficients to analytes (PCE, TCE, and cis-DCE) and interferences (carbon tetrachloride, toluene, and chloroform) are summarized in Figure 20. Normalization of all partition coefficients for different vapors to the partition coefficient of TCE showed a noticeable difference in response pattern of materials to analyte and interference vapors. A more quantitative analysis can be performed using principal components analysis (PCA) tools as shown in Figure 21. PCA is a multivariate data analysis tool that projects the data set onto a subspace of lower dimensionality with removed collinearity. PCA achieves this

objective by explaining the variance of the data matrix $\mathbf{X}$ in terms of the weighted sums of the original variables with no significant loss of information. These weighted sums of the original variables are called principal components (PCs). Upon applying the PCA, the data matrix $\mathbf{X}$ is expressed as a linear combination of orthogonal vectors along the directions of the principal components:

$$\mathbf{X} = \mathbf{t}_1 \mathbf{p}_1^T + \mathbf{t}_2 \mathbf{p}_2^T + \dots + \mathbf{t}_A \mathbf{p}_K^T + \mathbf{E} \quad (1)$$

where $\mathbf{t}_i$ and $\mathbf{p}_i$ are, respectively, the score and loading vectors, K is the number of principal components, $\mathbf{E}$ is a residual matrix that represents random error, and T is the transpose of the matrix.

Figure 20. Results of analysis of materials performance with respect to response to analytes and interferences. Visualization of relative material sensitivities as normalized partition coefficients for different vapors to the partition coefficient of TCE.

Figure 21. Application of PCA tools for determination of differences in the response pattern of the sensor materials toward analytes (PCE, TCE, and cis-DCE) and interferences (carbon tetrachloride, toluene, and chloroform). (A) scores and (B) loadings plots of the first two principal components.

In this analysis, we used data from all replicates of eight types of different films. The capability for discriminating of six vapors using the eight types of polymers was evaluated using a scores plot (see Figure 21A). It demonstrated that these six vapors are well separated in the PCA space when these eight types of polymers are used for determinations. To understand what materials induce the most diversity in the response, a loadings plot was constructed (see Figure 21B). The bigger the distance between the films of the different types, the better the discrimination ability of the sensor array that includes these films. For example, films of materials T and X introduce the most diversity in the recognition ability of the sensor array. In contrast, materials Q and R have very similar response pattern to the six vapors and their combination in the sensor array will be less useful. The loadings plot also demonstrates the reproducibility of the response of replicate films of the same materials. Such information served as an additional input into the materials selection for the tertiary screen.

Using the experimentally obtained partition coefficients and assuming in the first approximation a linear response of the sensors over the studied concentration range, the response of the sensor array with some of the lead materials identified in the secondary screen (R, T, D, and X) was modeled. This analysis was performed for vapors concentrations ~100 times smaller than those used earlier [3]. The number of elements in the sensor array was also four, the same as in the earlier array. Results of these simulations are presented in Figure 9. The results demonstrated that the newly developed materials using HT experimentation were capable of quantifying selectively several closely related chlorinated vapors in presence of interferences at part per billion concentrations.

Figure 22. Results of simulations of sensor responses to increasing concentrations of analyte and interference vapors. Maximum vapor concentrations are around 1 ppm.

Selection of Coatings

The use of chemical sensor arrays for the detection and quantification of volatile organic compounds is becoming increasingly common due to their small size and cost. These devices operate by arranging multiple partially selective sensors into an integrated sensor system. The data obtained from the array is then used by multivariate statistical methods to calculate analyte concentration or estimate the presence or absence of a particular analyte. Among the types of chemical sensor array technologies available today, polymer-coated acoustic wave devices have drawn considerable interest due to their high sensitivity for key analyte vapors.

Surface acoustic wave (SAW) and thickness shear mode (TSM) devices are the two most common types of acoustic wave sensors. For chemical sensing purposes, SAW and TSM devices are coated with a thin polymer film. As analyte

vapors sorb into the film, the characteristics (e.g., frequency) of the acoustic wave are measured. The Sauerbrey equation shown in equation 2 describes the change in frequency as a function of the concentration of the analyte vapor, the thickness and density of the film, and the partition coefficient.

$$(2) \quad \Delta f_v = \Delta f_s C_v K / \rho_s$$

In this equation K is the partition coefficient, Δf_s is the frequency shift due to the coating, ρ_s is the density of the coating, C_v is the concentration of the analyte vapor, and Δf_v is the expected frequency shift. The partition coefficient (K) can be rationalized based on the structure and properties of the film material. A chemical sensor array is created using multiple acoustic wave devices, each consisting of a different polymer films with diverse K values.

For each sensor application, critical design choices must be made -- such as the number of acoustic wave devices and the selection of which coatings to use in the array. In this sensor design, the number of sensors was limited based on the size of the well to a maximum of 8. More practically, a smaller number is available for data analysis since two of the sensors in the array are used for temperature and drift correction. From the six remaining sensors, net analyte signal (NAS) was used to calculate estimated detection limits for selected combinations of coatings. The coatings combinations with the lowest detection limits will be used in the prototype for laboratory and field-testing.

In 1986, Lorber first introduced the net analyte signal (NAS) concept [11]. Traditional analytical chemistry metrics such as signal-to-noise, limit of detection, sensitivity, and selectivity were originally developed for univariate signals (e.g., a single sensor). However, these simple metrics assume a direct one to one relationship between the sensor output and concentration of the analyte species of interest (i.e., perfect selectivity). This assumption does not hold for partially selective sensors when presented with a sample containing multiple components. In such cases, Lorber generalized these univariate metrics for the multivariate case by defining the NAS as the part of the analyte signal that is orthogonal to the space spanned by the interfering components in a complex mixture (i.e., contravariant vector). Stated differently, NAS is the gross analyte response *useful* for calibration. The calculation of the net analyte signal requires a pure component response from each analyte or, ideally, the sensitivity (i.e., slope of univariate calibration curve) for each sensor for each contributing species in the sample.

In general, the NAS for analyte i is computed using the matrix of sensitivities minus the analyte of interest (D_{i-1}), the pseudo-inverse of D_{i-1} , (D^+), the sensitivity response of analyte i , d_i and the identity matrix (I) as shown in equation 3.

$$\text{NAS}_i = (I - D_{i-1} D^+)d_i \quad (3)$$

Once the NAS for each analyte is determined, the selectivity (SEL) is computed by dividing the vector norm of NAS_i by the vector norm of the analyte sensitivities (d_i). The selectivity value varies between 1 (perfect separation) and 0 (complete overlap). Sensitivity (SEN) is simply the vector norm of the NAS. From SEL and SEN, limits of detection (LOD) can be determined. For this application, the strength of NAS lies in its ability to compress multivariate data into common scalar values. Thus, a particular combination of coatings can be tested to compute their multivariate K and plugged into the Sauerbrey equation to estimate frequency shifts and eventually detection limit.

Using the HTS tools described in the previous section, nine polymers were available for use in the sensor probe. The partition coefficients for the nine polymers and three analyte and interference vapors are shown in Table 4. In addition to the partition coefficients shown in Table 4, partition coefficients were also measured for common organic solvents that may act as an interference: chloroform (CLF), carbon tetrachloride (CTC), and toluene (TOL).

Table 4. Material Available for Coating Selection

Material	TCE	PCE	Cis-DCE
A	20854	15408	22430
B	20198	15325	21924
C	16248	12882	17587
D	37702	28193	40370
E	9714	3249	8499
F	6266	3989	7506
G	6949	2421	7365
H	7553	4334	8763
I	20365	16213	22764

From this list of nine sensor materials all possible three-sensor array combinations were tested. For a given combination of coatings, the multivariate sensitivity was calculated for a number of different possible scenarios: (1) TCE as the target analyte with PCE, DCE, CLF, CTC, or TOL acting as interferences in a binary mixture; and (2) TCE and PCE as the target analytes with DCE, CLF, CTC, or TOL acting as interferences in a three-component mixture. For each scenario and coating combination, the appropriate partition coefficients are placed into matrix format and used to calculate NAS and hence multivariate sensitivity (SEN). The units of SEN are the same as the partition coefficients and can be used in the Sauerbrey equation to calculate a predicted frequency shift. For these simulations, 100,000 Hz were used for frequency shift due to coating and 1 was used for the density of the material. This frequency shift is estimate of the “pure” signal in a complex mixture. Using an estimated noise level of 0.1 Hz

a detection limit can be calculated by estimating the amount of signal needed to be 3 times the noise level.

The results of this simulation indicated that a number of coating combinations performed well for different scenarios. However, the combinations H/E/D and G/E/D, and F/E/D were consistently among the best. For challenging three-components mixtures, the F/E/D combination performed the best based on mean sensitivity for the target analytes. Based on this criterion, this combination was chosen for use in the laboratory and field-testing. Table 5 shows the simulation results for this combination of coatings assuming a six-sensor array filled with three coatings repeated twice and the simulation parameters described earlier. The multivariate sensitivity of the best combination was 3.45 (in logarithmic units), which represents a 23% improvement over a combination of Siltem and two commercial materials.

Table 5. Coating Selection Simulation Results

Multivariate Limit of Detection TCE (ppbw)	Interference(s)
2.9	PCE
1.0	DCE
1.0	CTC
0.8	CLF
3.9	PCE and DCE

Membrane Selection

A critical component of the sampling design is the semi-permeable membrane that separates the groundwater and vadose zone vapors to be sampled from the sensor array sampling chamber. The design calls for a membrane that excludes water while allowing permeation and transport of chlorinated VOCs into the sampling chamber. Microporous, hydrophobic membranes are known to offer many advantages for this application.

Microporous membranes are generally those sheets of materials that have a sponge-like structure in three dimensions. Connections among the openings in the material create tortuous paths that constitute the membranes pores. Current manufacturing technology permits the production of a highly uniform interstitial pore geometry, which allows a “pore size” to be assigned to a given membrane. The pores allow gases and vapors to pass through the membrane while restricting the passage of particles larger than some size consistent with the pore size. Membranes referred to as hydrophobic repel water and other aqueous liquids owing to the chemical property of the material of construction. Membrane thickness is usually measured with micrometers and expressed as mils or microns. The proper thickness for a given application is the optimum between two often conflicting needs. Thinner membranes offer better flow rates, but this

is at the expense of sealing and handling convenience. To maximize airflow and minimize handling and sealing difficulties, manufacturers combine membranes with support materials, which are typically made from non-woven media, such as polypropylene or polyester.

Water intrusion pressure, also called water breakthrough, is a measure of the force required to push water through a membrane. Water intrusion, expressed in units of psi, is particularly relevant in our application, as the membrane must withstand pressures created by a depth of water. Membranes are commonly manufactured using polymers with low surface energy, or they can be post-treated with low-surface-energy coatings after manufacturing. Examples include polytetrafluoroethylene (PTFE), a low-surface-energy polymer, or Repel treatment, which places fluorocarbons on exposed membrane surfaces. The very low surface energy of the membrane and the small pore sizes prevent water from filling the pores. Thus, the membranes are very effective barriers to the passage of water.

Two limitations of these microporous, hydrophobic membranes were investigated in this study. First, although liquid phase water will effectively be excluded, vapor phase water will pass through the membrane and accumulate in the sampling chamber. Methods to control this water vapor transport were investigated. Secondly, there will be a trade-off between the pore size of the membrane and the pressure at which water will be forced into the membrane. A larger pore size will offer increased transport, but with water infiltration at a lower pressure. The mechanical integrity of selected microporous, hydrophobic membranes was evaluated at pressures corresponding to depths up to 300 feet below the water table.

A decision was made to avoid the use of heating or sintering colloidal polytetrafluoroethylene (Teflon) powder into stainless steel screen or porous discs. The Membrane Interface Probe (MIP), manufactured by Geoprobe Systems, employs such a sampling port that is heated to approximately 120°C. Variance in the porosity of microporous membrane structures created in heating Teflon powders is often quite high and the use of a manufactured hydrophobic, microporous membrane with a controlled pore size placed on a support backing of porous stainless steel was selected to provide better sampling control.

Figure 23 lists microporous, hydrophobic membranes that were recommended for use in this application by technical representatives from two leading manufacturers of such membranes, W.L Gore and Pall Specialty Materials. Samples of these membranes were obtained and tested under a variety of test conditions, as described below.

PTFE Membranes

Manufacturer	W.L. Gore					
Sample Desc.	0.02um PTFE on Non-woven PET	0.1um PTFE on PP scrim	100% PTFE or "White Crush" *	ePTFE membrane	ePTFE membrane	ePTFE membrane
Thickness (mil)	5.5 - 11.0	3.0 - 8.0	11.8	1.3-2.5	2.0-4.0	3.0
thickness (um)	125-250	75-200		25-60	50-100	75.0
thickness (mm)			0.30	0.025 - 0.06	0.05 - 0.1	0.075
Pore size (um)	0.02	0.10	2.0	0.1	0.2	0.02
WEP (psi)	250	**	12.80	90	45	250
Gurley # (sec)	300 ave	19 ave	70	11-16 ave	11 to 18 ind.	700 ave
IPA Bubble Point (psi)	50	30		25	15	50

Manufacturer	Pall Corp.	
Sample Description	PTFE/collendered polyester laminate*	PTFE/collendered polyester laminate
Thickness (mil)	~7	~7
Thickness (um)	190.0	190.0
Thickness (mm)	0.19	0.19
Pore size (um)	0.02	0.2
WBT (psi)	>75	>75
IPA Bubble Point (psi)	40 minimum	40 minimum

Stainless steel porous discs for membrane support

Manufacturer	Mott Corp.
Sample Description	porous 316L ss discs
Thickness (mm)	1.57
Pore size (um)	2, 5, 10, 20, 40 , 100
tensile strength (psi)	10,000- 4,000 for 2 -100 um

Figure 23. Membrane material selection options.

Two 70mm test filter assemblies (Figure 24) were purchased from Mott Corp., Farmington, CT. This assembly offered in a compact design the following features for testing: an all-stainless (316)/Teflon gasket construction, easy assembly using an upper and lower clamp, a high pressure rating (150 psig), 0.25 in NPT inlet and outlet connectors, and a lower housing that accepted a 2.37 in diameter porous stainless steel (316L) disc available in a wide variety of porosity from 0.2 to 100 μm and 1.57 mm thickness. Commercial membranes could be easily cut and fitted to the outside surface of the porous SS discs to provide a rigid support to the membrane. No effort was required or taken to seal the membranes to the porous disc support or Teflon gasket. Heat sealing, sonic welding and the use of adhesives are commonly used to seal membranes. With use of the Mott test cell, the PTFE membranes sealed very well onto the Teflon gaskets and no leaks were detected at the seal points.

Mott test filter assembly

Pressure rating: 150 psig

SS support discs porosity: 20, 40, 100 μm

Disc diameter: 2.37 in

Active disc area: 4.41 in²

Teflon gaskets (3)

Figure 24. Mott test cell.

Water-Phase CVOC Diffusion Testing

The lower housing of one of the Mott test filter assemblies was cut away to allow the supported membrane to be fully exposed to an aqueous solution (Figure 245). The active membrane/disc area was 4.41 in² (28.5 cm²). As a QCM sensor/sensor array was not available at the time of this early testing, a metal oxide semiconductor (MOS) sensor (Universal Sensor and Devices, LAV-Series Gas Sensor Transmitter coupled with a VS-1HC MOS sensor) was used to monitor TCE diffusion into the sensor/cell headspace. The MOS sensor was calibrated to 0-100 ppm toluene and was used to provide a fast relative CVOC response. Response time to TCE was approx. 5-10 sec. Labview software was used to collect the data.

Figure 25. Experimental set-ups used for water-phase testing (left) and high pressure water-phase testing (right)

Aqueous solutions of TCE were prepared by the standard addition method. The aqueous TCE solution (10.0L) was contained in a glass tank with a glass plate cover. The MOS sensor was placed inside the Mott assembly to give a watertight seal. The assembly was lowered onto a metal stage resting in the water tank (Figure 25). The stirring of the aqueous TCE with a magnetic stirrer was stopped prior to the Mott assembly being lowered into the tank, so as not to create a vortex on the membrane. Care was also taken so that no air pockets were created on the PTFE membrane surface as the assembly was lowered into the water. This could be accomplished by lowering the assembly on its side until it was completely submerged under water before rotating it right side up.

Diffusion rate data for four PTFE membranes are shown in Figure 26. The pore size of the stainless steel porous disc was kept constant at 100 μm for each of these experiments, so that only PTFE thickness, pore size, and laminate structure were variables. The TCE diffusion curves are remarkably similar at this concentration (~ 0.7 ppmw or ~ 50 ppmv at 25°C). Complete diffusion of TCE into the headspace occurred within 1 h and greater than 90% of the TCE diffused within 16-26 min. Both laminated and non-laminated PTFE membranes gave similar diffusion curves at 25°C . Lower concentrations of TCE were not examined given the calibration range provided by the MOS sensor.

The temperature dependence of the TCE diffusion rate through PTFE (3 mil thickness and 0.02 μm pore size) is shown in Figure 27. There is a small temperature dependence, but complete TCE diffusion is observed within ~ 1 h. The dependence of support disc porosity (100 μm vs. 40 μm) was also examined. Figure 28 shows that the 100 μm porous disc afforded complete TCE diffusion within 40 min., a small improvement over the 40 μm disc. Based on this test, 100 μm stainless steel porous disc was selected for vapor-phase TCE diffusion testing.

