Integrated Optic Chemical Sensor for the Simultaneous Detection and Quantification of Multiple Ions

**Final Report
March - September 1995**

Edgar Mendoza

September 1995

Work Performed Under Contract No.: DE-AR21-95MC32111

U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
Washington, DC

For

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Physical Optics Corporation
Torrance, California

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September 1995

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EXECUTIVE SUMMARY

This final report summarizes the work performed by Physical Optics Corporation (POC) on the DOE contract entitled "Integrated Optic Chemical Sensor for the Simultaneous Detection and Quantification of Multiple Metal Ions" (Contract No. DE-AR21-95MC32111). *This project successfully demonstrated a multi-element integrated optic chemical sensor (IOCS) system capable of simultaneous detection and quantification of metal ions in a water flow stream.*

POC's innovative integrated optic chemical sensor technology uses an array of chemically active optical waveguides integrated in parallel in a single small IOCS chip. The IOCS technique uses commonly available materials and straightforward processing to produce channel waveguides in porous glass, each channel treated with a chemical indicator that responds optically to heavy metal ions in a water flow stream. The porosity of the glass allows metal ions present in the water to diffuse into the glass and interact with the immobilized indicators, producing a measurable optical change. For the "proof-of-concept" demonstration, POC designed and fabricated two types of IOCS chips. Type I uses an array of four straight channel waveguides, three of which are doped with a metal sensitive indicator, an ionophore. The undoped fourth channel is used as the reference channel. Type II uses a 1×4 star coupler structure with three sensing channels and a reference channel.

Successful implementation of the IOCS technology is expected to have a broad impact on water quality control as well as in the commercial environmental monitoring market. Because of the self-referenced, multidetection capability of the IOCS technique, POC's water quality sensors are expected to find markets in environmental monitoring and protection, ground water monitoring, and in-line process control. Specific applications include monitoring of chromium, copper, and iron ions in water discharged by the metal plating industry. Other immediate commercial markets include the chemical process control market, various segments of the chemical manufacturing market, and the environmental monitoring market.

1.0 INTRODUCTION

This final report summarizes the work performed by Physical Optics Corporation (POC) under the DOE contract entitled, "Integrated Optic Chemical Sensor for the Simultaneous Detection and Quantification of Multiple Metal Ions." *In the course of this R&D project, POC conducted a proof-of-concept demonstration of a self-referenced multi-element integrated optic chemical sensor (IOCS) system capable of detecting multiple metal ions in water.* The goal of this R&D project was to develop an integrated optic chemical sensor unit (based on an optical chip) capable of simultaneously detecting and quantifying metal ions in hazardous liquid waste, as shown in Figure 1-1. The sensor chip uses an array of chemically active channel waveguides in a ruggedized, cost-effective unit capable of detecting in seconds any contaminants in a hazardous waste stream or other effluent. The multi-element sensor unit is self-contained and easy to operate, and requires minimal operator training. It is suitable for on-line monitoring in waste processing and treatment plants, in field applications, and in the laboratory. This compact, rugged, inexpensive unit capable of rapidly identifying liquid waste contaminants should find wide use in environmental and occupational applications ranging from the monitoring of waste processing and treatment, to hazardous waste identification, to groundwater monitoring.

Figure 1-1

Multi-element integrated optic chemical sensors. (a) Integrated optic sensor with a laser diode source and optical fibers; and (b) detail, showing the monolithic integrated optic sensor chip package.

The IOCS technique uses a novel photolithographic processing technology to produce channel waveguides in photosensitive porous glass. Each waveguide channel is treated with a fluorescence- or absorbance-based chemical indicator that responds optically to metal ions in water.

The porosity of the glass allows metal ions present in the water to diffuse into the glass and interact with the immobilized indicators, producing a measurable optical change. For the proof-of-concept demonstration, POC designed and fabricated two types of IOCS chips. Type I uses an array of four straight channel waveguides, three of which are doped with a metal sensitive indicator, an ionophore. The undoped fourth channel is used as the reference channel. Type II uses a 1×4 star coupler structure with three sensing channels and a reference channel.

In the course of this R&D project, POC investigated sensor chemistries for heavy metals such as lead, cadmium, cobalt, copper, zinc, and nickel. The selected chemistries were used for the proof-of-concept demonstration of a multianalyte IOCS system. Each of the active channel waveguides of the IOCS was doped with a metal ion sensitive ionophore. Figure 1-2 shows typical results obtained using phthalocyanine metal complexes as indicators for the detection of heavy metals in water. In this figure, a cobalt phthalocyanine indicator, immobilized in a porous glass substrate, shows optical changes in the presence of cobalt ions (1 mg/l) in an aqueous environment.

Figure 1-2
Metal ion detection in water using phthalocyanine metal complex
indicators adsorbed into a porous glass substrate.

The microporosity of the channel waveguides allows the metal ions to diffuse directly into the optical path of the waveguide, producing a measurable change in the optical and photophysical properties of the indicator. The magnitude of the optical change is proportional to the concentration

of the analyte. In this study, research focused on the proof-of-concept demonstration of the ability to fabricate self-referenced multianalyte IOCS chips on a porous glass substrate -- such as those shown in Figure 1-1. The ultimate aim of this R&D project is to develop IOCS technology for the low-cost mass production of water quality sensors.

Fabrication of an IOCS involves several processing steps: 1) fabricate integrated optic structures in porous sol-gel glasses, 2) identify and characterize metal ion sensitive fluorescent or colorimetric indicators, and 3) test the IOCS for the detection of metal ions in solution and in aqueous flow streams. All three of these steps have been successfully demonstrated. Further development of the IOCS technology will involve the engineering development of the IOCS chips and a field deployable optoelectronic module. The critical step in the engineering development of the IOCS technology will involve optimizing the sensor chemistries suitable for detection of metal ions in water at low parts-per-million concentrations. Based on the groundwork laid in this stage, this task can be readily accomplished.

POC views this study as the first step in developing the IOCS technology as a family of sensor products based on this as yet uncommercialized technology. POC foresees the development of this technology as occurring in four major stages:

Stage I	Proof-of Principle
Stage II	Technology Development
Stage III	Final Product Engineering and Test Marketing
Stage IV	Market Introduction and Scale-up

This contract represents a six-month research and development effort required to complete Stage I of the project. POC will pursue further funding for each of the remaining stages in the form of government contracts from DOE and/or other agencies and from commercial sources.

In the next stage -- "Technology Development" -- POC will design and fabricate a field deployable IOCS system using the self-referenced multielement sensor chips demonstrated in Stage I. The focus will be on optimizing the sensor chemistries investigated in Stage I, on identifying new chemistries for detecting other transition metals and heavy metal ions, on developing a compact field portable optoelectronic and signal processing sensor read-out module, and on conducting extended field testing at a DOE hazardous waste management facility.

Successful implementation of the IOCS technology is expected to have a broad impact on the commercial environmental monitoring market. Because of the self-referenced multidetection capability of the IOCS technique, POC's water quality sensors are expected to find markets in environmental monitoring and protection, ground water monitoring, and in-line process control. A particularly promising application is the monitoring of chromium, copper, and iron ions in water discharge produced by the metal plating industry. Other immediate commercial markets include the process control market, various segments of the chemical manufacturing market, and the environmental monitoring market. The primary users of this technology will be those involved in the direct use of water as a resource, such as in industrial and residential applications. This includes the aluminum, automotive, chemical, food processing, mining, pulp and paper, petroleum, steel, and textile industries, utility companies, municipal water and sewage systems, and commercial, institutional, and residential water treatment plants.

According to Environmental Business International, Inc., instrumentation for water quality control constitutes almost 40% of the total environmental monitoring market. An estimated market of \$1.16 billion dollars is expected for 1996 [1]. IOCS technology offers a unique capability for simultaneous detection and quantification of metal ions in liquid waste water at very competitive prices. Stage III will be entirely targeted at this market, with the introduction of a low cost field deployable IOCS unit. Although water quality control devices are commercially available, the proposed IOCS technology offers the advantages of in-line process control and mass production at a very competitive price. For this reason, we estimate that POC will begin to displace current systems within six months after product introduction. With a preliminary target price of \$7,500 for the basic instrument and a 25% market penetration, we expect to generate annual revenues of at least \$15 million within five years after introduction.

1.1 Project Objectives Met

The goal of this R&D project was to fabricate and test an IOCS chip capable of identifying and quantifying at least three metal ions in water at low concentration levels, and to investigate questions related to the Stage-II engineering development of a field-deployable IOCS unit. To do this, POC proposed to fabricate and demonstrate a "proof-of-concept" bench prototype IOCS system for the detection of heavy metal ions in water. This section discusses the experimental results achieved in the course of demonstrating the IOCS technology. Objectives 1 through 3 correspond to the objectives listed in the Stage I proposal [2].

Objective 1. Determine the most suitable optical arrangements for a field-installable IOCS metal ion monitoring system, including wavelength differentiation schemes, IOCS chip designs, and optoelectronics

In the course of this R&D project, POC designed a complete IOCS system consisting of two key components: an IOCS chip and an optoelectronic detection and signal processing system. The IOCS chip uses four channels: three channels doped with heavy metal ion sensitive indicators, and a fourth, undoped, channel for self-referencing. Two IOCS chip designs have been investigated. The IOCS chip is encapsulated in a durable plastic package that allows the sensing chip to be positioned in any water flow stream. The package design allows the sensing elements of the chip to interact directly with the water stream. The IOCS chip is connected to a fiber optic cable, which transmits the optical signals produced by each of the sensor elements of the chip to a remote sensor read-out optoelectronic detection system. The optoelectronic detection and signal processing system consists of two modules: a sensor read-out module and a data management module. Two detection approaches have been investigated for the sensor read-out module, depending on the type of chemical indicator used. For fluorescence-based indicators, a phase fluorimeter has been designed to measure the decay lifetime of the fluorescence-based sensor elements immobilized in the IOCS chip. For the absorption-based indicators, a dual wavelength ratiometer has been designed to measure the intensity changes produced by the adsorption of metal ions into the sensing element of the IOCS chip. The data management module controls both the phase fluorimeter and the ratiometer, and measures the optical activity of each of the sensing channels of the IOCS chip in real time. The optoelectronic and signal processing unit is packaged into a compact module that can be connected to a portable computer via an RS-232 communication port.

Objective 2. Develop one or more workable IOCS chips

POC designed and fabricated two types of four-channel IOCS chips: Fabrication of IOCS chips involves the following processing steps: 1) fabricate integrated optic structures in a porous glass substrate, 2) immobilize metal ion sensitive indicators into the porous channel waveguides of the chip, and 3) test the IOCS for the detection of metal ions in solution and in aqueous flow streams. All three steps were successfully demonstrated.

Two types of photosensitive porous glasses were investigated: sol-gel glasses and porous Vycor glass. These glasses were made photosensitive by adsorption of an organometallic photosensitizer into the porous network of the glass by means of chemical vapor deposition. When the glass is

exposed to light, the adsorbed photosensitizer permanently modifies the chemical morphology of the glass, producing a permanent change in its refractive index. This modification of the index of refraction make it possible to fabricate integrated optic structures capable of guiding light in a porous glass substrate. The integrated optic structures were photolithographed onto the photosensitive glasses by contact printing to photogenerate the channel waveguides. Contact photomasks were designed and fabricated on a high contrast chrome mask procured from Photoscience, Inc. Straight channel waveguides and 1×4 star couplers, 200 μm to 1000 μm in width, were fabricated on the photoactive porous glasses.

POC developed a technique for immobilizing the selected metal ion indicators into the porous channel waveguides. In brief, this technique requires the following steps: mask the IO chip with a protective coating to expose the active channels of the chip and to protect the reference channels from the environment, 2) immobilize the metal ion sensitive indicators by diffusing a concentrated solution of the indicator through the porous structure of the waveguide channels, and 3) test the IOCS chips using bench-top instrumentation.

Objective 3. Combine optical, chemical, and signal processing technology into a working demonstration of the IOCS technique, and demonstrate that its performance is suitable for use in hazardous waste monitoring and control

POC demonstrated that the IOCS chips were capable of detecting the target metal ions -- lead, copper, and cobalt -- at a concentration level of 1.0 mg/l in a water flow stream. To accomplish this, POC connecterized the IOCS chips with standard 400 μm multimode optical fibers and then encapsulated the connecterized chip in a specially designed, environmentally rigid, plastic package. The packaged IOCS chip was tested using bench-top instrumentation for the quantitative detection of heavy metal ions in a water flow stream. The optical chip detected the target metal ions with typical response and recovery times under a minute.

