Draft Final Report to

NASA, Kennedy Space Center
Advanced Projects Office

From

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150 West University Blvd.
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March, 1998

Dr. Charles Bostater
I. Introduction & Background

This NASA grant was funded as a result of an unsolicited proposal submission to Kennedy Space Center. The proposal proposed the development and testing of a shallow water optical water quality buoy. The buoy is meant to work in shallow aquatic systems (ponds, rivers, lagoons, and semi-enclosed water areas where strong wind wave action is not a major environmental factor. The proposal stated that the project was based upon the integration of a proprietary and confidential sensor and probe design that was developed by KB Science and Engineering and is currently patented by KB Science. The buoy's purpose was to collect hyperspectral optical signatures for analysis and resulting estimation of water quality parameters such as chlorophyll-a, seston and dissolved organic matter (DOC). The ultimate goal of the project was to develop a buoy that would integrate a probe to measure upwelling light from a source and thus relate this backscattered light to water quality parameters.

During the project period a buoy was constructed and integrated the confidential and proprietary probe or sensor design as originally proposed. A picture of the buoy, probe and various components have been previously provided to Kennedy Space Center employees (K. Poinbeouf and D. Britt) at their request.

During the project period of three years, a demonstration of the buoy was conducted. The last demonstration during the project period was held in November, 1996 when the buoy was demonstrated as being totally operational with no tethered communications line. During the last year of the project the buoy was made to be solar operated by large gel cell batteries. Fund limitations did not permit the batteries in metal enclosures as hoped for higher wind conditions, however the system used to date has worked continuously for in-situ operation of over 18 months continuous deployment.

The system needs to have maintenance and somewhat continuous operational attention since various components have limited lifetime ages. For example, within the last six months the onboard computer has had to be repaired as it did approximately 6 months after deployment. The spectrograph had to be repaired and costs for repairs were covered by KB Science since no funds were available for this purpose after the grant expired. Most recently the computer web page server failed and it is currently being repaired by KB Science. In addition, the cell phone operation is currently being funded by Dr. Bostater in order to maintain the system’s operation. The above points need to be made to allow NASA to understand that like any sophisticated measuring system in a lab or in the field, necessary funding and maintenance is needed to insure the system’s operational state and to obtain quality assurance and control of the data collected.

Future needs include the development of a maintenance agreement with KB Science and Dynamac Corporation at KSC to insure the system is properly operated and quality assured and data checked as well as to cover routine maintenance costs on a regular basis. These costs are estimated at approximately 20-25K per year based upon the costs over the last 12 months to replace key electronic components and manpower costs associated with operation of the buoy.
Publications Completed During Grant Period

Publications made during the grant period which describe the research (supported in part by the NASA grant) activities of the Marine & Environmental Optics & Remote Sensing Center are listed below. Support was used for several students listed in the conference proceedings. The first paper listed is the major paper that describes the buoy project and copies are available from Dr. Bostater.


Other related publications:


Other reports which document activities supported (in part) by the grant are published and publicly available from University Microfilms International, UMI Dissertation Service, a Bell & Howell Information Company or by requesting copies from librarians at university or government library. The thesis reports are listed below:


  **Note**: This student working on Ph.D. at University of Rhode Island, Marine Science Program involved with deep ocean buoy research with a leading world expert.


  **Note**: Student now works at NASA, Kennedy Space Center as a remote sensing specialist.


  **Note**: Student now works at NASA, Goddard Space Flight Center and NOAA’s National Hurricane Center as a remote sensing/meteorological scientist.


  **Note:** Student now works at Kennedy Space Center.

• Development and Sensitivity Analyses of A Remote Sensing Fluorescence Model for Water Quality Applications in Coastal and Marine Environments (*In Progress*).

  **Note:** This student now works at Kennedy Space Center.


• A Remote Sensing & Environmental Optics Model of Florida Coastal Scrub Plant Communities in Central Florida, Carlton Hall (*In Progress*).

  **Note:** Student works at Kennedy Space Center, NASA

**Dr. Bostater has also served on master and doctoral committees throughout the university during the grant period as indicated below. These reports are available at the Florida Tech library.**


• Spatial Analyses Using GIS For Queen Conch Larval Settling in the Bahamas, 1996.

