FIBER OPTIC CHEMICAL SENSORS

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OCTOBER 1993
FINAL REPORT
MAY 1989 - MARCH 1991

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This final report describes a database that supports the development, engineering and manufacturing of dependable chemical sensors which include fiber-optics in the design and which are suitable for use in the field by technicians. Inexperienced investigators using the database can start with the state of the art rather than starting over each time a requirement for a new chemical sensor is established. The expectations are shorter development times and reduced development and engineering costs.

Spectroscopy  Chemometrics
Absorption Spectroscopy  Ultraviolet Spectroscopy
ATR Spectroscopy  NIP Spectroscopy

Unclassified  Unclassified  Unclassified

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PREFACE

This report was prepared by the Laboratory for Inline Process Analysis, Kenneth E. Johnson Research Center, University of Alabama in Huntsville, Huntsville, AL 35899 under Contract No. F08635-89-C-0288, for the Air Force Engineering and Services Center (AFESC), Suite 2, 139 Barnes Drive, Tyndall Air Force Base, Florida 32403-5319. The work was performed between May 1989 and March 1991. The AFESC project officer was Bruce Nielsen.

This final report describes a database that supports the development, engineering and manufacturing of dependable chemical sensors which include fiber-optics in the design and which are suitable for use in the field by technicians. Inexperienced investigators using the database can start with the state of the art rather than starting over each time a requirement for a new chemical sensor is established. The expectations are shorter development times and reduced development and engineering cost.

This technical report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

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SECTION I
INTRODUCTION

A. OBJECTIVES

The goal for this research effort was a database that supports the development, engineering and manufacturing of dependable chemical sensors which include fiber optics in the design and which are suitable for use in the field by technicians. Inexperienced investigators using the database can start with the state of the art rather than starting over each time a requirement for a new chemical sensor is established. The expectations are shorter development times and reduced development and engineering cost.

B. BACKGROUND

1. General History

The need for increased communication system capacity at reduced cost per message unit has spurred the development and installation of hundreds of operating lightwave communication systems around the world. Compared to wire systems, optical fiber transmission systems operate with less energy per unit-message unit-mile, lower signal attenuation per unit distance, higher bandwidth for increased signal capacity, lower shock hazard, less influence from spurious radiation, smaller size, less weight, and many other advantages. These advantages have encouraged improvements in light sources; optical fibers, cables, and connectors; photodetectors; dispersion devices, for example small gratings; graded index lens; and multiplexers.

The availability of new and improved optical components has enabled significant progress toward the development of photonic sensors employing fiber optics. These sensors can detect acoustic and magnetic fields, temperature, pressure, liquid level, and many other parameters. Department of Defense researchers have developed many effective devices that have resulted in greater safety and efficiency aboard aircraft, on navy vessels, and sensors for underwater detection. The Army has developed missiles guided by optical fiber communication channels.
Analytical chemists, particularly spectroscopists, recognized the potential applications of these optical developments. Optrodes (optical electrodes) at the end of optical fibers to be used for chemical analyses were described. An early application at Oak Ridge National Laboratories (ORNL) was related to the use of quartz fibers to carry optical signals for spectroscopic measurements to and from solutions at high radiation levels which made conventional sampling techniques impossible. The chemical composition (seven components) of a process stream was controlled in real time using a dedicated computer and eight filters rotating at speeds of several cycles per second. Quartz fibers of the highest purity were required for this application because impurities in the quartz cause radiation damage to the fiber which results in signal attenuation. This example of process control using small quantities of fibers preceded the building of facilities to manufacture the larger quantities of fiber required to support the telecommunication devices. Today pure quartz fibers are very important to the modern telecommunication industry.

Subsequent adaptations of spectrophotometry for remote in situ analyses have revolutionized processes for the production of many chemicals. Real-time analyses replace the time-consuming practice of collecting a sample, taking it to the laboratory, and waiting for the analyses. Multicomponent analyses of production processes for major constituents and some minor components are well developed techniques.

Dr. Tomas Hirschfeld and associates at the Lawrence Livermore National Laboratories (LLNL) began the development of a class of fiber optic chemical sensors designated as FOCS. FOCS were characterized as small chemical laboratories placed at the end of an optical fiber. The optical fiber was used to observe a color change, chemical precipitation, or an absorption of a new chemical species as a chemical reaction occurred. The various chemical reactions occurred in small ampules on the end of the fiber or in a modified cladding provided on a short section near the end of the fiber. A creative and well-executed research program demonstrated the feasibility of chemical selectivity and detection of minor and trace components. The LLNL work is documented in internal reports, patents, and abstracts of talks at professional meetings. Relatively few publications, however, are found in technical journals. Technology transfer from LLNL proceeded along two paths. License rights were negotiated
with several companies. A smaller portion of the work was pursued by the Environmental System Laboratories at Las Vegas (EMSL/LV).

Commercial activities split primarily into two groups; one group was interested in process development in chemical manufacturing, and a second group was interested in "sticks" (small needle devices that can be placed in the body to make in situ measurements). The companies interested in chemical processing have reported increase productivity through the use of proprietary devices. However, the activity is within the company as an engineering and service activity. A small number of companies have introduced packaged instruments on the market.

A separate approach was taken by Mr. David LeFebre when he founded Guided Wave Inc., El Dorado Hills, California. He recognized the need for a spectrophotometer that supported fiber research and established a company with the objective of developing, manufacturing and distributing a spectrophotometer. Most of the photonic sensor systems developed within the chemical manufacturing industry are believed to use the Guided Wave spectrophotometers as a component of the system.

In 1986 The University of Alabama in Huntsville, UAH, organized the Center for Applied Optics. Dr. John Caulfield was selected as the first director. Dr. Caulfield had been a professional associate of Dr. Tomas Hirschfeld at Block Engineering during the development of the Fourier Transform Infrared (FTIR) Spectrophotometer. The first cooperative effort between Dr. Caulfield and Dr. Arendale, UAH Professor of Chemistry, was a small contract, Dr. Arendale as Principal Investigator, with Dr. Bernie Bulkin at Standard Oil Co., Cleveland Ohio. Dr. Hirschfeld had recently died of a heart attack. The work statement provided for review and documentation of technology related to fiber optic sensors for measurement of chemical analytes. To aid in this work, Dr. Stan Klainer, a third colleague of Dr. Hirschfeld and Dr. Caulfield, was employed as a subcontractor on the program. Dr. Stan Klainer was operating as ST&E in Livermore, California and also had contracts at LLNL. Dr. Arendale was serving as a consultant with United Space Boosters, Inc., in Huntsville Alabama. USBI, Inc. is a division of
United Technologies Inc. The United Technologies Research Center has an outstanding fiber optics program. The union of these four approaches was expected to have great promise.

A decision was made by Standard Oil not to extend the effort with the University of Alabama in Huntsville Center of Applied Optics to include the development of improved new sensors. Principal stumbling blocks were disagreements on proprietary and patent rights. A major problem was identification of the property of ST&E vs LLNL. ST&E was formed to manage the activities of Dr. Hirschfeld and Dr. Klainer separate from their activities at LLNL. Although Dr. Klainer was appointed an Adjunct Scientist in the Center of Applied Optics, he did not wish to accept the University's patent policy. The work of Dr. Klainer and Dr. Arendale separated at this point.

The technical report and the UAH proposal to Standard Oil Company prepared by Dr. Arendale were not widely distributed. These documents summarize the state of the art that existed in late 1986 when the proposal which resulted in this Air Force contract was prepared. Selected portions from these two documents have been reproduced as APPENDIX A of this report.

2. Contract Work Statement

The Laboratory for Inline Process Analyses of the University of Alabama in Huntsville initiated research under contract F08635-89-C-0288 8 July, 1989 to develop "Advanced FOCS Sensors." Objectives of the effort were as follows: The first phase was to develop FOCS design data bases. The second phase was to determine design parameters and functions, such as Beer's Law, for the design of aromatic hydrocarbon FOCS. The design parameters and databases were to be organized such that they can be readily updated and utilized for developing FOCS for new analytes. The third phase was to consist of laboratory verifications of models using optical components. Phase IV provided for breadboard constructions and testing of FOCS using design databases and models. The final phase was the development of specifications for one or more prototype instruments based on the tested breadboards.
C. APPROACH

This research program was divided into five parts. The initial efforts were related to the collection and critiques of available literature references. The Principal Investigator's collection of references and reprints was augmented with additional references using the literature base of the Redstone Scientific Information Center. The references were collected into an intelligent database using askSam, a computer program from askSam Systems, Inc. At this point, critique of the references was the basis for selection of theory applicable to the research effort. A decision was made to investigate all classes of chemical sensors which include fiber optics in the design rather than limit the investigation to FOCS. Laboratory experiments were performed to validate that the selected theory was applicable. Selected components were collected and tested as breadboard configurations. Based on these experiences, recommendations were formulated for specifications that can be used for the procurement of environmental monitoring systems which include fiber optics.
SECTION II
DATABASE

The initial task was to organize the available data (several hundred publications collected by Professor Arendale) into a database that could be made available to a larger community. The collection had become so large and was growing so fast that personal memory was no longer practical as a guide to searches. A search was made for methods for organizing and searching the references to meet the objectives for this contract. Placing the information in a computerized database was an easy decision.

A. CHOICE OF SOFTWARE FOR PREPARING THE DATABASE

The contract requirement for the Data Base/Computer software product is:

The tabular data shall be produced in a MS-DOS text file format, with only ASCII printable characters and blanks in the text. The data shall have the text positions of the fields defined in a fixed format to allow its importation into file management programs both in the microcomputer and the minicomputer (DBASE, FORTRAN, BASIC, and C are presently envisioned).

The files are to be delivered in the MS-DOS 360K 5 1/4 inch floppy disk format. Files that are too large for a single disk shall be partitioned into several files capable of fitting on the media, rather than using the MS-DOS backup and restore facilities (prevents compatibility problems with different versions of MS-DOS).

Since FORTRAN, BASIC, and C programs can be written to read an ASCII file of known format, limitations to format contained in the work statement are specified by the dBASE requirement. The dBASE format is almost a de facto standard for spreadsheet and database programs. Therefore, a prime software requirement was the capability to import and export dBASE files. This requirement did not eliminate any program that was seriously considered.
DATA JUNCTION, software licensed by Tools & Technology Inc., Austin, Texas came to our attention. This software converts files from the format of all the higher sales volume database and spreadsheet software to other supported formats. The software is sufficiently well recognized that a new company will often make arrangements to be included in the list of programs supported as a means of making market penetration.

The software chosen for in-house work was askSam, a program developed by Seaside Software, Inc, now askSam Systems Inc., Perry, Florida. askSam is a free-form information manager. A few basic elements of structure can be used to create a highly structured database, or a word-wrapped, scrollable textbase. Information is broken down into files, which are broken into documents and/or records which may contain textual information and fielded data. askSam accepts assorted data types, from simple words to scientific notation, and from structured fields to unstructured text. These features were combined to produce an intelligent database with elements of artificial intelligence, AI.

B. DESCRIPTION OF askSam AS RELATED TO CONTRACT OBJECTIVES

askSam is a unique product that combines the features of a database management system and some of the features of a text editor or word processor. Unlike other database management systems, askSam handles structured as well as unstructured data. Unlike word processors, askSam handles highly structured data. askSam can be used as both a database manager and a free-form information manager. With askSam, you enter and store free-form text, then write short programs to retrieve the organized information you want. With askSam you do not have to anticipate what you need to include in your information base. The information is written in a way that makes the most sense to you, using the words you want, anywhere on the screen. With askSam, you can retrieve single characters, multiple words, or entire documents. You can do Boolean searches, arithmetic, logical, date and time comparisons. askSam includes the necessary programming features that it can be used as a complete database applications development tool.
1. Description of "METHOD" File

For some reason, now forgotten, the database file for this collection of reprints and Xerox copies was called "METHOD". Figure 1 is a reproduction of the screen that shows the record for a selected reprint. At the top of the screen are the operations which can be performed. Choosing UPDATE DOCUMENT would start the program editor word processor, to allow changes in the recorded material. Other commands permit the scanning forward or backward through the records in the file, and the selection or making of records.

Below the line is the record for a document. The search engine can be used in case-sensitive mode. Therefore, information can be coded by the use of case as well as form. The @JOURNAL statement was placed at the beginning of this record in upper case as a marker to be used when programming searches and printouts. When printing bibliographies, different forms are used for books, journals, and correspondence. If a bibliography were being printed and a search had hit on this record, then the record would be searched for @JOURNAL to determine how to format the reference. If @BOOK was found a different format would be used. The next field is No. Selecting the sequence by which references are to be filed in an open-ended file is difficult. With askSam, each reprint is filed in a separate folder and folders are numbered in consecutive order. As the typist processes a reprint, it is put into the next file folder. Before computerization of this collection of material, some manual sorting had been conducted. To maintain this information for individuals familiar with the collection of reprints, each of the parts of the collection was assigned a number using the first digit of the four-digit number.

