Fluorescence of Contaminants in Soil and Groundwater
Using a Time-Resolved Microchip Laser System

by

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ABSTRACT

In this study, unique fiber-coupled microchip laser technology developed at MIT's Lincoln Laboratory was evaluated for practical application in a new in-situ sensor that utilizes laser induced fluorescence (LIF) to detect, identify, and quantify contaminants in subsurface environments. A multi-phase laboratory testing program was carried out to delineate the limits of the sensor's capabilities and provide fundamental insight into the factors controlling its performance in soil and groundwater. Robust and objective procedures were also developed to analyze data acquired with the sensor.

Laboratory investigations were performed using a versatile experimental apparatus designed to simulate the in-situ interface between the LIF sensor and contaminated media while providing complete control of test conditions. The experimental apparatus was used to analyze the influence of contaminated media properties on in-situ LIF observations, and to investigate issues associated with signal interference, sensor design, and data acquisition. Properties of contaminated substances given primary consideration included contaminant concentration and solution composition for the aqueous media, and grain size, type, color, mineralogy, and organic content for the soils.

Experimental results indicate that the sensor can detect aromatic hydrocarbons such as benzene, toluene, and (o)-xylene at part per million levels in aqueous solutions with, at most, a factor of five decline in performance when used in the presence of coarse soils. Fluorescence lifetimes as short as 2.5 ns can be determined without the need to deconvolute excitation and emission signals. Test results also show that soil has no measurable effect on the determination of contaminant fluorescence lifetimes or the general form of contaminant emission wavelength profiles. However, for a given contaminant concentration in the pore space of a soil with a narrow grain size distribution, decreases in soil grain size are accompanied by a decrease in the magnitude and variability of observed LIF signals. For soils containing a wide range of particle sizes, in-soil LIF observations are primarily influenced by effects associated with the smallest particles present in the soil. These trends were found to be a primary function of the volume of pore fluid in a soil specimen that is in the direct path of laser excitation energy. Soil organic content and optical characteristics such as reflectivity also have potential influence on in-soil LIF observations, although on a secondary basis. Results of additional LIF tests performed on two and three compound aqueous solutions demonstrate that both the emission wavelength and the time decay characteristics of a chemical mixture fluorescence signature can be represented by superimposing the individual contributions of the solution components.

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List of Symbols

ABBREVIATIONS and ACRONYMS

ADC  Analog to Digital Converter
ASA  Available Surface Area
ASTM American Society for Testing and Materials
BBC  Boston Blue Clay
BBO  Beta Barium Borate
BTEX Benzene, Toluene, Ethylbenzene, Xylene
CCD  Charge Coupled Device
DFM  Diesel Fuel Marine
E - W Emission - Wavelength
EEM  Excitation Emission Matrix
I - T Intensity - Time
KTP  Potassium Titanyl Phosphate
LIF  Laser Induced Fluorescence
MFS  Manchester Fine Sand
PAH  Polycyclic Aromatic Hydrocarbon
PMT  Photomultiplier Tube
PV   Pressure Volume
SCAPS Site Characterization and Analysis Penetrometer System
SEM  Scanning Electron Microscopy
SNR  Signal to Noise Ratio
SSA  Specific Surface Area
USCS Unified Soil Classification System
UV   Ultra Violet
WTI  Wavelength - Time - Intensity
WTM  Wavelength - Time Matrix
YAG  Yttrium Amber Garnet

SYMBOLS - English

A  Amplitude
a  Absorptivity
a_i  Fraction of solution fluorescence signal from component i
b  Path Length
c  Speed of Light, Concentration
C  Proportionality constant
C_{pf} Bulk pore fluid concentration
d  Groove spacing on spectrometer grating
D, Relative density
E Energy, Total energy
e Void ratio
e_{max} Maximum void ratio
e_{min} Minimum void ratio
f F number, ratio of focal length to clear aperture
f_{gs} Ratio of soil and aqueous solution fluorescence signals
f_{oc} Fraction of organic carbon
f_{om} Fraction of organic matter
h Planck's constant
\mathcal{H} Hamiltonian operator for total energy of an atom
\mathcal{H} Hamiltonian operator for total energy of a molecule
I Intensity
i Angle of incidence
I_a Absorbed intensity
I_e Emitted intensity
I_o Incident intensity
I_T Transmitted intensity
K Kinetic energy
k_d Water / soil partition coefficient
K_{oc} Organic carbon / water partition coefficient
K_{ow} Octanol / water partition coefficient
k_q Rate constant for oxygen quenching
L Fluorescence intensity in oxygenated solution
l Azimuthal quantum number
L_o Fluorescence intensity in deoxygenated solution
m Mass, Magnetic quantum number, Order of spectra
M Multiplicity, Molarity
n Principal quantum number, Electron shell number
N Number of atoms in a molecule
n_i Compaction lift number
p Momentum
Q' Concentration of dissolved oxygen in solvent
r Angle of reflectance of diffraction
s Spin quantum number, Displacement
S Absolute value of spin angular momentum for a molecule
S_i Singlet excited energy state
T Period of wave motion
t Time
T_i Triplet excited energy state
U_n Percent undercompaction of layer n
\( V \) Volume, Potential energy
\( v \) Speed of an electron
\( x \) Displacement, Location
\( X \) Contaminant concentration in water or soil pore fluid

**SYMBOLS - Greek**

\( \phi_r \) Quantum yield
\( \lambda \) Wavelength
\( \nu \) Frequency
\( \sigma \) Standard deviation
\( \tau \) Fluorescence lifetime
\( \psi \) Wavefunction representing the energy state of an atom
\( \Psi \) Wavefunction representing the energy state of a molecule
CHAPTER 1

INTRODUCTION

1.1 Introduction

Effective remediation of contaminated soil and groundwater requires detailed knowledge of the subsurface environment. Investigations of a site's hydrogeology, soil conditions, and the nature and extent of contamination form the basis of all remediation efforts. Subsurface reconnaissance can be accomplished in two primary ways: 1) through sampling and subsequent analyses, and 2) in real time using in-situ methods. While the former approach has the benefit of providing a controlled laboratory testing environment, the samples required for laboratory tests are inevitably subject to disturbance. Further, there are also practical limits on the number of samples that can be acquired which make it difficult to thoroughly characterize a contaminated site, particularly within a given budget. In contrast, in-situ measurements, although generally less precise, occur under actual field conditions and offer the potential to form a more detailed picture of the subsurface. Thus, in most subsurface investigations, there is a compromise between the quality of obtained data and its tendency to be representative of the site under investigation.

Site explorations are founded on a fundamental decision to acquire data of a particular level of detail and quality with a specified budget and within a given time frame. The decision to obtain high or low level data is generally a function of the design goals of a given project. That is, more complex and/or costly problems typically require more detailed information to facilitate safe and efficient solutions. For example, macro-scale hydrogeologic conditions can be ascertained using observation wells and piezometers, while hydraulic properties of specific soil strata can only be obtained from various forms of in-situ pumping tests or laboratory hydraulic conductivity tests performed on soil samples. Similarly, generalized profiles of soil stratigraphy can be developed rapidly in the field during soil boring operations using split spoon samples. However, more specific soil classifications require laboratory tests such as
grain size analyses and Atterberg limits. This argument carries over to remediation problems in that qualitative information can be used to identify contaminants, but effective cleanup can only be performed on the basis of quantitative data.

Remediation efforts are typically expensive endeavors in which clean-up strategies for soil and groundwater are closely linked to site-specific conditions. Further, the cost of remediation procedures is typically a direct function of the volume and severity of contamination. For these types of problems, high quality, detailed site characterization is always desirable.

In the past only laboratory-based gas chromatography and mass spectroscopy provided reliable estimates of chemical concentrations in soil and groundwater. These techniques, although accurate, are expensive and require samples extracted from the subsurface. As in soil sampling, sample disturbance is always a problem. Borehole contamination, small changes in sample temperature, exposure to light, and volatilization can all influence the results of chemical analyses. Therefore, ex-situ chemical analyses require quality control and careful evaluation to ensure that test results are truly indicative of site conditions. This process is open to substantial subjectivity and can often make remediation decisions difficult.

In the geotechnical arena, advances have been made toward high resolution, real-time in-situ characterization of soil strata and their hydraulic properties through the use of probe type devices, such as the piezocone. These devices consist of a series of hollow steel rods interconnected to form a long pencil-like probe that is pushed into the ground to investigate subsurface conditions. One segment of this probe, usually at the tip, houses instrumentation that characterizes the physical properties of the penetrated medium, such as soil strength, soil type, and pore water pressure. Signals generated by downhole instrumentation are carried to the surface using an umbilical cable that passes through the center of the steel rods composing the overall probe. Once at the surface, the data can be interpreted to provide indications of changes in soil properties with depth.

Recent developments in laser and fiber optic technology now permit the extension of this probe technology to chemical analyses via remote fiber-coupled optical spectroscopy. A fiber optic cable can be incorporated in the umbilical line of a probe device to transmit light
directly to the location of contamination and carry, for example, excited fluorescence energy to detection devices located within the probe or above ground. The distinctive nature of an optical phenomenon such as laser induced fluorescence (LIF) has the potential to provide both qualitative and quantitative characterization of in-situ contaminants in real-time using in-situ probe or monitoring devices.

Direct remotely deployed fiber optic sensors that make use of optical spectroscopic techniques, such as LIF, can characterize subsurface contamination without many of the problems or expense associated with conventional sample extraction techniques and subsequent ex-situ analyses. However, the use of optical spectroscopic profiling and monitoring devices has not become routine practice for two primary reasons. First, the ultimate performance of existing systems has been limited by a variety of technological factors. Second, the engineering profession currently lacks a thorough understanding of the measurements made with these devices. At present, the devices all make use of large cumbersome lasers that deliver excitation energy to a target medium at low repetition rates; characteristics that all inhibit practical application of the technique. In addition, existing fluorescence sensors all utilize ultra violet (UV) excitation sources located above the ground surface that subsequently lose energy and therefore detection sensitivity as the UV travels below ground via fiber optic cable. In addition to these technology based issues, enormous quantities of data are acquired with spectroscopic equipment and it is often unclear what fraction of in-situ contamination is actually generating the observed signals. With limited laser excitation capabilities it has been difficult simply to detect chemicals in the subsurface, let alone interpret the subtle properties that affect observations of contaminant fluorescence signatures.

Recent advances in laser technology at MIT’s Lincoln Laboratory offer the potential to alleviate many of the above mentioned problems of existing remote monitoring/detection systems. The new laser technology makes use of a fiber optic cable to couple a near infra-red 1 Watt diode pump to a series of millimeter scale crystals that generate 200 ps pulses of ultraviolet and visible radiation (266 nm and 532 nm) when driven by infra-red radiation. The laser operates at a repetition rate of approximately 10 kHz with an average power of several mW and a peak power of 10 kW. The small size of the microchip laser crystals allows them to be
packaged into a 3 cm x 0.8 cm cylinder with an output window that can be easily deployed within a standard site exploration device such as a cone penetrometer. Due to the efficient propagation of infra-red radiation through fiber optic cable, the diode pump can be located hundreds of meters away from the microchip laser module with virtually no transmission energy loss, thereby facilitating the generation of UV and visible radiation directly at the location of in situ contamination. The high repetition rate of the device provides enhanced signal quality through real-time signal averaging that can be very valuable for subsurface profiling operations. Further, the short laser pulse width permits identification of compounds with even the shortest fluorescence lifetimes (~ 2.5 ns) without the need for sophisticated data analysis.

Without the equipment limitations characteristic of earlier remote spectroscopic systems, it is now possible to investigate factors, such as soil matrix effects, fluorescence signal interference, and probe/soil interface issues, that influence the in-situ observations made with such a device and, in that way, approach a level of understanding that will facilitate practical use of spectroscopic techniques for real time in-situ chemical analyses.

1.2 Thesis Scope and Objectives

The work included in this thesis is part of a larger project sponsored by the Idaho National Engineering and Environmental Laboratory (INEEL). The overall project scope included the development and deployment of a contaminant sensor that utilizes both laser induced fluorescence (LIF) and Raman spectroscopy to detect, identify, and quantify chemicals in soil and groundwater. Funds provided by INEEL were used to support research efforts at MIT’s Lincoln Laboratory and at the main MIT campus. The research pursued by this multidisciplinary team had several goals: (1) advance the state of microchip laser technology, (2) characterize the performance capabilities of a microchip laser contaminant sensor, (3) determine the influence of test medium properties on contaminant spectroscopic measurements, and (4) deploy a prototype sensor in a variety of field modes to perform subsurface profiling, long-term contaminant monitoring, and down-hole contaminant analyses.

This thesis focuses on a limited portion of the overall INEEL project goals. In particular, the work presented herein investigates several fundamental issues that establish the
practicality and overall applicability of an in-situ LIF probe. Primary attention is given to the interpretation of soil matrix effects on observations of fluorescence displayed by contaminants present in the pore fluid of soils. In-situ spectroscopic contaminant measurements are analyzed to determine factors that may interfere with fluorescence signal acquisition, and also to identify potential correlations to contaminant concentration, soil grain size, soil type, color, and mineralogy. Additional emphasis is placed on understanding the significance of the interface between the LIF probe and the test medium under investigation. Finally, further attention is also given to exploration of the spectroscopic characteristics of multi-compound chemical solutions after developing a database of single compound fluorescence signatures.

The aforementioned issues were investigated through a three phase experimental testing program that made use of a unique apparatus designed to simulate the interface between an in-situ LIF probe and the contaminated test medium. The first phase of the testing program established a database of single contaminant aqueous solution fluorescence signatures that was later used as a datum from which to evaluate the influence of the soil matrix. This stage of testing also led to the development of robust and objective data analysis procedures. The second testing phase consisted of a parametric study designed to assess the impact of soil properties on the fluorescence signatures of single compound solutions present in the pore space of a soil matrix. Finally, the third phase of the program investigated the fluorescence characteristics of multi-compound solutions.

All analyses were performed using the BTX compounds (benzene, toluene, and (o)-xylene) as contaminants. These chemicals are primary constituents of fuels and are also very common groundwater and soil pollutants. In aqueous solutions, the BTX compounds have very short fluorescence lifetimes (< 7 ns) and are therefore difficult to identify using conventional laser systems. Their routine identification in this study emphasizes the versatility and sensitivity of the MIT/Lincoln Laboratory LIF probe used for this study.

Throughout this thesis, soil properties affecting the observed fluorescence response of contaminants in the soil matrix are characterized in a framework consistent with tests and terminology routinely used in the geotechnical and environmental engineering profession. The author hopes that this procedure will facilitate the use of any findings made in this study and encourage their rapid acceptance by practicing engineers. In this way, remote optical
spectroscopy may go beyond the realm of research and become a standard site investigation tool.

1.3 Organization

This thesis is organized to provide the reader with a theoretical and conceptual understanding of the phenomenon under investigation and a familiarity with the equipment and materials used throughout the testing program prior to a description of the actual test results. Findings obtained during the three phases of the testing program are then presented in self-contained chapters that highlight the specific characteristics of each testing stage as well as the general conclusions drawn from specific test phase results. The final chapter summarizes all of the conclusions derived from the testing program as a whole, and assesses the overall potential of a LIF based in-situ contaminant detection/monitoring system. An outline of the chapters and their general content follows.

Chapter 2 provides the theoretical background that serves as the foundation of fluorescence based contaminant identification techniques. This discussion outlines the energy absorption and emission processes that result in fluorescence and the relationship between observed fluorescence radiation and the structure of a fluorescing molecule. Note also that Chapter 2 provides definitions for a great deal of the fluorescence terminology that is used throughout the remainder of this thesis.

Chapter 3 presents a detailed review of existing laser induced fluorescence systems. The discussion highlights the differences between existing systems and the system utilized for this testing program. Results of previous studies focusing on LIF system detection of contaminants in aqueous solutions and soils are also critically evaluated. This chapter establishes the current state of practice in the area of LIF contaminant measurements and also illustrates established methods for analyzing and interpreting the results of such tests.

Chapter 4 provides a complete explanation of all aspects of the experimental equipment and testing procedures utilized throughout the duration of this testing program. This discussion serves as both a practical and conceptual guide to the use of the three primary equipment groups involved in the LIF experiments; namely, the specimen testing apparatus, the spectroscopic hardware, and the data acquisition and automation systems.
Chapter 5 is used to thoroughly characterize the materials and specimen preparation techniques used during the experimental testing phases of this study. Physical and engineering properties of the contaminants of interest are presented along with the results of grain size analyses, index tests, x-ray diffraction studies, and scanning electron microscopy tests used to describe the soils utilized in this program.

Chapter 6 describes the results of the aqueous solution phase of the testing program. Specific procedural details are discussed in addition to a variety of factors that influence the measurements obtained during a LIF test. The results of LIF tests performed using alternate means of data acquisition are also presented and used to establish limits on the ability of the MIT/Lincoln Laboratory LIF sensor to detect, identify, and quantify selected contaminants in aqueous solution. Particular attention is also given to a complete description of data handling and analysis procedures used to derive parameters of interest, such as fluorescence lifetimes, and total fluorescence signals.

Chapter 7 presents the results of a parametric study designed to evaluate the influence of soil properties on observed fluorescence signatures of contaminants present in the pore space of a soil matrix. This chapter demonstrates the variability in observed fluorescence signals that stems from soil grain size and also indicates the influence of soil type, color, mineralogy, and organic content on LIF measurements. Results from this phase of the testing program demonstrate the relationship between in-situ LIF measurements and the actual level of contamination present in the subsurface.

Chapter 8 provides an overview of the applicability of superposition techniques to a LIF analysis of multi-compound chemical solutions. Fluorescence signatures predicted for various mixtures of fluorescing compounds in aqueous solution on the basis of single compound test results are compared with actual experimental measurements of mixed chemical solutions.

Finally, Chapter 9 summarizes the results of this study and supplies recommendations for future research to be carried out in the area of in-situ LIF contaminant detection and monitoring.
CHAPTER 2

THEORY

2.1 Introduction

Luminescence can be defined as the emission of light by an atom or molecule following absorption, by that atom or molecule, of light of somewhat higher energy. There are two classes of luminescence, namely fluorescence and phosphorescence. The work presented in this study focuses solely on fluorescence, so consideration of that realm of luminescence will compose the bulk of the following text. However, the reader should be aware of the fact that the conceptual differences between fluorescence and phosphorescence are minimal. The processes outlined below in the context of fluorescence apply equally to phosphorescence. The only differences between fluorescence and phosphorescence stem from the nature of the excited energy states and energy dissipation mechanisms involved in the respective phenomena. One should also recognize however, that these differences, although subtle, have considerable physical significance on the observed characteristics of luminescent bodies. The contrast between fluorescence and phosphorescence is most apparent in that observable radiative emission from a phosphorescing atom or molecule continues as much as 100 times longer than that from a fluorescing atom or molecule following the removal of excitation energy.

The study of luminescence spans the fields of spectroscopy, photochemistry and quantum mechanics. The broad interest in luminescence can be considered both a consequence and a cause of the fact that luminescence is prevalent in numerous aspects of science, technology, and even daily life. Whether you are in a laboratory pursuing a deeper understanding of atomic or molecular structure, in a classroom trying to differentiate the pH of water samples with litmus paper, or in a Laundromat acknowledging that your freshly laundered clothes look “whiter-than-white,” virtually everyone has witnessed some form of luminescence. The fact that luminescence involves the emission of light is perhaps obvious;
however, the explanation and significance of this radiation requires greater attention. Although the detail provided by a quantum mechanical analysis of polyatomic fluorescence is unnecessary for the scope of this research effort, an investigation of fluorescence initiating with the fundamental principles of physics and quantum mechanics elucidates many characteristics of the phenomenon and also clarifies the usefulness and application of luminescence based techniques in science and engineering.

The following discussion develops the fundamental principles required to characterize the fluorescence phenomenon. Particular attention is given to describing a model for atoms, extending this model to describe molecules, and outlining the concept of an energy state, the process of light absorption, competing mechanisms of energy dissipation, and the interpretation of fluorescence emission energy.

2.2 A Model for the Atom

For a brief period of time early in the twentieth century, atoms were believed to consist of electrons that circled around a nucleus in fixed orbits, not unlike the motion of planets about the sun. This theory, introduced by Niels Bohr in 1913, included the important premise that an atom could exist only in discrete energy states. Bohr recognized that changes in the energy state of an atom induced by light could only occur in discrete steps that were integral multiples of a unit termed a quantum (Jaffe and Orchin, 1962). Although Bohr’s model had numerous advantages over previous ways of conceptualizing the makeup of matter, the idea of a planetary atom also suffered from a critical flaw. In 1927, W. Heisenberg illustrated that it is impossible to simultaneously measure the exact position and velocity of an electron in an atom, and thus the predictable nature of the fixed, traceable orbit theory proposed by Bohr did not accurately represent the nature of an atom. Around this same time in history (1924) de Broglie equated Einstein’s formula for energy,

$$E = mc^2$$

(2.1)

where m is the mass of the particle and c is the speed of light, with Planck’s relation that demonstrated the wave-particle duality of light.
\[ E = h\nu \]  
(2.2)

where \( h \) is Planck's constant and \( \nu = c/\lambda \) is the frequency of the electromagnetic radiation (\( \lambda \) is the wavelength of the electromagnetic radiation) thereby obtaining,

\[ \lambda = \frac{h}{mc}. \]  
(2.3)

which demonstrates that waves can be associated with particles. De Broglie then argued that for an electron, for example, \( c \) should be replaced in Equation 2.3 by \( \nu \), the speed of the electron, resulting in,

\[ \lambda = \frac{h}{mv}. \]  
(2.4)

which indicates that particle behavior, such as that of electrons, can be treated in the context of wave mechanics. This formula was confirmed experimentally in 1926, at which time Schrodinger first proposed a wave mechanical description for the atom. Schrodinger's atomic model was based on the premise of the wave nature of electrons and the concept that although one could not specify the exact position of an electron, one could still indicate the likelihood of finding an electron in a given region of space (Jaffe and Orchin, 1962).

Building on the wave mechanical description of the electron, Schrodinger related the behavior of electrons in the structure of an atom to that characterized by the equations of standing or stationary waves as established in classical mechanics. In the definition of a standing wave, wavelength, \( \lambda \), is equated to the distance, \( L \), between the standing wave boundaries and the number, \( n \), of half-wavelengths within the wave boundaries by the relation \( \lambda = 2L/n \). Thus a standing wave of wavelength \( \lambda \) can exist between two boundaries a distance \( L \) apart only if \( L \) is some integer multiple of \( \lambda/2 \). Similarly, atoms can exist only in discrete states characterized by specific levels of energy. By relating the integral standing wave solutions leading to resonance to the discrete allowable energy states of an atom, Schrodinger, for the first time, permitted an explanation for the absorption and emission phenomenon witnessed by those studying the interaction of atoms and light. This lead, ultimately, to the development and thorough understanding of spectroscopy techniques.
A standing wave can be characterized by the following wave equation,

\[ s = A \cos \frac{2\pi x}{\lambda} \cos \frac{2\pi t}{T} \]  

(2.5)

where \( s \) is displacement, \( A \) is the maximum amplitude, \( x \) indicates direction along the wave axis, \( \lambda \) is the wavelength, \( t \) is time, and \( T \) is the period of the wave motion. This equation is the product of a position function and a time function. Viewing a stationary time-independent state, the amplitude of this wave equation can be given by,

\[ \psi = A \cos \frac{2\pi x}{\lambda} \]  

(2.6)

where \( \psi \) is termed a wavefunction or amplitude function as defined in wave mechanics (Sandorfy, 1964). Taking the second derivative of this equation with respect to \( x \) yields,

\[ \frac{d^2 \psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} A \cos \frac{2\pi x}{\lambda} = -\frac{4\pi^2}{\lambda^2} \psi. \]  

(2.7)

Thus, rearranging terms

\[ \frac{1}{\lambda^2} = -\frac{1}{\psi} \frac{d^2 \psi}{dx^2} \frac{1}{4\pi^2}. \]  

(2.8)

Now relating the classical formula for kinetic energy, \( K = \frac{1}{2}mv^2 \)

(2.9)

with the de Broglie relation (Equation 2.4), one can obtain an expression for kinetic energy within the context of the wave description of a particle such that,

\[ K = \frac{h^2}{8\pi^2 m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2}. \]  

(2.10)
Schroedinger then suggested that the kinetic energy term, $K$, could be replaced with the difference between the total energy, $E$, and the potential energy, $V$, of the particle under consideration. This substitution yields,

$$E - V = -\frac{\hbar^2}{8\pi^2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2}.$$

(2.11)

Equation 2.11 can be rearranged as follows,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{\hbar^2}(E - V)\psi = 0.$$

(2.12)

This equation characterizes the condition of a particle limited to movement in only one direction. In actuality, a particle such as an electron is free to move in three dimensions. It is therefore important to differentiate the amplitude function, $\psi$, with respect to all three Cartesian directions. This can be symbolized using the Laplace operator,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2},$$

forming

$$\nabla^2\psi + \frac{8\pi^2m}{\hbar^2}(E - V)\psi = 0,$$

(2.13)

which is the time-independent Schroedinger equation in three dimensions describing the energy state of a particle in space at a particular instant in time (Sandorf, 1964). Note that the calculation of spectral intensities involved in absorption and/or emission processes would also require use of the time-dependent Schroedinger equation. However the time-dependent Schroedinger equation will not be derived at this time since it is unnecessary for the conceptual understanding of the atomic model sought in this discussion.

Equation 2.13 may be rewritten as follows:

$$-\frac{\hbar^2}{8\pi^2m} \nabla^2\psi + V\psi = E\psi$$

(2.14)

in order to isolate the quantity
\[ \mathcal{H} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V, \]  

(2.15)

which is the quantum mechanical Hamiltonian operator for total energy. The operator, \( \mathcal{H} \), is derived from the classical Hamiltonian expression for total energy,

\[ H = \frac{1}{2m} p_x^2 + \frac{1}{2m} p_y^2 + \frac{1}{2m} p_z^2 + V, \]  

(2.16)

where \( m \) is the mass of the particle and \( p_i \) is the momentum of the particle in the \( i \) direction, by respectively replacing the components, \( p_x, p_y, \) and \( p_z \), of the momentum in \( H \)

with the partial differential operators \( \frac{\hbar}{2\pi i} \frac{\partial}{\partial x}, \frac{\hbar}{2\pi i} \frac{\partial}{\partial y}, \) and \( \frac{\hbar}{2\pi i} \frac{\partial}{\partial z} \) (where \( i = \sqrt{-1} \))

according to the Second Postulate of Quantum Mechanics [7]. This procedure yields,

\[ H = \frac{1}{2m} \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial x} \right)^2 + \frac{1}{2m} \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial y} \right)^2 + \frac{1}{2m} \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial z} \right)^2 + V \]

\[ = -\frac{\hbar^2}{8\pi^2 m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V, \]

which is identical to Equation 2.14. Therefore, using the quantum mechanical Hamiltonian, Equation 2.13 may be rewritten in its most elegant form as

\[ \mathcal{H} \psi = E \psi. \]  

(2.17)

Written in the form illustrated in Equation 2.17, the Schrodinger equation demonstrates that an energy state represented by the wavefunction, \( \psi \), must be characterized by an energy, \( E \), that is an eigenvalue of the quantum mechanical Hamiltonian operator for total energy (Murrell, 1963). Thus, only specific levels of energy are valid states of existence for a system represented by a given set of wave functions.

Additional limitations on the acceptable eigenvalues and corresponding wavefunctions utilized in Schrodinger’s equation result from the fact that the electron motions incorporated
in Equation 2.17 are still subject to the conditions exerted by Heisenberg’s Uncertainty Principle. Both Schrodinger and Born recognized that the wave description of electron motion put forth in Schrodinger’s atomic model offered the possibility of characterizing electron position in a probabilistic sense (Sandorfy, 1964). However, this application would require the wavefunctions used to describe electron motion to be finite, single-valued, and continuous (Sandorfy, 1964). These conditions limit the physically acceptable solutions of Schrodinger’s equation and again support the discretization of energy states in the atomic model.

The probabilistic interpretation of the wavefunction is another extrapolation from classical theory. Just as the square of wave amplitude is proportional to energy density in electromagnetics, Born postulated that the square of the wavefunction could serve as a probability density indicating an electron’s position (Dykstra, 1992). Born therefore stated that, for a wavefunction \( \psi \), the quantity

\[
\rho = \psi^* \psi \, d\tau = \psi^2 \, d\tau
\]  

(2.18)

where \( \psi^* \) is the complex conjugate of \( \psi \), indicates the probability of finding an electron in the volume element \( d\tau \) (Sandorfy, 1964). Thus, the integral of \( \psi^2 \) over all space must equal one,

\[
\int_0^\infty \psi^2 \, d\tau = 1
\]  

(2.19)

and the wavefunction is said to be normalized (Sandorfy, 1964). Equation 2.19 is now considered the Fourth Postulate of Quantum Mechanics (Dykstra, 1992) and the term “orbital” denotes a region in space where there is a greater than 90% probability of finding an electron as defined in Equation 2.18 (Hercules, 1966).

Acceptable solutions of the Schrodinger equation, which can be extremely difficult to obtain for complex systems, provide the basis for the definition of so-called quantum numbers used to discretize the energy states of an atom. The energy states of an atom are associated with the distribution of its electrons in relation to its nucleus as characterized by the
wavefunctions, $\psi$. To describe an atom, a wavefunction must be obtained for each electron in the atom which accounts for the state of that electron as defined by four quantum numbers: $n$, $l$, $m$ and $s$. The meaning of each of these quantum numbers is described below.

The principal quantum number, $n$, describes the average distance of an electron from the nucleus of an atom. This therefore defines the energy of the electron and, in turn, the energy of an electron shell. The principal quantum number may theoretically hold any integer value greater than or equal to one (e.g. $n = 1, 2, 3, \ldots$) where $n = 1$ defines the K shell, $n = 2$ defines the L shell, etc. (Jaffe and Orchin, 1962).

The quantum number $l$ is termed the azimuthal number and it is a measure of the total angular momentum of an electron due to its motion about the nucleus of an atom. The azimuthal number determines the shape of the electron orbitals and may hold values of $0, 1, 2, \ldots (n - 1)$, where $n$ is the principal quantum number. A value of 0 corresponds to an s orbital, 1 to a p orbital, 2 to a d orbital, and 3 to an f orbital. Note that although $l$ may theoretically be greater than 3, to date, no atom has been discovered or created that possesses more than the four orbital shapes designated by s, p, d, and f. The letters s, p, d, and f, indicate the nature of spectral lines observed from the respective orbital types which may be sharp, principal, diffuse or fundamental (Jaffe and Orchin, 1962). Combinations of orbitals make up the electron shells of an atom, where, for example, the K shell contains only s orbitals and the L shell contains both s and p orbitals (Sandorfy, 1964).

The number $m$ is the magnetic quantum number. The magnetic quantum number accounts for the magnetic field established by the motion of an electron around the nucleus of an atom, and is thus related to the angular momentum of the electron. It may have values of $0, \pm 1, \ldots, \pm l$, where $l$ is the azimuthal quantum number. For a given electron, the value of the magnetic quantum number describes the precessed angle of the rotational axis of the electron in a magnetic field. This angle dictates any interaction between the electron and external electric or magnetic fields that in turn influences the orientation of the electron’s orbital relative to the nucleus (Toon and Ellis, 1978).

The fourth quantum number, $s$, indicates the spin of an electron and is the by-product of work by Dirac intended to account for relativistic effects in the description of the atom (Whitten et. al., 1988). The spin quantum number accounts for the fact that an electron
actually spins about its own axis and therefore possesses intrinsic angular momentum. The spin number may hold values of $\pm 1/2$ depending on whether or not the electron spin reinforces or opposes the electrons motion in orbit about the nucleus (Jaffe and Orchin, 1962).

With the energy and physical state of electrons defined it is possible to theoretically "assemble" an atom under the guidance of a few more rules of the atomic theory. Although the principal quantum number has no mathematical limit, the number of shells composing an atom, and thus the maximum value of $n$ for an atom, is determined by the ionization level of electrons surrounding a given nucleus. After reaching a certain distance from the nucleus, an electron's electrostatic interaction with the nucleus is negligible and the electron is considered ionized (Suppan, 1994). This is essentially a measure of how much force a nucleus can exert on an electron to maintain it as a component of the atom. Once a limit is established on $n$, the atom will consist of this limiting number of shells. Each shell will contain a number of subshells determined by the value of $n$ for that shell. In addition, each shell will be further discretized into $n^2$ orbitals. For example, if an atom has a limit of three shells ($n_{\text{max}} = 3$), the second shell ($n = 2$) or L shell, will include two subshells, s and p. The s subshell will contain one 2s orbital, and the p subshell will contain three 3p orbitals ($3p_x$, $3p_y$, $3p_z$) for a total of $n^2$ or four orbitals. When conceptualizing the final makeup of an atom one must follow the Aufbau Principle which states that an atom is “built up” around the nucleus by filling orbitals with electrons in order of increasing energy (Whitten et. al., 1988). An atom's electron configuration is completed by assigning electrons to their respective orbitals according the Pauli Exclusion Principle and Hund’s Rule. The Exclusion Principle states that no two electrons in the same atom can possess the same values of the four quantum numbers (Jaffe and Orchin, 1962). Hund’s Rule indicates that no two electrons may occupy a given orbital in a subshell until all orbitals of that subshell have at least one electron and all of these electrons have parallel spin (Jaffe and Orchin, 1962). Application of the above concepts completes the quantum mechanical description of an atom.

2.3 Extension of Basic Principles to Describe a Molecule

The quantum mechanical description of an atom outlined in Section 2.2 can be extended, conceptually, to treat the multi-particle system of a molecule. For a molecule, the
number of degrees of freedom involved in characterizing its state of energy is drastically increased over those required for the description of an atom. Each of the electrons in each atom of the molecule is, as before, described by the values of the four quantum numbers. In addition, molecules are also subject to the phenomenon of molecular vibrations. For a polyatomic molecule composed of N atoms there are typically 3N-6 vibrations or 3N-5 vibrations for a linear molecule (Sandorfy, 1964). Further, each vibrational state can also be associated with several rotational and translational energy conditions. All of these variables play a role in determining the total energy state of the molecule, which is still discrete in nature.

In this context, the Schrodinger equation can be interpreted to represent the relationship between a molecule’s state of energy and its defining wavefunctions as follows,

\[ \hat{H}\Psi = E\Psi \]  

(2.20)

where the wavefunctions, \( \Psi \), now represent the energy states of the molecule, \( \hat{H} \) is the quantum mechanical Hamiltonian of the molecule, and the eigenvalues, E, are the energy levels of the molecule (Murell, 1963). However, as the complexity of the system under investigation increases, the practicality of the Schrodinger equation suffers. For an atom such as hydrogen, with only one electron and one nucleus, it is possible to center a set of coordinate axes on the nucleus and calculate a representative wavefunction to describe the motion of hydrogen’s electron. As the number of particles involved in a system increases, the task of creating realistic wavefunctions becomes fruitless. Typically approximations are made to simplify problems involving complex multi-particle systems. These approximations often include neglecting vibrational, rotational and translational energies all together, and dealing solely with electron energies. However, the nature of the solution obtained from such an exercise also becomes increasingly qualitative.

For these reasons, analytical studies of molecular energy states are rarely pursued. Instead, the theoretical foundation provided by a detailed understanding of the structure of an atom assists in the interpretation of molecular spectroscopic data acquired experimentally. This is exactly the approach adopted for this research study.
2.4 Energy States and Light Absorption

The term energy state denotes a specific condition of position and motion for all of the nuclei and electrons that form a molecule (Toon and Ellis, 1978). The energy of a molecule can be approximated as the sum of three primary components: electronic energy, vibrational energy, and rotational energy, as follows,

\[ E_{\text{Total}} = E_{\text{Elec}} + E_{\text{Vib}} + E_{\text{Rot}}. \]  

(2.21)

Electronic energy refers to the energy derived from electron movement and charged particle interactions within the molecule and accounts for the majority of the total energy within a molecule. Vibrational energy is generally about one tenth of the electronic energy (Sandorfy, 1964). Vibrational energy results from the attractive and repulsive forces generated as atoms within a molecule move toward and away from each other. Finally, rotational energy describes energy associated with the motion of a molecule about its own axis (Toon and Ellis, 1978). This factor may often be one or two orders of magnitude lower than the vibrational energy (Sandorfy, 1964). Note that a component of translational energy also exists. However, this contribution to total energy is relatively insignificant and is often neglected in discussions of molecular energy.

As mentioned in Section 2.3 the energies included in Equation 2.21 are quantized. The distinct electronic configurations that can be attained by a molecule are each associated with several vibrational conditions. Similarly, each vibrational condition may include an array of possible rotational modes. For simplicity, all of these specific conditions are referred to as energy levels. Thus, a molecule may exist at any one of several possible electronic energy levels, each of which is associated with many vibrational energy levels that are subsequently related to a range of rotational energy levels. Figure 2.1 illustrates this cascading distribution of energies for a single electronic energy level, \( S_1 \). If a molecule were to exist at electronic energy level \( S_1 \), then selection of any one of the vibrational levels shown in the figure along with one of its respective rotational levels would constitute a possible energy state. Note that the energy difference between consecutive vibrational energy levels tends to decrease as the energy of the vibrational level increases. The exact opposite phenomenon occurs for the rotational energy levels.
Figure 2.1: Hierarchy of Molecular Energy Contributions for One of Many Possible Electronic Energy Levels.

Electronic energy levels exist in two forms termed electronic states. Electronic states should not be confused with formally defined energy states. An electronic state refers only to the general condition of the electrons in a molecule while an energy state specifically accounts for all of a molecule's energy components. Thus, there are a variety of potential energy states within a given electronic state. It is not uncommon to categorize energy states in association with an electronic state and its set of possible vibrational and rotational sublevels. Thus, for example, Figure 2.1 could be said to illustrate the possible $S_1$ energy states of a molecule.

The two types of electronic states that can be attained by a molecule are referred to as singlet and triplet states. The definitions of these states stem from a quantity called multiplicity, that accounts for the orbital angular momentum of a given electron configuration (Guilbault, 1990). Multiplicity, $M$, is defined by the equation,

$$M = 2S + 1$$  \hspace{1cm} (2.22)
where $S$ is the absolute value of the total spin angular momentum of the molecule, or rephrased, the sum of the spin quantum numbers of all of the electrons in the molecule. In the case of a typical polyatomic molecule that has an even number of electrons with paired spins (that is for every electron with $s = -1/2$ there is also another electron with $s = +1/2$) the value of $S$ is zero resulting in $M = 1$. This is termed the singlet electronic state and is the electronic energy condition maintained by most molecules in their state of lowest energy or ground state. If the spin of a single electron in the molecule is reversed, there will be a set of two unpaired electrons and $S$ will take on a value of one resulting in a multiplicity of three. This is the triplet electronic state (Guilbault, 1990).

The singlet and triplet electronic states can both achieve excited forms under the appropriate conditions. A molecule’s transition to an excited electronic state corresponds to a change in the distribution of electrons among the orbitals of the molecule. Molecules having multiple orbitals may therefore have several possible excited states. These excited electronic states are also characterized by the energy hierarchy described above.

The excitation of a molecule from a singlet to an excited singlet electronic state occurs when a molecule absorbs a photon of light within a particular range of frequencies. Since each electronic energy level of a molecule consists of many vibrational and rotational sublevels, more than one frequency of light is capable of inducing an excited electronic state. The frequency of light required for a specific electronic state transition is simply equal to the difference between the energies of the initial and final states of the transition. This concept is generally expressed using Planck’s relation (Equation 2.2) to determine the energy, $E$, required of the exciting photon, where

$$E = h\nu = E_f - E_i$$

and $E_f$ and $E_i$ are the energies of the final and initial states, respectively. Alterations of the electronic states of molecules require absorption of high energy photons in the visible and ultraviolet regions of the spectrum (Jaffe and Orchin, 1962). The process of light absorption occurs in approximately $10^{-15}$ seconds (Jaffe and Orchin, 1962).

Excitation to a triplet electronic state from the ground state of a molecule (which, as mentioned earlier, is typically a singlet state) is highly unlikely, and has a probability of
occurring that is one millionth of that of a singlet state excitation (Hercules, 1966). As a result, triplet excited states are generally the by product of a process called inter-system crossing from an excited singlet state.

![Jablonski Diagram](image)

**Figure 2.2**: Jablonski Diagram for a Diatomic Molecule (adapted from Guilbault, 1990).

A schematic of the ground and excited states of a molecule can be provided by a Jablonski Diagram. A Jablonski Diagram for a diatomic molecule might look like that pictured in Figure 2.2. Note that the Jablonski diagram is a very simplified illustration of molecular energy conditions, that depicts only electronic states. The actual energy associated with any given electronic state is still subject to variation due to changes in vibrational and rotational sublevels within each electronic state. Thus, for example, the first excited singlet, S₁, illustrated in Figure 2.2 can be viewed as a simplification of the entire image depicted in Figure 2.1.

The combination of all acceptable frequencies of light that may be absorbed by a molecule constitutes its absorption spectrum. An absorption spectrum for benzene is illustrated in Figure 2.3. The spectrum is characterized by somewhat broad peaks that result from the small incremental differences in the energies of the exciting photons capable of
Figure 2.3: Absorption Spectrum for Benzene (Rendell, 1987).

Inducing an electronic transition. At any selected wavelength, the ordinate of the absorption spectrum, referred to as the absorbance, corresponds to the relative probability that the molecule will absorb light of that particular frequency (Rendell, 1987). The likelihood of absorption is related to the probability of the existence of a particular excited state as described in the wavefunctions discussed in Section 2.2. For an atom, which is obviously not subject to molecular vibration or rotation, the absorption spectrum would consist only of a set of lines corresponding to the frequencies required to induce electronic state changes. Note, however, that even the spectral absorption lines of an atom will have some definite width due to atomic collisions, uncertainty in the actual position of the atom during an excited state of finite duration (the Uncertainty Principle), and motion of the atom relative to the observer (Suppan, 1994).

2.5 Competing Mechanisms for Energy Dissipation

Once a molecule is in an excited electronic state, several mechanisms compete to dissipate the energy of the molecule and re-achieve the inherently stable ground state
condition. These mechanisms can be divided into non-radiative and radiative processes. By definition, the radiative processes emit light and lead to the luminescence phenomena. Several of the possible radiative and non-radiative energy dissipation mechanisms of an excited molecule are illustrated in the detailed Jablonski diagram shown in Figure 2.4. These mechanisms are discussed in detail below.

![Jablonski Diagram]

**Figure 2.4:** Competitive Mechanisms of Energy Dissipation in an Excited Molecule.

The energy imparted upon a molecule through the absorption of light of an appropriate frequency will typically lead to the formation of an excited electronic state in which the vibrational and rotational energies are also greater than their potential minimum. The amount of energy converted into emitted light is then determined by the rate constants of competitive mechanisms for dissipating all energy in excess of that characteristic of the ground state. In
liquid solutions, no mechanism is more efficient than thermal relaxation. Within $10^{-13}$ to $10^{-11}$ seconds following light absorption, all vibrational energy in excess of the lowest vibrational level of the excited state will dissipate in the form of heat (Hercules, 1966). This means that if photon emission (radiative energy dissipation) is to occur at all, it will always occur from the lowest vibrational level of an excited electronic state.

The limits placed on radiative mechanisms can often become even more restrictive in molecules that are subject to the process of internal conversion. Internal conversion involves energy dissipation through coupling of the vibrational motions of a high order excited electronic state with the vibrational motions of a lower order excited electronic state. In this situation a molecule excited to the second excited singlet, for example, will most likely lose energy in a non-radiative fashion until it reaches some vibrational level of the first excited singlet. At this point, thermal relaxation will take over and the molecules energy state will decay into the lowest vibrational level of the first excited singlet. Thus, in most molecules, photon emission originates from the lowest vibrational level of the lowest excited singlet regardless of the excited state achieved in the initial absorption process (Hercules, 1966).

Once at the lowest vibrational energy level of the first excited singlet the remaining excess energy of the molecule may result in the emission of a photon. This radiative process, known as fluorescence, can initiate from any of the rotational and translational energies of the lowest vibrational level of the first excited singlet and will return the molecule to any configuration of the vibrational, rotational, and translational levels of its ground state. The energy of the emitted photon will be equivalent to the energy difference between the initial and final states of the molecule, in a manner similar to that described for absorption by Equation 2.23. The variety of potential state transitions involved in the radiative emission process accounts for the broad nature of a fluorescence emission spectrum. In general, each peak of a fluorescence emission spectrum corresponds to one of the vibrational energy levels of a molecule’s ground state (Guilbault, 1990).

It is important to recognize that even when a molecule is in the lowest vibrational condition of the first excited singlet, there is still no guarantee that the remaining excess energy of a molecule will manifest itself as fluorescence. Excess molecular energy characteristic of an excited singlet state can also dissipate through another radiative
mechanism. As discussed in Section 2.3, changes in the spin characteristics of electrons in an excited molecule may induce the process of inter-system crossing, which will populate a triplet excited state of a molecule. Thermal relaxation and internal conversion processes then tend to reduce the energy of the molecule to the lowest vibrational level of the lowest excited triplet. From this point, photon emission may occur leading to the radiative phenomenon termed **phosphorescence** that will return the molecule to some condition in its ground state (Guilbault, 1990).

Collisional and diffusion controlled processes such as quenching and excimer fluorescence can also often affect the nature of the first excited singlet-to-ground state transition that typically leads to fluorescence. The process of quenching involves an electron transfer from an excited molecule (donor) to a quencher (receptor). This results in the formation of an ion pair which dissociates from the donor, leaving the donor in a lower energy state. Aromatic compounds are particularly sensitive to oxygen quenching (Hercules, 1966). Excimer fluorescence occurs when an excited molecule combines with another molecule in the ground state creating atypical energy conditions that can lead to radiative emissions over large regions of the spectrum. This phenomenon is most prevalent in neat or highly concentrated chemical solutions. The intensity of excimer fluorescence is known to increase with the square of the concentration of the fluorescing compound. Excimer fluorescence is know to occur in many aromatic hydrocarbons including the BTEX compounds under investigation in this study (Hercules, 1966).

Fluorescence emission from the first excited singlet is also jeopardized by non-collisional energy losses resulting from vibrational coupling between the excited states of neighboring molecules. Further, to the dismay of the spectroscopist, there are even some cases in which a photon emission destined to be observed as fluorescence may be immediately absorbed by another molecule in a process called inter-molecular radiative energy transfer (Hercules, 1966).

Overall, it is apparent that two key conditions must be satisfied for a molecule to display fluorescence. First, the molecule must be excited by light of a frequency that has considerable probability of being absorbed in accordance with the molecule’s absorption spectrum. Second, the molecule’s rate of radiative decay from the first excited singlet to the
ground state must be competitive with the rates of other radiative and non-radiative energy dissipation processes.

2.6 Interpretation and Application of the Fluorescence Phenomenon

The previous sections of this chapter deal with theory that represents general luminescence phenomena. This section, instead, focuses solely on fluorescence, which is the central subject of this research study.

The absorption and emission processes outlined in Sections 2.4 and 2.5 demonstrate the relationship between the frequencies of incident radiation required for molecular excitation and the resulting frequencies of fluorescence emission. It is apparent that, in general, absorption is representative of an energy transition from a molecule’s ground state to some excited electronic state. However, transitions to the first excited singlet tend to occur with far greater regularity than transitions to any of the higher excited electronic states. Thus the majority of photons absorbed by a molecule possess energies that represent the vibrational spacing of the first excited singlet. Similarly, nearly all photons emitted from a molecule as fluorescence stem from transitions between the lowest vibrational energy level of the first excited singlet and any of the vibrational and rotational energy levels of the molecule’s ground state. Thus, an absorption spectrum serves as a map of the vibrational energy levels of a molecule’s first excited singlet and an emission spectrum similarly illustrates the vibrational structure of the molecule’s ground state (Berlman, 1965). For many compounds, the vibrational structure and frequencies of the ground and excited states are quite similar. Under this circumstance the absorption and emission spectra of many molecules tend to appear as near mirror images of each other. Note that some form of energy loss is involved in all absorption-emission processes. Therefore, the emission spectrum of a molecule is shifted to longer wavelengths than the absorption spectrum. This property is illustrated for anthracene in Figure 2.5 (Rendell, 1987). In this regard, any peaks in a molecule’s fluorescence spectrum that are not mirrored in the molecule’s absorption spectrum must be the result of experimental scatter or impurities in the system (Guilbault, 1990). Note that the point of overlap of the two spectra marks the transition between the lowest vibrational level of the ground state and the lowest vibrational level of the first excited singlet (Jaffe and Orchin, 1962).
Figure 2.5: Absorption and Emission Spectra of Anthracene (Rendell, 1987).

A measure of a molecule's likelihood to display fluorescence when in an excited state is provided by the quantum efficiency or quantum yield of the molecule (Konstantinova-Shlezinger, 1965). The quantum yield, \( \phi_f \), is defined as follows,

\[
\phi_f = \frac{\text{Number of Photons Emitted}}{\text{Number of Photons Absorbed}}.
\]  

(2.24)

Since each absorbed photon excites one molecule, the quantum yield can be interpreted as the fraction of excited molecules that will fluoresce. The quantum yield can, of course, have a maximum value of one. The usefulness of the quantum yield parameter stems from the fact that it is independent of the wavelength of exciting radiation used to induce fluorescence up to some limiting wavelength, \( \lambda_0 \), beyond which \( \phi_f \) drops rapidly to zero. This property of the quantum yield is referred to as Vavilov's Law (Konstantinova-Shlezinger, 1965).

Despite the fact that the quantum yield remains constant over a range of excitation wavelengths, the intensity of fluorescence peaks will still vary with the relative strength of the absorption line corresponding to the wavelength of excitation in use. However, the relative
shape of the peaks is independent of the excitation wavelength since the shape of the emission spectrum is a by-product of the quantum yield.

The quantum yield of a molecule can be used in conjunction with Beer's Law describing the absorption properties of a medium to establish approximate relationships between the concentration of a target medium in a solution and the observed fluorescence intensity from that solution. This procedure is outlined below.

Beer's Law states that the amount of light absorbed by a medium is related to the number of absorbing molecules in the path of the light. This can be formulated as follows,

$$\frac{I_T}{I_0} = 10^{-abc}$$  \hspace{1cm} (2.25)

where $I_0$ is the intensity of the incident light, $I_T$ is the intensity of the transmitted light, $a$ is the absorptivity of the medium, $b$ is the cell length, and $c$ is the concentration of the medium in the path of excitation (Jaffe and Orchin, 1962). One can now assume that all light that is not transmitted must be absorbed. Thus, the intensity of the transmitted light is related to the intensity $I_A$ of the absorbed light by

$$I_T = I_0 - I_A.$$  \hspace{1cm} (2.26)

From Equation 2.24, $I_A$ can be assumed to be proportional to the intensity of fluorescence emission, $I_E$, such that,

$$I_A \propto C \frac{I_E}{\Phi_f}.$$  \hspace{1cm} (2.27)

where $C$ is a proportionality constant used to account for the conversion from photon counts to intensity. Then, substituting Equation 2.26 into Equation 2.25 yields,

$$1 - \frac{I_A}{I_0} = 10^{-abc} \quad \rightarrow \quad I_A = I_0(1 - 10^{-abc})$$  \hspace{1cm} (2.28)
Therefore, relating Equation 2.27 with Equation 2.28 it is apparent that the intensity of fluorescence emission from a solution containing a given medium is proportional to the concentration of that medium in the solution.

As a final note on the interpretation of fluorescence phenomenon it is important to recognize that the intensity of fluorescence emissions decays with time after removing the source of excitation. The emitted intensity can be determined at any time, \( t \), using the following equation,

\[
I(t) = I_0 \, e^{-t/\tau}
\]  

where \( I(t) \) is the fluorescence emission intensity at time \( t \), \( I_0 \) is the intensity during excitation, and \( \tau \) is the mean decay period. The mean decay period is defined as the time, \( t \), at which \( I(t)/I_0 \) is equal to 1/e. The decay period provides a measure of the lifetime of an excited state in a molecule and is inherently related to the structure of the molecule and its susceptibility to competitive mechanisms of energy dissipation. Energy that is absorbed by a molecule will be lost through available energy dissipation mechanisms to return the excited molecule to its ground state. However, each mechanism is associated with a probability of occurrence that dictates its capacity to dissipate energy over time. Thus each energy dissipation can be described by a rate constant. If energy can be dissipated most rapidly in a non-radiative fashion, there will be little opportunity to manifest fluorescence. In contrast, if energy is lost slowly by non radiative mechanisms their will be greater opportunity over time for the energy to dissipate in a manner that will result in observable fluorescence. The relative influence of radiative and non radiative energy dissipation mechanisms tends to vary among chemicals. As a result the fluorescence decay period or lifetime can often be used to help distinguish between different chemical compounds.

Applications of the concepts outlined in this section will be detailed in the discussion of experimental results provided in Chapters 6, 7, and 8.
CHAPTER 3

BACKGROUND

3.1 Introduction

Researchers currently employ three basic techniques for remote in-situ contaminant identification and/or monitoring using optical spectroscopy. These techniques vary considerably in their versatility and include the use of fluorescent tracers, optrodes, and a class of procedures which may be termed direct methods (Kenny et. al., 1987). Fluorescent tracers are generally the least desirable of the three approaches to monitoring since they cannot be used to identify specific contaminants. Tracers merely indicate the potential movement and relative change in concentration of a contaminant over a given region without any direct indication of the contaminant's actual status. In contrast, optrodes are generally chemical-specific devices which make use of often irreversible chemical reactions to indicate the presence and concentration of a contaminant. Optrodes typically require knowledge of the nature of in-situ contamination prior to use and are therefore quite limited in their range of application. The direct methods, which include laser-induced fluorescence (LIF), are by far the most useful tools for contaminant detection and monitoring. When incorporated into in-situ devices, direct optical spectroscopic methods can be used to explore unknown sites and detect or monitor a multiplicity of compounds.