III. Web Page Development For Project

Copies of relevant web pages developed for the buoy project are attached and can be downloaded by anyone obtaining the source files. Any one having problems obtaining the source files can contact Dr. Bostater for assistance. The web site for the buoy is located under http://probe.ocn.fit.edu. Web pages were developed to integrate the buoy real time data availability via the web site for the Environmental Optics and Remote Sensing Lab.

The web pages are running under two Silicon Graphics workstations. The web pages under the site at www.ocn.fit.edu or system flux.ocn.fit.edu is owned by KB Science who contributed to the success of this project and has provided modem, ISDN, CPU and hard disk space for the projects success. Two of the Silicon Graphics workstations used during this project and purchased under this grant have been returned to Kennedy Space Center as agreed upon.

Additional documentation for the project is included in the Appendix of this final report.

IV. Summary & Conclusions

A shallow water quality buoy has been developed and is available for use to help assess the effects of rocket launches on nearby ponds and water systems at Kennedy Space Center. The next phase of an operational project needs to be established for the transfer of the buoy system to Kennedy Space Center for testing before and after rocket launches as originally proposed before the project began. In order to conduct this phase of the operation of the system, proper quality assurance and control of the system's performance is critical. This is needed to insure that the data obtained from the system provides accurate and reliable data when compared with other standard methods of water and wastewater analysis as prescribed by the US EPA and other agencies at the state and federal governmental levels. It is proposed that a teaming arrangement be created between KB Science (a small business who holds a patent for building the probe used on the buoy) and Dynamac Corporation. The purpose of this arrangement would be to transfer the system to NASA and for operation of the system in a concerted effort to measure water quality parameters in the vicinity of the KSC rocket launch complex. This NASA funded project would thus allow the determination of data QA/QC and limited data access from outside of the NASA KSC complex.
Appendix & Attachments
REAL TIME MONITORING OF WATER QUALITY PARAMETERS USING A REMOTELY SENSED DATA SYSTEM: DATA ACQUISITION, TRANSMISSION, ANALYSIS, DISPLAY, AND ARCHIVING

Ted McNally, Melissa Keller, and Charles Bostater
Marine and Environmental Optics Laboratory, Center for Remote Sensing
Marine and Environmental Systems Division
Florida Institute of Technology
150 W. University Blvd.
Melbourne, FL 32901

ABSTRACT

The science of remote sensing and advances in computer technology and communication systems have made it possible to monitor water quality parameters (chlorophyll-a, seston, and dissolved organic matter) in real time. The fundamental processes involved in such monitoring are acquisition of the remotely sensed data by the sensor, transmission of the data from the field to a more centrally located site, analysis and calibration of the data to determine water quality parameters, display of these parameters as a function of time, and archival of the data for immediate or future environmental decision making. Various methods for performing each of the five processes are described and evaluated. In addition, a case study is described that is based upon a specially designed shallow water optical buoy and a high resolution solid state spectrograph that measures light over 252 channels from 362 to 1115 nm as the data acquisition sensor. The data is transmitted from a remote location to Florida Tech where it is analyzed and correlated to water quality parameters using derivative spectroscopy described by Bostater (1991). The data is then displayed, in real time, and archived on an SGI Indigo² UNIX-based workstation. The system described provides real time remote sensing (ground truth) or reference data as inputs to satellite and aircraft remote sensing systems via access to the Internet based data archive.

1.0 INTRODUCTION

Increasing awareness of the truly global nature of environmental problems has led to an explosion in the amounts and types of data requested by physical scientists of all branches. The spatial and temporal resolutions of the data needed to address these

*Presented at Eco-Informa '96, Lake Buena Vista, Florida, 4-7 November 1996.
problems were imposing obstacles before the advent of remote sensing as a science. In today's world, increasing use is being made of technological and scientific advances in remote sensing to gather the data necessary to make intelligent environmental decisions. To effectively monitor any facet of the environment in real time requires significant planning and foresight. Specifically, decisions in five areas of operation of the data collection system need to be made. These five areas are data acquisition, transmission, analysis, display, and archiving. This paper begins with a discussion of each of these areas and ends with a case study of a shallow water optical buoy designed to measure chlorophyll, seston, and dissolved organic matter in real time in remote locations. Throughout, the emphasis is on optical remote sensing systems.