The AU field is for the author names. The search routine does not require this field identification, but the field identifier can be used as any other combination of letters. The writing of programs for printouts is simplified using field identifications. The fixed field formats are stored in templates. Entry of information is made faster by using a macro command to add a template to the screen so that data is always entered on the same line. TI is title. Note that the titles are typed with key words beginning with capital letters. The abstract may also contain these same words, but the words would be in lower case. Therefore, abstracts and titles can be searched separately with false drops occurring only when a word is capitalized because it
Optical fibers, analytical chemistry, and fluorescence spectroscopy have been integrated to form the new technology of remote fiber fluorimetry. Among the many potential applications of this technology is the measurement of volatile organochlorides in ground water and in the vadose zone. The key to this application was the development of a fiber optic chemical sensor (FOCS) with sub-ppm sensitivity for, at least, chloroform and trichloroethylene (TCE). We present here the concept and instrumentation of remote fiber fluorimetry, the design and laboratory evaluation of an organochloride FOCS, and preliminary field results of the application of the FOCS to contaminated well water.
is the first word in a sentence in the abstract. JN[ represents journal. By consistently entering a journal in the same format, a search can be made for all articles in the database appearing in a selected journal. A search could also be made for all publications in a given year by a selected author. VO[, IS[, and PG[ are for volume, issue, and pages. The AIS entry in the IS[ field is a code that this information was missing at the time this entry was made. As we refined the database, a search for these codes was used to make a list to be taken to the library.

KEY[ is for key words. These were entered in upper case. A list of key words is shown as Table 1. This particular list of keywords represents the Principal Investigator's, PI's, initial interests at the time the entries were assigned. The keywords are entered in upper case to allow searches by keywords. Since each record can be edited as desired, new key words can be added as information is obtained to indicate that a new keyword is desirable. The Principal Investigator uses key words to allow retrieval of groups of documents. For an example, a key word is added so that all references used in a paper or report can be retrieved. Since the keywords are in upper case, it is possible to search for a word and select that it should occur in the title, the abstract, or as a keyword. The switch on the search can also be set to ignore case doing the search and report any occurrence of the word as all caps, caps and lower case, or lower case. ABS[ contains the abstract. Although this feature is extremely useful it does not appear in the project database. This type field, variable length, is not easily adaptable to dBASE format. Distributing abstracts may also violate copyrights of some journals. This feature was extremely useful and time-saving as we searched the database for the selection of theory applicable to this research project and as we planned the experiments for validation of the theory.

2. Early Observations

As the papers were sorted and notations made for the word processors, some observations were obvious. An example would be Figure 2.

This illustration, or an adaptation, occurs in many publications. Although it gives a conceptual idea of the equipment used, details of the actual equipment were not given. The Principal Investigator saw a model on a visit to LLNL and made some notes, but these notes were of little use when we started our work on validation of theory.
### TABLE 1. KEYWORDS USED IN "METHOD" DATABASE
(COUNT OF REFERENCES SHOWN IN PARENTHESES)

<table>
<thead>
<tr>
<th>1000 SOFTWARE ALGORITHMS (201)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. PLS (12)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2000 SPECTROSCOPIC PROCEDURES (185)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ABSORBANCE (14)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3000 LUMINESCENCE (138)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. FLUORESCENCE (73)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4000 WAVEGUIDE PROBES (11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ATR (16)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>5000 ANALYTIC CHARACTERISTICS (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. AROMATICS (1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>6000 COMPONENTS (151)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. GENERAL (119)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>7000 MICROSENSORS (12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ELECTRONICS (1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>8000 OTDR (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. STANDARD (1)</td>
</tr>
</tbody>
</table>
Dr. Hirschfeld was a prolific publisher; a list that was compiled shortly after his death showed over 700 publications with approximately 50 publication related to FOCS. There are few refereed publications in the FOCS group. Also there is a very high ratio of patent applications compared to the other areas of Dr. Hirschfeld's research interests. Early patents were assigned to LLNL. Latter patents were assigned almost randomly: one was assigned to Mr. Myron Block, his former employer at Block Engineering, one with Dr. David Honig and Dr. Hiefje to Indiana University Foundation, and one to the University of Washington, Center for Process Analytical Chemistry. Dr. Hirschfeld was a respected scientist. He gave exciting and optimistic talks describing the future of FOCS. As an investigator in the field it became imperative to attend symposia arranged for by FACSS, PITTCOM, SPIE and ACS to learn of the advances in the state-of-the-art. An experimenter talking with other attendees was aware that there was extensive activity.

Most frustrating to the objectives of this project is to attend meetings and to meet with old acquaintances and to hear that they are involved in patent infringement lawsuits which are preventing the introduction of products on the market. On the other hand, industries which have in-house staffs that can develop equipment and who do not plan to market instrument systems are using photonic sensors with favorable results to solve problems and increase profits.
C. THE COUNCIL FOR INFRARED SPECTROSCOPY DATABASE

The Council For Near Infrared Spectroscopy maintains a database available at $700 or at a discount price to members. This group has used PC-File software, Buttonware, Inc. shareware. Current purchasers of this database receive a licensed copy of PC-FILE 5.0. The database is distributed in four parts:

1. 1905 - 87 (1499 hits)
2. 1987 - 88 (558 hits)
3. 1988 - 89 (314 hits)
4. 1989 - 90 (Search in progress)

This database grew from the searches made by Professor W. Fred McClure, North Carolina State University, Raleigh, North Carolina. Professor McClure's primary interest was agricultural products. His technical interest was the use of Fourier Transform. For most of his work, he applied chemometric procedures to the interferograms as obtained rather than the transform.

Professor McClure was active in the formation of the Council of Near Infrared Spectroscopists. Recently this group became more closely affiliated with the International Committee on NIRS. In addition to the database, the group sponsors both national and international meetings as well as short courses and symposia. It also participates in the publication of books.

The database has always used Buttonware software. PC-FILE started as shareware. PC-FILE 5.0 is a respected product. The files are compatible with dBASE. Dr. Arendale purchased the first 1400 references from Professor McClure. After the database was adopted as a CNIRS project, several companies made donations to the cost of the searches. Key words have been added and several individuals have supported Dr. McClure.

CNIRS is associated with the Society of American Spectroscopists, SAS. SAS includes many associated groups. The ASTM Subcommittee E-13.09 on Fiber Optics in Molecular Spectroscopy meets each year at FACSS and Pittcon.

Newcomers to the field of fiber optic chemical sensors should consider participation with CNIRS.
SECTION III
THEORY

Qualitative ideas related to the development of satisfactory FOCS and photonic sensors were developed as the documents were coded and collected into the Database. The second task was to select applicable theory as related to the publications, related information, and experience. A review of optics literature and procedures was first. The second subject was spectroscopic instrumentation. The third area was related to methods for handling weak signals and the problems related to signal/noise ratio.

A. REVIEW OF APPLICABLE OPTICS THEORY

Arendale and Jeffreys (1) at the University of Alabama in Huntsville Research Institute in 1967 conducted an experimental study related to reflected energy from laser illuminated targets under U.S. Army Grant DA-ARO-D-31-124-12761. The University of Alabama in Huntsville was one of the first institutions to become active in the study of remote spectroscopy and spectroradiometry.

Measurement of the characteristics of scattered radiation can provide significant information about a surface.

1. Reflection of Radiation From a Nonabsorbing Surface

The first consideration in the study of reflected energy from a particular surface must be an evaluation of the general reflection characteristics. Most texts on illumination engineering recognize two extremes of reflected energy, specular represented by (A) and Labertian represented by (B) in Figure 3. If a surface is polished (microscopically smooth) it reflects; that is, the angle between the reflected ray and the normal to the surface will equal the angle between the incident ray and the normal. A perfectly reflecting surface, will reflect all of the energy with the same angular dispersion as the incident beam. If a material has a rough surface or is composed of minute crystals or pigmented particles, the reflection is diffuse. Individual rays obey the laws of specular reflection; but, since the surface is rough or the particles may be in different planes or different orientations, the light is reflected in all possible
A Labertian surface is defined as a surface where the intensity of reflected energy is independent of the angle of observation. Lambert's Law (based on many observations and not theory) can be stated:

\[ I_r = I_o \cos \theta \cos \psi \]
where $I_0$ is the intensity of the radiation at normal incidence, $\theta$ is the angle of incidence, and $\psi$ is the angle of observation. Many combinations of specular and diffuse radiation are observed from real surfaces. Four frequently observed patterns are shown in Figure 3 as C, D, E, and F.

Much work has been done, particularly by illumination engineers to describe the intensity of radiation from a surface under various lighting conditions. Also, many references can be found to studies of polarization upon specular reflection. Fresnel's formulas for the reflection of polarized radiation can be found in most textbooks on optics. Although these theories are applicable to reflection spectroscopy and spectroradiometry, applications to sensors related to aquifers is limited. Therefore, further review is not included in this report.

2. Effect of an Absorbing Film on a Reflecting Surface

When the reflecting surface absorbs radiation at a given frequency, or if an absorbing thin film covers the surface, the chemical composition can often be identified. The use of polarized monochromatic radiation (obtained from monochromators) to measure the index of refraction and the absorption coefficient of thin films is an important scientific tool. Chemical analyses by spectroradiometry and reflection spectrophotometry have become important tools available to the material scientist.

3. Absorption by Transparent Substances

When monochromatic light is passed through an absorbing medium with the incident collimated beam normal to the surface, the intensity of the ray decreases exponentially. This phenomena frequently follows the Beer - Lambert Law:

$$A = \log \frac{I}{I_0} = ECL$$

where $A$ is the absorptivity, $I$ is the intensity of light passing through the sample, $I_0$ is the original intensity, $E$ is the absorptivity coefficient, $C$ is the concentration expressed in moles/liter, and $L$ is the path length. Spectrophotometry is a well-developed science. Instrument manufacturers compete to incorporate advancing technologies.
4. **Reflection and Refraction of a Beam**

When a ray traveling in a low index of refraction medium strikes a non opaque surface of higher index of refraction, some of the light is reflected and some of the light is refracted. This condition is represented in Figure 4.

[Diagram of reflection and refraction at air-water interface]

Figure 4. Reflection and Refraction at Air - Water Interface

\[ n_{\text{air}} < n_{\text{water}} \]

\( \theta_i \) and \( \theta_r \) represent the angle of incidence and the angle of reflection. \( \theta_i \) is the angle of refraction. All angles are measured from the normal to the surface. The laws governing reflection and refraction can easily be found from experimentation.

1. The reflected and refracted rays lie in the plane formed by the incident ray and the normal to the surface at the point of incidence.

2. For reflection: \( \theta_r = \theta_i \)

3. For refraction, \( \sin \theta_i / \sin \theta_r = n_{21} \) where \( n_{21} \) is a constant called the index of refraction. The index of refraction of one medium with respect to another varies with wavelength. Because of this fact, refraction, unlike reflection, can be used to analyze a beam of light into its component wavelengths. The Laws of Reflection and Refraction can be derived from Maxwell's equations. These laws should hold for all regions of the electromagnetic spectrum.
The path of a beam traveling in a higher index of refraction medium passing to a medium of lower index of refraction is shown in Figure 5.

Figure 5. Total Internal Reflection

As the angle of incidence, θ, is increased, a situation is reached (see ray e) at which the refracted ray points along the surface, the angle of refraction being 90°. For angles of incidence larger than this "critical angle", no refracted ray exists, giving rise to a phenomenon called total internal reflection. The critical angle is found by putting $\theta_2 = 90^\circ$ in the law of refraction.

$$n_1 \sin \theta_1 = n_2 \sin 90^\circ$$

$$\sin \theta_1 = \frac{n_2}{n_1}$$

Total internal reflection does not occur when the ray originates in the medium of lower index of refraction.

5. Multiple Total Internal Reflections

If a ray enters a nonabsorbing rod at an angle greater than the critical angle then the ray can pass through the rod without attenuation. This condition is represented in Figure 6.
The acceptance angle is defined by the critical angle. The numerical aperture, NA, is calculated by the following formula

$$NA = \sin \theta = \sqrt{\frac{n_1^2 - n_2^2}{n_1}}$$

The cone of light exiting the other end of the rod will be defined by a similar cone. If the entrance cone is smaller than the acceptance cone, the exit cone will usually fill the full cone. If there are bends in the fiber there will be energy losses to the cladding as shown in Figure 7.

The losses to the cladding represent loss of signal and the cladding modes also perturb the signal. If the cladding modes carry a high percentage of the energy, the exit cone can appear as a doughnut. Frequently the cladding is removed for a short distance before the detector so that only core radiation reaches the detector.
6. Conclusion

Fiber acceptable for remote spectroscopy must be carefully selected. Some flaws that are undesirable are shown in Figure 8.

![Figure 8. Losses in a Fiber](image)

These flaws must be eliminated from fiber used for photonic sensors and from transmission lines to or from a sensor. Absorbing impurities reduce the length of fiber that can be used. Small particles in a fiber cause scattering. Fiber manufacturing has improved so that quartz fibers are available from many manufacturers. There is not a single quartz fiber that can transmit in the complete range of interest to spectroscopists. A fiber containing residual hydroxyl, OH, groups is required if the region in the ultraviolet from 190 to 250 nanometers is important. For spectroscopy in the near infrared region, NIR, all hydroxyl groups must be removed from the silica. There is a hydroxyl absorption band in the second overtone region at approximately 1450 nanometers that is extremely difficult to eliminate.