This discussion focuses solely on research efforts concerned with contaminant detection and monitoring using laser-induced fluorescence. Recent research endeavors in this area can generally be divided into two major categories according to the complexity of the contaminated media under investigation. The first category, comprising the majority of existing work, is directed toward the identification and quantification of contaminants in aqueous solutions. The second category targets the complications revealed when contaminants are present in soil environments. Note that chemical detection and monitoring
operations in unsaturated or vadose zone soils can be very complex since contamination may be present in the solid, liquid, and/or gas phase of the porous media.

A great deal of research on laser induced fluorescence is concerned with equipment development and proof-of-concept work (Chudyk et. al., 1985; Hillrichs et. al., 1994; Kenny et. al., 1987; St. Germain et. al., 1993), signal enhancement (Vo-Dihn et. al., 1992), and data handling and correction (Ewald et. al., 1983; Draxler and Lippitsch, 1994). The goal of this study, however, is to utilize laser technology which overcomes many of the disadvantages of existing systems and concentrate on interpreting and understanding the data generated by that technology. As a result, the literature review which follows focuses most heavily upon research which has attempted to explain the effects of media properties on laser-induced fluorescence measurements. The review is prefaced by a brief description of several existing research efforts concerned with remote spectroscopic methods of contaminant identification and monitoring. An outline of existing research results which are pertinent to concerns in the current research program follows; the research results are organized by contaminated media (aqueous solutions and contaminated soils).

3.2 Existing Remote LIF Contaminant Identification and Monitoring Systems

At least eight research groups are presently developing fieldable LIF systems for contaminant identification. To date, four of these groups have actually field tested a sensor, while the other efforts remain at a laboratory development stage. Successful field tests with laser probes have been conducted by the Naval Ocean Systems Center (NOSC) (Apitz et. al., 1992; Lieberman et. al., 1993; Lieberman et. al., 1990; Knowles and Lieberman, 1995; Inman et. al., 1990), the United States Air Force in conjunction with North Dakota State University (NDSU) (Gillispie and St. Germain, 1992; Gillispie et. al., 1993), and Tufts University (Chudyk et. al., 1989; Goldberg, 1989; Lin et. al., 1995). Both the Navy and Air Force/NDSU programs have tested their devices on the United States Army's Site Characterization and Analysis Penetrometer System (SCAPS) which combines the capabilities of a cone penetrometer with a variety of mechanical, geophysical, and optical sensors for subsurface profiling. LIF field tests have also been performed by the German Institute for Experimental Physics (IEP) in Kiel, Germany (Bublitz et. al., 1995; Bublitz and Schade, 1995).
at a variety of sites using a fiber optic sensor and a mobile laboratory. Note that these tests were conducted on samples extracted from the subsurface since the IEP LIF device is not yet configured for subsurface investigations. However, IEP's development of a mobile lab does mark a significant step toward fielding a complete in-situ system. Contaminant detection using LIF is also being pursued by workers at the Denmark Water Quality Institute (WQI) who have constructed a laboratory prototype fluorimeter that is part of a program aimed toward the development of an in-situ instrument (Eisum and Lynggaard-Jensen, 1990). Other LIF based contaminant sensors are at earlier stages of development in the laboratories of the Institute of Atomic Physics (IAP) in Bucharest, Romania (Moise et. al., 1995); the Institute for Physical and Theoretical Chemistry (IPTC) in Braunschweig, Germany (Roch et. al., 1995); and the Institute for Hydrochemistry (IHC) at the Technical University of Munich in Munich, Germany (Kotzick et. al., 1995). All of the systems, with the exception of the IHC and IPTC units, have been used to detect, identify, and quantify contaminants in aqueous solution. At this time, the IHC and IPTC groups have not demonstrated the ability to perform time-resolved spectroscopy techniques required for contaminant identification. The characteristics of each of the above mentioned systems are summarized in Table 3.1. Table 3.1 also indicates the contaminants detected with each system and the nature of the contaminated media studied with each device.

Close inspection of Table 3.1 reveals that the existing LIF systems share several fundamental similarities. Each system makes use of a pulsed laser to permit temporal characterization of the fluorescence phenomenon. The lasers also generally emit radiation at ultra-violet wavelengths where a majority of common soil and groundwater pollutants fluoresce. And, finally, nearly all of the systems utilize some configuration of fiber optic cables to transmit excitation energy and collect specimen emissions. Although not presented in Table 3.1, it is important to note that except for the AF/NDSU, NOSE, and Tufts systems, all of the research groups make use of cleaved fiber optic cables to deliver and collect light. In contrast, the AF/NDSU, NOSE, and Tufts systems excite and collect through a window, generally sapphire or quartz, that lies between the contaminated medium and the fibers. The literature does not indicate if the exciting and/or collected energy is focused in these systems.
Noting these similarities, it is also important to recognize that some systems incorporate significant variations from the norm. For example, second generation devices developed by IEP and Tufts make use of Raman shifters to create multiple excitation wavelengths from a single laser source and in turn obtain additional contaminant characterization information in the form of excitation emission matrices (EEMs). The multiple excitation wavelengths provide further insight into the identity of contaminants by illustrating the characteristics of a compound's absorption spectrum. As discussed in Chapter 2, the amount of fluorescence energy emitted by a compound is directly related through its quantum yield to the amount light that the compound absorbed. Since the amount of light absorbed by a compound varies according to its absorption spectrum, changes in the intensity of observed fluorescence caused by variations of the excitation frequency can be used to characterize the absorption characteristics of contaminants under investigation. This testing technique evolved from laboratory experience that demonstrated a need for additional identification information when attempting to discern individual chemicals in multi-compound mixtures.

Another important system variation apparent in Table 3.1, which may also stem from research experience, is the use of multiple collection fibers to gather specimen emission energy. Both the AF/NDSU and NOSC systems utilize six collection fibers in contrast to the single fiber used by the other groups. Perhaps not coincidentally, among those research groups listed in Table 3.1, the AF/NDSU and NOSC teams have also performed the greatest amount of research to investigate the effects of the soil matrix on in-situ fluorescence measurements, and are therefore most likely to appreciate the benefits of spatial averaging provided by a multifiber collection system. The six collection fibers surround the individual excitation fiber. In this way, the collection fibers gather emission response over a large area, relative to the excitation zone. Further, although not confirmed, the back scattering configuration of this system might enhance performance by permitting light collection in a region that completely surrounds the zone of excitation.

Although some groups have taken significant steps to improve the performance of their sensors, many of the systems listed in Table 3.1 still share several disadvantages which limit their ability to remotely detect and/or identify several common soil and groundwater pollutants, such as the BTEX compounds, which are of primary interest in this study. Since
<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>Laser Type</th>
<th>Emission Wavelength</th>
<th>Pulse Width (Repetition)</th>
<th>Laser Output Power</th>
<th>Delivery/Collection Method</th>
<th>Excitation: Collection Fibers</th>
<th>Detected Contaminants</th>
<th>Detection Limits</th>
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<tr>
<td>AF/NDSU&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Nd:YAG pumped dye laser</td>
<td>266 nm multi UV and visible</td>
<td>5 - 7 ns (10 Hz)</td>
<td>300 µJ</td>
<td>optical fiber</td>
<td>1:6</td>
<td>BTEX PAHs</td>
<td>ppm</td>
<td>aqueous solutions contaminated soils</td>
</tr>
<tr>
<td>WQI&lt;sup&gt;b&lt;/sup&gt;</td>
<td>nitrogen and dye lasers</td>
<td>265 nm selectable 230-900 nm</td>
<td>&lt; 1 ns (N/A)</td>
<td>N/A</td>
<td>optical fiber</td>
<td>-</td>
<td>aromatic compounds</td>
<td>ppm</td>
<td>aqueous solutions</td>
</tr>
<tr>
<td>IPTC&lt;sup&gt;c&lt;/sup&gt;</td>
<td>nitrogen dye laser ion</td>
<td>337 nm 380 nm</td>
<td>500 ps (N/A)</td>
<td>120 µJ</td>
<td>optical fiber</td>
<td>1:1</td>
<td>mineral oil crude oils</td>
<td>ppm</td>
<td>powders alumina, quartz, sand</td>
</tr>
<tr>
<td>NOSC&lt;sup&gt;d&lt;/sup&gt;</td>
<td>nitrogen gas</td>
<td>337 nm</td>
<td>0.8 ns (10 Hz)</td>
<td>1.4 mJ</td>
<td>optical fiber</td>
<td>1:1</td>
<td>heavy fuels PAHs</td>
<td>ppm</td>
<td>aqueous solutions contaminated soils</td>
</tr>
<tr>
<td></td>
<td>nitrogen</td>
<td>337 nm</td>
<td>3 ns (N/A)</td>
<td>300 µJ</td>
<td>optical fiber</td>
<td>1:6</td>
<td>PAHs</td>
<td>N/A</td>
<td>aqueous solutions in sea water</td>
</tr>
<tr>
<td>IAF&lt;sup&gt;e&lt;/sup&gt;</td>
<td>nitrogen</td>
<td>337 nm</td>
<td>700 ps (0.5 - 10 Hz)</td>
<td>150 µJ</td>
<td>optical fiber</td>
<td>1:1</td>
<td>crude oil diesel oil kerosene</td>
<td>ppt</td>
<td>aqueous solutions contaminated soils</td>
</tr>
<tr>
<td>IEP&lt;sup&gt;f&lt;/sup&gt;</td>
<td>nitrogen</td>
<td>337 nm</td>
<td>248 nm 276 nm 317 nm</td>
<td>2 ns (100 Hz)</td>
<td>0.2 mJ</td>
<td>optical fiber</td>
<td>1:1</td>
<td>diesel fuel BTEX PAHs engine oil</td>
<td>ppm ppm</td>
</tr>
<tr>
<td>IHC&lt;sup&gt;g&lt;/sup&gt;</td>
<td>nitrogen</td>
<td>337 nm</td>
<td>N/A</td>
<td>120 µJ</td>
<td>optical fiber</td>
<td>1:1</td>
<td>PAHs</td>
<td>ppb</td>
<td>aqueous solutions</td>
</tr>
<tr>
<td>Tufts&lt;sup&gt;h&lt;/sup&gt;</td>
<td>Nd:YAG</td>
<td>266 nm</td>
<td>4-15 ns (5 Hz)</td>
<td>0.2 mJ</td>
<td>optical fiber</td>
<td>1:1</td>
<td>BTEX aromatics</td>
<td>ppb</td>
<td>aqueous solutions contaminated soils</td>
</tr>
<tr>
<td></td>
<td>Nd:YAG w/ Raman shifter</td>
<td>10 beams 258 - 379 nm</td>
<td>0.2 mJ</td>
<td>optical fiber</td>
<td>1:1</td>
<td>BTEX aromatics</td>
<td>ppb</td>
<td>contaminated soils</td>
<td></td>
</tr>
</tbody>
</table>

a) Gillispie et. al., '92; Gillispie and St. Germain, '93  
b) Eising and Lynggaard-Jensen, '90  
c) Roch et. al., '95  
d) Apitz et. al., '92; Knowles et. al., '95; Inman et. al., '90  
e) Moise et. al., '95  
f) Bublitz et. al., '95; Bublitz and Schade, '95  
g) Kotzick et. al., '95  
h) Chudyk et. al., '95; Goldberg, '89, Kenny et. al., '87

Table 3.1: Existing Remote Spectroscopic Contaminant Identification and Monitoring Systems
the excitation sources of all of the systems outlined in Table 3.1 remain distant from the investigated region in field applications (note that the nitrogen and dye lasers used by the Denmark research group are assumed to be too large for "down-hole" in situ applications), each of these systems must propagate excitation radiation to the target location using fiber optic cable. The ultraviolet excitation is therefore subject to considerable attenuation in the fiber optic cable (on the order of 20 dB for 30 m of fiber) which reduces the fluorescence emission from target compounds and deteriorates the detection capabilities of the system. This problem can become especially significant with the long lengths of fiber optic cable required for deep in situ investigations. Several of the existing fluorescence based systems also have relatively long excitation pulse widths which inhibit the observation of fluorescence decay profiles for short-lived contaminants such as benzene. Finally, many of the existing excitation sources operate at low repetition rates which are not conducive to the benefits of real-time signal averaging. All of these disadvantages are overcome by the laser system used for this testing program which is described in detail in Section 4.3.2.

3.3 Remote Optical Spectroscopy for Aqueous Solutions

Several researchers have demonstrated that contaminants such as PAHs, BTEX compounds, and heavy fuels can be detected in aqueous solutions at part per million levels or less using remote laser induced fluorescence (Apitz et. al., 1992; Chudyk et. al., 1985; Eismum and Lynggaard-Jensen, 1990; Gillispie et. al., 1993; Goldberg, 1989; Kenny et. al., 1987; Bublitz et. al., 1995; Bublitz and Schade, 1995; Kotzick et. al., 1995). Results from these studies have been interpreted in a variety of ways to afford both qualitative and quantitative information about chemicals present in an aqueous solution. Fluorescence results, however, require substantial data handling to harness all available information provided by the phenomenon. This complexity arises from the fact that fluorescence can be characterized by time information in addition to data on fluorescence emission wavelengths and intensities. The fluorescence response of an aqueous solution can be analyzed in varying degrees of detail in accordance with the objectives of a given study.

If a solution contains only one compound and the identity of that compound is known, the area beneath the fluorescence emission wavelength (EW) profile of the solution may be
integrated to yield a total fluorescence signal that can be used to determine the concentration of that chemical in the solution (Goldberg, 1989). The EW profile is simply a plot of time-integrated fluorescence intensity versus emission wavelength. Example plots of total fluorescence signal versus log of concentration are shown in Figure 3.1 for gasoline and phenol in pH = 7 buffered water. Note that the trend illustrated at low concentrations in both plots of Figure 3.1 is quite similar to the exponential increase in signal with log of concentration that would be predicted by Beer’s Law (Chudyk et. al., 1991) as discussed in Chapter 2, Section 2.6.

![Figure 3.1: Relationship between Total Fluorescence Signal and Concentration for Laboratory Tests Performed on Aqueous Solutions of Gasoline and Phenol (Goldberg, 1989).](image)

If a solution contains only one compound and the identity of that compound is unknown, there is a possibility that it can be identified by the shape or form of its EW profile. However, as illustrated in Figure 3.2, the fluorescence emission profiles of many compounds, such as the BTEX compounds which are of interest in the proposed research, tend to overlap and are therefore indistinguishable.

As a result, fluorescence systems must often invoke an additional level of equipment sophistication to make use of fluorescence lifetimes for contaminant identification. The lifetime of a compound is defined as the amount of time required for the fluorescence emission intensity to drop from its maximum to a value of 1/e times the maximum after discontinuing
Figure 3.2: Fluorescence Emission Profiles of the BTEX Compounds Obtained During Early Trials of the MIT/Lincoln Lab LIF Probe.

Excitation. These decay times can be very fast and are often distinctive for a given compound. BTEX compounds, for example, can be easily distinguished on the basis of their fluorescence lifetimes: benzene, 2.4 ns; toluene, 5.3 ns; and p-xylene, 11.9 ns (Gillispie et. al., 1992). Figure 3.3 illustrates the fluorescence decay curve of benzene. Once a compound’s fluorescence lifetime has been determined, the integrated area of the time resolved fluorescence peak at a given emission wavelength can be used as a measure of signal intensity that can then be related to the compound’s concentration in a solution (Chudyk et. al., 1991).

When an absolute fingerprint of a chemical is required for identification, fluorescence emission wavelength-time-intensity profiles (WTIs) can be generated by collecting fluorescence lifetime signatures at a series of selected emission wavelengths (Gillispie and St. Germain, 1992). These plots capture all of the identification information provided by a chemical’s fluorescence response at a fixed excitation frequency. Example WTI profiles for benzene, toluene, and p-xylene are shown in Figure 3.4.

Wavelength-time-intensity profiles can be especially useful when analyzing multi-component solutions. The data contained within a WTI can be selectively processed to create
Figure 3.3: Fluorescence Decay Curve of Benzene Obtained During Early Trials of the MIT/Lincoln Lab LIF Probe.

Figure 3.4: Wavelength-Time Intensity Profiles for Benzene, Toluene, and (p)-Xylene [Intensities in a.u.](Gillispie and St. Germain, 1992).
fluorescence contour plots on a time versus wavelength coordinate system or to generate intensity versus wavelength plots at any time during the fluorescence process. Each of these plots can help isolate fluorescence contributions from individual contaminants in a multi-compound solution. These ideas can be illustrated using an example case originally presented by Gillispe and St. Germain (1992) that is reproduced in Figure 3.5.

Part (a) of Figure 3.5 illustrates a WTI obtained for a mixture of benzene and p-xylene. The WTI for the mixture does little to highlight the individual fluorescence signatures of the two constituent chemicals. However, in Part (b) of Figure 3.5, fluorescence contours plotted from WTIs of benzene, the benzene/p-xylene mixture, and p-xylene illustrate the form of the individual fluorescence responses that contribute to the cumulative response of the benzene/p-xylene mixture. The benzene component contributes most heavily to the mixture's response at wavelengths less than ~272 nm and at early times less than ~20 ns. It is also apparent that p-xylene is responsible for all of the mixture's response at times in excess of ~25 ns. This point is emphasized in Part (c) of Figure 3.5 which shows plots of intensity versus wavelength for the benzene/p-xylene mixture at two separate times: 15 ns and 35 ns. The solid line in the figure is a trace of the fluorescence emission profile of an aqueous solution containing only p-xylene at a time of 35 ns. A comparison of the p-xylene trace with that of the benzene/ p-xylene mixture at 35 ns shows that the two curves are virtually identical, again illustrating that the mixture's response at long times is due almost entirely to p-xylene. Note that interpretation of WTI profile can become far more complex than illustrated in this example as the number of chemicals in a solution increases.

An alternate fluorescence signature that can also be used to identify individual chemicals in multi-compound solutions is that provided by an excitation emission matrix (EEM). Of course an EEM can only be generated by using a LIF system that can produce multiple excitation energies. However, if this technology is available, one can create a three dimensional plot fluorescence intensity as a function of excitation wavelength and emission wavelength. As illustrated for anthracene in Figure 3.6, the EEM of a compound can be very distinct. Note that the broad features in the excitation domain result from the fact that emission wavelength signatures for anthracene were acquired at discrete excitation.
Figure 3.5: Analysis of Wavelength-Time-Intensity Data (Gillispie et al., 1992).
(a) WTI Profile for a Mixture of Benzene and (p)-Xylene.
(b) Intensity Contours from the WTI Profiles of the BX Mixture and its Components.
(c) Emission Profiles at Selected Times for the BX Mixture and its Components.
Figure 3.6: Excitation-Emission Matrix of 62.4 μM Anthracene in Cyclohexane (Lin et. al., 1995).

wavelengths in approximately 15 nm intervals. The actual change in anthracene's fluorescence emission as a function of excitation wavelength is quite smooth.

Although general methods of interpreting and utilizing fluorescence response data have been outlined above, several researchers have indicated that fluorescence results can often be complicated by factors which alter the apparent fluorescence response or fluorescence characteristics of target compounds in solutions. For example, Chudyk et al. (1985) point out that fluorescence signals obtained from aqueous solutions can be severely obscured by scattering of a system’s excitation source, fluorescence from humics in natural waters, and the Raman line of water. While the interference caused by humics can be a very complex problem, difficulties associated with scattering and water line interference can typically be alleviated by using cutoff filters.
Another factor which can interfere with the typical fluorescence response of compounds in solution is fluorescence quenching caused by the presence of oxygen in a solution. Oxygen quenching affects both the intensity and the lifetime of fluorescence emissions. When a solution contains only one compound with fluorescence characteristics and oxygen is the only quenching molecule the ratio of the fluorescence intensity in a deoxygenated solution, \( L_o \), to that in an oxygenated solution, \( L \), is given by,

\[
\frac{L_o}{L} = 1 + \tau k_q [Q']
\]  

(3.1)

where, \( \tau \) is the mean decay time of fluorescence generated in a deoxygenated solution, \( k_q \) is the rate constant for quenching by oxygen, and \( Q' \) is the concentration of dissolved oxygen in the solution solvent (Berman, 1965). Although values of \( L_o/L \) vary for different compounds, the ratio ranges from 1 to 7 for most molecules. Thus the fluorescence intensity of a compound in an oxygenated environment is always less than or equal to that of the compound under deoxygenated conditions. Since quenching effectively reduces the potential occurrence of fluorescence, oxygen quenching also tends to reduce the fluorescence lifetime of compounds. For example, the fluorescence lifetime of naphthalene decreases from 41 ns in deoxygenated solution to 36 ns in air saturated water (Gillispie and St. Germain, 1992; Meidinger et. al., 1993). Note that quenching effects caused by oxygen in aqueous chemical solutions are generally insignificant for BTEX compounds, altering their fluorescence lifetimes by only a fraction of a nanosecond (Meidinger et. al., 1993).

3.4 Remote Optical Spectroscopy for Contaminated Soils

Although others have indicated that chemical saturated soils tend to display spectroscopic responses that are notably different from those of neat or aqueous chemical solutions (for example, Gillispie, et. al., 1993; Moise et. al., 1995; Roch et. al., 1995; Bublitz et. al., 1995; Bublitz and Schade, 1995), investigations of the effects of soil properties on remote fluorescence measurements have only been carried out at the Naval Ocean Systems Center (NOSC) in San Diego, California. The remote spectroscopic system used by the NOSC is outlined in Table 3.1.

Research at the Naval Ocean Systems Center has concentrated on the effect of soil properties on the fluorescence response of pure fuel products in saturated soils. Investigations
have been performed to evaluate the influence of soil type, grain size, specimen thickness, soil moisture and wetting effects, and "specimen aging effects." These studies, however, focused only on the intensity and emission wavelength characteristics of pure fuel product fluorescence. No attempt was made to examine aqueous solutions of contaminants or to evaluate the influence of soil properties on the decay characteristics of contaminants in soils. Unless noted otherwise, all of the experiments performed by the NOSC group to evaluate soil-related factors made use of air-dried soil specimens contaminated with known mass fractions of pure fuel products in quantities lower than necessary to achieve full soil saturation. Each of the influences on fluorescence response investigated at the Naval Ocean Systems Center is discussed individually below.

An investigation of the effects of soil type on the fluorescence intensity emitted by soil specimen contaminated with diesel fuel marine (DFM) revealed that sands generally display greater fluorescence response for a given change in contaminant concentration than clays. This premise is illustrated in Figure 3.7 where the steepest curve applies to sand and the two mildly sloping plots characterize clays (Apitz et. al., 1992). Additional tests performed with mixtures of sand and clay revealed that very small mass fractions of clay (less than 4% total mass) drastically reduced the fluorescence response of contaminated soil mixtures at given concentrations of DFM relative to the sand specimen (see Figure 3.8) (Apitz et. al., 1992).
The effects of grain size were evaluated for both sands and clays by analyzing the fluorescence response of DFM in specimen created from selected grain size ranges of each material. For both materials, the specimen created from the coarsest grains (25-50 mesh) generally displayed the strongest intensity for a given DFM concentration relative to the other particle size ranges; fine particles (140+ mesh) exhibited the mildest response. Note that regardless of the soil type or grain size, experimental measurements indicate that the fluorescence signal of contaminated soils emanates from only the first monolayer of soil grains in contact with the laser system window (Apitz et. al., 1992).

![Graph](image)

**Figure 3.8:** Fluorescence Response of Diesel Fuel Marine in Sand/Clay Mixtures (Apitz et. al., 1992)

Apitz et al. (1992) initially hypothesized that the soil type and grain size effects seen in the above mentioned experiments might be related to the specific surface area (SSA) of the soil particles. However, after normalizing their test data by values of the respective soil SSAs determined by nitrogen gas adsorption, Apitz et. al. (1992) recognized that the SSA values for the tested clays were as much as 350 times greater than those measured for the tested sands. Thus, the differences in SSA were far greater than the differences in observed fluorescence behavior between the various soils and was in effect overcompensating for any impact that soil particle area might have on fluorescence measurements.

Apitz et. al. (1992) then suggested that the soil type and grain size effects seen in the above mentioned experiments might be related to what they term the available surface area
(ASA) of the soils comprising the test specimen. Apitz et al. emphasize that the ASA is very different from the more common soil parameter termed specific surface area (SSA). ASA refers to the surface area of a particle that is actually available for contact by a contaminant, when that contaminant is likely to display more viscous behavior than the nitrogen gas usually used to determine the total surface area of soil particles in a SSA measurement. In essence, contaminants such as diesel fuel marine are likely to span the gaps of particle interstices, thereby providing substantially more contaminant exposure to excitation energy with less contaminant than would be required to fill the interstices and achieve the same effect. At this time there are no laboratory techniques available to measure the ASA of a soil so it is difficult to prove this concept.

However, Apitz et. al. (1992) propose that the concept of an available surface area effect is supported by experimental observations of the effect of water on the fluorescence response of a soil/contaminant system. Experimental evidence demonstrates that the presence of water in a soil/contaminant system tends to magnify the contaminant’s fluorescence response. These effects are most marked in clays but also prevalent in sands. Therefore, Apitz et. al. (1992) suppose that small amounts of water may fill many of the interstices of soil particles if added to a soil prior to contamination, and, over time, may displace contaminants from soil particle interstices if added following contamination. The net effect of closing-off soil particle interstices results in an enhanced contaminant fluorescence response at low specimen water content, which is consistent with the assumed effects of ASA stated by Apitz et. al. (1992). Additional experiments performed by Apitz et. al. (1992), however, show that as the weight percent of water in a soil specimen increases, the fluorescence response of the contaminated soil decreases. In fact, continued addition of water to specimen of varied soil composition but similar contamination ultimately reduces the spread in fluorescence response resulting from differences in soil type (Apitz et. al., 1992).

When contaminated soils are not given access to water, Apitz et al. (1993) suggest that the contaminants may actually soak into the interstices of soil particles. Experiments performed on contaminated soils and their extracts indicated that the fluorescence response of the soils decreased over time by an amount far greater than that displayed by the extracts (Apitz et. al., 1993). In this case, the amount of contaminant visible to a fluorimeter
excitation beam is believed to be reduced over time as the specimen “ages” and the contaminant “migrates” out of view. Note that although extract tests were also performed by Apitz et. al. (1993), the net decline in fluorescence signal attributed to contaminant/soil particle interaction must be assessed carefully since slight variations in handling and specimen storage can influence the manner in which contaminants degrade and volatilize over time.

Although the presence or lack of water in a soil system can, in itself, significantly effect the fluorescence response of contaminated soils, soils that are not fully saturated may often house contaminant vapors which can add to the complexity of any remote investigations based on optical spectroscopy. Chudyk et al. (1991) indicate that contaminants in vapor phase can be detected using laser induced fluorescence at part per million levels. Laboratory experiments conducted using Tuft’s fieldable fluorimeter demonstrated that toluene and xylene can be detected in vapor phase samples created in equilibrium with water. Example fluorescence emission spectra for toluene are presented in Figure 3.9 for various vapor concentrations of the contaminants. The integrated area of the time resolved fluorescence peaks can be used as a measure of signal intensity and thus as an indication of contaminant concentration in the vapor phase (Chudyk et al., 1991). Note that none of these vapor phase experiments involved any soil. Therefore, many questions remain regarding the influence of soil particles on vapor phase contaminant detection in vadose zone soils.

![Fluorescence Emission Spectra of Vapor Phase Toluene](image)

**Figure 3.9:** Fluorescence Emission Spectra of Vapor Phase Toluene (Chudyk et al., 1991).
3.5 Overview

The previous research review was intentionally detailed to emphasize that remote optical spectroscopy offers great potential for in-situ contaminant investigations. Several researchers have demonstrated that contaminants can indeed be detected, identified and quantified in aqueous and soil systems. However, it is also clear from existing research that in-situ fluorescence measurements are extremely sensitive to minor changes in the condition of the material under investigation. The large number of factors that have already been shown to influence in-situ fluorescence measurements of pure chemicals are sure to be of even greater significance as the concentration of a chemical in aqueous solution declines and the effects of the soil matrix begin to mask the distinguishing characteristics of contaminants. It is therefore apparent that reliable in-situ fluorescence measurements will require the use of all available fluorescence information in the intensity, time and wavelength domains to counteract complications associated with the in-situ matrix.

Although recent research efforts have established a large base of soil characteristics that influence fluorescence observations, it is also clear that there are many more issues that must be resolved before remote spectroscopic measurements can become routine engineering practice. There are no significant questions regarding the possibility to induce in-situ contaminant fluorescence. However, there are many questions related to understanding the meaning and significance of in-situ fluorescence measurements. To be practical, remote sensing systems must be easily transferable from one location to another. This constraint establishes the need for calibration of remote monitoring devices, so that a system can be efficiently adapted to the conditions prevalent at any given site. Calibration procedures are ultimately dependent upon an understanding of the effects of in-situ properties on the observations made with the device for contaminant detection and identification.
CHAPTER 4

LABORATORY EQUIPMENT AND TESTING PROCEDURES

4.1 Introduction

Several types of equipment were required to achieve the goals of this project due to the nature of the phenomenon under investigation and the variety of materials targeted for study. Observation of laser induced fluorescence events, which occur on extremely fast time scales, necessitated the use of sophisticated electronics. Further, since the materials investigated in this research effort included both solids, in the form of soil particles, and liquids, in the form of toxic, highly volatile chemicals, increased demands were also imposed on the testing apparatus. The need to accommodate a variety of test specimen, combined with a desire to carry out multiple testing scenarios, mandated that all mechanical devices be designed in a flexible, yet robust fashion.

The apparatus developed for this study can be divided into three primary groups, each of which has several sub-components. The first equipment unit is termed the specimen testing apparatus. This assembly is designed to provide a controlled testing environment for fluorescence investigations of a variety of specimens. The second experimental system comprises spectroscopic hardware used to induce and observe fluorescence. The last of the primary equipment groups includes all components required for data acquisition and experiment automation.

Each sub-component of the three testing systems is described individually in the following pages. This discussion is followed by an explanation of the testing procedures which simultaneously utilize all three equipment systems. The chapter concludes with brief descriptions of automation software and data handling procedures.
4.2 Specimen Testing Apparatus

4.2.1 Introduction

Two different specimen testing devices were utilized in this study. The first device is simple in design and reserved solely for analysis of liquid specimens under no-flow conditions. For the purpose of this discussion, this device will be referred to as the liquid test cell. The second device is more complex and versatile. It is used to investigate chemical fluorescence in the presence of soils and is referred to as the soil testing apparatus. Each testing unit is described in detail below.

4.2.2 Liquid Test Cell

The liquid test cell provides a simple and efficient means of evaluating the fluorescence of neat and aqueous chemical solutions. The device was designed with several criterion in mind. It had to be small to minimize the volume of waste generated during testing, sealed to prevent contaminant volatilization, easy to clean, and most importantly, capable of being coupled to the laser probe. (Note that the laser probe is described in detail in Section 4.3.2). The device, illustrated in Figure 4.1, consists of a small rectangular stainless steel block clamp that is placed around the probe containing the fiber-coupled laser. The test medium is placed

![Diagram of liquid test cell]

Figure 4.1: Liquid Test Cell
Figure 4.2: Schematic of the Soil Testing Apparatus.
in a cylindrical hole in the clamp located directly above the laser output window of the probe. The hole contains approximately 1.5 cm$^3$ of solution. To prevent specimen loss through leaks around the probe/clamp interface, a Teflon gasket is placed between the clamp and the laser probe. Volatilization of the test medium from the top of the unit is prevented using a stainless steel cap and fluorocarbon rubber o-ring.

4.2.3 Soil Testing Apparatus

The soil testing apparatus addresses the goals of this research program through a flexible design that includes three components: a specimen chamber; a contaminant reservoir system; and a contaminant flow control system. A schematic illustration of this setup is provided in Figure 4.2. Each component adds specific capabilities to the system as a whole and is discussed individually.

4.2.3.1 Specimen Chamber

The specimen chamber was designed in accordance with criteria similar to those established for the liquid test cell. The capability to couple with the laser probe was again of great importance, as well as the need to prevent contaminant losses, minimize waste, and facilitate cleaning. However, unlike the liquid test cell, the specimen chamber also had to meet the specific needs of soil testing. It had to accommodate the non uniform end conditions of soil specimens and permit specimen saturation and/or the flow of liquids through test specimens without loss or disruption of soil particles. The chamber also had to be large enough to permit soil specimen preparation using techniques such as pluviation and under compaction.

The specimen chamber designed to meet the above mentioned criteria is a cylindrical stainless steel vessel that can house a liquid, dry soil, or wet soil specimen (see Figure 4.3). The chamber holds a cylindrical specimen that is 2.54 cm in diameter. Holes extend through the end caps of the specimen chamber (see Figure 4.4) to permit liquid flow through the test specimen if desired. Each end of the test specimen is placed in contact with a porous metal disc that facilitates dispersion of liquid flow across the entire area of the test specimen from one end of the chamber to the other. Stainless steel springs are used to ensure contact
between the porous discs and the soil specimen. Fluorocarbon rubber o-ring seals located on each end cap ensure that there is no leakage from the specimen chamber.

**Figure 4.3:** Specimen Chamber

**Figure 4.4:** Specimen Chamber End Caps

**Figure 4.5:** Coupling of the Laser Probe with the Specimen Chamber.
The specimen chamber also has a circular arc indentation machined perpendicular to its long axis. This indentation allows the chamber to be coupled with a probe containing a fiber-optic laser system (see Figure 4.5). This transverse mounting configuration brings the sapphire laser window of the probe in contact with the specimen contained inside the test chamber. The integrity of the connection between the probe and the test chamber is maintained with a block clamp and a Teflon gasket.

4.2.3.2 Contaminant Reservoir System

Water and aqueous solutions of contaminants are stored in four reservoir units. Each unit consists of a sealed stainless steel beaker containing a Teflon bag (see Figure 4.6). The reservoir unit has two access ports; one inlet to the space between the exterior of the Teflon bag and the interior of the steel beaker, and one outlet from the interior of the Teflon bag. Liquids are contained within the Teflon bag and either forced or drawn out of the bag outlet while the interior of the steel beaker is pressurized with air. The reservoir units have a pressure capacity of 5 atm. Each of the four reservoir units may contain a different contaminant solution or simply clean water that can be directed through the specimen.

Figure 4.6: Contaminant Reservoir
chamber. The outlets of all four units are linked, through a valve manifold, to the inlet end of the specimen chamber. A sampling port is located along the path from the reservoirs to the specimen chamber to monitor input chemical concentrations. The air pressure within the steel beakers is controlled with a pressure regulator and monitored with a pressure transducer and dial gage.

4.2.3.3 Flow Control System

The principal component of the flow control system is a MIT designed pressure volume controller (PV controller). This device is essentially a piston within a cylinder that is actuated by a DC analog motor (see Figure 4.7). For this particular application, the piston and cylinder are made of stainless steel. The piston/cylinder unit is connected to the outlet port of the specimen chamber and can be used to induce flow through the test specimen. Liquid may be drawn through the test specimen from the reservoirs or liquid contained in the cylinder of the pressure volume controller may be pushed through the test specimen.

![Diagram of MIT Pressure Volume Controller](image)

**Figure 4.7: MIT Pressure Volume Controller**

The pressure volume controller is used in conjunction with an electronic control unit that regulates the voltage provided to the PV controller’s DC analog motor. The electronic
control unit therefore determines the speed and direction of piston movement on the pressure volume controller. The flow control system, which includes the PV controller and the electronic control unit, can be operated in either of two modes to regulate flow through a test specimen irrespective of the flow direction.

In the first approach, termed an analog feedback mode, the flow control system can be used to maintain a constant hydraulic head difference across the test specimen. Once a constant air pressure is applied to the reservoir tanks at the inlet end of the test chamber, the PV controller can be used to maintain a constant pressure (different from the inlet pressure) at the outlet end of the test chamber. This is achieved through the use of an analog feedback control loop involving the electronic control unit, the PV controller, and a pressure transducer placed between the outlet of the PV controller and the outlet of the test chamber. The user selects a specific pressure transducer reading that serves as a target for the control system. Deviations from this selected setting are then monitored by the electronic control unit. Based on the magnitude of the difference between the measured and desired transducer readings, the electronic control unit alters the voltage sent to the motor on the pressure volume controller. In this way, the electronic control unit actuates the PV controller’s piston to maintain the selected pressure at the test chamber outlet.

In the second operational mode of the flow control system, the piston of the PV controller can be moved at a constant velocity under open loop motor control. In this scenario, based on a user selected setting, the electronic control unit simply sends a constant voltage to the DC motor on the PV controller. Under this control method, fluid can be drawn out of the test chamber outlet while a constant pressure is simultaneously applied at the inlet end of the test chamber by the reservoir system. This scenario can also be performed in reverse by forcing fluid through the test specimen with the piston of the pressure volume controller. Pushing fluid through the test specimen with a single pressure volume controller does however limit one’s ability to test with multiple fluids.

The pressure volume controller is capable of displacing up to \( \sim 115 \text{ cm}^3 \) of fluid in a single stroke. This volume translates into as many as 8 to 30 pore volumes of fluid for a typical soil test specimen depending on the specimen length and void ratio. The pressure volume controller can generate pressures in excess of 60 atm. However, it is important to
recognize that the pressure capacity of the tubing and contaminant reservoirs (∼ 5 atm) used in the overall soil testing apparatus limit the safe operating conditions of the system as a whole.

4.2.3.4 Operation of the Soil Testing Apparatus

The overall soil testing apparatus outlined above can be used to evaluate a wide range of issues associated with the subsurface performance of an optical spectroscopy contaminant monitoring system. The test chamber can hold both liquids, and soils of varying type and grain size. The accompanying flow control system can be used to saturate any soil test specimen. In addition, the multiple reservoir system permits an analysis of fluorescence signals as a function of aqueous concentration. An added advantage of the multiple reservoir system is that the concentration of contaminants in the pore fluid of a soil specimen can be altered without changing the geometry of the soil mass. Finally, when combined with the multiple reservoir system, the flow control system can be used to simulate remediation processes by periodically changing the concentration of contaminants that flow through the test chamber. (Note that, for user safety, all testing equipment is contained in a chemical fume hood rated to draw a minimum of ∼ 3 m³/min of air).

4.3 Spectroscopic Hardware

4.3.1 Introduction

The spectroscopic system includes all of the devices necessary to induce and observe fluorescence. The fluorescence phenomenon is excited in target media using a fiber-coupled microchip laser system designed at MIT Lincoln Laboratory. Fluorescence emissions from test media are directed through a fiber optic cable to a CVI CM110 1/8 Meter Monochromator for spectral analysis. Light entering the monochromator is observed using two Hamamatsu H-5783-03 photosensor modules that include both a photomultiplier tube (PMT) and regulated high voltage power supply. Operation of the entire spectroscopic system is outlined below.
4.3.2 System Overview

Operation of the spectroscopic system can best be described by tracing the path of excitation and emission radiation through all of the system's components.

A fluorescence measurement is initiated by generating excitation energy. In this system excitation energy is first developed by converting electrical power to 808 nm radiation using an SDL Incorporated Model 2372-P3 laser diode pump based on semiconductor technology. Power for the diode pump is provided by a Light Control Instruments (LCI) Model 560 Laser Diode Driver that supplies the diode with a current of 2780 mA. The operating temperature of the diode is optimized using a large heat sink and a resistance based LCI Model 350 Temperature Controller (operative setting ~ 16 kΩ). The 808 nm radiation is coupled into a fiber optic cable and directed to a microchip laser unit housed in what is termed the laser probe.

The microchip laser probe was developed entirely at MIT Lincoln Laboratory. The probe itself actually consists of a microchip laser housed within a stainless steel cylinder intended to simulate a section of a standard geotechnical exploration device called a piezocone. The laser is coupled to the housing with a threaded fitting that contains a sapphire window and a UV silica focusing optic. A schematic of the internal laser optics and the probe housing is provided in Figure 4.8. The 808 nm radiation from the diode pump is used to

![Figure 4.8: Schematic of Laser Probe Optics and Housing](image)
pump a Neodymium: Chromium: Yttrium Aluminum Garnet (Nd:Cr:YAG) microchip laser in the probe that generates 1064 nm radiation. Light from the microchip laser is directed at two nonlinear, frequency-doubling crystals, KTP (Potassium Titanyl Phosphate) and BBO (Beta Barium Borate), to produce second and fourth harmonics of the incident beam at 532 nm and 266 nm. The laser operating principle is outlined in Figure 4.9. The laser is passively Q-switched and provides 200 picosecond light pulses at a repetition rate up to 6 to 8 kHz. After exiting the laser, the light beam is directed onto a filter that redirects the ultraviolet component of the beam (as well as ~10% of the 532 nm and 1064 nm radiation) out the probe’s sapphire window. Fluorescence emission excited in the target medium is then gathered through the sapphire window and imaged onto the tip of a 550 μm core silica return fiber.

![Figure 4.9: Microchip Laser Operating Principle](image)

The return fiber from the probe carries the fluorescence emission to a set of fiber coupled f number matching optics located at the entrance slit of a CVI CM110 1/8 meter scanning monochromator. The CM110 is characterized by an f/3.3 aperture and can accommodate two diffraction gratings on one dual grating turret. This research made use of a 2400 g/mm grating blazed at 250 nm that provided a maximum resolution of 0.2 nm.
The path followed by the fluorescence emission through the monochromator is pictured in Figure 4.10. Fluorescence emission that enters the monochromator is aimed at a UV silica beam splitter designed to send approximately 4 to 8% of the incident light to a PMT mounted perpendicular to the direction of the entering beam. This PMT is used to establish a trigger signal that prepares the data acquisition equipment for an upcoming signal from the detection PMT. The remaining \(\sim 90\%\) of the beam falls on a convex mirror with a 110 mm focal length and is then directed onto the monochromator's diffraction grating. Upon incidence with the grating, the beam is diffracted and a specific wavelength of light, \(\lambda\), is directed onto another equivalently sized convex mirror. The wavelength of the light leaving the grating is defined according to the Grating Law (Colthup, Daly, Wiberly, 1964) as follows,

\[
\lambda = d \left( \sin i \pm \sin r \right) / m
\]  

(4.1)
where \( m = 1, 2, 3, \ldots \) = the order of the spectra, 
\( i = \) the angle of incidence, 
\( r = \) the angle of reflectance or diffraction, 
\( d = \) the distance between grating grooves, and

the two trigonometric functions in Equation 4.1 are summed when \( i \) and \( r \) are on the same side of the grating normal, while their difference applies when \( i \) and \( r \) are on opposite sides of the grating normal as defined in Figure 4.11.

![Blaze Normal](image)

**Figure 4.11:** Definition of Terms for the Grating Law.

The theoretically monochromatic light leaving the grating (in reality there is some finite dispersion) and reflecting off the second convex mirror is incident upon one final bending mirror before being directed out the exit slit of the monochromator onto a second PMT used for signal detection. Both the trigger PMT and the detection PMT are mounted to the monochromator using custom light tight mounts that eliminate stray light.

Each PMT in the system is a Hamamatsu H5783-03 photosensor module as stated earlier. This model of PMT operates over a supply range of 250V to 1000V DC and is characterized by a radiant sensitivity of 21 \( \mu \)A/nW, a dark current of 0.5 nA, and a rise time of 0.65 ns (when operated at 800V). The PMT makes use of the photoelectric effect to convert light energy into electrical energy. This concept is illustrated in Figure 4.12. A potential is
set up across the cathode and anode of the photomultiplier tube by the supply (control) voltage. When a photon activates the cathode of the PMT, a photoelectron leaves the cathode and traverses the dynodes of the PMT resulting in a current at the anode. Each dynode releases many photoelectrons for each impacting photoelectron in a cascading fashion and thus provides gain. Current for the dynodes is provided by a bias network linked to the power supply, thus the gain across the tube is a direct function of the supply potential. The current through the tube can be monitored using a load resistor. The resulting voltage serves as a signal that can be observed by the data acquisition system.

4.4 Data Acquisition System

4.4.1 Introduction

There are several means of acquiring data to characterize fluorescence phenomenon. The choice of the collection method depends on the intended use of the data. The experimental setup utilized for this study provides three different data acquisition options: (1) data may be acquired using an MIT constructed 22 bit AD1170 analog to digital converter
linked directly to the detection PMT; (2) a Stanford Research Model SR430 Multichannel
Scaler Averager may be used to acquire and store PMT signals directly to a personal
computer file; or (3) a LeCroy 9362 1.5 GHz 10 GSa/s Oscilloscope can be used to capture
fluorescence signals and store them on floppy diskette. Each device has specific advantages
that make it useful for acquiring different aspects of the fluorescence phenomenon. However,
all of these techniques depend on an Excel PLUS 486 personal computer equipped with four
serial communication ports to control equipment operation and data handling. The following
sections detail the attributes and operational details of each data collection method.

4.4.2 AD1170 Data Acquisition Card

In one variation of the fluorescence experiments performed in this study, high signal to
noise ratio measurements of fluorescence emission-wavelength profiles were obtained using an
Analog Devices model AD1170 twenty-two bit analog to digital converter (ADC). The ADC
is an integral part of an eight channel data acquisition card designed in the MIT Geotechnical
Laboratory by Dr. Thomas Sheahan in 1991. The data acquisition card is used by placing it in
one of the expansion slots of a standard DOS compatible personal computer, and can be
accessed through a user configured input/output address. During experiments performed using
the AD1170, fluorescence emission from target media is analyzed through the scanning
monochromator at selected points over some emission wavelength range. At each
measurement point, corresponding to a specific emission wavelength, the monochromator
maintains its wavelength position while the signal from the detection PMT is directed to the
input of the ADC and integrated over a period of 300 ms. This integration period provides a
measure of the average PMT signal over 3000 laser pulses. The high degree of averaging
provided by the AD1170 helps eliminate anomalies in the signal and provides a more reliable
and repeatable representation of the test media’s emission wavelength profile. The
fluorescence intensity measurements acquired at each selected wavelength of an emission scan
are stored in a file on a personal computer that controls the scanning monochromator as well
as the data acquisition card. Note that the data acquisition technique does not provide any
insight into the fluorescence decay characteristics of the test materials.
4.4.3 LeCroy 9362 Digital Storage Oscilloscope

A LeCroy 9362 1.5 GHz digital storage oscilloscope was incorporated into the data acquisition system used in this testing program to obtain fluorescence decay data, and in turn, allow a thorough characterization of the fluorescence signatures of test media. The oscilloscope is capable of capturing up to 10 GSa/s on a single channel and can therefore provide many data points on the fluorescence decay curves of even the most rapidly decaying compounds studied in the program. Due to the high repetition rate of the laser used to excite fluorescence in test media, and the short duration of fluorescence decay phenomenon, data acquisition using the oscilloscope is synchronized with the laser excitation pulse to maximize data collection efficiency. The oscilloscope is operated in a single-shot mode that acquires fluorescence information from a detection PMT for a user specified duration ranging from 2 ns to 10000 seconds following a trigger signal provided by a trigger PMT.

The scope can acquire a fluorescence decay curve with 10 ps time resolution for time intervals up to 200 μs. Input signals from the detection PMT are digitized using an 8 bit ADC that provides ~ 0.08 mV resolution when the scope is operated at its most sensitive voltage setting of 2 mV/division. PMT output current directed to the scope’s primary detection channel is monitored across a 50Ω load to minimize time distortion of the incoming signal. The scope can average the signal versus time traces generated by up to 1000 trigger events. Thus, when the scope is used to observe fluorescence phenomenon, the fluorescence emission from up to 1000 laser pulses can be averaged for any given measurement. In a typical scanning scenario, a personal computer is used to adjust the position of the monochromator grating and to control the oscilloscope’s acquisition characteristics. Data acquired with the scope is stored directly on a 1.44 Megabyte 3.5” diskette located on-board the oscilloscope.

Although the LeCroy 9362 provides excellent decay time measurements for fluorescing compounds, its limited averaging capability and inability to limit the effects of noise make it difficult to use to detect the infrequent, low voltage fluorescence signals characteristic of low concentrations of test compounds.
4.4.4 SR430 Multichannel Scaler Averager

A Stanford Research model SR430 multichannel scaler averager was used during this study to capture fluorescence signals from specimen containing very low concentrations of target compounds. The scaler averager was configured as a photon counter to detect PMT signals emanating from infrequent fluorescence events characteristic of sub-ppm contaminant concentrations. In this mode, the scaler averager is used to observe signals from the fluorescence detection PMT for a minimum of ~ 5.3 μs and a maximum of ~340 s following a trigger signal from the trigger PMT. Thus, data acquisition using the SR430 may be limited in duration and synchronized with laser excitation in a manner similar to that described for the digital storage oscilloscope. However, for the SR430, the observed signal is not simply digitized for a finite time after triggering. Instead, the incoming signal is directed to a discriminator that compares the signal magnitude with a user selected voltage threshold during each of numerous time bins used to divide the observation period. There is no dead time between these time bins so no signal information is lost. The time bins may be from 5 ns to 10.5 ms in duration. Signal pulse pair resolution within a given time bin is 10 ns. The SR430 counts, as events, input signal pulses within a given time bin whose absolute value exceeds the absolute value of the threshold. The SR430 requires a minimum input pulse amplitude of 10 mV which is greater than the PMT response associated with a single photon impact. Therefore, to achieve single photon counting capability, all detection PMT signals go through a Stanford Research model SR445 fast preamplifier prior to entering the SR430. The amplifier is characterized by a 300 MHz bandwidth and 1.2 ns rise and fall times. The amplifiers operational speed, although slower than the PMT, helps preserve the time characteristics of fluorescence detection signals while achieving the signal input requirements of the photon counter.

When acquiring data with the SR430, a record is stored to keep track of the total number of events counted in each bin following a given trigger signal. Each acceptable trigger begins a new record. The SR430 will ignore all trigger signals while completing a count for a given record. Bin counts for up to 65536 records may be accumulated and stored to an on-board floppy disk or to a file on the personal computer used to control the SR430. When used in conjunction with the scanning monochromator, accumulated records of fluorescence
signal observations can be recorded at selected wavelengths over a scanned range. This activity can be carried out under complete computer control using a DOS compatible PC.

The discriminator based acquisition technique used by the SR430 provides a useful method to eliminate background noise from collected data, which is particularly important for low level infrequent signal detection. For example, if the discriminator threshold is set to the signal magnitude expected from a single photon, all signals received below that threshold will be ignored thereby eliminating potentially misleading information. This is especially useful to eliminate signals generated by PMT dark currents which are generally smaller in magnitude than the signals associated with the detection of a single photon. However, it is important to recognize that any signal in excess of the threshold will be counted as a single event. Thus, with a threshold setting characteristic of a single photon, one would be unable to distinguish the arrival of a single photon from that of say two or three photons arriving in a time period shorter than the pulse pair resolution of the device. This limitation implies that one must run several scans of a test specimen at different threshold levels to determine the actual number of photons arriving as a function of time, and thus provide even an approximate definition of the fluorescence decay characteristics of a compound. When this concept is combined with the fact that the counter also discretizes decay information into minimum intervals of 5 ns, which is a considerable fraction of most decay lifetimes, it is apparent that the photon counter is more useful for detect/\textit{n} \textit{n}-detect applications than quantitative analyses of contaminant concentrations.

4.5 General Testing Procedures

The laboratory equipment described previously was used to perform two basic classes of tests. Tests were carried out to investigate (1) the fluorescence properties of neat and aqueous solutions under no-flow conditions and (2) the fluorescence signatures of chemicals and solutions in the presence of soils with and without flow. Each of these experiments had several variations to evaluate specific specimen properties, however only the general test procedures followed for each test class will be described here. Any alterations of the general methods are discussed in conjunction with specific test results. The following sections individually detail the fundamental procedures of the three test classes.
4.5.1 No-flow Solution Tests in the Liquid Test Cell

The following steps outline the procedure for LIF tests performed on neat and aqueous solutions using the liquid test cell.

1. Clean the laser window, liquid test cell, and Teflon gasket using ethanol, then rinse all components thoroughly using distilled demineralized water.

2. Prepare desired chemical solution in accordance with the techniques outlined in Section 5.3.1 of Chapter 5. (remember to use hazardous chemicals only within a certified chemical fume hood).

3. Place prepared solution in liquid cell and close cell being sure to overfill the chamber so that no head space exists after tightening the threaded cap.

4. Turn on the LASER IN USE sign to alert all lab personnel that a test is in progress.

5. Turn on the central control computer, the laser modulation computer, the spectrometer, the PMT power supply, power and signal monitoring voltimeters, and all data acquisition equipment required for the particular test (i.e. oscilloscope and/or photon counter and amplifier).

6. Check the power supply to the trigger and detection PMTs. The trigger PMT should run at a control voltage of 500 V and the detection PMT should operate at 800 to 900 V.

7. Using the code TEST.bas on the control computer check the position of the spectrometer grating to ensure that it is not located on or near (+ 2 nm) any of the laser line harmonics (266 nm, 532 nm, 1064 nm) or the diode laser line (808 nm).