1.2 Success Criteria

Successful completion of this R&D project resulted in the demonstration of the "proof-of-concept" of the integrated optic chemical sensor (IOCS) system. To accomplish this, POC fabricated an IOCS system and tested it by simultaneously identifying and quantifying trace amounts of inorganic contaminants in aqueous samples. Specifically, we demonstrated the detection of low

concentration levels (~1.0 mg/l) of heavy metal ions in water. Success was demonstrated by meeting two milestones:

1. Formation of integrated optic channel waveguides in a porous glass substrate
2. Demonstration of integrated optic chemical sensors using highly specific metal ion indicators.

1.3 Major Milestone Status

The first milestone, "Formation of integrated optic channel waveguides in a porous glass substrate," was successfully met. Integrated optic channel waveguide structures were photolithographed onto porous sol-gel and Vycor glasses. These waveguides, capable of guiding a He-Ne laser beam, demonstrated attenuation losses on the order of 1.5 dB. The channel waveguides were then incorporated into integrated optic metal ion sensors for the successful second milestone demonstration.

Table 1-1 Milestone Status

WBS No.	Person	Name	Start	Finish	% Complete
1.2.2	EM	1.2.2 Milestone I - Demonstrate IO Waveguides	3/27/95 5:00 pm	6/27/95 5:00 pm	100%
1.3.2	EM	1.3.2 Milestone II - Demonstrate IOCS for Metal Ion Detection	9/27/95 5:00 pm	9/27/95 5:00 pm	100%

2.0 BACKGROUND

2.1 Sensors for Water Quality Control and Hazardous Waste Management

People have been exposed to hazardous waste contaminants since long before the industrial revolution. Environmental pollution problems in the industrial sector perhaps began with the release into the ground of dyes and other organic chemicals developed from the coal industry in Germany in the 1800s. In the 1900s, the variety of chemical waste increased drastically from the production of steel and iron, lead batteries, and petroleum refining. The World War II era ushered in massive production of chlorinated solvents, pesticides, polymers, plastics, paints, and wood preservatives. The Love Canal hazardous-waste site attracted major public concern in 1979 and

initiated the hazardous-waste control decade of the 1980s. This site had received 20,000 metric tons of chemical waste containing at least 80 chemicals, and had a serious impact on nearby residents. By 1989, state and federal governments had spent approximately \$140 million to clean up the site and relocate all of its residents. Since then, several other sites have received national attention including, Woburn, MA (tannery and glue making chemicals dating back to 1850), the Stringfellow Acid Pits near Riverside, CA, the Valley of Drums in Kentucky, the Brio chemical waste site in Houston, TX, Times Beach, MO (the town was abandoned because of dioxin contamination) and most recently the Westinghouse Hanford, WA, and Savannah River, GA, waste sites.

In a 1984 report, *Protecting the Nation's Groundwater from Contamination* [3], the Office of Technology Assessment listed more than 30 potential sources of water contamination. Figure 2-1 shows the priority rankings of the sources and various contaminants as reported by the U.S. Environmental Protection Agency (EPA) [4]. State inventories showed that more than half of the states and territories listed underground storage tanks, septic tanks, agricultural activities, municipal landfills, and abandoned hazardous waste sites as major threats to groundwater. Other sources include industrial landfills, injection wells, regulated hazardous waste sites, land applications, road salt, saltwater intrusion, brine pits at oil and gas wells, and surface impoundments.

(a) Contamination sources

(b) Contaminants

Figure 2-1

Frequency of various contamination sources and contaminants as major water quality threats [4].

Table 2-1 lists major pollutants according to the Environmental Protection Agency. Most of these materials dissolve in water to some degree. Large quantities of organic compounds produced by

industry, agriculture, and municipalities have created the greatest potential for groundwater contamination. The inorganic compounds occur in nature, and may come from natural sources as well as human intervention. Metals from mining, industry, waste water, agriculture, and fossil fuels can present serious problems in groundwater. Of the inorganic contaminants in groundwater, those of greatest concern are nitrates, ammonia, and trace metals. Nitrates in groundwater originate from nitrate sources on land, and are associated with fertilizers and the disposal of sewage water. Because nitrate concentrations are not limited by solubility constraints, nitrates are highly mobile in groundwater.

Table 2-1 Environmental Protection Agency (EPA) List of Priority Pollutants in Groundwater [5]

Base-Neutral Extractables	
Acenaphthene	Diethyl phthalate
Acenaphthylene	Dimethyl phthalate
Anthracene	2,4-Dinitrotoluene
Benzidine	2,6-Dinitrotoluene
Benzo[<i>a</i>]anthracene	Di- <i>n</i> -octyl phthalate
Benzo[<i>b</i>]fluoranthene	1,2-Diphenylhydrazine
Benzo[<i>k</i>]fluoranthene	Fluoranthene
Benzo[<i>ghi</i>]perylene	Fluorene
Benzo[<i>a</i>]pyrene	Hexachlorobenzene
Bis(2-chloroethoxy) methane	Hexachlorobutadiene
Bis(2-chloroethyl) ether	Hexachlorocyclopentadiene
Bis(2-chloroisopropyl) ether	Hexachloroethane
Bis(2-ethylhexyl) phthalate	Indeno[1,2,3- <i>cd</i>] pyrene
4-Bromophenyl phenyl ether	Isophorone
Butyl benzyl phthalate	Naphthalene
2-Chloronaphthalene	Nitrobenzene
4-Chlorophenyl phenyl ether	<i>N</i> -Nitrosodimethylamine
Chrysene	<i>N</i> -Nitrosodiphenylamine
Dibenzo[<i>a,h</i>] anthracene	<i>N</i> -Nitrosodi- <i>n</i> -propylamine
Di- <i>n</i> -butyl phthalate	Phenanthrene
1,2-Dichlorobenzene	Pyrene
1,3-Dichlorobenzene	2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin
1,4-Dichlorobenzene	1,2,4-Trichlorobenzene
3,3'-Dichlorobenzene	

Acid Extractables

<i>p</i> -Chloro- <i>m</i> -cresol	2-Niropenol
2-Chlorophenol	4-Nitrophenol
2,4-Dichlorophenol	Pentachlorophenol
2,4-Dimethylphenol	Phenol
4,6-Dinitro- <i>o</i> -cresol	2,4,6-Trichlorophenol
2-4-Dinitrophenol	Total Phenols

Volatiles

Acrolein	1,2-Dichloroethane
Acrylonitrile	1,1-Dichloroethylene
Benzene	<i>trans</i> -1,2-Dichloroethylene
Bis(chloromethyl) ether	1,2-Dichloropropane
Bromodichloromethane	<i>cis</i> -1,3-Dichloropropene
Bromoform	<i>trans</i> -1,3-Dichloropropene
Bromomethane	Ethylbenzene
Carbon tetrachloride	Methylene chloride
Chlorobenzene	1,1,2,2-Tetrachloroethane
Chloroethane	1,1,2,2-Tetrachloroethene
2-Chloroethyl vinyl ether	Toluene
Chloroform	1,1,1-Trichloroethane
Chloromethane	1,1,2-Trichloroethane
Dibromochloromethane	Trichloroethylene
Dichlorodifluoromethane	Trichlorofluoromethane
1,1-Dichloroethane	Vinyl chloride

Pesticides

Aldrin	Dieldrin	PCB-1016 ^a
α -BHC	α -Endosulfan	PCB-1221 ^a
β -BHC	β -Endosulfan	PCB-1232 ^a
γ -BHC	Endosulfan sulfate	PCB-1242 ^a
δ -BHC	Endrin	PCB-1248 ^a
Chlordane	Endrin aldehyde	PCB-1254 ^a
4,4'-DDD	Heptachlor	PCB-1260 ^a
4,4'-DDE	Heptachlor epoxide	Toxaphene
4,4'-DDT		

Inorganics

Antimony	Chromium	Nickel
Arsenic	Copper	Selenium
Asbestos	Cyanide	Silver
Beryllium	Lead	Thallium
Cadmium	Mercury	Zinc

Arsenic, cadmium, lead, chromium, zinc, and mercury are metal pollutants of major concern in groundwater. Table 2-2 lists the metal ion constituents in groundwater and the EPA acceptable concentrations for water quality standards. Most of the metal pollutant constituents result from industrial activities and discharges from mining, metal plating, plumbing, coal, gasoline, and pesticide related industries. Many of these metals are very toxic to humans, especially cadmium, lead, and mercury. Cadmium and zinc are common water and sediment pollutants in areas associated with industrial installations. Major sources of lead have been leaded gasoline and lead piping. Mercury is associated with discarded batteries, laboratory products, and lawn fungicides. Arsenic is discharged by phosphate mining, and is a by-product of copper, gold, and lead refining.

These metals are of concern in groundwater because of their pH and solubility characteristics in aerobic systems. Metals occur as cations in groundwater of low pH, and have a greater mobility in acidic waters. Mobility tends to decrease as the solid phase is approached. Mobility in metals is also increased by complexation of metal ions, and nearly all trace metals in groundwater are influenced by redox conditions, especially when complexation occurs. Heavy metals are particularly toxic in their chemically combined forms, and some, notably mercury, in their elemental form. Chromium plumes have been identified at a number of industrial facilities where metal plating is the predominant activity. For example, the U.S. Air Force Hughes Plant 44 Site in Tucson, AZ, has a major chromium plume migrating more than 150 ft. below the surface in a sand gravel aquifer.

Table 2-2

Metal Ion Constituents in Groundwater, and EPA Acceptable Concentrations for Water Quality Standards [6]

Inorganic Constituents	Concentration Range (mg/l)
Aluminum	10-1000
Ammonia	10-10000
Arsenic	<5
Barium	<10
Cadmium	<1
Calcium	100-3000
Chlorine (Total - Includes chloride)	300-3000
Chromium	<1
Copper	<10
Iodine (Total - Include organic iodine)	<15
Iron (Total)	1-1000
Lead	<5
Magnesium	100-1500
Manganese	0.01-100
Mercury	<0.2
Nickel	0.1-100
Nitrate (NO ₃ ⁻)	0.1-10
Potassium	200-1000
Selenium	<5
Silver	<1
Sodium	200-1200
Sulfate	10-1000
Zinc	0.1-100
Phosphates	1-100
Organic nitrogen	10-1000
Total dissolved organic carbon	200-30000
COD (chemical oxidation demand)	1000-90000
Total dissolved solids	5000-40000
pH	4-8

Ground water and hazardous waste must be characterized to identify physical, chemical, and radioactive components that can interfere with particular treatment techniques and final waste forms. Real-time techniques are required for on-line waste processing and for effective, universal monitoring of worker exposure. Normally, hazardous wastes are characterized by conventional analytical techniques (e.g., chromatography, mass spectroscopy, atomic absorption), which are labor-intensive in sample collection, and time-consuming with respect to laboratory work. Up to several hours of operator or technician time are needed to obtain the sample, log it, and carry/ship it to the analytical laboratory. Because this is unacceptable in terms of cost (\$50 to \$100 of labor and \$250 per analysis) and long turnaround times, significant quantities of contaminated waste may be allowed to be dumped back into a site without adequate treatment.

The solution to this problem is a real-time, in-line analyzer, capable of simultaneously monitoring multiple analytes. When perfected, such sensors could be placed at various locations along an aqueous waste processing stream (see Figure 2-2). In practice, a sensor would be placed at the pump head, and others at various stages of treatment, to monitor the cleansing process and to identify failures in specific areas of the treatment train; the last sensor would be placed at the effluent side of the treatment system to verify compliance with outflow goals.

Figure 2-2
In-line use of integrated optic chemical sensors (IOCS) in hazardous waste treatment plant.

2.2 Existing Technologies for Water Quality Control and Hazardous Waste Management

Measurement of the ever-increasing number of organic and inorganic contaminants in complex environmental matrices at ever-increasing levels of sensitivity requires the development and evaluation of innovative techniques for field screening, sampling, and sample handling. There is a special need for rapid, low-cost field methods to support hazardous waste site monitoring and characterization. Laboratory evaluation and field validation of existing and emerging technologies for off-site measurement of toxins at or around hazardous waste sources represent key needs as well. Groundwater monitoring methods for improved detection of contaminants constitute another major challenge, especially for *in situ* applications.

The role of and need for field screening methods to identify and quantify contaminants in environmental media are growing rapidly. Global leaders face the tremendous task of remediating thousands of hazardous waste sites -- the legacy of our much less environmentally-aware predecessors. Field screening methods that generate real-time information on the nature and extent of contamination improve the cost-effectiveness of remediation. Many of these same methods offer information at the point of exposure, thereby improving our ability to assess risks to human health and the environment.