Probably the single most important parameter related to the performance of optical fibers is the surface between the core and the cladding. If the silica fiber comes in contact with moisture in the air as it leaves the drawing furnace, small cracks form. These cracks reduce tensile strength and decrease signal strength. Fiber is drawn in a moisture free inert atmosphere. The lower index of refraction required for the cladding is often obtained by drawing the fiber into a fluorine atmosphere. This not only removes the OH groups by reaction, but the fluorine diffuses into the quartz providing the desired lower index of refraction coating.
that serves as the defining cladding. To prevent the penetration of moisture that would cause microcracks which would result in attenuation of signal and low tensile strength in the fiber a buffer is usually added. Polymer coatings, usually proprietary to each manufacturer, are added.

Microbends divert signal energy into cladding modes. Many excellent sensors for measuring microstrain have used this feature. A simple strain sensor is shown in Figure 9.

![Figure 9. Microstrain Sensor](image)

The attenuation of signal due to microbends represents an almost uncontrollable loss of signal in optical fibers used to connect sensors to the light source and detector. Better precision is obtained when the fiber is supported by cabling. One cable is shown in Figure 10.

![Figure 10. A Complete Cable](image)

The use of uncabled fiber for experiments reported in the literature was judged to be a major factor that prevents reproducibility by other laboratories. When uncabled fiber is
used, the fiber should be supported in a fixed position and the sample carried to the fiber. The un-cabled fiber should not be moved from sample to sample.

Guided Wave, Inc. manufactures fiber, cables, and has been vested in successful applications of the spectrophotometers that they manufacture. The Laboratory for Inline Process Analyses was one of the initial customers to use the Guided Wave, Inc. spectrophotometers for chemical analyses. The Laboratory instrument and cables have been updated frequently as improvements were made. Since fiber and cables, possibly the best obtainable, were available for this experimental program, fibers from other manufacturers were not tested except as sensors. The resources from this contract were used to evaluate other components of the desired system. Procedures recommended by Guided Wave, Inc. representatives were used.

B. REVIEW OF SPECTROSCOPIC TECHNIQUES

Telecommunication networks use lasers at a single frequency for each channel of information. Many frequencies can be passed over a single fiber optic cable at the same time without interference. Although lasers have been developed for many frequencies, the number is small compared to the absorption features for molecules. To use these lasers as energy sources, the spectroscopist would be limited in the number of molecules that could be observed. The spectroscopist prefers to use white light, which contains all frequencies, since each molecule has a distinctive absorption pattern that is as singular to the molecule as fingerprints are to humans. In theory, a spectroscopist could identify as many different chemical species as the number of wavelengths that are recorded. This is one reason that spectroscopy is so powerful as an analytical tool. Figure 11 shows the type of information that can be obtained by spectroscopists in several regions of the electromagnetic spectrum.
Figure 11. Interaction of Molecules With Electromagnetic Energy

1. Absorption Spectroscopy

Absorption spectrophotometry is the measurement of the attenuation of a beam of light as it passes through an absorbing medium. Spectroscopy is usually characterized by the wavelength of the illuminating electromagnetic energy. One division is ultraviolet, UV, spectroscopy covers the region from 190 to 400 nanometers, visible, VIS, 400 to 900 nanometers, the near infrared, NIR, 900 to 1600 nanometers, the infrared from 1600 to 2500 nanometers, and the far infrared the region to 40 microns. With new types of sources and detectors being announced almost daily, there is vigorous competition between spectrophotometer manufacturers. Research has passed from the design of stronger sources to the design of attenuators to protect some of the newer more sensitive detectors from saturation. These developments are causing major redirection in research efforts. The availability of stronger signals and more sensitive detectors has decreased the observation times from hours to milliseconds. It would be impossible to take advantage of these technological improvements if there were not parallel developments in computer technology.
The advancement in performance of sources and detectors, has made possible a decrease in instrument size. As recently as 5 years ago a spectrophotometer occupied its own air-conditioned room. The base was isolated from room vibrations. Today spectrophotometers are being packaged in units that can be carried by one person. The instruments are being placed in stressed cases and the manufacturers claim they can be dropped from reasonable heights without damage. These instruments can be carried into the field under harsh environments.

2. Scattering of Radiation

Many types of scattered radiation can be used for the quantitization of analytes. Luminescence spectrophotometry includes the phenomena of fluorescence and phosphorescence. The earliest investigations were limited to ultraviolet excitation. The higher energy photons obtained from hydrogen lamps and arc sources were required for the quantum excitation of electrons. The observations were usually limited to aromatic molecules or molecules with conjugated unsaturation. The stronger sources and more sensitive detectors available today have increased the working range and the number of molecules that can be observed. Since this is a scattering phenomenon the signal is usually obtained at right angles to the exciting beam. When a molecule absorbs the energy of the exciting radiation, it passes into an excited state. Each excited state has a characteristic stability. From some molecules, the photon is released immediately; for others the emission is delayed. Measuring the decay time is the basis for time resolved fluorescence or phosphorescence. These measurements depend on pulsed radiation and measuring decay times.

An important spectroscopy related to scattered radiation is Raman spectroscopy. When a molecule is irradiated, it enters a virtual excited state. Energy can be absorbed by many energy levels and released at different wavelengths as the molecule drops to other energy levels. The energy of the virtual state is sufficient that vibrational energy levels are involved. Raman spectroscopy is synergistic with mid-IR spectroscopy. Raman spectroscopy can take advantage of sources and detectors in the near UV, visible, and NIR. The Raman signal is the weakest of the scattered signals described for a given number of molecules. Raman spectroscopy has probably benefited more than any spectroscopy from the availability of the newer high-energy lasers that furnish the monochromatic energy required. Raman spectroscopy also can take
advantage of the new, very sensitive detectors in the 700 nanometer range. The largest improvement in Raman instrumentation design is the availability of holographic edge filters that eliminate the need for long path length and double monochromators to filter out the exciting radiation that scatters and masks the Raman signal. Over the past 10 years, observation times for Raman spectroscopy have dropped from hours (sometimes 24 hours) to milliseconds. A resurgence of interest in Raman spectroscopy occurred when the first lasers became available to replace the arc lamp. Until recently, however, the instruments were still very large and cooling water was required. One investigator, Dr. Mike Carrabba, EIC, Inc. is predicting that he will have a Raman spectrometer that can be carried as a backpack into the field within the next 2 or 3 years.

3. Conclusions

The Guided Wave, Inc. Spectrophotometer available in the laboratory was considered adequate to support the research effort related to sensors and using single optical fibers. Resources provided by this contract were not used to evaluate alternate design of spectrophotometers as the literature review did not provide descriptions of superior performance.

C. REVIEW OF CHEMOMETRIC TECHNIQUES

Most instruments today use a computer to supervise routine operations that previously required the presence of a technician. Today a laboratory microcomputer can accomplish tasks that once required a mainframe computer. When the decision is made to use a computer for routine operations and a computer is dedicated to an instrument there are significant blocks of time when the computer is waiting for the timer to indicate that the next operation is to be performed. This time can be used for calculations. These considerations have led to the development of real-time instrumentation. The measurements no longer require an attendant, and the answer for the quantitization of an analytes are immediately available. This information can be used to control an industrial process or to sound an alarm that a chemical is leaking into the environment.
1. Removing Noise From Low Signal/Noise Spectra

A major problem with photonic sensors is the low signal/noise recordings that are obtained. When analog signals are recorded, the mass of the recorder pens or the gauge smooths the signal. Resistance-capacitance filters can also be used. When computers are used, discrete values are recorded. Data are available only for the time periods when the analog to digital conversions are made. As contrasted to analog recordings, no information is available concerning what has happened in the time period between the points. The human eye and mind can recognize patterns. When the computer makes the conversion at a specified time, this may also be a time at which a noise transient occurs. Two decisions are required: (1) How close together will the points be and (2) how many replications of the conversion will be made so that an average may better represent the instantaneous value without the associated noise. If the noise is Gaussian and enough measurements are taken, the noise will approach zero. When recording spectra, the spectroscopist must choose between slow scans averaging many values as the recording is made and taking points rapidly and adding several scans. The advantages of each method will be described with the experimental data in the next section. The data must always be smoothed. Again there are many different algorithms. Choice of the method for recovery of true data from the noise may be the most important criteria when evaluating instrumental methods. Two of the most widely used methods are Savitsky-Golay smoothing and Fourier smoothing. There is no correct answer. Each data set must be evaluated on its merits.

2. Removal of Outliers and Interferents

When working with samples of unknown origin, substances not included in the calibration or training set may be present as interferents. The developer of the method tries to make the calibration as robust as possible. When working with whole spectra methods, the nonfitting spectra are usually referred to as outliers. There are no absolute measurements. Therefore, statistical methods are used to evaluate the uncertainty of the method. Descriptive statistics methods are usually used for this purpose. The uncertainty is expressed as a function of the distribution of the values of the measurement. The uncertainty of the measurement is usually expressed as the standard deviation. A range of plus or minus two standard deviation includes 95 percent of the observations. When greater assurance is required, additional determinations
are made and the values added. Developments in statistical evaluation have led to algorithms where measurements are made at a number of points on either side of the desired measurement and a trend analysis is performed. This is particularly valuable where peak heights are measured. A small instrumental error treated as the abscissa can cause a large error in the evaluation of an analyte. This has led to a group of methods referred to as whole spectrum procedures. Instead of using only a few points in a spectrum, the entire spectrum is used.

3. Multivariate Statistics

One of the biggest advances in statistical methods has been the development of multivariate statistics. The literature is full of references to such algorithms as PLS, partial least squares. An incomplete enumeration of some of these methods is shown as Figure 12.

<table>
<thead>
<tr>
<th>LEAST SQUARES</th>
<th>FACTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>K MATRIX</td>
<td>SIMCA</td>
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<tr>
<td>REVERSE MATRIX</td>
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<td>PCA</td>
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<tr>
<td>PLS - 1</td>
<td>PLS-2</td>
</tr>
<tr>
<td>PCR</td>
<td></td>
</tr>
</tbody>
</table>

Figure 12. Listing of Multivariate Methods Available

These algorithms evaluate the variance-covariance matrix. A group of samples, is evaluated for the largest source of variance. This variance is removed and then the next largest source of variance is determined. These vectors are usually referred to as factors. These are mathematical processes and often it is difficult to associate the abstract factors obtained from variance measurements with causality. Malonowski (2) has described a method called target factor analysis where the abstract vectors can be assigned with higher certainty. Powerful methods for the detection of analytes are possible without rotation and/or translation of the abstract vectors into recognizable real-world vectors.
4. Models

Reproduced as Appendix B is a discussion of the different types of models that have been considered for this research effort. As will be described in the next section, we depend heavily on statistical or empirical models. A statistical model can always be found that fits a data set. The successful use of these models depends on the choice of the training or calibration set. Any variable that may be found in real samples must vary in the training set. It is not necessary to know the exact values. The major effort is placed on quantitization of the analytes of interest. The calibration accuracy is reproduced in the unknown set.

5. Conclusions

Chemometrics is an interdisciplinary effort that combines statistics, computer science, and chemistry. Academic administration often dictates that chemometrician are located with the analytical chemists. The Principal Investigator, a spectroscopist by training, taught the graduate analytical chemistry course in chemometrics at The University of Alabama in Huntsville.

The conclusion reached by the Principal Investigator was that the available spectrophotometers and fiber optic cables were adequate and represented the state of the art. The major portion of the experimental effort should be concentrated on sensor designs. The evaluation of the data would include as many of the available chemometrics computer algorithms as resources permitted.
SECTION IV
EXPERIMENTAL WORK TO VALIDATE THEORY

In SECTION III, THEORY, three areas of technology were evaluated as possible sources of the delays that have been experienced in the maturation of FOCS technology. These areas were optics, spectroscopy, and failure to incorporate advances in computer technology and new software algorithms. The optical fibers and spectrophotometers available in the Laboratory for Inline Process Analyses were judged adequate for the experimental evaluations related to photonic sensors. The study of the literature did not indicate that chemometric techniques had been used for data reduction. Experiments were conducted using selected photonic sensors described in the database and multivariate analyses procedures were used during data reduction.

A. USE OF MULTIVARIATE ANALYSES

Multivariate analyses and/or analyses of variance methods have been recognized and used for many years. The popular software product SPSS (Statistical Programs for the Social Sciences) is now in the eleventh version. Nearly all of the algorithms used in the applications software available for multivariate statistical evaluation of data, directly or indirectly, use the variance-covariance matrix. Therefore, the programs are searching for variance. The search techniques are supported by statistical theory. The techniques isolate abstract factors. The identification of the meaning of these abstract factors in the real world is the responsibility of the user. Methods have been described for rotating the orthogonal axes so that the investigator may have a better chance of recognizing the sources of variance. This remains a difficult problem in the social sciences. First, the person being observed is often affected by the presence of the observer. Second, the number of samples in the population is small. When these procedures are used to discover sources of variation in the physical sciences, neither of these problems exists. The experimenter can change the experimental conditions, but the presence of the experimenter is not believed to change the response of the molecules. The predominant theory in the physical sciences, related to physical change, is the Kinetic Molecular Theory. A hypothesis of this theory is that molecules can be described as statistical populations. Also, a mole of molecules contains $10^{23}$ molecules. Chemical systems should meet the assumptions of the statistical procedures.
1. Advances in Analytical Chemistry

Analytical chemists, who have available to them the most advanced instrumentation can provide analyses for smaller samples and more dilute solutions than their predecessors. Implementation of computer programs based on multivariate statistical algorithms makes it possible to obtain reliable information from long data vectors that contain large amounts of extraneous information, for example, noise and/or analytes for which there is no requirement for control.

