

NASA SAMPLE PROPOSAL

(FIGURE AND TABLES ARE UNAVAILABLE)

TPL-P-3314

SBIR 93-1 SOLICITATION

FORM 9.B – PROJECT SUMMARY

PROPOSAL NUMBER 93-1 SUBTOPIC NUMBER – 12.07 AMOUNT REQUESTED \$70,000

TITLE OF PROJECT

Miniature Solid State Sensors for Chemical Contaminants in Liquids

TECHNICAL ASBTRACT (LIMIT 200 WORDS)

NASA has a serious unmet need for microminiature sensors capable of in situation, real-time analysis of contaminant levels in regenerative life support systems. Surface derivatized piezoelectric sensors can detect less than 10(-11)g of analyte using detectors weighing only 0.02 g with power consumption of 1 to 2 mW per sensor [1,2]. However, piezoelectric sensor technology has not resulted in the development of the ultra-high sensitivity, microminiature sensors needed by NASA for regenerative life support systems. The reasons include unsatisfactory sensor selectivity, poor sensor baseline recovery, degradation of sensor performance with time, and in the case of the bulk mode devices needed for liquid phase sensors, difficulties in signal processing due to the complexity of the output signal which leads to effects such as mode hopping.

TPL proposes to develop innovative sensor architectures, surface chemistries, electronics and software techniques to solve the problems that limit piezoelectric sensor performance. This will lead to miniature, low power, self-calibrating, high selectivity piezoelectric sensor systems suitable for detecting trace contaminants in the liquid phase suitable for space-based systems.

POTENTIAL COMMERCIAL APPLICATIONS

The new, high performance sensor technology would be applicable to a wide range of sensors for chemicals, corrosion and other properties. Environmental monitoring, oil refining, chemical manufacturing, automotive control, and industrial process control are among the potential uses.

KEY WORDS (LIMIT 8): Piezoelectric, Sensor, Shear Horizontal, Acoustic Plate Mode, Contaminant

NAME AND ADDRESS OF OFFEROR (Firm Name, Mailing Address, City/State/Zip):

TPL, Inc.

3768 A/B Hawkins NE

Albuquerque, NM 87109

PRINCIPAL INVESTIGATOR

Timothy C. Tiernan

TABLE OF CONTENTS

SECTION

PROPOSAL COVER

PROJECT SUMMARY

1. IDENTIFICATION AND SIGNIFICANCE OF THE INNOVATION
2. PHASE I TECHNICAL OBJECTIVES
3. PHASE I WORK PLAN
4. RELATED R/R&D
5. RELATIONSHIP WITH PHASE II OR OTHER FUTURE R/R&D
6. COMMERCIAL APPLICATIONS POTENTIAL
7. COMPANY INFORMATION
8. KEY PERSONNEL
9. CONSULTANTS AND SUBCONTRACTS
10. SIMILAR GRANT APPLICATIONS, PROPOSALS, OR AWARDS
11. PREVIOUS NASA SBIR AWARDS RECEIVED

SBIR PROPOSAL SUMMARY BUDGET

1.0 IDENTIFICATION AND SIGNIFICANCE OF THE INNOVATION

Surface derivatized piezoelectric sensors can detect less than 10 exp. (-11)g of analyte using detectors weighing only 0.02 g with power consumption of 1 to 2 mW per sensor [1,2]. However, piezoelectric sensor technology, has not resulted in the development of the ultra-high sensitivity, microminiature sensors needed by NASA for regenerative life support systems. The reasons include unsatisfactory sensor selectivity, poor sensor baseline recovery, degradation of sensor performance with time, and in the case of the bulk mode devices needed for liquid phase sensors, difficulties in signal processing due to the complexity of the output signal which leads to effects such as mode hopping. TPL proposes to develop innovative sensor architectures, surface chemistries, electronics and software techniques to solve the problems that limit piezoelectric sensor performance. This will lead to a miniature, low power, self-calibrating,

high selectivity piezoelectric sensor system suitable for detecting liquid phase analytes in either ground based or space-based systems.

Chemical derivatization of the piezoelectric device surface with a well-bonded, thin film that is highly selective to species such as organic contaminants in water, gives the theoretical capability for rapid measurements with an accuracy of parts per billion. This is due to changes in the oscillation frequency of the crystal in response to increased surface mass resulting from binding of the analyte to the derivatized crystal surface. The superiority of bulk mode devices in the liquid phase compared to the better characterized SAW mode devices arises from the difference in orientation of the acoustic oscillations through the crystal. The SHAPM waves move parallel to the crystal surface which prevents them from being damped at the interface between the crystal surface and the surrounding liquid.

During Phase I, new electronic and software techniques will be developed for exciting the sensor and monitoring its output. The new substrate will allow sensor refresh techniques to be developed that allow the sensor to be self-calibrating thus preventing problems associated with baseline drift. New methodologies will be developed for analyzing the sensor response that allow major improvements in sensor system selectivity. New fabrication techniques will be developed that make the sensors more durable increasing long-term performance in the field. The new concepts will be used to fabricate prototype SHAPM sensors for detection of organic contaminants such as urea in water samples. This approach will show the feasibility of using APM based sensors for regenerative life support systems.

1.1 BACKGROUND

1.1.1 Piezoelectric Devices

A piezoelectric sensor has a pair of interdigital finger transducers (IDT) on Piezoelectric substrate [3,4]. The IDT's form an acoustic antenna array which launch and receive surface and bulk waves through an interaction region where wave velocity is altered by surface mass loading (Figure 1). The mass induced change in velocity is then measured either as a change in the transit time of a pulse, a change in phase with respect to a reference frequency, or a change in frequency of an oscillator in which the sensor provides the feedback path. In order to produce constructive wave generation the finger spacing between the polarity elements must be an integral multiple of the wavelength. For single finger elements the fingers are typically $\frac{1}{4}$ wide spaced $\frac{1}{4}$ apart with alternate fingers connected in common. To reduce reflections from the underside of the fingers and to reduce mechanical stiffening due to metalization, fingers $\frac{1}{8}$ wide space $\frac{1}{8}$ apart connected in alternating pairs are frequently used. The bandwidth of the resurfacing transducer $BW = f/N$ where f is the center frequency corresponding to the element pitch and N is the number of element pairs. The passband shape is the Fourier transform of the finger overlap with uniform overlap resulting in a $(\sin x)/x$ band shape being the most common.