Vapor-Phase CVOC Diffusion Testing

A second, unmodified Mott test filter assembly was used to determine vapor-phase TCE diffusion rates through various PTFE membranes supported on a 100 μm 316L stainless steel porous disc. The membrane/disc area exposed to the TCE vapor was 4.41 in^2 (28.5 cm^2). As in the water-phase tests, a metal oxide semiconductor (MOS) sensor (Universal Sensor and Devices, LAV-Series Gas Sensor Transmitter coupled with a VS-1HC MOS sensor) was used to monitor TCE diffusion into the sensor/cell headspace. The MOS sensor was calibrated to 0-100 ppm toluene and was used to provide a fast relative CVOC response. Response time to TCE was approx. 5-10 sec. Labview software was used to collect the data.

Figure 26. Water-Phase TCE Diffusion Curves

Figure 27. Temperature Dependence of Water-Phase TCE Diffusion

Figure 28. Dependence of Water-Phase TCE Diffusion on Stainless Steel Support Pore Size

A vapor stream of 9.5 ppm TCE in air (Air Products) was introduced into the exterior of the membrane/support capped end of the Mott test cell, using an inlet T that carried the TCE vapor near the membrane surface under ambient pressure conditions. No pressure was applied across the membrane/support in these vapor-phase tests. An Environics 4040 system was used to control the vapor flow rates that entered the cell.

Figure 29 shows vapor-phase TCE diffusion curves across four PTFE membranes, supported on a 100 μm 316L SS porous disc relative to no membrane. The diffusion rates appear quite similar for all PTFE membranes. Complete diffusion of TCE occurred within 10 min. The diffusion curves are distinctly retarded relative to the case of no membrane placed on the SS support. The presence of a laminate backing on two to the PTFE membranes did not affect the diffusion behavior under these ambient pressure/temperature conditions.

Figure 30 shows the strong dependence of diffusion time on flow rate. Not surprisingly, the higher flow rate (200 ccm vs. 50 ccm) resulted in a much faster diffusion time. However, both equilibrium conditions were achieved within 20 min at either flow rate.

Figure 29. Vapor-Phase TCE Diffusion Curves

Figure 30. Dependence of Vapor-Phase TCE Diffusion on Flow Rate

Water Vapor (Humidity) Transport Testing

The same apparatus used in the water-phase testing (a fully exposed membrane/support resting on a metal stage placed in 1 large glass tank) was used to determine the rate of humidity transport across the PTFE membranes and into the test cell headspace. A multi-probe thermohygrometer (Cole-Parmer A-37990-30) fitted with a 6 mm x 1000 mm flexible probe was substituted for the MOS sensor. From 21 to 30 °C, the accuracy of the hygrometer was given as $\pm 2\%$. Figure 31 shows the rate of humidity transport across four PTFE membranes when the cell was submerged under 7.5 inches of water (0.3 psi). The relative humidity rapidly increased from ~25% RH to ~90% RH within 15 min. None of the tested membranes excluded water vapor, as was expected.

Figure 31. Water Vapor Transport Across PTFE Membranes

The effects of humidity on the performance of polymer-coated surface acoustic wave sensor arrays have been investigated at GE and in other laboratories. Responses to relative humidity were found to be important. Sorption of water vapor by polymer coatings on TSM sensors may lead to large shifts in baseline frequencies. At high ambient humidity levels, the concentration of sorbed water

may be large enough to affect the interaction of the coating with the target vapor. The responses of the TSM device to organic and water vapors may not be additive. It is also likely that our device will be deployed in a variety of different scenarios in which the humidity level to be sampled varies (e.g., soil vapor monitoring and groundwater monitoring).

Effort was undertaken to investigate what commercial desiccants might be used to remove or minimize the effect of humidity within the sensor head space. At the point of this study, it was not yet determined whether the probe design would use a shutter to protect the membrane from long-term exposure to groundwater or high humidity soil gas. It was also considered that a desiccant could be added to the analyte trap in the system purge mechanism to provide a means to remove water vapor from accumulating in the sensor headspace over time.

Inorganic salts and their aqueous solutions are commonly used to set relative humidity levels to some constant. Examples of some common salts and their target relative humidity include calcium chloride (29% RH), sodium iodide (39% RH), and lithium chloride (11% RH). Silica gel, porous polymer resins, and pelletized inorganic salts such as calcium sulfate (Drierite®) also may be used to absorb and store water.

Using the water-phase test set-up, calcium chloride and a variety of silica gel materials were placed in the test cell headspace (Figure 32), along with the digital hygrometer to monitor the influence of the desiccants when the test cell was submerged in water. Figure 32 shows that when 30cc silica gel (Aldrich, 3-9 mesh) was loaded into the cell headspace (140cc), the humidity was controlled to less than 25% RH over 48h. Shorter-term tests (2h) using calcium chloride similarly controlled the humidity within the cell from 23.1 to 24.4% RH. It was important to note that the temperature of the silica gel did not increase appreciably ($\Delta T = 0.4^{\circ}\text{C}$ over 22h) upon exposure of the membrane to water. The effect of temperature on TSM performance, like humidity, can be significant. Indicating silica gel desiccants (Alfa Aesar) proved to be useful in that the incorporation of cobalt chloride and its color change from blue (activated) to violet (10% moisture absorbed) pink (19%) to pale pink (28%) as it absorbed water provided a convenient means to monitor the need for replacement of the dessicant.

Figure 32. Silica Gel to Control Water Vapor Transport

High-Pressure, Water-Phase Testing

An important requirement of any membrane to be used to protect a sensor probe at depths up to 300 feet below the water table is its stability and performance at pressure. In an initial assessment, a PTFE membrane on a non-woven PET support (0.02 μm pore size, W.L. Gore) was subjected to 43 psi, the pressure the membrane would have to withstand at a depth of 100 ft. The apparatus described in the vapor-phase CVOC test was used, except that the test cell was inverted, 0.7 ppm TCE in water was loaded on top of the membrane to completely fill the test cell headspace, and air pressure from a compressed air cylinder was used to increase the pressure on the membrane to 43 psi. A 40 μm SS porous disc was used for this test after an initial test deformed a 100 μm porous disc. The TCE diffusion curve is shown in Figure 33. An increase in diffusion time from ~45 min to ~120 min was observed as the pressure increased. One explanation is that the membrane's porosity is deformed and is decreased at this higher pressure. All non-laminated PTFE membranes allowed some water to pass through the supported membrane. Figure 34 shows the TCE diffusion curve measured for a PTFE (0.02 μm pore size) on a polyester laminate

support at test pressures of 43 and 100 psi. These pressures correspond to water depths of 100 and 250 feet.

The use of silica gel to control the humidity within the test cell was shown to be effective even when the membrane saw pressures of 43 to 100 psi (250 feet of water) (Figure 35). The relative humidity approached 50% after 10h, and was higher than that seen at 0.3 psi (~25 % RH). It however was not the 90% RH seen in the absence of silica gel even at 0.3 psi.

These studies indicated that microporous, hydrophobic membranes of PTFE, when supported on a stainless steel porous disc (40 μm pore size), offer acceptable diffusion rates in both water and vapor phases. When further mounted on a polymer support such as polyester, PET, or polypropylene, these PTFE membranes can withstand the pressures to be encountered when such sampling devices are deployed at depths up to 250 ft below the water table. Figure 23 lists the top candidate PTFE membranes studied. The PTFE membranes with the smallest pore sizes, highlighted in yellow, were shown to afford the highest mechanical integrity (sealing and handling), especially under high-pressure conditions.

Figure 33. Aqueous TCE Diffusion under High Pressure Conditions

Figure 34. Aqueous TCE Diffusion under High Pressure Conditions

Figure 35. Water Vapor Transport Across PTFE Membranes under High Pressure Conditions

Membrane Seals

Membrane seal methods were explored using a considerable number of sample membranes and adhesives. Manufacturer's information was consulted but it became apparent that actual testing of full-scale membranes was required.

A mounting ring was needed to prevent torsional shearing forces to be applied to the membrane as the membrane seal was compressed. To secure the mounting ring to the membrane, several adhesives were tried. Inconsistent results were obtained. In particular, visual inspection of the seal proved the least effective method of examination. A hand-operated vacuum pump and fixture was assembled for performing rudimentary tests of the membrane seal. A twenty-four hour cure time was required for the adhesive once bonded to the mounting ring.

The membrane was supported by a perforated stainless steel disk. A perforated disk was chosen given the distortion observed on the sintered supports employed during pressure tests of the membrane. The edge of the disk

was relieved to accommodate an o-ring seal. The disk was reversible so that a metal-to-metal seal as well as the o-ring seal could be tried.

The best results were obtained using a special adhesive provided and applied by the manufacturer (W. L. Gore Co.). The initial allowance for the o-ring compression was insufficient to prevent leakage through the polyester backing. The membrane holder face was relieved so that additional pressure could be exerted on the membrane. A good seal was obtained. The membrane seal was visible on inspection by a “cloudy” circle completely around the polyester backing above the seal.

The maximum rate at which the probe could dive and be retrieved was studied. The anticipated failure mode was for the membrane to be forced away from the anvil plate upon being retrieved. To study this potential problem, a test cell was assembled. A set of valves was arranged with an accumulator so that the accumulator volume could be pressurized, then isolated from the compressor. The contents of the accumulator could be added to the test cell by opening a second valve. The test chamber pressure could be raised at a rate controlled by the valve cycling. A similar technique was used to lower the test chamber pressure. The maximum pressure for the test chamber was limited to 65 psig. It was determined that for the maximum operating speed for the winch that the membrane seal was adequate.

Instrument Deployment System

The probe is operated in the well using a winch supported by a tripod-mounted block. The laptop-controlled winch (22 kg not including cable, 10.4 (w) x 18.3 (l) x 14.5 (h) inch footprint) can be programmed for automated delivery and retrieval of the probe. The winch is battery operated and capable of raising and lowering the probe at speeds up to 12 ft/min. The winch also contains an integrated depth wheel with visual display.

For this application, the winch required calibration for the 1/10-inch Teflon coated cable. Calibration was performed by dropping a dummy probe down a 69-foot stairwell in the K-1 building at the Global Research Center. The actual distances dropped and the distances estimated by the winch were noted as the probe was lowered to each floor. A univariate calibration curve was generated to convert winch distance units into actual units ($y = 0.9863x - 0.0982$). A plot of the winch units vs. distance used to build this calibration curve is shown in Figure 36. The calibration curve had an R^2 value of 1.0. Both winches were found to have the same calibration curve.

Figure 36. Calibration curve for the winch. The x-axis is the distance as measured by a tape measure. The y-axis is the units listed on the display of the winch.

In addition to overall depth it was also necessary to calibrate the winches for the rate. This was done by measuring the rate at several winch setting and creating a univariate calibration curve as shown in Figure 37.

Communication/Recharging Station

Wireless communication with the probe is accomplished at the wellhead using an induction link. The induction link consists of a base station and a probe section as shown in Figure 38. The base station is used to provide power for battery charging and to provide a two-way communications link with the probe. A standard serial data interface is provided as another option for communication. For the prototype unit, the data rate was limited to 110 baud operation via the induction link versus 9600 baud for direct serial connection. The induction link was used to determine the probe's operating status and to initiate data collection during field tests. No direct electrical connection (e.g., via a tether cable) is required to service the probe. This feature allows the probe to remain sealed – simplifying decontamination and decreasing the likelihood of leaks occurring at critical seal points.

Figure 37. Calibration curve for winch delivery rate. The x-axis is the speed setting on the winch. The y-axis is the rate in units of Feet/Min.

The base station is connected to a power source and a control computer (i.e., a laptop computer). The station is torus-shaped allowing passage of the probe through its center. The probe is positioned by the winch in such a way as to link the onboard coil with the wellhead station coil. This point is located a few inches below the drawbar at the top of the probe. The wellhead station is capable of sensing and indicating contact with the probe. Once, the communication path has been established, battery charging begins. Simultaneously, command and data information can be passed over the link to upload data and download a new measurement schedule. The operational status of the probe can be determined using diagnostic commands entered over the link.

Figure 38. Photograph of induction link system.

The induction link consists of a pair of coupled coils. One coil is internal to the probe; the second coil is external to the probe. The coupled coils act as a transformer to accomplish the two-way (duplex) transfer of data and the one-way transfer of power. Positioning the probe coil within the external coil provides an electrical pathway from the external base station to the probe. Flux lines that mutually link the two coils provide the pathway.

A transmitter is built into the base station. The transmitter frequency is automatically adjusted to match the resonant frequency of the coupled coils. Operating at resonance maximizes the energy transfer across the link. While charging the batteries, the unmodulated transmitter output is linked to the receiver coil in the probe. The ac voltage induced in the receiver coil is rectified and applied to the battery. A 200 milliamperere charging current is available to the battery. Near full charge (as indicated by the battery terminal voltage), the charging current is reduced to a “trickle” charge level.

To communicate between the base station and the probe, the amplitude of the transmitted signal is changed (modulated). The receiving coil and detector circuits in the probe demodulate changes in the signal level. Serial data can be communicated to the probe by modulating the transmitted signal.

To send data from the probe to the base station, the coil current is monitored in the base station while the probe changes the receiving coil impedance by switching a fixed load in and out of the circuit. The base station senses the change in coil current at the transmitter to demodulate the serial message from the probe. The induction link operates at a nominal frequency of 100 kHz.

Proper positioning of the coil produces a maximum in the coil coupling. The linear positioning range of the coil is about 1.5 inches for good communications. The probe communicates using standard ASCII characters. A terminal emulator (e.g., Hyperterminal) may be used to communicate with the probe. Custom software (written in QuickBASIC 4.5) has also been used to interface the probe.

DFSS Subsystem Optimization

During the construction of the sensor probe subsystems, system level optimization was performed. The primary focus of this optimization was on decreasing the detection limit of the system for mixtures of TCE and PCE. To enable this study, the transfer function (i.e., model) used to predict detection limit in the coatings selection study was utilized. This transfer function makes use of the Sauerbrey equation and requires the partition coefficients from the coatings suite, coating thickness, and the density to estimate the frequency shifts for sensors in the array at a given analyte concentration. From the estimated frequency shift and a noise estimate the detection limit can be determined.

Simulation studies were done first to understand the relationships among the factors impacting detection limit. Figure 39 shows the result of those simulations. This figure illustrates that in order to meet the detection limit goal the sensor array must have both a good array of coatings and low noise sensor /electronics.

Figure 39. Simulation results showing the effect of partition coefficient and noise on the predicted detection for a polymer-coated acoustic wave sensor. The dashed line indicates the target detection limit of 5 ppbw.

Prior to finalizing construction and assembly of the prototype an assessment of the overall performance of the system was conducted. This was performed using values for noise, partition coefficient, thickness, and density taken from experimental measurements. The average short-term (1 hour) baseline noise of a 150 KHz thickness coated crystal was 0.35 Hz as measured in an environmental chamber for an overnight stability run. A density of 1 was used as a compromise value since it is near the mid-point of the range spanned by commonly used polymers. For example, Siltem has a density of 1.18, while polyisobutylene (PIB) has a density 0.92. The multivariate sensitivity for the best coatings suite (F/E/D) was 3.45 (logarithmic units) for a TCE as the analyte and PCE as the interfering species. The sensitivity for a single-component solution of TCE is 4.2 (logarithmic units). Based on these values, the predicted detection for TCE in the presence of PCE is 6.25 ppbw and 1.1 ppbw for TCE only. Improvement to the system will require reducing the noise level to less than 0.3 Hz in order to achieve the target detection. Based upon this data, full construction and assembly of the sensor probe is warranted.

RESULTS AND DISCUSSION

Laboratory Testing

Sensor Probe Configuration

A total of three sensor probes were constructed for testing. For laboratory testing, only one of the three sensor probes was available for use (Probe #2). Probes 1 and 3 were used in field-testing because they had the additional memory card for long-term data storage. Due to electronic failures, only Probe #1 was operational in the field and all field-testing data was obtained using that probe.

The sensor arrays contained 8 TSM devices. Seven of the sensors were 10 MHz TSM devices while the remaining sensor was a 7.158 MHz temperature sensor (sensor #1 in each probe). Six of the 10MHz crystals were coated with different sorbent polymer films via the dip coating procedure to a nominal thickness of 100-150 KHz. The remaining crystal was left uncoated and sealed. Table 6 lists the configuration of the 3 sensor probes indicating the thickness of the coatings (in KHz) and sensor material used in each probe. The naming scheme for the coatings is the same as those used earlier in Table 4.

Table 6. Configuration of Sensor Probes for Laboratory and Field Testing

Sensor #	Probe 1	Probe 2	Probe 3
1	Temperature	Temperature	Temperature
2	D (165)	E (148)	D (115)
3	D (191)	F(184)	D (110)
4	E (137)	D (70)	E (156)
5	E (183)	D (100)	E (153)
6	Uncoated	Uncoated	Uncoated
7	F (132)	H (125)	F (172)
8	F (108)	D (112)	F (167)

Data Acquisition

Laboratory testing was conducted in an environmental chamber set at 20°C. The temperature stability of the chamber was approximately +/- 0.5°C. The sensor probe sits inside the environmental chamber area. A serial cable is used to connect the laptop computer with the sensor probe. Power to the sensor probe is provided via a standard electrical outlet inside the environmental chamber. A custom written Quickbasic 4.5 program (GETST8A.bas) was written to provide

data collection and storage. This program acquires a complete set of IFM responses (4 per sensor channel) and records the outputs from the environmental sensors every ~39 seconds. The collected data is saved in a text file and saved to a laptop computer for subsequent analysis.