Today, data are obtained as the records of human observations and the digitized output of many sensors. This raw data becomes useful information when it relates to the system under observation. A highly useful technique is to relate the data to a MODEL. Several types of models are described in APPENDIX B. For many individuals, a model that simulates the process being monitored is the most useful. The minimum requirement for the model that we seek is that it integrate the database of past experiences with the system and the data currently being gathered and then to determine if the process is in the control region where observed variations are normally distributed. The model should also predict the near future condition of the system, and most important, for manufacturing plants, the product should satisfy the intended use.

Knowledge comes from confirmation of mental models that describe the past and/or predict the future. This statement is the heart of the Total Quality Management, TQM, movement in the Department of Defense and the Deming Method for quality. Dr. W. Edwards Deming (3) recently defined knowledge:

A statement conveys knowledge if it helps us to predict or to explain what has happened in the past. Nor there is knowledge in that statement. There are facts, of course. The dictionary is full of information. The number of prime numbers less than 100 is a number. You can put them down and count them. This is dictionary knowledge. It doesn't predict anything. Knowledge means prediction or explanation of past events. Physics is
knowledge. Chemistry (is knowledge). Science is knowledge because it explains and predicts what will happen in the future under certain conditions or explains what has happened in the past. I predict if I drop this pen it will fall to the table. A prediction, it conveys knowledge.

Sometimes prediction carries with it a high degree of belief. Sometimes extremely high as the statement about gravity that I just made. Associated with any prediction is degree of belief. How strong do we believe it. We plan, make plans for today for tomorrow. We are predicting today. We will find out later how good our prediction was.

......There is no such thing as an absolute measurement.

Science advances with the ability to measure. A significant portion of engineering activity is related to measurement. The human desire to see further and further and to see smaller and smaller objects drives advanced technology. Advances in technology have resulted in many new types of instruments for use by the analytical chemist. The microscope when combined with the FT-IR spectrophotometer or a Raman spectrophotometer allows identification of particles as small as $10^{-12}$ grams of a pure material embedded in the surface of a different host. Using the hyphenated techniques such as GC-MS, LC-MS, GC-MS-MS, GC-UV, and many others, concentrations of parts per trillion or less of analyte can be quantitated in samples of microliters. Do these advances represent blessings or curses? At times those individuals who are responsible for protocols with respect to litigable procedures and standards may consider these advances as curses. Particularly, if the new measurements create new paradigms.

When working with small quantities and concentrations that push the limits of detection, the information is embedded in signals characterized by low signal-to-noise ratio. This can lead to lack of understanding and difficulties in communicating with individuals who hold to the tradition that a measurement can be made to an absolute standard. Many have not
been introduced to the techniques of multivariate statistical analyses as provided to the analytical chemist by Wold, Kawolski, Malinolski, Massart, Martens, and their many associates (4).

One example of a problem where statistics plays an important role is the quantitization of an analyte at low concentrations where the signal is obtained at poor signal/noise ratio. Shown on Figure 13 are some of the required decisions.

![Figure 13. Statistics of the Blank vs the Statistics of the Analyte](image)

For this example we show measurements on the blank containing no analyte and measurements on the sample as being normally distributed. Plus or minus three standard deviations about the means includes 99.9 percent of the measurements. For an enforceable litigable procedure, it is necessary to set some minimum level of detection. If we are concerned about an environmental pollutant, it is desirable to set the lowest possible limit for quantitization consistent with known hazards. For such purposes, the limits of detection may be set at ten standard deviations for the blank. Although this may be the best compromise for the litigable limit, it is of little use to the plant technician who must prevent an analyte being added to a river or an aquifer.

2. Quantitization of Multiple Analytes

The Beer-Lambert relationship

\[ A = \log \frac{I_a}{I} = E \times c \times L \]
where \( A \) is the absorptivity, \( I \) is the measured power after a collimated beam of light has passed through an absorbing medium, \( I_o \) is the power before any light has been absorbed or scattered, \( E_a \) is the molar absorptivity coefficient, \( C \) is the concentration of the analyte in moles/liter, and \( L \) is the path length is the basis for calibration of single analytes. A simplified absorption spectra of three analytes is shown in Figure 14.

![Figure 14. Spectra of Three Analytes](image)

Spectra for several mixtures of the three analytes are shown in Figure 15.

![Figure 15. Spectra for Mixtures of Three Analytes](image)

Since the absorption peaks in the three analytes do not overlap, the spectrum of the mixture can be analyzed for each component. The matrix equation for the absorptions is shown in Figure 16.
Beer's Law \[ A_i = \sum_{j=1}^{k} k_{ij}c_j + e_i \]

K-Matrix \[ A = KC \]

\[
\begin{bmatrix}
A_1 \\
A_2 \\
A_3 \\
A_4 \\
A_5 \\
A_6
\end{bmatrix} = \begin{bmatrix}
k_{11} & k_{12} & \ldots & k_{1n} \\
k_{21} & k_{22} & \ldots & k_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
k_{m1} & k_{m2} & \ldots & k_{mn}
\end{bmatrix}
\begin{bmatrix}
c_1 \\
c_2 \\
c_3 \\
c_4 \\
c_5 \\
c_6
\end{bmatrix}
\]

Figure 16. K Matrix for Beer's Law

Compared to the Beer-Lambert Law equation given above, the matrix equation has been simplified by assuming a constant path length or a path length of 1 centimeter, and combining \( E \times L \) into the constant \( K \). The experimental problems relate to being sure the spectrophotometer is setting at the correct wave length for the highest point on the absorption peak and that there is no effect from noise. If the noise is Gaussian, with an equal number of positive and negative noise signals being added to the desired signal, the effect of noise can be minimized by averaging several measurements. The reproducibility of the spectrophotometer wave length setting is usually a function of design and the operator has minimal control. The spectrum obtained by smoothing a spectrum using a 7-point Savitsky-Golay routine and subtracting the smoothed spectrum from the original spectrum is shown on Figure 17.

Figure 17. Noise as Found Using 7-Point Savitsky-Golay Smooth
Note that there is severe random noise at both ends of the spectrum where the signal-to-noise ratio was the poorest. However, the noise appears random and therefore meets the definition of Gaussian distribution. When a single peak is used, we use the combined signal-plus-noise observation that may be correct, high, or low. We accept the value and plot statistical control charts for the observations. If this is the measurement for a process control variable, we cannot take corrective action based on this measurement. The UCL, upper control limit, and the LCL, the lower control limit, control our actions. If the value is between the UCL and the LCL, we do not tamper with the system as the measurements are following a normal statistical distribution. Can we improve the observation by correcting for noise? Sure. Take data at several frequencies on each side of the observation point and make a statistical fit for the shape of the peak. It is the practice in this laboratory to take data at as many frequencies as the computer storage register will allow and make a statistical fit to the spectrum. This is frequently done by applying principal component analysis. The concept of principal component analyses is shown in Figure 18.

Figure 18. Representation of Principal Component Analyses

If three samples were being considered, the absorption values could be plotted on the $\lambda_1$ axis. The absorptivities for the same three samples measured at a second wavelength could be plotted on
the $\lambda_2$ axis. Unless there is an interaction between the components in the three samples then the ratio for the measured values would be the ratio of the absorptivities of the pure samples at these $\lambda_2$ wavelengths. Therefore, by vector addition, the three samples could be represented by three points on the $\lambda_1 \lambda_2$ axis. This principle can be extended to three wavelengths. The human mind can recognize a pattern in three dimensions. A computer can calculate the points to represent spectrum in many dimensions. As stated above, we often use as many points as the buffer in the computer will accommodate. The principal component axis that the computer calculates is the axis of best fit for all of the frequencies used. If the measurement at a given frequency includes noise in addition to the signal for that frequency, it would represent a variance from the best-fit line. Therefore, by use of the whole spectrum, we find the best representation for the spectrum using all observed spectral points. The first principal component may be subtracted from the variance - covariance matrix and the process repeated. We then find the second component. This is an abstract mathematical computation. The removal of principal components can be continued until we have a component or components for the noise. These are of little interest. Two questions must be answered. How many of the components are real components and what is the spectra of the real components? Many procedures have been proposed to answer the first question. The Screen plot is frequently used. Each component represents less and less of the variance. When the sum of the variance becomes large and little improvement is gained by adding another component, then a good compromise is reached.

The question of what the principal components represent is more difficult. Target factor analysis represents one method (2). If the analyst expects that a component is present and has the spectrum of that component, this spectrum can be multiplied into the variance - covariance matrix to find the rotation required to yield this spectrum. It is possible to use this method to construct a rotation matrix and identify the concentration of each component. This procedure requires the $K$ Matrix, the extinction coefficient spectrum for each component in the mixture. Frequently the spectrum of some of the components in a mixture are not available and other methods must be used.

Unless the analyst wishes to establish a relationship with an interpretation based on causality, it is not necessary to identify the components or factors to perform quantitative
analyses for known components. To use this method a calibration set is required that meets the following conditions:

1. Typical samples are available for the training set.

2. The samples span each of the individual phenomena that can be controlled.

3. The samples are randomly selected to insure a chance of spanning the noncontrollable phenomena.

3. Application to Interferents

The application of multivariant analysis to the problem of interferents can be describe using Figure 19.

![Figure 19. Spectra of Analyte and Interferent](image)

An absorption peak in the spectrum of an analyte is represented by Curve A. The spectrum of a known or unknown interferent is represented by Curve B. The typical single point measurement technique measures the absorption at the point of maximum absorptivity. The measured value of A for a sample will depend on the ratio of the amount of the uncontrolled interferent. To minimize interference the number of points to be measured can be increased. If Spectrum A was measured as several hundred points, then the principal component analysis would find the interferent to be noise unless it had an identical spectrum. These considerations form the basis for taking as many points as the computer that we are using will allow. We
recognize that this is an overkill. The alternative is to take one point and, when the procedure is shown to be unreliable, add additional points. When the two approaches are maximized, the optimized number of points should be the same for both approaches. The question is which is the cheapest and quickest method of obtaining the desired precision. Method selection depends on the problem. If an experienced analyst is working with well-defined samples, the first method can be the quickest. When working with samples and processes where there is minimum information, only the second method can be successful. Most of the high-profit-producing applications in industry have come from the latter group. This is particularly true when reactions are continuing in the container while a sample is waiting for analysis. The greatest payoff often occurs when observing industrial processes and some upset occurs. Continuous quick analyses with many possibly redundant pieces of information always are the first analyses to recognize a signature pointing to the source of the problem.

4. Selection of Training Set

When using empirical or heuristic models, the important considerations are the Calibration Objects (training set). The calibration model

\[ Y = f(X) \]

that predicts \( y \), from the \( x \)-variables is determined from the training set. The experimenter must ensure that the calibration set contain enough information to solve the selectivity problems involved. For simple problems only a few calibration objects are needed. But in general, the less the analyst knows about the objects being analyzed and the instrumentation being used, the larger the calibration set needed to ensure a reliable prediction ability. The calibration objects must be representative for the population of objects from which \( Y \) values are to be predicted later, both with regard to average quality and to variability. A significant VARIABILITY must also be included in the calibration objects. The level of EVERY major independent component or phenomenon, that may cause interference effects in future \( X \)-data, must vary in the Calibration Object set. The actual level of these objects does not have to be known.

These rules can be illustrated with data from work that the Laboratory For Inline Process Analyses has done on iodine speciation. (This work was supported by NASA Marshall
Space Flight Center under Contract NAS-36955 D.O. 52.) Iodine in aqueous solution can exist as HI, I\(_{-1}\), I\(_{2}(aq)\), I\(_{3}\), HIO, IO\(_{-1}\), HIO\(_{3}\), IO\(_{4}\), IO\(_{5}\), and/or H\(_{2}\)IO\(_{4}\). These species represent oxidation numbers for iodine of -1 to +7. These species compete with H\(_{2}\)O, dissolved O\(_{2}\) and dissolved H\(_{2}\) for electrons. Further competition for electrons occurs when organics are present. The redox sensitivity is believed to be responsible for many conflicts related to analytical procedures for determining iodine concentration. Determination of all species simultaneously and in real-time is possible, highly desirable, and most likely the only way that the species responsible for biocidal action can be controlled. The concentration of each species is immediately available and there is no opportunity for the concentration of a species to change while a sample awaits analysis. The requirements for a successfully controlled system are related to the requirements for solving simultaneous equations. A single unknown quantity can be evaluated with one equation. If required to solve for two unknowns a minimum of two independent equations is required. Solving for ten unknowns requires a minimum of ten independent equations.