New technologies in field screening are increasingly gaining wide attention. Immunoassay technology has matured considerably, and immunoassay kits are being used extensively in the field. Gas chromatography (GC) remains the most popular field screening technology for organic compounds. Improvements in GC technology continue to be made commercially in conjunction with various sampling methods. Mass spectroscopy (MS) in combination with GC has drawn the attention of commercial developers to potential environmental applications. Many more opportunities are appearing for using transportable GC/MS units in the field, and man-portable GC/MS devices are being projected for the future. Fiber optic sensors, biosensors, and ion mobility spectroscopy also continue to draw the attention of the developer and user communities.

Techniques currently used to monitor liquid hazardous wastes are compared with POC's IOCS technology in Table 2-3 [7]. As employed today, these methods are incapable of *in situ* analysis. All require the sample to be extracted and transported to a remote laboratory. In the course of transportation and subsequent handling and preparation for analysis, many factors can affect the integrity of the sample. Sample contamination, "stirring" of contents by multiple sampling operations, post-collection changes in samples, and the time, effort, and possibility of sample

confusion arising from the need to transport samples to a central laboratory facility all argue for the use of continuous *in situ* measurement.

Several types of spectroscopy -- IR, near infrared (NIR), UV, luminescence, and Raman -- can all be adapted, with the aid of optical fibers, for *in situ* measurement. In situations where concentrations are relatively high, these techniques can be used directly to measure contaminants by monitoring their inherent optical properties. These techniques have been demonstrated for remote detection of metal ions in underground water monitoring [8,9,10]. However, for hazardous waste monitoring where the waste stream contains a wide variety of chemicals, these techniques do not have the resolution capability to distinguish among the components of the waste stream. This is why we propose to use a multi-waveguide approach that allows simultaneous detection of several metal ions, facilitating efforts to distinguish concentrations of individual contaminants.

Numerous groups have studied the luminescence properties of porphyrins and phthalocyanine derivatives [11,12]. The use of these compounds in sensors, however, has generally been limited to electrochemical devices [6]. POC's IOCS technique would allow these compounds to be used in a multianalyte configuration, overcoming previous cross-response difficulties that have limited their use in practical devices.

Table 2-3 Current Analytical Techniques

Technique	Acronym	Qualitative Analysis		Quantitative Analysis	
		Individual Elements	Multiple Elements	In-Situ Analysis	Sensitivity
1. Integrated Optic Chemical Sensors	IOCS	√	√	√	≤ 100 ppm
2. Infrared Spectroscopy	IR		√	√	0.1%
3. Raman Spectroscopy	Raman		√	√	0.1%
4. Ultraviolet Spectroscopy	UV		√		1%
5. Atomic Absorption and Emission Spectroscopy	AA	√	√		1 ppm
6. Luminescence Spectrophotometry	LS		√		1 ppm
7. Mass Spectrometry - Low Resolution - High Resolution - Automated GC/MS	MS LRMS HRMS GC/MS		√ √ √		1 ppm 100 ppm ≤ 1 ppm ≤ 1 ppm
8. Nuclear Magnetic Resonance Spectroscopy	NMR		√		1 %
9. Chromatography - Thin Layer - Liquid - Gas	TLC LC, HPLC GC		√ √ √		1 ppm 1% 1 ppm 1 ppm
10. Combustion Analysis	CA	√			
11. Thermal Analysis	TGA/DTA		√		1%

2.3 Multi-Element Integrated Optic Chemical Sensors

The use of integrated optic chemical sensors (IOCSs) in water quality control and hazardous waste management applications offers many advantages, the most prominent being that they offer multi-analyte sensing capability in a miniaturized format, and that they are self-referenced. The benefits of POC's IOCSs arise from their use of optical indicators, waveguides, and novel integrated structures. Indicator-based sensing ensures a high degree of selectivity and sensitivity. The use of waveguides makes the light path easy to control without the need for bulky optical components. *In contrast to previously described IOCSs, which use evanescent fields to probe specifically sensitized films on the waveguide surface [13,14,15], POC's novel*

porous IOCSs intrinsically detect the analyte by allowing reversible diffusion into the optical path of the channel waveguides themselves.

POC's IOCS technology (see Figure 2-3) for water quality control and hazardous waste management is based on fabricating chemically active channel waveguides in porous sol-gel glass substrates. The Stage I sensor chips contained four channels as shown in Figure 2-3, one for each of the selected heavy metal ion analytes plus a reference channel. Each of the active channel waveguides of the IOCS chip is doped with a metal ion sensitive indicator, making this a highly selective water quality detector. The micro-porosity of the channel waveguide allows the metal ion analyte to diffuse directly into the optical path of the waveguide, producing a measurable change in the optical properties (absorption or fluorescence) of the indicator dye. The magnitude of the optical change, either intensity-based or fluorescence lifetime-based, is directly related to the concentration of the metal ion analyte.

In the "Proof-of-Concept Stage," we investigated several types of metal ion indicators: 1) phthalocyanine metal complexes, 2) metalloporphyrin complexes, and 3) metal chelating agents. These compounds have been selected for investigation because of their proven metal ion affinity, selectivity, and sensitivity to parts-per-million concentration levels [16,17,18,19,20]. POC's consultant, Dr. DeLyle Eastwood, an expert in environmental sensing using fluorescence based indicators, advised POC on the selection of the most suitable indicators for the development of the proposed IOCS system.

Figure 2-3
Multi-element IOCS for hazardous waste monitoring.

3.0 TECHNICAL DISCUSSION

The goal of this Stage I effort was to demonstrate that the integrated optic chemical sensor (IOCS) technology is suitable for the fabrication of self-referenced multi-element chemical sensors for heavy metal ion detection in water flow streams. The experimental results produced to demonstrate the IOCS technology are described in the following sections. Section 3.1 describes the methodology involved in the design of integrated optic structures in porous silica glasses, Section 3.2 describes POC's proprietary method of fabricating integrated optic devices, Section 3.3 describes the chemistry and the optical properties of metal ion indicators, Section 3.4 describes the methodology involved in fabricating IOCS chips, and Section 3.5 describes the experimental tests that verified their performance in the detection of metal ions in a water stream.

3.1 Integrated Optic Chemical Sensor Design

The aim of this project is to develop a new family of integrated optic chemical sensors (IOCSs). IOCSs are based on microfabricated optical chips capable of simultaneously detecting and quantifying multiple metal ions in aqueous waste. They can be used for on-line monitoring of metal ion traces in the course of processing and decontamination of groundwater. The critical advantage of IOCS systems is that they are self-referencing. The proposed IOCS system for metal ion detection comprises a 1×4 star coupler integrated optic structure photolithographed onto a photosensitive porous sol-gel glass. Three of the arms of the star coupler are doped with metal ion sensitive fluorescent indicators, each with high selectivity to a particular ion, while the fourth channel is used as a reference to compensate for environmental fluctuations. In Stage I of this project, an IOCS chip for the detection of three metal ion analytes -- lead, cadmium, and arsenic -- was fabricated for the proof-of-concept demonstration. In the second stage, the sensor chip will be expanded to cover the large range of metal ions commonly found in groundwater systems.

The proof-of-concept demonstration of the proposed IOCS system is being carried out in two iterative stages. In Stage I, a four-channel IO sensor chip (Figure 3-1) was fabricated and tested for metal ion response in the concentration range from 0.1 mg/l to 10 mg/l. This chip uses four straight channel multimode waveguides (100 μm to 1000 μm width) doped with the fluorescent indicators. Three channels are used as active sensors and the fourth as a built-in self-reference. This design was used to characterize the sensor fabrication and metal ion response parameters. Stage II (Figure 3-2) will extend the design developed in Stage I into a fully integrated optic structure. This design will incorporate a 1×4 splitter so that only one light source is required to excite the fluorescent indicators, making this sensor truly self-referenced.

The remainder of Section 3.1 addresses the design of the integrated optic waveguide.

Figure 3-1
Stage I - Four-channel integrated optic sensor design.

Figure 3-2
Stage II - 1 x 4 star coupler metal ion sensor design.

The integrated optic waveguide design was one of the most challenging tasks of the project, since several of the waveguide parameters -- effective refractive index, V-number, and attenuation and absorption coefficients -- had to be characterized. Multimode channel waveguides in the range of 100 μm to 1000 μm and 1 $\times$ 4 splitters with splitting angles in the range of 2° to 10° were designed. The optical properties of the waveguides were characterized both theoretically and experimentally. A mathematical model that describes diffuse channel waveguides was initiated to lay the groundwork for the Phase II development effort.

The mathematical analysis of photolithographed diffused channel waveguides plays an important role in designing the fundamental IOCSs shown in Figures 3-1 and 3-2. These channel waveguides have two-dimensional gradient index profiles, and the scalar wave equation for these waveguides does not have closed form field solutions. Therefore, to study the light propagation characteristics of these waveguides, either direct numerical methods or approximate methods must be derived. In order to develop a model that can predict the behavior of the photoinduced channel

waveguides requires an understanding of the fundamental concepts of light propagation in planar waveguides.

The planar waveguide is the most fundamental element of an integrated optic device. As in optical fibers, light guiding in planar waveguides is based on the phenomenon of total internal reflection (TIR). In planar waveguides, this is accomplished by creating regions of higher refractive index than that of the bulk medium. In its simplest form, the ratio of the index of refraction within these regions to that of the bulk defines the sine of the critical TIR angle θ_c :

$$\sin \theta_c = \frac{n_1}{n_2} , \quad (3-1)$$

where n_1 is the index of refraction of the bulk medium and n_2 that of the guide. As a result, light that enters the region of higher refractive index within the critical angle is guided through the bulk of the medium. While any number of techniques might be used to modify the refractive index of a material, the material or technique must have low optical loss at the working wavelength, and must be compatible with systems of high spatial resolution.

3.1.1 Diffused Channel Waveguides

Models to predict the propagation behavior of diffused channel waveguides use numerical methods based on finite difference [21] or finite element [22] analysis. These methods give highly accurate results, but they involve extensive computation and do not lead to simple analytical solutions.

A simple analytical method for the analysis of diffused channel waveguides has been postulated by Sharma and Bindal [23]. Their method gives the refractive index distribution as

$$n^2(x,y) = n_s^2 + 2n_s \Delta n \cdot f(x)g(y) \quad y > 0 \quad (3-2)$$

$$= n_c^2 \quad y < 0, \quad (3-3)$$

where n_s is the substrate index, Δn is the peak index change, n_c is the cover index, and $f(x)$ and $g(y)$ are profile functions along the waveguide width and the depth, respectively. $f(x)$ and $g(y)$ are given by the following formulas:

$$f(x) = \frac{\operatorname{erf}\left(\frac{x + \frac{W}{2}}{\sqrt{2D}}\right) - \operatorname{erf}\left(\frac{x - \frac{W}{2}}{\sqrt{2D}}\right)}{2\operatorname{erf}\left(\frac{W}{2\sqrt{2D}}\right)}, \quad (3-4)$$

$$g(y) = \exp\left(\frac{-y^2}{2D^2}\right) \quad [24] \quad (3-5)$$

where W is the initial strip width and D is the diffusion depth. When dealing with a dielectric that is inhomogeneous, the method of applying the scalar wave equation separately in each region,

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + (k^2 n^2 - \beta^2)E = 0, \quad (3-6)$$

determining the modal fields, and satisfying the boundary conditions at the dielectric interfaces is no longer valid. This is because the lack of homogeneity within the medium does not allow for decoupling of the scalar field components, which would allow for a separable field dependence in the x - and y -directions. Thus, we must either deal directly with the more complicated wave equation [25]:

$$(\nabla_t^2 + n^2 k^2 - \beta^2)\bar{E}(x, y) = -\left(\nabla_t + i\beta\bar{z}\right)(\bar{E}_t \cdot \nabla_t \ln n^2), \quad (3-7)$$

where $\nabla_t^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$, $\nabla_t \equiv \bar{x} \frac{\partial}{\partial x} + \bar{y} \frac{\partial}{\partial y}$, $\bar{E}_t = E_x \bar{x} + E_y \bar{y}$, and $\bar{E}(x, y)$ is the electric field vector as a function of the transverse coordinates x and y , k is the wavenumber, and β is the propagation constant; or use an approximate method. Several papers [26,27,28] deal with modes of diffused channel waveguides, and these methods will be examined in the Technology Development Stage to determine the modal distribution of the sol-gel waveguides.

3.1.2 Weakly Guiding Approximation Model

As a first approximation in the design and modeling of star coupler structures, we decided to focus on the simplest case, a Y-branch structure. In order to determine preliminary design specifications

for an integrated optic (IO) Y-branch power splitter, we referred to recent work by Rasmussen et al. [29], in which the design of single-mode, weakly-guiding integrated optic power splitters is described in terms of normalized parameters. Although our waveguides will be designed to be multimode rather than single-mode, we believe that the procedure discussed here will yield a good first-order design whose accuracy can be enhanced as the project progresses into Stage II. The potential pitfalls in applying a single-mode model to a multimode design are discussed later in this section.