2.0 FUNDAMENTAL PROCESSES

2.1 DATA ACQUISITION

When designing a data acquisition system for remote sensing applications, it is important to take into account four fundamental resolutions of the system. Slater (1980) gives these four fundamental resolutions as temporal, spatial, radiometric, and spectral. Temporal resolution refers to the time scale of the sampling system. For instance, to measure atmospheric or oceanic turbulence, the sensor would have to be capable of recording data at time intervals less than one second. However, satellites such as the Advanced Very High Resolution Radiometer (AVHRR) measure parameters such as sea surface temperature at much greater time intervals (each point is measured every 8 hours). Spatial resolution refers to the smallest area that the sensor system can resolve. Again, turbulence measurements would need spatial scales on the order of centimeters, while satellite scales use much greater (on the order of 10s of kilometers). Radiometric resolution refers to how many discrete steps the full range of values is divided into. Radiometric resolution can be expressed in bits where 8 bit resolution gives 256 discrete levels, 10 bit gives 1024 levels, etc. Spectral resolution refers to the bandwidth of sensor systems, i.e., how many different channels are sampled, and the bandwidth of each channel. Water quality parameters are sampled more accurately with a high number of channels in the visible spectrum (from about 400-700 nm) with a small bandwidth (of 1 to 2 nm), while parameters such as sea surface temperature are routinely measured with high bandwidths and fewer channels. All four of these parameters need to be considered before the choice of a sensor can be made.

2.2 DATA TRANSMISSION

After the data has been acquired at a remote location, it must be transmitted back to a more central location for processing. Major considerations for the transmission of the data are the data throughput rate (how much data is being passed)
and how often is data being returned to the central location. Data that is not transmitted continuously and that can be sent in small batches less than 10 megabytes can be sent via modem and phone line, while continuous streams of data consisting of larger batches are generally sent by radio or microwave.

2.3 DATA ANALYSIS

When the central location receives the data, the raw measurements from the sensor must be translated into useful parameters to study the medium of interest. In the case of optical sensors, the fundamental parameter of interest is the irradiance reflectance, but radiance is also used. However, the sensor measures not only the medium of interest, but also measures light scattered into the sensor for the atmosphere without ever reaching the medium of interest. This path radiance must be accounted for and filtered from the signal to get an accurate reading. Various methods for accounting for the path radiance are beyond the scope of this paper, but the interested reader is referred to Duntley et al. (1957), Sturm (1981), Klemas and Philpot (1983), and Stumpf (1987) for two of the techniques that can be used.

For an optical sensor, once the path radiance has been subtracted, the radiance converted to irradiance, and the irradiance reflectance calculated, the reflectance spectrum is analyzed to determine the parameter of interest. For example, radiance from three channels of the AVHRR satellite can be used in a simple linear equation to determine sea surface temperature (Robinson, 1985). In the case of determining water quality parameters such as chlorophyll, where hyperspectral, small bandwidth sensors are used, more involved techniques can be used. One such technique (Bostater, 1991) involves derivative spectroscopy, where the derivative of the reflectance spectrum is calculated between various bands, and by regressing these band ratios to measured data, optimal bands or channels can be selected to measure the parameter of interest. Whatever technique is used, periodic ground truthing or in situ analysis is required to develop and maintain the algorithm.

2.4 DATA DISPLAY

For environmental resource managers and regulatory agencies, display of the data in a coherent, easily understandable form is very important. Figure 1 shows the form used to display the data from the shallow water optical buoy described in the next section. The form of this display provides a good example of the types of displays desired by environmental managers. With reference to Figure 1, the large window displays the raw data, in this case the digital count from the sensor measuring the amount of light upwelling from the water as a function of wavelength. The display of raw data is important in that it allows for a quick, basic check on the accuracy of the processed data. The first smaller window in the upper right of the screen displays the...
4.0 REFERENCES


Figure 1. Screen capture showing the graphical display of real time output from a shallow water optical buoy.

Figure 2. The shallow water optical buoy.
Shallow Water Optical Buoy

The buoys are operated and maintained as a collaborative project between NASA, Kennedy Space Center, Dynamac Corp, KB S&E and Florida Tech.