The gain of the transducer array is given by, $G = 4(rA(e))$, where a is the effective aperture measured in wavelengths. For rectangular arrays, G is a maximum for a square IDT pattern. The insertion loss of the array reaches a minimum below a certain bandwidth, $BW(max)$. The minimum number of IDT pairs, $N(min)$ required to achieve that bandwidth are shown in Table I.

In an infinity thick substrate only the surface Rayleigh wave (SAW) will be generated. For a finite thickness, three other main bulk modes may be generated, the shear horizontal acoustic plate mode (SHAPM), the antisymmetric shear vertical (A), and the symmetric longitudinal (S) waves (Figures 2). The number of allowed modes, their spacing and velocity are determined from the wave equations and mechanical properties. The electromechanical coupling efficiency of the modes is estimated from the fractional change in velocity dV/V due to surface metalization.

The amplitude of each type of wave depends on a number of factors including type of piezoelectric material, cut, wave propagation direction in relation to the

axis of the crystal and coupling efficiency between the electrodes and the crystal. Figure 3 illustrates the presence of the different wave types at different frequencies.

Analysis of the frequency response of a piezoelectric substrate provides several insights into the problems encountered with sensors based on these devices. For a given device the speed of the various acoustic waves, and the IDT spacing are both fixed. The frequency relationships for the acoustic waves are therefore also fixed. In quartz, if the SAW mode is given a frequency of 1 then the SHAPM mode will have a nominal frequency of 1.12, the asymmetric shear mode will be 1.6 and the longitudinal shear mode will be 1.8

The amplitude of these waves is a measure of the efficiency of the energy transfer of the wave through the crystal. Most sensor research has been conducted using oscillator circuitry to excite the sensor. As analyte accumulates on the sensor surface the frequency response of the device is changed and the oscillation frequency of circuit goes down. Oscillator circuits are simple and inexpensive to build but have serious limitations. They tend to lock onto a frequency the value of which is determined by a fixed tuning of their impedance. However, since the piezoelectric sensors have many frequencies at which they can efficiently transfer energy (i.e. SAW, SHAPM, etc.), it can be difficult to make the oscillator lock on to the desired mode. This is not usually a problem with SAW mode because it has a far higher amplitude than its close neighbor the SHAPM mode. When sensors using the APM modes are attempted, problems with oscillator circuitry become even more difficult to solve. This is one of the reasons why SAW based sensors are more advanced than APM mode devices.

The major problem encountered with APM based sensors is mode hopping [5,6]. Acoustic plate modes are actually a set of waves that cause the crystal to oscillate at a number of slightly different frequencies simultaneously (Figure 4). These frequencies are called modes. As the mass loading is increased the modes will all shift to a lower frequency. A resonator circuit tuned to one mode will track that frequency peak until mass loading causes the next higher mode to become close enough to the tuned frequency of the resonator circuit. At this point the resonator will lock onto the next higher mode and the frequency output by the circuit in response to increased mass will appear to jump to a higher frequency. This is known as "mode hopping". Problems associated with mode hopping have seriously limited the performance of sensors made based on bulk modes.

1.1.2 Piezoelectric Sensor Sensitivity

The relative mass sensitivity for piezoelectric devices with thin surface coatings is given by the relation $S(m) = df/(dm f)$. In the case of SAW sensors, $S(m) = Kf$ where K is a material constant. In the case of zero order bulk waves, $S(m) = -1/(2M)$ where M is the substrate mass per unit area. Thus SAW sensitivity increases with increasing frequency while bulk mode sensitivity increases with decreasing substrate mass. In the case of the SHAPM, decreasing mass by decreasing substrate thickness also increases mode spacing. For the antisymmetric acoustic plate mode (A(o)) decreasing thickness decreases phase velocity and the operating frequency for the substrate. Decreasing the thickness

of APM devices below approximately $\frac{1}{2}$ wavelength results in poor coupling between the IDT and the acoustic waves.

1.1.3 Commercialization of Piezoelectric Sensors

Saw based organic chemical sensors for gas phase detection have been studied by a number of groups including those at Sandia National Laboratories, the Naval Research Laboratory [7,8]. These sensors have proved very sensitive to a wide range of organic vapors. The lack of selectivity, characterized by response to a range of molecules with similar chemistries, was one factor that prevented the majority of the sensors from becoming commercial successes. A second problem encountered during development was poor recovery to baseline when the analyte was removed for the sensor environment.

To date, the only actual commercial product based on piezoelectric, mass sensor technology is a SAW microbalance developed for Langley Research Center by Femtometrics of Costa Mesa, CA. This device actually uses a SAW resonator, a specialty designed substrate that enhances the SAW mode amplitude and refines its frequency response. The device does not use a chemically derivatized surface and is not susceptible to baseline drift due to residual analyte.

Although a significant amount of research has been conducted for the development of APM based sensors, no APM sensor based products are currently on the market. In addition to the drift and long term stability problems

associated with basic SAW devices, APM's have serious additional problems including mode hopping, complexity of the output waveform, amplitude degradation and shift with mass loading and acoustoelectric coupling when used with ionic solutions [9]. The result of this coupling is a reduction in oscillation amplitude to unusable levels. These and other effects make the development of APM based liquid sensors a difficult but potentially highly rewarding prospect.

2.0 PHASE I TECHNICAL OBJECTIVES

The primary objective of Phase I is to demonstrate the feasibility of detecting trace organic contaminants in water by making major advancements in piezoelectric based sensors. Questions concerning the design and operation of the sensor substrate, mechanisms for exciting and reading the sensor, methods of analyzing the data, chemistry of the derivatized surface, priming and binding of the derivatized layer to the piezoelectric, and response of prototype sensors to known concentrations of organic materials in water will be examined and quantified. To answer these questions, the Phase I research will focus on the following specific objectives:

1. Design and fabrication of prototype sensor substrates with the characteristics need for improved performance.
2. Development of new methods for exciting the sensors and monitoring their response.
3. Fabrication of prototype sensors for testing performance enhancement concepts.
4. Testing the response of the sensors to trace organic materials water.