In Figure 20, the spectra of KI, I\(_{2}(aq)\), and KIO\(_{3}\) are shown.

![Figure 20. Spectra of KI, I\(_{2}(aq)\), and KIO\(_{3}\).](image)

A factor analysis of this data in 1801 dimensional space should show at least five factors since we anticipate factors for HIO and I\(_{3}\) for which methods of making standard solutions are not
available. When the factors for these components are identified and rotated we will obtain the spectra of molecules unavailable on the storeroom shelf. The PLSplus, version 1, routine that is part of the SpectraCalc software collection was used for this analysis. Shown in Table 2 is the data obtained when the training set consisted of samples of I$_2$(6 levels), KI(2 levels), and KIO$_3$. The data is reasonable for the principal variable, but the values for the other species were less precise than desired. Table 3 shows the improvement when the training set contained I$_2$(6 levels), KI(5 levels), KIO$_3$(5 levels), KI$_3$(KI plus I$_2$5 levels), and six mixtures using these samples. The spectra taken at 0.2 nanometer steps between 190 nanometers and 550 nanometers. Thus the analyses are being made in 1801 dimensional space. This is a severe overkill. However, the results for all components are as expected. In this set we gave the software the iodine values in ppm. The calibration algorithm is looking for variance in the spectra (x-points) to match to the known Y values that were supplied. Note that in this data set we are analyzing for three knowns out of a possible ten species that could be in the solution. It was not necessary to know the values for the other seven as we assumed that the species were at thermodynamic equilibrium. The I$_2$(aq) samples probably contained many of the total number of species, but they were described to the software as being I$_2$(aq). Analyses for every species will require additional standard solutions and additional method for preparing and analyzing the solutions in the training set.

This example is described to illustrate the power of multivariate analyses and empirical models. The responsibility of the observer to know the data set and to have knowledge of the system is illustrated.

B. DESCRIPTION OF THE SPECTROPHOTOMETER

The Laboratory for Inline Process Analyses uses the spectrophotometers manufactured by Guided Wave, Inc. Guided Wave, Inc was founded by Mr. David LeFebre in May 1983 to manufacture research grade spectrophotometers. Mr. LeFebre's immediate past experience had been in research and manufacturing of optical fibers. Developments have concentrated on using single-strand fibers to connect the spectrophotometer to the sensor. In early spring 1984, the Principal Investigator purchased one of the first five of the Model 100 instruments manufactured. The Model 100 was the first to optimize the optical components to the
### TABLE 2. MULTIVARIATE CALIBRATION STANDARDS

$\text{I}_2(\text{aq}), \text{KI AND KIO}_3$

<table>
<thead>
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<th>Component</th>
<th>Concentration</th>
<th>Analysis of d:\sc\data\NASI1.spc</th>
<th>The calibration matrix is IODHA.cal</th>
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<td>IODINE(aq)</td>
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### TABLE 3. MULTIVARIATE CALIBRATION

**TRAINING SET MIXTURES OF I₂, KI, AND KIO₃**

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<td>IΟ₃⁻</td>
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</table>
characteristics of energy transmission over fibers. All feedback from users has been taken seriously and used in developing new models. The Model 300 double beam instrument, on the market for about one year, was an attempt to include the needs of all users. The original instrument purchased by UAH has been updated on three occasions as the Model 150, Model 200, and Model 260 were developed. A specification for the Guided Wave model 260 and Model 300 spectrophotometer is given in Appendix C.

Many spectrometer manufacturers have provided attachments to their line of spectrophotometers to allow the use of fibers. Many of the manufacturers use bundles of fiber. The spectrophotometers are multiuse instruments. Although the Principal Investigator has followed these developments through literature references, visits by representatives, and visits to trade shows, no attempt has been made to compare performance as a part of this report.

Some features of the Guided Wave instruments are described in the following sections to illustrate the requirements on an instrument which is to be used with single-strand fiber optics and to provide examples of the apparatus used to obtain the experimental data.

1. The Optical Bench

The design of classical spectrophotometers includes slits, mirrors, gratings or prisms to disperse the radiation, and a detector. There is a loss of energy at the surface of each component. Since the energy carried by a fiber is small, as many surfaces as possible are eliminated. The essential elements of the fiber spectrophotometer are shown in Figure 21.
Figure 21. Scanning Fiber Spectrophotometer.

The light source is a tungsten halogen bulb or a deuterium lamp. The light source is large with respect to the diameter of the fiber core. Lenses are used to focus the energy from the source onto the fiber. The entrance cone into the fiber is controlled by the numerical aperture of the fiber. The fiber transmits the energy to the sample. Shown in Figure 21 is a transmission probe where the energy from the exit cone of the fiber is focused onto a concave mirror. The mirror focuses the energy back onto a second fiber that carries the energy to the spectrophotometer. The cone of energy from the fiber falls on a holographic concave diffraction grating. Since this cone is fixed by the characteristics of the fiber, the size of the grating that can be filled with light is determined by the distance from the end of the fiber to the grating. To reduce stray light in the grating chamber, a square aperture is used so that the cone of light just fills the square grating. The longer the distance from the aperture to the grating, the larger the area of light available but the lower the intensity. The Guided Wave instruments are 0.25-meter spectrophotometers. A characteristic of holographic concave gratings is that the reflected energy can be focused to a spot for only two wavelengths. The grating in this spectrophotometer has been designed so that the distance between these spots is sufficient that two detectors can be mounted on the instrument at the same time. The software can be set to change between the two detectors at any selected wavelength. The pattern of the radiation is shown in Figure 22.
Figure 22. Radiation Pattern at the Detector Slits

This is the only point at which slits are used in this spectrophotometer.

2. Gratings and Detectors

Changing a grating or detector only takes a few minutes. Therefore, observations can be made from the ultraviolet to the near infrared with the same instrument by choice of gratings and detectors. When quartz fibers are used, the useful region is from 200 - 250 nanometers to 2.2 micrometers. Zirconium fluoride fibers are available to extend the observation region to 3.2 micrometers in the infrared. To cover the full range at high resolution photomultipliers, silicon, germanium, and lead sulfide detectors are required. To cover the entire range diffraction gratings at 1200, 800, 600, 300 lines/mm are used. A component selection guide from the Guided Wave, Inc. literature is shown as Figure 23.

3. Experimental Setup and Sample Probes

The spectrophotometer is remote from the sample as the spectrophotometer is connected to the sample by a flexible fiber optic cable and the sample is connected to the
COMPONENT SELECTION GUIDELINES

LIGHT SOURCES
- Deuterium
- Tungsten-Halogen

FIBEROPTIC CABLES
- C2(NUV-Vis)
- C3(Vis-NIR)

GRATINGS
- 1200 Lines/mm (250°)
- 800 Lines/mm
- 600 Lines/mm
- 300 Lines/mm

DETECTORS
- PMT-Solar Blind
- PMT-UV-Vis
- PMT-Extended
- Silicon
- Germanium
- Lead Sulfide

WAVELENGTH (nm)

UV  Visible  NIR

- Peak operation
- Optimum range
- Extended range, performance degrades.

Figure 23. Diffraction Gratings and Detectors
spectrophotometer by a second fiber optic cable. This provides flexibility equal to the imagination of the experimenter. Standard probes and components as shown in Figure 24 are used to gain experience with the concepts. As the real-time problem is defined specialized components are designed to interface the system with the fibers that carry the information.

4. Analyses of Benzene, Toluene, and Xylene

Classical absorption analyses for benzene, toluene and xylene were made using the described equipment and quantitated using multivariate analyses. For these analyses, a probe, Guided Wave, Inc. Part #1RP2 SO - 6, consisting of a lens that formed the cone of light coming from the fiber into a 1-centimeter collimated beam was placed on the side of a standard 5 x 1-centimeter, 1 x 1-centimeter, or millimeter x 1 centimeter quartz absorption cell. A similar probe was placed on the opposite side to pick up the collimated beam and focus the light onto the optical fiber that returned to the spectrophotometer. Spectra were taken in both the ultraviolet and the near infrared. Spectra were obtained using neat solutions, mixtures of benzene-toluene-xylene, aqueous solutions made using the mixtures, and solutions made in Jet A fuel. These spectra have been reproduced as Figures 25 through 39. Examinations of the Figures show that each component shows its characteristics spectrum as expected. The analytical results obtained using the PLSplus, version 2, in the SpectrCalc collection are shown as Tables 4 and 5.
Figure 25. Benzene (0.5 ml/liter water)
5 cm Absorption Cell UV-VIS

Figure 26. Toluene (0.5 ml/liter water)
5 cm Absorption Cell UV-VIS
Figure 27. Xylene (0.5 ml/liter water)
5 cm Absorption Cell UV-VIS

Figure 28. 1:1:1 Benzene, Toluene, Xylene
5 cm Absorption Cell UV-VIS
Figure 29. Benzene (neat)
ATR Dip Probe NIR

Figure 30. Toluene (neat)
ATR Dip Probe NIR
Figure 31. Xylene (neat)
ATR Dip Probe NIR

Figure 32. 1:1:1 Benzene, Toluene, Xylene (neat)
ATR Dip Probe NIR
Figure 33. Jet A Fuel (neat)
1mm Absorption Cell NIR

Figure 34. Benzene (neat)
1mm Absorption Cell NIR
Figure 35. Toluene (neat)
1mm Absorption Cell NIR

Figure 36. Xylene (neat)
1mm Absorption Cell NIR
Figure 37. 5:2:2:1 Jet A BTX
1mm Absorption Cell NIR

Figure 38. 5:1:1:2 Jet A BTX
1mm Absorption Cell NIR
Figure 39. 5:2:1:2 Jet A BTX
1mm Absorption Cell NIR
TABLE 4. UV ABSORBANCE (190NM - 550NM)

The calibration matrix is BTXM.cal

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<td>toluene</td>
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<td>toluene</td>
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<td>xylene</td>
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<td>Concentration</td>
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<td>xylene</td>
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<td>toluene</td>
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<tr>
<td>xylene</td>
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### TABLE 5. NIR SAPPHIRE PROBE (900NM - 2000NM)

The calibration matrix is BTXM.cal

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<td>.164532</td>
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<tr>
<td>xylene</td>
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TABLE 5. (CONCLUDED) NIR SAPPHIRE PROBE (900NM - 2000NM)

Analysis of C:\sc\data\szb10.spc
Prediction error: 9.1321
Component    Concentration
benzene      .110085
toluene      .260646
xylene       .129268

Analysis of C:\sc\data\szb11.spc
Prediction error: 2.93533
Component    Concentration
benzene      .114971
toluene      .125375
xylene       .259653
5. **Analyses of Trichloroethylene and Related Compounds**

Recently we were asked if the absorption technique could be used for trichloroethylene and related compounds. The NIR spectra are shown in Figures 40 and 41. The technique can be readily adapted to the chlorinated hydrocarbons.

C. **FIBER OPTICS AND RELATED OPTICAL PROBLEMS**

Our earliest evaluations, Appendix A, had indicated the possibility that improvements in Fiber Optic Chemical Sensors could be made through appropriate changes in the optics. The experimental work described above indicates that acceptable results can be obtained with the Guided Wave, Inc spectrophotometer and fiber cables. In this section we describe some problems and the methods by which the problems were eliminated or reduced to an acceptable magnitude.

1. **Temperature Fluctuations and Microbends**

   As described in Section II, a bend in the fiber causes some of the energy to leave the fiber core and pass into the cladding. As shown in Figure 9 this phenomena can be used to design devices that can measure microstrain. These devices can be used to measure mass when calibrated, can be placed in mechanical models to measure stress distributions, and have been made into instruments to measure acoustics. Errors can be minimized for chemical sensors by use of well-buffered cables that prevent microbends. If possible, we take the sample to the probe so that each measurement is made with the cable in a fixed position. When real-time measurements are being made, a fixed cable arrangement can be used. When movement of the cable cannot be avoided, movement of the cable is included as a variable in the calibration set. Since readings are taken at multiple wavelengths and all wavelengths are not affected proportionally by movement of the cable, the multivariate search methods allot some of the frequencies to the fiber variations while finding other more reliable frequencies to use in quantitating the analytes of interest.
Figure 40. Trichloroethylene (neat)
1mm Absorption Cell NIR

Figure 41. Trichloroethylene (neat)
Dip Probe NIR
The light beam passes down the fiber core in a number of modes. These modes depend on diameter and length of fiber. As the temperature is raised, a fiber expands in diameter and length causing a change in the magnitude of the signal which is observed. If we are dealing with low signal to noise ratio, temperature variation can be important. Changes in material properties with temperature are reversible and reproducible. When temperature changes must be included, a temperature measurement is substituted for a wavelength value. A publication described one application where a sensor was excellent for measuring temperature when strain was constant and one wavelength was used. When temperature was held constant, the sensor was excellent for measuring strain using the same wavelength. The solution was simple, use one wavelength to quantitate temperature and a second wavelength to quantitate strain. We did not encounter an example during this experimental work where temperature measurement was required. Since an excess of wavelengths over the minimum required and multivariate analyses techniques are used, the software is protecting us from this problem by assigning wavelength to temperature. As we optimize the technique and move toward a minimum number of frequencies we expect to observe the temperature effects.