Our initial integrated optic circuit design is a simple Y-branch power splitter (see Figure 3-3). The size of the chip containing the IO circuit will be 40 mm × 5 mm × 2 mm; thus, the overall length of the IO circuit is 40 mm. The thickness A of the input channel will range from 50 mm to 500 mm, as will the corresponding thicknesses a_1 and a_2 of the output channels (note that we assume $a_1 = a_2$). The shape of the Y-branch bend will be a cosine profile, which has been demonstrated to be optimal [30]. More specifically, following the setup in Figure 3-3, the bend profile can be described as:

$$y(x) = D \cos[\pi(1-x/L)], \quad (3-8)$$

where $D = (d - a_n)/2$, $n = 1, 2$, and d is the branch separation distance. The length L of the Y-branch is then defined as the distance between the zero-slope points of the cosine profile. Next, following the procedure outlined in Ref. [23], certain constant values are assigned, including d , λ (input source wavelength), n_{co} and n_{cl} (core and cladding refractive indices), and A . Using these values, the following parameters can be calculated:

$$\Delta n = n_{co} - n_{cl}, \quad (3-9)$$

$$B = (2A/\lambda) \div (2n_{cl}\Delta n). \quad (3-10)$$

Figure 3-3
Integrated optic Y-branch power splitter.

B is the normalized frequency (more commonly referred to as the V-number, but without the multiplicative factor of π), and once it has been calculated another quantity F_S can be determined graphically (see Figure 3-4). Given F_S , L can then be found from Eq. (3-11):

$$L_1 = p \div \{ [F_S \lambda d (n_{cl})^{1/2}] / [2(\Delta n)^{3/2}] \} . \quad (3-11)$$

For single- or few-mode waveguides, the above procedure is easily performed using the loss plot in Ref. [23] (reproduced here as Figure 3-4). This plot is suitable for the design of a power splitter whose bending loss α is either 0.1 dB or 0.01 dB. However, for multimode waveguides ($B \gg 1$) a problem arises; specifically, the range of B in Figure 3-4 is quite small ($0.6 < B < 1.4$), and thus F_S cannot be determined from this plot. One possible solution to this problem is to extrapolate the F_S vs. B curve beyond the value of $B_{\max} = 1.4$; however, this must be done carefully, because if an "unnatural" function such as a higher-order polynomial is used to fit the curve over the given range of data points, the behavior of the fitting function is unlikely to be truly representative of the F_S vs. B relationship beyond $B_{\max}$.

Figure 3-4
 F_S vs. B for fixed losses of $\alpha = 0.1$ dB and 0.01 dB [24].

In addition to characterizing the Y-branch design, we have also been able to develop some basic design specifications for the channel waveguide sections both before and after the power splitter. For a multimode Y-branch power splitter we would like to design the waveguide so that the power distribution among branches is independent of as many factors as possible. By specifying a minimum length for each straight section both before and after the splitter section, we hope to eliminate the input mode-phase distribution as one dependence factor for the Y-branch power distribution. The remainder of this section details the basic theory behind these design specifications.

Consider an input source whose power distribution is equally dispersed among all modes. The initial phase coherence of the source will cease to be localized when the difference among the phases of the neighboring modes is

$$\Delta\beta L = \pi/2 \quad , \quad (3-12)$$

where $\Delta\beta$ is the difference between propagation constants of neighboring modes and L is the transmission length. For a multimode waveguide we can approximate β in the following manner:

$$\beta \cong k[n_{cl}^2 + (n_{co}^2 - n_{cl}^2)(1 - m^2/m_{max}^2)]^{1/2} , \quad (3-13)$$

where k is the wavenumber, m is the mode number, and m_{max} is the number of the highest-order mode supported by the waveguide. Next, taking the differential of β with respect to m , we arrive at

$$\Delta\beta = (k^2/\beta) (n_{co}^2 - n_{cl}^2)(m|\Delta m|/m_{max}^2) . \quad (3-14)$$

Applying the weakly-guiding condition with $\beta/k \cong n_{co}$ and setting $\Delta\mu = 1$, we can combine Eqs. (3-12) through (3-14) to obtain the following:

$$L_m = b^2 n_{co} / \lambda m , \quad (3-15)$$

with λ being the wavelength in vacuum. Thus, to determine a minimum length for the input section of the waveguide we set $m = 1$, which yields

$$L_{min} = b^2 n_{co} / \lambda . \quad (3-16)$$

Furthermore, referring back to the initial assumption of an equal input power distribution among all modes, we can determine an approximate average length L' by summing L_m over all the modes and dividing the summation by m_{max} . This leads to

$$L' = \sum_m \left(b^2 n_{co} / \lambda m \right) / m_{max} . \quad (3-17)$$

This expression can be evaluated by realizing that $m_{max} = B$, the normalized frequency, for a weakly-guiding waveguide and by determining a sum for the finite series

$$\sum_m (1/m), m \in [1, m_{max}] . \quad (3-18)$$

Using MATHCAD™ software, we were able to obtain an expression for this series:

$$\sum_m (1/m) = \psi(B+1) + \gamma , \quad (3-19)$$

where the ψ function is defined as

$$\psi(x) = d/dx \{ \ln[\Gamma(x)] \} , \quad (3-20)$$

and $\gamma = 0.57721556649$ (Euler's constant). Using these expressions, an average length L' can be arrived at:

$$L' = \frac{b\sqrt{n_{co}}}{8\Delta n} [\psi(B + 1) + \gamma] . \quad (3-21)$$

3.2 Fabrication of Integrated Optic Devices in Porous Silica Glasses

Fabrication of integrated optic structures in porous silica glasses can be described in terms of two processing steps: fabricating the photoactive porous silica glass, and then photolithographing the integrated optic structures into the photosensitive glass. Section 3.2 discusses the technological aspects of each of these processes.

3.2.1 Fabrication of Photoactive Sol-Gel Glasses

Photoactive silica glasses are made in a two-step process: fabrication of stable porous sol-gel glasses, followed by vapor doping of the porous glasses with an organometallic photosensitizer. In the course of Stage I, we have demonstrated the ability to process stable porous silica sol-gel monoliths from solution chemistry, and to photosensitize these glasses using organometallic precursors. Also, a commercially available porous silica glass, Corning Glass Code No. 6530, was used as a backup for the photodeposition of waveguide structures. The following sections discuss in detail the processing technology for fabricating photosensitive glasses.

3.2.1.1 Processing of Porous Sol-Gel Silica Glasses

The sol-gel process for silica involves mixing a silicon alkoxide $[\text{Si}(\text{OR})_4]$, water, and alcohol. On mixing this becomes a true solution (the term "sol," which means a dispersion of colloidal particles, is not correct; nevertheless, the term is used). Acid or base is added to catalyze the reaction.

R represents a proton or other ligand, and ROH is an alcohol. Depending on the proportion of water and catalyst present, this reaction may not go to completion and therefore silicic acid, Si(OH)_4 , is only partially formed. Soon after the onset of hydrolysis, condensation polymerization begins. This is represented by the reactions:

and

Under acidic conditions, polymerization leads to the formation of highly branched chains, whereas adding a base leads to more condensed clusters. After a period of time that depends on concentrations and reaction temperature, the sol-gel transition is reached. This is when the viscosity of the solution rises rapidly and a gel forms. This gel can then be dried to a microporous solid having interconnected porosity.

The sol-gel chemistry for producing silica porous glasses has been investigated extensively [31]. The most common sol-gel processing techniques involve mixing tetraethylorthosilicate (TEOS), ethanol (ETOH), and water in stoichiometric quantities. In the first two months of this project, preliminary empirical studies were performed using a variety of molar proportions and processing conditions to produce stable monoliths. These monoliths were fabricated using the processing scheme shown in Figure 3-5. This scheme was then slightly modified, as discussed below, as the sol-gel monoliths proceeded through the various processing stages, i.e., drying, aging, and curing. The modification was required in order to ensure crack-free monoliths.

The first step in this process was to mix the sol-gel precursor materials, TEOS, ETOH, and H_2O , in stoichiometric molar concentrations. Table 3-1 shows the molar concentrations of the chemical compositions thus far investigated. The criteria for selecting the molar concentrations was to vary the $\text{H}_2\text{O}/\text{TEOS}$ molar ratio R from 1 to 8 while maintaining good miscibility of the precursor reagents. This is a critical step, since water and TEOS have poor miscibility. Only by having the correct molar proportions in the H_2O -TEOS-ETOH system is good miscibility achieved.

Figure 3-5
Sol-gel processing for production of porous glass monoliths.

Table 3-1 Molar Ratio Concentration for the Formation of Sol-Gel Monoliths

Chemical Composition	Mole Fraction			Ratio of (Water/TEOS)
	TEOS	ETOH	Water	
1	0.188	0.719	0.093	0.494
2	0.158	0.607	0.235	1.484
3	0.137	0.524	0.339	2.474
4	0.120	0.462	0.418	3.464
5	0.107	0.413	0.480	4.453
6	0.098	0.595	0.306	6.041
7	0.101	0.794	0.103	7.851

The sol-gel solutions were mixed for one hour at room temperature, and then transferred to a specially designed plastic mold. This polycarbonate plastic mold (see Figure 3-6) allows the production of near-net-shape monoliths that require only minor post-processing steps, i.e., cutting and polishing. The end result is a sol-gel silica wafer $1\text{ cm} \times 4\text{ cm} \times 2\text{ mm}$. This mold, developed under a NASA Small Business Innovation Research project ^[32], allows the production of a total of 20 monoliths per batch.

Figure 3-6
Polycarbonate mold for casting near-net-shape sol-gel monoliths.

These casting molds have a screw-cap system that maintains a sealed environment throughout sol-gel curing. From each of the sol-gel chemical compositions prepared, three monoliths were cast. The cast sol-gel solutions were allowed to gel for approximately two weeks, or until the gel had shrunk away from the walls of the container. At this point, two or three small orifices were opened on the cover of the container to allow the solvent to evaporate slowly. As the ethanol evaporated, the gel shrank for approximately two more weeks. At this stage, the gel had shrunk approximately 40% from its original volume. The next step was to age the gel by placing the plastic containers in an oven and heating them to 120°C at a rate of $0.1^{\circ}\text{C}/\text{min}$. The aged gels were then transferred to porcelain crucibles and heat treated to 700°C at a rate of $1^{\circ}\text{C}/\text{min}$. Figure 3-7 shows the cast sol-gel monoliths after heat treatment to 700°C . The end result of this process was

an environmentally stable porous silica glass. The monoliths were 4.3 cm in length by 1.0 cm in width by 4 mm thick. This corresponded to a shrinkage of 45% from their original solution volume.

Figure 3-7
Porous sol-gel silica glass monolith after heat treatment at 700°C.

3.2.1.2 Porous Vycor Glass

The Stage I project plan included demonstrating the use of an alternative porous silica glass on which the planar waveguides could be photolithographically deposited, independent of the processing of the sol-gel monoliths. The time constraints of the Stage I project made this backup substrate necessary, since the sol-gel processing takes typically from one to two months to produce stable monoliths, and therefore the Stage I schedule allows only one opportunity to produce the desired glass structures. The porous silica glass selected was Corning's Vycor glass (Code No. 7930), which was selected because its microstructure and surface chemistry resemble those of porous sol-gel glasses. The most important difference between Vycor glass and sol-gel glasses is that a 3% boron phase is present as part of the Vycor glass matrix. The boron phase represents an impurity in the fabrication of high optical quality silica glasses. POC received porous

Vycor glass slabs ($4\text{ cm} \times 1\text{ cm} \times 2\text{ mm}$) from Corning, Inc., and integrated optic structures were photolithographically deposited on these monoliths.

3.2.2 Doping of Photosensitive Organometallic Compounds onto Porous Silica Glasses

Organometallic photosensitizer is doped onto porous silica glasses by diffusion control. In this process a low vapor pressure organometallic photosensitizer is adsorbed into the porous network of the glass by low pressure chemical vapor deposition. Two organometallic compounds, iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) and trimethyltiniodide ($((\text{CH}_3)_3\text{SnI})$), were investigated. Since these reagents exhibit sufficient volatility at room temperature, they were vapor deposited onto porous sol-gel and Vycor glasses by sublimation, using the vapor deposition chamber sketched in Figure 3-8. In this setup, the porous glass sample was first mounted vertically using a Teflon sample holder, which in turn was mounted on a petri dish. The photoactive organometallic compound was then injected onto the petri dish, and a bell jar was quickly placed over it to produce a sealed environment. Typically, $100\text{ }\mu\text{l}$ of the compound was injected into the vapor deposition chamber. The organometallic compound rapidly vaporized, filling the entire chamber with its vapor, which was then readily adsorbed by the porous silica glass. The extent of diffusion of the compound into the porous network of the glass was controlled by the length of time the glass was left inside the vapor chamber. For the $\text{Fe}(\text{CO})_5$ compound, diffusion times were typically from three to five minutes, while for the $(\text{CH}_3)_3\text{SnI}$ diffusion, times were approximately two hours. Immediately after doping, the photosensitized glass was exposed to light. If the impregnated glass sample is not immediately exposed to light, the adsorbed compound in time desorbs from the glass surface. The rate of adsorption and the number of moles adsorbed were followed by measuring the absorption spectrum of the glass as a function of exposure time.