The buoy systems utilized in this water quality monitoring project are designed to provide water quality data in shallow inland and coastal water types. The buoys utilize an optical sensing system to measure upwelled or backscattered light. The optical data are also being used to relate critical hydrological optical data to airborne and satellite sensors in order to study the earth as a system. Data collected is sent from onboard computers to a Silicon Graphics powered Internet Site. The raw data is processed and water quality parameter concentrations calculated using state of the art standard procedures for estimating water quality parameters from the optical data. The water quality algorithms are based upon radiative transfer theory and modern spectroscopy techniques and are calibrated to standard methods used for water & wastewater analyses. Buoys are being located in the coastal lagoonal systems of the Bananna River and planned for locations in the Indian River Lagoon region of Florida’s Space Coast shown in the map below. Clicking on the numbers on the map, or the links on the right will take you to a page with the data for the existing and proposed locations. (Click on station #1 as an example). The other locations are not active for public viewing at this time.

Select the station you are interested in:
Station Locations:

- Station #1
- (Insert Physical Location here)
- Station #2
- (Insert Physical Location here)
- Station #3
- (Insert Physical Location here)
- Station #4
- (Insert Physical Location here)
- Station #5
- (Insert Physical Location here)
- Station #6
- (Insert Physical Location here)

To view the latest data that has been sent via cellular communications to the internet site, (i.e., Chlorophyll-a, Seston or Suspended Particulate Matter, Dissolved Organic Matter or carbon, or the time averaged or sequential hyperspectral signatures) use the links below to display a plot of the processed data. For additional information (e.g., parameters and archived plots and data) access the individual station pages from the map or listings shown above.

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<th>Buoy 3</th>
<th>Buoy 4</th>
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Station Locations:

- Station #1
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- Station #4
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- Station #5
  - (Insert Physical Location here)
- Station #6
  - (Insert Physical Location here)

To view the latest data that has been **sent via cellular communications** to the internet site, (i.e., Chlorophyll-a, Seston or Suspended Particulate Matter, Dissolved Organic Matter or carbon, or the time averaged or sequential hyperspectral signatures) use the links below to display a plot of the processed data. For additional information (e.g., parameters and archived plots and data) access the individual station pages from the map or listings shown above. If you have a Java enabled browser you may view buoy data by clicking here.

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<th>Buoy 1</th>
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<th>Buoy 4</th>
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This page was last revised on 21 March 1997
To view archived data, select a month, day, hour, and parameter from the tables below and click the "View Plot" button.

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</table>

This page was last revised on 14 May 1997
Station #1

This space can have specific information about this location.

Latest Available Data

The next five images are links to the latest plots of the data in raw, averaged, and processed form gathered by the optical buoy at Station 1. The processed data relates to concentrations of chlorophyll, seston, and dissolved organic matter (DOM). To access archived data, please fill out the form below these images and submit your request.

Raw Data

Averaged Data

Chlorophyl Data
INSTRUCTIONS

This form may be used when reporting inventions, discoveries, improvements or innovations to NASA. Use of this report form is optional; provided, however, that whatever report format is used contains the essential information requested herein.

In completing each section, use whatever detail deemed appropriate for a "full and complete disclosure," as required by the New Technology or Property Rights in Inventions clause. For further guidance as to what constitutes a satisfactory report, please refer to NHB 2170.3, Documentation Guidelines for New Technology Reporting.

Available additional documentation which provides a full, detailed description should be attached, as well as any additional explanatory sheets where necessary.

1. TITLE   Shallow Water Optical Water Quality Buoy

2. INNOVATOR(S) (Name and Social Security No.) *

   Charles Bostater  email: bostater@probe.ocn.fit.edu

3. EMPLOYER (Organization and Division)

   Florida Tech, College of Engineering, DMES, Environmental Optics & Remote Sensing Lab

4. ADDRESS (Place of Performance)

   150 West University Blvd. Melbourne FL 32937

http://www.ocn.fit.edu

SECTION I - DESCRIPTION OF THE PROBLEM THAT MOTIVATED THE TECHNOLOGY DEVELOPMENT

(Enter A. - General Description of Problem Objective; B. - Key or Unique Problem Characteristics; C. - Past History/Prior Techniques; D. - Limitations of Prior Technique)

A. The problem proposed for development and testing was the utilization of a confidential sensor & probe previously developed by Dr. Bostater (US Patent Granted) for use on a flotation collar or buoy for collection of water quality data. The buoy system is designed for shallow water environments only.