8. Prepare the data acquisition instruments for the test:

   For the oscilloscope:
   a. Check to ensure that the trigger PMT is connected to Channel 2 and the detection PMT is connected to Channel 1.
   b. Check for 50 Ω coupling on both scope channels.
   c. Set trigger mode to falling edge.
   d. Set trigger channel to 2 and select trigger level [− 300mV].
   e. Define storage trace as average of detection channel readings.
   f. Select number of points used to digitize storage trace.
   g. Select number of traces used to create average trace.
   h. Direct waveform storage to floppy diskette in ASCII spreadsheet format.
For the photon counter:
   a. Check to ensure that the trigger PMT is connected to the trigger input (10 kΩ) and the detection PMT is connected to the signal input (50Ω).
   b. Select a time bin width for counting.
   c. Choose the number of bins collected per trigger (bins/record).
   d. Choose the number of triggers evaluated (records/scan).
   e. Select the trigger level [-1.6 mV] and mode [falling edge].
   f. Select the discriminator level.

For the AD1170:
   a. Select the desired bit precision.
   b. Choose the measurement integration time.

9. Turn on the laser diode temperature controller: Push the POWER rocker switch and then push the OUTPUT button.

10. Turn on the laser diode driver: Push the POWER rocker switch, turn the ENABLE key clockwise, and then push the OUTPUT button.

WARNING!!!! - The laser may now be active!

11. If the diode laser is to be modulated externally, select and run the desired modulation code on the modulation computer (Codes are discussed in Section 4.6 of this Chapter).

12. Using the code TEST.bas on the control computer select a data acquisition option and initiate the test.

At the conclusion of a test always remember to TURN OFF the LASER and PMT POWER SUPPLY before disassembling or handling any of the equipment.

* When turning off the laser first turn off the diode laser driver - toggle the OUTPUT button off, turn the ENABLE key counter clockwise to the off position, and push the POWER rocker switch to the off position - then turn off the laser diode temperature controller - toggle the OUTPUT button off and push the POWER rocker switch to the off position.

4.5.2 Soil Tests With and Without Flow in the Soil Testing Apparatus

Tests that investigated the effects of soil properties on the fluorescence signatures of contaminants were performed in the soil testing apparatus. No flow tests were conducted by closing off the ends of the soil chamber after bringing the soil specimen to a desired water
content and contaminant concentration. Tests involving flow incorporated the contaminant
reservoir and flow control systems discussed in Sections 4.2.3.2 and 4.2.3.3, respectively.
The procedure provided below outlines the actions required to perform tests using the soil
apparatus and flow system. Due to the similarities between all tests in this study occasional
reference is made to previously described procedures.

1. Clean the laser window, the specimen chamber and its end caps, and the Teflon
gasket using ethanol and then rinse all components thoroughly using distilled
demineralized water.

2. Disassemble, clean, and reassemble the pressure volume controller.

3. Disassemble the reservoir unit(s), clean the Teflon contaminant bags, and
reassemble the units.

4. Flush all flow lines with distilled demineralized water.

5. Prepare the soil chamber for specimen preparation:
   a. Thoroughly clean all components.
   b. Place a stainless steel spring in the bottom end cap.
   c. Place a porous stone on top of the end cap.
   d. Secure the end cap to the soil chamber.
   e. Mate the laser probe to the soil chamber using the Teflon gasket and two
      block clamps. Be sure to align the laser window with the opening in the soil
      chamber.
   f. Position the soil chamber and laser probe on the test stand for specimen
      formation.

6. Create the soil specimen using the method appropriate for the soil type as
described in Section 5.3 of Chapter 5.

7. Trim the end of the soil specimen flush with the end of the soil chamber.

8. Secure the second end cap with a spring and porous stone on the end of the
specimen chamber.

9. If running a dry soil test or a test at a pre-prepared water content close off the
end caps of the specimen chamber and SKIP TO STEP 17.

10. Prepare a chemical solution for testing in accordance with the techniques
outlined in Section 5.3.1 of Chapter 5.
11. Fill the Teflon reservoir bag with approximately 500 ml of the contaminant solution.

12. Connect all flow lines between the reservoir unit and the soil chamber.

13. With the pressure volume controller outlet open, increase the air pressure in the reservoir unit until contaminant solution flows through the specimen.

14. Once flow is visible at the outlet of the specimen chamber, close the pressure volume controller outlet and increase the air pressure to 4 ksc to saturate the specimen - leave for 8 hours.

15. If desired, perform test under no-flow conditions, close off the specimen chamber and SKIP TO STEP 17.

16. To begin flow turn on the flow control unit and adjust the drive potentiometer to achieve a desired piston velocity on the pressure volume controller and thus provide a constant flow velocity through the soil. (OPTION: analog feedback can be used to maintain conditions of constant gradient across specimen).

17. See steps 4 through 12 of Section 4.5.1.

4.6 Automation Software

The experiments carried out for this testing program were performed under computer control. Two computers were used to automate test progress and data acquisition. One computer was dedicated to external modulation of the diode laser and another was responsible for spectrometer control and data acquisition. These machines made use of software written in Quick BASIC to perform their respective tasks.

4.6.1 Laser Modulation

For some tests performed during this program the diode laser was externally modulated using a program called PULSE.bas. This program was run as an executable file on a 386 IBM Model 50 PS/2 personal computer. The code PULSE.bas, that is provided in Appendix A, was used in conjunction with the LCI Laser Diode Driver to control the current supplied to the laser diode and thereby regulate the diode’s repetition rate (or modulation). The diode lases at a current threshold of approximately 2780 mA. When this current is
supplied continuously to the diode, the diode will lase with a repetition rate ranging from approximately 6 to 8 kHz. Unfortunately, due primarily to temperature fluctuations in the diode cavity, the diode does not modulate consistently at these high repetition rates under conditions of constant current supply. Therefore, the current supplied to the diode by the laser diode driver was lowered to 2710 mA, a value slightly less than the diode lasing threshold of ~2780 mA, and the current was periodically driven over threshold under computer control. The lasing current was achieved by directing TTL signal pulses from one of the datalines of the PS/2’s parallel communications interface to the external modulation port of the diode driver. In this way, TTL logic “high” signals were used to supply additional current to the diode and in turn cause the diode to lase. The TTL signals were derived from the binary decomposition of decimal numbers sent out the PS/2’s parallel port. The code PULSE.bas repeatedly sends decimal values out the parallel address that alternate between logic high (1) and logic low (0) at a rate that the user can alter to modulate the laser over a range of frequencies from approximately 100 Hz to 1.6 kHz. Note that the upper bound on this modulation capability is solely a by product of the computer communication speed. Theoretically the computer could be used to modulate the diode up to its maximum natural rate of 6 to 8 kHz, although temperature effects would again have a negative influence.

4.6.2 Spectrometer Control and Data Acquisition

Overall testing activities were controlled using a code called TEST.bas. This software was run as an executable file on a Model 486 EXCELPLUS IBM compatible personal computer. The code provides an interface to the spectrometer, the AD1170 data acquisition card, the LeCroy 9362 oscilloscope, and the Stanford Research SR430 photon counter. The sophistication of experiments that can be controlled using TEST.bas varies and the user is provided with six different testing options. The code can be used to perform the following tasks:

- Reposition the spectrometer grating
- Monitor PMT signals on the AD1170 at a single monochromator position over time
- Scan across a wavelength range and monitor PMT signals on the AD1170
- Scan across a wavelength range and monitor PMT signals with the photon counter
• Scan across a wavelength range and monitor PMT signal amplitude and temporal characteristics on the oscilloscope
• Scan across a wavelength range and monitor PMT signals on both the photon counter and the oscilloscope

All of these options are achieved through a series of subroutines in TEST.bas that segment the experimental tasks. One subroutine is used to move the spectrometer grating and additional subroutines are used to acquire data with each device required to execute the test option selected by the user. These action subroutines are linked in the code through delay loops and timing statements to provide an array of measurement options. Additional subroutines are used to enhance the user interface by providing on-screen menus, opportunities to characterize data files, and continuous on-screen updates of test progress. When using the AD1170 or the photon counter, data acquired during a test is processed by the host personal computer and stored to a file on the hard drive. Data acquired using the oscilloscope is stored, unprocessed, to a 3.5 inch floppy diskette located on-board the scope. The source code for TEST.bas is provided in Appendix B.

4.7 Data Handling

The phenomenon of laser induced fluorescence can be thoroughly characterized in terms of three quantities, namely the intensity of the fluorescence emission, the wavelength at which that emission occurs, and the rate at which the intensity decays over time. The intensity and time characteristics of the fluorescence emission can be derived from the response of a photomultiplier tube used to observe the emission. The output of the PMT is a current that can be captured as a voltage across a load resistor and be monitored using any of the data acquisition systems discussed earlier. The wavelength associated with a given emission, often presented in nanometers, is determined using a spectrometer as discussed in Section 4.3.2.

The quantities measured throughout this testing program were, in all cases, stored to a file on either the hard drive of the control computer or the diskette drive of the oscilloscope. All stored data files were formatted in a fashion that allowed them to be imported by a variety of commercially available plotting and spreadsheet packages. Since data acquired using the AD1170 and the photon counter can be accessed by the host computer, it was processed prior
to storage. Data acquired using the oscilloscope could not be directly accessed by the control computer during testing and therefore required post processing.

Data obtained with either the AD1170 card or the photon counter consisted of only wavelength and intensity measurements. The wavelength measurements did not require any correction. However, the intensity measurements were corrected for the spectral response of the PMT. When using the AD1170, intensity corrections were made directly within the code TEST.bas. Data acquired with the photon counter was processed after testing. The PMT response curve used for the intensity correction process is provided in Figure 4.13. This curve presents the PMT anode radiant sensitivity as a function of observed wavelength. The anode sensitivity provides a relative measure of the PMT response to a given amount of incident energy at any given wavelength.

Figure 4.13: Spectral Response Curve for the Hamamatsu H5783-03 Photosensor Module (adapted from product data sheet, Hamamatsu Photonics, 1995).
The oscilloscope was used to acquire traces of emission intensity versus time at selected emission wavelengths. Each one of these traces was an average of the emission signal generated by a user defined number of laser pulses. Each average trace was stored to a separate file on the scope's diskette drive as an unsegmented block of numbers written in scientific notation. Following completion of the test, the data files on the scope's diskette were processed using a code called DATA.bas (see Appendix C). The code opens each individual data file on the storage diskette and parses the data block into values of intensity and time. Each set of intensity and time measurements is then associated with the wavelength of the emission measurement (obtained from the spectrometer) and stored in a three dimensional array. The array is then processed as a whole. All time measurements are converted to nanoseconds and zeroed to a user selected point prior to signal detection. All intensity measurements are corrected for the spectral response of the PMT. At each wavelength, the intensity versus time measurements are smoothed within a moving average window. The window size used in the smoothing process can be adjusted by the user, although typically 7 measurements were averaged in the window. Note that no averaging was performed in the wavelength domain. Once the data correction and processing is complete, a limited data set is created that makes use of approximately 50 data points equally spaced in time to characterize the intensity versus time traces acquired at each of the observed wavelengths. This limited data set is then printed to a file that can ultimately be accessed by commercial plotting and spreadsheet packages.
CHAPTER 5

MATERIALS AND SPECIMEN PREPARATION

5.1 Introduction

The fluorescence experiments carried out during this study made use of aqueous chemical solutions and soil specimen contaminated with varying levels of target compounds. The following sections describe the nature of the test media and the techniques used for specimen preparation.

5.2 Materials

5.2.1 Chemicals

The chemicals of interest in this study comprised the our major BTEX compounds, namely: Benzene, Toluene, Ethylbenzene, and (o)-Xylene. The BTEX compounds are members of a group of chemicals known as aromatic hydrocarbons. BTEX compounds are major components of gasoline and other fuels and are therefore very common environmental pollutants. These compounds are particularly prone to volatilization and have low aqueous solubilities. These physical characteristics, combined with the fact that the BTEX compounds are often found as subunits of more complex chemicals, generally limit their appearance in the environment to less than neat concentrations. Therefore, the majority of experiments performed in this testing program made use of solutions with contaminant concentrations at or below aqueous saturation levels.

All chemicals used in this study were reagent grade. The chemicals were purchased from J. T. Baker, and are declared to be 100% pure by the manufacturer (with the exception of ethylbenzene [98%]). Selected physical and engineering properties of the BTEX compounds which are relevant to this study are summarized in Table 5.1. The structural and molecular formulas for the BTEX compounds are provided in Figure 5.1.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight (g/mol)</th>
<th>Density (g/cm³)</th>
<th>Solubility (g/L)</th>
<th>Henry’s Constant (atm m³/mol)</th>
<th>Neat Molarity (mol/L)</th>
<th>Equilibrium Molarity (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>78.11</td>
<td>0.8736</td>
<td>1.780</td>
<td>$5.5 \times 10^{-3}$</td>
<td>11.30</td>
<td>$2.28 \times 10^{-2}$</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.14</td>
<td>0.8669</td>
<td>0.515</td>
<td>$6.6 \times 10^{-3}$</td>
<td>9.44</td>
<td>$5.59 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>106.17</td>
<td>0.8670</td>
<td>0.152</td>
<td>$8.7 \times 10^{-3}$</td>
<td>8.19</td>
<td>$1.43 \times 10^{-3}$</td>
</tr>
<tr>
<td>(o)-Xylene</td>
<td>106.17</td>
<td>0.8802</td>
<td>0.175</td>
<td>$5.1 \times 10^{-3}$</td>
<td>8.29</td>
<td>$1.65 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 5.1: Selected Physical and Engineering Properties of the BTEX Compounds

**Figure 5.1:** Structural and Molecular Formulas for the BTEX Compounds
5.2.2 Soils

A wide variety of soils were utilized to determine the influence of soil properties on the fluorescence signatures of BTEX compounds found in subsurface environments. The soils were selected to represent a range of soil types, grain sizes, and colors that are likely to be encountered in the field.

Tested materials included two sands, two clays, a silt, and pure industrial quartz (treated as a somewhat ideal soil). All of the soils were characterized according to standard geotechnical tests and classified using the Unified Soil Classification System (USCS). Three trials of Atterberg limits were performed on all fines according to ASTM Standard D4318. Two sets of sieve analyses (ASTM D421) and hydrometer analyses (ASTM D422) were used to define grain size curves for all materials. Three organic content combustion tests and two specific gravity determinations were also carried out for each soil according to ASTM Standards D2974 and D854, respectively. In addition, scanning electron microscopy (SEM) and x-ray diffraction tests were used to examine particle geometry and mineralogy.

<table>
<thead>
<tr>
<th>Soil</th>
<th>USCS Classification</th>
<th>Specific Gravity</th>
<th>Organic Content</th>
<th>Atterberg Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>Manchester Fine Sand</td>
<td>SP-SM</td>
<td>2.67</td>
<td>0.68</td>
<td>0.03</td>
</tr>
<tr>
<td>Ticino Sand</td>
<td>SP</td>
<td>2.67</td>
<td>1.52</td>
<td>0.04</td>
</tr>
<tr>
<td>Boston Blue Clay</td>
<td>CL</td>
<td>2.79</td>
<td>3.21</td>
<td>0.03</td>
</tr>
<tr>
<td>Venezuelan Clay</td>
<td>CH</td>
<td>2.81</td>
<td>6.90</td>
<td>0.05</td>
</tr>
<tr>
<td>Regional Silt</td>
<td>CL-ML</td>
<td>2.75</td>
<td>18.15</td>
<td>1.15</td>
</tr>
<tr>
<td>Granular Silica</td>
<td>ML</td>
<td>2.65</td>
<td>0.15</td>
<td>0.00</td>
</tr>
<tr>
<td>Silica Flour</td>
<td>SP</td>
<td>2.65</td>
<td>0.15</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 5.2: Selected Physical and Engineering Properties of Tested Soils.

The materials utilized in the testing program are described individually below. For reference all soil properties are also displayed using summary tables and plots. The grain size distributions for the sands and clays are provided in Figures 5.2 and 5.5, respectively. The grain size curves for all of the quartz mixes are provided in Figure 5.10. Points representing each of the fine soils are plotted on the plasticity chart given in Figure 5.6 according to the results of the Atterberg limit tests. SEM micrographs are also displayed for each soil. Finally,
the USCS classification, Atterberg limits, specific gravity values and organic contents of each soil are provided in Table 5.2.

**Manchester Fine Sand:**

Manchester Fine Sand (MFS) is an SP-SM medium to fine sand collected by the Plourde Sand and Gravel Company in Hooksett, New Hampshire approximately 16 km north of Manchester along the banks of the Merrimack River (Andersen, 1991). As evidenced by the grain size distribution illustrated in Figure 5.2, the fines content of the material exceeds 5% and therefore warrants the dual USCS classification provided. The material is also obviously poorly graded. MFS is beige in color with frequent speckles of black. This coloration is indicative of the large silica and feldspar content with traces of mica. SEM micrographs (Figure 5.3) demonstrate that the MFS grains are angular to subangular in nature and generally equidimensional. X-ray diffraction results indicate that the particles are composed of aluminum and silicon (again confirming the presence of feldspar) and potassium which balances the negative charge associated with the silica-aluminum replacement. Manchester Fine Sand also has a low organic content (0.68%).

**Ticino Sand:**

Ticino Sand (TS) is a clean, coarse river sand imported from Italy (Chauhan, 1995) that is poorly graded and has a USCS designation of SP. A review of the grain size curve presented for the material in Figure 5.2 demonstrates that 50% of the particles exceed 0.5 mm in diameter. The large size of the particles is shown in the SEM photos of Figure 5.4 which also demonstrate that the grains are subrounded to subangular in shape. Ticino sand has very inhomogeneous coloration. Individual sand grains can be black, white, beige, yellow, or orange. X-ray diffraction results show the presence of silicon, aluminum, potassium, calcium, and iron which are indicative of silica, feldspar, dolomite or another carbonate mineral, and some iron oxides. At 1.52%, the organic content of Ticino Sand is more than double that of Manchester Fine Sand.
Figure 5.2: Grain Size Distributions for Manchester Fine Sand and Ticino Sand.

Boston Blue Clay:

Boston Blue Clay (BBC) is a blue-green marine illitic clay with a CL designation that was deposited in the Boston basin about 12,000 to 14,000 years ago. The BBC used during this testing program was obtained from the base of the excavation for the MIT Biology Building (Building #68) (Berman, 1993). Despite its classification as a clay, approximately 45% of the material lies within the silt grain size range as shown in Figure 5.5. With a liquid limit of $47.0 \pm 0.4\%$ and a plastic limit of $23.8 \pm 0.9\%$ material plots above the A-Line in the low plasticity zone of the Plasticity Chart provided in Figure 5.6. BBC has an organic content of $3.21\%$. The particles are flaky and platelike as shown in Figure 5.7, and range from approximately 0.5 to 100 microns in size. X-ray diffraction tests show evidence of isomorphous substitution by aluminum, potassium, iron, calcium, and magnesium.
Figure 5.3: SEM Image of Manchester Fine Sand (Magnification 20x).

Figure 5.4: SEM Image of Ticino Sand (Magnification 20x).
**Venezuelan Clay:**

Venezuelan Clay is a highly plastic CH clay. It is yellow to orange in color. The material has a liquid limit of $60.2 \pm 0.5\%$ and a plastic limit of $21.7 \pm 0.4\%$. These properties lead to a position above the A-Line in the high plasticity zone of the Plasticity Chart given in Figure 5.6. The grain size distribution for Venezuelan Clay is illustrated in Figure 5.5. As shown in Figure 5.8, the particles are flaky, platelike, and range from 0.5 to 100 microns in size. X-ray diffraction demonstrates the presence of aluminum, potassium, and iron as substitution elements. Organic content determinations on the material reveal an organic content of 6.90%.

![Graph showing particle size distribution]

**Figure 5.5:** Grain Size Distributions for Boston Blue Clay, Venezuelan Clay, and Regional Silt.

**Regional Silt:**

The Regional Silt is a CL-ML material that was obtained in Lexington, Massachusetts. It is a silt with about 20% clay sized particles as demonstrated in Figure 5.5. The silt plots in the CL-ML region of the plasticity chart with a liquid limit of $23.5 \pm 0.1\%$ and a plastic limit
of 18.0 ± 0.5%. The material is light brown to gray in color. The SEM photos in Figure 5.9 show that the material is composed of rounded, subrounded, and platelike particles. Elements present in the soil include silicon, calcium (in high quantities), potassium, and iron. The silt has an organic content in excess of 18%.

![Plasticity Chart Illustrating Characteristics of Tested Soils](image)

- ○ Boston Blue Clay
- □ Venezuelan Clay
- ◊ Regional Silt

**Figure 5.6:** Plasticity Chart Illustrating Characteristics of Tested Soils.

**Industrial Quartz:**

Five different grades of pure industrial quartz (SiO₂) were acquired for use in this testing program. These materials were quarried in Quebec and processed in Ontario, Canada. X-ray diffraction results confirm the purity of these materials, indicating the presence of only silicon. Figure 5.10 illustrates the grain size distributions of each of the grades. The four digit grade notation, XXYY, indicates that YY% of the material is retained on a number XX U.S. standard sieve. Thus, for example, the 2075 grade indicates that 75% of the particles are retained on a number 20 sieve. The term silica flour is used to describe a pulverized grade of the quartz. The relative size and subangular shape of the particles characterizing the various
Figure 5.7: SEM Images of Boston Blue Clay:
a.) Magnification 641x.
b.) Magnification 2030x.
Figure 5.8: SEM Images of Venezuelan Clay:
(a.) Magnification 641x.
(b.) Magnification 2030x.
Figure 5.9: SEM Images of Regional Silt:
a.) Magnification 641x.
b.) Magnification 2030x.
quartz grades are shown in the SEM photos of Figures 5.11 and 5.12. During the testing program, the quartz materials were considered as somewhat ideal soils. The different grades of quartz span a range of grain sizes from clay through silt and up to medium sand. With an organic content of 0.15%, homogenous mineralogy and uniform white coloration, this material in particular permitted a thorough analyses of grain size effects without influences from other “soil” properties.

![MIT Classification Diagram](image)

**Figure 5.10:** Grain Size Distributions for Industrial Quartz Materials

### 5.3 Specimen Preparation Techniques

#### 5.3.1 Chemical Solutions

All chemical solutions were prepared using reagent grade chemicals and distilled demineralized water. On occasion, neat solutions were tested. However the majority of the experiments were carried out using aqueous solutions with contaminant concentrations at or below aqueous saturation levels. Since all of the BTEX compounds have densities less than that of water, saturated single compound solutions were created by maintaining a volume of
Figure 5.11: SEM Images of Industrial Quartz:
(a) Silica 2075 Magnification 20x.
(b) Silica 7030 Magnification 20x.
Figure 5.12: SEM Images of Industrial Quartz Powder:
   a.) Magnification 641x.
   b.) Magnification 2030x.
pure free product on the surface of water contained in a vial. These mixtures were allowed to
equilibrate so that the contaminant concentration in the water would reach saturation levels.
All such saturated solutions were stored in 40 ml amber glass vials with Teflon/silica septa. A
volume of free product was kept on the water surface to maintain equilibrium conditions over
long time periods.

The equilibrium solutions served directly as test media and were also used as stock
solutions to create all dilutions. Due to the volatility of the compounds, dilutions were tested
immediately after creation. All dilutions were prepared on a molar volume basis. That is, a
known volume of a given molar solution was expanded to a larger volume of lower molarity
using distilled demineralized water. This dilution technique is commonly represented by the
equation:

$$M_1V_1 = M_2V_2$$

(5.1)

where $M$ and $V$ represent molarity and volume, respectively, of the source (1) and diluted (2)
solutions in consistent units. For all test concentrations requiring multiple dilutions,
intermediate solutions were created in containers under zero headspace conditions to minimize
contaminant losses during preparation. Specimen volumes varied according to the nature of
each test. General aqueous solution tests made use of ~ 2 ml of solution, soil tests utilized 5
to 30 ml of solutions and flow tests required up to 500 ml of solutions.

5.3.2 Soil Specimen

5.3.2.1 Introduction

Three primary soil types were used in this testing program; namely sands, silts and
clays. The granular and fine grained materials required two distinct specimen preparation
techniques which are outlined below. The following techniques were generally applied
according to material type for all tests involving soils, however additional steps and/or method
modifications were sometimes required for tests targeting specific goals of the project. For
example, sands used to study the spectroscopic effects of grain size were sieved to yield
materials with a desired grain size distribution prior to specimen formation. Also the desired
water content of fine grained materials was sometimes achieved using aqueous contaminant
solutions rather than pure water for tests used to investigate soil wetting effects. These and other modifications and/or additions to basic procedures are discussed in detail in conjunction with the results of specific tests.

5.3.2.2 Granular Soils

Granular specimens investigated in the soil testing apparatus were prepared using a technique called multiple sieve pluviation. This preparation method provides control of the relative density, $D_r$, of the soil, and thus creates a specimen at a desired void ratio. The relative density of the specimen is defined in terms of the maximum, minimum, and specimen void ratio as follows:

$$D_r = \frac{e_{\text{max}} - e}{e_{\text{max}} - e_{\text{min}}} \times 100(\%)$$  \hspace{1cm} (5.2)

![Diagram of Multiple Sieve Pluviation Apparatus](image)

**Figure 5.13:** Multiple Sieve Pluviation Apparatus.

When preparing a specimen, oven dried soil is allowed to pour freely through a round opening in a soil reservoir located on top of a pluviator. The pluviator consists of a hollow plexi-glass
cylinder that is 16 inches long (~ 40 cm) located atop four screens spaced 3/4 inches (~ 2 cm) apart in the vertical direction. The four screens have openings corresponding to a No. 10 US Standard Sieve (2 mm). Soil that pours from the reservoir falls through the pluviator cylinder and the screens, randomly bouncing into soil chamber to form the specimen. A cone is placed on top of the soil chamber to deflect particles that do not directly enter the chamber after falling through the pluviator screens. The rate at which the soil falls through the screens determines the density of the soil specimen. This rate can be altered by changing the diameter of the opening in the soil reservoir. Larger openings lead to faster deposition rates and, in turn, to looser specimen. Reservoir openings used in this program ranged from 0.16 to 0.64 cm. Note that during the pluviation process, the laser probe is coupled to the soil chamber to ensure contact between the test media and the probe window. The equipment used in this procedure is illustrated in Figure 5.13.

5.3.2.3 Fine Grained Soils

Clay and silt specimen were prepared using the under compaction technique developed by R. S. Ladd (1978) to achieve uniform void ratios throughout the specimen. According to this procedure, a soil specimen is prepared, from the bottom upwards, in several layers or lifts of increasing percent compaction. In this way, the under compaction technique attempts to account for the fact that the compaction of each lift tends to further densify all prior lifts. The percent compaction of a given lift is dictated by the following equation:

\[ U_n = U_{ni} - \left[ \frac{U_{ni} - U_{nt}}{n_t - 1} \right] \times (n - 1) \]  \hspace{1cm} (5.3)

where

- \( U_{ni} \) = percent under compaction selected for first layer,
- \( U_{nt} \) = percent under compaction selected for final layer (usually zero)
- \( n \) = number of layer being considered
- \( n_i \) = first (initial) layer
- \( n_t \) = total number of layers (final layer).

As illustrated in Equation 5.3, the percent under compaction of each lift decreases linearly as the overall height of the specimen increases. The percent undercompaction for the first layer
\( U_{nl} \) which ultimately leads to a uniformly compacted specimen must be determined empirically and is material dependent.

For the tests in this program, the standard 10.16 cm tall by 2.54 cm diameter soil specimen was compacted in five lifts. The percent undercompaction for the first lift required to achieve uniform soil density throughout the completed specimen varied with soil type, but typically ranged from 0 to 5%. As with the granular specimen, the compaction process was performed directly in the soil test chamber which was securely coupled to the laser probe. Special attention was given to ensure that lift samples did not coincide with the location of the test window. The equipment used for this procedure is illustrated in Figure 5.14 and is described in detail by R. S. Ladd (1978).

![Diagram of Undercompaction Equipment](image)

**Figure 5.14:** Undercompaction Equipment.
CHAPTER 6

AQUEOUS SOLUTIONS

6.1 Introduction

The microchip laser probe was used in conjunction with the liquid test cell to conduct laser induced fluorescence (LIF) tests on aqueous solutions containing various concentrations of benzene, toluene, and (o)-xylene (BTX). These tests involved one contaminant and were performed under no flow conditions (multi-compound solutions are discussed in Chapter 8). The purpose of these experiments was threefold; to determine the ability of the microchip laser probe to detect, identify, and quantify BTX contamination in water; to assess factors such as laser penetration depth and electrical and optical noise that influence the performance of the probe in the field; and to facilitate the development of a database containing the fluorescence characteristics of BTX compounds in aqueous solution for comparison with the signatures in the presence of soils.

Specific experiments were performed to address each of the above mentioned goals. General fluorescence tests were performed in accordance with procedures detailed in Chapter 4, Section 4.5 to determine the detection, identification, and quantification capabilities of the laser probe. In addition, more specialized experiments, referred to as laser penetration tests, were carried out to determine the region of the test medium interrogated by excitation radiation emitted beyond the laser probe window. The non-standard procedures followed for these tests warrant further description and are therefore discussed within this chapter.

Two data acquisition schemes were used throughout the aqueous testing program to obtain all of the information necessary to characterize BTX fluorescence and the LIF probe's performance. The first system made use of the LeCroy 9362 digital storage oscilloscope to collect fluorescence data with 200 ps time resolution. Results obtained using the oscilloscope were analyzed to determine the fluorescence lifetimes and emission wavelength signatures of the BTX compounds in aqueous solutions. The combination of lifetime and emission
wavelength information is related to the contaminant; therefore, data acquired with the oscilloscope was used to establish the limits of the laser probe's identification capabilities for the compounds of interest. The second data acquisition technique utilized the Stanford Research model SR430 photon counter, that yields fluorescence data with greater signal sensitivity, but poorer time resolution, than the oscilloscope. Due to the poor time resolution of the photon counter, only emission wavelength data was collected with this device. Although this type of information cannot necessarily be used to identify a particular BTX contaminant, it can demonstrate the presence of a fluorescing substance in solution, and it is thus useful for detect/non-detect applications of the LIF probe. With this justification, the added sensitivity of the photon counter was utilized to determine the ultimate detection capabilities of the microchip laser system. Data acquired with both the oscilloscope and the photon counter were also used to assess the relationship between the magnitude of fluorescence signals excited in a test medium and the concentration of a contaminant in that medium. This information defined the ability of the probe to acquire reliable quantitative data on contaminants in aqueous solution.

The results of all phases of the aqueous solution testing program are described in detail in the following sections. The overall scope of this program is outlined in Section 6.2. Section 6.3 describes specific operational settings and procedural details associated with the general testing apparatus described in Chapter 4 that are unique to this phase of testing. Section 6.4 assesses the factors that influence the measurements obtained with the data acquisition equipment and ultimately affect the interpretation of the test results. Section 6.5 provides a summary of all of the results obtained from the general fluorescence experiments. Section 6.6 is used to analyze the test results that characterize the identification, quantification, and detection capabilities of the laser probe. Finally, the details of the laser penetration tests are discussed in Section 6.7.

6.2 Scope of Aqueous Solution Testing Program

This phase of the testing program involved a total of 50 LIF tests performed on aqueous solutions of individual BTX compounds. Six of these experiments were laser penetration tests and the remainder were general fluorescence tests. Numerous background
scans of distilled demineralized water were also carried out during this experimental phase (every 2 to 4 tests) to assure that test solutions were not subject to contamination. For both of the LIF test categories, experiment repeatability was evaluated by performing multiple tests on selected contaminant solutions. The following discussion outlines the specific contaminant solutions and data acquisition techniques used to conduct the laser penetration tests and the general fluorescence tests.

The laser penetration tests were all performed on aqueous solutions containing equilibrium concentrations of individual contaminants. Two tests were performed using each of the BTX compounds. Data acquisition during the laser penetration tests was carried out using the high speed oscilloscope.

The general fluorescence tests were performed on a broad range of contaminant solutions and made use of either the high speed oscilloscope or the photon counter for data acquisition. Overall, 38 of the general fluorescence tests were performed using the high speed oscilloscope, while the remainder made use of the photon counter. To clarify the fundamental characteristics of each of these tests, all of the general fluorescence experiments performed for the aqueous solution testing program are summarized in Table 6.1.

Table 6.1 illustrates the number of general fluorescence tests performed at selected aqueous concentrations for each of the BTX compounds. The tests are separated on the basis of the technique employed to collect data. Note that ND, or “non-detect,” is used in the table to designate tests performed that did not yield useful results.

<table>
<thead>
<tr>
<th>Compound</th>
<th>EQ Concentration (ppm)</th>
<th>General Fluorescence Tests</th>
<th>High Speed Oscilloscope</th>
<th>Photon Counter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Concentration (ppm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Benzene</td>
<td>1780</td>
<td></td>
<td>ND</td>
<td>1</td>
</tr>
<tr>
<td>Toluene</td>
<td>515</td>
<td></td>
<td>ND</td>
<td>1</td>
</tr>
<tr>
<td>(o)-Xylene</td>
<td>175</td>
<td></td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

ND = Non-Detect

**Table 6.1:** Summary of General Aqueous Solution Testing Program.
Limits on the concentration ranges evaluated for each compound were established on the basis of two factors. The upper testing limit was determined by the fact that homogeneous contaminant solutions can not be created reliably at concentrations in excess of the aqueous solubility of the compounds. The lower testing limit, however, was selected somewhat more arbitrarily. When testing a given compound, experiments were initiated at concentrations believed to be below the detectable limits of the acquisition equipment. The concentration used for subsequent tests was then increased until a noticeable fluorescence signature was obtained. The lowest test concentrations for each compound listed in Table 6.1 therefore mark the first concentration at which a fluorescence signature was observed. However it must be noted that tests were performed at discrete levels of concentration, therefore the first observable signature is not necessarily the lowest concentration for contaminant detection. For example, aqueous solution tests were also performed at concentrations of 100 ppm, 250 ppm, and 300 ppm for benzene, 1 ppm for toluene, and 100 ppb for o-xylene; but, the results of these tests resembled the general background signature of water. These tests were therefore considered “non-detect” cases and the next most convenient concentration was evaluated. Thus it should be apparent that the lower test limits do not in any way define the absolute sensitivity of the laser probe. A rigorous interpretation of device sensitivity is presented later in this chapter.

6.3 Equipment Settings and Procedures

As mentioned above, the aqueous solution testing program comprises the laser penetration experiments and the general fluorescence investigations. Experiments performed in both of these testing categories made use of the laser, spectrometer, photomultiplier tubes, and data acquisition equipment described in Chapter 4. For these tests, the light generated by laser induced fluorescence was chromatically dispersed using the CVI CM110 spectrometer equipped with 2.4 mm entrance and exit slits which provided spectral resolution of approximately 2 nm. The trigger PMT was operated at a control voltage of 500 V and the detection PMT was run at a control voltage of 850 V. Throughout this testing phase, the diode laser was passively Q-switched at a repetition rate between 6 and 8 kHz, and, therefore, was not specifically controlled. For both the laser penetration tests and the general
fluorescence tests, all aqueous solutions were prepared as described in Section 5.3.1 of Chapter 5. Further, both groups of experiments were conducted in the liquid test cell, which was coupled to the laser probe as illustrated in Figure 4.1.

Although the primary procedures and equipment used for the general fluorescence tests have already been outlined in Chapter 4, and briefly reiterated above, the following sections describe the specific equipment settings and detailed observation procedures utilized for data collection when performing the battery of tests listed in Table 6.1. Conditions maintained during the tests performed using the high speed oscilloscope are discussed independently from those upheld when using the photon counter. Note that the details of the laser penetration tests are discussed in conjunction with the results of those investigations in Section 6.9 of this chapter.

6.3.1 Data Acquisition Using High Speed Oscilloscope

Several equipment settings and measurement procedures were customized specifically for the aqueous solution experiments performed using the high speed oscilloscope. These factors included the sampling rate, voltage setting, and timebase of the oscilloscope as well as the number of laser pulses averaged for a given fluorescence measurement and the measurement acquisition interval in the wavelength domain. Each of these parameters is discussed individually below.

When using the LeCroy 9362 digital storage oscilloscope for general fluorescence testing, data were collected at a sampling rate of 5 GSa/s (see Chapter 4, Section 4.4.3). The voltage setting of the scope (i.e. volts/div.) was selected to accommodate the maximum signal level encountered during each test and was maintained throughout the duration of a test. The fluorescence signal was monitored on a timebase setting of 5 ns/div resulting in an acquisition period of 50 ns. Approximately 5 to 10 ns of this time consists of pre-excitation data and the remainder captures the decay in fluorescence intensity subsequent to the laser pulse.

The operational settings selected for the scope provided more than adequate temporal resolution to observe the fluorescence phenomenon under investigation in this study. At a sampling rate of 5 GSa/s, the high time resolution of the scope is evidenced by the time signature of the water Raman line presented in Figure 6.1, which is approximately 2 ns in
width at half-maximum. Since the Raman phenomenon involves only light scattering, rather than absorption and emission, Raman scattering signatures such as the water Raman line are necessarily of shorter duration than any possible fluorescence emission. Therefore, the scope’s ability to capture a pulse that rises and falls as quickly as the water Raman line demonstrates that, at the selected sampling rate, the scope can clearly characterize longer duration phenomenon such as the fluorescence emissions of BTX compounds. Further the overall 50 ns acquisition period associated with the selected sampling rate is more than adequate to capture the decay of BTX compound fluorescence signatures which have fluorescence lifetimes less than 10 ns.

![Graph showing time signature of water Raman line](image)

**Figure 6.1:** Time Signature of Water Raman Line.

Throughout the aqueous testing program fluorescence intensity measurements were obtained at 2 nm intervals over the wavelength range of 274 nm to 350 nm. This wavelength measurement interval adequately captures the broad features of BTX compound fluorescence. At each measurement interval (i.e. every 2 nm) the average fluorescence signal resulting from 500 laser pulses was acquired and stored. Studies of signal averaging demonstrated that averaging additional laser pulses did little to improve measurement quality.
6.3.2 Data Acquisition Using the Photon Counter

The photon counter was also used to observe fluorescence signals at 2 nm intervals over the wavelength range of 274 nm to 350 nm. Data was collected by comparing the fluorescence signal intensity to the value of the photon counter’s discriminator threshold over a finite period of time following excitation of the test medium. After performing several tests on water to optimize the signal to background ratio achieved with the device, the discriminator threshold was set at a level of -2.4 mV for the duration of the aqueous solution testing program. For all of the general fluorescence tests performed using the photon counter, the device was operated at the limits of its temporal capabilities. Fluorescence signals were acquired in discrete 5 ns time bins for a period of 5 µs (the shortest storage period available). Counts resulting from 10,000 laser pulses were allowed to accumulate in each of the time bins. The first 6 time bins recorded pre-excitation data. The counts recorded in each of the following 6 time bins (bins 7 through 12) were then summed to arrive at a total fluorescence signal for each measurement. The resulting signal is representative of the fluorescence activity over a 30 ns time interval.

6.4 Factors Influencing Test Measurements

Early stages of the aqueous solution testing program revealed a number of factors that can influence the intensity, wavelength, and/or time characteristics of fluorescence observations. These factors include the presence of background signatures, electrical and optical interference, and limitations of the data acquisition and optical systems. Each of these factors is discussed individually below, along with their potential impact on fluorescence measurements and possible means of overcoming their effects.

6.4.1 Background Signatures

Fluorescence emission of the BTX compounds occurs over the wavelength range of approximately 275 nm to 340 nm. Therefore fluorescence studies of aqueous solutions of BTX compounds inevitably encounter the water Raman line, which peaks at approximately 292 nm to 294 nm. The water Raman line produces a fairly strong signal that can be particularly troublesome when attempting to detect fluorescing compounds at low
concentrations. This feature is illustrated in Figure 6.2 (a) which displays a WTI profile for a 1 ppm solution of o-xylene without accounting for the effects of the water Raman line. Initial observations make it seem as though there is a very strong fluorescence signature available at this low contaminant concentration. However, an equivalently scaled scan of distilled demineralized water (Figure 6.2 (b)) reveals that a large portion of the observed signal in part (a) of the figure is actually derived from the water Raman line. Fortunately the signal produced by the water Raman line is extremely repeatable since it is associated with the molecular structure of water. Therefore, for all tests performed in the aqueous solution

![Graphs](image)

**Figure 6.2:** Effect of Water Raman Line on Aqueous Solution Fluorescence Signatures. 
(a.) WTI Profile for 1 ppm (o)-Xylene Before Subtraction of Water Raman Line.  
(b.) Signature of Water Raman Line.  
(c.) WTI Profile for 1 ppm (o)-Xylene After Removal of Water Raman Line.
testing program, the signal associated with the three dimensional signature of the water Raman line is mathematically subtracted from fluorescence test data. Figure 6.2 (c) illustrates the effect of this subtraction process. At this low contaminant concentration, the volume under the WTI curve has been reduced by nearly 25%. Of course, the significance of the water Raman line decreases as the concentration of a contaminant in solution, and thus the associated fluorescence signal, increases.

6.4.2 Electrical and Optical Interference

Electrical and optical signals that obscure LIF test measurements exist in two primary forms. Some of these signals occur at a particular frequency or are synchronized with the pulse of radiation used to excite the fluorescence experiment while others are random in nature.

Synchronous and frequency based interferences can result from stray laser light in the optical system, electrical ringing in signal transmission lines, and combinations of resistance and impedance inherent in the system electrical components. These types of interference are illustrated in Figure 6.3, which displays a scan of water that has not been subject to any signal processing. As shown earlier in Figure 6.2 (b), only the water Raman line should be present in

![Graph showing the influence of scattered laser light and electrical interference.](image_url)

**Figure 6.3:** Background Scan of Water Illustrating Influence of Scattered Laser Light and Electrical Interference.
the trace depicted in Figure 6.3. However, the profile displays a signal ridge that traverses the entire wavelength spectrum, mirror-like images of the primary signal peak (most notably a negative dip in the signal following the primary pulse), and an obvious sinusoidal pattern over the entire acquisition period. The ridge-like feature in Figure 6.3 is the by-product of scattered laser light in the monochromator as evidenced by its presence at all observed wavelengths and its very short time signature. The mirror images of the primary signal, referred to as electrical ringing phenomena, are present only when the laser is in operation and are therefore associated with the signal pulse caused by laser excitation of the test medium. The consistent sinusoidal pattern in the baseline exists at all times in the signature and is therefore a by product of the measurement circuitry.

Interference caused by scattered laser light can be reduced or completely eliminated in a LIF system using optical filters or a spectrometer with high light rejection capabilities. However, reductions in scattered light must often be weighed against tolerable losses of fluorescence signal. The same light rejection properties of a spectrometer that eliminate stray light may also significantly impair the overall detection capabilities of a LIF system. Similarly, the amount of light reduction that can be affected using optical filters depends on the relative position of the laser line and that of the desired fluorescence emission. All optical filters remove some finite bandwidth of radiation and have characteristic transmission curves that inevitably influence neighboring wavelength observations. In the experimental system used in this testing program, scattered laser light was eliminated through the use of two optical filters. A Schott glass WG280 filter that was placed immediately in front of the return fiber within the microchip laser probe and a solar blind filter was placed in front of the detection PMT at the exit slit of the monochromator. The WG280 filter prevented the 266 nm excitation energy from generating signals directly at the detection PMT and also from exciting fluorescence in the core or cladding of the probe’s return fiber. The solar blind filter eliminated the microchip laser line at 532 nm and the diode pump line at 808 nm. Although these filters eliminated or reduced light that could be misinterpreted as fluorescence from a contaminant, they also limited the observable light wavelengths to a range of approximately 290 nm through 325 nm at only 70% transmission.
Signal disruption caused by electrical ringing is a function of the impedance of the overall wiring system used to convey electrical signals from a detector to a measurement device. Locations of minor impedance mismatching in this cabling act as loads that generate secondary signals that appear as mirror-like images of the true signal traveling through a transmission line. These effects can have a significant impact on the shape (and therefore decay properties) of the fluorescence profile. However, since the ringing is a by-product of a physical characteristic of the measurement system it is extremely repeatable and can be easily eliminated through mathematical subtraction.

The sinusoidal baseline apparent in Figure 6.3 stems from the influence of the detection and measurement circuitry on the observed signal. In a multi-component measurement system, such as that used in this program, interference can arise with a specific frequency related to the overall resistive and capacitive characteristics of the system. Again, since these effects are directly linked to the physical design of the equipment, they can be eliminated mathematically.

Random noise, by definition, has no particular time history. This type of interference is typically unrelated to the excitation pulse in a LIF test and is thus present at all times throughout the experiment. Examples of random noise include signals generated by ambient light which reaches the detection system, signals created by thermionic currents in the PMT, and general electrical interference. All of these factors combine to establish a baseline noise signal. These signals cannot be easily subtracted and generally impose the ultimate limits on the performance of equipment. For example, in a LIF system, contaminant detection can only be achieved at concentrations which, when excited, emit enough fluorescence radiation to create a signal in excess of the noise baseline. In addition, noise signals can have a significant impact on the tail end of a fluorescence decay curve and thereby obscure the true decay properties of the medium under investigation.

Random noise factors can generally be reduced or eliminated by adequately shielding and grounding electrical components of the measurement system and by shrouding all optical detectors from ambient light sources. In the experimental setup used for this testing program shielding was achieved by utilizing coaxial cable for all signal lines and wrapping the PMT
detectors in a foil Faraday cage linked to ground. In addition an opaque shroud was used to cover the entire optical system and thus limit its exposure to ambient light.

6.4.3 Equipment Limitations

For a given level of laser power, the performance of the LIF probe is ultimately based on the limitations of the measurement system used with the device to collect data. The measurement system must have sufficient time resolution to capture the decay characteristics of the fluorescence phenomenon, the sensitivity to detect contaminants present at low concentrations, and the spectral resolution to observe changes in the wavelength characteristics of the fluorescence signal. For the LIF tests performed in this study, spectral resolution is of minor significance due to the innate similarities in the emission wavelength profiles of BTX compounds. However, time resolution and signal sensitivity play a critical role in establishing the identification, quantification, and detection limits of the laser probe. Often, however, the best performance in all of these categories cannot be achieved with a single measurement device. Therefore, as a precursor to analyzing the results of the fluorescence tests performed on aqueous solutions, it is important to note that the capabilities of the laser probe are entirely dependent upon its accompanying data acquisition system and thus vary accordingly. The specific limitations imposed on the performance of the LIF probe by the different data acquisition devices used throughout this program are discussed in detail in Section 6.6.

6.5 Summary of General Fluorescence Test Results

The following discussion defines and summarizes the parameters of interest obtained from each of the general fluorescence tests. The procedures used to obtain these parameters are also described as necessary. Results collected with the oscilloscope and the photon counter are presented individually.
6.5.1 Results of Aqueous Solution Tests Performed Using the High Speed Oscilloscope

The WTI curve from each test performed using the high speed oscilloscope was analyzed to determine the total fluorescence signal excited in the test medium (a value termed the "concentration indicator"), the wavelength and magnitude of the peak fluorescence emission, and the fluorescence lifetime of the compound in solution. The values of these parameters obtained for each of the 40 fluorescence tests performed using the high speed oscilloscope are summarized in Table 6.2. Note that each test is listed by name and accompanied by the aqueous concentration of the single compound used in the tested solution. WTI profiles and a comprehensive summary of the data acquired from each of these tests are provided in Appendix D.

The total fluorescence signal excited in the test medium was determined by integrating under the WTI profile using the trapezoidal rule. The WTI curve was first transformed into an emission wavelength spectrum by performing trapezoidal integration on each of the intensity-time traces comprising the profile. At each measurement location, the area under the intensity-time trace was treated as an ordinate of the emission wavelength spectrum. The trapezoidal rule was then used again to evaluate the area under the emission wavelength spectrum which is equivalent to the volume under the WTI profile. This procedure is illustrated in Figure 6.4.

In order to limit the influence of background noise on the total fluorescence calculation, each intensity time trace was integrated over a limited range in which its amplitude exceeded 1.6 times the standard deviation of the background noise (1.6 $\sigma$) associated with the measurement equipment. Assuming that the random noise component of the background, which cannot be effectively subtracted from a WTI profile, can be characterized by a normal distribution, the 1.6 $\sigma$ criterion should include approximately 90% of the noise. The background level was evaluated by obtaining the standard deviation ($\sigma$) relative to the mean of 10 full spectrum background signatures, a data set containing over 100,000 points. The 10 background signatures used in this calculation were acquired at different times throughout the aqueous solution testing program. As a result the standard deviation of the background level derived from the set of 10 background signatures was considered to be representative of testing conditions during all of the aqueous solution experiments.
<table>
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<tr>
<th>Compound</th>
<th>Test Name</th>
<th>Aqueous Concentration (ppm)</th>
<th>Lifetime (ns)</th>
<th>Peak Emission Wavelength (nm)</th>
<th>Signal (a.u.)</th>
<th>Concentration Indicator (a.u.)</th>
</tr>
</thead>
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<tr>
<td>Benzene</td>
<td>BEQa</td>
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<td>2.7</td>
<td>292</td>
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<td>0.033</td>
</tr>
<tr>
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<td>BEQb</td>
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<td>290</td>
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<td>292</td>
<td>7.91E-05</td>
<td>0.008</td>
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</table>

Table 6.2: Results of Aqueous Solution Tests Performed Using the Oscilloscope.
Figure 6.4: Procedure Used to Determine Total Fluorescence Signal.

The volumes obtained using the trapezoidal integration procedure are presented in arbitrary units (a.u.) since the fluorescence signals recorded in the WTI have been adjusted to account for the spectral response of the PMT. For the purpose of discussion, this volume measurement, or total fluorescence signal, is referred to as a "concentration indicator."

Fluorescence lifetimes were calculated from each WTI profile according to the following procedure. Representative intensity-time traces were extracted from the WTI profile and then normalized to a peak amplitude of unity. The extracted traces were selected
on the basis of two criteria: (1) the peak intensity of the trace was at least 50% of the peak fluorescence emission recorded in the overall WTI profile, and (2) the peak intensity of the trace was at least 4 times the background noise level of the WTI profile, where the background noise level is again defined as 1.6 times the standard deviation of the random background signal. All of the extracted and normalized intensity time traces were then averaged to form a single intensity-time trace. The peak amplitude of this trace was then located in the time domain and all of the data in a range from 1 ns after the peak to a point where the intensity drops below the background noise (1.6 σ) were considered representative of the decay characteristics of the tested medium. This limited data set was again normalized to a peak value of unity and the point of maximum amplitude was considered to occur at time t = 0. (The first nanosecond of data following the peak was ignored to ensure that a decay constant was determined for the fluorescence phenomenon without incorporating any measurement effects, such as rollover of the PMT signal, caused by measuring a rapidly rising signal which suddenly begins to decay). A decay curve of the form I(t) = ae^{-\alpha t} was then fit to this limited data set using a least squares routine. The parameter \( \alpha \) is defined as the fluorescence lifetime. This procedure is illustrated in Figure 6.5.

Note that when performing unweighted least squares non-linear regression on a data set displaying exponential decay the ordinate values of the data set decrease rapidly with increasing values of the abscissa. Thus the variance and, in turn, the least squares residuals decrease in this same manner. Therefore large valued data points tend to have more weight in the regression analysis than those of small amplitude. This characteristic is advantageous when attempting to limit the influence of low level background noise on a curve fit calculation.

6.5.2 Results of Aqueous Solution Tests Performed Using the Photon Counter

The photon counter was utilized as an alternate data acquisition device to improve the quality and reliability of results obtained with the LIF probe when testing low concentration solutions. A limited set of six tests was performed with this device. The counts recorded at each of the measurement points (i.e. every 2 nm) in the photon counting experiments provide the data to form an emission wavelength signature. The total number of counts involved in this signature, or the "area" under the emission wavelength profile, is related to the
Figure 6.5: Procedure Used to Determine Fluorescence Lifetimes:

a.) Locate intensity-time traces with peaks greater than 50% of the WTI peak and at least 4 times as large as the background noise.
b.) Isolate these traces from the WTI profile and capture their peak amplitudes.
c.) Normalize all selected IT traces by their respective peaks.
d.) Rezero time scale of decay curve: $t_0 = t_{peak} + 1\, \text{ns}$ and truncate data set at 1.6 $\sigma$.
e.) Fit the data with a decay curve of the form $I(t) = ae^{-t/\tau}$. 
concentration of the contaminant in solution. This value is again referred to as a "concentration indicator." Note that the total counts associated with a background scan of water were always subtracted from the aqueous solution data to ensure that the concentration indicator obtained with the photon counter was as representative as possible of contaminant fluorescence emission. The emission wavelength associated with the maximum signal count, and the total number of counts in the emission wavelength signature for each of the photon counting tests are summarized in Table 6.3.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Test Name</th>
<th>Concentration (ppb)</th>
<th>Peak Emission Wavelength (nm)</th>
<th>Concentration Indicator (counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(o)-Xylene</td>
<td>X5MPCa</td>
<td>5000</td>
<td>294</td>
<td>21659</td>
</tr>
<tr>
<td></td>
<td>X5MPCb</td>
<td>5000</td>
<td>294</td>
<td>24523</td>
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<td>X1MPCA</td>
<td>1000</td>
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<td>5022</td>
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<td>X5HBPCb</td>
<td>500</td>
<td>292</td>
<td>2950</td>
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Table 6.3: Results of Aqueous Solution Fluorescence Tests Performed Using the Photon Counter.