Figure 3-8
Chemical vapor deposition apparatus.

The photochemical reactions of the selected organometallic compounds adsorbed onto porous silica glasses has been previously investigated [33]. The reaction can be summarized as follows:

where M is a metal, i.e., iron or tin, X is a photolabile chromophore, i.e., CO or halogen, and R is a volatile organic group. Exposing the compound to light induces a photochemical reaction in which the M-X bond breaks, producing a highly reactive metal intermediate (M $\cdot$). The reactive metal intermediate is typically a metal radical, though in some circumstances it may be a metal ion. The metal intermediate reacts rapidly with the abundant silanol (Si-OH) groups of the porous glass surface, producing a chemical bond between the metal and the available oxygen. Binding of the metal to the silica group is the key step in forming gradient index patterns in silica glasses. The next step is to remove the organic component (R) by thermal treatment. The end product is a metal oxide permanently bound to the silica matrix.

3.2.3 Photolithography of Integrated Optic Structures onto Porous Glasses

Integrated optic channel waveguide structures were photolithographed onto photoactive sol-gel and Vycor glass slabs by exposing a photosensitized porous glass through a contact photomask using a mercury arc-lamp source. The experimental setup used for the photolithography experiments is shown schematically in Figure 3-9.

Figure 3-9
Photolithography setup for photodeposition of channel waveguides onto porous glasses.

Trimethyltiniodide was used to produce tin oxide channel waveguide structures, and iron pentacarbonyl was used to produce iron oxide channel waveguide structures. Exposure of the tin-based compounds produced a transparent metal oxide, while exposure of the iron-based compound produced a reddish-brown oxide. Both photodeposited metal oxides changed the refractive index of the glass network, allowing the structure to guide light. Figure 3-10 shows a 1×4 star splitter structure waveguide photodeposited onto a porous silica glass slab. Note that the glass surface is flat -- it is the refractive index variation that gives rise to the appearance of relief on the surface.

Figure 3-10
1 x 4 star splitter structure photolithographed onto a porous glass slab.

3.2.4 Characterization of the Optical Properties of Photoinduced Channel Waveguides

Characterizing the optical properties of the photoinduced channel waveguides is essential for a complete description of the sensor performance. The parameters to be considered are the width, the spectral transparency, the magnitude and shape of the refractive index profile, and the optical losses. The waveguide width is a function of the photomask resolution and of the processing conditions, i.e., concentration of the organometallic precursor adsorbed into the glass, excitation wavelength, and exposure time. Two refractive indices must be considered: those of the glass substrate and of the index layer. The refractive index of silica sol-gel glasses is 1.46, while that of Vycor glass is 1.5. The refractive index of the photoinduced layer depends on the metal oxide deposited. However, it has been previously demonstrated to differ by as much as 0.1 from the index of the glass substrate. A very small difference between the refractive indices of the substrate and the layer is enough to permit light waveguiding, as shown in Figure 3-11. The change in the index of refraction is directly proportional to the concentration of the organometallic precursor on the glass, the excitation intensity, and the exposure time. The resulting refractive index is a gradient profile, since the deposition of the adsorbed organometallic compound is diffusion-controlled.

Figure 3-11
He-Ne laser beam launched into a 600 μm channel waveguide photo
deposited onto a porous Vycor glass slab.

The transparency of the waveguide is close to that of the silica substrate in the visible and the infrared, as shown in Figure 3-12. Attenuation losses of 1.5 dB at the He-Ne wavelength were measured for a one-inch section of 600 μm wide straight channel waveguide using the experimental setup shown in Figure 3-13. These losses are largely due to coupling losses and light scattering at the interfaces. An upper bound on the losses caused by light absorption in the waveguiding material, i.e., the "inherent" waveguide transmission losses, can be conservatively estimated at 1.2 dB by estimating coupling losses to be 3% to 4% (0.15 dB) per optical interface. This implies a loss factor <0.5 dB/cm.

Figure 3-12
Optical transmission spectra of silica substrate and iron oxide waveguide.

Figure 3-13
Experimental setup for measuring optical losses in channel waveguides.

3.2.5 Power Splitting Characteristics of 1×4 IOCS Chip

The purpose of this testing was to characterize the optical power attenuation resulting from the propagation loss and fan-out efficiency of IOCS chips. Test results were obtained using the experimental setup shown in Figure 3-14.

Figure 3-14
Experimental setup for optical power attenuation measurements.

Initially, we measured the fan-out efficiency of a 1×2 IOCS chip using a 670 nm wavelength laser to launch light into the channel waveguide and using an optical power meter connected to a fiber mounted on a translation stage to measure the laser power coming out of each of the two fan-out channels. The experimental procedure was to couple the laser light into the waveguide and, using the translation stage to align the fiber with each fan-out channel, to find the maximum power output. These results are summarized in Table 3-2.

Table 3-2 Optical Attenuation and Splitting Efficiency of 1×2 IOCS Chip

	Test 1	Test 2	Test 3	Test 4	Test 5
Channel 1 (μW)	192	187	200	315	320
Channel 2 (μW)	142	160	170	275	320
Splitting Ratio	1.35	1.16	1.17	1.14	1.00

These results show the optical power measurements of five consecutive tests on the same integrated optic chip. The tests show progressive improvement in attenuation efficiency because of improved coupling of the source and optical fibers to the integrated optic splitter. At the end of test 5, we achieved the maximum power efficiency with a 50:50 splitting ratio.

Similarly, we measured the fan-out efficiency of a 1×4 channel waveguide using the 670 nm laser diode to launch light into the channel waveguide, and using the optical power meter connected to a

fiber mounted on a translation stage to measure the laser power coming out of each of the four fan-out channels. The results are shown in Table 3-3.

Table 3-3 Optical Attenuation and Splitting Efficiency of 1×4 IOCS Chip (μW)

	Test 1	Test 2	Test 3	Test 4	Test 5
Channel 1	49	51	53	45	64
Channel 2	70	96	100	80	133
Channel 3	99	78	36	50	46
Channel 4	—	—	40	—	53

The results shown in Table 3-3 show that the best optical alignment was achieved in test 5. Based upon these results, we calculated an average optical power for the 1×4 splitter of $0.74 \mu\text{W}$, with an average splitting efficiency of 0.99.

Finally, we measured the optical power attenuation through one straight $600 \mu\text{m}$ channel of the IOCS chip using the 670 nm laser diode. The attenuation was measured using the cut-back procedure of measuring output power, cutting the waveguide to a shorter length and then measuring the output power again to calculate loss (in dB) per centimeter. These results are summarized in Table 3-4.

Table 3-4 Optical Attenuation of a $600 \mu\text{m}$ Straight Channel of the IOCS Chip

Channel Length (mm)	Output Power (mW)	Loss (dB/cm)
38	0.32	—
18	1.0	4.8
9	1.4	1.5

In summary, the results of these tests demonstrated that the optical power attenuation of the IOCS chip is on the order of 1.5 dB/cm . Using a 1×2 splitter we obtained a 50:50 splitting ratio with an average power of $320 \mu\text{W}$. Similarly, the 1×4 splitter showed an average optical power of $0.74 \mu\text{W}$, with an average splitting efficiency of 0.99.

3.3 Chemistry and Optical Properties of Metal Ion Indicators

3.3.1 Metal Ion Chemical Indicators

Several types of fluorescence- or absorption-based chemical indicators are suitable for metal ion detection, including phthalocyanines, chelating agents, metalloporphyrins, and near-infrared compounds. Of these, phthalocyanines and chelating agents are the most commonly investigated. The initial months of this project focused on fluorescence-based phthalocyanines and chelating agents, which have been widely investigated and are commercially available from Aldrich, Inc. and Molecular Probes, Inc. Although these compounds are highly sensitive to metal ions, they usually respond to the charge of the metal ion. As a result there is cross-response for metal ions with the same charge, e.g., Cd^{2+} and Pb^{2+} . For this reason we conducted a preliminary investigation of the metalloporphyrin and crown ether indicators. In order to expedite this search, we made use of the consulting services of Dr. DeLyle Eastwood of Lockheed Environmental Sciences, Inc. Dr. Eastwood is a leader in the field of environmental monitoring, and in particular in the use of these compounds for metal ion detection.

The following sections discuss in detail the principle of metal ion indicator chemistry, and the chemistries of phthalocyanines and chelating agent indicators.

3.3.1.1 Metal Ion Sensing Fundamentals

The general principle of operation for metal ion detection using optically active indicators involves the chemical interaction of the indicator In with the target metal ion M to form a complex ion MIn:

The response range is defined by the equilibrium constant K_d for the metal-indicator reaction,

$$K_d = [\text{MIn}]/[\text{M}][\text{In}] ,$$

and corresponds roughly to:

$$pM = \log K_d + 1$$

The above reaction is analogous to the response of $pH = pK_a \pm 1$ observed in immobilized pH indicators. When $pM < \log K_d - 1$, the indicator is essentially saturated with metal ions, and further increases in the metal ion concentration produce very little change in the observed optical signal. Similarly, when $pM > \log K_d + 1$, most of the indicator is in the uncombined state, and further decreases in the metal ion concentration produce very little change in the observed optical signal. These principles have been discussed in great detail in previous reviews of optical sensing of metal ions [34,35].

For the optical detection of metal ions, researchers have developed a family of indicators referred to as "ionophores" that selectively bind to the particular metal ion. Typically, ionophores are macrocyclic molecules with an ion binding cavity of discrete dimensions. Hence, selectivity is based on the molecule cavity and the metal ion size. The connection between the metal ion moiety and the ionophore is a very important aspect of "molecular probe" design, which involves searching for the ionophore structure whose photophysical properties undergo the largest perturbation upon binding with the metal ion. The metal ion may be linked to the ionophore via a spacer, but in many cases atoms or groups of atoms belonging to the ionophore participate in the complexation. Crown ethers are the best known class of ionophores. However, many other types of molecules, including cryptans, chelators, podants, and coronads can be used as ion selective ionophores. The ion binding properties of ionophores have been summarized by R. M. Izatt, and co-workers in a major review [36].

Recently, new ion selective probe molecules have been developed based on the principle of fluorescence photoinduced electron transfer (PET). Figure 3-15 illustrates how a metal ion can control a photoinduced charge transfer to a fluorophore in which the metal ion is an electron donor and the fluorophore plays the role of an electron acceptor. In PET detection, the metal ion typically quenches the fluorescence emission of the fluorophore. This family of compounds is particularly attractive for use in lifetime-based metal detection, since typically these fluorophores have long-lived excited state intermediates.

Figure 3-15
Principle of metal ion recognition using photoinduced electron transfer in donor-acceptor systems [37].

3.3.1.2 Phthalocyanine Metal Ion Indicators

The phthalocyanines, naphthocyanines, and their metal derivatives are near infrared fluorophores [38,39]. This property makes them ideal candidates for the development of integrated optic chemical sensors because of the commercial availability of light sources and detectors that operate at these wavelengths. Metal-derived phthalocyanine compounds are available commercially from a number of sources including Aldrich Chemical Inc., K & K Labs, Fisher Scientific, and Eastman Kodak. Most recently Diatron Corporation in California has introduced a new class of phthalocyanine derivatives reputed to have much improved properties in this regard [40]. The luminescence properties of some phthalocyanine metal complexes of interest are summarized in Table 3-5; Figure 3-16 shows a typical luminescence spectrum for these complexes.

Table 3-5 Luminescence Bands for Phthalocyanine Complexes [41]

Phthalocyanine Complex	Fluorescence (cm ⁻¹)	Phosphorescence (cm ⁻¹)	Phosphorescence Lifetime (μsec)	Φ _F * (approx)	Φ _P * (approx)
Pd	15070	10100	25	5x10 ⁻⁴	3x10 ⁻³
Pt	?	10590	7	?	1x10 ⁻²
Cu	?	9390	<3	<10 ⁻⁴	1x10 ⁻³
VO	?	8500	?	?	~5x10 ⁻⁶
Mg	14640	~9000	~1000	0.6	~5x10 ⁻⁶
Zn	14640	9150	1100	0.3	1x10 ⁻⁶
Cd	14440	9120	350	3x10 ⁻⁸	2x10 ⁻⁴

*Φ_F= quantum yield of fluorescence; Φ_P= quantum yield of phosphorescence

Figure 3-16

Singlet absorption (—) and phosphorescence excitation spectra (x) of Pt-phthalocyanine [35].