A more annoying problem related to temperature has been molecular association in the dilute solutions. The wavelength maxima shift with temperature. When this problem occurs, temperature is included in the data vector.

2. Modification of Cladding

A number of sensors are described in the literature where the sensor consists of a core with a cladding with special properties. In Section III we described the energy rays as passing along the fiber if the light strikes the cladding at an angle greater than the critical angle. It has been shown that although the energy is totally reflected there is an evanescent energy wave that penetrates microinches into the cladding. Reflection is attenuated if the cladding has an absorption band at a wavelength in the illuminating radiation. Many experiments have been devised that demonstrate and use this phenomenon. Most of these designs also use the change in NA associated with the change in the ratio of refractive indices of the core and cladding. Several different arrangements are shown in Figure 42.
The sensor shown as A in Figure 42 has the buffer removed and the sample is in contact with the fiber. For this arrangement, the ATR, attenuated total reflection spectra of the sample is recorded. The sensor shown as B has a special cladding placed between the core and sample. If the sample or a component of the sample is absorbed by the cladding, the ATR spectrum is obtained as this analyte reaches the core. If the sample is soluble in the cladding the cladding will swell. If the sample has a higher index of refraction than the cladding material, then \( n_s \) may become greater than \( n_i \) and all energy may be absorbed. The sensor shown as C has the core of one fiber terminated within the sample. A second core is placed next to the fiber bringing the light into the sample region. This second fiber picks up portions of the energy. This twin core type of sensor can be used for special types of analytes. Initially, we considered some of these arrangements, but became less interested as successful analyses where obtained using classical spectrophotometric measurements. When a fiber is drawn from the furnace, an inert atmosphere is used to prevent moisture from causing microcracks and hydroxyl groups on the surface. Unless the experimenter has available a drawing furnace, it appears to be extremely difficult to obtain reproducible sensors using these approaches. Removing the manufacure's cladding and substituting another cladding has resulted in many extremely interesting research papers. When sufficient use is generated, a fiber manufacturer may be persuaded to add one of these fibers to the product line.

3. A Sensor Using a Silicone-Clad Fiber

Fiberguide Industries, Inc. manufacturers a nylon buffer, siloxane clad fiber for the telecommunication industry that we have used to fabricate a sensor. A schematic is shown in Figure 43.
The coil is wound from 3 meters of Fiberguide Industries fiber APC400N with 1.5 meters used in the sensor leaving two 1.5 meter fiber leads. This fiber is a low-hydroxy pure quartz fiber with a 400-micrometer core, 100-micrometer proprietary siloxane cladding, and a 100-micrometer nylon buffer. After the coil is wound, the nylon buffer in the coil area which is used for sensing is removed by immersing the probe in boiling propylene glycol. The fiber is threaded through small holes to give support and to prevent non reproducible microstrain. Our design is similar to the design reported by Degrandpre and Burgess (5).

Both the Guided Wave Model 200 and Model 300 spectrophotometers were used. With the Model 200 spectrophotometer a 600 l/mm grating and silicon and germanium detectors were used to record the spectrum from 800nm to 2000nm in 1nm increments. A silicon halogen lamp was used as the source of illumination. With the Model 300 a 470 l/mm grating and a proprietary detector was used to record the spectra from 800nm to 1750nm.

The sensor is connected to the spectrophotometer using the two 0.75-meter fiber-optic leads from which the nylon has not been removed. The ends of the fiber are cleaved with a sharp knife leaving a smooth optical surface perpendicular to the fiber. The fiber is mounted to the spectrophotometer port with a fiber clamp and adjusted with respect to the
spectrophotometer optics by moving in or out until the maximum signal is obtained. The leads and sensor sections are made from a continuous length of fiber. When the final sensor parameters are determined, SMA 905 connectors will be used to connect the sensor to the spectrophotometers. (The minimum order requirement for a SMA 905 for each core size prevents having all sizes available.)

The signal is recorded as a digital signal. The Model 200 is a single-beam spectrophotometer and a reference spectrum is required. The reference spectrum for gases is taken in air. The reference spectrum for aqueous solutions is water. Since the cladding is hydrophobic organophilic, the reference spectrum is the ATR (attenuated total reflection) spectrum of the siloxane cladding. Since the spectrum being obtained are ATR spectrum, total reflection does not occur at the wavelengths where the cladding has absorption bands. Therefore, less light passes to the detector. When the sensor is placed in the presence of organic liquids or vapors, the organophilic-hydrophobic cladding absorbs the organic and the cladding swells. Since there is less of the siloxane in the distance that the evanescent wave penetrates, more light remains in the fiber in the regions where the absorption were found in the reference spectrum. When the spectra are plotted as AU (absorption units) vs wavelength, regions of negative absorption appear. These bands can be used as internal standards to measure the swelling and hence the volume of the organic. When the organic material diffuses to the core, the ATR spectrum of the organic is obtained. The absorption bands can be quantitated using the methods available for quantitization of ATR spectrum.

The quantity of organic that can be absorbed will be related the solubility of the organic in the cladding material and will change with the chemical composition of the cladding. In air or in aqueous solutions the quantity will also be a function of the equilibrium constant for the distribution between the cladding and air or water. For benzene, toluene, and xylene, the solubility in the siloxane is much greater than in water or air. The sensors, therefore, are very sensitive. The cladding acts as an integrating sensor. Since the organics are easily removed with acetone, the activity of the sensor can be restored by soaking in acetone and air drying.
Some spectra for benzene, toluene, xylene, Jet A, and trichloroethylene are shown as Figures 44 through 51. A quantitization using PLS-2 is shown in Table 6.

**TABLE 6. EXPERIMENT SUMMARY FROM SOH2.RPT**  
(NEAT MIXTURES 1 MM ABSORBANCE CELL)

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69
Figure 44. Benzene (1 nm/liter water)
Coil Above Solution (30 minutes)

Figure 45. Toluene (1 ml/liter water)
Coil Above Solution (30 minutes)
Figure 46. Xylene (1mM/liter water)
Coil Above Solution (30 minutes)

Figure 47. 1:1:1 BTX (1mM/liter water)
Coil Above Solution (30 minutes)
Figure 48. Ratios of Jet A, BTX; Coiled Fiber Sensor;
(1mL/1000mL Water); above solution
Figure 49. Ratios of Jet A / BTX; Coiled Fiber Sensor; (2mL/100mL Water); Sensor immersed.
Figure 50. Trichloroethylene (neat)
Coiled Fiber Sensor NIR

Figure 51. Trichloroethylene (0.1ml/liter water)
Coiled Fiber Sensor
SECTION V

BREADBOARD DESIGNS

The contract provided for the testing of selected components in breadboard configurations. For FOCS configurations a breadboard consist of a sensing element, fiber optic connections, and a read-out device. All of the experiments reported in Section IV included a computer and spectrophotometer (the read-out devices), fiber optic cables, and a sensing device. The sensing device used commercial components. Analyses were obtained for the required analytes without the use of chemical reactions at the end of the fiber. Therefore, each experiment was a breadboard configuration where standard spectroscopic techniques were successful.

The only modifications required for laboratory or field use of the systems would be length and type of fiber or transducer design to fit specific experiments. This section describes an apparatus designed to test a sensor in an aqueous environment. All of the parameters which are required to simulate a natural environment are provided. This apparatus can be used during the qualification program for a system, and for quality assurance measurements during manufacture and delivery of a system.

A. DESCRIPTION OF TEST APPARATUS

The apparatus shown in Figure 52 is used to evaluate the minimum number of sensors required to determine that a process is operating within statistical control. A system that is operating within statistical control has a defined identity and a defined capability. It is a random process. Its behavior in the near future is statistically predictable in the absence of an unforesee action that knocks the process out of statistical control. The apparatus can also be used for experiments to identify the statistical variations as measured simultaneously by many different sensors exposed to a completely defined condition. The capability to jolt or upset the system and follow the return to a stable system is also provided. After a system has been calibrated, the apparatus can then be used to simulate full scale equipment when engineering experiments are required for design or redesign of the system. The system was fabricated from commercially available components by the UAH glassblower. The following features are provided:
3-way Stopcock

Teflon Impeller

Pump

Four 1 cm Pyrex Ports for Probe Sensors

Quartz Windows

2" Pyrex Flanged Pipe

Charging Port

Clamp

Figure 52: System Test Apparatus

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1. **Charging Port** The tube and two way stopcock at the lower left is used to fill the system. To fill the system with water that does not contain dissolved oxygen, the system is flushed with an inert gas. Nitrogen can be used if nitrogen fixation is not being investigated. Helium or argon can be used if both nitrogen and oxygen must be excluded. When the apparatus is free of active gases, the sample bottle is pressurized and the apparatus is filled with a degased solution. Both the two-way and three-way stopcocks are then closed to the atmosphere.

2. **Septum** Openings can be closed with septa as required. Samples may be taken or reagents added using a syringe and a needle placed through a septum. These ports may be used to adjust pH by adding acid or base. Carbon dioxide can be added when needed to simulate the atmospheric carbonate cycle or to adjust acidity. Oxygen can be added as required to adjust oxidation potential. The ports can be used to take samples without exposing the samples to atmospheric stimuli. The ports are used to add reagents to jolt a system and to follow the return to statistically described behavior. If temperature changes are expected, a syringe partially filled with solution is left in place at one of the ports to accommodate the differential expansion of glass and solution.

3. **Test Section** Glass tubing can be placed in either leg of the system if active devices are required for an experiment.

4. **Impeller** The solution within the system is circulated using the variable speed motor. The Teflon® coated impeller is magnetically driven.
5. **Sensor ports** Four ports are shown. These ports are used to hold sensors. Sensors currently available include pH, pI', pI2, pO2, pCO2, conductivity, and pE. Four can be used simultaneously.

6. **Spectroscopic windows** A five centimeter path length is provided for spectroscopic measurement. UV grade quartz, NIR grade quartz, and sapphire windows are used. A window at right angles to one pair of ports is used for fluorescence measurements. Absorption probes, Guided Wave, Inc. Part # 7TP 2S - 5, with 1 and 2 centimeter path lengths are placed through the sensor ports when required for an experiment.

7. **Spectrophotometer** A fiber-optic cable is used to connect the light source to a window and a second fiber cable completes the path to the spectrophotometer. Detectors include a photomultiplier, silicon, germanium, and lead sulfide. Available gratings include 1200, 600, and 300 l/mm. Combinations of these gratings and detectors makes possible the recording of high-resolution spectra from 190nm to 2200nm. Resolution in the UV region is 0.05 nanometers and 2 nanometers resolution in the lead sulfide NIR region. Specifications for the spectrophotometers are given in Appendix C.

8. **Additional detectors** A sapphire-tipped ATR probe designed for three passes of the evanescent wave, Guided Wave, Inc. Part # 1AT4 SO -6B, is available for the visible and NIR regions. Fiber ATR probes, as described in Section IV, are also used.

9. **Temperature control** The temperature is controlled by wrapping the system with tubing through which water is circulated. Experiments have been run at 40°C.
Experiments are designed so that at least two sensors should respond to a given chemical species. If an acid is generated, the event should be recorded at least as a change in level of pH and conductivity sensors. In addition, organic acids often show changes in the UV or NIR region of the spectrum. Should biomass form within the system or deposit on the windows used for spectroscopic observation, it should be readily detected unless it forms in the same thickness on each type of material used in the construction of the apparatus. The fiber optic ATR cell requires diffusion of the organic material into the siloxane buffer. The NIR ATR absorption spectrum and the NIR absorption spectrum would not be expected to show the same response for high molecular species such as biomass. Organic species containing active hydrogens such as hydroxyl, hydrogen adjacent to carbonyl, or amine groups will show strong NIR absorption. Since hydrophilic compounds will not diffuse into the siloxane cladding, the opportunity for differentiation is provided. Phenols, cresols, etc. will have strong UV signatures. Most compounds containing the benzene ring can be quantitated in the UV.

The objective is to observe in real-time a sufficient number of signals so that there is enough knowledge of the system to predict the behavior of the system in the near future.

B. DESIGN OF UV NIR PROBE

The design of a combined UV NIR probe that could be used in the field is shown in Figure 53.
A Teflon® spool is placed around the stainless steel shaft of an one or two centimeter absorption probe. A fiber-optic ATR sensor is wound on the spool. UV spectra can be recorded using the absorption probe, and NIR ATR spectra can be recorded using the fiber on the spool.

C. CONCEPT FOR AN INTEGRATED SYSTEM

Shown in Figure 54 is a concept of an integrated system that may be applicable to Air Force Bases.