5. Development of a preliminary design for the Phase II field prototype instrument system.
6. Preparation of the Phase I final report.

3.0 PHASE I WORK PLAN

3.1 TASK 1 – APM SUBSTRATE DESIGN AND FABRICATOIN

The first step in developing an extremely high performance sensor system based on piezoelectric sensor technology is the design and fabrication of a piezoelectric substrate incorporating innovative techniques that lead to the required performance capabilities. By analyzing the characteristics responsible for piezoelectric substrate performance it is possible to design a substrate with maximum sensitivity, high signal amplitudes, immunity to mode hopping, and acoustoelectric coupling when used in ion containing liquids.

For effective sensing of gas phase analytes, SAW mode devices have already proven to have most of the required characteristics. The major limitations are involved with inadequate selectivity and baseline drift. APM devices for use in the liquid phase have more serious limitations involving poor signal strength,

difficulty in sensor readout, mode hopping and others. The work to improve sensor response will be applicable to both APM and SAW devices.

In piezoelectric devices, the shear horizontal mode exhibits a cutoff frequency independent of plate thickness given by $F_c = (C_{66}/\rho) \exp^{-1/2}$ where $C_{66} \exp^{-2} = (C_{55}/C_{66}) - (C_{56}^2/C_{66}^2)$, C_{66} is the anisotropic factor, ρ is the density and C_{ij} are stiffness. For the higher order modes $F_m = F_c [1 + (m^2 \rho^2)/(2C_{66} h^2)] \exp^{-1/2}$, where m is the integer mode number and h is the plate thickness. Constructive interference from the IDT requires the bulk mode wavelength $\lambda(b)$ be related to the emission angle θ by $n\lambda(b) = \lambda(o) \cos \theta$, where n is an integer. The velocity of the wave $v(b) = \lambda(b) f(b)$, thus the bulk mode frequency is $f(b) = n v(b) / \lambda(o) \cos \theta$, where $n = 1$ for the fundamental mode. The horizontally polarized wave does not change polarization upon reflection from the surface boundary thus mode conversions do not occur. The bounce length $L(b) = 2h / \tan \theta$ and the spacing between IDT's is an integral multiple $nL(b)$.

The antisymmetric (A) and symmetric (S) waves for certain materials and cuts may support low pass modes where the zero order antisymmetric wave $A(o)$ phase velocity tends to zero with decreasing thickness while $S(o)$ approaches a constant. As the plate thickness increases the phase velocity of all modes $A(n)$ and $S(n)$ must asymptotically approach the SAW velocity. The vertical shear antisymmetric waves and the longitudinal symmetric waves have displacements in the plane of reflection thus a portion of the energy undergoes mode conversion resulting in vertical shear and longitudinal waves resulting at each reflection. The coupling factor for higher order modes is generally small, thus the zero order modes are of primary interest. For a plate thickness more than a few wavelengths the $A(o)$ and $S(o)$ modes are generated almost equally and have velocities very near the SAW velocity. As the thickness decreases the coupling of one or the other may be strongly dominant.

In the case of the piezoelectric crystal LiNbO₃, the SHAPM mode is most strongly generated in the Z-cut X-propagating substrate with thickness $h=3l(\theta)$ with angle $\theta = 21.8$ degrees and $L(b) = 15l(\theta)$. The antisymmetric mode dominates the Y-cut Z-propagating substrate for $h=l(\theta)/2$ with a coupling efficiency of 5.6%. The symmetric mode with $h= l(\theta)/2$ dominates the X-cut Y-propagating substrate with a coupling efficiency of 15% , as well as the Y-cut X-propagating substrate with a coupling efficiency of 13.5%. Based on the above analysis, a piezoelectric substrate will be designed and fabricated that takes advantage of the effects of materials and physical characteristics on acoustic wave propagation. The device will be of Z cut, X propagating LiNbO₃. Its nominal oscillation frequency will be selected such that the pseudo SAW mode enhances the SHAPM providing good SHAPM signal amplitude. The substrate will be thin and low mass to enhance SHAPM mode separation and mass sensitivity. The number of IDT's will be selected to maximize the bandwidth

without causing excess bounce length. The IDT pattern will be square for high gain and use split fingers to minimize spurious reflections (Figure 5). Another problem encountered with APM liquid phase sensors is acoustoelectric coupling. If there are ions in the liquid under test, the conductive nature of the solution allows the APM to dissipate its energy to the liquid resulting in reduced oscillation amplitude and unacceptable signal to noise ratio for the sensor. TPL has recently examined a solution to this problem first developed at Sandia that appears to have great promise. A very thin layer (20 angstroms) of conductive metal is deposited on the APM surface before the analyte sensitive polymer film is applied. The layer of metal has sufficiently low mass to pose no significant reduction in oscillation frequency and amplitude yet it effectively shields against acoustoelectric coupling when properly grounded.

3.2 TASK 2 – SENSOR EXCITATION AND DATA ANALYSIS

The second aspect of APM sensor technology that has prevented high performance is the inability to accurately monitor the response of the device to mass loading. To enhance sensor accuracy and prevent deleterious effects such as mode hopping, TPL will investigate and develop several new approaches for sensor excitation and response monitoring.

3.2.1 – NEW METHODS OF DATA GENERATION AND ANALYSIS

A promising technique for monitoring piezoelectric sensor response involves a circuit which sends a short (approximately 5 us) pulse of high frequency sine waves into the crystal and monitors the time required for the pulse to appear at the output transducer. The frequency of the sine wave will be the nominal frequency of the shear horizontal APM mode for the crystal. The time required for the signal to reach the output transducer is a measure of the velocity of the wave in the crystal. Mathematical analysis shows that mode velocity is directly related to device frequency and mass loading. The uncertainty of the arrival of the signal will determine the degree of accuracy for the mass loading measurement. A number of techniques including a precision voltage comparator, and degree of correlation circuitry between the input and output waves will be investigated in the determination of the accuracy possible with this method.