An Excel macro was written to convert the raw IFM sensor outputs into frequency by choosing one of the two outputs that has a linear response. IFM outputs closest to 0 fall within the linear portion of the IFM response. For the Phase I prototype the selection of the appropriate IFM output is done by hand, but the process will be automated in subsequent versions of the prototype. Subtracting the frequency of the uncoated reference crystal from the coated crystal being analyzed corrects for drift and other noise sources. The resulting product is the corrected data used for laboratory testing, chemometric algorithm development, and field-testing. For simplicity, analysis and field data was performed only two of the sensors in the array.

Desiccant/Membrane Optimization

To determine the optimal configuration of the sensor probe a two-level, two-factor experimental design was performed. The variables studied were the presence and absence of the membrane and the desiccant material. Each experiment was repeated once as shown in Table 7. TCE gas standards (10 ppm) were used for this study. For each measurement, TCE vapor was introduced into the sensor headspace for up to an hour, followed by a longer period of dry nitrogen purge. For each measurement the signal was calculated as the frequency shift before and after vapor exposure for sensor #2 in the array. The noise was the overnight baseline standard deviation frequency shift. The same noise value was used for all measurements. Using the signal and the noise values, an estimated detection limit for TCE in water using Henry's law at 20°C was done. The detection limit was the y response used in the analysis of the experimental design. Table 7 shows the factor settings of the experimental design and the calculated detection limit. In this table, 1 indicates that the factor was present during that experiment while a 0 indicates that it was absent.

Table 7. Experimental Design

Experiment #	Membrane (yes/no)	Desiccant (yes/no)	Detection Limit (ppbw)
1	1	0	7.9
2	0	0	7.9
3	0	1	8.3
4	1	1	23.8
5	1	0	7.6
6	0	0	7.6
7	0	1	8.9
8	1	1	28.6

Analysis of the data listed in Table 7 revealed an unexpected interaction effect. When desiccant and membrane are used together 50% or more of the TCE response is lost. This can be illustrated graphically in Figure 40, which shows an interaction plot. The y-axis in each of these plots is detection limit and the x-axes are the presence or absence of that factor. If there were no interaction effect the two lines would be parallel to each other. This data suggests that the desiccant soaks up significant amount of TCE and effectively competes with the sensor for access to the analyte. Based upon these experiments, it was decided that desiccant would not be used for further testing of the Phase I prototypes.

Figure 40. Interaction effect plot.

Calibration

Sensors based on polymer-coated acoustic wave devices need to be calibrated for the analyte of interest in the presence of expected interferences. Because we are unable to control humidity in the field measurement, the sensor must be calibrated for a saturated humidity environment (>90% RH). To mimic the measurement of TCE in a groundwater well, the sensor probe was lowered into a beaker filled to the top with an aqueous calibration standard. To reduce errors caused by evaporation of the TCE from solution, a Teflon coated lid was fitted to the probe and used to seal off the headspace. The Teflon lid area was further sealed with Teflon coated tape. Analyte vapors will permeate across the membrane along with humidity until equilibrium is established inside the headspace of the sensor array. A total of 11 calibration samples were prepared ranging from 0 to 7.3 ppm. Four of these samples were blank (0 ppm TCE).

A subset of the data is shown in Figure 41. In this plot, the x-axis is the time elapsed from the moment the distal tip of the sensor became submerged. The y-axis is the frequency shift sensor #2. In these plots two consistent trends are evident. First, within seconds after being placed in water, the frequency shift changes rapidly. This is caused by the transport of water vapor (humidity) through the membrane. The second observation is that after approximately 15 minutes the frequency continues to change but the rate decreases. Experiments done on optimization of the membrane indicated that water tends to permeate the membrane at a rate much faster than chlorinated solvents. Within 15 minutes the humidity inside the headspace reaches equilibrium (fully saturated). The rate of change seen in the data is proportional to concentration. For example, in Figure 41 the yellow curve is the sensor response to 7.3 ppmw of TCE. It is clear that the slope of the curve starting at approximately 1 hour is larger than the lower concentration samples and is constant. We are exploiting this rate difference as a first level discriminator against water interference and to providing a function to convert frequency shift into concentration of TCE in water. The second level of discrimination is to take advantage of the differences in partition coefficients between the coated polymers as was done in the experimental section to select the polymer materials. The multivariate nature of the sensor was not exploited in the laboratory and field-testing of the Phase I prototype.

Figure 41. Raw sensor data for subset of calibration set.

Chemometrics

For the Phase I prototype, calibration was done using just a single sensor in the array. Using the response curves from the 11 samples a calibration matrix was created. Nine discrete time points were selected from the curve (0, 5, 15, 60, 90, 180, 360, 480, 540 minutes) and were used as input to a stepwise multiple linear regression (MLR) algorithm. From this calibration matrix, a four-term model was chosen as optimal. The terms in the model include the frequency shift at 5 minutes, 90 minutes, 480 minutes, and an offset. Using this model an R^2 of 0.99 was calculated. Figure 42 shows the results of the calibration curve as the actual concentrations versus the model predicted concentrations. The standard error of the model is 0.111 ppmw TCE. The majority of this error comes from one sample that was predicted as 1.4 ppmw but was actually 1 ppmw. There are numerous error sources in preparation of the calibration standards and in placement of the sensor probe in the standard solution so this amount of error is not surprising.

Figure 42. Predicted vs. actual concentrations for the sensor probe tested against TCE in water.

The detection limit for the calibrated probe was computed by using the four blank samples. The average and standard deviation predicted concentration for the four blank samples is 2.2 +/- 2.8 ppbw. One definition of detection limit is the concentration that can be distinguished statistically from the blank samples. Based on this definition the limit of detection is 6.7 ppbw.

Preliminary Field Test

A preliminary field was conducted at the GE Power Systems Schenectady site February 5, 2003. In this field test, the entire AIMS setup was deployed at a groundwater monitoring well (DM-421G). For this well, the water level was at 9.31 feet below the surface and the mid-point of the screened section was 20.2 feet below surface. One of the key findings of this test was that there was a leak in the membrane assembly section causing the probe to fill with water when submerged. The leak caused the coatings to be removed from the sensor and damaged all of the crystals in the array. Subsequent analysis showed that in addition to the lower assembly area the IFM was damaged which rendered all of the sensor data unusable.

Although the TSM sensors failed to work, the environmental sensors were operational. The temperature sensor equilibrated under water at 10°C, which agreed with independent readings made with a YSI temperature probe. Temperature of the well water is a critical parameter in the application of Henry's law. The other promising observation from this test was that the entire system was operational, even in adverse conditions. The air temperature at the site was approximately 24°F with more than a foot of snow on the ground. We found that the winch and tripod were easy to set up and the winch was able to raise and

lower the probe in a two-inch monitoring well containing a passive diffusion-sampling bag.

Following the preliminary field test, the membrane seal section was modified to reduce the leaking problems. To obtain a better seal the raised portion of the membrane assembly was reduced by 0.02 inches. This modification allowed the O-ring to make stronger contact with the back of the membrane. This modification was tested by repeating the experiments at the preliminary field and extensive laboratory testing. The tests confirmed that the modified design is far less prone to leaking than the earlier design.

Field Test

A pilot field test was conducted at the DOE Savannah River Site in two phases as described in the field test plan found in the appendix. The test plan listed a total of 8 wells available for testing. However, due to electronic problems with the probe, the system was only deployed in only three wells and data collected from just two of them. The characteristics of the 3 wells tested at SRS are shown in Table 8.

Table 8. Well Characteristics

Well ID	Water column (ft) ^a	Mid-Point Screen (ft) ^b	Screen Length (ft) ^c	Size (in) ^d	TCE Conc. [ppb] ^e
MSB87B	47	164	5.0	2	< 1
MSB32B	83	125	5.0	2	< 1
ASB8C	30	164	5.6	4	163.5

^a total amount (depth) of water in the well

^b distance between the top of the well head and the mid-point of the screened section of the well.

^c length of the screened section in the well.

^d diameter of the well casing (inches)

^e concentration of TCE in the well measured using passive bag and off-site laboratory analysis or historical values

The setup of the AIMS system is straightforward and is detailed in the test plan in the appendix. A brief description will be given here for completeness. The main components of the system are the (a) sensor probe, (b) instrument delivery system, and (c) communication/recharging station. Once at the site, setup involves unpacking and assembling the winch and its battery pack (Figure 43). Next the tripod is assembled and placed directly above the well to sampled. Site setup takes about 10-30 minutes depending weather conditions and the terrain. To initialize data collection on the probe, the induction link is used to establish communication with the probe via the laptop. This can be done either on the tripod or in a vehicle located near the well (for example see Figure 44). Once

data collection has been started the probe is attached to the winch cable and placed inside the well as shown in Figure 45. The winch is used to lower the probe to the mid-point of the screen and is returned after 6-8 hours equilibration time. For these tests, the probe was lowered at a rate of 12 (winch units), which corresponds to approximately 2.4 ft/min. It should be possible to drop the probe at much faster rates (e.g., 12 ft/min) without damaging the membrane. Figures 46 and 47 show deployed systems at MSB87B and ASB8C.

Figure 43. Photograph of winch and battery pack.

Figure 44. Photograph of induction link being used to communicate with the sensor probe.

Figure 45. Photograph of the AIMS sensor probe being inserted into a two-inch groundwater monitoring well (MSB87B) on February 28, 2003.

Figure 46. Photograph of the complete AIMS setup at MSB87B while the probe is equilibrating at the mid-point of the screened interval.

Figure 47. Photograph of the AIMS setup at ASB8C on March 20, 2003. In this picture, the probe is being returned to the surface.

There were a few changes made in the field to the protocols described in the test plan due to unforeseen problems with the sensor electronics and communication/recharging station. Laboratory testing revealed that the data downloading via the induction was only capable of transfer rates of 110 baud. To support field testing objectives, the sensor probe was removed from the well after each test, physically disassembled, and a serial connection operating at 9600 baud used to data downloading. Secondly, the wireless recharge was not fast enough to support the objectives of the field test. While the sensor data was downloaded to the laptop, the battery pack was recharged using a hardwire connection to house power. Also due to problems with the electronics on sensor probe #3 and the induction link, only probe #1 collected data downhole.

The first phase ("shake-out test") of the SRS test was initiated February 28. During this test AIMS was tested in two, two-inch ground water monitoring wells (MSB87B and MSB32B) as listed in Table 9. The winch and tripod were easily assembled at both locations. Sensor probe #3 was lowered into both wells to the mid-point of the screened interval. In both cases no leaks in the membrane area were discovered. However, no sensor data collection was performed due to electronic problems that required repair before the next round of testing.

Table 9. Field Test Schedule (Phase I)

Date	Well ID	Measured Water Level (ft)	Measured Total Depth of Well (ft)
Feb. 28	MSB87B	124.0	171.3
Feb. 28	MSB32B	48.87	133.5

The second phase of the SRS test was initiated March 17. During this test, probe #1 was tested in MSB87B and ASB8C on four consecutive days as shown in Table 10. The sensor probe was lowered in all four wells to the mid-point of the screened interval. In all cases no leaks in the membrane area were discovered. The elapsed times to reach water level and mid-point of the screen were calculated based upon the deployment rate of the probe. The elapsed time at which the probe reaches the water level is critical for field-testing since it indicates the point at which useful data begins. Data collected from the well as the probe is lowered was discarded.

Table 10. Field Test Schedule (Phase II)

Day	Well ID	Measured Water Level (ft)	Start Time	Elapsed Water Level (min)	Elapsed Time Mid-Point Screen (min)
March 18	MSB87B	123.64	09:12	53	71
March 19	MSB87B	N/A	08:36	70	87
March 20	ASB8C	138.08	09:52	63	74
March 21	ASB8C	N/A	08:52	64	74

The temperature sensor in the environmental sensor package provides a convenient tool for tracking the progress of the probe. Accurate measurement of water temperature is also necessary for proper application of Henry's Law. Figure 48 shows the output of the temperature sensor as a function time elapsed from the beginning of data collection. The first 28 minutes includes data collected above ground and just after deploying the probe in the well and is not shown. The four curves represents the four deployments of the probe. In each case, the temperature changed as the probe was dropped down the well, but eventually stabilized. The temperature at which the probe stabilized was 16°C for MSB87B on March 18 and 14°C for MSB87B on March 19 and ASB8C on March 20-21. On March 21, an AIMS probe was deployed simultaneously with an In Situ Mini-Troll temperature probe. The Mini-troll indicated that the water temperature was 18.5 °C. The differences between the two measurements indicate that the AIMS environmental sensors may need to be recalibrated. Despite the offset, the temperature sensor is a pretty reliable tool for tracking the deployment of the probe. The transition from air to water is usually noticeable and in all cases agrees within a few minutes of the times calculated from the deployment rate (Table 10).

Figure 48. Plot of temperature vs. elapsed time for the four wells.

Analysis of the other environmental sensor data was not successful. The humidity sensor indicated that even after submerged under water for more than 6 hours the humidity inside the probe was approximately 30%. At the surface, the humidity sensor indicated values between 20% and 30%, which is not consistent with the weather reports for the test days. The cause of the humidity failure is due to either very poor circulation of the air inside the sensor probe or poor calibration of the humidity sensors. The pressure sensor was not functional either.

Sensor frequency data is acquired and stored once the probe is turned on. To maintain consistency with the laboratory data, only data collected after the probe tip is submerged under water is used. As noted above, the temperature sensor and the calculated elapsed times agree within a few minutes of each other. It is also possible to use the sensor data itself to denote the time when the probe enters water. As discussed in the chemometrics section, water vapor causes a very large, sudden shift in the frequency of a polymer coated crystal. Thus, from the sensor data it is easy to find the exact moment the sensor becomes submerged. This latter method was used for analysis of all field data.

One of the goals of the field testing was to determine if the calibration curve collected on the laboratory data could be used to predict the concentration of TCE in the field data. To provide the most accurate reference value for

comparison a passive diffusion bag (PDB) was deployed in ASB8C on March 3, 2003. The PDB was placed in the well approximately 165 feet below the surface or about 1 foot below the mid-point of the screened interval. The PDB was removed from the well on March 21 after the last deployment of the sensor probe. As described in the test plan, duplicate samples were collected and submitted for off-site laboratory analysis. The laboratory results indicated that this well contained 163.5 ppbw (average of the two duplicate samples) of TCE. No other contaminants were found above 10 ppbw.

Figures 49 and 50 are the processed data from two of the polymer-coated sensors in the array (#2 and #4). The y-axis is the sensor frequency shift relative to the first data point. The x-axis is the time relative to the point in which data analysis is initiated. Two different wells (ASB8C and MSB87B) were sampled twice each on consecutive days. ASB8C contains 163 ppbw of TCE, while MSB8C is a “clean” well. This data indicates that there is good day-to-day reproducibility in the sensor responses and that there are significant differences in the responses between the two wells. However, when the data is applied to our existing TCE calibration curve the concentration is estimated to be 0 ppb. Visual inspection of the data reveals why the concentration is predicted the same for all measurements. If we refer to Figure 41 and the discussion in the chemometrics section, it was noted that the concentration of the TCE was proportional to the slope of the response curve after about an hour. Thus, the multivariate calibration model uses data points at 5 min, 90 min, and 480 min to pull out slope information. The field data has the same initial large change that occurs within the first 15 minutes but then levels off until the probe is removed from the well. Thus, the field data appear to be similar to the laboratory blank samples and it is not surprising that the calibration model predicts them near 0. The data is also noisier than the laboratory data indicating the need for better thermal management of the IFM or advanced signal processing strategies to compensate for the variation.

Because the induction link system failed before we could proceed to a higher concentration well it is unknown whether the differences that were found between the data for the two wells was due to concentration effects or some other physical difference (size, depth, etc). Additional field data is necessary to establish a stronger correlation. Once the factors affecting the field response are determined, laboratory protocols can be developed to conduct experiments that mimic the conditions seen in the field.

Figure 49. Processed data from sensor #4 collected during deployments in two wells (ASB8C and MSB87B) at the SRS field test. This data is relative to the time in which the sensor probe is under water.

Figure 50. Processed data from sensor #2 collected during deployments in two wells (ASB8C and MSB87B) at the SRS field test. This data is relative to the time in which the sensor probe is under water.

CONCLUSIONS

This report describes the Phase I effort to develop an automated system for making *in situ* measurements of chlorinated volatile organic compounds (CVOCs) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) in groundwater. The Phase I project objectives were to (A) adapt GE's sensor array technology to meet DOE needs; (B) integrate the sensor probe into an in-well monitoring system; and (C) demonstrate system capabilities during a pilot field test. The target applications for this technology include long-term monitoring (LTM) and rapid site characterization.