Data and references examined for the phthalocyanines indicated that cadmium, lead, and arsenic are relatively stable (although the lower oxidation state of arsenic is labile, especially in the presence of oxygen) and cadmium and the higher oxidation states of lead and arsenic do emit (both

fluorescence and phosphorescence) at least enough to make them candidates for laser-induced fluorescence (using He-Ne lasers or laser diodes).

3.3.1.3 Chelating Metal Ion Indicators

Molecular Probes, Inc., has developed a family of chelating indicators suitable for heavy metal ion detection. These indicators produce a fluorescence change in the presence of metal ions in solution. The mechanism involves complex formation between a bidentate ligand and a solvated metal ion:

Trace amounts of heavy metals such as Hg^{2+} , Pb^{2+} , and Cd^{2+} can be readily identified with an indicator such as the BTC-5N, as shown in Figure 3-17. When excited near 415 nm, the fluorescence emission intensity increases and its emission wavelength shifts in the presence of micromolar concentrations of Ba^{2+} , Cd^{2+} , La^{3+} , Pb^{2+} , and Zn^{2+} , while the fluorescence signal remains unaffected by similar concentrations of Al^{3+} , Bi^{3+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} and Mn^{2+} .

Figure 3-17
Fluorescence emission spectra of BTC-5N heavy metal ion indicator:
(a) in increasing concentrations of Zn; (b) in 25 μM solutions of cadmium, zinc, barium, and lead.

BTC-5N heavy metal indicator will respond to metal ions in solution. Because the binding affinity constant (K_d) and fluorescence wavelength are specific to each of the sensitive metal ions, BTC-5N can differentiate each of these compounds using conventional dual wavelength ratiometric techniques. Table 3-6 shows the spectral characteristics and binding affinities of the BTC-5N indicator.

Table 3-6 Spectral Characteristics and Binding Affinity of the BTC-5N Heavy Metal Indicator

Ion	K_d (μ M)	Fluorescence (nm)
Cd ²⁺	0.1	505
Hg ²⁺	0.4	500
Zn ²⁺	0.2	517
Pb ²⁺	6.3	521
Ba ²⁺	68	523

3.3.2 Spectroscopic Characterization of Selected Metal Ion Indicators in Solution

After a literature review of the spectroscopic characteristics and metal ion affinity constants (K_d) of several types of heavy metal optical indicators, we decided to concentrate on the phthalocyanine and chelating metal ion indicators because these indicators have suitable optical responses to heavy metals. We contacted several chemical companies, including Aldrich Chemicals, Eastman Kodak, Fisher Scientific, Metalloporphyrin Products, ICN, Sigma, and Organometallics Inc., to procure the phthalocyanine complexes for lead, cadmium, and arsenic. Although we were able to obtain the lead and cadmium phthalocyanine complexes, we were not able to locate sources for phthalocyanine complexes for arsenic. As an alternative, we procured phthalocyanine complexes for copper and cobalt in order to demonstrate the multielement detection ability of the proposed integrated optic chemical sensor for heavy metal ion detection. These metal ions were selected because of their importance in environmental ground water protection. We also procured the Molecular Probes heavy metal indicator BTC-5N for characterization and testing. Table 3-7 lists the compounds investigated.

Table 3-7 Metal Ion Sensitive Indicators Selected for Solution Spectroscopic Characterization

	Phthalocyanine Metal Complexes
Aldrich Chemicals	Co-phthalocyanine Cu-phthalocyanine Pb-phthalocyanine Pb-tetrakis(4-cumylphenoxy)phthalocyanine
	Metal Ion Chelators
Molecular Probes	BTC-5N

3.3.2.1 Solubility Study

The major difficulty encountered in conducting the spectroscopic characterization of the selected compounds was finding a suitable common solvent for all of the selected compounds. The phthalocyanine indicators are notorious for their poor solubility in most common organic solvents. Therefore, a preliminary set of experiments was necessary to determine the solubility of these compounds in several organic solvents. Table 3-8 shows the results. The Molecular Probes indicator is water soluble, so no solubility studies were performed for this indicator.

Table 3-8 Solubility of Phthalocyanine Metal Complexes in Common Organic Solvents

Phthalocyanine Complex	Ethanol	Methanol	Acetonitrile	Toluene	Hexane
Pb	vp	vp	vp	vg	vp
Pb-tetrakis	p	p	p	vg	vp
Cu	g	g	p	vp	vp
Co	vg	vg	g	p	vp

vg-very good, g-good; m-medium; p-poor; vp-very poor

Other solvents tested but not listed in Table 3-5 included acetone, dimethylformamide, butyl acetate, and tetrahydrofuran. These solvents were tested only on a preliminary trial basis, and not all of the indicators were dissolved in any one of them. The solubility experiments involved preparing a 1×10^{-5} M solution of the indicator in a solvent. A very good solvent was one that completely dissolved the indicator without traces of a precipitate. A good solvent was one that dissolved the indicator when stirred manually or with an ultrasound sonicator. A medium solvent

was one that requires extensive stirring. A poor solvent was one that dissolved some of the indicator, leaving a precipitate. A very poor solvent was one in which the indicator precipitated completely without any dissolution.

3.3.2.2 Spectroscopic Data

The optical spectrum of each of the phthalocyanine metal complex indicators investigated is shown in Figure 3-18. Similarly, Figure 3-19 shows the optical spectrum of the metal ion chelator indicator in solution. The absorption peak wavelengths for the indicators are summarized in Table 3-9.

Figure 3-18
Optical spectrum of phthalocyanine metal complexes in solution.

Figure 3-19
Optical spectrum of BTC-5N indicator in solution.

Table 3-9 Absorption Peak Maxima of Selected Metal Ion Indicators

Metal Ion Indicator	Absorption maximum (nm)
Lead phthalocyanine	708
Lead tetrakis(4-cumylphenoxy)phthalocyanine	710
Copper phthalocyanine	670
Cobalt phthalocyanine	658
BTC-5N	452

3.3.3 Spectroscopic Characterization of Metal Ion Indicators Adsorbed into Porous Silica Glass

The next step in characterizing the spectroscopic properties of the selected metal ion indicators was to immobilize the indicators in a porous silica glass substrate and determine their spectroscopic properties under a variety of environmental conditions, i.e., dry, immersed in water, and in an aqueous system in the presence of metal ions. Table 3-10 lists the chemical indicators investigated.

The indicators were immobilized in porous Vycor glass rods (1/16 in. diameter by 1 in. length) for characterization of the spectroscopic properties of the immobilized indicators.

Table 3-10 Immobilized Metal Ion Sensitive Indicators Selected for Spectroscopic Characterization

Phthalocyanine Metal Complexes	Absorption Maximum (nm)	Target Metal Ion
Co-Phthalocyanine	658	Co
Cu-Phthalocyanine	670	Cu
Pb-Phthalocyanine	708	Pb
Pb-tetrakis (4-cumylphenoxy) phthalocyanine	710	Pb
Zn-Phthalocyanine	682	Zn
Ni-Phthalocyanine	608	Ni
Ni-tetrakis(4-cumylphenoxy)phthalocyanine	610	Ni
Cd-Phthalocyanine	670	Cd
Metal Ion Chelators		
BTC-5N	452	Cd, Pb, Zn, Ba
Xylenol Orange	425, 590	Pb

3.3.3.1 Test Setup

The spectroscopic properties of the immobilized indicators were characterized using the experimental setup shown in Figure 3-20.

Figure 3-20
Experimental setup for characterizing the spectroscopic properties
of immobilized metal ion indicators in a porous glass substrate

In this setup, a white light source is used as the analyzing lamp and an optical spectrum analyzer is used to collect the absorption spectrum in the region from 400 nm to 900 nm. The light from the analyzing source is guided via optical fibers to the porous glass rod containing the immobilized indicator and to the optical spectrum analyzer. Two laser sources orthogonal to the analyzing source, a He-Ne laser (630 nm) and a laser diode (670 nm), excite the fluorescence spectrum. A plastic cylinder, used as a water reservoir, allows the introduction of 10 ml of water or of an aqueous solution containing metal ions. A small drain allows the removal of the water or solution.

3.3.3.2 Preparation of Test Samples

The porous Vycor glass rods used to characterize the spectroscopic properties of the immobilized indicators were procured from Corning, Inc. These rods were used because they exhibit morphological properties similar to those of sol-gel glasses, and thus they are good for rapid characterization of the selected indicators. The Vycor rods were cut to 1 in. in length and both

ends were polished. After polishing, the rods were cleaned in a hot hydrogen peroxide solution for half an hour, followed by extensive rinsing in hot distilled water. The rods were then heat dried at 300°C for twelve hours. After heating, the rods were stored in a vacuum dessicator until they were impregnated with the metal ion indicators.

The metal ion indicators were impregnated into the porous network of the glass rods by sonicating the rods in a concentrated ($\sim 1 \times 10^{-4}$ M) solution of the indicator. Following this procedure, the rods with the entrapped indicator were transferred to a beaker containing distilled water and sonicated for 30 minutes. This removed any indicator not entrapped in the porous network of the glass, and avoided leaching of the indicator in the course of the spectroscopic characterization experiments. After rinsing, the impregnated glass rods were dried in a convection oven at 70°C for one hour. The rods were then placed in a vacuum dessicator until the time for them to be tested.

The impregnated glass rods were mounted in a specially designed sample holder, as shown in Figure 3-21, and then installed on the water reservoir of the experimental test setup shown in Figure 3-20. The sample holder allows the glass rod to be installed and coupled to an optical fiber bundle rapidly and without the use of epoxy. The sample holder is a machined stainless steel rod with orifices to allow water to diffuse into the porous glass rod.

Figure 3-21
Sample holder for spectroscopic characterization of metal ion indicators immobilized into porous glass rod.

3.3.3.3 Spectroscopic Data

The spectroscopic results of characterizing the immobilized indicators are discussed in this section. Figure 3-22 shows the optical spectrum of a dry Vycor glass rod (1 in. in length) in the region from 450 nm to 1450 nm. This spectrum shows three small absorption bands in the region from 850 nm to 1150 nm. These peaks correspond to the light source, and are not intrinsic in the spectrum of Vycor glass. A strong absorption peak at 1400 nm indicates the presence of chemiadsorbed water on the surface silica groups of the glass. This spectrum was used as a reference.

Figure 3-22
Optical spectrum of a dry porous glass rod.

Figure 3-23 shows a typical optical spectrum of a phthalocyanine-based metal ion indicator immobilized in the porous network of a silica glass rod. Two superimposed spectra are shown in this figure. The top spectrum is that of a clean porous glass rod, while the bottom spectrum is of the immobilized indicator. Comparison of the two spectra reveals the presence of a new absorption band centered at 670 nm. This absorption band is a characteristic signature of most phthalocyanine-based metal ion indicators. Changing the metal chromophore of the indicator can shift the position of the absorption band slightly, as shown in Table 3-10. Similarly, Figure 3-24 shows the optical spectrum of the metal ion chelating indicators immobilized into the porous silica glass.

Figure 3-23
Optical spectrum of copper phthalocyanine immobilized into a porous silica glass rod.

Figure 3-24
Optical spectrum of metal ion chelating indicators immobilized into a porous silica glass rod.

Once the metal ion indicators were immobilized in the porous glass, they were tested for their optical response to the target metal ion dissolved in the aqueous solution. In these experiments, chloride salts of the target metal ions were dissolved in water at a concentration of 1 mg/l. Figure 3-25 shows a result typical of these tests. This figure shows the spectroscopic

characterization results for the immobilized cobalt phthalocyanine indicator. First we obtained the transmission spectrum of the immobilized indicator both in the dry state and when the glass rod was immersed in water, as shown in Figure 3-25(a). This figure shows the Co-phthalocyanine absorption peak maximum at 762 nm and a small shoulder at 687 nm. These results demonstrate that this indicator is readily adsorbed into the porous glass matrix. Figure 3-25(b) shows the spectrum of the immobilized Co-phthalocyanine in water and when exposed to a water solution containing 1 mg/l of cobalt ions. This figure shows the optical response of the immobilized indicator after 15 and 30 minutes of exposure to the metal ion. These results indicate that the Co-phthalocyanine indicator can detect the presence of cobalt ions in an aqueous environment.

(a) Dry and Wet Spectra.