The part of greatest concern is the length of the fiber optic links. If certain portions of the spectrum are required, then the lengths between the sensors and computer would be very short. For example, if the UV region from 190 nanometers to 250 nanometers is required, the fiber length would possibly be limited to less than 10 meters if white light is used. There is evidence that this could be raised to several hundred meters if predispersed illumination is used. Lengths would also be limited if information is required near the hydroxy absorption bands. Small dedicated hardened computers are available. One of these computers could be located near a cluster of sensors and the information coded at a different wavelength or to an electrical signal. An alternate configuration would place a small dedicated hardened computer at the site of each group of sensors. The purpose of this computer would be to collect data and convert the data to a format that could be passed over standard optical transmission lines.
SECTION VI
OBSERVATIONS AND CONCLUSIONS

The past 10 years has seen a period of rapid growth in instrumentation supporting analytical chemists. During the early 1980's, Dr. Tomas Hirschfeld and his colleagues began experiments with fiber optic chemical sensors (FOCS). Experimentation using these novel sensors spread rapidly into university laboratories and into the laboratories within the chemical industry. Parallel efforts were initiated in the fiber optic industry and by the manufacturers of medical instrumentation. Instrument manufacturers accepted the challenge. New markets had been created. Some of these activities with emphasis on sensors and instrumentation as applied to measurements related to the environment are described in this report.

During the same period, developments in the personal computer industry were an additional source of excitement. Investigators in even a small research laboratory today have available the computational power that only a few years earlier was reserved for the large research installations. Today, this computational power is found in portable computers with self contained power packs that can be used by investigators in the field sciences. Calculations can be made on site. Software algorithms related to multivariate analyses are now available for the portable computers.

The technological advancements have been evaluated and components selected for an instrument that can give immediate analytical results in the field. Significant time will be saved during site evaluation related to environmental concerns as field instrumentation replaces the practice of collecting samples and sending them to a laboratory for evaluation. Reduction in cost at remediation sites will be realized as immediate analyses are available. Expensive equipment will not set idle while analyses are being performed at an off site laboratory. The use of the equipment and procedures described in this study should be particularly effective in monitoring a site that awaits remediation or a site following remediation.

This research began at a time when many specialized instruments were being considered. FOCS were described as small chemical laboratories at the end of an optical fiber. The
The conclusion reached in this study is that computer manufacturers, instrument manufacturers, and software houses have made innovative tricks unnecessary. (Applications to medical science excluded). When a goal is defined, sufficient research results are available so that the task is an engineering task not a research task. Unfortunately, each polluted area has its specific problems that must be considered. The task that lies ahead must be a team effort as the higher educational system has not provided interdisciplinary talent in sufficient numbers.

The analytical system selected during this study consist of a portable general purpose spectrophotometer. Gratings and detectors can be interchanged readily in the field so that the spectrophotometer can be used over the range of 190 nanometers to 2200 nanometers. This covers the ranges associated with ultraviolet, visible, and near infrared spectrophotometry. The light source housed in the spectrophotometer is connected by a fiber optic cable to the sensor which is in contact with the analyte. A second cable returns the electromagnetic radiation to the detector. The spectrophotometer is connected to a portable computer. The computer software controls the repetitive operations and calculates the analytical values for the analytes using multivariate algorithms.

The selected components can be configured for classical absorption spectroscopy and fluorescence spectroscopy. With the addition of a laser source, Raman spectroscopy would be possible. The choice of a flexible spectrophotometer permits as many spectral points as required to be acquired. Multiple points allow the software algorithms to correct for many sources of variance. The work described in this report used many redundant points. Through the use of multiple points precision was obtained. The ability to take many points increases the flexibility. New hardware is not required when the analyte changes. As use of the system increases, the database should contain the calibration data for all analytes of general interest.

When samples contain many analytes, it may be necessary to separate the components into groups. In the near infrared region, NIR, the quartz fiber used for the core makes a good attenuated total reflection, ATR, component. The ATR spectrum of a compound resembles the absorption spectra and is characteristic of the compound. The work of Degrandpre and Burgess (5) using a coated fiber that is hydrophobic and organophilic has been repeated during this investigation. Degrandpre and Burgess teaches that, "the polymer cladding is a critical
component of an evanescent-field fiber optic sensor. The cladding should provide mechanical strength, be selective for an analyte or group of analytes, have good chemical stability, and have good optical qualities such as transparency and low scattering. In order to work in the evanescent mode it must have a refractive index lower than the core index. Obviously, there will be many polymers that fit these criteria. The limited number of polymer claddings and core combinations that are commercially available dictate that researchers must develop their own manufacturing capabilities. As the result of our investigations, we add that the cladding must be added to the quartz core during the drawing operation while the fiber is in the inert atmosphere of the drawing furnace. The UAH Laboratory For Inline Process Analyses has received experimental fiber from the Guided Wave, Inc. plant. The theories have been confirmed and many new fibers are available. Since the aromatics have a higher index of refraction than quartz, the concentration range is limited before cutoff in the core. Therefore, we are also considering glasses with higher index of refraction than quartz.

The advantages of multivariate analyses are numerous. Probably the most important advantage is that many analytes can be quantitated using a single spectrophotometric system. With multivariate analyses and statistical models, analyses for the analytes of interest are obtained. All other analytes and sources of variation are considered noise. The analyst must accept the responsibility that the calibration set contains all sources of variance. It is important to carry redundant data rather than minimize the number of spectral points too early in an investigation and risk undesirable variation from interferents and non reproducible procedures.

A disadvantage of the recommended multivariant procedures is the requirement for a well characterized training set that has been analyzed by an acceptable analytical procedure. This disadvantage will decrease as use of the system increases and the database grows.

The present decade has seen many innovative changes applicable to determinations made by analytical chemists. This report has stressed the developments in spectrophotometers, computers, and computer software. An analytical system has been recommended that will expedite environmental analyses. The system will be useful during site characterization, remediation, and site monitoring.

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APPENDIX A

OPTRODE DEVELOPMENT
(From a UAH Report prepared in 1986)

A. BACKGROUND AND PROBLEM DEFINITION

1. Introduction

The Center for Applied Optics at The University of Alabama in Huntsville and their subcontractor ST&E, Inc. have completed a three month study to define the state of the art related to Optrodes and, more specifically, FOCS. This study was made at the request of Dr. Bernard Bulpin, Director, Analytical Sciences Laboratory, Standard Oil Research and Development Company.

The study has confirmed the observation that most of the published studies related to FOCS have their roots at the Lawrence Livermore National Laboratories (LLNL). Dr. Tomas Hirschfeld (LLNL) did much to popularize the ideas. Efforts were primarily directed at FOCS research concepts and as a result, few, if any, of these FOCS reached the commercial market. Considerable engineering effort remains to be completed.

2. Problem Statement

FOCS are small chemical laboratories placed at the end of a fiber optic. For chemical analyses these optrodes should be specific to the chemistry confined within the light path at the end of a fiber. Our studies indicate that many chemistries have been tested under laboratory conditions, but few, if any, have made the complete journey through engineering, manufacturing and then to the commercial market. In fact, the laboratory work is often suspect, as it has been difficult, if not impossible to repeat the experiments and obtain data similar to that reported in the literature. On the other hand, private communications indicate that several types of optrodes have been successfully adopted to industrial use. A uranyl optrode (based on LLNL research) is in use at Union Carbide and a copper optrode (started by ST&E but completed by Guided Wave, Inc.) is in place at Hughes Aircraft.
Our evaluation of FOCS identified the following as needed future research and engineering objectives of interest to Standard Oil:

1. Check viability of relevant optrodes
2. Specific optrode chemistry (proprietary)
3. Improved ruggedness
4. Increased lifetime
5. Better reproducibility between FOCS
6. Better protection from contamination
7. Better control of pore size of membranes

Significant advances toward meeting these objectives are possible. The problems are common to the engineering of optical systems. Several organizations at the recent FACSS meeting pointed out to us that they felt the most important deficiency within their organization was lack of an optics engineering group. More realistically, however, the need is for a team of chemists and optical engineers, working in tandem, if the FOCS are to become a practical useful devices. The CAO-ST&E team that completed the recent study, consists of chemists, optical engineers, and analysts and is uniquely qualified to attack these problems. The team, contains individuals who have been connected with FOCS development since the beginning and the optical specialist that constitute the CAO.

B. STATEMENT OF WORK

1. Approach to Capturing and Improving FOCS Technology

The engineering objectives give in Section A have been carefully considered. All FOCS have similar shortcomings. This observation led to consideration of common components. Signal to noise ratio is low. Either the signal strength at the source must be increased or the available signal must be used more conservatively. Significant effort has been placed on obtaining increased signal strength. The Livermore group has investigated several approaches. It will be the goal of this development effort to capture as much of this experience as possible. Reproducibility has been a major problem. ST&E, since personnel have been associated with the research, will be responsible for manufacturing the initial sensors and will
provide written procedures. Using the written procedures CAO will attempt to reproduce the ST&E results. The CAO will concentrate their developmental effort on the fiber optic components. Different cores, claddings and/or protective coatings may be used. UAH will attempt to distinguish between the populations of FOCS available for testing. FOCS made at UAH will be tested at ST&E.

Inadequate noise management is believed to cause a major portion of signal degradation. The optimum system will include compromises on fiber size, cladding, buffering, and/or tensile strength. Larger fiber cores transmit more light but lead to noise from modal mixing. Mode strippers have proven useful in separating signal from noise. Although photons are lost in strippers, frequently, an overall gain in signal strength and purity can be achieved. Although they are more expensive, bundles of small fibers will be considered. Signal lost in a single fiber may be high, but the signal will be greater if the geometry of collection can be improved or if less signal is lost to higher modes.

Big improvements have been made in obtaining useful information through the use of appropriate software algorithms. The analog approach to read-out is the simplest. When only a single parameter is measured information can be obtained concerning the statistical distribution of values. When two parameters are measured, two dimensional plots can be made. The human can often distinguish patterns. A few individuals can recognize patterns when three dimensions are considered. Once the information is digitized, computer programs can be used to find patterns in multiple dimensional space. The different methods of data reduction will be compared. Trade-offs in cost between the simplicity of a FOCS using analog output possibly digitized, and systems containing more intensive computer utilization will be considered.

Some of the unsatisfactory results are believed to originate from a standardization problem. Some of the variations between measurements may result from values being compared to an improper standard. This problem may become obvious as different spectrophotometers are used.

The adapter being used by ST&E to couple light into and out of the optrode does not appear to be a source of noise. This adapter will be used until a shortcoming is observed.
Engineering is required so that the adapter will be versatile enough to be used on a number of spectrophotometers. The first adaptation will be to the Guided Wave Inc. Optical Wave Guide Spectrophotometer, since UAH has experience with this spectrophotometer in measuring optical quantities related to fiber transmissions. Use of this spectrophotometer for comparing current spectral data transmission over fiber with previous results, should quickly identify the sources of problems.

2. A Bolder Experimental Approach

FOCS development has necessarily used fibers and technology that have been developed for the communication industry. Use of different types of fibers has been considered under Section B.1. Investigation of the sensor at the distal end of the fiber, however, was limited to capturing existing technology. New approaches to manufacturing the active parts of the sensor are proposed. Normally the core has a slightly greater index of refraction then the cladding. The chemical specificity is often derived from a chemical interaction with the cladding. If experimentation is limited to claddings that match the currently available glass, quartz, or plastic core materials, selection of claddings is limited. We propose to select the appropriate cladding, and then make an appropriate core material. The core material may be a single crystal, a specialty glass, or a powdered material compressed at high pressure until optically transparent. The cladding will then be deposited by a technique common to optical technology, for examples, by evaporation, sputtering, or plating.

Historically, many chemistries have been proposed and reported in the literature but few have actually worked properly. Unfortunately, the chemistries are so varied that it is impossible to focus on a single cause or a few specific causes for poor reproducibility. One of the reasons that FOCS have not progressed faster is the wide variety between the chemistries so that no commonality exists.

The data from the overhead transparencies used for the briefing related to this report follow on the next page.
TOMAS HIRSCHFELD
1939 - 1986

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OPTRODES

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TYPES OF OPTRODES

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<td>Beltsville, MD</td>
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<td>Irvine, CA</td>
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<td>Kelsius, Inc.</td>
<td>San Carlos, CA</td>
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<tr>
<td>Guided Wave, Inc.</td>
<td>El Dorado Hills, CA</td>
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ORGANIZATIONS WHICH MAY COMMERCIALIZE OPTRODE

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<tr>
<td>Guided Wave, Inc.</td>
<td>El Dorado Hills, CA</td>
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ADVANTAGES OF FIBER SPECTROSCOPY

- Small Physical Size
- Geometric Flexibility
- Environmental Versatility
- Real Time Analyses
- Multiple Analyses
- Sample Integrity
- Instrument Reliability
- Analyte Specificity
- In-Vivo and In-Situ Analyses
- EMI Insensitive

FUTURE ENGINEERING REQUIREMENTS FOR FOCS

Achieve Ruggedness
Increases Lifetime
Provide Reproducibility Between FOCS
Control Pore Size of Membranes
Protect Against Contamination

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APPENDIX B

MODELS

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MODELS

Models may be divided into three general types: (1) quantitative or analytic, (2) qualitative, and (3) heuristic or empirical.