Recent advances in the speed, and reductions in power consumption and price of microprocessor electronics make possible the use of digital signal processing (DSP) for the determination of APM sensor response. Digital signal processing is a method of refining desired signal characteristics using high speed analog to digital converter circuitry (ADC) and sophisticated, real time, software analysis, DSP can emulate any analog process in addition to providing a nearly unlimited array of linear/nonlinear processing techniques that are difficult or impossible to implement using analog signal processing. The DSP approach involves three areas; stimulation of the sensor to provide information about the resonance peaks, detection of the desired information in the sensor response, and

compensation for spurious sensor responses. These following techniques will be used:

1. Exciting the sensor with an rf pulse and measuring the delay in propagation due to mass loading. When this technique is used with analog circuitry it suffers from the pulse dispersion and subsequent pulse arrival time ambiguity. Transmission line theory provides for the existence of an rf pulse shape that will be relatively unaffected by dispersion. The effects of alternative rf pulse techniques will be examined in order to isolate the correct non-dispersive rf pulse shape. When isolated this pulse shape will eliminate ambiguities in pulse delay by allowing more effective pulse detection techniques.
2. A more effective time pulse detector based on "matched filter" DSP techniques. Given a known pulse shape with unknown delay and amplitude, an optimal pulse detector can be designed providing for very accurate determination of actual pulse arrival time.
3. Using DSP concepts, the sensor can be considered a frequency-filtering element with a response controlled by chemical loading. If a known input signal is used, the effects of sensor filtering can be determined. Auto-regression and resonance peak analysis algorithms will be developed to provide detailed information on the sensor response. Using this information, tracking of many individual sensor resonance peaks will be performed instead of the single resonance peak tracked with standard resonance circuitry that leads to mode hopping.
4. A separate detection of environmental temperature, pressure and humidity factors will be conducted and regression analysis performed on the results. Trends associated with these factors can be compensated for with software once their formats are understood.

3.2.2. PATTERN RECOGNITION

Substantial improvements in overall sensor flexibility and reliability can be achieved by relating measurements from several different sensors. Use of multiple sensors can both sharpen selectivity and broaden the range of discernible chemicals. Outputs from the sensor array form a "pattern" which can

be compared to other known patterns to deduce the actual concentration of the various contaminants in the environment [10].

Two approaches to this pattern recognition problem will be considered: non-parametric decision theoretic methods and neural networks. These approaches are complementary, the decision theoretic approach tends to decompose patterns by chemical and neural networks evaluate patterns for all chemicals simultaneously without an implied decomposition, Development of high performance pattern recognition is an iterative process with the results of each iteration suggesting methods of improving performance such as the need for new

sensors, the removal of redundant sensors, the need for improved training sets, etc.

1. Decision theoretic pattern recognition assumes that environmental information can be effectively represented by a pattern vector and that given suitable evaluation criteria the pattern can be assigned to a cluster of related patterns. The approach used will be non-parametric in that the distribution of pattern cluster members is not considered to be consistent and will not be used in characterizations. The following efforts will be performed: calculation of pattern normalization, test for redundant sensors, training of discriminant functions, evaluation of sensor importance to overall performance.

2. Neural networks attempt to imitate human pattern matching capabilities. This approach has proven very effective in recognizing complex patterns such as the ones produced by sensor arrays in actual environmental conditions. The following efforts will be performed: selection of network structure and training method, training of the network, evaluation of network to determine the importance of each sensor to overall performance.

3.2.3 SELF-CALIBRATION

A major factor in baseline drift not related to environmental effects on the sensor substrate is caused by the accumulation of residual analyte molecules on the derivatized surface of the sensor. A solution to this source of drift is the incorporation of a sensor refresh cycle for the sensor. A cycle would involve refreshing the sensor to a known baseline by actively driving off the residual analyte followed by reading the sensor response to a known, calibrated baseline. Two methods for refreshing the sensor will be investigated. The first will involve heating the sensor. Since sensitivity is a function of mass per unit area a small sensor can have the same sensitivity as a large one. The amount of energy required to heat a 0.02g sensor would therefore be extremely small and quick to apply. A simple, miniature resistive device would be pulsed by the microprocessor to heat the surface providing the energy needed to liberate residual bound analyte.

A second approach to the refresh would involve the use of conductive polymer films as the surface derivatization. Conductivity in these materials is known to be affected by the degree of oxidation of the polymer. The conductive polymer could

be made selective for organics by developing an anionic substituent specific for the contaminant. The advantages of a conductive polymer are twofold. First, transition between the oxidative state and neutral forms of the polymer can be accomplished by the application of a suitable electric potential. This allows the sensor to be actively driven to a known oxidative state where analytes would be unbound from the sensor surface. The polymer film could then be conveniently returned to a known oxidative with known sensitivity free of

residual analytes, thus significantly increasing sensitivity and reproducibility of the sensor. Second, because of the conductive nature of the material, the substrate could be coated by electro polymerization. This allows the film to be actively engineered with respect to both morphology and thickness yielding an extremely thin but porous coating that improves sensor sensitivity, response rate, and recovery time.

3.2.4. ELECTRONIC TEST INSTRUMENTATION

The electronics TPL will use for the evaluation of sensor response will be composed of a network analyzer coupled through an GPIB interface to a high performance frequency counter and a personal computer. The network analyzer is able to excite the input electrodes and sense the amplitude of the output signal over a frequency range of .001 Hz to 500 Mhz.

A personal computer will be used to control the network analyzer and collect the data generated. Parameters such as excitation frequency, voltage and bandwidth will be selected. The output of the network analyzer will be transferred to the PC in both tabular and spectral form for detailed analysis. As the sensors are developed the PC will be able to perform rapid, automated analysis of the data using DSP and other techniques. This will provide the needed information for the calculation of the performance potential made possible with the proposed methods for improved sensors.