Due to the amount of information obtained from a single fluorescence experiment, the data derived from many of these tests was used to characterize more than one aspect of the laser probe's performance. The results displayed in Tables 6.2 and 6.3 are therefore referenced repeatedly throughout the remainder of this chapter.

6.6 LIF Sensor Performance in Single - Compound Aqueous Solutions

6.6.1 Results of Contaminant Identification Tests

Identification of a BTX compound in aqueous solution requires knowledge of the fluorescence lifetime and emission wavelength signature of that compound. With the equipment available in this testing program, this level of information could only be obtained from tests performed using the high speed oscilloscope. Examples of the type of data collected with the scope are presented in Figures 6.6 through 6.8. These figures show
representative WTI curves for various aqueous concentrations of each of the BTX compounds. Each of the figures includes three WTI profiles: one illustrates the fluorescence signature obtained from an equilibrium solution of the contaminant and water, another shows an example of the profile for a typical intermediate concentration, and the third plot provides the WTI profile for the lowest contaminant concentration observed with the oscilloscope.

![ WT profiles for benzene ]

**Figure 6.6:** WTI Profiles for Selected Aqueous Concentrations of Benzene.

a.) Equilibrium Solution: 1.78 ppt.

b.) Intermediate Concentration: 1 ppt.

c.) Lowest Concentration Observed: 500 ppm.

For all three of the studied chemicals, the WTI curves are generally very smooth for concentrations of the target compounds near aqueous equilibrium. The curves become more
erratic as the concentration decreases. This variability stems from two factors. First, as the concentration of the contaminant in solution decreases, the laser excitation pulse excites fewer molecules. Thus, the natural variability in molecular excitation states is not necessarily averaged out in the final stored intensity-time trace. Within the averaging capabilities of the equipment used in this program, this aspect of variability could not be eliminated. This phenomenon typically leads to irregularities in the intensity of the traces obtained at different emission wavelengths that is visible as roughness in the wavelength-intensity plane of the WTI

![Graphs](image)

**Figure 6.7**: WTI Profiles for Selected Aqueous Concentrations of Toluene.
- a.) Equilibrium Solution: 515 ppm.
- b.) Intermediate Concentration: 50 ppm.
- c.) Lowest Concentration Observed: 5 ppm.
curve. The second, and most important, factor contributing to variability in the WTI curve is electrical and optical noise. As the contaminant concentration decreases, the fluorescence excited in the test medium also decreases and the magnitude of the resulting signal generated by the detector PMT begins to approach the level of noise present in the measurement system.

![Graphs showing WTI Profiles](image)

**Figure 6.8: WTI Profiles for Selected Aqueous Concentrations of (o)-Xylene.**

a.) Equilibrium Solution: 175 ppm.

b.) Intermediate Concentration: 10 ppm.

c.) Lowest Concentration Observed: 1 ppm.

Further comparison of the WTI profiles in Figures 6.6 through 6.8 demonstrates that there is very little difference in the emission wavelength characteristics of BTX compounds. This point is emphasized in Figure 6.9 which displays typical emission wavelength signatures...
for each of the BTX compounds. These E-W profiles have been normalized to their respective peak amplitudes to facilitate comparison.

Note that the optical filters used during this testing program affect the emission spectra of all compounds in exactly the same manner. Therefore, although the filters influence the absolute shape of measured spectra in non-constant transmission ranges (less than ~290 nm and greater than ~325 nm), the filters do not alter the relative differences between the emission spectra of the BTX compounds.

![Normalized Emission Wavelength Profiles for the BTX Compounds](image)

**Figure 6.9:** Normalized Emission Wavelength Profiles for the BTX Compounds obtained from Tests on Equilibrium Aqueous Solutions.

Close inspection of Figure 6.9 reveals that there are some subtle differences among the curves displayed for each contaminant. In particular, there are slight differences in the width of the E-W profiles for the BTX compounds. For the profiles displayed in the figure the values of full width at half maximum for benzene, toluene, and o-xylene are approximately 23 nm, 24 nm, and 25 nm, respectively. Further, the E-W profile of o-xylene peaks after that of either benzene or toluene. This observation is supported by a review of the data listed in Table 6.2 which demonstrates that the observed peak locations for the E-W profiles of benzene, toluene, and o-xylene are 292 ± 1 nm, 293 ± 1 nm, and 294 ± 1 nm, respectively.
Unfortunately, several factors limit the value of the subtle differences between the E-W profiles of the BTX compounds. First, the small differences in emission profile width displayed in Figure 6.9 cannot be assessed on a reliable basis without the use of a spectrometer with higher resolution than that used in this study. Further, the peak wavelength data listed in Table 6.2 demonstrates that the minor differences in the E-W profiles of the BTX contaminants are likely to be overshadowed by measurement variation in a field scenario. Although the average peak wavelengths of the E-W profiles show some signs of distinction, the spread in the peak locations obtained from individual tests on each compound tend to overlap, and, in fact, the standard deviation of the data is less than the spectral resolution of the monochromator used to conduct the experiments. It can therefore be concluded that E-W profiles alone do not display enough individuality to be useful for field identification of the BTX compounds using the currently available equipment.

![Graph showing fluorescence decay curves](image)

**Figure 6.10:** Representative Fluorescence Decay Curves of the BTX Compounds obtained from Tests on Equilibrium Aqueous Solutions.

The remaining parameter that offers the possibility for contaminant identification is the fluorescence lifetime. Values of fluorescence lifetime calculated from the fluorescence test data are summarized in Table 6.2. Given that the highest quality test data for each compound was achieved using equilibrium solutions, the results of the equilibrium tests have been used to
determine the fluorescence lifetime representative of each of the BTX contaminants. Representative decay curves obtained from equilibrium solution tests are displayed in Figure 6.10 for each of the three compounds. The curves for toluene and o-xylene are very smooth, while the decay curve for benzene displays evidence of sinusoidal interference. This remnant of interference is apparent in the benzene signature due to the generally low magnitude of the benzene fluorescence emissions. Small differences between the background signature subtracted from actual test data and the data itself are inevitable. For benzene, the measured signal is already quite small, therefore the byproducts of background subtraction are more apparent in the benzene signature than in the signatures of toluene or o-xylene. This effect becomes evident in the decay profiles of all compounds as the magnitude of the emission signal decreases in conjunction with a decrease in the concentration of the compound in solution.

Analysis of the experimental measurements from equilibrium solution tests indicate that benzene in aqueous solution has a fluorescence lifetime of \( 2.7 \pm 0.2 \text{ ns} \) while toluene and o-xylene display lifetimes of \( 6.3 \pm 0.1 \text{ ns} \) and \( 6.6 \pm 0.2 \text{ ns} \), respectively. The lifetimes obtained for benzene and toluene agree quite well with the values of 2.4 ns and 5.3 ns published by Gillispie and St. Germain (1993) for these contaminants in aqueous solution. The author is not aware of any published findings regarding the fluorescence lifetime of o-xylene in aqueous solution. It is clear that benzene can be rather easily differentiated from either toluene or o-xylene. However, the sub-nanosecond variation between the lifetimes of toluene and o-xylene make it difficult to distinguish between these two compounds.

The difficulty of differentiating between two lifetime values that are so similar is emphasized in Figure 6.11. This figure displays the decay curve of toluene along with two mathematically generated decay curves having decay constants of 5.5 and 6.5 ns. Data points from the experimental curve lie directly on both of the boundaries established by the generated curves. It is therefore apparent that a strictly objective method, such as that presented in Section 6.4.1., must be used to consistently determine fluorescence lifetimes from test data so that contaminants may be reliably identified. Note that the absolute value of the lifetime derived from a curve fitting procedure is not as important as the ability of a curve fitting procedure to yield consistent results when applied to a variety of experimental data. Once a
procedure is determined and a characteristic lifetime is associated with a given contaminant, that contaminant can then be reliably identified using the results of the curve fitting routine.

![Fluorescence Lifetime Curve](image)

**Figure 6.11: Variability in Fluorescence Lifetime Determination.**

It becomes more difficult to reliably determine a fluorescence lifetime, and subsequently identify a compound, as the concentration of a compound in solution decreases. Figure 6.12 displays an intensity time trace obtained from a fluorescence experiment performed on a 1 ppm solution of o-xylene. The overall shape of this curve is significantly affected by noise in the measurement system. As the concentration of a contaminant in solution decreases it may still be possible to obtain fluorescence data, but the lifetime determined from that data may no longer be representative of the contaminant under investigation. As a result, it is necessary to establish a minimum signal level above the noise that will facilitate reliable and repeatable calculations of lifetimes that agree with those obtained from the equilibrium solutions. This signal level must exceed that required simply for detection of the contaminants. The signal level must also be great enough to include several reliable data points on the decay curve of the test compound.

The minimum signal level required for repeatable determinations of fluorescence lifetimes was determined by analyzing the sensitivity of the curve fitting procedure used in this program to different assumptions of background noise levels. Given that noise can drastically
alter the shape of a decay curve, it is desirable to curve fit using only data that exceed the noise level yet also represent a large enough portion of the decay curve to facilitate an accurate curve fit.

![Fluorescence Decay Curve](image)

**Figure 6.12:** Fluorescence Decay Curve for 1 ppm Aqueous Solution of (o)-Xylene.

Figure 6.13 illustrates the influence of background noise level assumptions on the exponential curve fitting procedure described above. The points presented in Figure 6.13 were obtained by repeatedly fitting exponential decay curves to the data from each of the aqueous tests under a variety of background noise level assumptions. Since background noise has an adverse influence on the curve fit results, the exponential curve was fit only through data having a large enough intensity to exceed a selected noise band. Under the assumption that the background noise can be characterized by a normal distribution, the rejected noise band was varied over a range from 1 to 10 times the standard deviation of the background noise observed throughout the aqueous phase of the testing program. Although this range is greater than one would actually apply in practice, it demonstrates the dependence of the curve fit results on the fraction of the decay curve used in the fitting operation.
Figure 6.13: Effect of Background Noise on Fluorescence Lifetime Determinations.

To carry out this exercise, the entire data set for each test was first fit with an exponential decay curve. This fitted curve, a smooth and continuously decreasing function, was then used to identify points in time at which the intensity of the fluorescence signal would be expected to drop below each of the studied noise bands. In this way, a truncation point for the data set was established for each noise criterion without the influence of noise that might cause the data to plummet below the noise band at a time far earlier than the phenomenon it represents. The truncation point and the peak intensity of the data set were then used to calculate the fraction of the peak fluorescence intensity embedded in the assumed noise band. Figure 6.13 illustrates the relationship between the accuracy of the decay constant obtained from a curve fit and the fraction of the peak fluorescence intensity embedded in the assumed noise band. The curve fit accuracy is presented using a normalized lifetime ratio that illustrates the variation in a curve fit decay constant from the decay time that was generated from large signal equilibrium data. The numerator represents the difference between the decay constant
obtained from a particular test, $\tau$, with a given noise band and the mean lifetime obtained from equilibrium data, $\tau_{\text{mEQ}}$. The denominator is simply the mean equilibrium lifetime.

As evidenced by Figure 6.13, repeatable determinations of fluorescence lifetimes can be performed on at least one of the intensity time traces obtained from a contaminant WTI profile if the level of background noise in the WTI curve is less than approximately 25% of the curve’s peak amplitude. Within this range of less than 25% noise, lifetimes are determined within $\pm 10\%$ of the equilibrium values with a confidence of approximately 70%. Note that this level of error precludes the effective distinction of compounds such as toluene and o-xylene.

The criterion determined for consistent curve fitting of the fluorescence decay profiles establishes the ultimate identification limits of the LIF probe for each of the BTX compounds. The standard deviation of the background noise for all of the tests performed in this phase of the testing program is approximately $6.3 \times 10^{-6}$ a.u.. Again assuming that the background noise is random normal in nature, a noise envelope can be established at a signal value of $1.6 \sigma$ which includes approximately 90% of the noise signal. Therefore a minimum WTI peak amplitude of approximately $4.0 \times 10^{-5}$ a.u. (i.e. $4 \times 1.6 \times 6.3 \times 10^{-6}$) is required to identify a compound on the basis of its fluorescence lifetime. Thus, the identification limits of the LIF probe for benzene, toluene, and o-xylene are $\sim 225$ ppm, 4 ppm, and 2 ppm respectively. (Note that these limits are determined from relationships established in Section 6.6 of this chapter that describe the quantification capabilities of the LIF probe). These limits can, of course, be enhanced by increasing the laser power, increasing the light throughput of the spectroscopic system, or further limiting the level of background noise in the measurement system.

6.6.2 Results of Contaminant Quantification Tests

As outlined above and described in detail in Chapter 2, the total fluorescence signal generated during a LIF experiment is proportional to the concentration of the fluorophore in solution. The total fluorescence signals obtained in the experiments performed using the high speed oscilloscope and the photon counter are represented by the concentration indicators listed in Tables 6.2 and 6.3, respectively. In the following discussion the data acquired using the oscilloscope are discussed independently from those obtained using the photon counter.
Concentration indicators determined from data collected with the oscilloscope can be used to generate relationships between the concentration of each of the BTX compounds in solution and the observed total fluorescence signal as illustrated in Figures 6.14 through 6.16. In all cases, the experimentally observed fluorescence signals are linearly proportional to the concentration of the contaminant in solution. The lines drawn through the data in Figures 6.14 through 6.16 are the results of linear regression analyses. The quality of the fit is indicated by the regression coefficient displayed with each figure. Note also that the equations of the linear regression lines are presented with the figures.

Although each of the curves display a similar trend, it is obvious that different concentrations of each of the BTX compounds are required to achieve a given signal level. Unfortunately, since the compounds cannot be observed over the same concentration range, it is not possible to compare the fluorescence signal levels of all three compounds at any given concentration using experimental data. However, a comparison of the slopes of the linear regression lines fit through the data reveals that, for a given concentration, o-xylene yields approximately 2.5 times more fluorescence signal than toluene and over 380 times more signal than benzene.

**Figure 6.14:** Linear Relationship between Total Fluorescence Signal and Aquacous Concentration for Benzene.
**Figure 6.15:** Linear Relationship between Total Fluorescence Signal and Aqueous Concentration for Toluene.

Regression:
\[
\text{Signal} = 2530 \times \text{Concentration (decimal equivalent)}
\]
\[r^2 = 0.995\]

**Figure 6.16:** Linear Relationship between Total Fluorescence Signal and Aqueous Concentration for (o)-Xylene.

Regression:
\[
\text{Signal} = 6450 \times \text{Concentration (decimal equivalent)}
\]
\[r^2 = 0.989\]
The differences in fluorescence behavior among the BTX chemicals are a function of two primary factors. First, as illustrated by the absorption spectra for each chemical (see Figure 6.17), the BTX compounds all have substantially different absorptivities for the 266 nm excitation radiation used in these experiments. O-xylene will absorb nearly 13 times more 266 nm radiation than benzene, and approximately 1.4 times as much as toluene. Second the quantum yields of each of the compounds differ. Although there are significant solvent dependencies, the quantum yield of o-xylene is approximately 1.1 times that of toluene and 3.5 times that of benzene (Murov et. al., 1993). These factors demonstrate that for a selected concentration, the number of photons absorbed and subsequently re-emitted (with some losses) as fluorescence, by o-xylene should be approximately 1.5 times that of toluene and 45 times that of benzene. These factors, however, only provide a rough indication of the overall fluorescence behavior represented by the total fluorescence signal underlying a WTI profile. Although the number of transitions from the ground state to an excited state and back to ground state via radiative emission serves as the foundation of the fluorescence signal, the energy associated with each of the radiative transitions is a function of the actual structure of the molecule under investigation and not simply the number of photons involved.

Figure 6.17: Absorption Spectra of the BTX Compounds (adapted from Berlman, 1965).
Based on the linear relationships presented above, it is possible to obtain the limit at which the probe can reliably determine the concentration of a known contaminant in aqueous solution. As the concentration of a contaminant in solution decreases the fluorescence radiation emitted by the material will decrease uniformly at all wavelengths therefore the general shape of the WTI profile would be expected to remain approximately the same, and would simply scale according to the peak height. This concept is confirmed in Figure 6.18 which depicts the linear relationships between the peak amplitudes of the WTI profiles and the concentration of the contaminants in solution.

Regression:
\[ \text{Signal} = 0.179 \times \text{Concentration (decimal)} \]
\[ r^2 = 0.922 \]

Regression:
\[ \text{Signal} = 11.3 \times \text{Concentration (decimal)} \]
\[ r^2 = 0.995 \]

Regression:
\[ \text{Signal} = 24.0 \times \text{Concentration (decimal)} \]
\[ r^2 = 0.841 \]

Figure 6.18: Linear Relationships between WTI Peak Intensity and the Concentration of a Contaminant in Solution.
Since both the peak signal and volume of the WTI profile relate well to concentration it is possible to evaluate the performance of the LIF sensor by comparing these two values. When the magnitude of the WTI peak no longer scales with its volume than it is clear that factors other than fluorescence, such as noise, are contributing significantly to the volume calculation. At this point the concentration calculations are no longer valid and it is not possible to reliably quantify observations made using the LIF probe. This quantification limit is difficult to assess. However, Figure 6.19 demonstrates that, on a log-log scale, the linear relationship between WTI peak amplitude and the volume under the WTI curve breaks down as the peak signal approaches 1 to 2 \( \times 10^{-4} \) a.u. Notice that this limit is more severe than that observed for the determination of fluorescence lifetimes. This results from the fact that only a single high quality intensity time trace is required to achieve reasonable decay time estimates. However, concentration measurements make use of the entire wavelength spectrum over time. Thus, in essence, a large portion of the WTI curve must be composed of reliable data to yield accurate concentration measurements.

![Graph showing relationship between peak signal and volume under WTI profile](image)

**Figure 6.19** Relationship between the Peak Amplitude and Volume of WTI Profiles.

The quantification limits for the BTX compounds associated with the divergence points indicated in Figure 6.19 are approximately 750 ppm for benzene, 18 ppm for toluene, and 8 ppm for o-xylene. Note that these values were obtained by dividing the quantification
limits (a.u.) by the respective slopes of the regression lines drawn through the data of Figure 6.18.

The quantification limits mentioned above can be associated with a minimum signal to noise ratio (SNR) that is required when the LIF probe is used in conjunction with the oscilloscope. For the purpose of contaminant quantification this signal to noise ratio is given by the quotient of the minimum required peak signal (i.e. $2 \times 10^{-4}$ a.u.) to the assumed background noise level (i.e. $1.6 \sigma = 1.6 \times 6.3 \times 10^{-6}$) which results in an SNR of 20. These limits, however, do not necessarily mark the ultimate capabilities of the LIF system. The following discussion describes a small series of tests performed to assess the benefits afforded to the LIF system by applying photon counting techniques for data acquisition. The photon counter achieves greater quantification sensitivity than the oscilloscope, and also produces results that are very easily interpreted and subject to less ambiguity at low concentrations than those obtained using the scope.

The results of the photon counting tests performed on o-xylene were listed in Table 6.3 in Section 6.4.2. These results are shown graphically in Figure 6.20. For all 6 of these

![Graph showing photon counting results for o-xylene](image)

**Figure 6.20:** Results of Photon Counting Tests Performed on Aqueous Solutions of (o)-Xylene.
tests the water Raman line has been subtracted from the data. Although limited in scope, the
tests illustrate the quality of data that can be achieved at very low concentrations using the
photon counter. In particular, the 5 ppm and 1 ppm curves are obviously repeatable. The two
500 ppb curves are less similar. However, this difference most likely stems more from the
difficulty of creating a 500 ppb solution than from actual measurement error. The peak counts
recorded for the lowest concentration displayed (500 ppb) are 221 and 306 and the two 500
ppb curves include totals of 1474 and 2950 counts over the 39 observation points. The
background level recorded using the photon counter has a mean of \(~ 1\) count per observation
point. Since the photon counting process is most appropriately described by a Poisson
distribution, the standard deviation of this per measurement background is simply the square
root of the mean or also 1. When working with a Poisson process however the standard
device of the data is not very useful for establishing a level of confidence regarding the
likely count value associated with the background. However, the cumulative Poisson
probability distribution can be used to determine that there is a \(~ 92\%\) probability that the
background count will remain below a value of 2 if characterized by a mean of \(~ 1\). Thus,
assuming that this confidence level is acceptable, the 500 ppb tests are associated with a signal
to noise ratio at the peak of at least \(~ 110\) and an overall total count SNR of at least \(~ 18\) (i.e.
1474/(2*39)) at this same concentration. Although the overall SNR is not very high at the
500 ppb level it is important to recognize that an acceptable signal to noise ratio for photon
counting can be as low as 2 to 5 because of the processes unusually stable background and the
improbability of generating false positive results due to the binary nature of the counting
scheme (i.e. below threshold = 0; above threshold = 1).

The significance of this concept is most important for contaminant detection
(discussed in the following section); however, the LIF sensor’s quantification capabilities are
also enhanced using the photon counter. This point is made clear by interpreting the total
fluorescence counts recorded for each of the tests performed with the photon counter. As
shown in Figure 6.21, the total fluorescence counts are linearly proportional to concentration.
Thus if it was deemed acceptable to operate at a SNR of 2, where the noise is represented by
a value of 2 counts per measurement, a “concentration” measurement determined by the
\text{SNR} \times \text{Background} = 2 \times (2 \times 39) = 156 \text{ would signify the lowest possible}
quantification level achievable when using the photon counter for data acquisition with the LIF probe. Based on the slope of the regression line fit through the limited data set of Figure 6.21, the total count of 156 corresponds to an o-xylene concentration of 34 ppb.

![Graph showing relationship between total counts and concentration (ppm)](image)

Regression:
Total Counts = $4.6 \times 10^9 \times$ Concentration (decimal equivalent)

$r^2 = 0.990$

**Figure 6.21:** Relationship between Total Counts and Aqueous Concentration for Photon Counting Tests Performed on (o)-Xylene.

### 6.6.3 Results of Contaminant Detection Tests

Contaminant detection is the final performance characteristic of the LIF probe that can be evaluated from this phase of testing. The detection capabilities of the probe define the ultimate limits of its usefulness in practice. Often, once a contaminated site is identified and researched, the type of compounds in the ground are known and a simple detect/non-detect device can be very useful to locate zones of contamination for further, more detailed, study. In this regard, it is important for the LIF probe to provide reliable results. Therefore, when using the probe in a detect/non-detect application a detection criterion must be established to reduce the possibility of misclassifying a tested zone.

The criterion selected for detection using either the oscilloscope or photon counter for data acquisition were established to statistically eliminate the possibility of interpreting...
background noise as a fluorescence signal. Based on the assumption that the background noise included in the oscilloscope measurements is statistically normal, a detection criterion can be established which requires a minimum signal level of approximately three times the standard deviation of the background noise (3σ). The 3σ noise band theoretically includes approximately 99.9% of the background noise signal. Thus any signal detected in excess of this value could reasonably be interpreted as the by-product of fluorescence. When using the photon counter, based on the cumulative Poisson probability distribution, the noise level must be assumed to be 5 counts per bin to achieve an equivalent confidence level to that described for the oscilloscope.

![Graph showing the relationship between concentration (ppm) and peak count.](image)

**Regression:**

\[
\text{Total Counts} = 4.4 \times 10^8 \times \text{Concentration (decimal equivalent)}
\]

\[r^2 = 0.991\]

**Figure 6.22:** Relationship between Peak Photon Counter Measurements and the Aqueous Concentration of (o)-Xylene.

The detection limits for the BTX compounds when using the oscilloscope for data acquisition are therefore 100 ppm, 2 ppm, and 0.8 ppm, respectively \([(3\times6.3 \times 10^6) / \text{(slope of respective regression line in Figure 6.18)}]\). If the photon counter is used for data acquisition only the peak of the EW profiles would have to extend above the noise baseline. Therefore assuming a minimum required signal to noise ratio of 2, the single measurement count would have to exceed \(2 \times 5 = 10\) to signify a positive detection of o-xylene. Relating the peak of the
EW profile generated with the photon counter to the concentration of the contaminant in solution as in Figure 6.22, a peak count of 10 corresponds to an aqueous concentration of approximately 23 ppb for o-xylene.

6.6.4 Summary of LIF Sensor Performance Limits and Evaluation Criteria

Overall, the detection, identification, and quantification tests demonstrate the performance capabilities of the LIF sensor in aqueous, single compound solutions using either the high speed oscilloscope or the photon counter for data acquisition. The aqueous solution experiments have also lead to the development of several criteria that objectively define the limits of the sensor’s capabilities. These criteria and the sensor’s associated performance limits are summarized in Table 6.4. The performance limits are separated according to the nature of the data acquisition system employed during testing. The evaluation criteria used to establish the tabulated performance limits are summarized below each performance heading. Note that no photon counting experiments were performed on solutions of benzene or toluene. Further, no attempts were made to identify compounds using the photon counter.

<table>
<thead>
<tr>
<th>Compound</th>
<th>High Speed Oscilloscope</th>
<th>Photon Counter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Detection 3 ( \sigma )</td>
<td>Identification SNR &gt; 4</td>
</tr>
<tr>
<td>Benzene</td>
<td>100 ppm</td>
<td>225 ppm</td>
</tr>
<tr>
<td>Toluene</td>
<td>2 ppm</td>
<td>4 ppm</td>
</tr>
<tr>
<td>(o) - Xylene</td>
<td>0.8 ppm</td>
<td>2 ppm</td>
</tr>
</tbody>
</table>

Table 6.4: Summary of LIF Sensor Performance Limits and Evaluation Criteria.

6.7 Results of Laser Penetration Tests

The results described above for the general aqueous solution testing program provide a database that may be compared to the fluorescence signatures of the BTX compounds in the presence of soils. One of the primary factors that determines the magnitude of fluorescence observations generated from a solution of given concentration is the volume of that solution
interrogated by excitation radiation. When contaminants exist in the presence of soils, inevitably some of the volume typically excited in a matrix free solution will be occupied by the soil particles. The difference in signal levels observed between simply aqueous solutions and solutions in soil will therefore, to some extent, be related to the difference in the volume of the contaminant solution that is excited.

Under this premise, a series of specialized tests was performed during the aqueous testing phase of this program in an attempt to obtain an estimate of the depth of laser penetration into aqueous media. These tests were performed using the same liquid test cell used for all other aspects of aqueous solution testing. However, during the laser penetration tests, the cap of the liquid test cell was removed and a polished glass cylinder was put in its place. The glass cylinder was attached to the end of a micrometer incremented in thousandths of an inch. The micrometer permitted precise movement of the glass cylinder toward and away from the laser probe window. When performing a test to evaluate the depth of light penetration into an aqueous solution the test cell was partially filled with a contaminant solution and then the glass cylinder was gradually lowered through the solution until it contacted the laser probe window. As the cylinder descended toward the window it displaced the contaminant from the region in front of the window and thereby reduced the volume of the solution that was excited by the laser. The reduced volume resulted in a reduction in the fluorescence signal that was observed using the high speed oscilloscope. A total of six tests were performed as described above. Two trials were conducted with each of the three BTX compounds. The results of these tests are presented in Figure 6.23. From this figure it is clear that all of the solutions behaved in the same manner. As the glass cylinder was lowered into the test solution, the fluorescence signal remained constant and then rapidly dropped off in magnitude as the glass cylinder closed in on the probe window. The point where the signal begins to decrease marks the outer boundary of the zone of solution excited by the laser. When the glass cylinder begins to occupy this zone, the amount of contaminant excited decreases and so does the observed fluorescence signal. The curves in Figure 6.23 demonstrate that the zone of excitation extends to a distance of approximately 0.64 to 0.76 mm beyond the face of the probe window. Since the size of this zone is larger than many soil particles, significant signal reduction and/or interference can be expected when performing
LIF tests on contaminants present in a soil matrix. The application of these measurements is discussed in Section 7.4.3.

Figure 6.23: Results of Laser Penetration Tests.
CHAPTER 7

SOILS

7.1 Introduction

Numerous laboratory experiments were performed using the microchip laser probe and the soil test chamber to identify factors that might influence LIF measurements made in the subsurface. Tests were carried out, using both processed and natural materials, in a manner that simulated the interface between the laser probe and soil as it would occur in the field. This approach was pursued in an effort to link laboratory findings to real world applications of the LIF sensor. The soil tests helped evaluate the impact of a soil matrix on the performance capabilities of the probe and also determined the effect of soil properties on the fluorescence signatures of compounds observed in the presence of soils. Investigated soil properties included grain size, color, mineralogy, morphology, soil type, and organic content.

This phase of testing was pursued on a parametric basis. The testing program was therefore designed to identify the characteristics of soil that have the greatest influence on LIF measurements. As with any parametric study, an effort was made to investigate the significance of individual parameters whenever possible, and in this way build a progressively more complex understanding of soils' impact on fluorescence observations.

To isolate the effects of specific soil properties, LIF tests were performed on a variety of soils including the idealized material industrial quartz, Manchester fine sand, Ticino sand, Boston blue clay, Venezuelan clay, and a regional silt from the Massachusetts area. The wide grain size range, single mineralogy, and uniform coloration of industrial quartz made this material useful for a comprehensive study of soil grain size effects. Additional granular materials having narrower grain size distributions were also selected for study to follow up on the grain size trends identified during the quartz tests. These materials include Manchester fine sand and Ticino sand. Manchester fine sand has a somewhat less uniform mineralogy and
higher organic content than the quartz, and also differs in color. Ticino sand contains a wide range of minerals, is quite varied in color, and also has a much higher organic content than the quartz. LIF tests using MFS and Ticino sand were therefore compared with those performed using industrial quartz to illustrate the significance of mineralogy, soil color, and organic content. Since the quartz material also exists in a fine grained form as quartz flour, it was possible to compare quartz flour test results with those generated using Bostor blue clay, Venezuelan clay, and regional silt to investigate the effect of changes in soil type, soil color, and morphology while eliminating the impact of grain size. Although this group of soil types is by no means an all inclusive set of natural materials, it does provide a sampling of the range of soils that might be encountered in the field. (Note that the physical characteristics of all of the tested soils are described in detail in Chapter 5).

Due to the number of variables involved in the soil tests, several steps were taken to simplify the test program. Since the results of the aqueous solution testing program demonstrated that trends in the fluorescence behavior of all of the BTX compounds are quite similar, only aqueous solutions of o-xylene, the chemical with the highest quantum yield of the BTX compounds, were used during this phase of testing. Further, the strongly linear relationships of concentration versus fluorescence signal developed from the aqueous solution tests eliminated the need to evaluate a range of solution concentrations during the soil tests. Thus, only equilibrium concentrations of o-xylene (175 ppm) were employed for soil testing. These choices simplified test execution and also helped assure consistent test conditions throughout the program, which ultimately facilitated the comparison of individual test results.

All of the soil experiments were performed in accordance with the general testing procedures outlined in Chapter 4, Section 4.5. Procedural details specific to the soils tests are discussed within this chapter. In some cases, additional equipment modifications were implemented to further understanding of observed phenomena. These enhancements are discussed herein, as necessary.

Fluorescence induced during the soil tests was observed using a Hamamatsu H5783-03 photomultiplier tube attached to a CVI CM110 spectrometer as discussed in Chapter 4. Signals emanating from the detector photomultiplier tube were monitored using the LeCroy 9362 digital storage oscilloscope triggered by a second PMT. As described earlier, the high
speed oscilloscope provides measurements of the fluorescence signal intensity over time and therefore elicits all available information from a fluorescence experiment.

Throughout the soil testing program, the scope and the spectrometer were configured exactly as described in Sections 6.2 and 6.2.1 of Chapter 6. Since the soil test data were similar in form to that gathered during the aqueous testing program, all of the software developed for data reduction of aqueous solution tests was also utilized for the soil tests. Note that the confidence established during the aqueous solution tests in the capabilities of the probe, and in the robustness of the data reduction software, led to fewer duplicate tests in this stage of the program - although frequent background and standard solution checks were nonetheless performed regularly to ensure that the LIF probe was operating correctly.

Results from all of the soil tests are summarized and interpreted within this chapter. Section 7.2 presents an overview of the soil testing program and describes procedural details and equipment enhancements characteristic of the soil experiments. Section 7.3 provides a summary of the soil test results. Section 7.4 examines granular media and the effect of soil grain size on contaminant fluorescence observations. Results of additional tests performed on granular media to evaluate particle morphology, soil color, mineralogy, and organic content are summarized and analyzed in Section 7.5. Section 7.6 briefly examines the impact of soil type on LIF measurements made with the microchip laser probe. Finally, Section 7.7 describes the overall influence of soil on the performance of the microchip LIF sensor.

7.2 Scope and Description of Soil Tests

LIF tests were performed on a variety of soil specimens created from natural soils, preprocessed mixes of industrial quartz, or selected grain size ranges of these materials (for example, passing a No. 10 sieve and retained on a No. 20 sieve). The specimens were generally categorized as granular media (particles retained on a U. S. Standard No. 200 sieve) or material termed fines (particles passing a U. S. Standard No. 200 sieve). Tested soils included in the category of granular media are industrial quartz, Ticino sand, and Manchester fine sand. The fines tested in this program included Boston blue clay, Venezuelan clay, a regional Massachusetts silt, and sieved fractions of the quartz flour and Manchester fine sand.
Two types of soil tests were performed during this program. One test type was carried out using the specimen chamber, contaminant reservoir system, and flow control unit described in Chapter 4. This first test type, hereafter referred to as a standard soil test, was performed on both granular media and fines. A second type of test, termed a soil paste test, was performed only on fines and made use of the preliminary test cell discussed in Section 4.2.2 of Chapter 4. The two types of soil tests are described separately below (in Sections 7.2.1 and 7.2.2).

Table 7.1 summarizes the tests performed on each of the soils mentioned above. The table is organized by material with separate divisions for each test type. When appropriate the material classifications are subdivided into specific grain size ranges. The last two columns of the table provide the number of standard soil tests and soil paste tests performed on specimens created from each grain size range.

### 7.2.1 Standard Soil Tests

During all of the standard soil tests, the soil test chamber was coupled to the laser probe as illustrated in Figure 4.5. After coupling the test chamber and the probe, the test specimen was prepared in accordance with the pluviation and undercompaction procedures detailed in Chapter 5 for granular and fine grained materials, respectively. Following setup of the specimen, the soil in the test chamber was saturated with distilled demineralized water.

The saturation process was performed by allowing water to infiltrate the specimen from bottom to top under a low hydraulic head to avoid channeling through the specimen or along the side walls of the test chamber. This initial stage was particularly important when dealing with finer grained materials. Generally, a hydraulic gradient of less than 15 was utilized. Once the flow emerged from the far end of the specimen, the pore fluid line leaving the specimen chamber was closed and the pressure in the pore fluid was gradually raised to 4 atm so that all air in the specimen, which had not been pushed out during the infiltration phase, was forced into solution. Once saturated, at least two pore volumes of water were flushed through the specimen under low gradient conditions. A piston connected to the pore fluid line at the top of the specimen was drawn away from the specimen at constant velocity.
while the surface of a fluid reservoir connected to the bottom of the specimen was pressurized at slightly more than 4 atm. The piston velocity was maintained so that the hydraulic gradient across the specimen never exceeded 15.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Grain Size Range (mm)</th>
<th>Sieve Sizes</th>
<th>Number of Tests Performed</th>
<th>Soil Paste</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Passing (No.)</td>
<td>Retained (No.)</td>
<td>Standard</td>
</tr>
<tr>
<td>Industrial Quartz</td>
<td>2.00 - 1.19</td>
<td>10 - 16</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.19 - 0.84</td>
<td>16 - 20</td>
<td>1</td>
<td>-</td>
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<tr>
<td></td>
<td>2.00 - 0.84</td>
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**Table 7.1: Summary of Soil Testing Program.**

After saturation, a complete WTI scan of the water saturated soil specimen was acquired. This scan served as a background signature. The specimen was then infiltrated with
at least 2 pore volumes of equilibrium o-xylene solution under the same conditions as described above. Again a full WTI scan was performed, which provided an example of the LIF signature of o-xylene in a particular soil. As later became apparent, this WTI scan was subject to considerable variability depending on the properties of the soil specimen under investigation. Therefore, several additional stages were added to the soil testing procedure in an effort to bound the potential signal variability.

One of these additional steps required minor modification of the specimen chamber. A micrometer and an additional Teflon gasket were added to the clamp used to couple the specimen chamber with the laser probe. The Teflon gaskets permitted smooth movement of the probe across the surface of the specimen while maintaining pore pressures in excess of 1 atm. The micrometer allowed accurate tracking of the probe movement.

The micrometer controlled probe movement was utilized to perform a scan of the soil surface, and thus acquire an estimate of the potential variability in the fluorescence signal observed from a contaminated soil specimen as a function of the laser probe's position on the specimen. This "range test" was performed following the acquisition of the full WTI scan of the contaminant-saturated specimen. To perform the range scan, the pore pressure in the specimen was reduced to 1 atm and the stress on the coupling clamp was relaxed. The micrometer attached to the coupling clamp was then used to advance the laser probe across the soil specimen. In this way LIF measurements could be obtained at a variety of locations across the specimen. Generally, measurements were taken every 0.125 mm across the specimen over a range of approximately 5 mm. Since evidence from the aqueous solution tests and the full WTI scans of the soil testing program demonstrated that the peak intensity of the WTI profile was linearly related to the volume under the curve (or total fluorescence signal), there was no need to acquire a full WTI profile at each of the measurement locations across the soil specimen. Instead, only a single intensity-time trace at the 294 nm emission wavelength was acquired at each measurement location. The 294 nm intensity-time trace is generally at or very near the peak of o-xylene WTI. Therefore the peak of this trace can be used to extrapolate a total fluorescence signal associated with each of the range scan measurements.
After performing the range scan, the micrometer was used to position the laser probe at the location of an approximate minimum signal. At this point, the coupling clamp was fully tightened, the pore pressure was re-equilibrated to 4 atm, and another full WTI scan was acquired marking a "minimum" signal. Subsequently, the pressure was again reduced, the clamp was again relaxed and the micrometer was used to search for a maximum signal. The pore pressure was then raised again to 4 atm and a "maximum" WTI scan was acquired. Since the locations of minimum and maximum WTI scans were established subjectively by visually monitoring the peaks of individual intensity time traces on the oscilloscope, these scans did not represent the absolute maximum and minimum observable fluorescence signals in the presence of the soil under investigation. Instead the additional full WTI scans were completed to ensure that the in-soil LIF signature of o-xylene behaved as anticipated from trends observed in the aqueous solution experiments. These additional full scans, which covered a broad range of signal intensity, also provided further support of the linear relationship between the WTI peak and the total "volume" under the WTI curve. Note that once this relationship was satisfactorily established, the minimum and maximum scans were eliminated from the testing procedure.

After completing all of the full WTI scans and range scans on a given specimen, fluid that had flowed through the specimen was extracted from the outlet lines of the test system and placed in a sealed vial. Within 10 minutes of extraction the fluid was tested in the preliminary test cell to acquire a full WTI signature representative of the pore fluid in the specimen. When presenting results of the soil tests, all signals are normalized by the total fluorescence signal from the extract. This has two primary benefits. First, it allows each test to be compared without concern for long term fluctuations in the power characteristics of the laser or inconsistencies in the concentration of the pore fluid contaminant. Essentially each measurement is presented relative to the conditions present at the time of testing. This procedure also eliminates the need to account for soil sorption effects that have not yet been studied by placing all measurements in terms of the pore fluid composition.

In summary, there were six stages to the standard soil test performed for this program: (1) a background scan with water, (2) a full WTI scan of soil following contaminant saturation, (3) a range scan consisting of intensity-time traces acquired at fixed intervals of
displacement across the specimen, (4) the search for, and acquisition of, a "minimum" WTI curve, (5) the search for, and acquisition of, a "maximum" WTI curve, and (6) a full WTI scan of pore fluid extract. As mentioned above, not all six stages were completed for every soil specimen.

7.2.2 Soil Paste Tests

The soil paste tests provided an alternative to the long time periods required to ensure contaminant saturation of the large specimen used in the standard soil tests. The soil paste tests made use of less than 5 grams of fine grained material. The material to be tested was prepared approximately 48 hours prior to actual testing. To prepare the test specimen, approximately 5 grams of air-dried fines were placed in a 40 ml vial filled with equilibrium o-xylene solution. The vial was sealed with no head space and then vigorously agitated at the time of preparation. The soil/contaminant mixture was then allowed to sit, while sealed, for at least two days.

After equilibrating with the contaminant mixture, the soil became a paste. This paste was then placed directly on the laser probe window in the preliminary test cell for testing. The lid of the test cell was then closed and the test was performed. After completing a full WTI scan of the contaminated soil paste, the fluid in the preparation vial was also tested to demonstrate that sufficient contaminant was present in the vial to satisfy any sorption demands of the soil. This fluid signal was used to normalize the signal acquired during the soil paste test.

7.3 Summary of Soil Test Results

Given the above preface that describes the nature of the soil tests, the following discussion summarizes the results of the tests performed during the soil program. During each stage of the standard soil tests, and all stages of the soil paste tests, the oscilloscope was used to acquire either a full WTI scan or at least a peak intensity time trace that could be extrapolated to yield a total fluorescence signal. Each full WTI scan was analyzed to determine the total fluorescence signal excited in the test medium, the wavelength of peak
fluorescence emission, and the fluorescence lifetime of the compound in solution. These calculations were performed using the procedures outlined in Chapter 6, Section 6.4.1.

For all of the soil tests, all test result parameters were calculated after subtracting a background signature from the observed WTI profile of the tested contaminated media. These background scans were generally featureless with little, if any, evidence of influences other than electronic noise, optical noise, and electrical ringing. In fact, none of the soil tests demonstrated any significant background signature that could be attributed to the presence of soil. This observation helped to eliminate concerns over possible soil Raman signatures that might interfere with fluorescence observations. Further, in the majority of the soils tests, not even the water Raman line was visible. Only tests performed on the intermediate to large grain size, and therefore large pore size, specimens included enough interrogated volume to register a noticeable water Raman signature. (This observation will be described in more detail in the discussion of soil grain size effects presented later in this Chapter).

Table 7.2 summarizes the parameters of interest obtained from soil tests performed on specimens of industrial quartz. The results of the various stages of the soils tests are presented in separate groups of columns. The first two columns of the table identify the test and describe the size of soil particles used to form the specimens. The next three columns, columns 3, 4 and 5, provide the lifetime, peak emission signal, and concentration indicator derived from the first full WTI scan performed on the particular test specimen immediately following contaminant saturation. Note that the wavelength of peak emission is not tabulated because it remains at a value of 294 ± 1.2 nm for all of the soil tests performed using o-xylene as a contaminant. Columns 6 and 7 present the peak emission signal and concentration indicator obtained from the full WTI scans performed on the pore fluid extract. The lower and upper bounds of the signals recorded during the range scans are then presented in columns 8 and 9, respectively. Finally, columns 10 through 13 provide the peak emission signal and concentration indicators obtained from the minimum and maximum full WTI scans performed on a select group of specimens. WTI profiles and a comprehensive summary of the data acquired from each of the full WTI scans performed on quartz specimens are provided in Appendix E. Appendix F contains a summary of each of the range scan tests performed on specimens of quartz.
Table 7.3 presents the results of the soil tests performed on granular media other than industrial quartz. This includes all tests performed on specimens of Manchester fine sand and Ticino sand. Table 7.3 is organized in exactly the same manner as Table 7.2 with only two exceptions: (1) an additional column is included to differentiate soil type, and (2) no minimum or maximum WTI scans were performed on Manchester fined sand or Ticino sand. Note that Table 7.3 also includes the results for two unique tests, MFS1 and TIC1, that were performed on unsieved natural soils. Appendix G includes WTI profiles and a summary of the data acquired from each of the full WTI scans performed on specimens of Manchester fine sand and Ticino sand. The range scan tests performed on specimens of each of these soils are summarized in Appendix H.

Standard soil tests were also performed on fine grained materials. Two tests were conducted on specimens composed of silt particles passing a No. 200 sieve and retained on a No. 325 sieve. In addition, two tests were also performed on similarly sized particles of Venezuelan clay. In all four cases the obtained signatures resembled background noise. Thus the “results” of these tests are not tabulated.

The limited results of the soil paste tests are presented in Table 7.4. None of the full WTI scans of the soil pastes provided measurable LIF signals. However, for completeness, Table 7.4 presents the peak emission signal and the concentration indictor obtained from tests of the pore fluid of the respective soil pastes.

The data presented in the summary tables is sufficient to reconstruct any of the figures presented in the discussion of results that follows with only one exception. In particular, the range scan data presented in the tables can be used to define only the upper and lower bounds of the observed fluorescence signal rather than all of the individual observations. The author believes that these bounds indicate the observed trend without the need for a comprehensive list of the more than 800 individual readings obtained during the testing program.

Although the parameters of interest provided in Tables 7.2 through 7.4 are useful by themselves, one should be aware of two simple calculations that are applied to the data for the purpose of presentation throughout the discussion of results. The first calculation involves the extrapolation of total fluorescence signals from measurements of the peak fluorescence.
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<th>Conc. Indicator</th>
<th>Peak Signal</th>
<th>Conc. Indicator</th>
<th>Range Scan</th>
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<td>Q170bX</td>
<td>0.10 - 0.09</td>
<td>6.5</td>
<td>4.54E-04</td>
<td>0.100</td>
<td>1.51E-03</td>
<td>0.334</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Q200aX</td>
<td>0.09 - 0.07</td>
<td>6.3</td>
<td>1.50E-04</td>
<td>0.029</td>
<td>1.16E-03</td>
<td>0.235</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Q125aX</td>
<td>0.07 - 0.04</td>
<td>4.7</td>
<td>1.12E-04</td>
<td>0.020</td>
<td>3.96E-04</td>
<td>0.069</td>
<td>4.37E-05</td>
<td>7.76E-05</td>
<td>5.75E-05 0.008</td>
</tr>
</tbody>
</table>

Table 7.2: Results of Laser Induced Fluorescence Tests Performed on Industrial Quartz.
<table>
<thead>
<tr>
<th>Soil</th>
<th>Test Name</th>
<th>Grain Size Range (mm)</th>
<th>Lifetime $\tau$ (ns)</th>
<th>Peak Signal $S$ (a.u.)</th>
<th>Conc. Indicator $I$ (a.u.)</th>
<th>Pore Fluid Extract</th>
<th>Range Scan</th>
<th>Lower Bound (a.u.)</th>
<th>Upper Bound (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manchester Sand</td>
<td>M78aX</td>
<td>0.21 - 0.18</td>
<td>6.8</td>
<td>5.24E-04</td>
<td>0.122</td>
<td>1.20E-02</td>
<td>3.082</td>
<td>1.05E-03</td>
<td>4.42E-03</td>
</tr>
<tr>
<td></td>
<td>M100aX</td>
<td>0.18 - 0.15</td>
<td>6.5</td>
<td>1.38E-03</td>
<td>0.343</td>
<td>1.19E-02</td>
<td>3.037</td>
<td>6.19E-04</td>
<td>4.61E-03</td>
</tr>
<tr>
<td></td>
<td>M325aX</td>
<td>0.07 - 0.04</td>
<td>6.6</td>
<td>9.76E-04</td>
<td>0.228</td>
<td>1.36E-02</td>
<td>3.392</td>
<td>7.46E-04</td>
<td>2.48E-03</td>
</tr>
<tr>
<td></td>
<td>MFS1</td>
<td>Natural Soil</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.32E-03</td>
<td>1.265</td>
<td>4.98E-04</td>
<td>1.49E-03</td>
</tr>
<tr>
<td>Ticino Sand</td>
<td>T253aX</td>
<td>0.71 - 0.59</td>
<td>6.5</td>
<td>4.48E-03</td>
<td>1.114</td>
<td>8.91E-03</td>
<td>2.140</td>
<td>8.29E-04</td>
<td>8.82E-03</td>
</tr>
<tr>
<td></td>
<td>T34aX</td>
<td>0.59 - 0.42</td>
<td>6.4</td>
<td>2.81E-03</td>
<td>0.669</td>
<td>9.99E-03</td>
<td>2.451</td>
<td>4.08E-04</td>
<td>7.62E-03</td>
</tr>
<tr>
<td></td>
<td>T45aX</td>
<td>0.42 - 0.30</td>
<td>6.6</td>
<td>4.47E-03</td>
<td>1.098</td>
<td>1.28E-02</td>
<td>3.140</td>
<td>8.84E-04</td>
<td>8.41E-03</td>
</tr>
<tr>
<td></td>
<td>TIC1</td>
<td>Natural Soil</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.40E-03</td>
<td>2.005</td>
<td>5.42E-04</td>
<td>4.54E-03</td>
</tr>
</tbody>
</table>

Table 7.3: Results of Laser Induced Fluorescence Tests Performed on Manchester Fine Sand and Ticino Sand.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Test Name</th>
<th>Grain Size Range (mm)</th>
<th>Peak Signal $S$ (a.u.)</th>
<th>Conc. Indicator $I$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boston Blue Clay</td>
<td>BBC1</td>
<td>Natural Soil</td>
<td>6.66E-03</td>
<td>1.497</td>
</tr>
<tr>
<td>Venezuelan Clay</td>
<td>VEN1</td>
<td>Natural Soil</td>
<td>6.80E-03</td>
<td>1.614</td>
</tr>
<tr>
<td>Regional Silt</td>
<td>SLT1</td>
<td>Natural Soil</td>
<td>9.04E-03</td>
<td>2.183</td>
</tr>
</tbody>
</table>

Table 7.4: Results of Laser Induced Fluorescence Tests Performed on Soil Pastes.
emission at 294 nm. The second calculation pertains to the normalization of total fluorescence signals (or concentration indicators) by the total fluorescence signal obtained from WTI scans of contaminant pore fluid extracts. These two issues are discussed individually below.

(1) Since the peak of the 294 nm IT trace is typically the peak of the overall WTI curve for tests performed on o-xylene, the intensity time traces acquired at 294 nm during the range scans can be used to extrapolate total fluorescence signals associated with each measurement. Evidence from all of the full WTI scans performed on o-xylene pore fluid extracts and soils saturated with o-xylene demonstrates that there is a strong linear relationship between the peak emission signal of a WTI profile and the volume or total fluorescence signal under the curve. This relationship is illustrated in Figure 7.1, which presents data from over 100 full WTI scans. The fact that this relation holds in the aqueous solution extracts and in the presence of a variety of soils supports its use for analyses involving the range scan data. Note that the proportionality constant of 246.3 which relates the peak and total o-xylene fluorescence signals obtained during the soil testing program (see Figure 7.1) is virtually identical to the value of 241.1 that characterizes the o-xylene aqueous solution test data.

![Figure 7.1: Linear Relationship between Peak and Volume of WTI Profile.](image-url)
(2) As mentioned briefly above, Tables 7.2 through 7.4 present total fluorescence signals derived from full WTI scans of the contaminant pore fluid extract. The reported value of the total fluorescence signal, however, is not truly representative of the contaminant concentration in the pore space of the test specimen. In actuality, the extract solution incurs significant contaminant losses during the extraction process. When the contaminant was extracted from the test chamber fluid lines it was allowed to pour into a vial which, despite efforts, could not be practically maintained with a zero head space during the filling period. Further, the contaminant was later (within 10 minutes) withdrawn from the vial using a syringe and placed into the preliminary test cell. Filling the preliminary test cell required two syringe volumes and therefore the test solution was open to volatilization during this transfer operation. To assess the losses incurred during the extraction and transfer procedures special LIF tests were performed using only contaminant solutions in the soil test chamber. The soil test chamber was filled with equilibrium o-xylene solution and then flushed with two additional volumes. A full WTI scan of the solution in the chamber was then acquired. Immediately thereafter some of the solution was extracted and tested in the preliminary test cell following the exact procedures used during the soil tests. Three of these calibration tests were performed. They demonstrated that the signal in the extract was approximately 18.9 ± 1.6 % less than that observed when the solution was tested within the specimen test chamber. With this loss in mind, the total fluorescence values reported in Tables 7.2 through 7.4 were increased by 18.9% before use in the normalizing procedures involved in the data analyses presented later in this Chapter.

The information derived from the tests summarized above is analyzed in detail in the following sections.

7.4 Effects of Soil Grain Size on LIF Measurements

7.4.1 Introduction

Throughout the soil testing program, primary attention was given to developing an understanding of the impact of soil grain size on the observed fluorescence signature of contaminants in soils. As mentioned earlier, specimens used in the initial studies of soil grain
size were created from selected grain size ranges of industrial quartz and were saturated with an equilibrium solution of o-xylene. This material was selected for its uniform mineralogy, consistent coloration, and broad range of available grain sizes; parameters that all enabled a thorough study of grain size effects without influences from other characteristics of the soil. The specimens created using quartz were composed of particles that spanned a wide grain size range, from particles passing a U.S. Standard No. 10 sieve (2.0 mm) to particles retained on a U.S. Standard No. 325 sieve (0.07 mm). The particles used to prepare most specimens were obtained by sieving the quartz material to obtain particles trapped between two closely sized sieves, for example passing a No. 10 sieve and retained on a No. 16. The grain size ranges evaluated during the quartz tests are summarized in Table 7.1. Note that all of the quartz specimens were prepared using multiple sieve pluviation to create specimens of uniform density.