(b) In Water and in an Aqueous Solution Containing Cobalt Ions.

Figure 3-25
Optical spectrum of Co-phthalocyanine immobilized into a porous glass rod.

Similarly, Figure 3-26 shows the optical spectra of the immobilized copper phthalocyanine indicators immersed in water. As with the Co-phthalocyanine indicator, the figure shows the characteristic absorption peaks of the Cu-phthalocyanine indicator at 670 nm. In this figure, the optical response of the immobilized copper phthalocyanine indicator is shown both in water (lower

curve) and in an aqueous solution of copper chloride. This figure shows two important features: the intensity of the 670 nm absorption peak, which is the active peak of the phthalocyanine indicator, decreases in the presence of the copper ions; and the intensity of the absorption peak at 1260 nm remains unchanged. Based upon these two characteristics in the optical spectrum, we can perform dual wavelength ratiometric detection using the 670 nm absorption band as the active, metal ion sensitive band, and the 1260 nm absorption band as the reference band. This allows the development of a self-referenced sensor system.

Figure 3-26
Changes in optical spectrum of copper phthalocyanine immobilized into a porous silica glass rod in water and in a 1 mg/l copper chloride aqueous solution.

Similar optical intensity changes were observed using the other phthalocyanine metal ion indicators. The results, tabulated in Table 3-11, show the change in optical intensity at the active wavelength of the indicator as a function of the concentration of the target metal ion in solution (note that the intensity unit dB/mg/l becomes dB-1/mg). From these results it is observed that the cobalt and copper indicators have high sensitivity to the metal ions, the lead and cadmium indicators have medium sensitivity, and the nickel and zinc indicators have poor sensitivity. The two phthalocyanine tetrakis-(4-cumylphenoxy) derivatives for lead and nickel show no response to the selected target metals.

Table 3-11 Optical Changes of Phthalocyanine Metal Ion Indicators as a Function of the Metal Ion Concentration in Water

Phthalocyanine Metal Complexes	Absorption Maximum (nm)	Intensity Change (dB-I/mg)
Co-Phthalocyanine	658	-16.0
Cu-Phthalocyanine	670	-17.0
Pb-Phthalocyanine	708	-4.1
Pb-tetrakis(4-cumylphenoxy)phthalocyanine	710	NR
Zn-Phthalocyanine	682	-0.57
Ni-Phthalocyanine	608	-1.52
Ni-tetrakis(4-cumylphenoxy)phthalocyanine	610	NR
Cd-Phthalocyanine	670	-3.2

* NR - No response to target metal ions

The metal ion chelating indicators demonstrated a similar response to the target metal salt in solution. The active wavelength region of these indicators is typically in the 400 nm to 600 nm region. Figure 3-27 shows their typical optical response. This figure shows the optical response of xlenol orange immobilized in a porous glass rod in the presence of lead chloride. An isosbastic point at 500 nm indicates the formation of a metal ion complex between lead ions and the chelating indicator. Similar results have been obtained for the BTC-5N indicator. These results are summarized in Table 3-12.

Figure 3-27
Optical spectrum changes of xlenol orange immobilized into a porous silica glass rod in water and in a 1 mg/l lead chloride aqueous solution

Table 3-12 Optical Changes of Metal Ion Chelating Indicators as a Function of the Metal Ion Concentration in Water

Chelating Complexes	Absorption Maximum (nm)	Intensity Change (dB-I/mg)
BTC-5N	427	-1.3
Xlenol Orange	440	-2.0

In summary, the experimental data obtained in the course of the spectroscopic studies of the immobilized metal ion indicators indicated that the phthalocyanine complexes for cobalt, copper, lead, and cadmium exhibited the best dynamic response to the target metal ions. For the proof-of-concept demonstration of the IOCS technology it was decided to use the phthalocyanine complexes for cobalt, copper, and lead as the metal ion active indicators, since these compounds demonstrated the largest optical response.

3.4 Fabrication of Integrated Optic Chemical Sensor Chips

Two types of integrated optic chips were fabricated for the proof-of-concept demonstration, a 4 straight channel chip and a 1×4 star coupler chip. The procedure for fabricating IOCS chips involves the following steps: 1) mask the integrated optic chip with a protective coating to expose the active channels and to protect the reference channel of the chip, 2) dope each of the active channels of the chip with a metal ion sensitive chemical indicator, 3) package the IOCS chips, and 4) couple optical fibers to the channel waveguides. The following sections discuss these processing steps in turn.

3.4.1 Masking IOCS Chips with Protective Coating

The integrated optic structures -- the 4-straight-channel chip and the 1×4 star coupler chip -- photolithographed into porous silica glasses must be masked with a protective coating in order to define the active and reference channels. The protective coating mask defines the active channels for doping the metal ion indicators, and then protects the reference channel from exposure to the aqueous environment during use.

The integrated optic chips were masked by first covering the active channels and then depositing a gold coating onto the surface of the chip using a metal evaporator. Figure 3-28 diagrams this technique. The active channels of the chip were covered with a glass plate cut precisely to match the width of the channel. The glass plates were placed directly on top of the active channel waveguides to protect them from being coated in the metal plating process. (This process requires precise alignment of the protective glass slides onto the channel waveguides of the chip.) Figure 3-29 shows the IOCS chips immediately after the masking process. The chip with the covered channels was then placed in a metal evaporator and coated with a thin gold film. The thickness of the film ranged from $1 \mu\text{m}$ to $2 \mu\text{m}$.

Figure 3-28
Setup for masking integrated optic chemical sensor chips.

(a) Four straight channels.

(b) 1 x 4 star coupler.

Figure 3-29
Gold coated IOCS chips.

3.4.2 Doping IOCS Chips with Metal Ion Indicators

Once the IO chips were masked, they were doped with a concentrated solution of the selected metal ion sensitive indicators. Impregnating the metal ion indicators is one of the most delicate steps of the entire fabrication process, since cross-contamination of the sensing channels must be prevented. Each channel was impregnated by removing its glass slide cover, using a syringe containing the concentrated indicator solution to impregnate the metal indicator into the channel, and then re-covering the channel. This procedure is shown schematically in Figure 3-30.

Figure 3-30
Setup for doping chemical indicator into porous channel waveguides.

After the selected phthalocyanine indicators were impregnated into the porous channel waveguides of the IOCS chip, the optical spectrum of each of the channels of the chip was measured using a white light source and an optical spectrum analyzer. Optical fibers were butt-coupled to each of the channels of the waveguide both to deliver light to the chip and to transmit the optical signal from the channels to the spectrum analyzer. Figure 3-31 shows the spectral results obtained for each of the channels of the chip. This figure shows the characteristic optical spectrum of the immobilized indicators on the active channels of the chip and that of the reference channel.

Figure 3-31

Optical spectrum of the immobilized metal ion indicators on the waveguide channels of the IOCS chip.

Similarly, a 670 nm laser diode was used to characterize the fluorescence emission of the immobilized phthalocyanine indicators, as shown in Figure 3-32. This figure shows the spectrum of the reference channel and that of the cobalt and copper channels. The spectrum for the lead channel is not shown because no fluorescence emission was detected for this channel. The reference channel shows the spectrum of the laser excitation source at 670 nm. The cobalt and copper channels show the characteristic fluorescence spectra of phthalocyanine indicators in the range from 850 nm to 950 nm.

(a) Reference channel

(b) Co sensing channel

(c) Cu sensing channel

Figure 3-32
Fluorescence spectra of the immobilized phthalocyanine indicators on the waveguide channels of the IOCS chip.

These results demonstrate that either intensity-based or fluorescence-based detection, depending of the type of indicator, could be used to detect each of the metal ions. Both of these techniques have been used to detect the target metal ions in a water flow stream as discussed in Section 3.5.

3.4.3 Packaging IOCS Chips

Design of Integrated Optic Sensor Package -- For the proof-of-concept demonstration of the integrated optic metal ion sensor, we designed a generic package to enclose and protect the IOCS chip. This package (see Figure 3-33), made of black Delrin plastic, holds the IOCS chip securely in place and allows easy coupling of the light delivery fibers to the channel waveguides in the chip. Optical fibers connect the IOCS chip to a remote optoelectronic sensor readout box, which contains the light source and signal detection circuitry. The cover plate with a central orifice allows the metal ions present in a water outflow to interact with the waveguide sensor without obstruction, and it offers strain relief to the fibers. Figure 3-34 is a complete schematic drawing of the package with dimensions.

(a) Four straight channel chip

(b) 1 x 4 star splitter chip

Figure 3-33
Integrated optic sensor (IOS) packaging design.

Figure 3-34
IOCS packaging design.

3.4.4 Coupling Optical Fiber to IOCS Chips

The final steps involved in fabricating the IOCS chip are to align and couple the optical fibers to the IOCS chip, and then to encapsulate the IOCS device in the packaging material. The fibers were butt coupled to the waveguides and aligned using the setup shown in Figure 3-35. In this setup, the IOCS chip is placed in the bottom section of a specially designed plastic package that supports the chip in place. The optical fibers were positioned in place while the optical power through the chip was measured. When the power reached maximum, the fiber was glued to the glass chip using optical epoxy. The fibers were also glued to the plastic container to produce a rigid bond and to prevent their debonding from the chip. Each connectorized IOCS chips was finally packaged by encapsulating it in a waterproof epoxy resin, leaving an open window for the active channels of the chip to interact with the environment as shown in Figure 3-36. This low thermal expansion epoxy was used to pot the chip in the plastic mold and protect it from water permeation and any environmental effects.

Figure 3-35
Setup for coupling optical fibers to IOCS chip.

Figure 3-36
Epoxy-encapsulated sensor package.

3.5 Demonstration of Integrated Optic Chemical Sensor Response to Target Metal Ions

The packaged IOCS chips were tested for their metal ion sensing performance using the experimental setup shown in Figure 3-37. In these tests, each IOCS chip was immersed in a water reservoir and tested for response to each of the target metal ions. The objective of these tests was to demonstrate that integrated optic chemical sensors are capable of detecting low concentrations of heavy metal ions in aqueous environments. A 670 nm laser diode was used for both intensity-based and fluorescence-based detection.

Figure 3-37
Continuous flow cell test setup for measuring optical attenuation.

Intensity-based detection was used to monitor the intensity changes in the lead phthalocyanine indicator, since its absorption maximum occurs at this wavelength. Through the course of these tests, the optical power at 673 nm for both the reference channel and the lead sensing channel was measured in the absence and presence of lead ions (1 mg/l) in water, as shown in Figure 3-38. Figure 3-38 shows that the reference channel responds slightly (± 3.5 dBm) to the presence of lead ions, but that after a short time (~ 60 sec) the signal returned to its reference level. Similarly, the lead sensing channel responded to the presence of lead ions in solution. A total optical change of 13.7 dBm was measured, as shown in Figure 3-38(b).

(a) Reference channel

(b) Pb sensing channel

Figure 3-38
Intensity response of the IOCS chip to lead ions in solution using
670 nm laser diode as the analyzing source.

The 670 nm laser diode was also used to excite the fluorescence spectra of the copper and cobalt sensing channels at 890 nm as shown in Figures 3-39 and 3-40. Figure 3-39 shows that the copper ions quench the fluorescence intensity of the immobilized copper phthalocyanine indicator. An optical change of 12.4 dBm in the fluorescence intensity of the copper sensing channel was

observed, with a response time of approximately three seconds. No effect was observed in the optical intensity of the reference channel. Similarly, Figure 3-40 shows how the fluorescence spectrum of the cobalt sensing channel is quenched upon introduction of cobalt ions into the water flow stream. An optical change of 16.8 dBm in the fluorescence intensity of the cobalt sensing channel was observed, with a response time of approximately nine seconds. This figure also shows that the sensor recovers to its original fluorescence level once the cobalt ions have been removed from the water flow stream. A recovery time of twenty seconds was measured for this channel. The results and significance of this effort are summarized in Section 5.0, Conclusions.

Figure 3-39
Fluorescence response of the IOCS chip to copper ions in solution
using a 670 nm laser diode as the excitation source.

Figure 3-40
Fluorescence response and recovery of the IOCS chip to cobalt ions
in solution using a 670 nm laser diode as the excitation source.

4.0 BUSINESS PLAN

POC has established a business plan for development of our integrated optic chemical sensor (IOCS) product line. The IOCS fits well into the overall POC strategic business plan for optical sensors, as discussed in the following sections.

4.1 Commercial Applications

The low cost, small size, and anticipated excellent performance of the IOCS are particular advantages in instruments used for in-line monitoring and for field testing of reclaimed, recycled, and waste water or other liquid media. The ability to change analytes by simply exchanging the IOCS chip makes the sensor system extremely flexible. In addition, the IOCS is a self-referencing sensor system that can perform multianalyte detection.