A. QUANTITATIVE OR ANALYTICAL

A quantitative model consists of a mathematical representation of the dynamic features of a system as a set of differential equations, or a description in terms of state variables obtained from the knowledge of the fundamental physics and chemistry of the system. Stochastic techniques can be employed for systems with unpredictable behavior. Shown at the top of Figure B-1 are four quantitative models: (1) Most individuals are familiar with the equation representing an ideal gas. Data representing the state variables temperature, pressure, volume and mass can be correlated using the equation for an ideal gas. If any three of the properties are known, the fourth can be calculated. For example, mass can be evaluated by measuring the volume, temperature, and pressure of a sample of gas. (2) Beer's Law is the principal equation used by spectroscopists. If the spectrum of each component of a mixture is known and the compounds in the mixture do not react, then the percent of each component is calculated by a manipulation of matrices. (3) Constructing a quantitative model for a system—for measuring pH using a glass electrode or a hydrogen electrode is straightforward. The Nernst equation defines the relationship between the electropotential and the activity of the hydrogen ion. The Nernst equation also defines the change in potential with a change in temperature. Potential and current relate to the flow of electrons in conductors and are adequately described by Ohm's law. Many successful pH meters have been developed and marketed using these equations to construct the model. As demonstrated by these examples, model building is a useful technique used by many scientists and engineers. This type of model is successful if the relationships are shown are linear and the variables can be separated. A first order model can be quickly constructed and instruments developed, manufactured and calibrated. A closely related technique of model building is represented by the example taken from Diamond, William J., Practical Experimental Designs. This example represents a synthesized linear model. It is assumed that the variables are separable. Each of the individual functions is obtained by planning experiments where
BUILDING THE MODEL \((y = f(x))\) IS THE CRITICAL STEP

QUANTITATIVE OR ANALYTICAL

- Ideal Gas Law: \(PV = nRT\)
- Beer's Law: \(A = ELC\)
- Nernst Equation: \(E = E^0 - \frac{RT}{nF} \ln \left(\frac{[Red]}{[Ox]^b}\right)\)

**Tire Life (Diamond)**

\[
\text{Life of Tire} = f(\text{type of Rubber}) + f(\text{Curing Temp}) + f(\text{Additives}) \\
+ f(\text{Groove Design}) + f(\text{Mixing Procedure}) + f(\text{Size of Tire}) \\
+ f(\text{Car Design}) + f(\text{Roadbeds}) + f(\text{Operating Speeds}) \\
+ f(\text{Atmospheric Conditions}) + f(\text{Operator Of Car}) \\
+ f(\text{Maintenance}) + f(\text{Type of Rubber})
\]

\[
f(\text{Operating Speed}) = 87 \times \exp \left[7 - \left(\frac{\text{Speed} + (\quad)^2}{\text{Speed}}\right)^3\right]
\]

**QUALITATIVE**

A SYSTEM IS REPRESENTED OR DESCRIBED BY ITS COMPONENTS.
CAUSAL RELATIONSHIPS ARE EMPHASIZED (FREQUENTLY USED IN EXPERT SYSTEMS AND NEURAL NETWORKS)

**HEURISTIC OR EMPIRICAL**

A SET OF EQUATIONS ABOUT A SYSTEM GENERATED THROUGH EXPERIMENTATION, STATISTICS, AND VALIDATION

**Figure B-1 Models**
only one variable is changed at a time, that particular variables is modeled, and then the entire set of experiments is summed.

Quantitative of analytical models are sufficient for classical science and are particularly important to demonstrating causality. Science and technology have advanced our abilities to measure with greater precision, to see smaller objects, and to see objects at greater distance. Many examples are found where the variables interact and are not linear or separatable. Pure specimens of many of the chemicals in complex mixtures as found in nature are not available. Therefore, other methods of model building must be considered.

B. QUALITATIVE.

For a qualitative model a system is represented in terms of its components. The casual relationship between the components, corresponding to physical laws are emphasized. Functional descriptions of the components are utilized to generate rules and constraints for the entire system. This type of model can be demonstrated using the Ideal Gas Law. If the temperature and pressure of a volume of gas was being monitored in a container of fixed volume and a temperature rise is observed without an increase in pressure, as would be expected in a non reacting system, a chemical reaction in which the number of molecules of gaseous product is less than the number of molecules of gaseous reactants may be postulated. This would not be a valid conclusion if a transducer malfunctions. The first rule therefore could be: if the above condition is observed check for the malfunction of a transducer. This type of model is frequently used for AI and expert system algorithms. Model of this type will be useful in describing monitoring system where detecting and quantitating a change in an analyte is more important than the base line composition. This type of model is less useful for modeling diagnostic systems.

C. HEURISTIC OR EMPIRICAL.

The amount of information obtained from an univariate statistical analysis is limited. For a single type of measurement on several samples, the samples can be represented on an axis or number line representing all possible values of the measurement. With univariate statistical
techniques, some information can be learned about the one-dimensional distribution of these points. More information can be gained when the values of a separate measurement are known for these samples. It is then possible to plot the points in a plane. As additional dimensions are added, more information is available.

The human being is the best pattern recognizer in two dimensions, or sometimes three dimensions. As additional types of measurements are made on the samples of a population, the potential to gain information about the properties of the sample increases, but the human ability to "see" patterns rapidly decreases. The computer, however, is able to manipulate points in multidimensional space, perform operation on them, and recognize the patterns in the higher order space. Cluster analysis and pattern recognition algorithms are designed to model systems and determine or predict properties of systems that are not themselves directly measurable but are related to measurements on the systems and give information that is sought. The pattern recognition approach is oriented to discover hidden relationships and to develop accurate and useful prediction and classification models for aspects (properties of categories) that are difficult or impossible to measure, using features or variable that are easy and inexpensive to measure and a training set of knowns. As each individual has a characteristic fingerprint, each instrument, each transducer, and each sample has a characteristic data vector. If the data vectors for two instruments are the same, the instruments are identical. If the data are different for identical samples by several operators then the instruments or operators are responsible. If the data vectors are not identical, they can often be separated into two or more vectors that can be identified. This type of modeling is particularly useful for evaluating data taken using several instruments and several operators to identify malfunctioning instruments and/or unqualified technicians.

Empirical models have been used beneficially for near-infrared analyses (NIRA). Data vectors (spectra) are taken for samples of known composition. An empirical model is established, based on the variance covariance matrix. The content of unknown samples can then be quantitated (predicted). These models have been used extensively for analyses of agricultural products, drugs, and textiles.
Relationship between error of prediction and complexity of the calibration are shown on Figure B-2. As indicated, if only one observable is used, the error of prediction caused by interferants is high. As longer data vectors are used the error of prediction decreases. An example from spectroscopy is the use of a single wavelength and Beer's law vs the entire spectrum and Beer's law. When a factor analysis approach is used, the use of too many factors results in including noise in the data. The training set must match the experimental conditions.
Figure B-2. Prediction Error vs Complexity
APPENDIX C

SPECIFICATIONS OF SPECTROPHOTOMETERS
APPENDIX C

SPECIFICATIONS FOR SPECTROPHOTOMETERS

One classification for spectrophotometers is related to the handling of the reference spectrum. A single beam spectrophotometer requires that the reference spectrum be taken and stored. A double beam spectrophotometer has parallel light paths and alternates readings between the reference and the sample. There are advantages and disadvantages for each method. The Guided Wave, Inc. Model 200 used for most of the work described in this report is a single beam instrument. The Model 300 is a double beam instrument. Both of the Guided Wave, Inc. instruments are optimized to the characteristics of light transmission over fiber cables. These spectrophotometers gave better signal/noise ratio than was reported in the literature for other spectrophotometer designs.

A. SINGLE BEAM SPECTROPHOTOMETER

A portable scanning spectrometer employing an optical fiber link between the sample and the spectrophotometer is required. A selection of gratings and detectors are required to allow use of the spectrometer as a UV-VIS-NIR instrument over the range of 190 nanometers to 2200 nanometers. Kinematic mounts of detectors and gratings are required so that gratings and detectors may be readily interchanged and calibrated in the field. Operating characteristics include:

1. Distance between spectral points and number of readings averaged to be software adjustable.

2. Record 2000 points in a single scan in 30 seconds or less.

3. Spectrometer bandwidth selectable from 2 - 16 nanometers by changing entrance and exit slits.

4. Signal-to-noise of 50 microabsorbance units (RMS) or better at zero absorbance units through 2 meters of single strand optical fiber (core diameter 500 micrometers or less).
5. Industry standard SMA 905 connectors provided for optical cable connections.

6. IBM-PC compatible interface and software drivers.

7. Software to collect and display spectra and store spectra to disk.

B. DOUBLE BEAM SPECTROPHOTOMETER

A scanning spectrometer employing reference and sample optical links is required. Capabilities to include:

1. Record spectra between 700 nanometers and 1900 nanometers in a single scan in 10 seconds or less.

2. Spectrometer bandwidth not greater than 16 nanometers.

3. Signal-to-noise of 20 microabsorbance units or better at zero absorbance units through 2 meters of single strand optical fiber, core diameter 500 micrometers or less.

4. IBM-PC compatible interface and software drivers.

5. IBM-PC data terminal capable of being located at least 1 kilometer from the spectrophotometer.

6. Industry standard SMA 905 connectors provided for optical fiber connections.

7. Software to collect and display spectra and store spectra to disk.

8. Software with macro language allowing automated operation including customized data collection on, reduction, and display.
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Searches for the unavailable information was made if the material was pertinent to this contract.


Arena, Guiseppe; Rizzarelli, Enrico; Sasmartano, Silvio; and Rigano, "A Non-Linear Least-Squares Approach to the


Yamada, Haruka and Yamamoto, Yoichiro, "Illumination of Flat or Unstabled Samples for Raman Measurements using Optical Fibers," AJN, AVO, AIS, 4-5, 1980.


Ho, C.-N.; Christian, G.D. and Davidson, E.R., "Simultaneous


Saari, Linda A. and Seitz, Rudolf W., "pH Sensor Based on


Hirschfeld, Tomas; Deaton, Terrence; Milanovich, Fred and Klainer, Stanley, "Feasibility of Using Fiber Optics for Monitoring Groundwater Contaminants," Optical Engineering,


Smit, H.C. and Meites, Louis, "Factors Affecting the


Szabó, Klára; Nagypál, István and Fábián, István, "Unexpected Dependence of the Protonation Constant of 2,2'-Bipyridyl on Ionic Strength," Talanta, 30, 10, 801-804, 1983.


10

1984.


Fitch, Pamela and Gargus, Greg A., "Remote UV-VIS-NIR Spectroscopy Using Fiber Optic Chemical Sensing," American Laboratory, AVO, AIS.


Abraham, M.H; Doherty, R.M.; Kamlet, M.J. and Taft, R.W.,


Bernard, Jean-Jacques; Depresles, Emmanuel, "High-Resolution Correlation OTDR For Distributed Fiber-Optic Sensors and


Krohn, David A., "Fiber Optic Sensors: Phase Modulation,"


Goldman, Don S., "Chemical Sensor Development For Process and


Sherman, Glenn H.; Danielewicz, Edward J. and Rudisill, J.


Watson, Jr., Edgar, "On-line Analysis of Trace Contaminants


AAU, "NEW! A 12-bit Slow-Scan CCD Camera... at Half the Cost of Other Cooled CCD cameras," Laser Focus World, 25, 10, APG, 1989.


Barnes, R.J.; Dhanoa, M.S. and Lister, Susan J., "Standard Normal Variate Transformation and De-trending of


Clementi, Sergio; Bonelli, Daniela; Cruciani, Gabriele; Skagerberg, Bert;., "Chemometrics Strategy in Drug Design,"

Clifton, M.J., "A Viscometer For the Quality Control and Experimental Laboratory," American Laboratory, AVO, AIS, 11, 1989.


Del Fanti, Natalino; D'Alessio, Aldo; Pianca, Maurizio; Moggi, Giovanni; "FT-IR Study of Poly(vinylidene Fluoride-co-Hexafluoropropene)/Phthalate systems," Chimica Oggi, AVO, AIS, 15-17, 1989.


Ellerbe, Polly; Meiselman, Stanley; Snigoski, Lorna T.; Welch, Michael J., "Determination of Serum Cholesterol by a Modification of the Isotope Dilution Mass Spectrometric


Havel, Henry A.; Chao, Robert S.; Haskell, Royal J. and


Howard, Mark; Norris, Karl and Williams, Philip C., "Methods of Determining the True Accuracy of Analytical Methods," Analytical Chemistry, 61, AIS,


Kohen, Elli; Hirchberg, Joseph G. and Prince, Jeffrey, "Spatiotemporal Mapping of Fluorescence Parameters in Cell


Moss, Tuckerman, "Moving Power Down a Fiber," *Photonics*


Scheller, Frieder; Shcubert, Florian; Pfeiffer, Dorothea; Hintshce,, "Research and Development of Biosensors*," Analyst, 114, AIS, 653-662, 1989.


Sweedler, Jonathan V. and Denton, M. Bonner, "Spatially


Hessefort, Norbert; Hedstrom, Mark and Greive, William, "Characterization of Phenolic-Modified Oils Using Size-Exclusion Chromatography and a diode-Array Detector," LC-GC, 7, 2, 130-136, AYR.
Oliver, M., "Guided-Wave Optical Spectroscopy of Thin Films," 
AJN, AVO, AIS, 639-657, AYR.

Srinivas, S. and Lakshman, S.V.J., "BASIC Program for 
Evaluation of Wavenumbers for Wavelengths," American 
Laboratory, AVO, AIS, 23-25, AYR.
REFERENCES