The sensor probe utilizes an array of thickness shear mode (TSM) sensors coated with proprietary sorbent polymer films. To meet these objectives, high throughput screening tools and advanced chemometric methods were used to discover new sorbent polymer films and from the pool of available materials down-select to the optimal combination based upon detection of TCE in the presence of anticipated interferences such as PCE, DCE, chloroform, carbon tetrachloride, and toluene. The best 6-sensor array combination utilizing 3 different materials resulted in a 23% improvement in the multivariate partition coefficient for TCE compared to arrays of commercial materials. These new sensor materials enable detection and speciation of two and three component mixtures of CVOCs below the MCL (minimal concentration level) if noise levels in the probe can be reduced to previous benchmark values. A novel frequency measurement technique (instantaneous frequency measurement or IFM) was developed to reduce the size requirements of the sensor electronics. The short-term noise (1 hr) of the IFM was 0.35 Hz when used to measure the frequency of an 8 mm, 10 MHz TSM device coated with sorbent material. Long-term noise sources such as drift were greatly reduced by encasing the IFM in sand to increase its thermal time constant. The final sensor prototype was only 1.5 inches in diameter, enabling it to operate in 2-inch or larger groundwater monitoring wells. Design for Six Sigma (DFSS) tools were used to optimize the overall system design of the sensor probe to meet many of the user-specified criteria (e.g., detection limit, size, response time, etc.).

Once the sensor probes were constructed, laboratory testing was conducted to further optimize system performance and to assess capability. An experimental design concluded that putting desiccant in the headspace was detrimental to sensor response. Without desiccant in the headspace, humidity becomes a major source of variation. A unique calibration strategy was devised to overcome this interference by taking advantage of the differing diffusion rates between CVOCs and water. The frequency shifts at 5, 90, and 480 minutes after the probe was submerged in the aqueous sample was used to create a calibration curve for TCE. Using multivariate linear regression on the 11 samples collected, a correlation coefficient of 0.99 for a plot of the predicted concentrations vs. the actual concentrations was obtained. Using a series of blank standards, the

detection limit of the sensor probe was estimated to be 6.7 ppb ($\mu\text{g/L}$) for TCE in water.

To support the sensor probe during field-testing, an instrument delivery system and a communication/recharging station were also constructed. The instrument delivery system can be used to position the sensor probe in 2 inch or larger groundwater monitoring wells. A commercially available winch system was obtained and calibrated for use with 1/10 inch Teflon coated cable. A communication/recharging station was used to provide wireless battery recharging and communication to enable a fully automated system.

A preliminary field test was conducted at a GE remediation site and a pilot field test was performed at the DOE Savannah River Site (SRS). The preliminary field test uncovered problems with the membrane seal that caused the system to leak and fill with water when submerged for extended periods of time. This problem was fixed by redesigning the membrane assembly to obtain better contact with an O-ring. At SRS, the system was demonstrated in an uncontaminated (i.e., "clean") 2-inch well and in a 4-inch well containing with 163.5 ppb of TCE. Repeat measurements at the two wells indicated excellent day-to-day reproducibility. Significant differences in the sensor responses were noted between the two types of wells but they did not match the laboratory calibration data. The robustness of the system presented numerous challenges for fieldwork and limited the scope of the SRS pilot field test. However, the unique combination of trace detection and size warrants continued development of the technology. To the best of our knowledge this field test marks the first ever deployment of an acoustic wave sensor array inside a two-inch groundwater monitoring well.

The lessons learned from the pilot field demonstration at SRS also provided an opportunity to assess the state of the technology and to establish options to improve upon the existing design. The induction link system used for recharging and communication proved too cumbersome in the field. In fact, the failure of this critical component caused us to end the SRS pilot test prematurely. Even if a robust component were constructed, field testing requires flexibility and the induction link is more suitable for a commercial product in which the user does not require immediate access to raw data and can wait hours in order to download data and/or recharge the battery packs. For many applications, the ability to make multiple measurements during a single mission is not necessary. Thus, the piston and absorber canister were never tested and are not required for a useful product. These components add an additional two feet to the length of the sensor probe. The other component that adds significant length to the sensor probe is the battery pack, which measures nearly 3 feet in length. It is possible to solve all of these design issues if a vented cable is used. Real-time data access and power can be provided from the surface using the same instrument delivery system. The ability to monitor the status of the probe as it is positioned in the well would provide much needed feedback during field-testing.

In addition the vented cable can be used to bring a clean volume of air to the probe to enable multiple measurements during a mission and to help regulate humidity and temperature levels inside the probe. Removing the battery pack, system purge, and desiccant storage area would cut the overall length of the probe to approximately two feet which would increase portability and flexibility. Alternative designs have also been envisioned for humidity control such as Nafion tubing.

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LIST OF ACRONYMS AND ABBREVIATIONS

AIMS	Automated In-Well Monitoring System
cis-DCE	Cis-dichloroethylene
CLF	Chloroform
CTC	Carbon tetrachloride
CVOC	Chlorinated volatile organic compounds
DCE	Cis-Dichloroethylene
DNAPL	Dense non-aqueous phase liquid
DFSS	Design for Six Sigma Methodology
DOE	Department of Energy
GEGRC	GE Global Research Center
GC-MS	Gas chromatography-mass spectrometry
GUI	Graphical user interface
HTS	High throughput screening
IDW	Investigative derived waste
IFM	Instantaneous Frequency Measurement
KHz	Kilo-hertz
LTM	Long Term Monitoring
LOD	Limits of detection
MCL	Minimum concentration level
MHz	Mega-hertz
MIP	Membrane Interface Probe
MLR	Multi-linear regression
MNA	Monitored natural attenuation
MOS	Metal oxide sensor
NAS	Net analyte signal
PCA	Principal component analysis
PCE	Tetrachloroethylene
PDB	Passive diffusion bag
ppb	Parts per billion ($\mu\text{g/L}$)
ppm	Parts per million (mg/L)
ppbw	Parts per billion in water
PAWS	Portable acoustic wave sensor
PLL	Phase locked loop
PTFE	Polytetrafluoroethylene
QCM	Quartz crystal microbalances
RH	Relative humidity
SEL	Selectivity
SEN	Sensitivity
TCE	Trichloroethylene
TOL	Toluene
TSM	Thickness shear mode
SRS	Savannah River Site
UHF	Ultra High Frequency
VCO	Voltage controlled oscillator
VOC	Volatile organic compounds

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APPENDIX 1. TEST PLAN.

FIELD TEST PLAN

February 11, 2002

GE/Nomadics In-Well Monitoring System
for Vertical Profiling of DNAPL Contaminants

Work Performed Under Contract:
DE-AC26-01NT41188

Submitted By:
GE Global Research
P.O. Box 8
Schenectady, NY, 12301

Program Manager: Joseph J. Salvo
Phone Number: 518-387-6123
FAX Number: 518-387-7611
E-Mail: salvo@crd.ge.com

Principal Investigator: Ronald E. Shaffer
Phone Number: 518-387-4344
Fax Number: 518-387-7611
E-Mail: shaffer@crd.ge.com

Submitted To:
U. S. Department of Energy
National Energy Technology Laboratory
COR: Karen L. Cohen
E-Mail: cohen@netl.doe.gov

A. Project Description

Overview

An automated in-well monitoring system (AIMS) has been developed to characterize dissolved- and vapor-phase DNAPL (dense non-aqueous phase liquid) contaminants in the groundwater. The monitoring system takes advantage of low-cost chemical sensor array technology developed by researchers at GE Global Research Center for long-term monitoring of environmental contaminants in groundwater wells. GE has teamed with Nomadics Inc., who will provide engineering design support, prototyping and commercialization of the automated in-well monitoring system.

The contract with DOE NETL consists of ten tasks occurring in two phases. Phase I consists of project planning, test site selection, advanced engineering design work necessary to modify and integrate existing sensor technologies at GE and Nomadics, and a pilot field test at a selected DOE site. Phase II is optional and consists of activities leading to, and execution of, a large-scale demonstration of the GE/Nomadics in-well monitoring system at a selected DOE site.

Phase I Demonstration Site

In conjunction with DOE NETL, the DOE Savannah River Site (SRS) was chosen as the Phase I demonstration facility. Like a number of DOE and industrial remediation sites, SRS has numerous ground water monitoring wells requiring quarterly sampling and off-site laboratory analysis. According to the SRS site need statements SR00-3027, SR01-3029, and SR02-3029, long-term monitoring (LTM) of closed waste units will have significant future costs due to regulatory requirements for extended compliance monitoring. Using baseline technology, LTM will require expensive and time consuming field sampling and laboratory analysis. It was also noted that establishment of *in situ* remote monitoring methods will enable data to be collected more often and at substantial cost savings. In addition SR00-3021 describes the need for alternative sample collection and well installation technology that eliminates or significantly reduces aqueous or non-aqueous investigative derived waste (IDW). It was noted that the ground water sampling program at SRS involves about 10,000 samples per year and that IDW management is major task for the site.

One of the most prevalent classes of contaminants present in the ground water at SRS are dissolved volatile organic compounds (VOC). For a number of years, the waste handling practices at SRS often consisted of disposing of waste organic solvents directly into unlined pits and trenches, which resulted in extensive subsurface groundwater contamination. The two primary contaminants of concern are trichloroethylene (TCE) and

perchloroethylene (PCE), which range in concentrations in the various ground water monitoring wells across the site from a few ppb to the lower ppm. Dissolved-phase DNAPLs such as TCE and PCE are also commonly encountered at DOD, NASA, and many of the nations environmental superfund sites.

The need for LTM is becoming increasingly important because of the trend towards acceptance of monitored natural attenuation (MNA). MNA applies passive or natural remediation processes to an existing chlorinated VOC plume. The reductive dehalogenation process of chlorinated ethenes results in the breakdown of PCE and TCE into daughter products such as Cis 1,2, dichloroethylene (DCE) and vinyl chloride (VC). In a typical application, LTM is required for a minimum of 5 years, but is more likely to occur for 30 years or longer. A typical LTM program for MNA would be very expensive to operate using the baseline field sampling and off-site laboratory analysis. Traditional LTM techniques require semi-annual or quarterly sampling. The average cost for sampling and analysis has been estimated as approximately \$3000 per sample for a comprehensive suite of constituents (SR02-3029). Even for a smaller subset of analytes the analysis can run as much as \$500 per sample [1]. SRS has \$365M allocated for the 30-year LTM life-cycle. This cost can be significantly reduced using an *in situ* measurement system such as the one described in this test plan.

The AIMS system directly addresses some of the major technology concerns at SRS and many other government/industry environmental remediation sites. AIMS provides a cost-effective long-term monitoring or rapid site characterization strategy. The field test at SRS is critical to assess the capability of AIMS and provide a faster pathway toward product commercialization.

SRS Field Test Locations

Within the SRS complex, the field test will be restricted to ground water monitoring wells at two general locations. Figure 1 is a map illustrating the areas within the SRS complex with known groundwater contamination problems. A total of 8 ground water monitoring wells will be visited during the field test. Five of these wells are located in the A/M area and the other three are located in the TNX area. Figure 2 contains detailed maps of the TNX and A/M areas showing the location of the 8 individual wells. A full discussion of the characteristics is given later in the experimental design section. As noted above, SRS has general needs for LTM and rapid characterization of CVOCs in groundwater. However, these two locations were chosen because of the large CVOC plumes that are currently undergoing quarterly monitoring and proximity to remediation activities. These two areas also provide a large diversity of well monitoring

conditions (CVOC concentrations, co-contaminants, depths) necessary for meeting the objectives of the field test.

Figure 1. Map

Figure 2. (A) A/M area. (B) TNX area.

The TNX area is located near the southwestern quadrant of the site, approximately 0.25 miles east of the Savannah River. It is an industrial facility where pilot-scale testing and evaluation of chemical processes took place. Contamination resulted from the use of unlined seepage basins to dispose of wastewater, leakage from a network of process sewers, and leachate from various activities in the area. The TNX area groundwater is contaminated with chlorinated CVOCs, primarily TCE, PCE, and carbon tetrachloride. The CVOC plume covers eight acres and has a minimum thickness of 20 feet. Groundwater characterization indicates that contamination is limited to the shallow water table aquifer. According to the SRS web site, an interim record of decision was approved in 1994 for the clean up of the TNX area. A pump and treat system was installed to treat and inhibit further migration of the 500 ppb dissolved VOC plume.

The A/M area occupies 350 acres in the northern section of the site, approximately 1 mile from the SRS boundary. The area contains facilities used for the manufacture of reactor fuel and target assemblies, support services, laboratories and administration. During the operation of the manufacturing facilities (1950s-1980s), industrial chlorinated solvents, primarily TCE and PCE, were used in several stages of the fabrication process to degrease fuel assemblies. Wastewater from those operations flowed into the M-area settling basis and Lost Lake. The M-area settling basin is an unlined, man-made depression. Monitoring wells installed in 1981 showed that half of the solvents from the basin had seeped into the water table contaminating the groundwater. The A/M area groundwater cleanup program was started in 1983. Today an extensive network of groundwater wells consisting of over 400 wells is present throughout the A/M areas.

B. Technology Description

Overview

The automated in-well monitoring system (AIMS) consists of 3 primary components: (a) sensor probe, (b) instrument delivery system, and (c) communication/recharging station. An overview of the operation of the system is shown in Figure 3. The instrument delivery system consists of a winch to automatically lower and raise the probe at a specified rate to a predetermined depth below the surface. A tripod is used to keep the winch above the wellhead and make it easier to take the probe in and out of the well. The sensor probe contains the chemical sensor and accessories (battery, sampling handling, etc) to enable operation for extended periods of time in difficult to access environments. The communication/recharging station is positioned at the wellhead to provide wireless debriefing and recharging of the batteries on the sensor probe.

The communication station is also linked to a laptop PC for final data analysis and display.

Operational Concept

The operation of the AIMS system can also be described using Figure 3. Using the instrument delivery system, the sensor probe is positioned to predetermined depths (< 110 m) below the water table inside an existing groundwater monitoring well (2 inch diameter or larger). For this field test the sensor probe will be positioned near the mid-point of the screened interval of the monitoring well. The distal end of the probe (bottom) contains a semi-permeable membrane. As organic vapors cross the membrane into the sensor headspace they are detected. The sensor data are stored on-board the probe and retrieved only during the data debriefing portion of the mission. Once a measurement has been made, the sensor probe will undergo a self-cleaning or scrubbing cycle to remove organic vapors from the headspace. After sampling a predetermined number of depths, the sensor probe will be returned to the surface for data debriefing and battery regeneration. The on-board data logging system will begin debriefing once it is within the range of the receiver located at the well cap. After data debriefing, the battery used to operate the sensor probe will be recharged wirelessly. While the recharging is being completed the sensor data transferred from the probe to a laptop PC for detailed analysis and visualization.

Figure 3. Automated In-Well Monitoring System Concept

Sensor Probe Details

The sensor probe is a self-contained system capable of operation in difficult to access environments such as 2-inch or larger groundwater monitoring wells. Figure 4 shows photographs of the sensor probe (minus the battery pack and wireless communication package) assembled (A) and unassembled (B). The key subsystems in the probe are the: sample introduction, thickness shear mode (TSM) sensor array, sensor oscillator electronics, system purge, frequency measurement device, and data logging electronics.

Figure 4. Photographs of sensor probe.

The sample introduction subsystem consists of a semipermeable, hydrophobic membrane, a desiccant chamber, and small open chamber or sensor headspace. Membranes made of poly(tetrafluorethylene) (PTFE) are available commercially from W.L. Gore and Associates (www.gore.com). The outer face of the membrane is in direct contact with the groundwater to be sampled. Analyte is introduced into the probe by diffusion through the membrane. The membrane also serves to exclude water, which could damage the sensor electronics. Both Ho et al and Schabron et al have described a similar concept for creating an artificial headspace and for protection of sensor electronics [2,3]. PTFE membranes have been shown to provide mechanical integrity and favorable analyte transport properties [2,3]. A thin, porous metal disk is placed directly behind the membrane to help provide additional mechanical strength. Immediately above the membrane is a section containing silica gel desiccant beads. The desiccant beads serve to soak up water vapor, which acts as an interfering species in the chemical sensor measurement. The detection limit and speciation capability of the sensor array is optimized when the humidity levels have minimal variation [4-6]. The entire membrane and desiccant section can be changed quickly in the field by replacing the entire lower assembly which is held in place by three screws and slid over the electronics and TSM sensor array assemblies.

Using the sample introduction section described above, an artificial headspace is created. Henry's law states that the partial pressure or concentration of a volatile component in the headspace (P) is proportional to its concentration in aqueous solution (C) through H, which is Henry's law constant.

$$P = H \times C \quad (1)$$

This equation is used to convert the concentration detected in the vapor phase (e.g., ppmv) to the concentration of the VOC in the aqueous phase

(e.g., ppmw). The assumption used in this work is that the Henry's law coefficients can be corrected for the temperature of the aqueous phase and that variation with concentration is minimal. Table 1 contains Henry's Law coefficients for common VOCs at 25°C. It should be noted that there is often wide variation in the Henry's law coefficients reported in the literature. We plan to use coefficients that match best with the experimental laboratory work done with the sensor probe.

Table 1. Henry's Law Coefficients for common CVOCs

Compound	<i>H</i> (ppmw/ppmw) 25 °C
Trichloroethylene	88.8
Tetrachloroethylene	162
Methylene Chloride	29.2
Chloroform	33.0
Vinyl Chloride	11,000
Carbon tetrachloride	148
Toluene	69.0
Trans 1,2 dichloroethylene	57.4

Source: J.F. Schabron, J.F. Rovani, D.F. Moore, Chemical Sensor And Field Screening Technology Development: Downhole Photoionization Detection of Volatile Organic Compounds, Topical Report 1995-1996, DOE Contract No. DE-FC21-93MC30127, DOE/MC30127-5787.