7.4.2 Tests Performed on Quartz Specimens

Results of the LIF tests performed on the quartz specimens demonstrate that soil grain size, and indeed soil in general, has very little, if any, impact on the shape of the observed fluorescence signature of a contaminant. Typical normalized WTI profiles of o-xylene in the presence of quartz and in aqueous solution are presented in Figure 7.2. A comparison of these plots shows that the general shape of the aqueous and in-soil profiles are

![Figure 7.2: Typical Normalized WTI Profiles of (o)-Xylene in the Presence of Quartz (a) and in Aqueous Solution (b).](image-url)
indistinguishable. To emphasize the similarity between the aqueous and in-soil signatures, Figure 7.3 presents emission wavelength profiles for both of the WTI curves displayed in Figure 7.2. After normalizing the EW profiles to facilitate comparison it is clear that the emission characteristics of all of the test specimens are virtually identical, although the in-soil experiments show slightly more variability than the aqueous tests. Data analyses performed on all of the quartz tests indicate that the peak of the in-soil o-xylene WTI profile (synonymous in location with the peak of the EW profile) is located at 295 ± 2 nm which compares favorably to the value of 294 ± 1 nm recorded during the aqueous solution tests performed on o-xylene.

![Normalized Emission Wavelength Profiles](image)

**Figure 7.3:** Normalized Emission Wavelength Profiles for (o)-Xylene in Quartz and in Aqueous Solution.

Further evidence of soil's lack of influence on the shape of the emission signature of contaminants is provided by a review of Table 7.2 which presents the fluorescence lifetimes derived from WTI scans of the quartz specimens using the procedure described in Chapter 6, Section 6.5.1. The average o-xylene fluorescence lifetime obtained during quartz testing is 6.5 ± 0.3 ns (excluding test Q325a which had a particularly low signal). This value is very similar to the lifetime of 6.6 ± 0.2 ns determined during the aqueous testing program. Since there is no reason to believe that the observed behavior of other BTX compounds will differ
from that of o-xylene, it is clear that soil particles have no distinguishable influence on the form of a contaminant's emission signature.

Although soil has little influence on the shape of the observed fluorescence emission, there is a very noticeable effect of soil grain size on the magnitude of the observed signal. This is illustrated in Figure 7.4, which presents normalized fluorescence signals as a function of specimen particle size. Figure 7.4 includes the total fluorescence measurements (concentration indicators) from full WTI scans of quartz specimens obtained during three different test stages: (1) following contaminant saturation, (2) during the minimum scan, and (3) during the maximum scan. In addition, the figure also includes total fluorescence signals extrapolated from range scan data using the previously discussed linear relationship between the peak signal and the volume of an o-xylene WTI profile. All of the data included in Figure 7.4 are summarized in Table 7.2. Each soil test data point is normalized by the total fluorescence signal observed during a LIF test conducted on pore fluid extracted from the test specimen. The circular dotted data points represent the full WTI scan data and the hollow diamond symbols indicate values calculated from the range scan tests. Although a single test specimen

![Figure 7.4: Relationship between Soil Grain Size and Normalized Fluorescence Signal in Quartz Specimens.](image-url)
includes various sizes of soil grains, each test result is plotted in association with the smallest grain size retained by the sieves used to prepare the test specimen. Thus, for example, the total fluorescence signal obtained from a test performed on particles that passed a No. 20 sieve and were retained on a No. 30 sieve would be plotted at a grain size of 0.59 mm; the smallest grain size retained on a No. 30 sieve.

Figure 7.4 illustrates that for grain sizes approaching those characteristic of a large sand, a wide range of possible fluorescence intensities may be observed for a given concentration of contaminant in solution. For example, for grain sizes in the range of 0.80 to 2.00 mm the fluorescence signal recorded from a LIF test may represent anywhere from 4% to 100% of the true pore fluid contaminant concentration. As the grain size of the tested soil decreases, the variability in the observed signal also decreases. Over the particle size range of 0.04 to 0.20 mm the upper bound of the signals drops to approximately 30% of the true in-soil concentration and the lower bound appears to increase.

This experimental observation can be explained in terms of the region of the specimen interrogated by the laser. Given that the aqueous solution tests for laser penetration depth indicated that the laser penetrates approximately 0.75 mm into the test medium under ideal conditions, it is apparent that soil particles can easily obscure this zone. As illustrated in Figure 7.5, Part (a), for specimens comprised of large particles it is conceivable that the laser may focus on only a soil particle, only a contaminated pore space, or some fraction of both. Therefore, on a local basis, the LIF probe may measure a lack of any contamination, indicate the presence of the true contaminant concentration, or display some signal representative of a condition between these two extremes. As the particle size of the soil composing the specimen decreases, the region of the specimen interrogated by the laser contains more and more soil grains and also many pore spaces (see Part (b), Figure 7.5). Therefore, the upper bound of the observed signal decreases as more soil particles occupy the excitation area; and the lower bound achieves some minimum greater than zero, since some contaminated pore space is always in view of the laser. The lower bound may also include some signal generated by contaminant trapped in intra-particle voids or contaminant simply absorbed onto soil particle surfaces. (Note that these effects were not investigated during this testing program). For soils having higher organic contents the contribution to the baseline signal from sorbed
contamination will likely increase. However, the reader should note that a thorough study of sorption effects was not pursued during this program.

\[ a. \] 

\[ b. \] 

Note: Gray Circle Denotes Tested Zone

**Figure 7.5:** Illustration of the Influence of Soil Grain Size on Volume of Pore Fluid Contaminant Interrogated by the LIF Probe.

Further evidence of the mechanism leading to the variability of the in-soil fluorescence measurements is apparent when viewing the range scan data as a function of the probe's displacement across the test specimen. Figure 7.6 provides range scan measurements from 4 of the range scan tests, all performed on specimens composed of different sized quartz particles. These data are exactly the same as those represented by hollow diamond data points in Figure 7.4. For a given particle size, the data are plotted in the order that they were observed across the specimen surface. The horizontal scale is reported in mm of displacement across the test specimen. The sieve size range used to create the specimens analyzed in each test is presented along the left-hand vertical axis of each plot in the figure. The mean grain size of the test specimens is also indicated in each plot for comparison with the signal trend observed across the specimens. The mean grain size is defined as the average of the maximum and minimum grain sizes present in the specimen in association with the dimensions of the sieves used to bound the soil particles composing the specimen. All of the observations are again normalized by the signal from the pore fluid extract.
A review of Figure 7.6 demonstrates that the variability in the observed fluorescence signal is directly related to the position of the laser probe in contact with the specimen. For the large size particles the signal tends to remain low or remain high and then rise or fall quite rapidly. In a system composed of two media, that is soil and pore fluid, this data trend could be envisioned as a scanning situation in which the laser beam traverses a large soil grain or pore space before suddenly moving into the alternate media. For the smaller particle sizes the signal tends to remain quite smooth throughout the scan. Thus it appears that as the particles and pore spaces reduce in scale, the zone of the specimen illuminated by the laser includes a somewhat constant distribution of soil particles and contaminated voids.

Figure 7.6: Range Scan Measurements from Various Grain Size Specimens
The observation of significant changes in emission signal over very short distances within the larger soil matrices points to the need for spatial averaging whenever utilizing a LIF sensor to make true in-situ measurements. Spatial averaging may be achieved by simply taking many closely spaced measurements and averaging their results. Alternatively, the region of the soil analyzed for a single measurement may be increased in size so that the relative scale of the soil particles under investigation is minor when compared to the zone interrogated by the laser. This would limit observation variability and have an effect similar to that currently apparent when analyzing specimens composed of soil particles finer than approximately 0.2 mm.

7.4.3 Model of Grain Size Effects Based on Particle Geometry

The experimental observations and supporting hypotheses discussed above can be confirmed by examining a physical model that simulates the in situ conditions characteristic of a soil LIF test. An effective model can only be achieved after considering the importance of particle packing geometry. In a real soil specimen, the soil particles may be packed in a variety of ways that, on the particle scale, will lead to variability in the size and volume of localized pore spaces, and thus variability in the fluorescence emission observed from a selected contaminant concentration. However, for a given grain size, the upper bound of the fluorescence observations is unique. Signals lower than the maximum associated with a selected grain size can be generated in the presence of other smaller particles. Further, although the minimum of the overall signal versus grain size relationship may have some lower bound, minimum signals are generally unreliable metrics since they can often be dominated by noise. As a result, only the upper bound of the observed signal has the potential to yield insight into the actual in-situ contaminant concentration, given the size of the soil particles comprising the specimen. With this in mind it is desirable to model a particle packing configuration that exposes the maximum pore volume to the laser for any group of similarly sized particles. For simplicity the soil grains used to achieve this desired configuration can be modeled as spheres packed in a matrix. Since the particles are in contact with a flat window surface during a LIF test the largest fluorescence signal will be achieved when the maximum pore volume is exposed to the laser window. This condition exists when the particles are
positioned in a flattened body centered structure as illustrated in Figure 7.7. Notice that this configuration differs from a standard body centered cubic in that particles on the principal planes (i.e. 1 and 3 in the figure) of the unit cell are in contact with each other which opens the pore space exposed to the laser window.

![Diagram of Flattened Body Centered Structure]

**Figure 7.7:** Flattened Body Centered Structure of Modeled Soil Particle Field.

After establishing a particle geometry for a model test specimen, the LIF signal derived from an analysis of this specimen can be determined if one assumes a shape and size for the region of the specimen exposed to excitation energy at levels great enough to induce detectable fluorescence. This region will hereafter be referred to as the test zone. Since the laser used to perform the experiments in this program was focused just beyond the plane of the probe window, and the excitation radiation emanating from this window has a tendency to scatter or reflect from the central focus, the test zone was modeled as hemisphere extending in all directions radially from the center of the probe window into the test specimen. This test zone was then placed in contact with a field of soil particles arranged in the compressed body centered configuration described above to simulate a LIF test performed on a soil specimen.
For the model under discussion, the soil particles were simulated using spheres of unit radius arranged on two levels. For all of the calculations performed in this study, the test zone was assumed to be centered over a void in the soil particle field. Further, the volume of the test zone contributing to a LIF measurement was never allowed to extend beyond the upper surface of the soil particles within the test zone. Thus, only the pore space in the direct path of excitation energy was included in test zone volume calculations. A representative section of the particle field is illustrated in Figure 7.8. The two layer particle field is sufficient to delineate all soil particle surfaces exposed directly to the laser window and all continuous pore spaces that exist in a compressed body centered matrix.

![Particle Field](image)

**Figure 7.8: Representative Section of Particle Field Used to Model Soil Grain Size Effects.**

The volume of contaminated media contained in the test zone, which is directly proportional to the signal that would be obtained during a LIF test, was calculated for a wide range of soil grain sizes by changing the relative dimensions of the test zone and the soil particle spheres. In this model the particles were assumed to have a unit radius. Therefore a wide range of soil particle sizes was simulated by reducing or increasing the size of the test zone. Since the real soil particles evaluated in this testing program ranged from approximately 1/40th to 4 times the assumed zone of influence of the laser probe, similar test zone/soil particle ratios were modeled. Calculations of the modeled test zone volume for varying particle/test zone ratios produce the curve presented in Figure 7.9.
In Figure 7.9, the ratio of the detectable pore volume to the volume of the test zone is plotted versus the ratio of the particle radius to the test zone radius. Under ideal test conditions, the ratio represented by the ordinates of the normalized curve is equal to the value of the LIF signal that would be observed in soil saturated with contaminant solution divided by the signal observed in pore fluid extract, since these signals are both directly proportional to the volume of contaminant solution interrogated (barring other secondary effects described in more detail later). This normalized curve can be compared with the actual quartz test data described above by simply selecting a radius for the test zone in units of mm. Selection of the test zone size then translates the normalized curve left or right by establishing the particle sizes as a function of the test zone dimension. The best fit of the quartz data maxima is illustrated in Figure 7.10 and occurs if the test zone is assumed to be ~ 1.0 mm in diameter. The dimension of 1.0 mm is quite reasonable given the results of early tests on aqueous solutions that showed that the laser penetrates approximately 0.76 mm into the aqueous test media. Given that the actual shape of the test zone is not known and the, reasonable zone "diameters" could range from three quarters to one and a half millimeters. Since the best fit of the experimental data occurs with a test zone dimension less than that of a sphere having
radius 0.76 mm, it is possible that the assumption of a spherical test zone is not accurate. However, as evidenced by similarity between the shape of the model curve and the maxima of the quartz experimental data set it is clear that geometric effects related to soil grain size dominate the trends observed in situ contaminant measurements.

![Graph showing the relationship between signal in soil and signal in extract against minimum grain size in tested range (mm).](image)

**Figure 7.10:** Comparison of Experimental Data and Grain Size Model Results Using a 1.0 mm Diameter Test Zone.

### 7.5 Soil Properties with Secondary Influence on LIF Measurements

#### 7.5.1 Mineralogy

Additional tests on granular media other than quartz were performed to evaluate the importance of soil mineralogy, morphology, color, and organic content. Since the grain size ranges of many natural soils are not as broad as that of mechanically prepared materials such as industrial quartz, only limited grain size ranges could be tested using real soils. Nonetheless, grain size trends observed in quartz tend to be preserved in the presence of other
materials as evidenced by the curves presented for Ticino sand and Manchester fine sand (MFS) in Part (a) of Figure 7.11. The data presented in this figure are formatted in exactly the same manner as those shown earlier in Figure 7.4. Note that in Figure 7.11 diamond shaped symbols represent MFS test results and circular symbols indicate tests performed on Ticino sand.

The trend of signal versus grain size illustrated in the MFS and Ticino sand data is very similar to that observed in the quartz tests despite the many differences between the soil particles involved in the experiments. The upper signal bound observed on the MFS data is almost exactly the same as that observed for similarly sized quartz particles. Further, the total fluorescence signals observed in Ticino sand display an upper bound that decreases as a function of soil grain size in a manner similar to that observed in the quartz tests. These observations emphasize the primary influence of the effect of soil grain size on the LIF measurements.

Note that the above discussion has focused on granular materials sieved over a finite grain size range. In a field situation natural materials will predominate. Figure 7.11 (b) illustrates the results of range scan tests performed on specimens prepared using the full natural grain size distribution of MFS and Ticino sand. In both cases the natural soil tests display LIF signals similar to those observed from the range scan performed on the smallest grain size range of particles in the specimens. This observation indicates that the smallest particles present in a soil specimen will tend to control the magnitude of the observed LIF signal for a given concentration of contaminant in the soil pore fluid. This trend is consistent with the geometric model put forward earlier in that the volume of the pore spaces in a soil specimen will generally be a function of the smallest particle size present. Even in a material containing a mixture of very large and small particles, the small particles will tend to fill in the voids between larger particles creating a soil matrix more characteristic of the smallest particle size.

Despite the conceptual and predictive benefits of the geometric soil model used to interpret the LIF observations, Ticino sand provides evidence that other more subtle factors also influence the absolute magnitude of an in-soil fluorescence signal. Although the Ticino data display similar general behavior to quartz, the Ticino data also exhibit a slightly higher
Figure 7.11: Relationship between Soil Grain Size and Normalized Fluorescence Signal in Manchester Fine Sand and Ticino Sand.

upper bound than the signals recorded in similar tests on quartz with differences between the maxima of the two data sets ranging from 16 to 24%. An investigation of the distribution of the range scan data for all three of the granular materials indicates that this difference stems from factors other than simply data scatter or data extremes. Figure 7.12 (a) presents the results of the quartz range scan tests in the form of histograms associated with each tested grain size. The histograms are divided into 10% nominal ranges of the in-soil/extract signal ratio. A review of the quartz data histogram reveals that the quartz signal distributions are skewed toward in-soil/extract signal ratios on the order of 0-30%. In Figure 7.12 (b) a similar trend is observed for the MFS data which supports the congruence of LIF signal behavior displayed by these two materials. However, the Ticino data has a very different distribution. The Ticino data is more uniformly distributed across all observation values for each grain size with some concentration of observations over the range of 20-40%. This behavior is similar to that observed for the large 1.2 mm grains of quartz. In this way, LIF observations made in
Figure 7.12: Distribution of Measurements Acquired During Range Scan Tests Performed on Industrial Quartz (a), Manchester Fine Sand (b), and Ticino Sand (b).
Ticino sand specimens of a selected grain size exhibit characteristics similar to larger particles in ways more complex than simply a larger signal. This points to a fundamental addition to the grain size mechanism leading to the LIF signal in the Ticino sand. Some other soil trait must also influence the LIF measurement. There are several factors which may account for this disparity.

A variety of characteristics differ among quartz, MFS, and Ticino sand including general mineralogy, soil color, organic content, and particle morphology. MFS has a more varied mineralogy than quartz with notable percentages of feldspar and mica in addition to silica. However, the color of MFS is a fairly uniform beige with frequent speckles of black and in this way differs only slightly from the luminous white of pure quartz. The soil color and mineralogy of Ticino sand are drastically varied from that of quartz. Ticino sand displays very inhomogeneous coloration with black, white, beige, yellow, and orange soil grains. The mineralogy of Ticino sand is also quite complex with silica, feldspar, dolomite, carbonates, and iron oxides all adding to its composition. The organic content of the quartz is only 0.15% on a mass basis which is very low in comparison to the 0.68% organic content of MFS and the 1.52% value determined for Ticino sand. Finally, the particles of quartz and MFS are virtually identical in shape as evidenced by the angular and subangular grains pictured in the SEM images of Figures 5.3 and 5.11 in Chapter 5. The morphology of Ticino sand particles differs mildly from that of both quartz and MFS in that Ticino sand includes small quantities of oblong particles that are subangular to rounded in nature. The significance of the above mentioned differences must be interpreted in terms of their influence on the mechanisms that may lead to a change in the LIF signal observed from contaminants present in the pore fluid of the soils.

7.5.2 Morphology

Due to the subtlety of the differences in soil morphology between the granular materials under investigation it is unlikely that particle morphology plays a key role in establishing the difference in observed LIF signals between quartz and Ticino sand. Although irregularly shaped particles can be packed in generally looser states than similarly shaped particles due to the enhanced potential for particle bridging, the infrequent presence of oblong
particles in the Ticino sand precludes the possibility of this effect leading to anything more than occasionally large measurements. Significant and consistent variations in particle morphology between the quartz and Ticino sand particles would typically lead to noticeable variations in the density of the soil specimen created within similar particle size ranges of the respective materials. However, over the grain size range encompassing the Ticino sand tests (0.71 mm - 0.30 mm), there is less than a 5% average difference in porosity between the quartz and Ticino sand specimen. Therefore, particle morphology and its associated effect on specimen density, are improbable causes for the observed difference between the quartz and Ticino behavior.

7.5.3 Organic Content

Another possible explanation for the relatively high signal observed in the Ticino sand may be related to the organic content of the soil particles. As mentioned above, the organic content of Ticino sand is more than double that of MFS and approximately 10 times that of quartz. Organic content has the potential to contribute to the in-soil/extract signal ratio observed in a test specimen in three ways: (1) the organic matter itself may fluoresce, (2) contaminants in the pore fluid may sorb to the organic components of the soil particles providing locations of high contaminant concentration that will subsequently fluoresce when excited, and (3) the chemical absorbed onto the particle surfaces may detract from the pore fluid concentration which will in turn result in a lower pore fluid extract measurement and a high in-soil/extract signal ratio. Measurements of the background signatures of Ticino sand prior to contamination reflected no evidence of fluorescence; therefore the first of these three considerations is not plausible. Further, during testing operations equilibrium contaminant solution was continuously flowed through the test specimen providing a renewable supply of o-xylene that is unlikely to have been depleted. LIF tests performed on pore fluid extracted from the test specimen confirmed this hypothesis and demonstrated that the bulk pore fluid contaminant concentration remained unchanged throughout the soil test. Therefore, mechanism (3) can also be eliminated. Mechanism (2) however, remains feasible.

A comparison of Figures 7.4 and 7.11 demonstrates that the differences between the signals obtained in quartz and Ticino sand increase as the particle size decreases with a
differential of 16% at a grain size of ~0.59 mm and a differential of 24% at a grain size of ~0.30 mm. This trend is consistent with a phenomenon dependent on particle surface area. As the size of particles present in a test specimen decreases the surface area of the particles exposed to the laser increases. Figure 7.13 illustrates this concept with calculated values of surface area derived from the soil particle field used earlier to model grain size effects. These calculated values of surface area can be used in conjunction with the soil grain size model discussed earlier to illustrate the potential influence of contaminant sorption on the in-soil/extract signal ratio.

![Graph showing relationship between detectable particle surface area and particle radius/test zone radius.](image)

**Figure 7.13:** Results of Simulated Particle Field Surface Area Calculations.

The mechanisms underlying the development of observable fluorescence from soil sorbed contamination are difficult to assess. It is clear that the sorption of contaminants by soils can be interpreted using common partitioning theories such as those presented by Hemond and Fechner [H&F] (1994), and Schwarzenbach, Gschwend, and Imboden [SGI] (1993). However, the interpretation of the potential exposure of these sorbed contaminants to incident fluorescence-inducing excitation energy is not equally lucid.

The absorption of a contaminant such as o-xylene by organics bound to the surface of soil particles can be approximated using knowledge of partition coefficients that provide the ratio between a chemical’s concentration in two media. Partition coefficients between
chemicals in aqueous solution and other media are generally presented in terms of the octanol-water partition coefficient, $K_{ow}$, since octanol is readily available for laboratory experimentation. This is the case for o-xylene. The logarithm of $K_{ow}$ for o-xylene is commonly tabulated and is listed as 3.12 by Hemond and Fechner (1994). From $K_{ow}$, it is possible to use approximate relationships to obtain the organic carbon/water partition coefficient for o-xylene. A common relationship used to determine $K_{oc}$ for aromatics and polynuclear aromatics is the following:

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006$$

(H&F, 1994). Substituting a value of 3.12 into Equation 7.1 for $K_{ow}$ yields,

$$\log K_{oc} = 0.937 (3.12) - 0.006 = 2.92$$

such that, $K_{oc} = \sim 830$ ml of water/g organic carbon, where $K_{oc}$ is the ratio of the concentration of a compound on organic carbon (mg/g) to the concentration of that contaminant in water (mg/ml).

Using $K_{oc}$ and $f_{oc}$, the fraction of the soil that is organic carbon (mg/mg), it is possible to obtain the partition coefficient, $K_d$, for an organic compound such as o-xylene between water and soil

$$K_d = K_{oc} \cdot f_{oc}$$

(H&F, 1994). Generally, $f_{oc}$ is assumed to equal approximately one half of $f_{om}$, the fraction of the soil that is organic matter (mg/mg) (SGI, 1993). For Ticino sand $f_{om} = 1.52\%$ as discussed in Chapter 5, and, subsequently, $f_{oc} = 0.76\%$. Therefore $K_d$ is approximately 6.3 ml of water/g of soil which is equal to the ratio of the concentration of o-xylene on the soil particles (mg/g) to the concentration of o-xylene in the pore fluid (mg/ml).

Once the organic carbon/water and soil/water partition coefficients are determined an assumption must be made to account for the influence of sorbed contaminants on observable fluorescence. Two approaches to this problem are feasible and consistent with environmental engineering concepts. One might simply make use of $K_{oc}$ and assume that incident excitation
energy penetrates some finite depth into the organic matter on the surface of soil particles thereby exciting fluorescence in a zone of contamination characterized by the product of $K_{oc}$ and the bulk pore fluid contaminant concentration ($C_{pf}$). Alternatively, a thin aqueous boundary layer may be assumed to exist around the entire surface of the soil particles in which the contaminant concentration drops from the value on the soil particles, $K_d \cdot C_{pf}$, to the bulk pore fluid concentration, $C_{pf}$. The following discussion investigates these possibilities individually.

**Approach 1**

The first approach to account for the contribution of sorbed contamination to total observable fluorescence was pursued by using the organic content of the tested soils and an approximate specific gravity for the organics (say 1.3) to calculate an approximate thickness of the layer of organics on the soil particles. Since the organic content determinations presented in Chapter 5 were performed on full grain size ranges of the studied soils, additional organic content tests were performed on quartz, Ticino sand, and Manchester fine sand to determine soil organic content as a function of particle size. These tests revealed that particles in the No. 10 to No. 16 sieve range generally have one third the organic content of particles passing the No. 120 sieve with a rather continuous distribution in between. Using this information, approximate volumes of organic matter were calculated and assumed to surround the soil particles.

The volume of organic matter associated with a particle was calculated by first assuming that the soil particles were spherical in shape. For any particle size the volume was then calculated simply as $\frac{4}{3}\pi r^3$. The specific gravity of the soils, generally on the order of 2.65, was then used to determine a mass for any particular particle size. Then, using the organic content of the soil, the organic matter associated with a soil particle was determined on a mass basis. This organic mass was then converted into a layer of finite thickness surrounding the soil particle using an approximate specific gravity for the organics of 1.3.

The thickness of the organic layer coating the soil particles was then used as an approximation of the thickness of organics covering the surface area of soil particles exposed to laser excitation as determined using the particle field model results presented in Figure
7.13. For both Ticino sand and MFS these calculations revealed that the organic content of the soils is great enough to provide a layer of organic matter around the particles with a thickness in excess of $\sim 75$ nm. The results were similar for quartz, with only particles smaller than 0.3 mm displaying less than a $\sim 75$ nm layer of organic matter. Given that typical organic molecules range in size from 5 to 25 nm (SGI, 1993) it can be assumed that the organic layer consists of some finite number molecular layers in excess of three or four. Thus if it is assumed that laser light penetration into the organics is similar to that estimated for the soil particles, a depth of only one or two organic molecules may actually receive excitation energy. Therefore, it is possible that all of the soil particles possess enough organic matter to accommodate the maximum depth of excitation energy penetration. In this case all of the soils are in a limiting condition so that the benefit to their respective fluorescence signatures incurred from sorbed contaminants is identical. Thus, according to this approach, organic content cannot account for the differences in total fluorescence signals observed among the quartz, MFS, and Ticino sand. However, it should be noted that assuming the excitation energy penetrates approximately 20 nm into the organic layer and that the organic layer is composed of 50% organic carbon, the soil particle model demonstrates that the total fluorescence signal of all of the soils may be increased by 5 to 15% depending on the particle size under investigation.

**Approach 2**

As stated briefly above, an alternate method of accounting for the contribution of sorbed contaminants to fluorescence might consider the presence of a thin aqueous film or boundary layer around the soil particles that contains an elevated concentration of contamination relative to the bulk pore fluid of the soil. If it is assumed that the concentration in this boundary layer follows a linear gradient between that representative of the contaminants sorbed on the soil to that present in the bulk pore fluid the average contaminant concentration in this layer may be approximated by the average of these bounding conditions (determined with appropriate units, of course). In this case the contaminant concentration in the boundary layer is a direct function of the organic content of the soil as it relates to $K_d$. 

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Since the boundary layer is aqueous, it can be assumed that the laser excitation energy penetrates the full thickness of this layer. The thickness of this layer, however, is undefined and there is little precedent in environmental literature for its assumption. Viscinal water layers involved in chemical binding and ion exchange are typically assumed to be tens of nanometers in thickness (SGI, 1993). In contrast thin film models that describe chemical exchange between two media often make use of boundary layers on the order of microns (H&F, 1994). The appropriateness of either of these assumptions is argumentative. Without further investigation it would be inappropriate to assume a thickness for this layer, therefore Figure 7.14 is provided to illustrate the possible effect associated with this layer as a function of layer thickness. The lines presented in Figure 7.14 demonstrate the increase in the in-soil/extract signal ratio incurred by an increase in the assumed thickness of the soil boundary layer averaged over selected grain size ranges pertinent to the soils under investigation. The MFS curve reflects signal enhancement in the grain size range of 0.04 to 0.20 mm. The Ticino curve represents the average increase in signal over the particle size range from 0.3 to 0.6 mm. Note that all changes in the in-soil/extract signal ratio are defined relative to the signal.

Figure 7.14: The Effect of Particle Boundary Layer Thickness on Fluorescence Generated from Sorbed Contaminants.
ratio that would be observed in quartz of similar grain size. The effect of 0.15% organic content on the quartz curve is insignificant.

Overall, there are many unknowns involved in the manifestation of fluorescence from sorbed contaminants. However, the concepts outlined above indicate the potential for the sorbed material to contribute to LIF observations. This potential demonstrates that the effects of organic content warrant further investigation.

Although increases in the organic content of a soil may shift the curve of maximum observed LIF signals in an upward direction, due to the relatively thick boundary layer that would be required for organic content to raise a LIF signal by ~20% it is unlikely that organic content alone leads to the observed differences between the quartz and Ticino specimens of similar grain size.

7.5.4 Soil Color and Mineralogy

Another mechanism that would likely contribute to the intensity of an observed signal is related to the optical characteristics of the soil particles that are implied by soil color and that are a byproduct of mineralogy. The mineralogy of a soil is inherently linked to what is perceived as the soil color. Differences in soil mineralogy lead to differences in particle surface structure and roughness that in turn affect the absorption, transmission, and reflection properties of the soil. All of these light related characteristics have the potential to affect LIF measurements. Unfortunately, these properties are not easily ascertained for granular media. Typically absorption, reflectivity, and transmissivity are obtained for a material by performing an experiment in which a calibrated light source is directed toward a cuvette of liquid or a planar solid. Measurements are then made to determine the energy reflected from the surface of the test material and the energy transmitted through the material. The difference between the incident energy and the sum of the energy lost to reflection and that transmitted through the material is assumed to be absorbed. This type of experiment is impractical with soil particles, since the particles are often nearly opaque and generally irregular in shape. Transmission distances through particles are, consequently, very short and energy passing through the particles tends to scatter because opposite surfaces of the particle are not necessarily planar or parallel. Further, the granular nature of the particles prevents the
accurate separation of light losses associated with the passage of light through mineral matter and losses related simply to the scattering of light off particle surfaces. These characteristics make it difficult to obtain quantitative values for transmissivity and/or absorbance that pertain to the soil particles comprising a LIF test specimen. However, experiments can be performed to evaluate the approximate transmission properties of a soil matrix as a whole. When combined with measurements of the reflection and/or scattering characteristics of a granular medium it is possible to back calculate an approximate matrix absorbance value. Although measurements derived from tests performed on a soil matrix do not yield particle specific properties, they can be considered representative of the behavior encountered when a LIF test is performed on a soil specimen.

The following discussion presents the results of a battery of experiments performed to assess the optical characteristics of quartz, MFS, and Ticino sand. Although deterministic values are derived from these experiments, the above mentioned uncertainties necessitate a qualitative interpretation of the potential for soil particle reflection, transmission, and absorption to affect LIF signal measurements.

Reflectivity

Reflectivity is a practicably measurable optical property of granular media that may affect LIF signals and may also accurately account for the material's behavior as a mass. An approximation of the light scattering or reflection qualities of soil can be ascertained from soil color, as perceived by the human eye. Soils that appear bright to the human eye tend to scatter white light while darker colors tend to absorb white light. These characteristics point toward the behavior that might be expected when soils are exposed to ultra violet light. Since the difference between white light wavelengths and ultra violet wavelengths is quite small relative to the size of the soil particles investigated during the granular media tests, one would expect very little difference in the scattering behavior of the soil for white or ultra-violet light. Thus soils such as quartz that appear to the human eye as bright white would be expected to scatter or reflect more UV radiation than darker soils such as Ticino sand. This hypothesis is confirmed by a review of laboratory reflection/scattering experiments performed using ultra violet and white light sources.
Figure 7.15, Part (a) illustrates UV and white light spectral traces obtained during scattering experiments performed on uncontaminated specimens of quartz, MFS, and Ticino sand.

(a.)

![UV Light and White Light Spectral Traces](image)

(b.)

![Schematic of Scattering Test Setup](image)

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Figure 7.15: Results (a) and Schematic (b) of Scattering Tests Performed on Specimens of Quartz, Manchester Fine Sand, and Ticino Sand.

sand. The experimental setup used for these tests is illustrated schematically in Part (b) of Figure 7.15. The experiments were conducted by directing collimated light toward a soil specimen located a fixed distance from a collection fiber. Light collected by the fiber was directed to a spectrometer and observed using a PMT. Signals recorded by the PMT provided a relative measure of the reflectivity of the soils. The angle of light collection was varied from
10 to 80 degrees, in 10 degree increments, with no significant change in the ratio of observed signals between the soils. Soil grain size also had little impact on the ratio of the observations between soils.

For both the white light and ultra violet light test series, calculations of the total signal under the reflection curves indicate that the reflectivity of MFS is approximately 60% of that for quartz, while Ticino sand displays a reflectivity that is ~ 30% of the quartz value, again independent of collection angle and soil particle size.

The absolute values of reflectivity or scattering for the soils, however, are subject to variation with changes in collection angle and soil grain size. Figure 7.16 illustrates the effects of soil grain size and collection angle on the intensity of reflections observed from specimens of quartz that were tested using a calibrated white light source. Note that no significant interdependence of these parameters was observed nor was there significant variation as a function of soil type. Thus, using the relative reflectivity ratios described above and the grain size - incident energy and collection angle - reflected energy relationships presented in Figure 7.16 it was possible to determine absolute measures of reflectivity for any grain size of all three granular media tested throughout this program.

**Figure 7.16:** The Effects of Collection Angle (a) and Soil Grain Size (b) on Reflectivity Measurements Performed on Specimens of Quartz.

Additional tests were performed to assess the effect of wet soil and water filled pore space on the reflectivity measurements. For these tests the soil specimens were formed dry in
an open-top container and then soaked with water to cover all soil particles and fill all pore spaces. The surface of the soaked soil was then scraped flat to achieve a "level" test surface at the desired distance from the illumination beam and collection fiber. For all three tested soils the energy reflected from the wet specimens was approximately one third of that observed from dry specimens with wet to dry reflectivity ratios of 0.39, 0.35, and 0.33, respectively, for quartz, MFS, and Ticino sand.

Transmissivity

Although the transmissivity of individual soil particles cannot be accurately determined for granular media, it is possible to obtain a composite measure of the transmission properties of a soil/pore space system. Using an experimental configuration similar to that applied for standard transmission tests one can obtain measurements of light throughput for a soil specimen. The test configuration utilized for this type of experiment is illustrated schematically in Figure 7.17. In this test, a collimated white light source is directed toward soil particles contained in a glass cell of a particular width. Light emanating from the far side of the cell can be collected and considered as a measure of the soil system transmissivity.

![Figure 7.17: Schematic of Transmissivity Test Setup.](image)

Results of transmission tests performed on specimens of the three test soils are presented in Figure 7.18. All of the specimens were created using particles passing a U.S. Standard sieve No. 50 and retained on a U.S. Standard sieve No. 60. The figure illustrates changes in the light throughput of a soil system of fixed grain size as the cell width, and thus the number of soil particles across the cell, increases. Note that the smallest test cell dimension (0.9 mm) corresponds to a width of about three soil particles for the range of grains evaluated during this test series. A review of the test results reveals a nonlinear trend in the
transmission of light through the soil system. This observation may indicate that light is being lost both through absorption by the soil particles as well as scattering in the soil matrix pore space and points, again, to the difficulty in separating these two phenomenon. Note that the transmissivities presented in Figure 7.18 were all acquired using a calibrated light source and thus are presented in absolute terms as a fraction of the total energy incident upon the test specimen. Since the light source energy was evaluated through the empty test cell, this normalization process also accounts for the light lost through the empty test cell.

![Graph showing percent of total incident energy transmitted vs. transmission cell width.]

Figure 7.18: Results of Transmissivity Experiments Performed on Specimens of Quartz, Manchester Fine Sand, and Ticino Sand.

The amount of light transmitted through a defined region of a soil specimen will, of course, increase as the size of the soil particles comprising the specimen increases. If the soil particles are very small relative to the test region, transmission through the specimen will be a primary function of the transmissivity of the particles. However, as the particle size increases relative to the size of the test zone, the component of soil matrix transmission attributed to pore space will increase and begin to dominate the observed transmissivity. This concept is illustrated in Figure 7.19.

The results presented in Figure 7.19 were obtained by performing a series of transmission experiments in a test cell of fixed width on a variety of quartz specimens, each
composed of differently sized particles. The results are normalized by the transmissivity value obtained for the 0.25 mm soil particles which corresponds to soil passing a No. 50 sieve and retained on a No. 60 sieve. Thus, for example, the light passing through the 0.59 mm particle specimen is nearly 40 times more intense than that transmitted through the 0.25 mm particle specimen of the same thickness. The test cell used for these experiments was 2.6 mm in width, which is greater than four particle diameters for all of the tested specimens.

![Graph showing normalized transmissivity vs grain size](image)

**Figure 7.19:** Effect of Soil Grain Size on Transmissivity Measurements Obtained Using a Fixed Width Test Cell.

In the figure it is clear that for particles less than approximately 0.25 mm in diameter the soil matrix transmissivity is fairly moderate and is most likely a function of particle properties. For the larger sized particles (above a soil grain size of approximately 0.25 mm) there are very few particles in the light path and there is a dramatic increase in the light throughput of the specimens. In this region it is likely that pore space effects dominate the transmissivity measurements. Differences in this trend among soils of varying type are insignificant. Since previously discussed evidence demonstrates that the region of a specimen involved in a LIF test includes only two or three layers of soil particles it is likely that the influence of transmissivity on LIF measurements will scale with the pore space associated with the particle size of a given test specimen.
**Absorptivity**

Using the results of the reflectivity and transmissivity experiments described above, the energy absorbed by a soil matrix can be calculated from the difference between the energy incident upon the test specimen and the sum of the energy lost to reflection and transmission.

Table 7.5 provides the values of reflectivity, transmissivity, and absorptivity observed and/or calculated for specimens of quartz, Manchester fine sand, and Ticino sand. The values presented correspond to wet soil properties as described in the discussion of reflectivity. Note that the listed optical properties are associated with distinct grain sizes of each soil to facilitate interpretations of the impact of optical phenomenon on data and model results presented earlier in Figures 7.10 and 7.11.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Grain Size (mm)</th>
<th>Reflectivity (% of Total Incident Energy)</th>
<th>Transmissivity</th>
<th>Absorptivity* (% of Total Incident Energy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>0.59</td>
<td>5.1%</td>
<td>13.7%</td>
<td>81.2%</td>
</tr>
<tr>
<td></td>
<td>0.42</td>
<td>5.5%</td>
<td>7.6%</td>
<td>86.9%</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>6.4%</td>
<td>3.4%</td>
<td>90.3%</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>7.4%</td>
<td>1.7%</td>
<td>90.9%</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>8.3%</td>
<td>0.5%</td>
<td>91.2%</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>11.9%</td>
<td>0.2%</td>
<td>87.9%</td>
</tr>
<tr>
<td>Manchester Fine Sand</td>
<td>0.18</td>
<td>1.5%</td>
<td>0.7%</td>
<td>97.8%</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>1.5%</td>
<td>0.5%</td>
<td>98.0%</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>2.5%</td>
<td>0.1%</td>
<td>97.4%</td>
</tr>
<tr>
<td>Ticino Sand</td>
<td>0.59</td>
<td>0.5%</td>
<td>4.6%</td>
<td>94.9%</td>
</tr>
<tr>
<td></td>
<td>0.42</td>
<td>0.5%</td>
<td>2.5%</td>
<td>96.9%</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>0.6%</td>
<td>1.1%</td>
<td>98.3%</td>
</tr>
</tbody>
</table>

* Note: Absorptivity values are characteristic of three to four layers of soil particles.

**Table 7.5:** Approximate partitioning of incident light in soil specimens of quartz, Manchester fine sand, and Ticino sand.

With the measurements of soil optical properties presented above it is possible to analyze the potential influence of these parameters on the magnitude of observed LIF signals. This analysis requires an understanding of the way in which reflected, transmitted, and absorbed light may impact LIF observations. Comparisons of soil model simulations and
experimental results from, for example, the soil tests presented in Figure 7.10 illustrate that the majority of a LIF signal stems from excitation of contaminants located in the pore space of a soil directly exposed to excitation energy. Under this premise it is clear that light will, in general, pass through contaminated pore fluid and thus induce fluorescence prior to contacting soil particles or exiting the collection zone of the probe. However, it is possible that thin films of contaminated liquid trapped between soil particles and the LIF probe window may not constitute a large enough volume to fluoresce with an intensity that will measurably contribute to an overall observation. In these regions light may simply interact with soil particles with little or no LIF signal benefit. Thus, since it can be assumed that all of the tested soils have the same base signal resulting from simply geometric factors as illustrated in the soil particle model (Figure 7.11), differences in the observed fluorescence properties of these materials that result from optical characteristics can be interpreted by analyzing the fractions of reflected, transmitted, and absorbed light that contribute to a LIF measurement.

Accurate assessments of the fractions of reflected, transmitted, and absorbed light that contribute to LIF signals are very difficult to obtain experimentally. However, several factors can aid in the development of reasonable estimates for these values. For example, since much of the light transmitted through a two or three layer uncontained particle matrix passes through pore spaces, it is reasonable to assume that a high percentage (say 80% or more) of the transmitted light would have the potential to induce detectable fluorescence when the soil pores are filled with an aqueous contaminant solution. Further, a high percentage (say 90% or more) of the light categorized as absorbed in Table 7.5 could also feasibly result in detectable fluorescence based on the assumption that the majority of the light must pass through a significant volume of pore fluid before contacting soil. (Note that UV absorption by the particles and subsequent mineralogical fluorescence does not contribute to the observed LIF signatures as evidenced by the fact that background scans of the uncontaminated soils showed no detectable fluorescence in the wavelength range of interest to this study.) Finally, only moderate amounts (say less than 40%) of the light reflected or scattered from an uncontaminated soil specimen would be expected to contribute to fluorescence observations. The reflected or scattered fraction of incident energy might include some light whose energy was reduced (possibly due to multiple collisions) and would be incapable of inducing
fluorescence in observable zones as well as a substantial fraction of light completely redirected out of the probe collection zone.

Using the rationale described above and the assumptions that 40% of reflected/scattered incident light, 80% of transmitted incident light, and 95% of absorbed incident light contribute to LIF observations, the optical properties of Manchester fine sand and Ticino sand may be responsible for approximately a 5% increase in observed LIF signals over those recorded in quartz specimens composed of similarly sized particles. Even the most extreme assumptions for light fractions involved in LIF signal generation which would neglect all reflected energy and include 80% of the transmitted light and all of the absorbed energy account for only a 6 to 10% difference between the Ticino sand and quartz specimens. It is therefore clear that, although soil optical properties can be considered a contributing factor to the manifestation of LIF signals, their effect is minor and is obviously not the only secondary influence on LIF measurements.

In summary, grain size has a dominant effect on the intensity and variability of observed LIF signals in soil environments. The effect of grain size can be used to calibrate a LIF sensor and in turn obtain an approximate measure of the concentration of a contaminant in the pore fluid of a soil given a-priori knowledge of the soil particle size distribution. In addition to the grain size effect, in-soil LIF measurements are also influenced, on a secondary basis, by the presence of organics and the mineralogy of the soil as it relates to the optical properties of the soil grains. Although difficult to confirm, experimental evidence points to the possibility that increased organic content in a soil may lead to slightly enhanced LIF signal observations.

7.6 The Effect of Soil Type: Fine Grained Materials

Soil tests were also performed on specimens composed of particles passing the No. 200 sieve. This sieve size serves as the upper bound on particles termed fines. Tests on fines provided an opportunity to evaluate the capabilities of the LIF probe in silts and clays in addition to quartz and Manchester fine sand, and in that way, determine the effect of soil type on the measurements made with the LIF probe. As mentioned in Section 7.1, standard soil tests were performed on Venezuelan clay, the regional silt, and fine grained fractions of
industrial quartz and Manchester fine sand. Further, soil paste tests were carried out for Boston blue clay, Venezuelan clay, and the regional silt. None of the background scans of these materials displayed any signatures characteristic of the presence of the soils. Measurable fluorescence signals were achieved during tests performed on sieved fractions of both quartz and MFS that passed the No. 200 sieve and were retained on the No. 325 sieve. These data have already been presented in Figures 7.4 and 7.11, respectively. Unfortunately, all of the tests performed on clay or silt materials passing a No. 200 sieve (0.07 mm) showed negligible signal. Consequently, no results are presented for these tests.

The successful tests performed on fine grained quartz and MFS demonstrate that the LIF probe can be used effectively in the grain size range of 0.07 to 0.04 mm. In fact, as shown in Figures 7.4 and 7.11, measurements made in fine grained specimens of quartz and MFS indicate that 20 to 30% of the pore fluid extract signal can be observed in the presence of the soil. Further, the geometric soil model presented earlier predicts that a signal of 16 to 18% of the extract value should be obtained from a LIF test performed on material in the range of 0.07 to 0.04 mm. However, difficulties arise when the LIF probe is used in the presence of particles passing a No. 325 sieve (0.04 mm) as evidenced by the poor test results achieved with specimens of silt and clay. This problem may stem from several factors associated with the physical properties of silt and clay.

Both the silt and the clay contain very high fractions of extremely fine particles on the order of microns. A review of the grain size distributions presented in Chapter 5 for these materials demonstrates that over 85% of Venezuelan clay on a mass basis is finer than 10 microns and more than 55% is finer than 1 micron. Similarly, about 50% of the silt is finer than 10 microns and slightly less than 15% is finer than 1 micron. Since the silt and clay LIF tests made use of the full grain size distributions of these fine grained natural soils, it appears that these tests may actually demonstrate behavior characteristic of a significant extension of the grain size effect observed during experiments performed on large particle sizes.

The presence of very fine particles combined with the flat plate like shape of silt and clay grains produces a material that can achieve very tight packing configurations that potentially limit the observable contaminant pore space. Further, as illustrated earlier for the industrial quartz specimens, the finer the particles comprising a specimen the greater the
amount of incident energy reflected and scattered from the particle surfaces. Trends presented in Section 7.5.4, which related the optical properties of soils to LIF observations, indicated the potential for increased soil reflectivity to decrease LIF signal intensities. This effect combined with the strictly geometric limitations of ultra fine grains could easily limit the magnitude of LIF emissions to immeasurable levels using the current apparatus.

Note that the organic contents of Venezuelan clay and the regional silt are quite high with measured values of approximately 7% and 18%, respectively. This fact, however, does not aid in the explanation of the silt and clay LIF observations. As discussed in Section 7.5.3, the contribution to fluorescence gained from organic content is generally small, and also limited by the laser penetration depth into the organic medium. Thus, the high organic content does not necessarily imply a measurable signal. In contrast, limitations of available contaminant in the pore space of the silt and clay caused by absorption to the organics can also be discounted. Measurements of the pore fluid extracted from the fine grained specimens illustrated that more than enough contaminant was available to satisfy any sorption needs and still maintain high contaminant levels in the pore fluid.

7.7 The Effect of Soil on the Performance of the LIF Sensor

The results obtained from tests performed on equilibrium solutions of o-xylene in the presence of soils may be used to assess the impact of the presence of soil on the contaminant detection capabilities of the LIF sensor. Although power fluctuations of the laser experienced during this phase of testing preclude the development of definitive detection limits in soils, an assessment of detection limits in soils relative to those in aqueous solutions is still feasible. Under the reasonable assumption that in-soil LIF signals will decrease linearly in intensity with a decrease in concentration as in aqueous solutions, it is possible to establish a limit on the detection capabilities of the probe that is, of course, a function of soil grain size. This concept can be clarified as follows.

If, in a standard aqueous solution test, a signal S is generated by a solution having a concentration of X, when this same solution is used as a pore fluid in soil the observed LIF signal will be some fraction, $f_p$, of the signal recorded in aqueous solution as a function of the soil grain size. Thus if one examines the minimum signal, say $S_{\text{min}}$, required to confidently
detect a compound in aqueous solution, that signal will be related to some minimum
detectable concentration, $X_{\text{aqueous}_{\text{min}}}$, as described in Chapter 6, Sections 6.5 through 6.7.
Then, since the minimum signal required for detection in both soils and solutions is a function
of equipment capabilities and will not change as a function of test media (assuming similar
levels of electrical and optical noise in both cases), the minimum detectable in-soil
concentration, $X_{\text{soil}_{\text{min}}}$, can be calculated by the following formula;

$$X_{\text{soil}_{\text{min}}} = \frac{X_{\text{aqueous}_{\text{min}}}}{f_S}$$  \hspace{1cm} (7.3)

for any soil grain size. Effectively this function takes the reciprocal of the normalized signal
versus grain size curve and scales the result by the minimum detectable aqueous solution
concentration. Note that any consistent units of concentration can be used in Equation 7.3.
This same argument holds for identification and quantification limits as well.

If the laser had exhibited stable performance during the soil testing program similar to
that displayed throughout the aqueous test series, the curves presented in Figure 7.20 would
likely represent the detection capabilities of the probe in soil environments. These curves
were generated using the normalized signal versus grain size relationship provided by the
geometric soil model presented in Section 7.4 and the LIF probe detection limits for the BTX
compounds established in Chapter 6. A review of Figure 7.20 demonstrates that the detection
capabilities of the LIF sensor will be reduced by as much as a factor of 5 over the soil grain
size range of particles passing a U.S. Standard No. 10 sieve and retained on a U.S. Standard
No. 200 sieve. Slight variations in these limits can be expected for real soils since the
normalized signal versus grain size relationship is subject to change in relation to the organic
content and optical characteristics of the soil. A set of curves similar to those presented in
Figure 7.20 might be used to calibrate a probe and illustrate the expected signal from a wide
range of contaminant concentrations in the presence of a variety of soil grain sizes.
**Figure 7.20:** Approximate Detection Limits for BTX Compounds in the Presence of Soil as a Function of Soil Grain Size.

Curves similar to those presented in Figure 7.20 can also be created to represent the identification and quantification capabilities of the probe in soils. However, for simplicity, Table 7.5 summarizes approximate detection, identification, and quantification limits of the LIF sensor for each of the BTX compounds in a variety of soil conditions. The table illustrates the sensor's performance limits when using the high speed oscilloscope for data acquisition. The performance limits presented in Table 7.5 can be enhanced by more than an order of magnitude by employing a photon counter for data acquisition. For example, o-xylene detection limits range from approximately 25 to 125 ppb over the particle size range characteristic of coarse to fine sands when data is acquired with a photon counter. Further, use of a photon counter also improves the o-xylene quantification limits to values of approximately 35 to 180 ppb over the coarse to fine sand grain size range.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Soil Classification</th>
<th>Approximate Grain Size Range</th>
<th>Detection Limits (ppm)</th>
<th>Identification Limits (ppm)</th>
<th>Quantification Limits (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BENZENE</td>
<td>Coarse Sand</td>
<td>2.00 - 0.60 mm</td>
<td>100 - 150</td>
<td>225 - 325</td>
<td>750 - 1100</td>
</tr>
<tr>
<td></td>
<td>Medium Sand</td>
<td>0.60 - 0.20 mm</td>
<td>150 - 350</td>
<td>325 - 800</td>
<td>1100 - 2700</td>
</tr>
<tr>
<td></td>
<td>Fine Sand</td>
<td>0.20 - 0.07 mm</td>
<td>350 - 550</td>
<td>800 - 1200</td>
<td>2700 - 4000</td>
</tr>
<tr>
<td>TOLUENE</td>
<td>Coarse Sand</td>
<td>2.00 - 0.60 mm</td>
<td>2 - 3</td>
<td>4 - 6</td>
<td>18 - 25</td>
</tr>
<tr>
<td></td>
<td>Medium Sand</td>
<td>0.60 - 0.20 mm</td>
<td>3 - 7</td>
<td>6 - 15</td>
<td>25 - 65</td>
</tr>
<tr>
<td></td>
<td>Fine Sand</td>
<td>0.20 - 0.07 mm</td>
<td>7 - 10</td>
<td>15 - 20</td>
<td>65 - 100</td>
</tr>
<tr>
<td>(o) - XYLENE</td>
<td>Coarse Sand</td>
<td>2.00 - 0.60 mm</td>
<td>0.8 - 1</td>
<td>2 - 3</td>
<td>8 - 12</td>
</tr>
<tr>
<td></td>
<td>Medium Sand</td>
<td>0.60 - 0.20 mm</td>
<td>1 - 3</td>
<td>3 - 7</td>
<td>12 - 30</td>
</tr>
<tr>
<td></td>
<td>Fine Sand</td>
<td>0.20 - 0.07 mm</td>
<td>3 - 5</td>
<td>7 - 10</td>
<td>30 - 45</td>
</tr>
</tbody>
</table>

Table 7.6: Summary of LIF Sensor Performance Limits as a Function of Soil Grain Size.
CHAPTER 8

MULTI-COMPOUND SOLUTIONS

8.1 Introduction

A series of LIF tests was performed using the preliminary test cell to evaluate the ability of the microchip laser probe to differentiate individual compounds in a multi-contaminant solution. This capability can prove to be very useful in a field situation since contaminated sites are likely to contain a variety of compounds, many of which may often be unanticipated during an initial investigation. With the ability to extract information about individual compounds from a composite signature, remediation efforts and overall cleanup strategies can be more closely tailored to the specific nature of subsurface contaminants, and thus be more cost effective and efficient.

Field recognition of individual contaminant signatures in chemical mixtures undoubtedly requires detailed reference to a database. However, it is not practically feasible to test all compounds in the presence of all soils. Fortunately, trends presented in Chapter 7 indicate that this type of “all inclusive” database is also unnecessary. During a site exploration a database containing simply the aqueous signatures of all potentially encountered compounds could be referenced to determine the approximate makeup of a composite signature obtained from the contaminated region. This type of database does not yet exist. However, ideally, it would include emission wavelength and lifetime information for individual contaminants, as well as scaling parameters related to chemical concentration that, when combined with general knowledge of site soil conditions, could facilitate an approximate quantitative assessment of subsurface contamination. For such a database to prove useful, however, it is important to understand the fluorescence behavior of compounds in mixtures. The material presented in this chapter provides the foundation of this understanding.
The results of the multi-compound LIF tests performed during this phase of the testing program help interpret the way in which incident excitation energy is partitioned among multiple compounds in solution. Measurements of total fluorescence signals obtained from various mixtures of compounds are compared with the individual fluorescence signatures of the solution components in order to demonstrate the additive nature of total fluorescence signals. Further, an investigation of the decay characteristics of multi-compound fluorescence emissions as a function of emission wavelength indicates the potential to separate lifetimes and thus recognize individual compounds among additional fluorophores. The WTI matrices obtained from the multi-compound tests are analyzed manually at selected times and wavelengths of interest to illustrate experimental findings. As a result, not all of the tests are studied at the same level of detail.