B. The key problem was the creation of a flotation collar or ballast system that could incorporate a computer, solar panels, rechargeable batteries and a cellular phone system that could be automated for collection of hyperspectral signatures of the upwelling light from water and the real time communication of the data to a computer with data available via the world wide web for transmission anywhere in the world within a couple of minutes from the data being collected.

C. The buoy system was conceived after testing a confidential probe concept in a wastewater treatment facility.

D. The concept of an optical buoy is not new. Previous research has demonstrated the concept of floating optical sensors as a buoy system. This project was however the first system that utilized a patented probe design in conjunction with a hyperspectral sensor system which relays the optical signatures via cellular communications to a computer system where the data is immediately available over the world wide web. http://probe.ocn.fit.edu.buoy. The optical signatures are analyzed using algorithms or techniques derived from derivative spectroscopy. As such the system is a novel and unique innovation but the buoy system itself is not patentable.

* Supplying this information is voluntary, in accordance with Public Law 93-579 (Privacy Act of 1974). However, it is required for eligibility in the establishment of Space Act monetary awards.
A. A buoy was constructed jointly with funding from NASA and from KB Science & Engineering for a flotation collar with a donut type of shape. The buoy was painted a bright yellow color and 2 large gel batteries were mounted to the top of the flotation collar along with two large solar panels for recharging the batteries. In side of the collar is a 12 inch PVC pipe which holds a computer and cellular phone. A hyperspectral sensor provided by KB Science & Engineering is powered as part of the probe which the flotation collar holds.

B. The development of the system is complete. There are some improvements to the flotation collar that could be made by using materials that have a lesser degree corrosion in a marine or freshwater environment. Other than this, the system is operational for sending hyperspectral signatures via cellular communications to a computer.

C. The system operates as 2 components. One system is the flotation collar with the batteries, solar panels, computer and cellular phone. This system was developed for this NASA grant. The computer and cellular phone sends the sensor data to a remote computer system. The second system that was built for the flotation collar or buoy was an enlarged probe designed using confidential and patent pending probe technology by KB Science & Engineering.

D. The buoy system which supplies the power and computer and cellular link is fully operational as a stand alone operational unit and as such can be used to integrate other sensors. This aspect of the project was kept in mind during the buoy development process. As such, other sensors and instruments can be integrated on the buoy. However our goal was to design the buoy as a flotation collar to accept the optical probe. This is what makes the buoy system unique and novel or innovative, but not patentable since buoys have been made for many years.

E. The supportive theory is limited to the operation of the 2 systems. The first is based upon common buoy designs that demonstrate the use of flat discus buoys. The second part of the theory of operation has to do with the measurement of high resolution optical signatures of water based upon radiative transfer theory.

F. The engineering specifications can be found in any basic engineering book on design of floating objects or books and reports on design of buoys.

G. Equipment used in the buoy are rechargeable gel cell batteries, solar panels to recharge the cells. A dry air system to provide dry air to the non-contact backscatter probe, a single board computer with a cellular modem, PCMCIA card slot, and a cellular phone that can be automated and all equipment run via 12 or 6 volts.

H. The unit can not be operated in high wind wave conditions. The system is meant for shallow waters that are semi-enclosed aquatic systems, ponds, lakes and or lagoons. The aluminum flotation collar must be properly painted and originally constructed in such a manner that corrosion is minimized. The system has to have zinc's changed and removed periodically to assist in this manner. The flotation collar must be painted with anti-fouling paint and repainted occasionally (once a year or every 6 months) depending on the quality of the waters where the units are placed. The system should be quite suitable for location in water or aquatic systems near the vicinity of rocket launches for monitoring rocket launch impacts on aquatic systems when integrated with other sensors such as standard pH sensors, etc.
SECTION III - UNIQUE OR NOVEL FEATURES OF THE TECHNOLOGY AND THE RESULTS (OR BENEFITS OF ITS APPLICATION)

(Enter as appropriate A. Novel or unique features; B. Development or Conceptual Problems; C. Operating Characteristics, test data; D. Analysis of capabilities; E. Source of error; and F. Advantages/shortcomings)

3.