Directly above the sample introduction section is the TSM sensor array and associated electronics. The TSM sensor array consists of eight 10MHz TSM devices (also know as quartz crystal microbalances) [7-10]. Some of the TSM devices are used for temperature and electronic drift compensation, while the remaining devices contain GE proprietary polymer coatings on them [7]. Analyte vapors residing in the sensor headspace are sorbed into the polymer films and are detected by the TSM devices as a change in their oscillating frequency. The change in the oscillating frequency is inversely proportional to the concentration of the analyte in the headspace. Each TSM sensor contains a slightly different polymer film, which are partially selective toward TCE and PCE. Each TSM device has its own oscillator, which has been optimized for minimal drift, noise, and power consumption. To further compensate for potential noise sources the sensor probe also contains temperature, humidity, and pressure sensors. Near the top of the probe, just below the battery section, the rest of the sensor electronics is located. Two wires connect the oscillator output to a frequency-measuring device. The output of the frequency measurement device is collected by an on-board ATMEL processor, which provides both data handling and data storage capabilities.

Integral to the unattended probe operation is the ability to refresh the sensor array. At the end of a measurement cycle, the headspace volume is quickly replaced with clean gas by a positive displacement pump. Clean gas is obtained by passing gas from the headspace volume through an absorber bed contained in the pump. The pump is operated electrically by a small stepper motor located in a sealed compartment at the top of the assembly. The number of strokes and the stroking rate can be regulated by the microcontroller. Gas from the headspace volume is input to the pump by a tube opening below the crystal locations. Gas is returned to the headspace by a second tube, concentric to the input tube, opening near the crystal sockets at the top of the headspace to promote adequate mixing during the purification process. Operation of the purification pump continues until the sensors return to baseline conditions.

The power supply for the probe consists of an onboard, rechargeable Ni-Cd battery pack. The pack is maintained by an inductively coupled communications and battery charger – no direct electrical connection to the probe is required for data communications or battery charging. The probe electronics is capable of entering low power modes during transit to the measurement sites. Power for uploading data at the wellhead is provided by the charging system.

Instrument Delivery System Details

The probe is operated in the well using a winch supported by a tripod-mounted block. The laptop-controlled winch (22 kg not including cable, 10.4 (w) x 18.3 (l) x 14.5 (h) inch footprint) will be programmed for automated delivery and retrieval of the probe. The winch is battery operated and cable of raising and lowering the probe at 1.6 - 49 ft/min. The winch also contains an integrated depth wheel with visual display. A wellhead station is provided for accessing the probe for communications and battery maintenance. The operator establishes a communications link with the probe using the wellhead station and a control computer (e.g., a ruggedized laptop computer). A measurement schedule is downloaded to the probe indicating the time and measurement configuration for each test. The operator uses the winch to position the probe for each scheduled test. At the conclusion of the test sequence, the probe is returned to the surface. A communications link is established with the probe using the wellhead station. Data is uploaded from the probe while battery charging is performed.

Communication and Recharging Station Details

Communication with the probe is accomplished at the wellhead using an induction link. The link also serves to provide power to the battery for recharging. No direct electrical connection is required to service the

probe. This feature allows the probe to remain sealed – simplifying decontamination and providing a more environmentally impervious solution.

The wellhead station is connected to a power source and a control computer (i.e., a laptop computer). The station is torus-shaped allowing passage of the probe through its center. The probe is positioned by the winch in such a way as to link the onboard coil with the wellhead station coil. This point is located a few inches below the drawbar at the top of the probe. The wellhead station is capable of sensing and indicating contact with the probe. Once, the communication path has been established, battery charging begins. Simultaneously, command and data information can be passed over the link to upload data and download a new measurement schedule. The operational status of the probe can be determined using diagnostic commands entered over the link.

Measurement Sequence (“Mission”)

To use the sensor probe to make a measurements *in situ* the project leader must define a “mission” for that particular experiment. A mission is a set of instructions for the probe and instrument delivery system. Since the two systems cannot communicate with each other and there is no means of communicating with the probe once it leaves the base station, all steps in the process are based upon elapsed time from the beginning of the experiment. Key variables in the mission include the depth of the well, speed of descent/ascent, and number of replicate measurements. The mission profile is downloaded to the probe and the PC controlling the instrument deployment system. This mission is then executed and the probe returns back to the base position.

The key steps in the mission (measurement sequence) are outlined below.

1. Mission begins with a completely charged sensor probe at the well head (base position). The elapsed time is synchronized with the time in which the mission was downloaded to the probe.
2. Sensor probe is put in sleep mode.
3. Sensor Probe is rapidly lowered down the well at a pre-programmed rate until it reaches the water surface.
4. Once the probe reaches the water surface the instrument delivery system slows the rate of descent. A slow rate is chosen to minimize well disturbance and to allow pressure equilibration to occur at the membrane.
5. The probe is stopped near the mid-point of the screened interval and allowed to equilibrate for 4-8 hours.
6. Data acquisition on the probe begins.

7. The system purge is operated to remove any VOC vapors in the headspace of the sensor probe.
8. The probe is allowed to equilibrate for 2-4 hours. Analyte vapors permeate across the membrane and eventually reach equilibrium concentration inside the sensor headspace.
9. Steps 7 and 8 are repeated a total of 3 times or more times. Once the data collection sequence is finished the sensor probe returns to sleep mode.
10. Instrument delivery system slowly brings the sensor probe to the surface.
11. Once the probe reaches the water surface, it rapidly ascends to the well head.
12. Probe docks at the well head (base position).

Benefits

The baseline method for groundwater monitoring requires manual collection of a sample using either a pump or a sampling device such as a Kabis™ sampler. Once a sample is collected from the well it is typically sent off-site for laboratory analysis. This process can often take up to two weeks before results are returned to the site. The AIMS system provides a fast turn-around, cost-effective method for measuring trace concentration of chlorinated solvents in groundwater. Detection limits and accuracy of the AIMS system is expected to be comparable to that of sample collection and laboratory analysis. Because the AIMS method can be operated autonomously manual intervention is minimal increasing worker safety and decreasing overall labor costs. Similar to other *in situ* detection methods minimal sample handling is required (no well purging necessary) and the only investigative derived waste will occur when the probe is moved from well to well or during routine maintenance.

C. Field Test Objectives

The primary objective of the field test is to validate the performance of the AIMS system in groundwater monitoring wells representative of a large environmental remediation facility. A diverse group of monitoring wells was chosen, including wells of different sizes (2" vs. 4"), TCE concentrations (< 5 ppb to > 1 ppm), concentrations of co-contaminants (0% PCE to 40% PCE), and depths (< 86 ft below the water table). Although the system is capable of vertical well profiling, this capability will not be demonstrated during the field test. Specific objectives for field test are described below.

For each monitoring well, the AIMS sensor probe will be validated against results obtained from the baseline method. The baseline data will be used to assess the performance of the sensor probe for accuracy and speciation of TCE. One of the goals for this project is for the concentration measured by the sensor probe to be within 20% of the concentration measured by the reference method. This assessment can be done on a well-by-well basis and by considering all of the wells as group. For wells in which co-contaminants are present, speciation capability can be validated if the accuracy of the TCE measurement also meets the 20% criterion. Overall, the project will be deemed successful if the TCE concentrations determined *in situ* by the sensor probe are not statistically different from those obtained by the baseline method and from historical well sampling conducted by SRS.

A second objective of the field test is to establish detection limits for the measurement of TCE *in situ* using the AIMS probe. Detection limit, as defined here, is the concentration of TCE that provides a sensor response equal to 3 times the baseline (or background) noise level. The target for this project is to demonstrate a detection limit for TCE less below 5 ppbw, which is the minimum concentration level (MCL) established by the U.S. EPA. Since laboratory detection limits will be established for several common CVOCs during the control testing task, their estimated detection limits can also be calculated.

The diversity of wells selected will also demonstrate the ability to operate in wells of different depths and sizes. Since the width or depth of the well are not expected to impact the ability to provide accurate quantitative analysis of TCE, the test will be deemed successful if the probe is able to mechanically withstand all of the well conditions studied.

This field test will also provide practical knowledge necessary for establishing standard operating practices such as sensor equilibration times and system mobilization and demobilization. This information will be critical for performing cost analysis.

D. Experimental Design and Procedures

A total of 8 monitoring wells were selected for the field test (Table 2). This group was chosen in order to represent the wide diversity of wells found at large environmental remediation sites. Appendix 1 contains additional data from these wells including well water temperatures and concentration profiles.

Table 2. Well Parameters

Well ID	Water column (ft) ^a	Mid-Point Screen (ft) ^b	Screen Length (ft) ^c	Size (in) ^d	TCE Conc. [ppb] ^e	Interferences ^f
MSB87B	47	164	5.0	2	< 1	MC(2/14, 5.3), CM(1/14, 2.3)
MSB32B	83	125	5.0	2	< 1	CM (1/12, 1.4)
TBG5	6	47	20.0	4	1122	CTC (1/12, 0.9), DCE (8/20, 8.6), PCE (1/15, 4.0)
XSB2D	10	61	20.0	4	17.7	CLF (4/12, 1.8)
TNX10D	15	15	20.0	4	11.4	CLF (2/10, 1.2), MC (1/4, 4.1)
ASB8C	30	164	5.6	4	610	MC (2/8, 179), TOL (1/6, 87), PCE (1/8, 1.2)
MSB49B	86	221	5.6	4	130	DCE (16/19, 2.5), PCE (20/20, 73)
MSB31CC	29	170	4.7	4	2956	CTC (2/6, 1.6), CLF (1/6, 0.7), DCE (3/6, 6.5), MC (2/8, 81), PCE (10/10, 2212)

NOTES

^a water column is the amount (depth) of water in the well

^b mid-point screen is the distance between the top of the well head and the mid-point of the screened

^c Screen length is the length of the screened section in the well.

^d diameter of the well casing (inches)

^e average concentration of trichloroethylene (TCE) in the well during 2001-2002.

^f list of major interferences and co-contaminants in each well along with number of 'J' + 'good' detects and the number opportunities and maximum concentration from 1999-2002 [ppb]. Abbreviations are as follows: CTC = Carbon Tetrachloride; CLF = Chloroform; DCE = cis 1,2, - DCE; MC = methylene chloride; CM = Chloromethane; TOL = toluene; PCE = tetrachloroethylene;

Two AIMS will be deployed at the field test and operated concurrently on two wells as described in the schedule (Section K). According to the schedule a total of 3 days has been allotted for conducting a series of experiments at each individual well. To maintain schedule a third probe will be available as a backup if one of the probes should fail. As AIMS is moved from well to well a series of steps must be executed prior to the making the measurement and immediately following the measurement.

These steps in the experimental design are described below and shown graphically in Figure 5.

Figure 5. Flow chart describing the key steps in the experimental design.

Many of the steps shown in Figure 5 are described in greater detail elsewhere in the test plan, but a brief summary will be given here. The first step (Step A) in the experimental design is to deploy the diffusion sampling bag in the well. As discussed in Section F, the diffusion sampling bag will be used to validate the performance of the sensor probe. Step A should be conducted two weeks prior to setup and assembly of the instrument delivery system. During the first week of testing (“shakeout test”), no diffusion bags will be deployed so steps A and N will not be performed.

Steps B-C, J-N, and P-Q involve the mobilization and demobilization of materials and equipment. These steps are elaborated further in Section E. As discussed later in the schedule, steps B and C are estimated to require 0.5 days to complete.

Once the probe is in base position at the well head, the sensor probe is ready to make a measurement. As described earlier, the project leader defines a mission for that particular experiment. The mission profile is downloaded to the probe and the PC controlling the instrument deployment system. This mission is then executed and the probe returns back to the base position. At the base station, data collected from the

probe is sent to the laptop for storage and subsequent analysis and the batteries on the probe are recharged. If necessary, another mission can be downloaded and the process (steps D-H) repeated. According to the schedule, a total of 1.5 days has been allotted at each well to complete these steps in the process.

Once the probe is removed from the well (Step J), the sensor probe measurements are complete and demobilization of equipment should begin. Steps K and L require an iterative decontamination procedure. If the probe and/or cable contain residual VOC it cannot be used until it is clean. Time required to obtain confirmatory analysis of the absence of residual VOC has been factored into the schedule. One final demobilization task is Step Q. After each well, the membrane and desiccant section of the probe will be replaced with fresh materials. Demobilization (including steps L and Q) is described further in section E.

Once all the equipment has been unassembled the diffusion sampling bag can be pulled from the well according to the protocol described in Section F. Step O will be performed off-line on a laptop computer. None of the steps in the design are dependent upon completing this task and will be accomplished during quiet periods in the test plan.

After Step M is finished, at the discretion of the field test project leader, the instrument delivery system can be moved to the next well and prepared for the next set of measurements. However the sensor probe and cable cannot be placed inside the well until steps L and Q have been finished.

E. Site Preparation, Equipment, and Materials

Site preparation requires separate setup of the validation method and the operation of AIMS. SRS staff will prepare the 8 wells in Table 2 for diffusion sampling by unlocking the well caps (or providing keys) and removing all internal well parts. Early in the field test, diffusion sampling bags will be deployed in 6 of the 8 wells to act as a validation method. This process will be further detailed in section F (Sampling and Analysis Plan)

AIMS was designed to be transportable from well to well within a given site so the setup of the test equipment is straightforward. Site preparation (steps B and C in Figure 5) involves a number of steps. The instrument delivery system requires assembly of the tripod. The winch with Teflon coated cable attaches to the tripod. The sensor probe is physically placed at the top of the well head and is attached to the cable. External batteries are used to power the winch and the communication station and are positioned near the test area. After the systems are powered up and pass

a simple system check, the winch is then used to lower the probe down so that the top of the probe is just inside the wellhead (base position). The base position allows for wireless communication between the probe and the base station. In this configuration, the data can be downloaded from the probe, instructions sent to the probe, or batteries recharged.

Demobilization at the well location is composed of two steps: disassemble test equipment and decontamination. Since the tripod, winch, communication system, batteries, laptop, etc. do not come in contact with any contaminants from the well they do not have to undergo any type of decontamination and can simply be unassembled and moved to the next well. Reusable equipment such as the sensor probe and the cable connecting the sensor probe to the winch have to be decontaminated before they can be used at other wells or taken off the site. All PPE, disposable equipment, and related waste materials (disposable gloves and garments, tape, plastic sheets, etc.) will be placed into labeled containers for disposal as specified in Residuals Management section (Section I) of the field test plan.

Sensor Probe Decontamination Protocol:

- 1) Place sensor probe and sample containers on a plastic sheet.
- 2) Wash in detergent solution, then rinse.
- 3) Save final rinse solution for residual analysis.
- 4) Dry sample containers with paper towels (if necessary) and place on a clean plastic sheet.
- 5) Dispose of all washing and rinsing solutions as specified in Section I (Residuals Management) of the Field Test Plan.

Teflon Cable Decontamination Protocol:

- 1) Place a large sample collection container on a plastic sheet beneath the cable.
- 2) Soak a paper towel in detergent solution
- 3) Soak a paper towel in rinse solution
- 4) As the probe is being brought back to the surface, apply the two paper towels to the cable directly above the sample collection containers.
- 5) Once the cable is completely wound final rinse is applied directly to the spool and collected in a final rinse sample collection container.
- 6) Dispose of paper towels and all washing and rinsing solutions as specified in Section I (Residuals Management) of the Field Test Plan.

The collected final rinse material from the sensor probe and the Teflon cable are combined and submitted to an on-site analytical laboratory for analysis according to SRS practice. The entire decontamination

procedure will be repeated if residual contamination is detected in the composite final rinse (Step L in Figure 5).

Once decontamination is complete, the distal section of the sensor probe will be removed and replaced with another section containing fresh desiccant and a new membrane. Although laboratory studies done here at GE indicate that desiccant lifetime is much longer than 3 days (expected number of days between replacement), it was decided for this field test that replacing desiccant and membrane will greatly decrease the chances for cross-contamination and allow a more robust comparison between the TCE concentrations measured by the probe and those measured by the reference method. In a commercial product this step will need to occur less frequently.

F. Sampling and Analysis Plan

Polyethylene diffusion bag (PDB) samplers are now commonly used to determine concentrations of VOCs in groundwater wells. As they are passive devices that rely on the ambient movement of groundwater from the aquifer or water-bearing zone through the well screen, it was decided that this sampling method would be best suited for referencing with an in-well sensor probe. Well-purge sampling is the most widely employed “conventional” sampling method. It, in theory, removes stagnant well water and brings fresh water into the well from the adjacent aquifer formation(s), providing a flow-weighted sample adjacent to the borehole. Well-purge sampling may produce sample of high turbidity and the high degree of pumping stress mixes contaminants into the well from various contributing zones, and can induce movement of contaminants into the well from zones not adjacent to the well screen. To avoid such contaminant source uncertainties, the PDB method was thought to provide the best comparison with an in-well probe capable of discrete interval sampling. In fact, PDBs are often used for discrete level sampling for VOCs, where VOC stratification is present.

PDB samplers will be obtained from Columbia Analytical Services, Inc. They are made of LDPE plastic (typically 4 mils) in the shape of a tube that is filled with deionized water and sealed at both ends. The samplers are typically 18 inches in length and 1.25 inches in diameter; they hold between 220-350 mL of water. The PDB sampling procedures that will be followed are given in Appendix 2. That method follows the prescribed sampling techniques originally outlined in Vroblesky and Hyde [11]. More recent user’s guides are also available from the USGS [13] and the ITRC [13].