4.2 Market Analysis

The expected markets for the integrated optic chemical sensors (IOCSs) are many. They include the process control market, various segments of the chemical manufacturing market, and the environmental monitoring market. It is the intention of POC to focus initially on the environmental monitoring market.

According to Environmental Business International, Inc., instrumentation for purification and treatment of water and waste water constituted 37% of all environmental instrument sales in 1993 (\$1.8B) -- the largest market in the environmental monitoring field. Projections for this portion of the environmental instrumentation market through 1998 show an average annual growth of approximately 6%, with expected 1998 sales of \$2.4B (see Table 4-1).

Although the environmental industry as a whole is leveling out, expected growth in the water and waste water segment is still strong enough to support the introduction of our product. Indeed, as environmental instrumentation is moving away from laboratory analysis and toward continuous in-line monitoring and rapid field measurement, the IOCS is ideally placed to take advantage of this new trend.

The integrated optic chemical sensor offers a unique capability of simultaneous detection and quantification of metal ions in liquid waste water at very competitive prices. For this reason, we conservatively estimate that POC will begin to displace current systems within six months of market introduction. With a preliminary target price of \$7,500 for a basic instrument and 25% market penetration, we expect to generate revenues of approximately \$5,000,000 within five years after introduction.

Table 4-1 The Environmental Instrument Industry Continues to Grow

Environmental Industry Segment	Revenue (\$ Billions)									
	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998
Services										
Analytical Services	1.5	1.5	1.6	1.6	1.6	1.6	1.7	1.7	1.8	1.8
Solid Waste Management	23.5	26.1	27.0	28.2	29.4	30.6	31.9	33.4	34.7	35.9
Hazardous Waste Management	7.5	8.3	8.5	8.8	8.6	8.6	8.6	8.6	8.5	8.2
Remediation/Industrial Service	8.2	8.5	7.9	8.2	8.4	8.9	9.3	9.7	10.1	10.4
Consulting & Engineering	10.2	12.2	13.4	14.2	14.4	15.0	15.8	16.6	17.3	17.8
Equipment										
Water Equipment & Chemicals	11.7	12.1	12.5	13.0	13.2	13.8	14.5	15.3	16.1	16.8
Instrument Manufacturing	1.5	1.6	1.7	1.8	1.8	1.9	2.1	2.2	2.3	2.4
Air Pollution Control Equip.	3.6	3.7	3.7	3.8	3.8	3.9	4.1	4.3	4.4	4.6
Waste Management Equip.	9.8	10.4	11.0	11.4	11.2	11.1	10.9	10.6	10.3	9.8
Process & Prevention Techn.	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4
Resources										
Water Utilities	18.8	20.2	21.1	21.7	23.1	24.3	25.5	26.7	27.9	29.1
Resource Recovery	13.3	15.2	14.0	14.3	15.2	16.1	17.0	18.1	19.1	20.1
Environmental Energy Sources	1.6	1.8	1.9	2.0	2.1	2.3	2.6	2.9	3.2	3.5
Total Industry	111.5	122.0	124.7	129.6	133.5	138.9	144.9	151.0	156.8	161.9
Average Growth Rate (%)	11.7	9.5	2.2	3.9	3.1	4.0	4.3	4.2	3.8	3.3

from Environmental Business Journal, April 1994.

4.3 Marketing Plan

Physical Optics Corporation has conducted discussions with several municipal water and waste treatment agencies, and also with companies in the environmental remediation and control industry. The Los Angeles Industrial Waste Management Division has agreed to test our system in their facility. Positive results from this testing will give POC high visibility among potential customers, particularly in the lucrative water remediation and quality verification markets.

POC plans to launch a limited line of IOCS products targeted specifically at the water quality and remediation process control markets. The product will be introduced initially in POC's local Southern California market, the nation's largest water quality equipment market. We expect that the dual advantages of convenient location (to facilitate customer contacts) and high visibility (by virtue of our collaboration with several large local customers) will supply the impetus required to create rapid growth in IOCS system sales in the first two years after product introduction. As growth-derived revenue increases, POC will evaluate other markets; since the market for water quality sensors is truly global in scope, POC expects to be able to maintain a high rate of sales growth for well over a decade.

4.4 Physical Optics Corporation Record of Commercialization

Physical Optics Corporation has a long and successful history of converting SBIR developed technology into commercially viable products. Since our inception in 1985, we have had gained more than \$10.1 million in commercial sales resulting from the SBIR program, an outstanding record when one considers that the average product development cycle is at least seven years. As a result of this success, POC has been able to attract \$20.06 million in outside money for the support of product introduction. Seventy five percent of the money raised (\$15.04 million) has been used to fund the products resulting from Phase II projects that were completed by the end of FY 1994. The remaining moneys are earmarked for products developed as a result of more recent Phase II projects. By 1995, the commercial product mix due to our development efforts has resulted in six families of products, all of which are based upon our technological strength in optics. POC forecasts that by the turn of the century, our cumulative commercial sales will be in excess of \$50 million.

4.5 Management System

The management of this project is characterized by clear, well defined lines of authority, responsibility and communications. As Principal Investigator, Dr. Edgar A. Mendoza is responsible for the overall performance of the project. The project is managed by Dr. Robert Lieberman, who has oversight responsibility for all technical, financial, and management aspects of the project. Dr. Lieberman is POC's R&D Sensor Systems Vice President, reporting directly to the Senior Vice President for Research and Development, Dr. Ryszard Gajewski, ensuring that the project has high corporate visibility. All optical sensor work is performed within Dr. Lieberman's Sensor Systems Department. Dr. Mendoza also has ready access as needed to other POC personnel. Dr. Mendoza serves as POC's contact point with the DOE on all issues technical, managerial, and contractual.

The relationship between the IOCS project and POC's organization is outlined in Figure 6-1.

Figure 6-1
Project organization within POC.

4.6 Technical Support

The laboratories of the **Research & Development Division**, where the project has been performed, occupy 16,000 square feet. POC's R&D facility is designed to serve applications in various areas of photonics, including optical interconnects, optical computing, neural nets, information processing, and fiber optic device fabrication and testing. Our photonics laboratories

have all equipment necessary for fabricating and testing optical interconnects, including chip-to-chip, backplane, and reconfigurable modules using free space as well as waveguide implanted interconnects.

Specifically relevant to this project have been the facilities and equipment of the Sensor Systems Department. In particular, a full range of opto-electronic test equipment, numerous light sources and optical filters, fiber termination equipment, optical elements such as lenses and polarizers, positioning equipment, optical breadboards, and several types of detectors and preamplifiers have been available to fulfill the needs of the project. Major equipment that was of use in Stage I includes an Ando AQ6312B Optical Spectrum Analyzer, a Hewlett-Packard 8153A Fiber Optic Power Meter, a 175 MHz digital oscilloscope (LeCroy model 9400A), lock-in amplifiers, high temperature furnace (Termolyne Model 6000), Class 100 clean room, a variety of photolithography equipment, computer controlled micropositioning stages (Melles Griot), three IBM compatible laboratory computers, analog-to-digital conversion hardware and software, and machining facilities. Overall, the R&D Division has accumulated capital equipment valued at \$1 million.

4.7   Safety and Health Program, Environmental Protection Program, and   Quality Assurance/Quality Control Program

Safety and Health Program -- Physical Optics Corporation maintains a safe working environment for all employees. In addition to full compliance with the City of Torrance Fire Code and all federal, state, and local safety ordinances, the company maintains an active program of employee education and training with regard to both laboratory safety and general safe working practices. Training sessions are held for new employees within 30 days of employment. At least once a year, safety training classes are held for all employees, new or old. POC's facilities are inspected yearly by the Torrance Fire Department, and we maintain a complete on-line database of all hazardous, combustible, and flammable chemicals. This database permits real-time assurance of compliance with hazardous material storage limits. A complete collection of Material Safety Data Sheets (MSDSs) for all chemicals used on site is kept in a widely-publicized, fully accessible location. Proper safety equipment, ranging from gloves and face masks to certified fume hoods and respirators, is readily available to all employees whose work requires their use. Arrangements for emergency medical care, long-term disability insurance, and all other appropriate measures have been made, in case a workplace accident should occur.

Environmental Protection Program -- Physical Optics Corporation has a complete tracking system in place for monitoring hazardous chemicals used at our facilities. Our receiving process assigns a unique tracking number to each container of hazardous material, identifying where within POC's facilities it will be used. A computerized database is used to track hazardous chemicals. Hazardous waste is collected for regularly scheduled removal by licensed professional disposal services. POC recently installed a recirculating water cooling system for use with its chilled-water laser systems, bringing the corporation into full compliance with environmental waste-water regulations. As part of this installation, a "sample trap" was installed, allowing the chemical composition of our "outflow" to be monitored. POC has never been cited for violation of water-quality regulations.

Quality Assurance/Quality Control Program -- POC's quality assurance program, which is based upon MIL-Q-9858, is reviewed regularly by management. The company quality assurance procedures and practices document the areas of procurement, document control, material control, receiving inspection, manufacturing fabrication, calibration, corrective action, supplier quality assurance, statistical quality control and analysis, and workmanship standards among others. POC is dedicated to doing excellent work and delivering products of consistently high quality.

5.0 CONCLUSIONS

POC has successfully demonstrated the proof-of-concept of a self-referenced multi-element integrated optic chemical sensor (IOCS) chip capable of detecting heavy metal ions in a water flow stream. POC's innovative sensing technology is based on an array of chemically active optical waveguides integrated in parallel in a single small IOCS chip. The IOCS technique uses commonly available materials and straightforward processing to produce channel waveguides in a porous glass, each channel treated with a chemical indicator that responds optically to the presence of heavy metal ions in water. The porosity of the glass allows metal ions to diffuse from the water into the glass to interact with the immobilized indicators, producing a measurable optical change. For the proof-of-concept demonstration, POC designed and fabricated two types of IOCS chips. Type I uses an array of four straight channel waveguides, in which each of three channels is doped with a metal sensitive indicator, an ionophore, and the undoped fourth channel is used as the reference channel. Type II uses a 1×4 star coupler structure, again with three sensing channels and a reference channel. These chips were tested for their response to metal ions in a water flow stream. In the course of this contract period, all processing techniques required to fabricate IOCS chips have been investigated, and a variety of chemical indicators, including phthalocyanine metal

complexes and metal chelators, for metal ion detection have also been investigated. A firm foundation has been laid for the future engineering development of a compact optoelectronic readout module, and several potential spin-off markets have been identified.

Successful implementation of this technology is expected to have a broad impact on the government's environmental water quality program and in the commercial environmental monitoring market. Because of the self-referenced, multidetection capability of the IOCS technique, POC's water quality sensors are likely to find markets in environmental monitoring and protection, ground water monitoring, and in-line process control.

6.0 FUTURE TECHNOLOGY DEVELOPMENT

In the "Technology Development Stage," the integrated optic chemical sensor (IOCS) technology will be optimized with the goal of producing a fully autonomous, portable water quality control instrument. To accomplish this the following objectives have been set forth:

Objective 1. Design, build, and test a self-referenced integrated optic sensor chip for **lead, chromium, copper, and cadmium** ions that meets all of the specifications listed in Table 1-8. These sensors must be fully capable of operation at a water treatment plant at DOE's Savannah River Technology Center.

Objective 2. Design, build, and test optoelectronic support equipment interface the integrated optic sensors to the water treatment process control circuitry. The optoelectronic system will include a multiwavelength fiber optic frequency domain (phase) fluorimeter sensor readout system and signal processing. The optoelectronic system should be capable of stand-alone as well as integrated operation.

Objective 3. Integrate and package the integrated optic sensor, fiber optic leads, and optoelectronic system to form a complete water monitoring system. Perform laboratory tests to verify proper, crosstalk-free, operation of the integrated system.

Objective 4. Perform rigorous laboratory testing to verify the proper integration and reliability of IOCS system.

Objective 5. Demonstrate a bench-style prototype of the IOCS instrument suitable for mass fabrication and field deployment at the Savannah River Technology Center.

Table 6-1 Desired Performance for Metal Ion Monitoring in a Water Treatment Plant [3]

Target Heavy Metals	Potable (mg/l)	Hygiene (mg/l)	Accuracy (%)	Response Time (min)
Copper	1.0	1.0	1 - 5	1 - 5
Chromium	0.05	0.05	1 - 5	1 - 5
Cadmium	0.002	0.002	1 - 5	1 - 5
Lead	1.0	1.0	1 - 5	1 - 5

Once the IOCS chip is optimized, IOCS water quality sensors and other IOCS products will be introduced to the market. POC's technology will compete successfully with current technologies because of its low cost and suitability for mass production.

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