3.3 TASK – 3 FABRICATOIN OF THE PROTOTYPE SENSORS

Ultimately, the advanced sensor substrates and data analysis techniques will be applicable to sensors for a wide range of analytes. During Phase I, TPL will limit the coating materials use to conductive polymers and the analytes sensed to trace organics such as urea in water. The rationale for this approach is to study the potential for sensor performance based on the improvements outline in this proposal. A suite of refreshable sensors whose outputs are read using sophisticated DSP, pattern recognition, and neural network techniques could form the basis for a synthetic “nose” capable of monitoring a wide range of analytes with extremely high sensitivity and stable long term performance.

3.3.1. – PRIMING THE SENSOR SUBSTRATES

One of the major problems that has limited piezoelectric sensor performance is the lack of long-term stability. Adhesion between the analyte coating material and the piezoelectric substrate surface is critical for high durability. The strongest method for anchoring the sensitive film is to form a covalent chemical bond between the surface and the film. There are several methods that can be used to anchor materials such as polymers or ceramics to the APM device surface. A well-established technology exists for binding materials by derivatizing with silane

coupling agents [11, 12], proper choice of silane functionality allows a variety of materials to be chemically attached to glass-like surfaces. Glow discharge plasmas can be used to create the proper surface for chemically binding a variety of materials. TPL has the experience and equipment

to perform these priming techniques. The strength of adhesion will then be determined using standard ASTM mechanical testing procedures.

3.3.2. COATING THE PROTOTYPE SENSORS

The sensor coatings must form a reversible bond to the analytes for repeatable long-term performance. Three conductive polymers will form the basis for the substrate surface derivatizations, polypyrrole, polyaniline and polythiophene. Self-doping, organic contaminant attractive side chains will be incorporated to enhance analyte sensitivity without compromising the conductivity of the films. Polyaniline films will be prepared in 50 ml of 2 M sulfuric acid solution containing 0.1 M aniline. The applied voltage will range from -0.1 to $+0.90$ volts with scan rates in the 50 Mv/sec range. By varying the duration of the electroplating process it will be possible to adjust the morphology and thickness of the coating to obtain enhanced sensor performance characteristics. Polypyrrole films will be deposited in a 0.2 M potassium chloride solution containing 10 Mm pyrrole. A plating potential of 0.9 volts will be applied for different periods and the results observed and quantified. Other conductive polymers will be electro polymerized using techniques similar to those described. The films produced will be examined by obtaining voltammograms and performing scanning electron microscopy (SEM).

3.4 TASK 4 – LABORATORY TESTING OF THE PROTOTYPE APM SENSORS

The test apparatus will allow the prototype sensors to be exposed to a selected level of analyte under controlled temperature and humidity. A glass test cell, approximately 2 cc internal volume, will sensor under test. An aperture at the top of the housing will provide a good glass to sensor seal. Teflon tape will be wrapped around the sensor and glass aperture to produce a gas tight seal. The glass test cell will have Teflon fittings for 1/8 inch diameter tubing which connect it to a precision analyte stream generation system. Separate precision flow controllers deliver a precise amount of diluting material (water) to the mixing system. The sensors will be tested inside a temperature and humidity controlled environmental chamber. Temperature, humidity and pressure will be monitored by computer to determine correlations between these factors and sensor performance. Prototype sensors will be tested by exposure to the selected organics such as urea, at the 20 ppb to 200 ppm levels in water.

3.5 TASK 5 – PRELIMINARY SENSOR SYSTEM DESIGN

A sensor system design that incorporates all of the features described above will be formulated with a twofold purpose. 1) To determine the feasibility of the proposed instrument and predict its performance capabilities under actual field conditions. 2) To determine the technical difficulties and costs associated with full development and fabrication so that detailed and accurate projections can be made concerning the fabrication of the Phase II functional prototype of the instrument.

3.6 PERFORMANCE SCHEDULE

Task 1 will be completed two months after the beginning of work.

Task 2 will be completed three months after the beginning of work.

Task 3 will be completed four months after the beginning of work.

Task 4 will be completed five months after the beginning of work.

Task 5 will be completed six months after the beginning of work.

Task 6 will be completed six months after the beginning of work.

TPL will provide a final report containing the data, analysis, and conclusions based on the research conducted in tasks 1 through 5.

4.0 RELATED R/R&D

4.1 RELATED RESEARCH

The proposal research represents an extension of the efforts of TPL in the areas of piezoelectric sensor technology, specialty coatings, surface chemical modification processes, chemical synthesis, and surface chemical characterization techniques. It is also a direct extension of R&D work conducted at TPL and Sandia National Laboratories on acoustic wave devices. TPL has interacted quite extensively with the personnel of Sandia in the development of piezoelectric devices.

In 1991 TPL conducted a Phase I program for NASA with informal collaboration from personnel at Sandia National Laboratories. The focus of that program was the development of an organic contaminant sensor for the drinking water system in space station freedom based on APM piezoelectric sensors. The results were promising in that the prototype sensor was able to detect a number of analytes at ppb levels. However, Phase II was not funded. This was due to a number of factors including unsatisfactory sensor selectivity and poor sensor baseline recovery. The proposed solution to those problems was to incorporate a chromatography unit into the system to separate and concentrate the analytes prior to sensing. That approach was deemed too large, heavy, complex and expensive to be practical for the space station.

Since that program, TPL has made significant progress in the development of theoretical models and realistic approaches to the solution of the limitations of APM based sensor for liquid based measurements. The solutions proposed in this proposal are an outgrowth of that new and innovative thinking. The proposed new APM architecture with enhanced signal characteristics; new methods for self-calibration of the sensor, and advanced techniques for data analysis should make possible the simple, miniature sensor system needed by NASA.

TPL has recently been awarded a Phase II program from NASA to develop a SAW based sensor for hydrazine vapor in air. The goal of that program is a highly specific sensor for use in an environmentally controlled area. The Phase I

program was successful in the development of a surface chemistry with sensitivity to hydrazine.