The following sections of this chapter describe the multi-compound testing program. Section 8.1 summarizes the tests performed and briefly discusses exceptions to the general testing procedures presented in Chapters 4 and 6 that were followed while performing the multi-compound tests. Section 8.2 provides a general overview of the multi-compound fluorescence signatures and the information they contain. Section 8.3 illustrates the additive qualities of total fluorescence signals emanating from multiple compounds in solution. The decay characteristics of the composite fluorescence signatures are then described in detail in Section 8.4. Finally, Section 8.5 outlines the potential impact of the multi-compound findings on the practical performance of the LIF sensor.

8.2 Summary of Multi-Compound Testing Program

Due to the laser power fluctuations that plagued the latter portion of the soils testing program, a new laser probe was acquired to carry out the multi-compound tests. This probe was identical in design to the original probe; however, improvements in assembly and alignment techniques used during its construction provided the device with approximately 7 times more power than its prototype counterpart. To calibrate the new device and evaluate the influence of enhanced excitation energy, 15 tests on single compound solutions were performed at the onset of this testing phase. These tests were performed on aqueous
solutions of benzene, o-xylene, and naphthalene and are summarized in Table 8.1. Appendix I contains WTI profiles and a summary of the data acquired from each of the calibration tests.

A review of Table 8.1 demonstrates that the lifetime measurements obtained using the new probe compare favorably with those recorded during the aqueous solution tests. Benzene, o-xylene, and naphthalene were selected for this phase of testing because of the substantial difference in their fluorescence lifetimes that facilitates separation of their fluorescence signatures in multi-compound solutions. This point is illustrated by examining the lifetimes of these compounds. For the limited data set presented in Table 8.1 the mean lifetime values for benzene, o-xylene, and naphthalene, respectively, are 3.0 ns, 6.5 ns, and 42.2 ns. Note that slight increases in the lifetime of benzene relative to lifetime determinations presented in Chapter 6 are a byproduct of signal rollover associated with the benzene observations. As described in Chapter 6, the rapid rise and sudden fall of the short lived benzene signal inevitably leads to curvature at the crest of the data set where this change in signal direction occurs. With the new probe, the benzene fluorescence signals are more than an order of magnitude greater in intensity than previously recorded using the original probe. This increase

<table>
<thead>
<tr>
<th>Compound</th>
<th>Test Name</th>
<th>Aqueous Concentration (ppm)</th>
<th>Lifetime τ (ns)</th>
<th>Peak Emission Wavelength (nm)</th>
<th>Peak Emission Signal (a.u.)</th>
<th>Concentration Indicator (a.u.)</th>
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</thead>
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<tr>
<td>Benzene</td>
<td>MCBEQ1</td>
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<td>296</td>
<td>4.03E-03</td>
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<td>MCBEQ2</td>
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<td>MCB7501</td>
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<td>300</td>
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<td>1.49E-03</td>
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<td>(o)-Xylene</td>
<td>MCXEQ1</td>
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<td>296</td>
<td>3.95E-02</td>
<td>10.810</td>
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<tr>
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<td>6.5</td>
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<td>3.85E-02</td>
<td>10.391</td>
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<td>MCXEQ3</td>
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<td>3.52E-02</td>
<td>9.232</td>
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<td>0.499</td>
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<tr>
<td></td>
<td>MCXTM2</td>
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<td>6.5</td>
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<td>2.90E-03</td>
<td>0.603</td>
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<td>Naphthalene</td>
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<td>46.891</td>
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<td></td>
<td>MCNEQ2</td>
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<td></td>
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<td></td>
<td>MCN5M2</td>
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<td>40.8</td>
<td>320</td>
<td>5.68E-03</td>
<td>5.083</td>
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</table>

Table 8.1: Results of Calibration Tests Performed Using Equilibrium Solutions of Benzene, (o)-Xylene, and Naphthalene.

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in intensity also increases the signal rollover and results in approximately a 0.2 ns increase in the lifetime calculated for the compound. This change occurs only for short lived benzene and is within the typical range of lifetime measurement error (± 0.2 to 0.3 ns). Therefore, the rollover effect has no significant impact on the probe’s ability to differentiate contaminants.

The total fluorescence signals, or concentration indicators, from each of the calibration tests are plotted versus concentration for all three of the tested compounds in Figure 8.1.

**Figure 8.1:** Linear Relationship between Total Fluorescence Signal and Concentration for Aqueous Single Compound Solutions of Benzene, (o)-Xylene, and Naphthalene.

These data display a clear linear relationship between observed signal and concentration given that no fluorescence signal is expected from uncontaminated distilled demineralized water (as shown during the single compound aqueous solution testing program). The slope of the
benzene plot is approximately 0.6% of the slope of the o-xylene plot. This result is double the value of 0.3% obtained for the benzene/o-xylene response ratio during the aqueous solution testing program (see Chapter 6, Figures 6.14 and 6.16). However, it is important to recognize that the benzene/o-xylene response ratio derived from the plots in Figure 8.1 is of similar magnitude to that determined using the original probe; that is, both are close to half a percent. It is difficult to discern the significance of the observed variation in the response ratio with only two data sets (benzene and o-xylene) available for comparison. Unfortunately, naphthalene data was not collected with the original probe, so it is not possible to analyze additional contaminant data sets to evaluate the average signal enhancement provided by the increased power of the new probe. Further, the lack of laser power readings throughout the testing program precludes a direct comparison of the data in Figure 8.1 with that presented in Chapter 6. However, given that the above mentioned benzene/o-xylene response ratio is similar in magnitude to that obtained from an analysis of the Chapter 6 data and that there is a linear increase in fluorescence signal with an increase in contaminant concentration for all of the tested compounds, it is apparent that the new probe performs in a manner consistent with that observed for the original probe. With confirmation of the probe’s performance during single compound tests, it is possible to move forward and investigate the characteristics of multiple compound solutions.

The multi-compound testing program included 13 tests in all. Twelve tests were performed on mixtures of two compounds and one additional test was performed on a combination of three compounds. Test solutions for all of the multi-compound investigations were prepared using equilibrium solutions of the individual constituents. For the double compound tests, the individual equilibrium solutions were combined, on a volumetric basis, in ratios of 50%/50%, 25%/75%, and 75%/25%. Two tests were performed at each of the three ratios for mixtures of benzene and o-xylene and mixtures of o-xylene and naphthalene. The three compound test was performed on a 25%/50%/25% mixture of benzene, o-xylene, and naphthalene. These tests are summarized in Table 8.2. WTI profiles and important results of these tests are presented in Appendix J. Note that the results of these tests do not include lifetime measurements since the intensity time signatures vary at different emission
wavelengths and are often, although not always, a composite of multiple decay curves. This premise is investigated further in Section 8.4.

All of the multi-compound tests were performed using the preliminary test cell that holds a specimen volume of approximately 2 ml. Thus, for example, a 25/75 mix of o-xylene and naphthalene was prepared by combining 0.50 ml of o-xylene equilibrium solution with 1.50 ml of naphthalene equilibrium solution. During the preparation of the solution, precautions were taken to minimize losses due to volatilization. However, some losses were inevitable. In general, the multi-compound mixtures were prepared by adding solutions to the test cell according to their tendency to volatilize. The procedure for specimen preparation included the following 6 steps: (1) the solution that was least volatile and/or displayed the

<table>
<thead>
<tr>
<th>Test Name</th>
<th>Mixture Components</th>
<th>Peak Emission</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzene (o)-Xylene</td>
<td>Wavelength</td>
<td>Signal</td>
</tr>
<tr>
<td>BX551</td>
<td>50% 50% -</td>
<td>296</td>
<td>2.12E-02</td>
</tr>
<tr>
<td>BX552</td>
<td>50% 50% -</td>
<td>294</td>
<td>2.32E-02</td>
</tr>
<tr>
<td>BX721</td>
<td>75% 25% -</td>
<td>296</td>
<td>1.55E-02</td>
</tr>
<tr>
<td>BX722</td>
<td>75% 25% -</td>
<td>296</td>
<td>1.48E-02</td>
</tr>
<tr>
<td>BX271</td>
<td>25% 75% -</td>
<td>296</td>
<td>3.49E-02</td>
</tr>
<tr>
<td>BX272</td>
<td>25% 75% -</td>
<td>296</td>
<td>3.39E-02</td>
</tr>
<tr>
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<td>- 50% 50%</td>
<td>296</td>
<td>2.30E-02</td>
</tr>
<tr>
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<td>- 50% 50%</td>
<td>320</td>
<td>2.19E-02</td>
</tr>
<tr>
<td>NX721</td>
<td>- 25% 75%</td>
<td>320</td>
<td>3.17E-02</td>
</tr>
<tr>
<td>NX722</td>
<td>- 25% 75%</td>
<td>322</td>
<td>3.20E-02</td>
</tr>
<tr>
<td>NX271</td>
<td>- 75% 25%</td>
<td>296</td>
<td>2.20E-02</td>
</tr>
<tr>
<td>NX272</td>
<td>- 75% 25%</td>
<td>296</td>
<td>2.67E-02</td>
</tr>
<tr>
<td>B/XN252</td>
<td>25% 50% 25%</td>
<td>320</td>
<td>2.00E-02</td>
</tr>
</tbody>
</table>

**Table 8.2: Results of Multi-compound Solution Tests.**

greatest fluorescence signature was withdrawn from its preparation vial using a syringe and added to the test cell, (2) the lid of the test cell was then closed, (3) an appropriate volume of the second solution was then withdrawn from its preparation vial using a second syringe, (4) the test cell was then reopened, (5) the second solution was injected into the test cell to complete the total volume of the test solution, and (6) the lid of the test cell was resealed in a fashion that ensured zero head space within the test cell. For a two compound mixture the
test cell was generally filled and sealed with both solution components in less than 15 seconds. The equilibrium solutions used to form the contaminant mixtures were prepared following the general procedures outlined in Chapter 4.

Fluorescence emissions from the preliminary test cell were monitored using the Hamamatsu H5783-03 photomultiplier tube and CVI CM110 spectrometer described in detail in Chapter 4. Signals generated by the photomultiplier tube were again acquired using the LeCroy 9362 high speed digital storage oscilloscope. The scope and spectrometer were configured for data acquisition in a manner identical to that described in Chapter 6, Sections 6.2 and 6.2.1 with two exceptions. First, for all tests involving naphthalene the time scale of the scope was set to 20 ns per division, as opposed to the setting of 5 ns per division typically employed, to accommodate the extremely long fluorescence time signature of that compound. In addition, due to the enhanced signal quality afforded by the increased power of the new probe, only 50 laser pulses were required to generate a reliable signal in comparison to the 500 individual fluorescence traces averaged during the aqueous testing phase. Despite this difference in operational settings, all of the software for data acquisition, test control, and data reduction used in the previous aqueous and soils analyses was also utilized for the multi-compound tests.

8.3 Overview of Multi-Compound Fluorescence Signatures

The wavelength, time, intensity (WTI) signature of a multi-compound solution provides insight into the nature and constitution of the solution's components. This is apparent by comparing the individual profiles of o-xylene and naphthalene equilibrium solutions shown in Figure 8.2 with examples of the WTI curves for naphthalene - o-xylene mixtures presented in Figure 8.3. The naphthalene - o-xylene data were selected for this illustration as pronounced examples that highlight the traits present, albeit often at a more subtle scale, in all multi-compound solutions. Although not discussed herein, tests performed on the benzene - o-xylene mixtures display characteristics similar to those described below. However, since the individual equilibrium solutions of benzene and o-xylene produce comparably shaped fluorescence signatures, the effect of varying component ratios in these
mixtures is difficult to observe visually, although they are still apparent following an appropriate mathematical analysis.

Figure 8.2: WTI Profiles of (o)-Xylene (a.) and Naphthalene (b.) in Aqueous Equilibrium Solution.

The curves presented in Figure 8.3 demonstrate the way in which characteristics of individual contaminant signatures influence an overall solution profile as the relative proportions of the solution components are altered. In this series of plots there is a notable increase in long wavelength emissions as the naphthalene fraction of the composite solution is increased. Since this is a two compound solution proportioned on a volumetric basis, the increase in the naphthalene related signal is accompanied by a decrease in the shorter wavelength o-xylene emissions. These trends are reinforced in the time domain as illustrated in the intensity contour plots of Figure 8.4. The naphthalene component has a very long time signature compared to that of o-xylene. As the intensity of a signal increases, the time required for it to decrease below some absolute magnitude will also increase, although its decay characteristics do not change. Thus, examination of Figures 8.4 (a.) through (c.) illustrates the extension of the naphthalene signature in time that accompanies its increased presence in the solution. In Part (a) of Figure 8.4 the density of the contour lines in the shorter wavelength region characteristic of o-xylene emissions clearly identifies the peak of the overall composite solution profile. As the relative proportions of naphthalene and o-xylene are changed, moving through Figures 8.4 (b.) and (c.), there is a development of two
Figure 8.3: Wavelength, Time, Intensity Profiles for (o)-Xylene - Naphthalene Solutions Composed of (a) 75%/25%, (b) 50%/50%, and (c) 25%/75% Mixtures of (o)-Xylene and Naphthalene Aqueous Equilibrium Solutions.

Note: Contour Origin = 2 x 10^{-3} a.u., Contour Spacing = 2 x 10^{-3} a.u.

Figure 8.4: Intensity Contour Plots for (o)-Xylene - Naphthalene Solutions Composed of (a) 75%/25%, (b) 50%/50%, and (c) 25%/75% Mixtures of (o)-Xylene and Naphthalene Aqueous Equilibrium Solutions.
peak locations and then a change to a condition where the peak intensities are only associated with the long wavelength emissions of naphthalene.

The concepts explored here in a cursory manner are investigated mathematically and described in detail below. It is, however, important to note that in many instances useful information can be gained even from a rapid visual inspection of data. A quick overview of the temporal characteristics and emission peak locations of a fluorescence signature can often help limit the set of compounds that are included in a particular composite solution.

8.4 Interpretation of Total Fluorescence Signals in Multi-Compound Solutions

Empirical evidence demonstrates that total fluorescence signals generated during LIF tests performed on multi-compound solutions can be interpreted in terms of the signals obtained from tests on the individual components of the solution. As stated above, the multi-compound solutions were prepared on a volumetric basis such that distinct volumes of different compounds in equilibrium with water were combined to yield one composite solution. As a first approximation, barring any interaction effects between the two combined components, the total fluorescence signal observed from the composite solution may be considered a superposition of the individual signals observed from the solution components. Thus a 25%/75% solution of naphthalene and o-xylene would be expected to display a fluorescence signal equivalent to the sum of 25% of the signal generated during a test of the naphthalene equilibrium solution, and 75% of the total fluorescence observed from a test of the o-xylene equilibrium solution. In this way, predictions of the total fluorescence signal observed from multi-compound solutions can be made on the basis of the equilibrium solution measurements carried out to calibrate the new laser probe. Table 8.3 illustrates this premise. Each test is listed in conjunction with the observed total fluorescence signal and the signal that was predicted on the basis of the average of the equilibrium solution test results. The error in reference to the prediction is also tabulated for convenience.

The error in the predictions tends to be positive or very slightly negative for all of the benzene - o-xylene mixtures and negative for all of the naphthalene - o-xylene mixtures. The error is also negative for the three compound solution. In general, one would expect these
simple predicted values of total fluorescence to exceed the observations, due to the high potential for contaminant losses during specimen preparation. Note that earlier measurements

<table>
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<th>Test Name</th>
<th>Mixture Components</th>
<th>Concentration Indicator</th>
<th>Error in Prediction</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Benzene (o)-Xylene</td>
<td>Observed (a.u.)</td>
<td>Predicted (a.u.)</td>
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<td>BX551</td>
<td>50% 50%</td>
<td>5.152</td>
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<td>50% 50%</td>
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<td>75% 25%</td>
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</tr>
<tr>
<td>NX272</td>
<td>- 75% 25%</td>
<td>15.834</td>
<td>19.028</td>
</tr>
<tr>
<td>BXN252</td>
<td>25% 50% 25%</td>
<td>12.095</td>
<td>16.658</td>
</tr>
</tbody>
</table>

Table 8.3: Comparison of Predicted and Observed Total Fluorescence Signals for Multi-Compound Solutions.

described in Chapter 7 revealed that almost a 20% loss was incurred on tests of soil specimen pore fluid simply by extracting the specimen from the soil test chamber and injecting it into the preliminary test cell. As described earlier, when preparing a multi-compound solution for testing, at least two transfers of contaminant were required between a preparation vial and the test cell. Further, test BXN252 required three separate additions to the test cell during specimen preparation. Therefore errors associated with contaminant losses on the order of 20% are not unreasonable for the multi-compound tests. However, for the benzene-o-xylene mixtures the observed signal is, on average, 10% greater than predicted. This error, due to its direction more than its magnitude, demonstrates that some mechanism, other than contaminant losses, is contributing to the inaccuracy of the measured signal predictions.

Although the presence of one solute in water can effect the solubility of another solute in the same solution these types of interference and/or enhancements were not a factor in the multi-compound tests because of the employed method of specimen preparation. Both
benzene and o-xylene were already dissolved in water at conditions of equilibrium prior to being combined to create the multi-compound specimen. Thus any limitations on solubility were already enacted in the individual equilibrium solutions prior to formation of the composite solution. Further, although benzene, with its comparatively high solubility of 1780 ppm, may have had the potential to increase the solubility of o-xylene by acting as a cosolute or cosolvent (SGI, 1993), there was no possibility for the actual concentration of o-xylene in the contaminant mixture to increases since the combined specimen had no access to additional volumes of contaminant.

Despite the fact that the potential solubility enhancements afforded by benzene acting as a cosolute or cosolvent could not be realized, the presence of benzene may have had an impact on the quantum yield of o-xylene. As reported in the Handbook of Photochemistry (Murov et. al., 1993), for the same contaminant concentration, the quantum yield of o-xylene in a non polar solvent is approximately 28% greater than in a polar solvent. Therefore, since fluorescence emission is directly proportional to quantum yield, it is possible that increases in the presence of nonpolar benzene in the solution would be accompanied by increases in the observable fluorescence signature from the o-xylene fraction of a multi-compound solution involving these two contaminants. Further, since there is more than an order of magnitude difference in the aqueous solubilities of benzene and o-xylene, it is likely that there was more than enough benzene present in all of the dual compound mixtures to facilitate interaction between the two compounds. It is difficult to assign an exact value to the potential o-xylene signal enhancement attributable to the presence of benzene. However, even a 10 to 15% increase in quantum yield of the o-xylene fraction of the benzene - o-xylene mixtures can account for the majority of the disparity between the observed and predicted signals. As a note, an assumption of 15% volatilization losses and a 25% increase in the quantum yield of o-xylene in the presence of benzene leads to less than a 6% average difference between total fluorescence signal observations and predictions.

Overall, an investigation of the total fluorescence signals derived from multi-compound solutions demonstrates the additive nature of component signatures. This concept provides predictive power, that when refined, could lead to the formation of a large database of expected contaminant signatures created from the results of only a few simple tests. In
general, the trends observed in the test data can be considered representative of conditions in the field since most contaminated sites will contain contaminant concentrations at or below aqueous solubility levels at elevations below the water table. It is unlikely that the additive characteristics of fluorescence signatures can be applied to pure product combinations due to well documented interferences associated with excimer fluorescence. Thus in a field situation where there are unsaturated zones or areas where there are pools of pure product the behavior of fluorescence emissions is likely to be more complex than that studied in this testing phase. Note that excimer fluorescence (discussed in Chapter 2) was not investigated in this study.

8.5 Fluorescence Decay in Multi-Compound Solutions

In addition to a measurement of the total fluorescence emission generated in a specimen, the multi-compound WTI also provides valuable fluorescence decay information that can be used to help identify a solution’s constituents. However, multi-compound decay data requires significantly more interpretation than that derived from a single compound solution to yield accurate identification information. The decay characteristics of a multi-compound WTI profile tend to vary at different emission wavelengths. This variation stems from changes in each component’s contribution to the overall emission profile as a function of emission wavelength.

In a single compound solution, the decay of emission energy following excitation can be characterized by an exponential function of form $ae^{-bx}$ (Chapter 6). When more than one compound is present in a solution, the emission profiles of the individual components tend to overlap in some, if not all, regions of the observation spectrum. If the fluorescence emissions from two or more compounds coincide in the wavelength domain, the decay of the emitted energy in that region must follow a trend marked by the superposition of the independent component emissions. Experimental results from this phase of testing indicate that the superposition effect can be described by a summation of exponential decays. Thus, if the emissions of $i$ components coincide at a particular observation wavelength, at any time $t$ following excitation the normalized fluorescence emission, $I(t)$, can be characterized by:

$$I(t) = \sum_i a_i e^{-t/b}$$

(8.1)
where \( a_i \) denotes the fraction of the signal generated by component \( i \) at time zero, and \( \tau_i \) indicates the decay constant associated with component \( i \). This concept can be illustrated clearly by analyzing a series of examples.

A 50%/50% mixture of naphthalene and o-xylene, such as that examined in test NX551, provides an illustration of a two compound mixture for which there are regions of fluorescence emission from only one solution component and other zones involving emission overlap from both solution components. Part (a.) of Figure 8.5 depicts the peak fluorescence emissions as a function of wavelength for individual equilibrium solutions of o-xylene and naphthalene. Scaled versions (dotted lines) of these individual equilibrium curves are then presented in Figure 8.5, Part (b.) to illustrate the approximate contribution of the individual solutions to a 50%/50% aqueous mixture of the two contaminant solutions. The individual scaled curves are also summed and presented as a prediction (solid symbols) for comparison with the measured peak curve (open symbols) of test NX551. In this case, the prediction indicates slightly less influence from o-xylene and slightly more influence from naphthalene than the measured curve which depicts actual test data. However, it is apparent from the figure that, overall, the measured behavior matches the prediction quite well especially in terms of the two peak locations in the wavelength domain. Thus the regions of independent

\[ \text{Figure 8.5: Breakdown of Solution Components Contributing to the Fluorescence Response of a 50%/50% Aqueous Solution of Naphthalene and (o)-Xylene.} \]
and overlapping fluorescence emission indicated by the equilibrium solution curves are likely to provide a good indication of the type of decay behavior observed in the test data as a function of emission wavelength.

A review of Figure 8.5 (a.) indicates that over the emission wavelength range of 275 nm to ~285 nm or ~290 nm only o-xylene contributes to the mixture fluorescence emission. Similarly, in the range from ~335 nm to 350 nm naphthalene is the only solution component responsible for fluorescence emission. In the intermediate zone from ~290 nm to ~335 nm both contaminants are likely to influence the emission observations. This information is confirmed by an analysis of the decay characteristics of the 50%/50% naphthalene - o-xylene mixture at different wavelengths. Figure 8.6 presents intensity - time traces from test NX551 at selected wavelengths to demonstrate the variety of emission behavior that can be encountered even when only two compounds compose a solution. Wavelengths have been isolated within all three zones of interest described above. Note that the decay curves have also been normalized by their respective peak amplitudes to facilitate comparison.

Analysis of the curves presented in Figure 8.6 reveals that the decay profiles for the 286 nm and 338 nm emissions can be described using a single exponential decay constant. A fluorescence lifetime of 6.6 ns was calculated for the 286 nm emission trace using a least squares regression. This value accurately represents the fluorescence behavior of o-xylene. In

![Figure 8.6: Examples of the Variation in Fluorescence Emission Decay Encountered in the Data from a 50%/50% Naphthalene - (o)-Xylene Solution.](image)
addition, a lifetime of 39.4 ns was obtained for the 338 nm decay curve which compares favorably with the lifetime values calculated for naphthalene in the initial equilibrium solution tests presented in Section 8.2. The intermediate wavelength decay curves, all required a sum of two different exponential decay curves to achieve an accurate curve fit. Since the decay constants associated with both contaminants in the solution were already known all of the intermediate decay curves were fit using the decay constants obtained for the individual naphthalene and o-xylene time traces at 286 nm and 338 nm, respectively. At a given emission wavelength the proportion of the fluorescence emission attributed to each of the solution components is represented by the coefficient $a_i$ of the exponential decay term associated with each compound. The curve fits obtained for three of the selected intensity-time traces are illustrated in Figure 8.7. For all three of the plots presented in Figure 8.7, the open symbols

![Decay Curves](image)

**Figure 8.7:** Decay Constants Determined for 286 nm, 312 nm and 338 nm Intensity Time Traces from a 50%/50% Naphthalene - (o)-Xylene Solution.
signify measured data, and the solid lines represent the final curve fit through the data. For the 312 nm plot, dotted lines are also shown to indicate the individual contributions of the solution components to the overall decay profile. The form of the decay equation and decay constant(s) used in the fitting process are also provided in the figure.

The concepts illustrated using the naphthalene - o-xylene solution above are reiterated in an analysis of test BX722. In this test, there are no regions of single compound fluorescence as illustrated in Part (a.) of Figure 8.8. The emission profiles of benzene and o-xylene overlap completely within the wavelength range observed. As a result, all of the decay signatures obtained from the mixed solution must be characterized using the sum of two exponential curves. Only the leading coefficients of the exponentials change as the relative fluorescence contribution of the compounds varies with emission wavelength. Again a least squares regression algorithm can be used to find the values of all of the parameters required to characterize the decay of the fluorescence emission. An example of the fit achieved using calculated lifetimes of 2.9 ns for benzene and 6.5 ns for o-xylene at an emission wavelength of 296 nm is provided in Figure 8.8, Part (b.).

**Figure 8.8:** Fluorescence Response of a 75%/25% Aqueous Solution of Benzene and (o)-Xylene: (a) Solution Components, and (b) 296 nm Emission Decay Curve.
The premise that a sum of exponential equations can be used to identify individual components and their contribution to fluorescence in the two compound solutions can also be extended and applied to a three compound solution. This process is illustrated in Figure 8.9 using test BXN252. Part (a.) of the figure illustrates the superposition of the individual compound contributions that results in a predicted peak emission curve (solid symbols) as a function of emission wavelength. The observed peak emission curve (open symbols) is also presented for comparison. To illustrate the decay behavior of this three compound solution the intensity time trace at 306 nm is presented in Figure 8.9, Part (b.). Note that the decay curve has again been normalized by its peak amplitude. A review of Part (a.) of the figure demonstrates that the 306 nm trace includes contributions from benzene, o-xylene, and naphthalene. In this case a function including three exponential terms was used to fit the decay curve. The three decay constants determined for the fit are 2.9 ns, 6.5 ns, and 41.5 ns for benzene, o-xylene, and naphthalene, respectively. The fluorescence decay function and its parameter values are presented in the figure.

**Figure 8.9:** Fluorescence Response of a 25%/50%/25% Aqueous Solution of Benzene, (o)-Xylene, and Naphthalene: (a) Solution Components, and (b) 306 nm Emission Decay Curve.
From a review of the above examples, it is apparent that the time decay of the fluorescence response of a multi-compound solution at any emission wavelength can be represented by a sum of exponential equations of the form $a_i e^{-\frac{t}{\tau_i}}$ for the $i$ components of the solution where $a_i$ and $\tau_i$ are as defined earlier. The ability to obtain a unique solution for the parameters of this exponential formulation depends on the number of components in the solution and the amount of data available for analysis. Each data point on the decay curve of an intensity-time trace provides a target condition for optimization of the exponential equation parameters. As the number of components in a solution increases more data is required to obtain decay constants ($\tau_i$) and leading coefficients ($a_i$) with equivalent levels of confidence. Theoretically, for each solution component, a minimum of two data points are required to identify the two unknown quantities, $\tau_i$ and $a_i$. Of course, confidence in the choice of these parameters improves as the number of data points used for their determination increases. Ultimately, for a given acceptable confidence level, the number of components that can be identified in a solution will be a direct function of the wavelength and temporal resolution of the equipment used to collect the fluorescence observations.

8.6 LIF Sensor Performance in Multi-Compound Solutions

Overall, the experimental results from the multi-compound solution tests demonstrate that the fluorescence response of a mixed solution can be characterized by the superposition of the proportional responses of the solution’s components in both the time and emission wavelength domains. Although this concept was illustrated using contaminant mixtures of known composition, it is evident that the superposition techniques presented in Sections 8.3 and 8.4 can be used in conjunction with a detailed database of equilibrium solution test results to determine the source of a fluorescence signature measured in the field. This procedure might involve a number of steps that converge to provide an approximate composition of a test solution. Initial information on emission peak locations in the field data would immediately narrow the scope of potential solution components. Additional analyses could then identify the number of exponential terms and the value of the decay constants required to accurately describe the field data decay behavior as a function of emission wavelength. This would further limit the possible composition of the field signal. Finally, an iterative procedure
could be used to alter the proportions of the potential solution components until a match was identified on the basis of acceptable confidence levels. This type of technique is very similar to that used with other analytical tools such as a gas chromatograph and an x-ray diffraction system. Traits of the test specimen are prioritized and evaluated in a process of elimination until the most likely specimen composition is derived. The observations made during the multi-compound test phase demonstrate that the LIF sensor has the potential to operate in this analytical manner. Thus, the LIF sensor’s abilities to identify and quantify contaminants in solutions have substantial potential for application to practical problems.
CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 Research Overview

In this study, unique microchip laser technology developed at MIT's Lincoln Laboratory was evaluated for practical application in a new in situ contaminant sensor that utilizes laser induced fluorescence (LIF) to detect, identify, and quantify aromatic hydrocarbons in subsurface environments. The potential applications of the sensor, which include long term contaminant monitoring, subsurface profiling, and down-well investigations, all involve contact between the sensor and contaminated soil and/or groundwater. Since these natural contaminated media are inevitably inhomogeneous, the relative test conditions of individual LIF measurements tend to differ. This premise raises several questions regarding the impact of subsurface characteristics on in-situ LIF investigations. This study has therefore focused on the interpretation of in-situ spectroscopic contaminant measurements and their correlation to properties of the contaminated media.

A versatile experimental apparatus was designed and fabricated to simulate the in-situ interface between the LIF sensor and contaminated media while providing complete control of test conditions. This laboratory apparatus provided a means to proof test the new sensor and also permitted in-depth investigations of fundamental issues that have the potential to influence in situ optical spectroscopic measurements acquired with any sensor of similar design. The experimental apparatus was primarily used to analyze the influence of contaminated media properties on LIF observations, although issues associated with electrical and optical interference, laser penetration depth into the target medium, and data acquisition limitations were also addressed.

The BTX compounds, benzene, toluene, and o-xylene, were used throughout this study as test contaminants. These compounds are primary constituents of fuels and are therefore common pollutants. The BTX compounds also have the shortest fluorescence
lifetimes of any of the aromatic hydrocarbons. Thus, the probe's ability to detect and identify these compounds provides not only a significant illustration of its capabilities but also emphasizes its applicability to actual environmental concerns. The properties of contaminated substances given primary consideration included contaminant concentration and solution composition for the aqueous media and grain size, type, color, and mineralogy for the soils. The influence of particle morphology and soil organic content on LIF measurements was also considered on a secondary basis.

Two different data acquisition devices were used in conjunction with the testing equipment. The first and most versatile unit, a high speed oscilloscope, characterized the magnitude of a fluorescence signal as a function of time. The second device, a photon counter, provided exceptional signal sensitivity but very little temporal information. These two data acquisition units were utilized to evaluate the dependence of the LIF sensor's performance on the characteristics of its accompanying data acquisition system.

Proof testing of the prototype LIF sensor and continued evaluation of factors affecting its performance were carried out through a three phase testing program. In the first phase, 40 single compound aqueous solution tests were performed to determine the repeatability of LIF measurements, identify trends in the fluorescence behavior of compounds as a function of aqueous concentration, observe the form of specific contaminant signatures, assess the impact of interferences, establish robust methods for data analysis, and determine the sensor's ultimate detection, identification, and quantification limits for specific compounds in aqueous solution based on criteria developed through detailed data analysis. After developing confidence in the capability and reliability of the LIF sensor, soil tests were performed to delve further into the phenomenon under investigation and identify specific parameters controlling LIF observations in the presence of soils. Over 100 individual tests were conducted on specimen created from various grain size ranges of 6 different soils. The soil test results were compared with the findings of the aqueous solution test phase to highlight the influence of a soil matrix on in situ fluorescence measurements. Finally, a third test phase was pursued involving 15 tests conducted on two and three compound aqueous mixtures. This last testing phase was carried out using a second generation LIF probe design. The new probe benefited from improved assembly and alignment techniques that resulted in nearly an order of
magnitude more laser power than the original probe. The multi-compound tests extended the laboratory investigations closer to true field conditions, provided insight into the LIF sensor’s ability to identify individual compounds in multi-component solutions, and, through the use of a second probe, helped demonstrate that the general findings of the earlier two phases of testing were not specifically related to a particular probe or probe power level. Further, the multi compound tests illustrated the potential for contaminant interactions to affect LIF observations.

9.2 Results and Conclusions

As a whole, this study provided insight into the use of fluorescence spectroscopy for in situ contaminant analysis. The work yielded a detailed assessment of the specific capabilities of a prototype LIF sensor and also addressed several fundamental issues affecting any optical spectroscopic system designed for subsurface operation. Since the experiments performed throughout this study were divided into three primary categories according to the nature of the test media under investigation, the results and associated conclusions of these testing phases are discussed individually below. The following discussions detail findings from aqueous contaminant solution studies, investigations of contaminant solutions in the presence of soils, and experiments performed on aqueous mixtures of two and three compounds. The separate discussions are followed by an interpretation of their collective meaning with regard to the practicality and potential effectiveness of in-situ contaminant investigations.

9.2.1 Summary of Findings from the Aqueous Solution Testing Program

The simplicity of the aqueous solution tests facilitated investigations of a variety of general issues related to the design of the LIF sensor in addition to specific concerns about the use of the sensor for contaminant investigations in aqueous media.

The aqueous solution experiments demonstrated that the internal optical design of the LIF probe permitted sufficient transmission of fluorescence inducing radiation and collection of emission energy to detect benzene, toluene, and o-xylene at aqueous concentrations typically found in the environment. Further, successful LIF experiments performed on compounds such as benzene proved that the LIF sensor was capable of inducing identifiable
fluorescence in compounds with fluorescence lifetimes as short as 2.5 ns. The decay characteristics of the fluorescence emissions generated in the single compound solutions were also useful in characterizing the probe. All of the single compound fluorescence signatures displayed simple exponential decay over time thus demonstrating that the short 200 ps excitation pulse of the microchip laser induced common single photon fluorescence with no evidence of atypical effects. Finally, the more than 800 hours of operation and greater than 2500 estimated on/off cycles logged on the sensor during the aqueous testing program provided the first demonstration of the long term sustainability of a microchip laser based LIF system. Thus, the aqueous solution experiments served as proof tests that confirmed the general feasibility of the microchip laser based LIF sensor.

Experiments performed on aqueous solutions also demonstrated that many aspects of optical interference associated with, for example, scattered excitation energy and the Raman signature of water, were extremely repeatable and could therefore be eliminated through the use of optical filters or simply by mathematical subtraction. Overall, optical noise contributions to fluorescence measurements were limited to insignificant levels. Electrical interference components that were synchronous with the laser excitation pulse were also easily eliminated by subtraction. With these factors eliminated, it was apparent that only random electrical noise and the resolution of the data acquisition system limited the capabilities of the LIF sensor for a given level of per pulse excitation energy.

Using the equipment available during this study, specific detection, identification, and quantification limits were established for each of the BTX compounds in aqueous solution. The development of logical and robust data processing and analysis procedures also indicated that for any compound, all of these limits necessarily differ. Further, the performance limits of the probe were shown to be directly linked to the data acquisition system employed during testing. Table 9.1 summarizes the performance limits of the probe in association with the two data acquisition systems used in this study. Note that no photon counting experiments were performed on solutions of benzene or toluene. Also, no attempts were made to identify compounds using the photon counter.
Table 9.1: Summary of LIF Sensor Performance Limits.

The aqueous solution experiments resulted in the development of several criteria that objectively define the limits presented in Table 9.1. The limiting criteria vary in conjunction with the data acquisition system, but were always established in relation to the noise level of the system. The criteria that define the performance limits of the LIF sensor when used in conjunction with the high speed oscilloscope or the photon are described separately below.

When using the high speed oscilloscope for data acquisition, all of the oscilloscope performance limits were based on the noise band of the scope which was assumed to be statistically normal. For contaminant detection analyses, the noise band was assumed to include approximately 99.9% of the noise recorded by the scope (3 times the standard deviation of the mean of the measured noise band [3 $\sigma$]). For identification and quantification, the noise band used in SNR calculations was less restrictive and, statistically, included approximately 90% of the scope’s background noise (1.6 times the standard deviation of the mean of the measured noise band [1.6 $\sigma$]). Based on these assumptions, analysis of the aqueous solution data demonstrated that the signal generated from a contaminant’s fluorescence emission must exceed 99.9% of the scope’s background noise to qualify as contaminant detection. Further, a peak signal to noise ratio of at least 4 (SNR $> 4$, where N = 1.6 $\sigma$) is required of an intensity time trace at any observed emission wavelength to permit contaminant identification on the basis of fluorescence lifetimes that are repeatable within $\pm$10% of the mean lifetime recorded during equilibrium solution tests. The criterion established for quantification of contaminant concentrations was even more limiting. The peak of a contaminant’s Wavelength - Time - Intensity (WTI) profile must be at least 20 times
greater than the noise band of the data acquisition system (SNR > 20, where N = 1.6 σ) to permit quantitative analysis that is repeatable within ±10% of the mean total fluorescence signal obtained at a given contaminant concentration.

When using the photon counter for data acquisition, a signal to noise ratio greater than 2 (SNR > 2) was required for contaminant detection and quantification. The definition of noise for each of these categories, however, differs in relation to the confidence required for each measurement and is directly related to the Poisson cumulative distribution function that characterizes noise in a counting process such as that utilized by the photon counter when applied for fluorescence observations.

9.2.2 Summary of Findings from the Soil Testing Program

Soil tests were performed on specimen of quartz, Manchester fine sand, and Ticino sand saturated with equilibrium solutions of o-xylene. The industrial quartz was selected because its wide grain size range, single mineralogy, and uniform coloration facilitated a comprehensive study of soil grain size effects. Manchester fine sand and Ticino sand were chosen as additional granular materials having grain size distributions that were narrower than, yet coincident with, that of the quartz and could thus be used to follow up on the grain size trends identified during the quartz tests. Since Manchester fine sand and Ticino sand also have more varied color, less uniform mineralogy, and higher organic content than the quartz, these materials were additionally useful to illustrate the significance secondary soil properties on LIF observations.

A number of valuable findings were derived from the soil testing program. These tests demonstrated that soil properties had no measurable effect on the general shape of a pore fluid contaminant’s fluorescence signature in either the wavelength or time domain. Thus the fluorescence lifetimes determined for contaminants in the presence of soils do not differ from lifetimes calculated for the same contaminants in aqueous solution. Further, soil does not alter the emission wavelength characteristics of a contaminant signature. Based on this finding it is apparent that the LIF sensor does not induce and/or observe any soil related Raman effects. This was confirmed in soils with combustion based organic contents as high as 18%.
Other LIF tests also performed on specimen of quartz, Manchester fine sand, and Ticino sand saturated with equilibrium solutions of o-xylene illustrated that measurements of peak and total fluorescence signal made in the presence of soils are subject to considerable variability. Specifically, for a given contaminant concentration in the pore space of a soil specimen composed of uniformly sized soil grains, as the grain size of the soil decreases, so does the value of the maximum observed LIF signal. For example, total fluorescence signals obtained during tests performed on contaminant saturated quartz composed of particles smaller than 0.2 mm were only 25% of the values obtained from tests on the same contaminants in aqueous equilibrium solution. The in-soil signals were equivalent to the aqueous measurements only when the soil grain size exceeded approximately 0.9 mm. A geometric model was developed which showed that these findings were primarily related to the volume of pore fluid in a soil specimen that was directly accessible to laser excitation energy. For a natural soil containing a distribution of particle sizes, in-soil LIF signals tend to be characteristic of the values typical of the smallest particle size in the soil. Evidence from experiments on fine grained soils (primarily clay minerals) with greater than 98% of their particles passing a U.S. Standard No. 325 sieve (0.04 mm) illustrated that very small soil particles can completely mask all contaminant fluorescence observations.

Two additional soil related factors were investigated in greater detail. Hypotheses presented in Chapter 7 illustrated that fluorescence emanating from contaminants sorbed to soil particles had the potential to account for as much as a 15% increase in the magnitude of LIF signals generated in soils with an organic content as high as ~ 1.5% relative to soils with less than 0.15% organic content. Further, the optical properties of soil particles, namely absorption, transmission, and reflectivity, also have the potential to influence the LIF signal generated in pore fluid contaminants. Estimates based on measurements of soil optical characteristics imply that an order of magnitude difference in soil reflectivity might account for a 5 - 10% difference in LIF measurements performed on soils saturated with contaminant solutions. At this time, the significance of the effects associated with soil organic content and optical properties is a function of many assumptions including the assumed mechanism relating the soil properties to fluorescence observations. It is therefore clear that these factors require further investigation to facilitate a more accurate assessment of their impact on fluorescence.
measurements. However, it is equally clear that any effects stemming from soil organic content and optical properties are secondary to the influence of soil grain size described above.

In summary, all of the soil related factors pursued during the soil testing program combine to alter the detection, identification, and quantification capabilities of the LIF sensor relative to those in aqueous solution. Tests performed to estimate the depth of excitation energy penetration into a target medium demonstrated that the laser radiation reaches approximately 0.60 to 0.75 mm into the test medium. The fact that this dimension is greater than the size of many soil particles makes it clear that soil must influence in-situ optical spectroscopic measurements. Recognize, however, that the impact of soil on LIF observations is limited to an alteration of LIF signal magnitude and has no bearing on the emission wavelength or time decay characteristics of the phenomenon. Over the range of coarse grained soil particle sizes investigated, that is 0.07 mm to 2.00 mm, soil may reduce the detection, identification, and quantification capabilities of the LIF sensor by as much as a factor of five.

9.2.3 Summary of Findings from the Multi-Compound Solution Testing Program

The multi-compound solution tests demonstrated that, at concentrations below aqueous solubility, both the emission wavelength characteristics and the decay properties of a chemical mixture fluorescence signature can be represented by the superposition of the individual contributions of the solution components. The emission wavelength characteristics of the solution components are simply additive on the basis of the molar fraction, or concentration, of that contaminant in the total solution. Similarly, the decay of a multi-compound solution’s fluorescence emission at an emission wavelength shared by \( n \) components can be described by the sum of \( n \) exponential equations of the form \( a_i e^{-\tau_i t} \), where \( a_i \) denotes the fraction of the emission generated by component \( i \) at time zero, and \( \tau_i \) represents the decay constant associated with compound \( i \). The straightforward, additive nature of individual chemical fluorescence signatures in the emission wavelength and time domains confirmed for the multi-compound solutions supports the possible development of a
predictive model that can be used to analyze unknown contaminant mixtures on the basis of a limited set of data derived from tests performed on individual compounds.

9.2.4 Applications of LIF Sensor Technology

The specific findings and conclusions outlined above demonstrate the potential to utilize compact microchip laser technology to create a LIF sensor capable of performing in-situ contaminant analyses. By providing insight into the primary factors controlling the performance of the LIF sensor in aqueous and soil environments this experimental program also indicates the possible effectiveness of the sensor when applied in various capacities. Further, the testing and data interpretation techniques utilized in this research effort serve as a general means to evaluate the capabilities of any in situ investigation device based on optical spectroscopy.

At present, it is clear that an in-situ LIF sensor can be used effectively to investigate the presence of contaminants in aqueous solution and in the pore space of soils on a detect/non-detect basis. It is also apparent that chemical speciation and quantification can be readily achieved in aqueous contaminant mixtures through analyses of contaminant fluorescence lifetimes and emission wavelength characteristics. Although a complete database of fluorescence signatures for contaminants in aqueous solution does not yet exist to facilitate identification and quantitative analyses in complex systems, simple superposition effects that have been shown to govern multi-compound fluorescence behavior at or below aqueous solubility levels indicate that the creation of such a database is feasible. Extension of these capabilities to in-soil investigations, however, is more difficult. Using the prototype LIF sensor design, it is possible to reliably detect and identify contaminants in the presence of coarse grained soils. However, quantitative assessments of contamination in this media are likely to involve significant error and may require concurrent investigations of soil grain size. Further, using the present LIF sensor design, fine grained soils such as clays may completely obstruct in-soil LIF observations.

The detection, identification, and quantification capabilities of the LIF sensor in aqueous solution suggest that the current sensor design can be used effectively as a down-well investigation tool, although effects associated with pure product contamination have not yet
been explored. The sensor can also be applied as a long term monitoring device that is placed in or near a contaminated region and surrounded by material of known grain size. With detailed knowledge of the in-situ conditions neighboring the sensor even quantitative in-soil contaminant assessments are plausible. However, field application of the LIF sensor as a subsurface profiling probe that can provide reliable quantitative data with no foreknowledge of a test site is still some time away. Although more research is required to fully understand all of the issues that influence in-situ contaminant fluorescence observations, this study supports the concept of an in-situ microchip LIF contaminant sensor and demonstrates that in-situ LIF technology warrants further investigation.

9.3 Recommendations for Future Research

After evaluating the results of the experiments conducted throughout this study, it is apparent that several issues can be pursued to improve the design of the LIF sensor system as a whole and to further enhance the present understanding of contaminant fluorescence in subsurface environments.

The performance of the existing LIF sensor can be improved through a series of innovations that make the device more versatile and practical. Although the sensor is quite useful in its present state for in-situ monitoring and down-well investigations, its broader application as a quantitative subsurface profiling unit is inhibited by the influence of soil matrix effects, limitations on data acquisition speed, and for very deep investigations, propagation losses of collected fluorescence emission energy. It may be possible to overcome each of these difficulties through further research.

The first of the above mentioned issues requiring attention may prove to be the most difficult to address. Soil matrix effects in coarse grained soils have been shown to induce variability in in-soil LIF observations. This variability can lead to a miscalculation of subsurface contaminant concentration by as much as a factor of five. In some circumstances only approximate quantitative measurements are necessary. Thus the significance of the quantitative error linked to soil matrix effects will tend to be case dependent. However, the versatility of the LIF sensor can be inarguably improved by decoupling LIF measurements and soil matrix effects. This might be achieved by increasing the zone of the test medium.
interrogated for an individual measurement or by working with an unfocused laser. Either of these options would likely result in a more stable, yet reduced, fluorescence signal since the zone targeted for the measurement would tend to include many soil particles and thus many void spaces. Another approach to the problem might make use of a LIF system with a variable focal length. This design could incorporate a flexible or movable optic to alter the laser excitation zone in the test medium. In this case soil grain size information could be inferred from the change in the fluorescence signal observed as the target zone changed. Thus, the in-soil fluorescence signals would regain meaning on an absolute scale of contaminant concentration and facilitate in-situ quantitative analyses. Unfortunately, alterations of the LIF sensor interrogation zone are unlikely to improve sensor performance in fine grained materials. This problem might be overcome by effectively removing the fines from the sensor interrogation zone, perhaps through mechanical displacement of the soil or by in-situ examination of the soil pore fluid.

Improvements in the LIF sensor data acquisition process are less speculative than any of the concepts put forth to overcome soil matrix effects. Further, the benefits of enhanced data acquisition capabilities would influence all applications of the LIF sensor. Even though the LIF sensor makes use of a microchip laser that induces fluorescence with 200 ps pulses of excitation energy, the sensor's ultimate ability to perform real time signal averaging and thus improve signal quality is limited by the speed of the data acquisition system used in conjunction with the laser. Based on the experimental results obtained in this study it may not appear that improvements in signal quality are necessary for field application of the sensor. However the tests described in this study were all performed in the laboratory by averaging signal traces acquired on an oscilloscope at each of the monitored emission wavelengths. This system required approximately 25 seconds to obtain a single average intensity-time trace. This type of system is adequate for laboratory investigations, where measurements are often acquired on an individual basis in association with specific experimental configurations. In the field, however, multiple measurement, continuous push operations are desirable to facilitate subsurface profiling, enhance data gathering, and reduce equipment operation time and expense. Thus, measures must be taken to improve the speed at which data can be acquired. Enhanced performance of the LIF sensor in the field requires an analysis of the complete LIF
system. For specific sites, operations can be improved by targeting specific chemicals, limiting observation intervals in both the time and wavelength domain, and utilizing advanced data acquisition devices. The data acquisition device, however, provides the most general basis for overall improvement in system performance. For example, significant time savings can be realized by using a high speed data storage device and/or by acquiring data over the entire observation spectrum simultaneously using a photodiode array or charge coupled device (CCD) to detect emission energy. Note, however, that switching to a CCD or diode system may result in some loss of detection sensitivity. The significance of this loss will be project dependent and must be weighed against the time and cost savings offered by the enhanced acquisition technique.

Another equipment improvement that has the potential to significantly enhance the capabilities of the LIF sensor involves a method to eliminate propagation losses of fluorescence emissions transmitted through the LIF sensor return fiber. Although the microchip laser system used in this program eliminates a great deal of excitation energy losses by generating ultra violet radiation at the testing location, the fluorescence excited in contaminated media must still be collected and transmitted via fiber optic cable to a detection system located above ground. Substantial increases in instrument sensitivity can be afforded by eliminating these return fiber losses. One solution to this problem might incorporate a downhole spectrometer and/or detector system to convert the optical information into electrical signals very near to the excitation location. This approach does not alleviate the need for high speed signal processing to permit time resolved data analyses. However, problems associated with temporal distortions and signal amplification can be overcome more easily in the confined space of a profiling device when using electronics rather than optics. Further, by reducing analog signal travel requirements through down-hole signal processing, it may be possible to improve LIF system sensitivity to levels commensurate with photomultiplier technology.

Effective implementation of the system improvements described above may make it possible to take advantage of new developments in diode laser technology to create an in-situ sensor that is more sensitive and versatile than any existing system. The enhanced LIF sensor technology could be used in conjunction with higher power diode pumps to extend the
sensor's capabilities beyond fluorescence into the field of Raman spectroscopy. At this time the microchip laser is capable of generating both ultra violet and visible excitation energy. If either spectral emission proves to be capable of inducing useful Raman scattering then it would be possible to create a sensor that could utilize both fluorescence and Raman scattering to detect and identify contaminants. Simultaneous application of laser induced fluorescence and Raman scattering analyses would permit quantitative investigations of virtually any compound, including the problematic chlorinated solvents.

Overall, the results of this study have provided support to the concept of using laser induced fluorescence for in-situ contaminant investigations while simultaneously illustrating the significance and influence of many subsurface characteristics on fluorescence observations. There are, however, many more issues related to subsurface contaminant analyses that can and should be studied using the MIT/Lincoln Lab LIF sensor and the laboratory apparatus developed during this program. The fundamental areas requiring further exploration can be summarized as follows:

- investigate the relationship between soil organic content and observed in-soil contaminant fluorescence to identify underlying mechanisms that may influence emissions.
- distinguish between the performance characteristics of a remote detection/monitoring system in saturated and partially saturated soils.
- determine the effect of subsurface characteristics on the ability of a remote fluorescence system to detect vapor phase contaminants in the pore space of soils.
- differentiate fluorescence contributions from sorbed, in-water, and vapor phase contaminants in a multi-phase environment.
- thoroughly examine the fluorescence behavior of contaminants in multi-compound mixtures.
- evaluate the ability of the remote spectroscopic system to detect changes in in-situ chemical concentration affected by remediation operations.
- identify the factors limiting the performance of the LIF sensor in fine grained soils and establish techniques to investigate contaminants in that medium.