Although many VOCs equilibrate with the PDB sample water within 48 to 72 hours at temperatures of 10°C and above, the recommended minimum

equilibration period for PDBs is 14 days. A 14 day equilibration period will be used in all SRS wells, although it is recognized that the groundwater samples over that period will be a time-integrated average of 1-4 days prior to recovery.

Several days prior to the removal of the PDBs at 14 days, the sensor probe will be lowered to a short distance above the top of the PDB bag (Step F in Figure 5), very near or at the midpoint of the screen interval as shown in Figure 6. That distance will be determined based on results from a preliminary field test in Schenectady, NY. At the conclusion of sensor probe measurement cycle, the probe will be removed, followed by the PDB sampler. The PDB samplers will be carefully retrieved, cut open and its content will be decanted in volatile organic analysis (VOA) vials with HCl used as a preservative. Samples will be labeled and placed in an ice-cooled chest until delivery to a certified laboratory for analysis under chain-of-custody procedures. Samples will be analyzed by EPA method 8260B. For each well, a mean and standard deviation TCE concentration from the PDB sampling/validation method will be obtained.

Figure 6. Close-up conceptual view of a groundwater monitoring well with diffusion sampling bag and sensor probe deployed.

Quality assurance/quality control

Blind duplicate samples will be collected from well XXX, where two PDBs will be placed side by side in the well screen (Table 3). One source blank

will be collected by filling a preserved VOA vial with the content of a PDB sampler that was not exposed to groundwater.

Table 3. Field Test Verification Sampling and Quality Assurance/Quality Control Schedule

Well ID	PDB sample	PDB sample	PDB sample
	Lab 1	Lab 2	QA/QC
TBG5	X	X	duplicate
XSB2D	X	X	
TNX10D	X	X	
ASB8C	X	X	
MSB49B	X	X	
MSB31CC	X	X	
	X	X	PDB blank

G. Data Management, Analysis, and Interpretation

Data Management

The two primary sources of data generated in this field test are the sensor probe outputs and the CVOC concentrations for each well obtained from the reference method. At the end of each measurement (Step G in Figure 5), data stored on the probe will be downloaded electronically to the laptop computer for analysis and storage. The data stored on the probe may include, but are not limited to, the mean and standard deviation outputs of the frequency measuring device, converted relative frequencies, temperature, humidity, and pressure sensor readings and the like. The format for the raw data will be an ASCII text file that can be opened in Microsoft Excel or other commonly available spreadsheet program. Each data point will have an associated time stamp. Floppy diskettes will be used for back-up storage of the data from each measurement. Data from the diffusion bag sampling and off-site laboratory will be stored mainly in

the form of a field log notebook. A field log notebook will be kept by the principal investigator (or designated alternate). Copies of all data and logbooks will be available upon request.

Data Analysis

Once the sensor probe data have been saved to the laptop and data analysis can begin. Software has been written to automate much of the data collection, formatting, and analysis. The sensor frequency data from the probe will be input into a software package that uses multivariate statistical algorithms to calculate TCE concentration and an error estimate. If multiple missions were performed (Figure 5, Step J), a mean and standard deviation TCE concentration will be calculated.

As described above in the sampling and analysis plan, samples will be collected from six of the wells and sent to multiple analytical laboratories. As an alternative the replicate samples may be submitted to the same laboratory as blind replicates. For each well, a mean and standard deviation TCE concentration from the validation method will be obtained.

Finally, the TCE concentrations measured by the sensor probe will be compared to the TCE concentrations from the validation method. As a backup, historical data from all 8 of the wells can also be used for analysis and interpretation. Comparison of the concentrations between the reference method and the AIMS probe will be done using a combination of custom written Microsoft Excel macros, MATLAB, and the MINITAB statistical package. Correlation plots will be created to see if there is general agreement across the diversity of wells. Statistical paired *t*-tests will be performed on the TCE concentrations to determine if the difference between the two methods is statistically significant at the 95% confidence level. In addition to statistical testing, graphs of the raw sensor data (frequency shift at equilibrium for each coated sensor in the array) for each measurement will be made available.

Analyses of the differences between the AIMS probe data and the reference method will allow us to estimate the accuracy of the method. The target accuracy for the field test is 20%. Accuracy is just one of the performance criteria used in the judging the success of this field test. Accuracy is calculated using Equation 2, where $C_{reference}$ is the average TCE concentration for a given well measured by the reference method and C_{probe} is the concentration measured by the sensor probe at the same well.

$$\%Accuracy = \left(\frac{C_{reference} - C_{probe}}{C_{reference}} \right) \times 100 \quad (2)$$

Calculation of accuracy will be done on a well-by-well basis. This allows us to make assessment of whether accuracy is affected by the presence of co-contaminants such as PCE, DCE, and carbon tetrachloride. Speciation can be assessed by comparing the accuracies for the wells in which TCE is the primary contaminant (e.g., ASB8C, TGB5, TNX10D, XSB2D) versus those in which the % of co-contaminants is greater than 25% (e.g., MSB31CC, MSB49B).

Using the sensor response data from two “clean” wells, baseline or background signal variations can be established and used to calculate detection limits for field applications. Laboratory data will establish the relationship (e.g., a calibration curve) between sensor response and analyte concentration. Detection limit is defined here as the concentration of the analyte that would provide a sensor response equal to 3 times the baseline (or background) noise level. Detection limits for common VOCs should be below the minimum concentration level (MCL) established by the U.S. EPA. For TCE and PCE, the MCL is 5 ppb. Calculation of the detection limit will be performed using custom written Microsoft Excel macros.

H. Data Quality Objectives

In general, data quality objectives for this project are to generate data that will withstand scientific and technical scrutiny. Data will be generated using generally accepted procedures for analysis, data reduction, and documentation. Specific data quality objectives are summarized below for each of the field test objectives.

- The mean and standard deviation TCE concentrations determined by the AIMS probe should fall within 20% of the concentrations determined by the baseline method across the range of well types (co-contaminants, depths, sizes)
- The detection limit for TCE in groundwater should be less than 5 ppbw.
- The equipment should operate in field conditions for a variety of well types (2 and 4 inch wells, shallow to deep sampling locations). Successful operation at each well is defined as the ability to go through each of the steps in the experimental design (Figure 5) such that TCE concentrations are obtained.

I. Health and Safety

Personnel working on site during the field test at SRS will be 29CFR 1910.120-40 Hr. HAZWOPER trained and satisfied the SRS General Employee Training requirements. Personnel protection equipment (PPE) will be used as required by SRS and OSHA requirements. A project

safety and health plan has been approved and is on file at SRS (Q-SHP-2003-00002).

J. Residuals Management

Investigative derived waste (IDW) will be generated from two activities at each well and will be minimized as much as possible. Decontamination of the cable used as part of the instrument delivery system and the sensor probe itself will generate IDW. Recovery of the diffusion sampling bags will also generate IDW. Any PPE equipment used as part of these activities will also need to be disposed of properly. Waste handling instructions have provided by the site and can be found in the work clearance permit on file with Mark Amidon at SRS.

J. Reports

Within 48 hours after retrieving the sensor probe from each groundwater monitoring well, we will provide a “quick-look” report. This report will consist of the mean and standard deviation sensor concentration as measured by the probe. These concentrations will be compared to the historical TCE concentrations (see Appendix 1) for those wells and provided upon request.

Data from the passive diffusion sampling bags will not be available until after the field test has ended. This data will be made available in the draft final report for the project.

K. Schedule

The field test schedule is based upon our objective of validating the performance of the sensor probe is the widest possible diversity of wells. To attain this objective an aggressive schedule is planned to have an AIMS at each of the 8 wells listed in Table 2. Table 4 shows a calendar listing the order in which the wells will be sampled. The first 5 days of the test is a shakeout. The two wells accessed during this period are wells that have less than 1 ppb of TCE in them (i.e., “clean”). This week will be used to make sure that all of the equipment is mechanically operating. For the wells that will be used as part of the shake-out, 1 full day has been allotted for setup and installation, 1 day for testing, and 1 day cleanup and decontamination. Historical data will be used in place of diffusion sampling. The shakeout week will also be used to deploy the diffusion sampling bags in the remaining 6 wells. After the initial shakeout week, we will return 2/24 and stay for 2 weeks to sample the remainder of the wells. The experimental protocol (Figure 5) will be the same for all of the

wells. AIMS-1 will be located in the TNX area, while AIMS-2 will be used at wells in the A/M area. A total of 3 days have been allotted to spend at each well. This includes 0.5 days for setup, 1.5 days for testing, and 1 day for demobilization and decontamination.

Table 4. Field Test Schedule

Monday	Tuesday	Wednesday	Thursday	Friday
2/24 Ship equipment to SRS	2/25	2/26 Arrive at SRS	2/27 Training	2/28 Deploy Bags Setup AIMS
3/3 Shake-out AIMS1: MSB87B AIMS2: MSB32B	3/4 Shake-out AIMS1: MSB87B AIMS2: MSB32B	3/5 End Shake-Out	3/6 Fly home	3/7
3/10 Lab testing	3/11 Lab testing	3/12 Lab testing	3/13 Lab testing	3/14 Lab testing
3/17 Arrive at SRS AIMS1: TNX10D AIMS2: MSB49B	3/18 AIMS1: TNX10D AIMS2: MSB49B	3/19 AIMS1: TNX10D AIMS2: MSB49B	3/20 AIMS1: XSB2D AIMS2: ABS9C	3/21 AIMS1: XSB2D AIMS2: ABS8C
3/24 AIMS1: XSB2D AIMS2: ABS8C	3/25 AIMS1: TBG5 AIMS2: MSB31CC	3/26 AIMS1: TBG5 AIMS2: MSB31CC	3/27 AIMS1: TBG5 AIMS2: MSB31CC	3/28 Spare Fly home?
3/31 Equipment Pickup @ SRS	4/1	4/2	4/3	4/4

L. Regulatory Compliance

No issues anticipated.

M. Project Organization

Project Manager: Dr. Ronald E. Shaffer, GE Global Research
Office Phone: (518) 387-4344

Site/Field Safety Officer: Mr. Angelo Bracco, GE Global Research
Office Phone: (518) 387-6647

Site Coordinator: Mr. Mark Amidon, Bechtel Savannah River Inc.
Office Phone: (803) 952-7781

Personnel from GE Global Research in Niskayuna, New York, will have the primary responsibility for conducting the technical aspects of the

project. Dr. Ronald E. Shaffer, the principal investigator for this project will have primary responsibility for the overall technical direction of the field test. Dr. Shaffer will also be responsible for all of the data collected and analysis of the data collected during the field demonstration. Mr. Angelo Bracco is the Field Safety Officer and will also responsible for instrument mobilization/demobilization activities. Mr. Mark Amidon is the Savannah River Site coordinator.

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Appendix 1 A.

Additional Information on the 8 Groundwater Monitoring Wells

Table 1. Winter Well Temperature Characteristics 1999-2002

Well ID	Mean ^a	Std. Dev. ^a	Minimum ^a	Maximum ^a	# ^b
MSB87B	19.0	1.8	17.3	21.4	4
MSB32B	18.5	0.3	18.2	18.9	4
TBG5	24.8	1.8	23.1	27.2	4
XSB2D	20.6	1.1	18.9	21.7	5
TNX10D	20.9	1.4	19.4	22.4	4
ASB8C	18.3	0.3	18.1	18.6	3
MSB49B	19.0	0.9	17.6	20.0	7
MSB31CC	20.0	1.0	19.3	21.1	3

a. all temperatures are in °C.

b. number of temperature readings taken during the winter months (December, January, February, and March) from 2000-2002.

Appendix 1B.

Passive Bag Sampling Standard Operating Procedure

1.1. General

The following protocols will be followed when groundwater samples are collected by the passive bag sampling method (Vroblesky and Hyde, 1997) for verification groundwater sampling during the course of the filed test of the GE/Nomadics AIMS system.

All persons involved with the sampling program will be technically competent and familiar with the sampling procedures described herein. All persons will also be familiar with the site-specific Health and Safety Plan (HASP) and will also have completed Occupational Safety and Health Administration (OSHA) 40-hour training, including 8-hour annual refreshers, as appropriate.

1.2. Pre-Sampling Preparation

Prior to any sampling event, the following steps must be taken by personnel responsible for sampling:

1. Notify the appropriate parties of the sampling round at least one week prior to the proposed sampling date.
2. Review the sampling procedures and the site-specific HASP.
3. Assemble all equipment and materials necessary for sample collection as shown in Table 1-1.
4. Inspect the equipment to ensure that it is in working order and decontaminate sampling equipment, as appropriate.
5. Note and replace any equipment or materials that are in short supply or are showing indication of wear.
6. Establish a sampling team of at least two people.

Upon receipt of the sampling containers from the laboratory, inventory the containers to make sure appropriate containers were delivered, check if preservatives have been added, if necessary, and assess the general condition of containers.

Coolers containing wet ice will be utilized during the sampling activities and subsequent transportation to the laboratory to maintain the proper temperature of 4 degrees Centigrade (°C).

Table 1-1. Field Equipment

Sampling Equipment

- Personal safety equipment (e.g., steel-toed work boots, latex gloves, safety glasses)
- Insulated sample coolers containing prepared sampling containers, preservatives, and wet ice
- Water level indicator(s)
- Weighted nylon measuring tape.
- Stainless-steel snap hooks, unless dedicated in well(s)
- Stainless-steel weights (6-inch long by $\frac{3}{4}$ -inch diameter solid rod with hole), unless dedicated in well(s).
- Teflon®-coated stainless-steel wire or disposable nylon line, unless dedicated in well(s).
- Laboratory-grade deionized water.
- Paper towels.
- Methanol.
- Alconox.
- Ziploc bags.
- Polyethylene sheeting
- Distilled water.
- 5-gallon pail with lid.
- Tool box.

Documentation Equipment

- Prepared sample labels.
- Waterproof pens not containing organic solvents.
- Chain-of-custody forms.
- Custody seals.
- Field notebook.

Miscellaneous Equipment

- Compliance Monitoring Program Sampling and Analysis Plan.
- Site-Specific Health & Safety Plan.
- Well keys.
- Calculator.

1.3. Passive Bag Sampler Preparation

Prior to mobilizing to the sampling site, passive bag samplers are obtained from Columbia Analytical Services, Inc. ready for use or, alternatively, they may be created using the following procedure:

1. Create polyethylene bags by cutting the roll of 4 mil polyethylene flat tubing (2-inch wide) into approximate 18-inch long sections. Heat seal three sides of the polyethylene bags with the 24-inch impulse heat sealer.
2. Fill the polyethylene bag with approximately 150 milliliters (mL) of laboratory-grade deionized water, and heat seal the fourth side of the polyethylene bag, taking care to minimize or eliminate headspace.
3. Prior to transportation to the site, wrap the deionized water-filled polyethylene bags in clean polyethylene sheeting inside a cooler containing wet ice to preserve the integrity of the deionized water-filled polyethylene bags and minimize the formation of headspace inside the polyethylene bag.
4. Prior to mobilization to the site, review well construction details and water levels in each well to be sampled. Fabricate well-specific passive bag holders by measuring the line (i.e., nylon or Teflon®-coated stainless-steel wire) and attaching the snap hooks on the line such that the deionized water-filled polyethylene bag can be secured by the hooks within the screened or open rock interval of the well and the stainless steel weight will barely rest on the bottom of the well. For each passive bag holder, secure a stainless steel weight to the bottom of the line and attach the stainless steel snap hooks to the line at the appropriate measured locations to secure the deionized water-filled polyethylene bag. Place a knot at the top of the line to coincide with the top of the well casing to facilitate the proper placement of the passive bag sampler within the monitoring well. To minimize the potential for contamination, place each well-specific passive bag holder in a labeled ziploc bag upon completion for transport to the site. After the first sampling event, the holders may be dedicated to certain monitoring wells if Teflon®-coated stainless-steel wire is used.

1.4. Water Level and Total Depth Measurements

Prior to installing a passive bag sampler in a monitoring well, water level measurements and total depth measurements will be obtained with an electronic water level indicator and a weighted nylon measuring tape. The electronic water level measurement method involves lowering a probe into a well which, upon contact with the water, completes an electric circuit. At the instant the circuit is closed, the water level indicator provides an audible and/or visual alarm which indicates that the water has been contacted.

All water level and total depth measurements will be obtained in accordance with the following procedures. Latex gloves will be worn during all measurement activities.

1. Unlock the well cover and carefully remove to avoid having any foreign material enter the well.
2. Clean the water level probe and lower portion of cable, and test water level meter to ensure that the batteries are charged.
3. Lower the probe slowly into the monitoring well until the audible and/or visual alarm indicates the top of the water column.
4. Read the depth, to the nearest 0.01 feet, from the graduated cable using the marked measuring point on the monitoring well casing as a reference. Record the depth to water in the field notebook. If the well is dry or frozen, record that condition in the field notebook.
5. Collect duplicate water level measurements at a minimum of one monitoring well in every 20 monitoring wells [i.e., 5 percent (%)].
6. Measure the total depth of the well using a weighted nylon measuring tape and record the depth to the nearest 0.01 feet. Record the measurement in the field notebook.
7. Remove the probe from the monitoring well slowly. Clean the probe and lower portion of cable using clean paper towels saturated with distilled or deionized water. Repeat this procedure with the weighted nylon measuring tape.
8. Replace the monitoring well cap and lock the protective casing in place.