TPL was awarded a Phase I contract by the NSF to develop a SAW based sensor for monitoring CO₂ concentrations in seawater. A sensor based on the

solubility of CO₂ in polyalkoxphosphazene polymers was fabricated and tested and showed significant promise. A Phase II program is anticipated for the development of a field prototype sensor system.

Some of the technology developed during these research programs is applicable to the proposed program and should improve the probability for success.

However, the goals of the two programs are fundamentally different since the previous research is based on SAW sensors rather than SHAPM sensors. As previously discussed there are fundamental differences between the two device types. In general APM sensors have far more challenging obstacles impeding high performance but have the potential for use in the liquid phase, something SAW mode devices cannot do.

In addition to chemical sensor research, the Principal Investigator, Mr. Timothy Tiernan, has been involved in a wide range of research for the development of sophisticated instrumentation for automated sensing, and data acquisition. Prior to his work at TPL, Mr. Tiernan was employed at Radiation Monitoring Devices Inc. as the Manager of Biomedical Engineering. While there, he was responsible for research programs aimed at the development of a wide range of instrumentation for a number of applications including non-destructive analysis of fiberglass reinforced composites, analysis of bulk grain supplies using genetic engineering techniques, and development of a complex dosimetry system for flight personnel in low Earth orbit.

4.2 REFERENCES

5.0 RELATIONSHIP WITH PHASE II OR OTHER FUTURE R/R&D

5.1 ANTICIPATED PHASE I RESULTS

The result of a successful project will be the demonstration of the feasibility of major enhancements to piezoelectric based sensors that will allow them to be used for extremely rapid and accurate analysis of contaminants in liquids.

Development of the sensor fabrication and data analysis methodologies for the system during the Phase I program will form the basis for the development and fabrication of a field prototype monitoring instrument during Phase II.

5.2 SIGNIFICANCE OF PHASE I TO PHASE II

The phase I program will demonstrate the feasibility of using APM technology to analyze for trace organic contaminants in water. During Phase I, research will focus on performance enhancements for the sensor substrate, new electronics and software techniques for exciting and monitoring the sensor that result in

improved data analysis capabilities, new concept for maintaining sensor baseline stability and long term performance, surface derivatizations based on conductive polymers, and preliminary specifications for pattern recognition algorithms for data analysis. Prototype sensors will be fabricated and examined for their ability to perform the desired measurements in the laboratory.

During Phase II, the design of actual field prototype will begin. The phase I effort will provide the knowledge required to determine realistic performance specifications for the system and these will be fully developed. Sensors that were found to be lacking in certain performance characteristics will be improved. The

required electronics will be designed and fabricated so that a complete instrument for automated measurements can be fabricated for field-testing.

6.0 COMMERCIAL APPLICATIONS POTENTIAL

6.1 FEDERAL GOVERNMENT APPLICATIONS

In addition to NASA's need for regenerative life support, a simple yet accurate instrument for detection of organic contaminants in water that could be operated in the field or automatically at remote locations and provide real time data would have widespread application for the U.S. environmental program. It could provide critical information on the status of groundwater, aid in the demarcation of pollution sites, monitor the progress of cleanup efforts and provide data for correlation of water quality and biological activity. The proposed device would be simple and inexpensive enough for widespread use. The concept for the sensor is very flexible and could be applied to a wide variety of contaminants so that the basic sensor system could be used to monitor most of the pollutants found in the environment. It could also be used to evaluate antipollution programs that are being developed to prevent contaminants from entering the groundwater environment.

6.2 COMMERCIAL APPLICATIONS

Piezoelectric based sensors have numerous potential applications. The technology that will be developed with respect to surface treatment, packaging, data collection and analysis and overall performance would be applicable to a wide range of sensors for chemicals, corrosion and other properties. Oil refineries, nuclear reactors, and chemical plants have a large number of situations where sensor arrays capable of monitoring critical parameters would be invaluable. The potential accuracy and sensitivity of the proposed sensor technology suggest that it has the potential for application in many industrial and manufacturing processes.

The number of U.S. companies with interest sensors is extremely broad and includes major oil companies, water districts, automakers, chemical and glass manufacturers and many others. Because the APM sensor provides more potential sensitivity to mass changes than virtually any other chemical sensing technique, and because the surface modification schemes proposed here could

impart these devices with specificity for a large number of materials the potential market is very large.

Follow-on Phase III funding is expected to be obtained from a number of industrial concerns, including the limited partners of the venture capital fund, AMT Venture Partners, Ltd. Of Dallas, TX, that has an equity investment in TPL, Inc. The limited partners of AMT are some of the largest international companies concerned with sensor technology including DuPont – chemical sensors for industry, Showa Shell (Japan) – petrochemical industry, and Lubrizol - lubricant additives. This relationship provides TPL with direct access for probable strategic alliances that will provide the funding for additional development of sensors for

specific applications. Under this scenario, TPL is prepared to utilize the technology in-house to manufacture sensors for commercial applications.

7.0 COMPANY INFORMATION

7.1 TPL, Inc.

TPL was established in late 1989 by H.M. Stoller, its President and Chief Executive Officer. It has two major business areas; advanced materials and sensors R&D, and applications of energetic materials. The former is technically directed by Dr. Richard Brotzman, Director of Research, and includes programs in sol-gel ceramics, high technology polymers, chemical and radiation sensors, and reactive chemistry for adhesive applications, the latter is directed by Mr. Stoller. TPL currently has 19 employees and anticipates FY93 revenues in excess of \$2.4 million.

TPL's primary long-term objective is developing commercial products from its research and development efforts. To this end, a financial investment was obtained, in May 1991, from AMT Venture Partners, Ltd, Dallas, TX and its co-investor, the John Hancock Advanced Materials Fund. These venture capital firms and AMT's limited partners (11 international materials related companies, DuPont, Toray, St. Gebain, etc.) provide both the financial backing and strategic business relationships that will help us attain our objective.