In addition to laboratory exploration of the principles underlying the LIF sensor's capabilities, a great deal can also be learned from field trials of the device. For example, efforts could be
made to employ the device to examine landfill leachate, monitor remediation efforts, or observe the migration of contaminant plumes. Use of the sensor in field situations will highlight areas of practical significance that require improvement before the sensor can be used on a routine basis. As these topics are investigated many more questions will inevitably arise. However, continued understanding of the factors controlling the LIF sensor's performance and the fluorescence phenomenon may ultimately make in-situ optical spectroscopy a standard site investigation technique.
References


Appendix A

DIODE LASER EXTERNAL MODULATION PROGRAM
Diode Laser External Modulation Program - “PULSE”

DATE 1/22/97:  JOE SINEFIELD

PROGRAMS = "PULSE.BAS"

' This program is used to modulate the microchip laser
' at a repetition rate of ~ 1.1 kHz

CLS : LOCATE 8, 30: COLOR 5
PRINT "MODULATING DIODE LASER"
COLOR 20, 0
LOCATE 14, 23: PRINT "                       \""
LOCATE 15, 23: PRINT "----------------------------- * -- "
LOCATE 16, 23: PRINT "                   /\ "

' inform user that code is running

' send numbers (i.e. 6 and 4, for example) out address 956 to generate
' high and low TTL signals on pin 2 of output port (relative to pin 7)

' this TTL signal can then be used to externally modulate the LCI
' Model 560 Laser Diode Driver

FOR X = 1 TO 50000000
    OUT 956, 6
    OUT 956, 6
    OUT 956, 6
    OUT 956, 6
    OUT 956, 6
    OUT 956, 6
    OUT 956, 6
    OUT 956, 4
    OUT 956, 4
    OUT 956, 4
    OUT 956, 4
NEXT X

' inform user that code is no longer running

CLS : COLOR 7
PRINT "LASER MODULATION INACTIVE"
Appendix B

AUTOMATION SOFTWARE FOR LASER INDUCED
FLUORESCENCE TESTS
DATE 10/28/96: JOE SINFIELD

PROGRAM$ = "TEST.BAS"

\* This program is used for the following purposes:
\* < 1 > to control the stepper motor which rotates the grating
\* of the CVI CM110 spectrometer
\* < 2 > to acquire data from a Hamamatsu H5783-03 photomultiplier
\* tube using an AD1170 A/D converter
\* < 3 > to acquire data from an SR430 MULTI-CHANNEL SCALER
\* configured for photon counting
\* < 4 > to collect fluorescence decay curve data from a LeCroy
\* Model 9362 High Speed Oscilloscope

\* COPYRIGHT JOE SINFIELD OCTOBER 1996

\* ******** DEFINE VARIABLES ********

\* ADJVOLTS = PMT voltage adjusted for 3.6 mV background
\* ANSS$ = used as menu input variable
\* BIN1 & BIN2 = photon counting bin identifier
\* BITS = total number of bits in photomultiplier reading
\* CFA ... CFG = spectral response curve fitting parameters
\* CFX, CFY = spectral response variables (X=wavelength/100, Y=PMT response)
\* C = counter indicating the number of scan intervals entered by user
\* CHEMS$ = name of chemical under investigation
\* CHOICES$ = used as menu input variable
\* CMBWRT$ = command variable for SR430 AND LeCroy 9362 communication
\* CONCS$ = concentration of chemical under investigation
\* DATE$ = sate that experiment is performed
\* FILENAMES$ = results storage filename
\* HI = high byte of photomultiplier read@g
\* INFO = reading number (data line number in data storage file)
\* INFO (1000, 2) = test results storage array
\* INTBIT = A/D converter bit precision
\* INTERVAL(10) = array of scan interval data reading intervals (nm)
\* INTTIME = integration time of A/D converter
\* LO = low byte of photomultiplier reading
\* M = data acquisition channel counter
\* MID = middle byte of photomultiplier reading
\* NORMVOLT = PMT signal normalized for spectral response
\* NUMREAD = number of readings to take when monitoring PMT
\* OPERATORS$ = initials of person performing experiment
\* OPTIONS$ = used as menu input variable
\* Q$ = used as menu input variable
Automation Software for Laser Induced Fluorescence Tests - "TEST"

' READING = spectrometer wavelength (nm)
' READING(1000) = storage array for current READING
' READINT = reading interval for monitoring PMT
' SAMPLES = nature of sample under investigation (soil or aqueous solution)
' SAT = percent saturation of soil sample
' SATS = saturation status of soil sample (fully or partially saturated)
' SCANFLAG = flag (1) indicating last subinterval of scan
' SETUP = flag (1) indicating activation of data acquisition capability
' SOILTYPE$ = type of soil under investigation (sand, clay, etc.)
' SRNORM = spectral response normalizing value
' START(11) = array of scan interval starting points (nm)
' STOPFLAG = flag to indicate emergency shutdown of program
' STP(10) = array of scan interval stopping points
' TIMES = time of day that experiment is performed
' TRACEnC$ = counter to track floppy disk space
' VOLTS = voltage of data acquisition channel
' WAVELENGTH = user input wavelength
' WRTS = command variable for SR430 AND LeCroy 9362 communication
' G, H, I, J, K, L, X, Y = loop counters

********* CREATE PROGRAM ESCAPE USING F1 KEY *********

ON KEY(1) GOSUB EmergencyClose
KEY(1) ON

********* INITIALIZE VARIABLES *********

INITIAL = 0: READING = 0: SETUP = 0: TRACEnC = 0
REM DYNAMIC:INFO, READING
DIM START(11), STP(10), INTERVAL(10)
DIM INFO(1000, 2), READING(1000), NORMSTORE(20)

********* SETUP FIRST SCREEN *********

CLS: LOCATE 8, 18: COLOR 11
PRINT "LASER SPECTROSCOPY DATA ACQUISITION PROGRAM"
PRINT : PRINT
PRINT " " MIT GEOTECHNICAL LABORATORY"
PRINT : PRINT : PRINT
PRINT " " JOE SINFIELD COPYRIGHT 1996"
WATCH = TIMER

HoldScreen:
' Hold introductory message on screen for 5 seconds
IF TIMER < WATCH + 1 THEN GOTO HoldScreen

MainMenu:

' ******** CREATE OPENING MENU ********

COLOR 11: CLS : PRINT : PRINT : PRINT
PRINT " PICK AN OPTION FROM THE FOLLOWING MENU:"
COLOR 7
PRINT : PRINT " A > MOVE TO A SELECTED WAVELENGTH (nm)"
PRINT : PRINT " B > SCAN A WAVELENGTH RANGE (nm) AND MONITOR THE PMT"
PRINT : PRINT " C > SCAN A WAVELENGTH RANGE (nm) AND COUNT PHOTONS"
PRINT : PRINT " D > SCAN A WAVELENGTH RANGE (nm) AND COLLECT DECAY DATA"
PRINT : PRINT " E > MONITOR THE PMT"
PRINT : PRINT " F > SCAN, COUNT PHOTONS AND COLLECT FLUORESCENCE DECAY DATA"
PRINT : PRINT " G > QUIT"
COLOR 11: PRINT
INPUT "PLEASE ENTER YOUR CHOICE (e.g. A ): ". CHOICES

Choicelist:

IF CHOICES$ = "A" THEN GOSUB MoveSpec
IF CHOICES$ = "B" THEN GOSUB ScanMonitorPMT
IF CHOICES$ = "C" THEN GOSUB ScanCountPhotons
IF CHOICES$ = "D" THEN GOSUB ScanFluorescence
IF CHOICES$ = "E" THEN GOSUB MonitorPMT
IF CHOICES$ = "F" THEN GOSUB ScanCountFluorescence
IF CHOICES$ = "G" THEN GOSUB Quit

GOSUB Quit

MoveSpec:

' ******** SUBROUTINE TO MOVE TO A SELECTED WAVELENGTH ********

IF INITIAL = 0 THEN GOSUB Initialize ' setup communication w/ CM110
GOSUB Position ' determine current position

CLS
COLOR 11: LOCATE 6, 1
PRINT "YOU ARE CURRENTLY POSITIONED AT WAVELENGTH : 
COLOR 2: LOCATE 6, 45
PRINT USING "####.##": READING
LOCATE 6, 54: COLOR 11
PRINT "nm"

COLOR 11: LOCATE 8, 1
INPUT "ENTER A NEW WAVELENGTH POSITION IN NANOMETERS : ", WAVELENGTH

IF WAVELENGTH = READING THEN
COLOR 2: LOCATE 12, 1
INPUT "DO YOU WISH TO QUIT (Q) OR RETURN TO THE MAIN MENU (M)? ", OPTIONS
IF OPTIONS$ = "Q" THEN GOSUB Quit
IF OPTIONS$ = "M" THEN GOSUB MainMenu
END IF

GOSUB Move                    ' perform movement
GOSUB Menu                    ' menu options

IF ANS$ = "A" THEN CLS : GOSUB MoveSpec
IF ANS$ = "M" THEN GOSUB MainMenu
IF ANS$ = "Q" THEN GOTO Quit

ScanMonitorPMT:
'  ******** SUBROUTINE TO SCAN AND MONITOR PMT ********

GOSUB FileInfo                ' create data file
GOSUB DataAcqSetup            ' setup data acquisition
IF INITIAL = 0 THEN GOSUB Initialize ' setup communication w/ CM110
GOSUB Position                ' determine current position
GOSUB ScanParameters          ' enter scan intervals
IF Q$ = "N" THEN GOSUB ScanParameters ' on error try again
GOSUB Scan                    ' perform scan
GOSUB Menu                    ' menu options
IF ANS$ = "A" THEN GOTO Choicelist
IF ANS$ = "M" THEN GOTO MainMenu
IF ANS$ = "Q" THEN GOTO Quit
ScanCountPhotons:
‘ ******* SUBROUTINE TO SCAN AND COUNT PHOTONS *******
GOSUB FileInfo ‘ create data file
IF INITIAL = 0 THEN GOSUB Initialize ‘ setup communication w/ CM110
GOSUB Position ‘ determine current position
GOSUB ScanParameters ‘ enter scan parameters
IF Q$ = "N" THEN GOSUB ScanParameters ‘ on error try again
GOSUB Scan ‘ perform scan
GOSUB Menu ‘ menu options
IF ANS$ = "A" THEN GOTO Choicelist
IF ANS$ = "M" THEN GOTO MainMenu
IF ANS$ = "Q" THEN GOTO Quit

ScanFluorescence:
‘ ******* SUBROUTINE TO SCAN AND COLLECT FLUORESCENCE DATA *******
IF INITIAL = 0 THEN GOSUB Initialize ‘ setup communication w/ CM110
GOSUB Position ‘ determine current position
GOSUB ScanParameters ‘ enter scan parameters
IF Q$ = "N" THEN GOSUB ScanParameters ‘ on error try again
CLS
LOCATE 10, 4
INPUT "ENTER DELAY IN MINUTES BEFORE STARTING ACQUISITION: ". DELAY
CLS
LOCATE 10, 20
PRINT "WAITING FOR LASER POWER TO STABILIZE"

HOLD = TIMER + DELAY * 60
HOLDCNT = 0

DelayPeriod:
  HOLDCNT = HOLDCNT + 1
IF HOLDCNT / 10 = INT(HOLDCNT / 10) THEN
  LOCATE 12, 28
  TRACK = HOLD - TIMER
  PRINT "TEST WILL COMMENCE IN "
  LOCATE 14, 24
  COLOR 20
  PRINT USING "##": INT((TRACK) / 60);
  PRINT " MINUTE(S) AND ";
  PRINT USING "##": (TRACK) - (INT((TRACK) / 60) * 60);
  PRINT " SECONDS"
END IF

IF TIMER < HOLD THEN GOTO DelayPeriod

COLOR 2
GOSUB Scan                ' perform scan
GOSUB Menu                ' menu options

IF ANSS = "A" THEN GOTO Choicelist
IF ANSS = "M" THEN GOTO MainMenu
IF ANSS = "Q" THEN GOTO Quit

MonitorPMT:
' ********* SUBROUTINE TO MONITOR PMT *********

GOSUB FileInfo            ' subroutine to create data file

GOSUB DataAcqSetup        ' subroutine to setup data acquisition

IF INITIAL = 0 THEN GOSUB Initialize     ' setup communication w/ CM110

GOSUB Position            ' determine current position

' ~~~~ ENTER NUMBER AND TIMING OF READINGS ~~~~

CLS : LOCATE 8, 10
INPUT "HOW MANY READINGS WOULD YOU LIKE TO TAKE? ": NUMREAD
LOCATE 10, 10
INPUT "PLEASE ENTER THE READING INTERVAL IN SECONDS => ": READINT

FOR G = 1 TO NUMREAD
CLS : LOCATE 10, 5
PRINT " "; G; " OF "; NUMREAD; " READINGS COMPLETED AT "; READINT; " SECOND INTERVALS"
LOCATE 12, 30: PRINT "READING = "; VOLTS * -1; "Volts"

READTIME = TIMER

GOSUB ReadPMT  ' read PMT

ReadDelay:
IF TIMER < READTIME + READINT THEN GOTO ReadDelay

NEXT G

GOSUB EndAcqStore  ' end data acquisition/store results

GOSUB Menu  ' menu options subroutine

IF ANS$ = "A" THEN GOSUB MonitorPMT
IF ANS$ = "M" THEN GOSUB MainMenu
IF ANS$ = "Q" THEN GOSUB Quit

ScanCountFluorescence:
' ** SUROUTINE TO SCAN, COUNT PHOTONS, & COLLECT FLUORESCENCE DATA **

GOSUB FileInfo  ' create data file

IF INITIAL = 0 THEN GOSUB Initialize  ' setup communication w/ CM110

GOSUB Position  ' determine current position

GOSUB ScanParameters  ' enter scan parameters

IF Q$ = "N" THEN GOSUB ScanParameters  ' on error try again

GOSUB Scan  ' perform scan

GOSUB Menu  ' menu options

IF ANS$ = "A" THEN GOTO Choicelist
IF ANS$ = "M" THEN GOTO MainMenu
IF ANS$ = "Q" THEN GOTO Quit

Quit:
END
ScanParameters:
' ~~~~ PROVIDE USER INSTRUCTIONS FOR SCAN INTERVALS ~~~~~

CLS: LOCATE 2, 10: COLOR 2
PRINT "PLEASE ENTER THE SCAN PARAMETERS IN NANOMETERS (nm)"
COLOR 11: LOCATE 4, 16
PRINT "END BY ENTERING ZERO FOR ALL PARAMETERS"

' ~~~~ INITIALIZE SCAN PARAMETER STORAGE ARRAYS ~~~~~

C = 1: START(0) = 1: TRACECNT = 0
FOR X = 1 TO 10: START(X) = 1: STP(X) = 0: INTERVAL(X) = 0: NEXT X

' ~~~~ ENTER SCAN PARAMETERS ~~~~~

COLOR 2: LOCATE 14, 1: PRINT "START"
LOCATE 16, 1: PRINT "STOP"
LOCATE 18, 1: PRINT "INT"

WHILE START(C - 1) <> 0
COLOR 2: LOCATE 13, 10 * C: PRINT "--"
LOCATE 13, 2 + 10 * C: PRINT USING "##": C
LOCATE 13, 4 + 10 * C: PRINT "--"
COLOR 11: LOCATE 14, 10 * C: INPUT "", START(C)
LOCATE 16, 10 * C: INPUT "", STP(C)
LOCATE 18, 10 * C: INPUT "", INTERVAL(C)
C = C + 1
WEND

' ~~~~ DISPLAY INPUT SCAN PARAMETERS ~~~~~

CLS
COLOR 2: LOCATE 8, 10: PRINT "ARE YOU SURE ABOUT THESE PARAMETERS?"
COLOR 2: LOCATE 14, 1: PRINT "START"
LOCATE 16, 1: PRINT "STOP"
LOCATE 18, 1: PRINT "INT"

FOR Y = 1 TO C - 2
COLOR 2: LOCATE 13, 10 * Y: PRINT "--"

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LOCATE 13, 2 + 10 * Y: PRINT USING "##": Y
LOCATE 13, 4 + 10 * Y: PRINT "---"
COLOR 11: LOCATE 14, 10 * Y: PRINT USING "####.##": START(Y)
LOCATE 16, 10 * Y: PRINT USING "####.##": STP(Y)
LOCATE 18, 10 * Y: PRINT USING "####.##": INTERVAL(Y)
NEXT Y

' ~~~~~ CONFIRM INPUT SCAN PARAMETERS ~~~~~

COLOR 2: LOCATE 20, 10: INPUT "PLEASE ANSWER YES (Y) OR NO (N)", Q$

RETURN

Scan:

' ******** EXECUTE INTERVAL SCANS ********

FOR K = 1 TO C - 2

IF START(K) <= READING THEN ' move to round start position
WAVELNTH = START(K)
GOSUB Move
CLS
END IF

LOCATE 10, 20
PRINT "Monochromator Position = ". WAVELNTH: " nm"

' take initial reading

IF CHOICE$ = "B" THEN GOSUB ReadPMT
IF CHOICE$ = "C" OR CHOICE$ = "F" THEN GOSUB CountPhotons
IF CHOICE$ = "D" OR CHOICE$ = "F" THEN GOSUB FluorescenceDecay

IF STP(K) < START(K) THEN INTERVAL(K) = -INTERVAL(K)

' perform scans in intervals

FOR ROUND = 1 TO ABS((STP(K) - START(K)) / INTERVAL(K))
WAVELNTH = WAVELNTH + INTERVAL(K)
READING = WAVELNTH
GOSUB Move

LOCATE 10, 20
PRINT "Monochromator Position = ", WAVELNTH: " nm"

' take data readings

IF CHOICE$ = "B" THEN GOSUB ReadPMT
IF CHOICE$ = "C" OR CHOICE$ = "F" THEN GOSUB CountPhotons
IF CHOICE$ = "D" OR CHOICE$ = "F" THEN GOSUB FluorescenceDecay

NEXT ROUND

NEXT K

RETURN

ReadPMT:
' ********** SUBROUTINE TO READ PMT **********

INFO = INFO + 1
M = 0
OUT 776, M
OUT 768, INTTIME: WAIT 768. 1, 1
OUT 776, 15

' select the multiplexer channel for PMT
' perform conversion
' ground the input to the AD1170

LO = INP(768 + 1); MID = INP(768 + 2); HI = INP(768 + 3)
BITS = LO + 256 * MID + 65536 * HI
VOLTS = (BITS * 10 / 2 ^ (INTBIT + 7) - 5) * 1000

' read three data bytes - lo. mid. hi
' total number of bits
' convert to volts

' ********** ADJUST PMT SIGNAL FOR SPECTRAL RESPONSE **********

' The PMT spectral response curve is approximated by a 7th order
' polynomial of the form \( y = ax^7 + bx^6 + \ldots + gx + h \) where \( y \) (CFY)
' becomes a normalizing factor and \( x \) (CFX) = wavelength/100. The
' curve is log (response) - linear (wavelength) in nature.

CFX = WAVELNTH / 100
ADJVOLTS = VOLTS

' divide by 100 for curve fit
' adjust PMT readings for background
' constants for spectral response curve fit

CFA = -.0027364; CFB = .080532; CFC = -.986568; CFD = 6.499194
CFE = -24.78267; CFF = 54.32861; CFG = -62.3136; CFH = 28.81784
7th order polynomial spectral response curve fit

\[ CFY = CFA \times CFX^7 + CFB \times CFX^6 + CFC \times CFX^5 + CFD \times CFX^4 + CFE \times CFX^3 + CFF \times CFX^2 + CFG \times CFX + CFH \]

SRNORM = 10^7 CFY  \quad \text{\textsuperscript*}{\text{logarithmic curve fit therefore take antilog}}
NORMVOLT = ADJVOLTS / SRNORM  \quad \text{\textsuperscript*}{\text{PMT signal adjusted for spectral response}}
INFO(INFO, M) = VOLTS  \quad \text{\textsuperscript*}{\text{store normalized PMT signal}}
READING(INFO) = WAVELNTH
PRINT #5, READING(INFO), INFO(INFO, 0)
RETURN

EndAcqStore:

\text{******* SUBROUTINE TO END DATA ACQUISITION AND STORE RESULTS *******}

OUT 768, 176: WAIT 768, 1, 1 \quad \text{\textsuperscript*}{\text{re-enable background calibration}}
CLOSE #5
RETURN

Menu:

\text{******* SUBROUTINE FOR MENU OPTIONS *******}

BEEP: BEEP: BEEP
CLS
COLOR 7: LOCATE 10, 15: PRINT "WOULD YOU LIKE TO PERFORM THIS MENU OPTION AGAIN ... < A >"
LOCATE 12, 15: PRINT "RETURN TO THE MAIN MENU ......................... < M >"
LOCATE 14, 15: PRINT "OR QUIT ? .................................... < Q >"
PRINT : LOCATE 16, 10: COLOR 11: INPUT "PLEASE MAKE A SELECTION NOW. ". ANSS:
CLS
RETURN

FileInfo:

\text{******* SUBROUTINE TO INPUT DATA FILE INFORMATION *******}

INFO = 0 \quad \text{\textsuperscript*}{\text{initialize results storage counter}}

CLS : LOCATE 4, 1
INPUT "PLEASE ENTER A DATA STORAGE FILENAME FOR THIS TEST ". FILENAME$ FILENAME$ = FILENAME$ + ".RES"
OPEN FILENAMES$ FOR APPEND AS #5

LOCATE 6. 1
INPUT "PLEASE ENTER YOUR INITIALS ", OPERATORS$

LOCATE 8. 1
INPUT "WHAT TYPE OF SAMPLE ARE YOU TESTING? AQUEOUS SOLUTION (A) OR SOIL (S) ". SAMPLES$

IF SAMPLES$ <> "A" THEN

IF SAMPLES$ = "S" THEN LOCATE 9. 5: INPUT "IS THE SOIL FULLY SATURATED (F) OR PARTIALLY SATURATED (P) ? ", SATS$
IF SATS$ = "P" THEN LOCATE 10. 5: INPUT "WHAT IS THE PERCENT SATURATION? ". SAT
ELSE SAT = 100
IF SAMPLES$ = "S" THEN LOCATE 11. 5: INPUT "WHAT TYPE OF SOIL IS IT? ". SOILTYPE$
ELSE

LOCATE 14. 1: INPUT "WHAT CHEMICAL IS BEING INVESTIGATED? ". CHEMS$
LOCATE 16. 1: INPUT "WHAT IS THE CONCENTRATION? ". CONCS$
END IF

IF SAMPLES$ = "A" THEN SAMPLES$ = "AQUEOUS SOLUTION" ELSE SAMPLES$ = "SOIL SAMPLE"
IF SATS$ = "P" THEN SATS$ = "PARTIALLY SATURATED" ELSE SATS$ = "FULLY SATURATED"

WRITE #5. FILENAMES$, OPERATORS$, DATE$, TIMES$
IF SAMPLES$ = "SOIL SAMPLE" THEN WRITE #5. SOILTYPE$. SAMPLES$. SATS$. SAT. "% SATURATION"
IF SAMPLES$ = "AQUEOUS SOLUTION" THEN WRITE #5. SAMPLES$
WRITE #5. CHEMS$. "CONCENTRATION = ". CONCS$

RETURN

DataAcqSetup:
' ********** SUBROUTINE TO SETUP DATA ACQUISITION CAPABILITY **********

IF SETUP = 1 THEN RETURN

' 768 = decimal I/O address of AD1170 A/D converter
' 776 = decimal I/O address of multiplexer channel selector
' 15 = multiplexer connection to ground
INTTIME = 22
INTBIT = 15
OUT 768, 60: WAIT 768, 1, 1
OUT 768+1, INTBIT
OUT 768, 48: WAIT 768, 1, 1
OUT 768, 176: WAIT 768, 1, 1
OUT 776, 15
OUT 768, 184: WAIT 768, 1, 1
SETUP = 1
RETURN

' integration time of A/D converter
' bit precision
' set default calibration time
' load data format into 2nd byte
' lock in the loaded data format
' begin background calibration
' set input to AD1170 ground
' disable background calibration
' flag - setup complete

CountPhotons:

' ********** SUBROUTINE TO COUNT PHOTONS **********

INFO = INFO + 1

IF INFO = 1 THEN
OPEN "COM2:9600,N,8,2" FOR RANDOM AS #2' open com line

WRT$ = "OUTP 0"
PRINT #2, WRT$
END IF

WRT$ = "CLRS"
PRINT #2, WRT$

WRT$ = "SSCN"
PRINT #2, WRT$

' direct SR430 output to RS232 port
' reset data memory
' start scan with next trigger
' read serial poll status byte
' check if scan is complete

CheckStatus:

WRT$ = "*STB?"
PRINT #2, WRT$
FOR I = 1 TO 350000: NEXT I
INPUT #2, SP%
IF SP% MOD 2 = 0 THEN GOTO CheckStatus

WRT$ = "AUTS"
PRINT #2, WRT$

PRINT #2, "BINA?", 7
INPUT #2, BIN1
PRINT #2, "BINA?", 8
INPUT #2, BIN2
PRINT #2, "BINA?", 9

' autoscale SR430 display
' obtain count in bins
Automation Software for Laser Induced Fluorescence Tests - “TEST”

```
INPUT #2, B1N3
PRINT #2, "BINA?": 10
INPUT #2, B1N4
PRINT #2, "BINA?": 11
INPUT #2, B1N5
PRINT #2, "BINA?": 12
INPUT #2, B1N6

INFO(INFO, 0) = B1N1 + B1N2 + B1N3 + B1N4 + B1N5 + B1N6
READING(INFO) = READING
WRITE #5, READING(INFO), INFO(INFO, 0)
RETURN

EndCount:
   · · · · · · · · SUBROUTINE TO END COUNTING AND CLOSE RESULTS FILE · · · · · · · ·

   CLOSE #5
   RETURN

EmergencyClose:
   · · · · · · · · SUBROUTINE TO CLOSE FILES PRIOR TO EMERGENCY SHUTDOWN · · · · · · · ·

   IF CHOICE$ = "C" THEN GOSUB EndAcqStore  · · end acq. / store pmnt data
   IF CHOICE$ = "D" OR CHOICE$ = "F" THEN GOSUB EndCount  · · store counting data
   GOTO Quit

FluorescenceDecay:
   · · · · · · · · SUBROUTINE TO COLLECT FLUORESCENCE DECAY DATA · · · · · · · ·

   TRACECNT = TRACECNT + 1
   IF TRACECNT = 120 THEN GOSUB FloppyChange

   IF TRACECNT = 1 THEN
      SHELL "MODE COM3:96,N.8.2"
      CLS : LOCATE 10, 20
      PRINT "Monochromator Position = ", WAVELNTH: " nm"
   END IF
      · set scope to remote mode
   OUT 1000, 27  · ESC
   FOR D = 1 TO 500: NEXT D
```

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OUT 1000, 82  ' R
FOR D = 1 TO 500: NEXT D
END IF

FOR Q = 1 TO 2  ' clear sweep counter
  OUT 1000, 67  ' C
  FOR D = 1 TO 500: NEXT D
  OUT 1000, 76  ' L
  FOR D = 1 TO 500: NEXT D
  OUT 1000, 83  ' S
  FOR D = 1 TO 500: NEXT D
  OUT 1000, 87  ' W
  FOR D = 1 TO 500: NEXT D
  OUT 1000, 13  ' Carriage Return
  NEXT Q
FOR D = 1 TO 500: NEXT D

DELAY = TIMER + 20  ' time to take sweeps

Tracewait:
  IF DELAY > TIMER THEN GOTO Tracewait

  OUT 1000, 27  ' Clear command buffer
  ' ESC
  FOR D = 1 TO 500: NEXT D
  OUT 1000, 67  ' C

  OUT 1000, 83  ' store average trace to floppy
  ' S
  FOR D = 1 TO 500: NEXT D
  OUT 1000, 84  ' T
  FOR D = 1 TO 500: NEXT D
  OUT 1000, 79  ' O
  FOR D = 1 TO 500: NEXT D
  OUT 1000, 13  ' Carriage return

RETURN

FloppyChange:
  ' ********** SUBROUTINE TO PERMIT FLOPPY REPLACEMENT **********

CLS
COLOR 11: LOCATE 8, 20
PRINT "THE DISK IN THE OSCILLOSCOPE IS FULL"
LOCATE 10, 20: PRINT "PLEASE INSERT A NEW DISK OR QUIT"
LOCATE 12, 20: INPUT "ENTER YOUR CHOICE 'NEW' OR 'Q' (QUIT)", ANS$
IF ANS$ = "Q" THEN GOSUB Quit ELSE RETURN

Initialize:

' initialize communication with CM110 Spectrometer

IF INITIAL = 1 THEN RETURN
OPEN "COM1:9600, N, 8, 1, CS10000, DSO" FOR RANDOM AS #1
TRASH$ = INPUT$(LOC(1), #1)
WAIT &H3FE, 16, 0
INITIAL = 1
RETURN

MessageWait:

' wait for STATUS and CANCEL messages from CM110

IF LOC(1) <> 0 THEN GOTO MessageReceive
IF TIMER < WAITTIME THEN GOTO MessageWait
RETURN

MessageReceive:

' input message string from CM110

MESSAGES$ = "" ' clear message string
MESSAGES$ = INPUT$(1, #1) ' input message &

' NOTE: We could look at the message here but we don't need it.
' We are only trying to keep the input buffer clear.

RETURN

Position:

' QUERY position status of CM110 - output position as READING

TRASH$ = INPUT$(LOC(1), #1)
WAIT &H3FE, 16, 0
' wait for CTS to go low
PRINT #1, CHR$(56):  ' send QUERY command <56>
WAIT &H3FE, 16, 0  ' wait for CTS to go low
PRINT #1, CHR$(0):  ' send QUERY byte - Postion
POSITIONTIME = TIMER + 10  
GOSUB PositionWait
WAITTIME = TIMER + 20  
GOSUB MessageWait
WAITTIME = TIMER + 60  
GOSUB MessageWait
RETURN

PositionWait:

  ' wait for postion bytes from CM110

  IF LOC(1) >= 2 THEN GOTO PositionReceive
  IF TIMER < POSITIONTIME THEN GOTO PositionWait
  RETURN

PositionReceive:

  ' input position bytes from CM110 and output READING

  Position$ = ""  ' clear position string
  Position$ = INPUT$(2, #1)
  HIBYTE = ASC(MID$(Position$, 1, 1))
  LOBYTE = ASC(MID$(Position$, 2, 1))
  Position = LOBYTE + 256 * HIBYTE  ' Angstroms
  READING = Position / 10  ' Nanometers
  WAVELNTH = READING
  RETURN

Move:

  ' rotate CM110 grating to transmit selected wavelength

  TRASH$ = INPUT$(LOC(1), #1)
  WAIT &H3FE, 16, 0  ' wait for CTS to go low
PRINT #1, CHR$(16);       ' send GOTO command <16>
WAIT &H3FE. 16. 0        ' wait for CTS to go low
                      ' calculate bytes to send
HIGHBYTE = INT((WAVELNTH * 10) / 256)
LOWBYTE = INT((WAVELNTH * 10) - 256 * HIGHBYTE)
PRINT #1, CHR$(HIGHBYTE);   ' send HIGHBYTE
WAIT &H3FE. 16. 0        ' wait for CTS to go low
PRINT #1, CHR$(LOWBYTE);    ' send LOWBYTE
WAITTIME = TIMER + 20     ' wait and input status byte
GOSUB MessageWait
WAITTIME = TIMER + 600    ' allow movement, input cancel
GOSUB MessageWait
RETURN
Appendix C

DATA REDUCTION PROGRAM FOR LASER INDUCED FLUORESCENCE TESTS
'DATE 10/9/96:  JOE SINFIELD
' 3/1/97  Revised for advanced parsing
'4/15/97  Revised for baseline and noise criterion

PROGRAM$ = "DATA.BAS"

'This program is used to combine data files acquired using
'the LeCroy 9362 High Speed Oscilloscope. The files are
'imported individually and then combined to form one file
'formatted for three dimensional wavelength-time matrix
'plots.

' COPYRIGHT JOE SINFIELD, OCTOBER 1996

CLS
COLOR 3: LOCATE 8, 18
PRINT "THIS PROGRAM COMBINES OUTPUT DATA FILES FROM"
PRINT : LOCATE 10, 18
PRINT " THE LeCroy 9362 OSCILLOSCOPE"
FOR T = 1 TO 100000: NEXT T

CLS
LOCATE 8, 1
PRINT "IF YOUR DATA FILES ARE NOT IN THE DIRECTORY b:\lecroy_1.dir\"
LOCATE 9, 1
INPUT "THEN ENTER 'N' FOR NO; (DEFAULT = 'enter') :", ASK$

IF ASK$ = "N" THEN
  CLS
  LOCATE 10, 1
  INPUT "ENTER THE PATH NAME FOR YOUR DATA FILES (e.g. => A:\): ", PATH$
  ELSE
    PATH$ = "b:\lecroy_1.dir"
END IF

' Note: Data file names are assumed to be of the form STA???.TXT

FileInfo:

  CLS : LOCATE 10, 15
  INPUT "WHAT IS THE FIRST FILE NUMBER: ", STARTNUM
  LOCATE 12, 15
  INPUT "WHAT IS THE LAST FILE NUMBER: ", LASTNUM
  LOCATE 14, 15
  INPUT "ENTER THE STARTING WAVELENGTH (nm): ", WAVE
  LOCATE 16, 15
  INPUT "ENTER THE WAVELENGTH INCREMENT (nm): ", INC
'********* DIMENSION ARRAYS AND INITIALIZE VARIABLES *********

REM $DYNAMIC: TIM, AMPL, TEMPS, NORM, BOUND
DIM file$(254), T$(12), TIM(254), AMPL(254, 42), TEMPS(254)
DIM EW(150), BCKGRND(254, 42), PEAK(42), NORM(254, 42), BOUND(42, 3)
DIM VOLFLAG(42)

CreateFileNameArray:
FOR a = STARTNUM TO LASTNUM
   B = LEN(STRS(a)) - 1
   a$ = MIDS(STRS(a), 2, B)
   IF a < 10 THEN file$(a) = PATH$ + "STA00" + a$ + ".TXT"
   IF a > 9 AND a < 100 THEN file$(a) = PATH$ + "STA0" + a$ + ".TXT"
   IF a > 99 THEN file$(a) = PATH$ + "STA" + a$ + ".TXT"
NEXT a

CLS

ImportDataFiles:
FILECNT = 0
FOR file = STARTNUM TO LASTNUM

CLS : LOCATE 12, 2
PRINT "CURRENTLY PROCESSING DATA FOR FILE => ", file$(file)

OPEN file$(file) FOR INPUT AS #1

FILECNT = FILECNT + 1

RemoveHeader:
FOR C = 1 TO 10
   INPUT #1, TEXT$(C)
NEXT C

ConvertFirstTime:
IF FILECNT > 1 THEN GOTO ImportDataStrings
FIRST$ = MIDS(TEXT$(10), 5)
TIM(1) = VAL(FIRST$)

ImportDataStrings:
COUNT = 0
FOR K = 1 TO 600
   IF EOF(1) THEN GOTO FinalAmpConversion
   COUNT = COUNT + 1
   INPUT #1, TEMPS(K)
NEXT K

FinalAmpConversion:
AMPL(COUNT, FILECNT) = VAL(TEMPS(COUNT))  ' convert last AMPL value
ParseStrings:
 FOR STR = 1 TO COUNT - 1

 POINTCNT = 0
 LENGTH = LEN(TEMP$(STR))
 FOR L = 1 TO LENGTH
   CHECKS = MIDS(TEMP$(STR), L, 1)
   IF CHECKS = CHR$(46) THEN
     POINTCNT = POINTCNT + 1
     PNTHLDR = L
   END IF
   IF POINTCNT = 2 THEN
     EPOS(1) = L
     GOTO NegativeCheck
   END IF
 NEXT L

FindExponential:
 ECNT = 0
 LENGTH = LEN(TEMP$(STR))
 FOR L = 1 TO LENGTH
   CHECKS = MIDS(TEMP$(STR), L, 1)
   IF CHECKS = CHR$(101) THEN
     ECNT = ECNT + 1
     EPOS(ECNT) = L
   END IF
   IF ECNT = 2 THEN GOTO SplitEs
 NEXT L

NegativeCheck:
 NEGCHECKS = MIDS(TEMP$(STR), EPOS(1) - 2, 1)
 IF POINTCNT = 1 AND PNTHLDR = 3 THEN
     LBND = 2
     GOTO RecoverAmp
 END IF
 IF NEGCHECKS = CHR$(45) THEN LBND = (EPOS(1) - 2) ELSE LBND = (EPOS(1) * 1)
 GOTO RecoverAmp

SplitEs:
 ' divide strings including more than one number written in scientific notation
 NEGCHECK2$ = MIDS(TEMP$(STR), EPOS(2) - 2, 1)
 IF NEGCHECK2$ = CHR$(45) THEN LBND = EPOS(2) - 2 ELSE LBND = EPOS(2) - 1
 GOTO RecoverAmp

RecoverAmp:
 ' transform AMPL portion of string into a number
 L1 = LBND - 1
 L2 = LENGTH - LBND + 1
 AMPL(STR, FILECNT) = VAL(MIDS(TEMP$(STR), 1, L1))
 IF FILECNT > 1 THEN GOTO NextString
Data Reduction Program for Laser Induced Fluorescence Tests - “DATA”

TIM(STR + 1) = VAL(MID$(TEMP$(STR), LBND, L2))

NextString:
    NEXT STR

CLOSE #1

NEXT file

ImportBackground:
    ' import background data
CLS : LOCATE 10, 10: INPUT "Please enter the background filename (NO EXTENSION): ", BACK$
BACKFILES$ = "C:\QB45\" + BACK$ + ".CSV"
OPEN BACKFILES FOR INPUT AS #2
FOR R = 1 TO COUNT
    FOR C = 1 TO 39
        INPUT #2, BCKGRND(R, C)
    NEXT C
NEXT R

' wavelength range covered in test is:
    ' Start at: WAVE
    ' Finish at: WAVE + INC*(INT(LASTNUM-STARTNUM))
    ' Background data goes from 274 nm to 350 nm in 2 nm increments
    ' therefore the data column corresponds to wavelength/2 - 136

SignalAdjust:
    WAVECNT = 0
    X = WAVE - INC.
    FOR W = 1 TO (INT(LASTNUM - STARTNUM) + 1)
        X = X + INC
        BACKCOL = X / 2 - 136
        WAVECNT = WAVECNT + 1
    FOR TIMECNT = 1 TO COUNT STEP 1
        ' TIMECNT corresponds to row of data in background matrix
        CFX = X / 100
        CFA = -.0027364; CFB = .080532; CFC = -.986568; CFD = 6.499194
        CFE = -24.78267; CFF = 54.32861; CFG = -62.3136; CFH = 28.81784
        CFY = CFA * CFX ^ 7 + CFB * CFX ^ 6 + CFC * CFX ^ 5 + CFD * CFX ^ 4 + CFE * CFX ^ 3 + CFF
        * CFX ^ 2 + CFG * CFX + CFH
        SRNORM = 10 ^ CFY
        AMPL(TIMECNT, WAVECNT) = -1 * (AMPL(TIMECNT, WAVECNT) - BCKGRND(TIMECNT, BACKCOL)) / SRNORM

TimeAdjust:
    IF W = 1 THEN TIM(TIMECNT) = ((TIM(TIMECNT) - 5.49E-08) / 1E-09)
NEXT TIMECNT

' IF PEAK(WAVECNT) > WTIPEAK THEN WTIPEAK = PEAK(WAVECNT)

NEXT W

FindBaseline:
WTIPEAK = 0

FOR W = 1 TO (INT(LASTNUM - STARTNUM) + 1)
PEAK(W) = 0

BLINE = 0
FOR J = 1 TO 15
BLINE = BLINE + AMPL(J, W)
NEXT J
BLINEAVG = BLINE / 15
FOR T = 1 TO COUNT
AMPL(T, W) = AMPL(T, W) - BLINEAVG
IF AMPL(T, W) > PEAK(W) THEN PEAK(W) = AMPL(T, W)
NEXT T
IF PEAK(W) > WTIPEAK THEN WTIPEAK = PEAK(W)
NEXT W

'We now have a 3-D array of data that includes time, normalized
'intensity and wavelength measurements
'.
'There are 1 TO (INT(LASTNUM - STARTNUM) + 1) wavelengths
'Times are stored in the array TIM(time count)
'Amplitudes are stored in the array AMPL(time count, wave count)

StoreData:
CLS : LOCATE 12, 20
PRINT "ENTER A FILENAME FOR DATA STORAGE (INCLUDE PATH BUT NO EXTENSION): "
LOCATE 14, 20: INPUT STOR$ 

Boundaries:
FOR W4 = 1 TO (INT(LASTNUM - STARTNUM) + 1)
   BOUND(W4, 1) = 0; BOUND(W4, 2) = 0; BOUND(W4, 3) = 0
NEXT W4

MLTPLR = 1.645
Sigma = .0000063
CONFNDC = MLTPLR * Sigma
FOR W2 = 1 TO (INT(LASTNUM - STARTNUM) + 1)
   PEAKV = 0
   FOR T2 = 30 TO 60
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IF AMPL(T2, W2) > PEAKV THEN
    PEAKV = AMPL(T2, W2)
    BOUND(W2, 2) = T2
END IF
NEXT T2

IF PEAKV >= CONFDNC THEN VOLFLAG(W2) = 1 ELSE VOLFLAG(W2) = 0

NEXT W2

FOR W3 = 1 TO (INT(LASTNUM - STARTNUM) + 1)
    IF VOLFLAG(W3) = 0 THEN GOTO NewWave

LowerBound:
    FOR TL = BOUND(W3, 2) TO 1 STEP -1
        IF AMPL(TL, W3) < CONFDNC THEN
            BOUND(W3, 1) = TL + 1
        GOTO UpperBound
    END IF
    NEXT TL

UpperBound:
    FOR TU = BOUND(W3, 2) TO COUNT
        IF AMPL(TU, W3) < CONFDNC THEN
            BOUND(W3, 3) = TU - 1
        GOTO NewWave
    END IF
    NEXT TU
    BOUND(W3, 3) = COUNT

NewWave:
    NEXT W3

Integrate:
' calculate the area under each intensity time trace (trapezoidal rule)
' noise criterion => ignore below 1.645 Sigma (90% confidence)
' therefore ignore below 1.645*(6.3e-6) = ~ 1e-5

EWMAX = 0
FOR WCNT = 1 TO (INT(LASTNUM - STARTNUM) + 1)
    TAREA = 0
    IF VOLFLAG(WCNT) = 0 OR (BOUND(WCNT, 3) - BOUND(WCNT, 1)) < 3 THEN
        EW(WCNT) = 0
    GOTO NewWave2
    END IF
    FOR TCNT = BOUND(WCNT, 1) + 1 TO BOUND(WCNT, 3)
AMP1 = AMPL(TCNT - 1), WCNT
AMP2 = AMPL(TCNT, WCNT)
INCAMP = (AMP1 + AMP2) / 2
INCTIME = TIM(TCNT) - TIM(TCNT - 1)
INCAREA = INCAMP * INCTIME
TAREA = TAREA + INCAREA
NEXT TCNT
EW(WCNT) = TAREA

NewWave2:
  ' find wavelength at which we have the maximum amplitude of EW curve
WVL = WAVE - INC + INC * WCNT
IF WVL >= 280 AND EW(WCNT) > EWMAX THEN
  EWMAX = EW(WCNT)
  MAXHLDR = WCNT
END IF

NEXT WCNT

Lifetime:
  'normalize decay curves for lifetime calculations
NORMCNT = 0
FOR LFTWCNT = 1 TO (INT(LASTNUM - STARTNUM) + 1)
  IF PEAK(LFTWCNT) >= .5 * WTIPEAK THEN
    NORMCNT = NORMCNT + 1
    GOSUB Normalize
  END IF
NEXT LFTWCNT
GOTO LFTStore

Normalize:
  'this routine normalizes the intensity-time trace to a peak of unity and
  'positions the peak at a particular storage location
MAXAMP = 0
FOR LFTCNT = 1 TO COUNT
  IF AMPL(LFTCNT, LFTWCNT) > MAXAMP THEN
    MAXAMP = AMPL(LFTCNT, LFTWCNT)
    TIMHLDR = LFTCNT
  END IF
NEXT LFTCNT

SHIFT = 40 - TIMHLDR
IF SHIFT > 0 THEN GOTO Greater:
IF SHIFT = 0 THEN GOTO Equal:
IF SHIFT < 0 THEN GOTO Less:

Greater:
FOR SCI = 1 TO SHIFT
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NORM(SC1, NORMCNT) = 0
NEXT SC1
FOR SC2 = SHIFT + 1 TO COUNT
    NORM(SC2, NORMCNT) = AMPL(SC2 - SHIFT, LFTWCNT) / MAXAMP
NEXT SC2
RETURN

Equal:
FOR SC3 = 1 TO COUNT
    NORM(SC3, NORMCNT) = AMPL(SC3, LFTWCNT) / MAXAMP
NEXT SC3
RETURN

Less:
FOR SC4 = 1 TO COUNT + SHIFT
    NORM(SC4, NORMCNT) = AMPL(SC4 - SHIFT, LFTWCNT) / MAXAMP
NEXT SC4
FOR SC5 = COUNT + SHIFT + 1 TO COUNT
    NORM(SC5, NORMCNT) = 0
NEXT SC5
RETURN

LFTStore:
    'store fluorescence decay curve at wavelength of maximum amplitude
LFT$ = STOR$ + "L.T.DAT"
OPEN LFT$ FOR OUTPUT AS #1
FOR TCNT2 = 1 TO COUNT
    FOR ITCOL = 1 TO NORMCNT
        IF ITCOL = 1 THEN PRINT #1, TIM(TCNT2);
        IF ITCOL = NORMCNT THEN PRINT #1, NORM(TCNT2, ITCOL)
        IF ITCOL > 1 AND ITCOL < NORMCNT THEN PRINT #1, NORM(TCNT2, ITCOL);
    NEXT ITCOL
NEXT TCNT2
CLOSE #1

    'store boundary of integration zone
BNDS = STOR$ + "BD.DAT"
OPEN BNDS FOR OUTPUT AS #1
FOR XX = 1 TO 39
    PRINT #1, BOUND(XX. 1), BOUND(XX, 2), BOUND(XX, 3)
NEXT XX
CLOSE #1

Concentration:
    'calculate the area/volume under the WTI (trapezoidal rule)
VOLUME = 0
FOR WCNT = 2 TO (INT(LASTNUM - STARTNUM) + 1)
    INCEW = (EW(WCNT - 1) ÷ EW(WCNT)) / 2
    INCVOL = INCEW * INC

VOLUME = VOLUME + INCVOL
NEXT WCNT

EWStore:
' store emission wavelength data
EW$ = STORS + "EW.DAT"
OPEN EW$ FOR OUTPUT AS #1
PRINT #1, "CONCENTRATION INDICATOR: ", VOLUME
PRINT #1, "WAVELENGTH OF MAXIMUM EMISSION: ", WAVE - INC + INC * MAXHLD
PRINT #1, "THE PEAK OF THE WTI PROFILE IS: ", WTIPK, "(a.u.)"
FOR WCNT = 1 TO (INT(LASTNUM - STARTNUM) + 1)
   PRINT #1, (WAVE - INC + INC * WCNT), EW(WCNT)
NEXT WCNT
CLOSE #1

CLS
LOCATE 10, 20
PRINT "CONCENTRATION INDICATOR: "; VOLUME; " a.u."
LOCATE 12, 20
PRINT "MAXIMUM EMISSION AT "; WAVE - INC + INC * MAXHLD; " nm"
LOCATE 14, 20
PRINT "MAXIMUM AMPLITUDE: "; WTIPK; " a.u."
PRINT : LOCATE 16, 17
INPUT "PRESS ENTER TO CONTINUE", READYS

StoreLimitedData:
WTIS = STORS + ".DAT"
OPEN WTIS FOR OUTPUT AS #1

' This section arranges data in a file in the following way
'
'     Time Wavelength Intensity(w1) Intensity(w2) ....
'     T1 W1 I(w1)@T1 I(w2)@T2
'     T2 W2 I(w1)@T2 I(w2)@T2
'     etc etc etc etc etc

TIMECNT2 = -4: SKIPTIME = 5: WAVELENGTH = WAVE - INC: WNDW = 3
COUNTWAVE = 0: SKIPWAVE = 1

' SKIPTIME and SKIPWAVE determine data skipped in output file
' WNDW determines averaging window +/- WNDW

ROWMAX = INT(COUNT / SKIPTIME) + 1
WAVEMAX = INT((LASTNUM - STARTNUM) / SKIPWAVE) + 1
FOR DATAROW = 1 TO ROWMAX
   TIMECNT2 = TIMECNT2 + SKIPTIME
   COUNTWAVE = COUNTWAVE + 1
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IF COUNTWAVE <= WAVEMAX THEN WAVELENGTH = WAVELENGTH + SKIPWAVE * INC ELSE WAVELENGTH = 0

FOR DATACOL = 1 TO (WAVEMAX + 2) ' time is zeroed and converted to ns

IF DATACOL = 1 THEN PRINT #1, TIM(TIMECNT2); ((TIM(TIMECNT2) - 5E-08) / 1E-09);
IF DATACOL = 2 THEN PRINT #1, WAVELENGTH;
IF DATACOL < 3 THEN GOTO NextColumn

IF TIMECNT2 < (WNDW + 1) THEN
   AMPAVG = AMPL(TIMECNT2, DATACOL - 2)
   GOTO WriteIntensity
END IF

IF TIMECNT2 > (COUNT - WNDW) THEN
   AMPAVG = AMPL(TIMECNT2, DATACOL - 2)
   GOTO WriteIntensity
END IF

IF WNDW = 0 THEN
   AMPAVG = AMPL(TIMECNT2, DATACOL - 2)
   GOTO WriteIntensity
END IF

AMPAVG = 0
FOR WNDW = (-1 * WNDW) TO WNDW
   AMPAVG = AMPAVG + AMPL((TIMECNT2 + WNDW), (DATACOL - 2))
NEXT WNDW
AMPAVC = (AMPAVG / (2 * WNDW + 1))

WriteIntensity:
   IF DATACOL = (WAVEMAX + 2) THEN PRINT #1, AMPAVG ELSE PRINT #1, AMPAVG;

NextColumn:
   NEXT DATACOL

NEXT DATAROW

IF WAVEMAX > ROWMAX THEN
   WAVEPRINT = WAVE + (ROWMAX - 1) * INC * SKIPWAVE
   FOR EXTRAWAVE = (ROWMAX + 1) TO WAVEMAX
      WAVEPRINT = WAVEPRINT + INC * SKIPWAVE
   NEXT EXTRAWAVE
   PRINT #1, 0, WAVEPRINT
   NEXT EXTRAWAVE
END IF

CLOSE #1

END
Appendix D

RESULTS OF LASER INDUCED FLUORESCENCE TESTS PERFORMED ON SINGLE - COMPOUND AQUEOUS SOLUTIONS
**Test Name:** BEQa  
**Contaminant:** Benzene  
**Concentration:** 1780 ppm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.033 a.u.
- **Maximum Emission**
  - **Intensity:** $3.48 \times 10^{-4}$ a.u.
  - **Wavelength:** 292 nm
- **Lifetime:** 2.7 ns

**Intensity Contour Plot**

- **Contour Spacing:** $4.0 \times 10^{-5}$ a.u.
- **Contour Origin:** $4.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: BEQb

Contaminant: Benzene
Concentration: 1780 ppm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.030 a.u.
Maximum Emission
Intensity: $3.01 \times 10^{-4}$ a.u.
Wavelength: 290 nm
Lifetime: 2.8 ns

☐ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: BEQc

Contaminant: Benzene
Concentration: 1780 ppm

**Wavelength - Time - Intensity Curve**

Concentration Indicator: 0.029 a.u.
Maximum Emission
Intensity: $2.84 \times 10^{-4}$ a.u.
Wavelength: 292 nm
Lifetime: 2.5 ns

**Intensity Contour Plot**

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: B1Ta
Contaminant: Benzene
Concentration: 1000 ppm

Date Performed: March 24, 1997

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.017 a.u.
Maximum Emission
Intensity: 1.91 x 10^{-4} a.u.
Wavelength: 292 nm
Lifetime: 2.7 ns

Intensity Contour Plot

Contour Spacing: 2.0 x 10^{-5} a.u.
Contour Origin: 2.0 x 10^{-5} a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: BlTb

Contaminant: Benzene
Concentration: 1000 ppm

Date Performed: March 24, 1997

- **Wavelength - Time - Intensity Curve**

  - Concentration Indicator: 0.017 a.u.
  - Maximum Emission
    - Intensity: $2.13 \times 10^{-4}$ a.u.
    - Wavelength: 292 nm
  - Lifetime: 2.6 ns

- **Intensity Contour Plot**

  - Contour Spacing: $2.0 \times 10^{-5}$ a.u.
  - Contour Origin: $2.0 \times 10^{-5}$ a.u.

- **Intensity - Time Signature**

- **Emission - Wavelength Profile**
**Test Name:** BITc  
**Contaminant:** Benzene  
**Concentration:** 1000 ppm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.014 a.u.
- **Maximum Emission**  
  - **Intensity:** $1.71 \times 10^{-4}$ a.u.  
  - **Wavelength:** 290 nm  
  - **Lifetime:** 2.5 ns

**Intensity Contour Plot**

- **Contour Spacing:** $2.0 \times 10^{-5}$ a.u.  
- **Contour Origin:** $2.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: B1Td

Contaminant: Benzene
Concentration: 1000 ppm

Date Performed: March 25, 1997

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.016 a.u.
Maximum Emission
Intensity: $1.73 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 2.5 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: B750Ma

Contaminant: Benzene
Concentration: 750 ppm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.014 a.u.
Maximum Emission
  Intensity: $1.48 \times 10^{-4}$ a.u.
  Wavelength: 292 nm
  Lifetime: 2.4 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
**Test Name:** B750Mb

**Date Performed:** March 25, 1997

**Contaminant:** Benzene

**Concentration:** 750 ppm

- **Wavelength - Time - Intensity Curve**
  
  **Concentration Indicator:** 0.009 a.u.

  **Maximum Emission**
  - **Intensity:** $1.19 \times 10^{-4}$ a.u.
  - **Wavelength:** 292 nm

  **Lifetime:** 2.8 ns

- **Intensity Contour Plot**
  
  **Contour Spacing:** $2.0 \times 10^{-5}$ a.u.

  **Contour Origin:** $2.0 \times 10^{-5}$ a.u.

- **Intensity - Time Signature**

- **Emission - Wavelength Profile**
**Test Name:** B5HMa  
**Date Performed:** March 25, 1997

**Contaminant:** Benzene  
**Concentration:** 500 ppm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.009 a.u.
- **Maximum Emission**  
  - **Intensity:** $1.08 \times 10^{-4}$ a.u.  
  - **Wavelength:** 294 nm  
  - **Lifetime:** 2.8 ns

**Intensity Contour Plot**

- **Contour Spacing:** $2.0 \times 10^{-5}$ a.u.  
- **Contour Origin:** $2.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: TEQa  
Contaminant: Toluene  
Concentration: 515 ppm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 1.262 a.u.
Maximum Emission  
Intensity: $5.56 \times 10^{-3}$ a.u.  
Wavelength: 292 nm  
Lifetime: 6.3 ns

□ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-4}$ a.u.  
Contour Origin: $2.0 \times 10^{-4}$ a.u.