1.5. Passive Bag Sampler Installation

1. The procedures to be followed when installing the passive bag sampler:
2. Upon arrival at a monitoring well, don new latex gloves and remove a deionized water-filled polyethylene bag from the cooler.
3. Attach the deionized water-filled polyethylene bag to the line of the well-specific passive bag holder or the dedicated holder using the stainless steel snap hooks.
4. Slowly lower the passive bag sampler down the monitoring well until the stainless steel weight reaches the bottom of the well indicating that the sampler is properly positioned in the screened or open rock interval as confirmed by the knot at the top of the well casing.

5. Secure the line extending above the top knot either to the steel casing of the well's stickup or, for a flush mounted well, the locking cap.
6. Close and lock the monitoring well.
7. Record the date and time of placement of the passive bag sampler in the monitoring well in the field notebook.

1.6. Passive Bag Sample Collection

Following a minimum 14 day sampling period, the procedures to be followed when collecting the passive bag sample are as follows:

1. Prior to the removal of the passive bag samplers, don new latex gloves and remove the sample-filled polyethylene bag from the monitoring well using the attached line.
2. Remove the sample-filled polyethylene bag from the stainless steel snap hooks and dry with a clean paper towel.
3. Cut open the sample-filled polyethylene bag and pour the water directly into the sampling containers. Record sample identification, date, time, analysis required, project identification, sampler identification and client identification on each sample container. Place the sample containers in a cooler containing wet ice immediately after collection. All information should also be entered in the field notebook.
4. Return dedicated holders, if used, to the well after sampling activities are complete. Close and lock the well. Deliver the samples to the laboratory within 24-hours of collection.

1.7. Decontamination of Sampling Equipment

Prior to assembly of the passive bag sampler, decontaminate the stainless steel parts with an Alconox and tap water wash, tap water rinse, methanol rinse, and a distilled water rinse. After rinsing, dry the stainless steel parts with clean paper towels and place in a plastic bag, sealing to ensure that no outside contaminants are introduced prior to use during subsequent sampling activities.

APPENDIX 2.

DOCUMENT NUMBER:

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REVISION:

E3

TITLE:

Probe Terminal Communications Interface

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Nomadics, Inc.

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Introduction

This document defines the terminal commands used to interface with the AIMS probe. Terminal commands are simple text commands that can be entered using a software terminal emulation program such as HyperTerminal. HyperTerminal is included with the installation of most all versions of Microsoft Windows.

Terminal commands were chosen as the messaging protocol because it results in a simple and flexible communication scheme that can be easily extended. The use of terminal commands also makes it simple to develop software applications that communicate with the probe.

In order to establish communications with the probe, an RS-232 data link is used. This RS-232 data link may be connected to the AIMS in one of two ways:

1. Directly to the probe
2. Or connected to the deployment controller that will relay commands to and from the probe via the inductive communications link

The commands that communicate to the probe are identical regardless of how you are connected. The RS-232 baud rate must be fixed at 9600 baud (9600,N,8,1).

Commands

All commands must be terminated by a carriage return as indicated by the symbol ↵. If using a terminal emulator, press the Enter or the Return key to send a ↵. Please note that the carriage return character is a non-displayable control character to a terminal emulator.

The probe is designed to always respond to a command, including invalid commands. The probe will respond with one or more characters followed by a ↵. When an unsupported command is entered, the probe will reply with a u↵.

Command Documentation Syntax

Commands are shaded in gray. The syntax consists of the command character followed by any arguments.

Example:

```
commandCharacter <arg1Name:c> <arg2Name:###> <arg3Name:hhhh>
```

Arguments

The documentation for command arguments are enclosed in "<>" characters. The "<>" characters are not part of the actual command and are not entered when typing the command.

The number of characters in the argument are indicated by the "c" or "#" character following the argument name. A "c" indicates the argument takes a character, a "#" indicates the argument takes a numeric character "0" through "9", and a "h" indicates the argument takes a hexadecimal character.

In the example above, arg1Name takes a single character, and arg2Name takes three numeric characters, and arg3Name takes four hexadecimal characters.

Acquire

Initiates data acquisition of the crystal frequency data from either the sensor array or temperature crystal sensor located next to the delay line.

a

Parameters

None

Returns

a ←

Remarks

Currently 512 samples are acquired and stored in probe memory. Use the Data “d” command to request the data from the probe

Example

Tx: a←

Rx: a←

See Also

Data command “d” in section 2.3

Pressure

The pressure command reads the I2C pressure sensor output on Port A4 of the AD7417.

b

Parameters

None

Returns

The pressure sensor A/D reading as number string such as "6F", the minimum value is 0x000 to a maximum of 0x3FF (10 bits).

↵

Example

Tx: s ↵

Rx: 198 ↵

Celsius Temperature

Reads the AD7417 integrated I2C temperature sensor and converts the value into degrees Celsius.

c

Parameters

None

Returns

The temperature reading in Celsius as number string such as "22.5"

± ##.## ↵

Example

Tx: c↵

Rx: 22.0↵

Data

The data command returns one data sample from the probe memory up to the maximum samples acquired.

d

Parameters

None

Returns

The data sample data returned is a number in string format such as "123456".

When there is no more data to dump, the string "endofdata" is returned

↵

Remarks

Currently 512 samples are acquired and stored in probe memory. Use the "a" command to acquire data and the "d" Data command to request the data. It is not required that all the data be read from memory.

Example

Tx: d ↵

Rx: 123456 ↵

.

. ***Comment: Repeat 512 times or until "endofdata" is received***

.

Tx: a↵

Rx: endofdata↵

See Also

Acquire "a" command in section 2.1

Echo

Echoes the command and any characters following the command

e <stringToEcho:ccc...>

Parameters

<stringToEcho:ccc...> Optional, one or more characters to echo

Returns

The echoed string

Remarks

This is useful to test if communications is working without changing or causing any changes in the probe status

Example

Tx: e hello world↵

Rx: e hello world↵

Statistics

The statistic command is used to compute the average, residual average, and standard deviation of the data captured by the A/D converter.

f

Parameters

none

Returns

Average
Residual Average
Standard Deviation

Remarks

Three commands are required to obtain the computed values.

Example

```
Tx: f ↵  
Rx: #####.## ↵  
Tx: f ↵  
Rx: #####.##↵  
Tx: f↵  
Rx: #####.##↵  
Tx: endofdata↵
```

Power Control

The power command provides a means to turn on or off the power to the IFM and PLL circuits.

g [+/-]

Parameters

- + — turns on the power supply to the IFM and PLL sections of the probe
- — turns off the power supply to the IFM and PLL sections of the probe.

Returns

On initial power up of the probe controller the power is turned on to the IFM and PLL circuits.

Remarks

Example

Tx: g +↵
Rx: g +↵

-OR-

Tx: g-↵
Rx: g-↵

Humidity

The humidity command reads Port A3 of the AD7417 for the humidity sensor output.

h

Parameters

None

Returns

The humidity sensor A/D reading as number string such as “128”, the minimum value is 0x00 to a maximum of 0x3FF (10 bits).

←

Example

Tx: h←

Rx: 19E←

Remarks

The sensor device used is the Honeywell humidity sensor, model HIH-3610.

Customize PLL Data

The 'i' command allows extended capabilities for the manipulation of PLL configuration residing in the EEPROM of the ATMEL 103 processor.

i [mux] [pll command index] [pll command or comment]

Parameters

none

Returns

Remarks

Three commands are required to obtain the computed values.

Example

Tx: i ↵
Rx: i z ↵

```
//-----  
//parameter are order restricted  
//process register command.  
//  
// CMD  MUX  IDX  PLLSTRING  
// i   1   1-7  00000000  
// i   1   c   "comment"  
// i   1   p   Prints current command for mux  
// i   1   d   clears current mux  
// i   1   t   7.15MHz default commands  
// i   1   s   10.0MHz default commands  
// i   j       -clears all values  
// i   k       -prints all values  
// i   z       -defaults 1,9 @ 7.15MHz & 2-8 @ 10.0MHz.  
//-----
```

Clear EEPROM PLL Configuration Commands

The 'j' command is used to write non-PLL commands to the internal EEPROM of the ATMEL 103 processor.

j

Parameters

none

Returns

none

Remarks

The 'j' command returns the input character entered after the EEPROM has been written to. The time required to write the 9 channels of blank data will be about 1 second. The contents of the EEPROM may be printed by using the 'k' command. The results of this operation can be seen by using the 'k' command to print the contents of the PLL command store. The results will be similar to the output shown below the example. Any autonomous data collection at this point will result in garbage data being collected.

Example

```
Tx: j ↵
Rx: j ↵
Tx: k ↵
1:BLANK PLL CMD
1:BLANK PLL CMD
1:BLANK PLL CMD
1:BLANK PLL CMD
1:BLANK PLL CMD
1:BLANK PLL CMD
1:BLANK PLL CMD
1:Blank Description
...
...
...
9:BLANK PLL CMD
9:BLANK PLL CMD
9:BLANK PLL CMD
9:BLANK PLL CMD
9:BLANK PLL CMD
9:BLANK PLL CMD
9:Blank Description
```

Print EEPROM PLL Configuration Commands

The 'k' command is used to print the contents of the PLL commands stored in the internal EEPROM of the ATMEL 103 processor.

k

Parameters

none

Returns

none

Remarks

The 'k' command should be used to print the contents of the EEPROM PLL configuration.

Example

Tx: k ↵

Rx: k ↵

Latched

The latched command returns the PLL latch status.

I

Parameters

None

Returns

A string indicating the PLL latch status.

Returns either "PLL LATCHED" or "PLL NOT LATCHED"

Example

Tx: I<cr>

Rx: PLL LATCHED<cr>

Or

Tx: I<cr>

Rx: PLL NOT LATCHED<cr>

Motor Commands

Used to initiate pump motor motion and configure properties. All motor commands begin with an “m”

Motor Home Retract/Park

Moves payload to the desired home position of either retracted or parked (extended).

```
m <  
m >
```

Parameters

- > — retract the payload to the position closest to the motor
- < — Park the payload to the position farthest from the motor

Returns

A string indicating motor status is return while the command is being completed.

```
(M) ... Retracting↵  
(M) ... Parking↵
```

Example

Retract Purification Payload Canister:

```
Tx: m >↵  
Rx: (M) ... Retracting↵
```

Park Purification Payload Canister:

```
Tx: m <↵  
Rx: (M) ... Parking↵
```


Motor Move

Moves payload away or towards the motor the specified number of steps. If no steps are entered, the motor is moved a single step in the desired direction.

m <direction:c><numberSteps:###>

Parameters

<direction:c> - A character indicating the direction to move the motor

“+” - Extend away from the motor

“-” to retract towards the motor.

<numberSteps:###> - The number of steps to move the motor. This argument is optional. If no steps are entered, the motor will move a single step in the desired direction.

Returns

A string indicating motor delay status

(M) ... Delay = 4096↵

Example

To move 100 steps away from the motor:

Tx: m +100↵

To move 100 steps in towards the motor:

Tx: m -100↵

Remarks

The number of maximum travel steps for the pump motor is typically 275.

Motor Pump Cycle

Cycles the pump for the specified number of cycles.

m ~<numberOfCycles:##>

Parameters

<numberOfCycles:##> - A number specifying the number of cycles to pump. The maximum number of pump cycles is 99

Returns

A string indicating motor status
(M) ~Pumping: 16↵

Example

To move cycle the pump 8 times:

Tx: m ~8↵

Rx: (M) ~Pumping: 8↵

Remarks

The maximum number of pump cycles is 99

Motor Step Period

Sets the motor step period that determines the pump velocity

m !<stepPeriodTime:####>

Parameters

<stepPeriodTime:####> - A number specifying the motor step period

Returns

A string indicating motor delay status
(M) Delay = 2000↵

Example

To set the delay to 2000:
Tx: m !2000↵
Rx: (M) Delay = 2000↵

Remarks

The default is 4096

PLL

Configures the Phase Locked Loop (PLL). This command is intended for development only and should normally not be used.

p <deviceNum:#> <registerData:hhhhh>

Parameters

<deviceNum:#> - A single numeric character indicating which PLL device type the data is formatted for:

1 - LMX2316

2 - LMX2325

<registerData:hhhhh> - A hexadecimal string containing the destination and register data for the PLL chip. The bits containing the data are padded by an extra nibble pre-pended to the MSB of the hexadecimal string

Returns

The string, "exit PLL"

Remarks

This command is intended for development only and should normally not be used. See the National Semiconductor LMX2316 data sheet for a description of the N, R, and F register data.

<http://www.national.com/ds/LM/LMX2306.pdf>

Output Data from DataFlash Memory

The 'o' command and associated commands are used to control and extract data collected during the experiment.

Output Single record

The 'o' command with out any parameters is used will send a data record to RS232 port. Successive issuances of the 'o' command will index the internal record counter and the will output the next successive data record.

o

Parameters

none

Returns

The data record for one complete pass through the experiment in a comma delimited

Remarks

The following table represents the structure of the data being returned from the probe.

Standard deviation of a negative value indicates that the PLL was not locked when the samples were taken.

Data maybe collected via HyperTerminal capture or using QuickBasic.

2 bytes unsigned short	2 bytes unsigned short	2 bytes unsigned short	2 bytes unsigned short
Experiment Time in Seconds	Internal Probe Temperature	Internal Probe Pressure	Internal Probe Humidity
4 Bytes - Long	4 Bytes	4 Bytes	4 Bytes
Channel 1 Average for Frequency 1	Channel 1 Standard Deviation for Frequency 1	Channel 1 Average for Frequency 2	Channel 1 Standard Deviation for Frequency 2
4 Bytes	4 Bytes	4 Bytes	4 Bytes
Channel 1 Average for Frequency 3	Channel 1 Standard Deviation for Frequency 3	Channel 1 Average for Frequency 4	Channel 1 Standard Deviation for Frequency 4
4 Bytes	4 Bytes	4 Bytes	4 Bytes
Channel 2 Average for Frequency 1	Channel 2 Standard Deviation for Frequency 1	Channel 2 Average for Frequency 2	Channel 2 Standard Deviation for Frequency 2
.			
.			
.			
4 Bytes - Long	4 Bytes	4 Bytes	4 Bytes
Channel 9 Average for Frequency 3	Channel 9 Standard Deviation for Frequency 3	Channel 9 Average for Frequency 4	Channel 9 Standard Deviation for Frequency 4

Figure 1. Data Record Format

Example

Tx: 0 ↵

Rx: 46,92,104,336,-2428168,-52115,-1787794,-35699,-1542329,-17309,-1478925,-17188,-6

29487,9248,-2801640,21859,786946,3978,4361574,1972,-1983914,-20401,-1607102,-167

18,-1532629,-15799,-1478300,-16020,4454047,815,314379,16372,-3099479,144974,-594

881,5910,-1930213,-19706,-1557351,-16349,-1486844,-16046,-1436872,-15762,-200466

7,-17439,-1722365,-17590,-1701906,-17433,-1678745,-17109,-1578358,-17583,-132859

8,-16255,-1318672,-17948,-1313972,-16961,-1544532,-18215,-1296850,-18193,-129489

5,-16955,-1289674,-17605,1539367,10866,4012925,6659,-2117099,8736,-2573187,4429 ↵

Rest Record Index with Single Record Output

This command resets the internal record index and outputs the first record stored in memory.

o !

Parameters

! character

Returns

The first stored data record. Each record is followed by a carriage return.

Remarks

Use this command to reset the data counter to the first record stored in DataFlash. See the data format in figure x

Example

Tx: o !↵

Rx: 95,92,104,336,-2428168,-52115,-1787794,-35699,-1542329,-17309,-
1478925,-17188,-6
29487,9248,-2801640,21859,786946,3978,4361574,1972,-1983914,-
20401,-1607102,-167
18,-1532629,-15799,-1478300,-16020,4454047,815,314379,16372,-
3099479,144974,-594
881,5910,-1930213,-19706,-1557351,-16349,-1486844,-16046,-1436872,-
15762,-200466
7,-17439,-1722365,-17590,-1701906,-17433,-1678745,-17109,-1578358,-
17583,-132859
8,-16255,-1318672,-17948,-1313972,-16961,-1544532,-18215,-1296850,-
18193,-129489
5,-16955,-1289674,-17605,1539367,10866,4012925,6659,-
2117099,8736,-2573187,4429 ↵

Output Continuous

This command is used for dumping the entire contents of the DataFlash. Each data record is continuously read from memory until the last record is reached (End of Memory).

o %

Parameters

%

Returns

This command will continuously return data records via the serial interface until the end of memory is reached.

Remarks

The data record is in a comma delimited format.
The format of the data record is

Example

Tx: o %↵

Rx: 46,92,104,336,-2428168,-52115,-1787794,-35699,-1542329,-17309,-
1478925,-17188,-6
29487,9248,-2801640,21859,786946,3978,4361574,1972,-1983914,-
20401,-1607102,-167
18,-1532629,-15799,-1478300,-16020,4454047,815,314379,16372,-
3099479,144974,-594
881,5910,-1930213,-19706,-1557351,-16349,-1486844,-16046,-1436872,-
15762,-200466
7,-17439,-1722365,-17590,-1701906,-17433,-1678745,-17109,-1578358,-
17583,-132859
8,-16255,-1318672,-17948,-1313972,-16961,-1544532,-18215,-1296850,-
18193,-129489
5,-16955,-1289674,-17605,1539367,10866,4012925,6659,-
2117099,8736,-2573187,4429 ↵

·
·

Run

The run command is start the probe used to compute the average, residual average, and standard deviation of the data captured by the A/D converter.

r

Parameters

none

Returns

The run command will output the experiment counter and experiment time in seconds. Successive output will

Get

Measure Temperature

Measure Pressure

Measure

Channel Number

Remarks

The serial connection is not required for the main experiment loop to operate. The output will write to the serial interface. The processor speed will be set to normal rate of 4MHz.