TPL intends to remain a highly diversified materials technology company and commercialize its technologies, either through developing a manufacturing capability or licensing, depending on the particular business strategy adopted. A major advance occurred in June, 1992 when TPL was awarded a \$1.5 million contract to continue development of a high energy density storage dielectric polymer. This contract, an outgrowth of an SBIR program, is being accompanied by a TPL-funded business plan development which is formulating a commercialization strategy based on capacitor products.

TPL is pursuing the development of sensors and imaging systems based on novel technologies. Its research in the areas of new radiation detection materials

is expected to play a major role in the commercialization of the instrumentation concepts detailed in this proposal.

7.2 FACILITY/EQUIPMENT

TPL occupies over 10,000 square feet of office and laboratory space. Facilities of importance to the proposed program include:

1. Electronics Testing Laboratory containing an HP network analyzer model 4195 A with test kits, HP multi-input data acquisition system, computerized LCR meter, 350 Mhz and 100 Mhz digital oscilloscopes, capacitance meter, signal generator, plotter, impedance bridge, digital multimeters, computerized frequency counters, low and high voltage power supplies with ramp generator, a large selection of passive and active components, a variety of computational, analysis, plotting and database software, thinkjet printer, BP plotter, strip chart recorders, temperature and humidity controlled test chambers, BP microprocessor development system, a variety of data acquisition and

- control boards for PC computers, PC/AT and Hewlett Packard computer systems.
2. Synthetic Chemistry Laboratory containing hoods, glassware, heaters, balances, and inert atmosphere chambers, which provides the capability to do complete chemical synthesis of advanced polymers and sol-gel ceramics.
 3. Analytical Diagnostics laboratory containing a nuclear magnetic resonance (NMR) facility, gas chromatograph, Fourier Transform Infrared Analysis Spectrometer, UV-visible spectrometer, fluorescence spectrometer, Cahn Wet-Tek Surface Energy Measurement System, BloSym Corporation's molecular modeling of materials software and a Silicon Graphics Workstation which provides the capability to perform significant materials analysis.
 4. General high bay laboratory space which includes: United Mechanical Test Machine with 1200 degree F temperature capability; 12" X 12" hot press, 30 ton force and 600 degree F; metallography table, chemical hoods furnaces; storage cabinets; electronics laboratory; and sample preparation areas.

TPL is an industrial member of the NSF-sponsored Center for Micro-Engineered Ceramics, University of New Mexico. TPL presently has access to two laboratories at CMEC. The first is a fully equipped analytical chemistry lab which we use for both sol-gel ceramics and polymer synthesis work. The second laboratory contains an ultra high vacuum apparatus for the measurement of diffusion properties in ceramic coatings and optical equipment to conduct strain birefringence measurements in gels and polymers. As an industrial member of CMEC, TPL has direct access to all of their analytical equipment. A summary of this equipment follows: High field liquid FT-NMR spectrometers; GE NT-360, JEOL GX-400, Bruker AC-250P; Low field pulse NMR spectrometers; 10, 20, 4-60 Mhz Hitachi S-800 field emission SEM with low Z x-ray analysis; UNM

Electron Beam Microanalysis Facility, with JEOL 2000FX; TEM with TN5500 EDS, and a JEOL superprobe with 5 spectrometers; UNM Powders and Granular Materials Laboratory, with porosimeters, image analyzer, nitrogen sorption analyzer, particle size analyzers, adsorption instruments, gas permeation apparatus, TGA, DTA, DSC, dilatometer, single-crystal and powder x-ray diffractometers; Temperature-programmed desorption/Auger apparatus; Aerosol reactors for powder generation and gas-phase particle-size distribution analyzers.

The facilities and equipment used in this program will comply with environmental laws and regulations of the federal government, the State of New Mexico and local governments.

8.0 KEY PERSONNEL

8.1 TIMOTHY C. TIERNAN – PRINCIPAL INVESTIGATOR

Mr. Tiernan will be the principal investigator. Mr. Tiernan joined TPL in January, 1991 as a Senior Scientist. He played a major role in the conduct and analysis of

the experiments that resulted in the development of SAW based sensors for hydrazine and CO₂. While at TPL, Mr. Tiernan has also been involved in the development of neutron activation analysis instrumentation for industrial process control, and large pixel arrays made with hydrogenated, amorphous silicon. Mr. Tiernan's extensive experience in the engineering and development of commercial sensor systems and radiation detector products provides the necessary qualifications to direct the proposed program.

Previously, Mr. Tiernan was employed at Radiation Monitoring Devices Inc. as Instrumentation Manager. He was responsible for the development of a range of radiation detection and nuclear medical instrumentation. Under an Air Force contract, Mr. Tiernan led a team of scientists in the development of a complex radiation environment composed of alpha and beta particles, gamma rays and neutrons and provide separate dose information for each type of radiation. A prototype of the instrument was designed, fabricated, tested and delivered to the Air Force for their evaluation.

Mr. Tiernan has also been responsible for the development of instrumentation for commercial products. An example of an industrial device based on radiation detection techniques was the development of a system for analysis of bulk grain supplies. Under contracts with the NIH, instrumentation was developed for a number of nuclear medical applications. Two examples are: instrumentation for the analysis of cerebral blood flow in the intensive care situations and during surgical procedures in the operating room; a small, computerized, battery powered, hand-held probe for the location of radiolabeled tumors during surgery.

Mr. Tiernan has also been involved in the development of a number of radiation detection systems for industry including stack monitors for nuclear power plants, on line controls for nuclear waste storage facilities and coal mining operations. Mr. Tiernan has also been involved in the development of a number of radiation detection systems for industry including stack monitors for nuclear power plants, on line controls for nuclear waste storage facilities and coal mining operations. Mr. Tiernan earned his B.S. in biochemistry from the University of Maine in 1979 with a focus on biomedical engineering and instrumentation.