SECTION III (Cont.)
D. LIST THE DATES AND ANY PARTICULARLY PERTINENT PAPER AVAILABLE BUT NOT ATTACHED

E. DEGREE OF TECHNOLOGICAL SIGNIFICANCE (Check in you of technological significance of this technology)

☐ 1. MODIFICATION TO EXISTING TECHNOLOGY

BREAKTHROUGH

COMMENTS

SECTION IV - ADDITIONAL DOCUMENTATION (Include or list below any pertinent documentation which aids in the understanding or application of the new technology. IF NOT TOO BULKY OR DIFFICULT TO REPRODUCE, INCLUDE COPIES WITH THIS REPORT. For those references or additional documentation available but NOT included in this report (due to their being nonessential to a basic understanding of the new technology and which may be costly to handle) complete item A, below)

A. AVAILABLE DOCUMENTS

1. PAPERS, ARTICLES
2. CONTRACTOR REPORTS
3. ENGINEERING SPECS.
4. ASSEMBLY/MFG. DRAWINGS
5. PARTS OR INGRED. LIST
6. OPERATING MANUALS
7. TEST DATA
8. ASSEMBLY/MFG. PROCED.
9. COMPUTER TAPES/CARDS
10. OTHER (Specify)

B. INDICATE THE DATES OR THE APPROXIMATE TIME PERIOD DURING WHICH THIS TECHNOLOGY WAS DEVELOPED (i.e. conceived, constructed, tested, etc.)

C. LIST THE FIRST PUBLICATION OR PUBLIC DISCLOSURE OF THE TECHNOLOGY, AND DATES

SIGNATURE (S) OF INNOVATOR (S)
Subject: NASA Grant NAG10-0151, "DEVELOPMENT AND TESTING OF AN OPTICAL WATER QUALITY BUOY"

This is a reminder that complete closeout of the subject grant cannot be made until you have complied with the Patent Rights Clause by either reporting the new technology/inventions made under the subject grant or certifying that there were none.

As a commercialization incentive, this clause allows you to retain the rights to all technology/inventions resulting from your grant performance. However, they are required to be reported to NASA even if you do not plan or elect to seek patent protection. Also, each new technology/invention will be considered for publication in the NASA Tech Brief Journal, which provides proper credit and a minimum award of $150.00 to each innovator.

Compliance with this clause may be accomplished by completing and returning the enclosed Report of New Technology/Inventions (File 1002). This report should be sent directly to me with a copy to the KSC Contracting Officer. Copies of the detailed descriptions themselves need not be forwarded to the KSC Contracting Officer. You may provide the detailed description for each new technology listed by using the enclosed New Technology Report, NASA Form 666A, also available electronically on the internet at http://technology.ksc.nasa.gov/DOC/ntr.html.

If you have any questions on how to submit your new technology/invention or comply with the Patent Rights Clause, please call Ms. Joyce Haskell at (407) 867-6374. To avoid any delay in closing out your grant, it is requested that the Report of New Technology/Inventions be provided within two (2) weeks.
Enclosures:
File 1002
NASA Form 666A
REPORT OF NEW TECHNOLOGY/INVENTIONS
(Required by New Technology or Patent Rights Clause)

1. Name and Address of Contractor -

Florida Institute of Technology
Attn: Charles Bostater
150 W. University Blvd.
Melbourne, FL 32901-6988

2. Contract/Grant Number - NAG10-0151

3. List each New Technology/Invention by Title and Innovator's Name.

Shallow Water Optical Water Quality Buoy, Charles Bostater

NOTE: On the attached NASA Form 666A, fill out a detailed description (including drawings) for each New Technology/Invention listed.

4. List each New Technology/Invention on which Contractor elects to retain title.

The new technology (a buoy) utilizes a previous confidential probe which has been granted a US Patent to KB Science. Since optical buoys are not a new idea in general, the buoy system is considered new technology but is not patentable.

5. List subcontracts containing New Technology or Patent Rights Clause (if "None", so state). Provide name, address and subcontract number.

NONE

6. Certification is hereby made to the following: (check "a" or "b")

   a. New Technology/Inventions listed above are all of the items required to be reported.
   b. No New Technology/Inventions were made under the contract/grant identified above.

Dr. Charles Bostater
Name/Title of Authorized Contractor

Signature

Date: 5/4/98
## CAPITAL EQUIPMENT INVENTORY REPORT

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GRAND TOTALS: 32223.00

TOTAL UNITS: 32223.00

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GRAND TOTALS 2430.00 2430.00 TOTAL UNITS