Example

Tx: r ↵

Rx: ---EC: 184

ET:8554

0

y-1

exit PLL

exit PLL

exit PLL

exit PLL

Serial

This command returns the serial number from the probe.

s

Parameters

None

Returns

"Serial Number of the probe" ↵

Example

Tx: s ↵

Rx: Serial: 003↵

Compute Stats

The compute stats function calculates the statistics for the current A/D dataset.

t

Parameters

None

Returns

Use the “a” command prior to computing the stats.

Example

Tx: t ↵

Rx: t ↵

UART Communication Speed

The ‘u’ command is used to change the baud rate in which the probe communicates with the outside world.

u 9600

u 110

Parameters

none

Returns

A string is returned indicating the baud rate change.

Remarks

The current implementation of the data link hardware only allows the probe to communicate at 110 baud. The probe will automatically be configured to 110 baud with its powered up. Configuration of the probe to operate at 110 baud required the slowing main CPU clock. During the experimentation loop the CPU clock is restored to its original setting (4MHz) or when the probe is connected directly to the host. Each baud rate requires a specific HyperTerminal configuration be loaded. The data link does not support baud rates greater than 110 baud. 9600 baud communications required a direct connect to the probe hardware

Example

Tx: u 9600 ↵

Rx: 110 -> 9600 ↵

-or-

Tx: u 110 ↵
Rx: 9600 -> 110 ↵

Version

The version command returns the current firmware version string.

v

Parameters

None

Returns

“Firmware version string” ↵

Example

Tx: v↵

Rx: “Nomadics, Inc. V1.00:15 4K A/D XTAL” ↵

Erase DataFlash Memory

This command erases the contents of DataFlash memory.

W

Parameters

none

Returns

Remarks

This command should be issued when the processor is running at default clock rate of 4Mhz.

Example

Tx: w ↵

Rx: w ↵

Mu x

The multiplexer command selects the desired multiplexer channel.

x #

Parameters

- A number specifying the multiplexer channel (mux) to select

x [-, +, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9]

+ — The argument + is equivalent to 0

- — The argument - is equivalent to 9

0 — Turn all oscillator on.

1 — Turn oscillator 1 on.

2 — Turn oscillator 2 on.

.

.

.

8 — Turn oscillator 8 on

9 — Turn all oscillators off

Returns

x←

Example

To set the mux to channel 4:

Tx: x 4←

Rx: x←

Select Delay Line Temperature Crystal

The Delay Line Temperature command selects the delay line temperature crystal making its signal available to be measured by the A/D converter.

y[+/-]

Parameters

- + — force deselect of all sensor crystals and selects Delay Line Temperature Crystal channel for input to A/D.
- — deselect the Delay Line Temperature Crystal, this must be completed before selecting a sensor channel.

Returns

y+↵
y-↵

Example

Tx: y+↵
Rx: y+↵

Erase DataFlash memory

z

Parameters

none

Returns

Average
Residual Average
Standard Deviation

Remarks

Three commands are required to obtain the computed values.

Example

Tx: z ↵
Rx: #####.##

k
1:p18000d3
1:p110011c
1:p11084a9
1:p18000d2
1:p11084ad
1:p11084b1
1:p11084b5
1:7.15MHz Crystals
2:p18000d3
2:p1100190
2:p1108599
2:p18000d2
2:p110859d
2:p11085a1
2:p11085a5
2:10.00MHz Crystals
3:p18000d3
3:p1100190
3:p1108599
3:p18000d2
3:p110859d
3:p11085a1

3:p11085a5
3:10.00MHz Crystals
4:p18000d3
4:p1100190
4:p1108599
4:p18000d2
4:p110859d
4:p11085a1
4:p11085a5
4:10.00MHz Crystals
5:p18000d3
5:p1100190
5:p1108599
5:p18000d2
5:p110859d
5:p11085a1
5:p11085a5
5:10.00MHz Crystals
6:p18000d3
6:p1100190
6:p1108599
6:p18000d2
6:p110859d
6:p11085a1
6:p11085a5
6:10.00MHz Crystals
7:p18000d3
7:p1100190
7:p1108599
7:p18000d2
7:p110859d
7:p11085a1
7:p11085a5
7:10.00MHz Crystals
8:p18000d3
8:p1100190
8:p1108599
8:p18000d2
8:p110859d
8:p11085a1
8:p11085a5
8:10.00MHz Crystals
9:p18000d3
9:p110011c
9:p11084a9
9:p18000d2

9:p11084ad
9:p11084b1
9:p11084b5
9:7.15MHz Crystals

Appendix 2A – Quick Reference Command Table

Command	Syntax	Description
Acquire	a	Initiates data acquisition of the crystal frequency data
Pressure	b	Reads and returns the current value from pressure sensor. The returned value is a 10 bit A/D count. Scientific units conversion is required by the application program.
Celsius Temperature	c	Reads the temperature sensor value and returns it in computed degrees Celsius
Data	d	Returns one data sample from the probe memory.
Echo	e	Echo the command and any following data entered
Power	g [+/-]	Turn on power or off to the IFM & PLL subsystems.
Humidity	h	Reads and returns the current value from the humidity sensor. The returned value is a 10 bit A/D count. Scientific units conversion is required by the applications program.
PLL extended commands	i	Extended commands for configuration of the EEPROM PLL data. This option has only been partially tested and should be used for production.
Clear PLL Data	j	Clear the EEPROM PLL configuration.
Print PLL Data	k	Print PLL EEPROM configuration.
Latched	L	Returns string indicating latch status of the PLL; “PLL LATCHED” or “PLL NOT LATCHED”
Motor Home Retract	M >	Retract purification canister to the position closest to the motor
Motor Home Park	M <	Park purification canister to the position farthest from the motor
Motor Extend One Step	M +	Extend the purification canister one step away from the motor.
Motor Retract One Step	m -	Retract the purification canister one step toward the motor.
Motor Extend N-Steps	m +###	Extend the purification canister ### number of steps away from the motor.
Motor Retract N-Steps	m -###	Retract the purification canister ### number of steps away from the motor
Motor Pump Cycle	m ~##	Cycles the purification system ## number of cycles. (Maximum of 99 cycles)
Motor Step	m !####	Sets step period (pump velocity) to #### number of counts

Period		
Output Data	o	Output 1 data record at current record index.
Output Data Reset	o !	Reset data record index and output of 1 st data record.
Output Data Continuous	o %	Continuous data record output starting at current record index.
PLL	p #####	Program and configure the PLL registers.
Run	r	Run experiment until DataFlash memory is full or until the probe is powered down.
Serial	s	Returns the current serial number of the device.
Compute Stats	t	Compute the stats on the A/D dataset residing in memory.
<i>Baud</i>	u [9600/110]	Set the baud rate of the probe, either 9600 or 110 baud.
<i>Version</i>	v	Returns the current firmware data string
Erase	w	Erase contents of DataFlash Memory
MuX	x #	Selects the desired A/D mux channel 0 – Turn all channels on. 1-8 Selected channels 9 – Turn all channels off.
Delay Line	y[+/-]	Turns on/off the temperature crystal located near the delay line.
PLL default data.	z	Write default PLL configuration for the nine channels

Appendix 3. Induction Link Notes

Power Coupler Prototype Notes

L. Hoy
7/9/02

Transmitter Board

Overview

The transmitter board drives the transmitter coil to provide power to recharge the down-hole tool battery pack and support two-way data transfer between the docking station and the down-hole tool. The transmitter is designed to deliver only enough power to charge the 12v (10 cell NiCd) battery pack (~1.5 watt max.).

The transmitter circuit operates as an H-bridge driving an series-resonate LC network at about 100KHz. The transmitter frequency is automatically adjusted by a PLL circuit to maintain the LC network at series resonance. A voltage control loop regulates the voltage swing in the LC network to maintain a constant magnetic flux level inside the transmitter coil. Power coupling efficiency with a slotted, conductive housing over the receiver is about 25%.

Data transfer to the tool is done by amplitude modulation of the transmitter power. Data is received from the tool by sensing changes in the receiver coil load. Data transfer is half-duplex. The transmitter must not attempt to transfer data to the tool at the same time the tool is sending data to the docking station.

Power Input

The transmitter is designed to operate from a 12V battery. Correct operation requires that the input voltage be in the range 11.0v to 15.0v. Normal operating current is in the range of 200mA to 500mA while transmitting and 10mA to 30mA when disabled.

Enable Input

This signal is a 5v CMOS input. The transmitter circuit may be turned off by pulling the "Enable" input low. This input is pulled high on the board and may be left open if not used. When this input is pulled low, the drive pulses to the transmitter coil are disabled but the 100KHz oscillator chip continues to run. This input is not intended for data modulation.

Modulation Input

This signal is a 5v CMOS input. Driving this input high causes the transmitter power to drop by about 50%. It is pulled low on the board and so may be left open when not in use. It is important to note that the action of the modulator prevents proper charging of the tool battery. This input must be low during normal charging operation and pulsed high only when data transfer is required. The data channel formed by this input and the receiver in the tool can support toggle rates in the range 100Hz to 1000Hz but must be treated as an AC coupled channel where the polarity may be reversed.

Detector Output

This signal is a 5v CMOS output. This logic output changes state when the load on the transmitter coil changes. It will toggle synchronously with the modulation input signal applied to the receiver in the tool. The data channel formed by this output and the modulation input in the tool can support toggle rates in the range 100Hz to 1000Hz but must be treated as an AC coupled channel where the polarity may be reversed.

Voltage Adjustment

The voltage adjustment potentiometer sets the amount of power transferred to the receiver by controlling the AC voltage level on the transmitter coil. To set this adjustment, first, instrument the receiver to measure the battery charge current. Setup an oscilloscope to monitor the voltage on the LC network (attach probe to coil-capacitor common node). Position the receiver in the center of the transmitter coil such that the battery charge current is at a maximum. Any metallic housing for the receiver should be in place. Adjust the voltage adjustment potentiometer to produce the desired charge current (typically 50 – 100mA). Note that the voltage setting for the bare receiver coil (~50VAC for 100mA) will be much less than the voltage setting required if the receiver is in a conductive housing (~150VAC for 100mA).

Center Frequency Adjustment

The center frequency adjustment is provided to make sure the PLL that sets the operating frequency can tune the frequency range need to keep the transmitter LC network at resonance. With the receiver unit positioned in the transmitter coil, tune the LC network to resonate as near to 100KHz as possible. This is done by adding/subtracting small amounts of capacitance or adding/removing turns from the coil. When done adjusting the coil and capacitor, adjust the center frequency control (R15) to give 2.5v at the VCO control input (pin 9 of the '4046 PLL). Note: This adjustment was included because of uncertainties in C14 and the PLL chip tuning properties and may not be needed in the production version.

Coil and Capacitor Selection

The amount of power that can be transferred to the receiver depends on the reactance level of the LC network at resonance and the AC voltage across the coil. The choice is a trade-off between high current losses in the H-bridge or high voltage stress in the capacitor. The transmitter circuit is designed to generate ~1.5 watts in the receiver with the LC network operating in the range of 50VAC to 200VAC. To achieve a battery charging current in the range of 50 to 100mA with the above coil voltage, the prototype LC is set for a reactance value of about 130 ohms (.012uf/210uH at 100KHz). The power capability can be increased by adjusting the coil geometry and capacitance to give a lower reactance. However, this will increase the conduction losses in the H-bridge and lower the overall efficiency.

Transmitter Board Top View (with coil attached)

Transmitter Board Schematic – Page 1

Transmitter Board Schematic – Page 2

MODULATOR / DETECTOR

TLC 2272

Receiver Board

Overview

The receiver assembly consists of a loop antenna (L1 and L2) driving a full-wave rectifier. The rectified current is applied directly to charge the battery. The charge current is set by the voltage adjustment made at the transmitter. The inductors were chosen to give a very high open circuit voltage (50-70VAC) but have a high series impedance (~350 ohms at 100KHz), creating a relatively constant charge current into the battery.

Data is sent to the docking station by modulating the load on the receiving antenna coil. The data signal from the docking station is detected by monitoring the charge current. Data transfer is half-duplex. The receiver must not attempt to transfer data to the docking station at the same time the docking station is sending data to the tool.

Battery Connections

The prototype receiver is designed to charge a battery pack consisting of 10, C-size, NiCd batteries, with a trickle charge current input of 50 to 100mA. A protection diode (D6) is provided to limit the open circuit voltage to about 16v should the battery become disconnected or open.

+5v Supply

The charge current monitor and modulation detector circuits require +5v to operate. This must be supplied by the tool system. The +5v is not required if the current monitor or data detector is not used.

Charge Current Output

This is an analog output in the range of 0 to +5v. The output is interpreted as 100mA average charge current per volt. The current measured represents the current supplied by the receiver coil and not the total load current in the battery. The op-amp that processes this signal requires +5v to be supplied by the system controller.

Modulation Input

This is a logic level, MOSFET gate input. Pulling this input high shorts out the receiving antenna. The transmitter circuit senses this short as a load change in the transmitter coil. This input is pulled low on the board and so may be left open if not used. It is important to note that the action of the modulator prevents proper charging of the battery. This input must be low during normal charging operation and pulsed high only when data transfer is required. The +5v power is not required for this input to function. The data channel formed by this input and the transmitter in the docking station can support toggle rates in the range 100Hz to 1000Hz but must be treated as an AC coupled channel where the polarity may be reversed.

Detector Output.

This is a +5v CMOS output. This output changes state to indicate modulations sensed in the transmitter power level. It will toggle synchronously with the modulation input signal applied to the transmitter in the docking station. The op-amp that processes this signal requires +5v to be supplied by the system controller. The data channel formed by this output and the transmitter in the docking station can support toggle rates in the range 100Hz to 1000Hz but must be treated as an AC coupled channel where the polarity may be reversed.

Receiver Board Top View

RECEIVER

The diagram is a hand-drawn circuit schematic for a receiver, plotted on a grid background. At the top, the word "RECEIVER" is written and underlined. The circuit starts with an input transformer having two secondary coils, L1 and L2, each labeled "270µH". The secondary of L1 is connected to a diode bridge consisting of four diodes: D1, D2, D3, and D4. A MOSFET, labeled Q1, is connected to the bridge. The output of the MOSFET is connected to a 1N4002 diode, D5. A 10kΩ resistor, R1, is connected to the MOSFET's gate. A 16V LED, D6, is connected to the output of D5. A 0.1µF capacitor, C1, is connected to the LED's anode. The circuit also includes a 10kΩ resistor, R2, and a 10kΩ resistor, R3. A 10kΩ resistor, R4, is connected to the input of a first op-amp, U1A, which is a TLC2272. The op-amp is configured as a comparator, with its non-inverting input (pin 3) connected to ground and its inverting input (pin 2) connected to the output of the MOSFET. The output of U1A (pin 1) is connected to a 5V supply, labeled "CHARGE CURRENT 1V=100mA". A 0.1µF capacitor, C2, is connected to the output of U1A. A second op-amp, U1B, is also a TLC2272, configured as a comparator. Its non-inverting input (pin 5) is connected to ground, and its inverting input (pin 6) is connected to the output of the MOSFET. The output of U1B (pin 7) is connected to a 5V supply, labeled "DET. OUT". A 10kΩ resistor, R6, is connected to the input of U1B. A 0.1µF capacitor, C3, is connected to the input of U1B. A 10kΩ resistor, R7, is connected to the output of U1B. A 0.1µF capacitor, C4, is connected to the output of U1B. A 5V supply, labeled "+5V", is connected to the circuit. A "MOD IN" terminal is also shown. The circuit is powered by a battery, with terminals labeled "BATT+" and "BATT-".

Appendix 4. Schematics

4				3		2		1	
D						ITEM	QTY.	PART NO.	DESCRIPTION
						1	1	6.1	Bulkhead, Upper TSM Array
						2	1	6.2	Bulkhead, Lower TSM Array
						3	1	6.3	Tube Outer
						4	1	6.4	Membrane Holder
						5	1	6.5	Electronics, TSM Array
						6	1	6.6	Sensor Crystal Kit
						7	1	6.7	Fastener Kit
						8	1	6.8	Seal Kit
C									
B									
A						Nomadics, Inc.			
						Sensor Compartment, 6.0			
						SIZE	FSCM NO	DWG NO	REV
						SCALE 1 : 1		SHEET	1 OF 9
4				3		2		1

	4	3	2	1	
D					D
C					C
B					B
A					A
	4	3	2	1	

Material: 304 stainless
 tube, 1.5"OD x 0.050"
 wall thickness x 4.00"
 length, finish one end
 for three mtg. screws

	Nomadics, Inc.			
	Sheath, 6.4.1			
	SIZE	FSCM NO	DWG NO	REV
	SCALE	1 : 1	SHEET	7 OF 9

4				3				2				1							
D									ITEM	QTY.	PART NO.	DESCRIPTION							
									1	1	6.6.1	Crystal, Temperature Sensor, HC50							
									2	1	6.6.2	Crystal, Reference, HC50							
									3	6	6.6.3	Crystal, Sensor, HC50							
C																			
B																			
A																			
								SIZE	FSCM NO			DWG NO			REV				
								SCALE			1 : 1					SHEET	5 OF 9		
4				3				2				1							