Some of his publications pertinent to the current work include:

1. T.C. Tiernan, K.B. Kidd, R.W. Brotzman, "CO₂ Sensor System for Long-Term Ocean Monitoring," Final Report submitted to NSF, TPL, Inc. Contract No. ISI-9160100, November 1992.
2. T.C. Tiernan, R.W. Brotzman, H.M. Stoller, "High Sensitivity Hydrazine/N₂O₄ Detector System," Final Report submitted to NASA, TPL, Inc. Contract No. NAS9-18675, September 1992.
3. P. Waer, G. Entine, T. Hazlett, and T. Tiernan, "Small, Remote Cadmium Telluride Radiation Monitor," presented at the Health Physics Society Meeting Boston, MA, June 1988.
4. T. Tiernan, V. Nagarkar, G. Entine, J.G. Hardy, et al., "Portable Solid State, Real-Time Instrument for Space Dosimetry," presented at the Health Physics Society Meeting, Boston, MA, June 1988.

5. T. Tiernan, G. Entine, D.A. Stump, D.S. Prough, "Portable Real Time Analysis Systems for Regional Cerebral Blood Flow," IEEE Proc. Of Nucl. Sci., NS-35, No. 1, February 1988, pp. 698-702.
6. T. Tiernan, G. Entine, D.A. Stump, D.S. Prough, "Intra-Operative Regional Myocardial Blood Flow Monitor," Abstract, Soc. Of Nuc. Med. Symp., San Francisco 1988.

8.2 DR. RICHARD O'BRIEN –STAFF SCIENTIST

Dr. O'Brien will perform the chemical synthesis and polymer side chain modifications required to develop the surface chemistries needed for high sensitivity and selectivity to trace organics. Dr. O'Brien has extensive experience in synthetic chemistry with major emphasis on the development of new approaches to polymer modification. His current research involves the development of new types of polyalkoxyphosphazene polymers. He is also participating in the development of new pathways to cubanes.

Dr. O'Brien earned his Ph.D. in Chemistry from the University of Nebraska at Lincoln. He has extensive experience in the synthesis and characterization of organic, organometallic, and polymer compounds as well as significant academic training in these areas. He also holds an M.S. in Organic Chemistry from the

University of North Dakota and a B.S. in Professional Chemistry from South Dakota State University.

Before joining TPL, Dr. O'Brien was a Senior Research Scientist at Rieke Metals, Inc. His research included the preparation and characterization of functionalized organic molecules, organometallic reagents, and a wide variety of conducting polymers such as polythiophenes, poly 3-alkyl thiophenes, poly-para-phenylenes, and poly phenyl ketones.

1. R.A. O'Brien, R.D. Rieke, "Direct Metalation of p-Bromopolystyrene Using Highly Reactive Copper and the Preparation and Reaction of Highly Reactive Copper Bound to an Insoluble Polymer," J. Org. Chem. 55,788 (1990).
2. R.A. O'Brien, T. Chen, R.D. Rieke, "Chemical Modification of Halogenated Polystyrene Resins Utilizing Highly Reactive Calcium," J. Inorg. And Organomet. Polym. 2(3), 345 (1992).
3. R.A. O'Brien, T. Chen, R.D. Rieke, "Chemical Modification of Halogenated Polystyrene Resins Utilizing Highly Reactive Calcium and Formation of Calcium Cuprates in the Preparation of Highly Functionalized Polymers," J. Org. Chem. 57,2667 (1992).

8.3 DAVID W. CUTLER – SENIOR ENGINEER

Mr. Cutter will participate in the sign of the SHAPM sensor substrate, electronics and software needed for the development of the prototype piezoelectric sensors. Mr. Cutler has extensive experience with mathematical modeling of complex systems, digital signal processing techniques, and the development of sophisticated real time analysis methodologies based on neural networks. Mr.

Cutler is currently engaged in the development of chemical sensors for hydrazine and software based image enhancement techniques for silicon pixel arrays. Prior to joining TPL, Mr. Cutler was employed at E-Systems, Inc. During his 15-year term of employment, Mr. Cutler has held a number of positions covering the hardware, software, and systems designs. Mr. Cutler designed a number of digital control related instruments including a receiver interface for a Watkins-Johnson wideband receiver system, a control unit for a video crossbar switch, computer keyboards, a format convert for a "T1" like TDM multichannel digital audio system, and an embedded controller for a multichannel steerable beam antenna. He was the task leader for the 7-person hardware and software design team on a high integration card tester. This tester provided both debug and production test capability for a set of 13 cards averaging over 100 VLSI and other ICs per card.

Mr. Cutler was a senior team member of a 10-person team that implemented a multifunction receiver/modem. He provided leadership in the creation of a real-time, multiprocessing/multitasking operating system for this modem, implemented the receiver and modem functions, was a technical resource for the

coding of the data stream manipulation and EDAC functions, and provided an interface to other design and systems groups. He was responsible for the design of the "next generation" receiver/modem being designed at his leaving E-Systems.

Mr. Cutler has an M.S. in Electronics Engineering with concentration in Digital Signal Processing from Southern Methodist University, an M.S. in Systems Management from the University of Southern California, and a B.S. in Electronics Engineering from Louisiana Tech University.

9.0 CONSULTANTS AND SUBCONTRACTS

No consultants or subcontracts are proposed.

10.0 SIMILAR GRANT APPLICATIONS, PROPOSALS OR AWARDS

As mentioned previously, NASA has funded a Phase II program for the development of a hydrazine detector and NSF has funded a Phase I proposal for monitoring CO₂ in seawater. Both of these programs are based on SAW mode devices which are significantly different from APM mode sensors. In addition, the focus of those programs is on different types of measurement problems, a different detection medium (gas rather than liquid) and a different emphasis for the resulting instruments which makes that research significantly different from the proposed program for an APM based sensor.

11.0 PREVIOUS NASA AWARDS

NAS 10-11654, "A Repair Coating for Cryogenic Transfer Lines," 1990, Phase I, Kennedy Space Center

NAS8-38909, "Aerogel Processing of Ceramic Composite Membranes," 1991, Phase I, Marshall Space Flight Center

NAS8-38891, "Organic Contaminant Monitor," 1991, Phase I, Marshall Space Flight Center

NAS9-18675, "High Sensitivity Hydrazine/N₂O₄ Detector System," 1992, Phase I,
Johnson Space Center