□ Intensity - Time Signature  
□ Emission - Wavelength Profile
Test Name: TEQb

Contaminant: Toluene
Concentration: 515 ppm

Date Performed: March 18, 1997

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 1.419 a.u.
Maximum Emission
Intensity: $6.25 \times 10^{-3}$ a.u.
Wavelength: 294 nm
Lifetime: 6.3 ns

□ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-4}$ a.u.
Contour Origin: $2.6 \times 10^{-4}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: TEQc

Contaminant: Toluene
Concentration: 515 ppm

- Wavelength - Time - Intensity Curve

Concentration Indicator: 1.238 a.u.
Maximum Emission
   Intensity: $5.61 \times 10^{-3}$ a.u.
   Wavelength: 292 nm
   Lifetime: 6.3 ns

- Intensity Contour Plot

   Contour Spacing: $2.0 \times 10^{-4}$ a.u.
   Contour Origin: $2.0 \times 10^{-4}$ a.u.

- Intensity - Time Signature

- Emission - Wavelength Profile
Test Name: TEQd

Contaminant: Toluene
Concentration: 515 ppm

Date Performed: March 18, 1997

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 1.307 a.u.
Maximum Emission
Intensity: $5.88 \times 10^{-3}$ a.u.
Wavelength: 292 nm
Lifetime: 6.4 ns

□ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-4}$ a.u.
Contour Origin: $2.0 \times 10^{-4}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: THMa

Contaminant: Toluene
Concentration: 100 ppm

**Wavelength - Time - Intensity Curve**

Concentration Indicator: 0.254 a.u.
Maximum Emission
Intensity: $1.18 \times 10^{-3}$ a.u.
Wavelength: 292 nm
Lifetime: 6.2 ns

**Intensity Contour Plot**

Contour Spacing: $1.0 \times 10^{-4}$ a.u.
Contour Origin: $1.0 \times 10^{-4}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: THMb
Contaminant: Toluene
Concentration: 100 ppm

Date Performed: March 18, 1997

- Wavelength - Time - Intensity Curve
  - Concentration Indicator: 0.219 a.u.
  - Maximum Emission
    - Intensity: $1.04 \times 10^{-3}$ a.u.
    - Wavelength: 292 nm
  - Lifetime: 6.1 ns

- Intensity Contour Plot
  - Contour Spacing: $1.0 \times 10^{-4}$ a.u.
  - Contour Origin: $1.0 \times 10^{-4}$ a.u.

- Intensity - Time Signature

- Emission - Wavelength Profile
Test Name: THMc

Contaminant: Toluene
Concentration: 100 ppm

- **Wavelength - Time - Intensity Curve**

  ![3D Intensity Plot]

  Concentration Indicator: 0.266 a.u.
  Maximum Emission
  Intensity: $1.23 \times 10^{-3}$ a.u.
  Wavelength: 292 nm
  Lifetime: 6.1 ns

- **Intensity Contour Plot**

  ![Intensity Contour Plot]

  Contour Spacing: $1.0 \times 10^{-4}$ a.u.
  Contour Origin: $1.0 \times 10^{-4}$ a.u.

- **Intensity - Time Signature**

  ![Intensity - Time Signature]

- **Emission - Wavelength Profile**

  ![Emission - Wavelength Profile]
Test Name: THMd

Contaminant: Toluene
Concentration: 100 ppm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.225 a.u.
Maximum Emission
Intensity: $1.09 \times 10^{-3}$ a.u.
Wavelength: 292 nm
Lifetime: 6.2 ns

Intensity Contour Plot

Contour Spacing: $1.0 \times 10^{-4}$ a.u.
Contour Origin: $1.0 \times 10^{-4}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: TFMa

Contaminant: Toluene
Concentration: 50 ppm

Date Performed: March 21, 1997

- Wavelength - Time - Intensity Curve
  - Concentration Indicator: 0.114 a.u.
  - Maximum Emission
    - Intensity: $5.85 \times 10^{-4}$ a.u.
    - Wavelength: 294 nm
  - Lifetime: 6.1 ns

- Intensity Contour Plot
  - Contour Spacing: $5.0 \times 10^{-5}$ a.u.
  - Contour Origin: $5.0 \times 10^{-5}$ a.u.

- Intensity - Time Signature
- Emission - Wavelength Profile
Test Name: TTMa

Contaminant: Toluene
Concentration: 10 ppm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.027 a.u.
Maximum Emission
Intensity: $1.45 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.6 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
**Test Name:** TTMb

**Contaminant:** Toluene
**Concentration:** 10 ppm

**Date Performed:** March 17, 1997

**Wavelength - Time - Intensity Curve**

Concentration Indicator: 0.026 a.u.

Maximum Emission
- Intensity: $1.53 \times 10^{-4}$ a.u.
- Wavelength: 294 nm
- Lifetime: 5.9 ns

**Intensity Contour Plot**

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: TTMc

Contaminant: Toluene
Concentration: 10 ppm

Date Performed: March 18, 1997

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.021 a.u.

Maximum Emission
Intensity: $1.25 \times 10^{-4}$ a.u.
Wavelength: 290 nm

Lifetime: 6.1 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: TTMd

Contaminant: Toluene
Concentration: 10 ppm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.025 a.u.
Maximum Emission
Intensity: $1.61 \times 10^{-4}$ a.u.
Wavelength: 292 nm
Lifetime: 6.6 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: T5Ma

Contaminant: Toluene
Concentration: 5 ppm

Date Performed: March 21, 1997

- Wavelength - Time - Intensity Curve
  
  Concentration Indicator: 0.007 a.u.
  Maximum Emission
  Intensity: $1.05 \times 10^{-4}$ a.u.
  Wavelength: 292 nm
  Lifetime: 4.9 ns

- Intensity Contour Plot
  
  Contour Spacing: $1.0 \times 10^{-5}$ a.u.
  Contour Origin: $2.0 \times 10^{-5}$ a.u.

- Intensity - Time Signature

- Emission - Wavelength Profile
Test Name: XEQa

Contaminant: (o)-Xylene
Concentration: 175 ppm

Wavelength - Time - Intensity Curve

Concentration Indicator: 1.207 a.u.
Maximum Emission
Intensity: $4.95 \times 10^{-3}$ a.u.
Wavelength: 296 nm
Lifetime: 6.8 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-4}$ a.u.
Contour Origin: $2.0 \times 10^{-4}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: XEQb

Contaminant: (o)-Xylene
Concentration: 175 ppm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 1.022 a.u.
Maximum Emission
Intensity: $4.35 \times 10^{-3}$ a.u.
Wavelength: 294 nm
Lifetime: 6.5 ns

□ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-4}$ a.u.
Contour Origin: $2.0 \times 10^{-4}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: XEQc

Contaminant: (o)-Xylene
Concentration: 175 ppm

Date Performed: March 23, 1997

- Wavelength - Time - Intensity Curve

Concentration Indicator: 1.210 a.u.
Maximum Emission
Intensity: $4.96 \times 10^{-3}$ a.u.
Wavelength: 294 nm
Lifetime: 6.5 ns

- Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-4}$ a.u.
Contour Origin: $2.0 \times 10^{-4}$ a.u.

- Intensity - Time Signature

- Emission - Wavelength Profile
**Test Name:** XEQd

**Contaminant:** (o)-Xylene
**Concentration:** 175 ppm

**Date Performed:** March 23, 1997

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 1.063 a.u.
- **Maximum Emission**
  - **Intensity:** $4.39 \times 10^{-3}$ a.u.
  - **Wavelength:** 294 nm
- **Lifetime:** 6.5 ns

**Intensity Contour Plot**

- **Contour Spacing:** $2.0 \times 10^{-4}$ a.u.
- **Contour Origin:** $2.6 \times 10^{-4}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: XHMa

Contaminant: (o)-Xylene
Concentration: 100 ppm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.702 a.u.

Maximum Emission
Intensity: \(2.96 \times 10^{-3}\) a.u.
Wavelength: 296 nm
Lifetime: 6.7 ns

□ Intensity Contour Plot

Contour Spacing: \(2.0 \times 10^{-4}\) a.u.
Contour Origin: \(2.0 \times 10^{-3}\) a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
**Test Name:** XHMB

**Contaminant:** (o)-Xylene  
**Concentration:** 100 ppm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.664 a.u.
- **Maximum Emission**  
  - **Intensity:** $2.59 \times 10^{-3}$ a.u.  
  - **Wavelength:** 294 nm  
- **Lifetime:** 6.9 ns

**Intensity Contour Plot**

- **Contour Spacing:** $2.0 \times 10^{-4}$ a.u.  
- **Contour Origin:** $2.0 \times 10^{-4}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: XHMc

Contaminant: (o)-Xylene
Concentration: 100 ppm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.586 a.u.
Maximum Emission
Intensity: $2.54 \times 10^{-3}$ a.u.
Wavelength: 294 nm
Lifetime: 6.6 ns

☐ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-4}$ a.u.
Contour Origin: $2.0 \times 10^{-4}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: XFMa

Contaminant: (o)-Xylene
Concentration: 50 ppm

Date Performed: March 23, 1997

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.318 a.u.
Maximum Emission
Intensity: $1.41 \times 10^{-3}$ a.u.
Wavelength: 294 nm
Lifetime: 6.3 ns

Intensity Contour Plot

Contour Spacing: $1.0 \times 10^{-4}$ a.u.
Contour Origin: $1.0 \times 10^{-4}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: XTMa

Contaminant: (o)-Xylene
Concentration: 10 ppm

Date Performed: March 22, 1997

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.062 a.u.
Maximum Emission
Intensity: $3.43 \times 10^{-4}$ a.u.
Wavelength: 292 nm
Lifetime: 7.0 ns

□ Intensity Contour Plot

Contour Spacing: $5.0 \times 10^{-5}$ a.u.
Contour Origin: $5.0 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: XTMb

Contaminant: (o)-Xylene
Concentration: 10 ppm

Date Performed: March 22, 1997

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.073 a.u.
Maximum Emission
Intensity: $3.34 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.9 ns

☐ Intensity Contour Plot

Contour Spacing: $5.0 \times 10^{-5}$ a.u.
Contour Origin: $5.0 \times 10^{-5}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: XTMc

Contaminant: (o)-Xylene
Concentration: 10 ppm

Date Performed: March 23, 1997

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.077 a.u.
Maximum Emission
Intensity: \(3.39 \times 10^{-4}\) a.u.
Wavelength: 294 nm
Lifetime: 6.6 ns

☐ Intensity Contour Plot

Contour Spacing: \(5.0 \times 10^{-5}\) a.u.
Contour Origin: \(5.0 \times 10^{-5}\) a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: XTMd

Contaminant: (o)-Xylene
Concentration: 10 ppm

Date Performed: March 23, 1997

- **Wavelength - Time - Intensity Curve**

  Concentration Indicator: 0.092 a.u.
  Maximum Emission
  Intensity: $4.38 \times 10^{-4}$ a.u.
  Wavelength: 294 nm
  Lifetime: 6.6 ns

- **Intensity Contour Plot**

  Contour Spacing: $5.0 \times 10^{-5}$ a.u.
  Contour Origin: $5.0 \times 10^{-5}$ a.u.

- **Intensity - Time Signature**

- **Emission - Wavelength Profile**
Test Name: X1Ma

Contaminant: (o)-Xylene
Concentration: 1 ppm

Date Performed: March 22, 1997

- Wavelength - Time - Intensity Curve

Concentration Indicator: 0.004 a.u.
Maximum Emission
Intensity: $5.40 \times 10^{-5}$ a.u.
Wavelength: 294 nm
Lifetime: 6.6 ns

- Intensity Contour Plot

Contour Spacing: $1.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

- Intensity - Time Signature

- Emission - Wavelength Profile
Test Name: X1Mb

Date Performed: March 22, 1997

Contaminant: (o)-Xylene
Concentration: 1 ppm

- **Wavelength - Time - Intensity Curve**

  Concentration Indicator: 0.007 a.u.
  Maximum Emission
  Intensity: 8.91 x 10^{-3} a.u.
  Wavelength: 292 nm
  Lifetime: 6.8 ns

- **Intensity Contour Plot**

  Contour Spacing: 1.0 x 10^{-5} a.u.
  Contour Origin: 2.0 x 10^{-5} a.u.

- **Intensity - Time Signature**

- **Emission - Wavelength Profile**
Test Name: X1Mc

Contaminant: (o)-Xylene
Concentration: 1 ppm

Date Performed: March 23, 1997

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.005 a.u.
Maximum Emission
Intensity: $6.32 \times 10^{-5}$ a.u.
Wavelength: 292 nm
Lifetime: 6.8 ns

Intensity Contour Plot

Contour Spacing: $1.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: X1Md
Contaminant: (o)-Xylene
Concentration: 1 ppm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.008 a.u.
Maximum Emission
Intensity: $7.91 \times 10^{-5}$ a.u.
Wavelength: 292 nm
Lifetime: 6.6 ns

☐ Intensity Contour Plot

Contour Spacing: $1.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Appendix E

RESULTS OF FULL SCAN LASER INDUCED FLUORESCENCE
TESTS PERFORMED ON SPECIMENS OF INDUSTRIAL QUARTZ
Test Name: Q16aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 6, 1997

Soil: Industrial Quartz
Grain Size Range: 2.00 - 1.19 mm

- Wavelength - Time - Intensity Curve

Concentration Indicator: 0.196 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.829 a.u.

Maximum Emission
Intensity: $8.70 \times 10^{-4}$ a.u.
Wavelength: 296 nm
Lifetime: 6.7 ns

- Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

- Intensity - Time Signature

- Emission - Wavelength Profile
Test Name: Q16bX
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 6, 1997
Soil: Industrial Quartz
Grain Size Range: 2.00 - 1.19 mm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.238 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.918 a.u.
Maximum Emission
Intensity: $1.05 \times 10^{-3}$ a.u.
Wavelength: 296 nm
Lifetime: 6.4 ns

Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

Intensity - Time Signature
Emission - Wavelength Profile
**Test Name:** Q16cX  
**Date Performed:** May 7, 1997

**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm

**Soil:** Industrial Quartz  
**Grain Size Range:** 2.00 - 1.19 mm

- **Wavelength - Time - Intensity Curve**

  ![Wavelength - Time - Intensity Curve](image)

  - **Intensity Indicator:** 0.235 a.u.
  - **Normalized Concentration Indicator:** In-Soil / Extract = 0.500 a.u.
  - **Maximum Emission**
    - **Intensity:** $1.15 \times 10^{-3}$ a.u.
    - **Wavelength:** 296 nm
  - **Lifetime:** 7.0 ns

- **Intensity Contour Plot**

  ![Intensity Contour Plot](image)

  - **Contour Spacing:** $4.0 \times 10^{-5}$ a.u.
  - **Contour Origin:** $4.0 \times 10^{-5}$ a.u.

- **Intensity - Time Signature**

  ![Intensity - Time Signature](image)

- **Emission - Wavelength Profile**

  ![Emission - Wavelength Profile](image)
Test Name: Q16cXMN
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 7, 1997
Soil: Industrial Quartz
Grain Size Range: 2.00 - 1.19 mm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.018 a.u.
Normalized Concentration Indicator: In-Soil / Extract = 0.038 a.u.

Maximum Emission
Intensity: $1.16 \times 10^{-4}$ a.u.
Wavelength: 296 nm
Lifetime: 6.1 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-3}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
**Test Name:** Q16cXMX

**Contaminant:** (o) - Xylene

**Concentration:** 175 ppm

**Date Performed:** May 7, 1997

**Soil:** Industrial Quartz

**Grain Size Range:** 2.00 - 1.19 mm

**Concentration Indicator:** 0.489 a.u.

**Normalized Concentration Indicator:**

**In-Soil / Extract =** 1.040 a.u.

**Maximum Emission**

**Intensity:** $2.04 \times 10^{-3}$ a.u.

**Wavelength:** 294 nm

**Lifetime:** 6.8 ns

**Intensity Contour Plot**

**Contour Spacing:** $2.0 \times 10^{-3}$ a.u.

**Contour Origin:** $2.0 \times 10^{-4}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: Q12aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: April 29, 1997

Soil: Industrial Quartz
Grain Size Range: 2.00 - 0.84 mm

- **Wavelength - Time - Intensity Curve**

  ![3D Graph](image)

  - **Intensity (a.u.)**
  - **Time (ns)**
  - **Wavelength (nm)**

  - Concentration Indicator: 0.538 a.u.
  - Normalized Concentration Indicator:
    - In-Soil / Extract = 0.694 a.u.
  - Maximum Emission
    - Intensity: $2.30 \times 10^{-3}$ a.u.
    - Wavelength: 296 nm
  - Lifetime: 6.8 ns

- **Intensity Contour Plot**

  ![Contour Plot](image)

  - Contour Spacing: $2.0 \times 10^{-4}$ a.u.
  - Contour Origin: $2.0 \times 10^{-4}$ a.u.

- **Intensity - Time Signature**

  ![Intensities](image)

  - Time (ns)
  - Intensity (a.u.)

- **Emission - Wavelength Profile**

  ![Intensities](image)

  - Wavelength (nm)
  - Intensity (a.u.)
**Test Name:** Q12bX  
**Date Performed:** April 29, 1997

**Contaminant:** (α) - Xylene  
**Concentration:** 175 ppm

**Soil:** Industrial Quartz  
**Grain Size Range:** 2.00 - 0.84 mm

- **Wavelength - Time - Intensity Curve**

- **Intensity Contour Plot**

- **Intensity - Time Signature**

- **Emission - Wavelength Profile**

- **Concentration Indicator:** 0.688 a.u.  
  **Normalized Concentration Indicator:**  
  **In-Soil / Extract =** 0.862 a.u.  
  **Maximum Emission**  
  **Intensity:** $2.87 \times 10^{-3}$ a.u.  
  **Wavelength:** 294 nm  
  **Lifetime:** 6.7 ns

- **Contour Spacing:** $2.0 \times 10^{-4}$ a.u.  
  **Contour Origin:** $2.0 \times 10^{-4}$ a.u.
Test Name: Q12cX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: April 29, 1997
Soil: Industrial Quartz
Grain Size Range: 2.00 - 0.84 mm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.561 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.710 a.u.
Maximum Emission
Intensity: \(2.40 \times 10^{-3}\) a.u.
Wavelength: 294 nm
Lifetime: 6.2 ns

□ Intensity Contour Plot

Contour Spacing: \(2.0 \times 10^{-4}\) a.u.
Contour Origin: \(2.0 \times 10^{-4}\) a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: Q20aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Wavelength - Time - Intensity Curve

- Concentration Indicator: 0.068 a.u.
- Normalized Concentration Indicator: In-Soil / Extract = 0.220 a.u.
- Maximum Emission
  - Intensity: $3.17 \times 10^{-4}$ a.u.
  - Wavelength: 294 nm
  - Lifetime: 6.5 ns

Intensity Contour Plot

- Contour Spacing: $4.0 \times 10^{-5}$ a.u.
- Contour Origin: $4.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile

Date Performed: May 7, 1997

Soil: Industrial Quartz
Grain Size Range: 1.19 - 0.84 mm
Test Name: Q20aXMX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 7, 1997

Soil: Industrial Quartz
Grain Size Range: 1.19 - 0.84 mm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.289 a.u.
Normalized Concentration Indicator: 
In-Soil / Extract = 0.933 a.u.

Maximum Emission
Intensity: $1.21 \times 10^{-3}$ a.u.
Wavelength: 294 nm
Lifetime: 6.7 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-4}$ a.u.
Contour Origin: $2.0 \times 10^{-4}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
**Test Name:** Q20aXMN

**Date Performed:** May 7, 1997

**Contaminant:** (o) - Xylene

**Concentration:** 175 ppm

**Soil:** Industrial Quartz

**Grain Size Range:** 1.19 - 0.84 mm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.024 a.u.
- **Normalized Concentration Indicator:**
  
  In-Soil / Extract = 0.078 a.u.

- **Maximum Emission**
  - **Intensity:** $9.77 \times 10^{-5}$ a.u.
  - **Wavelength:** 296 nm
  - **Lifetime:** 6.5 ns

**Intensity Contour Plot**

- **Contour Spacing:** $2.0 \times 10^{-5}$ a.u.
- **Contour Origin:** $2.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
**Test Name:** Q225aX

**Contaminant:** (o) - Xylene

**Concentration:** 175 ppm

**Date Performed:** May 5, 1997

**Soil:** Industrial Quartz

**Grain Size Range:** 0.84 - 0.71 mm

**Wavelength - Time - Intensity Curve**

Concentration Indicator: 0.147 a.u.

Normalized Concentration Indicator:

In-Soil / Extract = 0.297 a.u.

Maximum Emission

Intensity: $6.60 \times 10^{-4}$ a.u.

Wavelength: 294 nm

Lifetime: 6.7 ns

**Intensity Contour Plot**

Contour Spacing: $4.0 \times 10^{-5}$ a.u.

Contour Origin: $4.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
**Test Name:** Q225bX

- **Contaminant:** (o) - Xylene
- **Concentration:** 175 ppm

**Date Performed:** May 6, 1997

- **Soil:** Industrial Quartz
- **Grain Size Range:** 0.84 - 0.71 mm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.131 a.u.
- **Normalized Concentration Indicator:**
  - In-Soil / Extract = 0.266 a.u.
- **Maximum Emission**
  - **Intensity:** $6.07 \times 10^{-4}$ a.u.
  - **Wavelength:** 292 nm
- **Lifetime:** 6.7 ns

**Intensity Contour Plot**

- **Contour Spacing:** $4.0 \times 10^{-5}$ a.u.
- **Contour Origin:** $4.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: Q225cX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 8, 1997

Soil: Industrial Quartz
Grain Size Range: 0.84 - 0.71 mm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.060 a.u.
Normalized Concentration Indicator: In-Soil / Extract = 0.194 a.u.

Maximum Emission
Intensity: $3.02 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.8 ns

□ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: Q225cXMN

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 8, 1997

Soil: Industrial Quartz
Grain Size Range: 0.84 - 0.71 mm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.050 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.161 a.u.

Maximum Emission
Intensity: $2.52 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.9 ns

□ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
**Test Name:** Q225cXMX

**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm

**Date Performed:** May 8, 1997

**Soil:** Industrial Quartz  
**Grain Size Range:** 0.84 - 0.71 mm  
**Concentration Indicator:** 0.260 a.u.  
**Normalized Concentration Indicator:** In-Soil / Extract = 0.840 a.u.  
**Maximum Emission**  
**Intensity:** $1.12 \times 10^{-3}$ a.u.  
**Wavelength:** 296 nm  
**Lifetime:** 6.9 ns

- **Wavelength - Time - Intensity Curve**

- **Intensity Contour Plot**  
  **Contour Spacing:** $2.0 \times 10^{-4}$ a.u.  
  **Contour Origin:** $2.0 \times 10^{-4}$ a.u.

- **Intensity - Time Signature**

- **Emission - Wavelength Profile**
Test Name: Q23aX

Contaminant: (o) - Xylene

Concentration: 175 ppm

Date Performed: May 3, 1997

Soil: Industrial Quartz

Grain Size Range: 0.84 - 0.59 mm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.146 a.u.

Normalized Concentration Indicator: in-Soil/Extract = 0.284 a.u.

Maximum Emission

Intensity: $6.68 \times 10^{-4}$ a.u.

Wavelength: 294 nm

Lifetime: 6.4 ns

Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.

Contour Origin: $4.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
**Test Name:** Q23bX

**Contaminant:** (o) - Xylene

**Concentration:** 175 ppm

**Date Performed:** May 4, 1997

**Soil:** Industrial Quartz

**Grain Size Range:** 0.84 - 0.59 mm

**Wavelength - Time - Intensity Curve**

Concentration Indicator: 0.268 a.u.

Normalized Concentration Indicator: 0.541 a.u.

Maximum Emission

Intensity: $1.19 \times 10^{-3}$ a.u.

Wavelength: 294 nm

Lifetime: 6.5 ns

**Intensity Contour Plot**

Contour Spacing: $1.0 \times 10^{-4}$ a.u.

Contour Origin: $1.0 \times 10^{-4}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
**Test Name:** Q23cX

**Date Performed:** May 5, 1997

**Contaminant:** (o) - Xylene

**Concentration:** 175 ppm

**Soil:** Industrial Quartz

**Grain Size Range:** 0.84 - 0.59 mm

**Wavelength - Time - Intensity Curve**

- Concentration Indicator: 0.310 a.u.
- Normalized Concentration Indicator: In-Soil / Extract = 0.574 a.u.
- Maximum Emission
  - Intensity: $1.34 \times 10^{-3}$ a.u.
  - Wavelength: 294 nm
- Lifetime: 6.4 ns

**Intensity Contour Plot**

- Contour Spacing: $1.0 \times 10^{-4}$ a.u.
- Contour Origin: $1.0 \times 10^{-4}$ a.u.

**Intensity - Time Signature**

- **Emission - Wavelength Profile**
Test Name: Q23dX
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 5, 1997
Soil: Industrial Quartz
Grain Size Range: 0.84 - 0.59 mm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.271 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.579 a.u.

Maximum Emission
Intensity: $1.26 \times 10^{-3}$ a.u.
Wavelength: 296 nm
Lifetime: 6.3 ns

☐ Intensity Contour Plot

Contour Spacing: $1.0 \times 10^{-4}$ a.u.
Contour Origin: $1.0 \times 10^{-4}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: Q253aX
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 12, 1997
Soil: Industrial Quartz
Grain Size Range: 0.71 - 0.59 mm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.055 a.u.
Normalized Concentration Indicator: In-Soil / Extract = 0.271 a.u.
Maximum Emission
Intensity: $2.75 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.6 ns

□ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: Q34aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: April 29, 1997

Soil: Industrial Quartz
Grain Size Range: 0.59 - 0.42 mm

- Wavelength - Time - Intensity Curve

<table>
<thead>
<tr>
<th>Intensity (a.u.)</th>
<th>Time (ns)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0e-3</td>
<td>10</td>
<td>275</td>
</tr>
<tr>
<td>8.0e-4</td>
<td>30</td>
<td>290</td>
</tr>
<tr>
<td>6.0e-4</td>
<td>40</td>
<td>305</td>
</tr>
<tr>
<td>4.0e-4</td>
<td>50</td>
<td>320</td>
</tr>
<tr>
<td>2.0e-4</td>
<td>60</td>
<td>335</td>
</tr>
</tbody>
</table>

Concentration Indicator: 0.152 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.253 a.u.

Maximum Emission
- Intensity: $6.64 \times 10^{-4}$ a.u.
- Wavelength: 294 nm
- Lifetime: 6.7 ns

- Intensity Contour Plot

<table>
<thead>
<tr>
<th>Contour Spacing</th>
<th>Contour Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^{-4}$ a.u.</td>
<td>$1.0 \times 10^{-4}$ a.u.</td>
</tr>
</tbody>
</table>

- Intensity - Time Signature

- Emission - Wavelength Profile
**Test Name:** Q34bX

- **Contaminant:** (o) - Xylene
- **Concentration:** 175 ppm

**Date Performed:** April 29, 1997

- **Soil:** Industrial Quartz
- **Grain Size Range:** 0.59 - 0.42 mm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.162 a.u.
- **Normalized Concentration Indicator:**
- **In-Soil / Extract** = 0.261 a.u.
- **Maximum Emission**
  - **Intensity:** $7.69 \times 10^{-4}$ a.u.
  - **Wavelength:** 294 nm
- **Lifetime:** 6.4 ns

**Intensity Contour Plot**

- **Contour Spacing:** $1.0 \times 10^{-4}$ a.u.
- **Contour Origin:** $1.0 \times 10^{-4}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: Q34cX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 9, 1997
Soil: Industrial Quartz
Grain Size Range: 0.59 - 0.42 mm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.014 a.u.
Normalized Concentration Indicator: In-Soil / Extract = 0.054 a.u.

Maximum Emission
Intensity: $9.56 \times 10^{-5}$ a.u.
Wavelength: 296 nm
Lifetime: 6.5 ns

☐ Intensity Contour Plot

Contour Spacing: $1.0 \times 10^{-5}$ a.u.
Contour Origin: $1.6 \times 10^{-5}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: Q34cXMN

Date Performed: May 9, 1997

Contaminant: (o) - Xylene
Concentration: 175 ppm

Soil: Industrial Quartz
Grain Size Range: 0.59 - 0.42 mm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.018 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.070 a.u.

Maximum Emission
Intensity: $1.04 \times 10^{-4}$ a.u.
Wavelength: 296 nm
Lifetime: 7.6 ns

□ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: Q34cXMX
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 9, 1997
Soil: Industrial Quartz
Grain Size Range: 0.59 - 0.42 mm

- Concentration Indicator: 0.123 a.u.
- Normalized Concentration Indicator: In-Soil / Extract = 0.477 a.u.
- Maximum Emission
  - Intensity: $5.10 \times 10^{-4}$ a.u.
  - Wavelength: 296 nm
  - Lifetime: 6.9 ns

- Intensity Contour Plot
  - Contour Spacing: $4.0 \times 10^{-5}$ a.u.
  - Contour Origin: $4.0 \times 10^{-5}$ a.u.

- Intensity - Time Signature
- Emission - Wavelength Profile
Test Name: Q45aX
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 4, 1997
Soil: Industrial Quartz
Grain Size Range: 0.42 - 0.30 mm

- **Wavelength - Time - Intensity Curve**

  ![3D Graph](image1)

  - Concentration Indicator: 0.084 a.u.
  - Normalized Concentration Indicator: In-Soil / Extract = 0.122 a.u.
  - Maximum Emission
    - Intensity: $3.92 \times 10^{-4}$ a.u.
    - Wavelength: 298 nm
  - Lifetime: 6.5 ns

- **Intensity Contour Plot**

  ![Contour Plot](image2)

  - Contour Spacing: $4.0 \times 10^{-5}$ a.u.
  - Contour Origin: $4.0 \times 10^{-5}$ a.u.

- **Intensity - Time Signature**

  ![Intensity Time Signature](image3)

- **Emission - Wavelength Profile**

  ![Emission Wavelength Profile](image4)
Test Name: Q45bX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 10, 1997

Soil: Industrial Quartz
Grain Size Range: 0.42 - 0.30 mm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.035 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.189 a.u.

Maximum Emission
Intensity: $1.73 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.8 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: Q45bXMN

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 10, 1997

Soil: Industrial Quartz
Grain Size Range: 0.42 - 0.30 mm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.030 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.162 a.u.

Maximum Emission
Intensity: $1.57 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 7.0 ns

☐ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
**Test Name:** Q45bXMX  
**Date Performed:** May 10, 1997

**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm

**Soil:** Industrial Quartz  
**Grain Size Range:** 0.42 - 0.30 mm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.080 a.u.
- **Normalized Concentration Indicator:**
- **In-Soil / Extract:** 0.433 a.u.
- **Maximum Emission**
  - **Intensity:** \(3.90 \times 10^{-4}\) a.u.
  - **Wavelength:** 292 nm
- **Lifetime:** 6.8 ns

**Intensity Contour Plot**

- **Contour Spacing:** \(4.0 \times 10^{-5}\) a.u.
- **Contour Origin:** \(4.0 \times 10^{-5}\) a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: Q56aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: April 29, 1997

Soil: Industrial Quartz
Grain Size Range: 0.30 - 0.25 mm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.050 a.u.
Normalized Concentration Indicator: In-Soil / Extract = 0.082 a.u.

Maximum Emission
Intensity: $2.92 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 5.2 ns

☐ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: Q56bX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: April 30, 1997

Soil: Industrial Quartz
Grain Size Range: 0.30 - 0.25 mm

- Wavelength - Time - Intensity Curve

Concentration Indicator: 0.099 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.134 a.u.
Maximum Emission
Intensity: $4.85 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.4 ns

- Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

- Intensity - Time Signature

- Emission - Wavelength Profile
**Test Name:** Q56cX

**Contaminant:** (o) - Xylene

**Concentration:** 175 ppm

**Date Performed:** May 9, 1997

**Soil:** Industrial Quartz

**Grain Size Range:** 0.30 - 0.25 mm

**Wavelength - Time - Intensity Curve**

**Concentration Indicator:** 0.030 a.u.

**Normalized Concentration Indicator:**

**In-Soil / Extract =** 0.099 a.u.

**Maximum Emission**

**Intensity:** $1.52 \times 10^{-4}$ a.u.

**Wavelength:** 292 nm

**Lifetime:** 6.3 ns

**Intensity Contour Plot**

**Contour Spacing:** $2.0 \times 10^{-5}$ a.u.

**Contour Origin:** $2.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: Q56dX

Date Performed: May 9, 1997

Contaminant: (o) - Xylene
Concentration: 175 ppm

Soil: Industrial Quartz
Grain Size Range: 0.30 - 0.25 mm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.017 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.075 a.u.

Maximum Emission
Intensity: $1.07 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.5 ns

Intensity Contour Plot

Contour Spacing: $1.0 \times 10^{-5}$ a.u.
Contour Origin: $1.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: Q56dXMN
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 9, 1997
Soil: Industrial Quartz
Grain Size Range: 0.30 - 0.25 mm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.008 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.035 a.u.

Maximum Emission
Intensity: 6.26 x 10^{-5} a.u.
Wavelength: 296 nm
Lifetime: 5.4 ns

☐ Intensity Contour Plot

Contour Spacing: 1.0 x 10^{-5} a.u.
Contour Origin: 1.0 x 10^{-5} a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: Q56dXMX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 9, 1997

Soil: Industrial Quartz
Grain Size Range: 0.30 - 0.25 mm

- **Wavelength - Time - Intensity Curve**

  ![Wavelength - Time - Intensity Curve](image)

  - Concentration Indicator: 0.038 a.u.
  - Normalized Concentration Indicator: In-Soil / Extract = 0.168 a.u.
  - Maximum Emission
    - Intensity: $2.77 \times 10^{-4}$ a.u.
    - Wavelength: 292 nm
  - Lifetime: 6.8 ns

- **Intensity Contour Plot**

  ![Intensity Contour Plot](image)

  - Contour Spacing: $2.0 \times 10^{-5}$ a.u.
  - Contour Origin: $2.0 \times 10^{-5}$ a.u.

- **Intensity - Time Signature**

  ![Intensity - Time Signature](image)

- **Emission - Wavelength Profile**

  ![Emission - Wavelength Profile](image)
**Test Name:** Q67aX

- **Contaminant:** (o) - Xylene
- **Concentration:** 175 ppm

**Date Performed:** May 10, 1997

- **Soil:** Industrial Quartz
- **Grain Size Range:** 0.25 - 0.21 mm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.011 a.u.
- **Normalized Concentration Indicator:**
- **In-Soil / Extract =** 0.073 a.u.

**Maximum Emission**

- **Intensity:** $6.58 \times 10^{-5}$ a.u.
- **Wavelength:** 298 nm
- **Lifetime:** 6.7 ns

**Intensity Contour Plot**

- **Contour Spacing:** $1.0 \times 10^{-5}$ a.u.
- **Contour Origin:** $1.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
**Test Name:** Q67aXMN  
**Date Performed:** May 10, 1997

**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm

- **Wavelength - Time - Intensity Curve**
  
  Concentration Indicator: 0.013 a.u.  
  Normalized Concentration Indicator:  
  In-Soil / Extract = 0.087 a.u.

  Maximum Emission  
  Intensity: $7.85 \times 10^{-5}$ a.u.  
  Wavelength: 292 nm  
  Lifetime: 6.6 ns

- **Intensity Contour Plot**
  
  Contour Spacing: $1.0 \times 10^{-5}$ a.u.  
  Contour Origin: $1.0 \times 10^{-5}$ a.u.

- **Intensity - Time Signature**

- **Emission - Wavelength Profile**
**Test Name:** Q67aXMX

**Contaminant:** (o) - Xylene
**Concentration:** 175 ppm

**Date Performed:** May 10, 1997

**Soil:** Industrial Quartz
**Grain Size Range:** 0.25 - 0.21 mm

**Wavelength - Time - Intensity Curve**

- Concentration Indicator: 0.036 a.u.
- Normalized Concentration Indicator: In-Soil / Extract = 0.240 a.u.
- Maximum Emission
  - Intensity: $1.90 \times 10^{-4}$ a.u.
  - Wavelength: 294 nm
- Lifetime: 6.2 ns

**Intensity Contour Plot**

- Contour Spacing: $2.0 \times 10^{-5}$ a.u.
- Contour Origin: $2.0 \times 10^{-3}$ a.u.

**Intensity - Time Signature**

- **Emission - Wavelength Profile**
Test Name: Q78aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 1, 1997

Soil: Industrial Quartz
Grain Size Range: 0.21 - 0.18 mm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.073 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.115 a.u.

Maximum Emission
Intensity: $3.79 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.3 ns

□ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.6 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: Q78bX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 1, 1997

Soil: Industrial Quartz
Grain Size Range: 0.21 - 0.18 mm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.039 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.068 a.u.

Maximum Emission
Intensity: $2.08 \times 10^{-4}$ a.u.
Wavelength: 296 nm
Lifetime: 6.3 ns

☐ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: Q120aX
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 1, 1997
Soil: Industrial Quartz
Grain Size Range: 0.15 - 0.12 mm

- **Wavelength - Time - Intensity Curve**

Concentration Indicator: 0.058 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.096 a.u.
Maximum Emission
Intensity: $2.87 \times 10^{-4}$ a.u.
Wavelength: 298 nm
Lifetime: 6.2 ns

- **Intensity Contour Plot**

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

- **Intensity - Time Signature**
- **Emission - Wavelength Profile**
Test Name: Q120bX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 1, 1997

Soil: Industrial Quartz
Grain Size Range: 0.15 - 0.12 mm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.074 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.116 a.u.

Maximum Emission
Intensity: $3.66 \times 10^{-4}$ a.u.
Wavelength: 296 nm
Lifetime: 6.2 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: Q140aX
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 10, 1997
Soil: Industrial Quartz
Grain Size Range: 0.12 - 0.10 mm

Concentration Indicator: 0.025 a.u.
Normalized Concentration Indicator: In-Soil / Extract = 0.098 a.u.
Maximum Emission
Intensity: $1.35 \times 10^{-4}$ a.u.
Wavelength: 296 nm
Lifetime: 6.4 ns

Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
**Test Name:** Q140aXMN

**Contaminant:** (o) - Xylene

**Concentration:** 175 ppm

**Date Performed:** May 10, 1997

**Soil:** Industrial Quartz

**Grain Size Range:** 0.12 - 0.10 mm

**Wavelength - Time - Intensity Curve**

- Concentration Indicator: 0.014 a.u.
- Normalized Concentration Indicator: In-Soil / Extract = 0.055 a.u.
- Maximum Emission
  - Intensity: $8.99 \times 10^{-5}$ a.u.
  - Wavelength: 298 nm
- Lifetime: 6.7 ns

**Intensity Contour Plot**

- Contour Spacing: $2.0 \times 10^{-5}$ a.u.
- Contour Origin: $2.0 \times 10^{-5}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
**Test Name:** Q140aXMX  
**Date Performed:** May 10, 1997

**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm

- **Wavelength - Time - Intensity Curve**

  ![Wavelength-Time-Intensity Curve](image)

  - **Intensity (a. u.):**
    - 2.0e-4
    - 1.5e-4
    - 1.0e-4
    - 5.0e-5
    - 0.0e+0
  - **Time (ns):**
    - 0
    - 10
    - 20
    - 30
    - 40
    - 50
  - **Wavelength (nm):**
    - 275
    - 290
    - 305
    - 320
    - 335
    - 350

- **Concentration Indicator:** 0.030 a.u.
- **Normalized Concentration Indicator:**
  - In-Soil / Extract = 0.117 a.u.

- **Maximum Emission**
  - **Intensity:** $1.55 \times 10^{-4}$ a.u.
  - **Wavelength:** 294 nm
  - **Lifetime:** 6.6 ns

- **Intensity Contour Plot**

  ![Intensity Contour Plot](image)

  - **Contour Spacing:** $2.0 \times 10^{-5}$ a.u.
  - **Contour Origin:** $2.0 \times 10^{-5}$ a.u.

- **Intensity - Time Signature**

  ![Intensity-Time Signature](image)

  - **Intensity (a.u.):**
    - 0.0
    - 0.5
    - 1.0
  - **Time (ns):**
    - 0
    - 10
    - 20
    - 30
    - 40
    - 50

- **Emission - Wavelength Profile**

  ![Emission-Wavelength Profile](image)

  - **Intensity (a.u.):**
    - 0.0e+0
    - 1.0e-3
    - 2.0e-3
  - **Wavelength (nm):**
    - 275
    - 290
    - 305
    - 320
    - 335
    - 350

371
Test Name: Q170aX
Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 3, 1997
Soil: Industrial Quartz
Grain Size Range: 0.10 - 0.09 mm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.087 a.u.
Normalized Concentration Indicator: 
In-Soil / Extract = 0.223 a.u.
Maximum Emission
Intensity: 4.00 x 10^-4 a.u.
Wavelength: 296 nm
Lifetime: 6.4 ns

Intensity Contour Plot

Contour Spacing: 4.0 x 10^-5 a.u.
Contour Origin: 4.0 x 10^-5 a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: Q170bX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 3, 1997

Soil: Industrial Quartz
Grain Size Range: 0.10 - 0.09 mm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.100 a.u.
Normalized Concentration Indicator: In-Soil / Extract = 0.250 a.u.
Maximum Emission
  Intensity: $4.54 \times 10^{-4}$ a.u.
  Wavelength: 294 nm
  Lifetime: 6.5 ns

□ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: Q200aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 4, 1997

Soil: Industrial Quartz
Grain Size Range: 0.09 - 0.07 mm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.029 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.103 a.u.
Maximum Emission
Intensity: $1.50 \times 10^{-4}$ a.u.
Wavelength: 294 nm
Lifetime: 6.3 ns

□ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: Q325aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 12, 1997

Soil: Industrial Quartz
Grain Size Range: 0.07 - 0.04 mm

□ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.020 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.242 a.u.

Maximum Emission
Intensity: $1.12 \times 10^{-4}$ a.u.
Wavelength: 292 nm
Lifetime: 4.7 ns

□ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-5}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
Test Name: Q325aXMN

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: May 12, 1997

Soil: Industrial Quartz
Grain Size Range: 0.07 - 0.04 mm

- Wavelength - Time - Intensity Curve

- Intensity Contour Plot

- Intensity - Time Signature

- Emission - Wavelength Profile

Concentration Indicator: 0.008 a.u.
Normalized Concentration Indicator: In-Soil / Extract = 0.097 a.u.

Maximum Emission
Intensity: $5.75 \times 10^{-5}$ a.u.
Wavelength: 296 nm
Lifetime: 5.7 ns

Contour Spacing: $1.0 \times 10^{-5}$ a.u.
Contour Origin: $1.0 \times 10^{-5}$ a.u.
**Test Name:** Q325aXMX  
**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm

**Date Performed:** May 12, 1997  
**Soil:** Industrial Quartz  
**Grain Size Range:** 0.07 - 0.04 mm

□ **Wavelength - Time - Intensity Curve**

![Wavelength-Time-Intensity Curve](image)

- **Concentration Indicator:** 0.018 a.u.
- **Normalized Concentration Indicator:**
  - In-Soil / Extract = 0.217 a.u.

- **Maximum Emission**
  - **Intensity:** $1.00 \times 10^{-4}$ a.u.
  - **Wavelength:** 292 nm
  - **Lifetime:** 5.3 ns

□ **Intensity Contour Plot**

![Intensity Contour Plot](image)

- **Contour Spacing:** $2.0 \times 10^{-5}$ a.u.
- **Contour Origin:** $2.0 \times 10^{-5}$ a.u.

□ **Intensity - Time Signature**

![Intensity-Time Signature](image)

□ **Emission - Wavelength Profile**

![Emission-Wavelength Profile](image)
Appendix F

RESULTS OF RANGE SCAN LASER INDUCED FLUORESCENCE TESTS PERFORMED ON SPECIMENS OF INDUSTRIAL QUARTZ
**Test Name:** Q16cXR  
**Date Performed:** May 7, 1997

- **Contaminant:** (o) - Xylene
- **Concentration:** 175 ppm
- **Soil:** Industrial Quartz
- **Grain Size Range:** 2.00 - 1.19 mm

![Signal in Soil vs. Displacement](image1)

---

**Test Name:** Q20aXR  
**Date Performed:** May 7, 1997

- **Contaminant:** (o) - Xylene
- **Concentration:** 175 ppm
- **Soil:** Industrial Quartz
- **Grain Size Range:** 1.19 - 0.84 mm

![Signal in Soil vs. Displacement](image2)

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**Test Name:** Q225cXR  
**Date Performed:** May 8, 1997

- **Contaminant:** (o) - Xylene  
- **Concentration:** 175 ppm  
- **Soil:** Industrial Quartz  
- **Grain Size Range:** 0.84 - 0.71 mm

---

**Test Name:** Q253aXR  
**Date Performed:** May 12, 1997

- **Contaminant:** (o) - Xylene  
- **Concentration:** 175 ppm  
- **Soil:** Industrial Quartz  
- **Grain Size Range:** 0.71 - 0.59 mm

---

Average of maximum and minimum grain sizes.
**Test Name:** Q34cXR  
**Date Performed:** May 9, 1997  
**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm  
**Soil:** Industrial Quartz  
**Grain Size Range:** 0.59 - 0.42 mm

---

**Test Name:** Q45bXR  
**Date Performed:** May 10, 1997  
**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm  
**Soil:** Industrial Quartz  
**Grain Size Range:** 0.42 - 0.30 mm

---

**Diagram Details:**
- **Signal in Soil / Signal in Extract**
- **Displacement (mm)**
- **Average of maximum and minimum grain sizes.**
**Test Name:** Q56dXR  
**Date Performed:** May 9, 1997  
**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm  
**Soil:** Industrial Quartz  
**Grain Size Range:** 0.30 - 0.25 mm

---

**Test Name:** Q67aXR  
**Date Performed:** May 10, 1997  
**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm  
**Soil:** Industrial Quartz  
**Grain Size Range:** 0.25 - 0.21 mm

---

Average of maximum and minimum grain sizes.
**Test Name:** Q140aXR  
**Date Performed:** May 10, 1997

- **Contaminant:** (o) - Xylene
- **Concentration:** 175 ppm
- **Soil:** Industrial Quartz
- **Grain Size Range:** 0.12 - 0.10 mm

---

**Test Name:** Q325aXR  
**Date Performed:** May 12, 1997

- **Contaminant:** (o) - Xylene
- **Concentration:** 175 ppm
- **Soil:** Industrial Quartz
- **Grain Size Range:** 0.07 - 0.04 mm

---

Average of maximum and minimum grain sizes.
Appendix G

RESULTS OF FULL SCAN LASER INDUCED FLUORESCENCE TESTS PERFORMED ON SPECIMENS OF MANCHESTER FINE SAND AND TICINO SAND
Test Name: M78aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: June 8, 1997

Soil: Manchester Fine Sand
Grain Size Range: 0.21 - 0.18 mm

Box Wavelength - Time - Intensity Curve

Concentration Indicator: 0.122 a.u.
Normalized Concentration Indicator: In-Soil / Extract = 0.033 a.u.

Maximum Emission
Intensity: $5.24 \times 10^{-4}$ a.u.
Wavelength: 296 nm
Lifetime: 6.8 ns

Box Intensity Contour Plot

Contour Spacing: $4.6 \times 10^{-5}$ a.u.
Contour Origin: $4.0 \times 10^{-5}$ a.u.

Box Intensity - Time Signature

Box Emission - Wavelength Profile
**Test Name:** M100aX

**Contaminant:** (o) - Xylene

**Concentration:** 175 ppm

**Date Performed:** June 9, 1997

**Soil:** Manchester Fine Sand

**Grain Size Range:** 0.18 - 0.15 mm

**Wavelength - Time - Intensity Curve**

![Wavelength - Time - Intensity Curve](image)

**Concentration Indicator:** 0.343 a.u.

**Normalized Concentration Indicator:**

In-Soil / Extract = 0.094 a.u.

**Maximum Emission**

**Intensity:** $1.38 \times 10^{-3}$ a.u.

**Wavelength:** 294 nm

**Lifetime:** 6.5 ns

**Intensity Contour Plot**

![Intensity Contour Plot](image)

**Contour Spacing:** $1.0 \times 10^{-4}$ a.u.

**Contour Origin:** $1.0 \times 10^{-4}$ a.u.

**Intensity - Time Signature**

![Intensity - Time Signature](image)

**Emission - Wavelength Profile**

![Emission - Wavelength Profile](image)
**Test Name:** M325aX

- **Contaminant:** (o) - Xylene
- **Concentration:** 175 ppm

**Date Performed:** June 8, 1997

- **Soil:** Manchester Fine Sand
- **Grain Size Range:** 0.07 - 0.04 mm

**Wavelength - Time - Intensity Curve**

- **Concentration Indicator:** 0.228 a.u.
- **Normalized Concentration Indicator:**
  - In-Soil/Extract = 0.056 a.u.
- **Maximum Emission**
  - **Intensity:** $9.76 \times 10^{-4}$ a.u.
  - **Wavelength:** 294 nm
- **Lifetime:** 6.6 ns

**Intensity Contour Plot**

- **Contour Spacing:** $1.0 \times 10^{-4}$ a.u.
- **Contour Origin:** $1.0 \times 10^{-3}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: T253aX  
Contaminant: (o) - Xylene  
Concentration: 175 ppm  

Date Performed: June 9, 1997  
Soil: Ticino Sand  
Grain Size Range: 0.71 - 0.59 mm  

Wavelength - Time - Intensity Curve

Concentration Indicator: 1.114 a.u.  
Normalized Concentration Indicator:  
In-Soil / Extract = 0.439 a.u.  
Maximum Emission  
Intensity: $4.48 \times 10^{-3}$ a.u.  
Wavelength: 296 nm  
Lifetime: 6.5 ns  

Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-4}$ a.u.  
Contour Origin: $4.0 \times 10^{-4}$ a.u.  

Intensity - Time Signature  
Emission - Wavelength Profile
Test Name: T34aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: June 9, 1997

Soil: Ticino Sand
Grain Size Range: 0.59 - 0.42 mm

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.669 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.227 a.u.
Maximum Emission
Intensity: $2.81 \times 10^{-3}$ a.u.
Wavelength: 296 nm
Lifetime: 6.4 ns

Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-4}$ a.u.
Contour Origin: $4.0 \times 10^{-4}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: T45aX

Contaminant: (o) - Xylene
Concentration: 175 ppm

Date Performed: June 9, 1997

Soil: Ticino Sand
Grain Size Range: 0.42 - 0.30 mm

- Wavelength - Time - Intensity Curve

Concentration Indicator: 1.098 a.u.
Normalized Concentration Indicator:
In-Soil / Extract = 0.291 a.u.

Maximum Emission
Intensity: $4.47 \times 10^{-3}$ a.u.
Wavelength: 296 nm
Lifetime: 6.6 ns

- Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-4}$ a.u.
Contour Origin: $4.0 \times 10^{-4}$ a.u.

- Intensity - Time Signature

- Emission - Wavelength Profile
Appendix H

RESULTS OF RANGE SCAN LASER INDUCED FLUORESCENCE TESTS PERFORMED ON SPECIMENS OF MANCHESTER FINE SAND AND TICINO SAND
Test Name: M78aXR

Contaminant: (o) - Xylene
Concentration: 175 ppm

Soil: Manchester Fine Sand
Grain Size Range: 0.21 - 0.18 mm

Displacement (mm)

Signal In-Soil / Signal in Extract

Average of maximum and minimum grain sizes.

Test Name: M100aXR

Contaminant: (o) - Xylene
Concentration: 175 ppm

Soil: Manchester Fine Sand
Grain Size Range: 0.18 - 0.15 mm

Displacement (mm)

Signal In-Soil / Signal in Extract

Average of maximum and minimum grain sizes.
**Test Name:** M325aXR  
**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm  
**Date Performed:** June 8, 1997  
**Soil:** Manchester Fine Sand  
**Grain Size Range:** 0.07 - 0.04 mm

**Graph:** Signal in Soil / Signal in Extract vs Displacement (mm)

---

**Test Name:** MFS1R  
**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm  
**Date Performed:** June 9, 1997  
**Soil:** Manchester Fine Sand  
**Grain Size Range:** Natural Soil

**Graph:** Signal in Soil / Signal in Extract vs Displacement (mm)

---

Average of maximum and minimum grain sizes.
**Test Name:** T253aXR  
**Date Performed:** June 9, 1997  
**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm  
**Soil:** Ticino Sand  
**Grain Size Range:** 0.71 - 0.59 mm

![Graph](image1)

---

**Test Name:** T34aXR  
**Date Performed:** June 9, 1997  
**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm  
**Soil:** Ticino Sand  
**Grain Size Range:** 0.59 - 0.42 mm

![Graph](image2)
Test Name: T45aXR  
Contaminant: (o) - Xylene  
Concentration: 175 ppm  
Soil: Ticino Sand  
Grain Size Range: 0.42 - 0.30 mm

Test Name: TIC1R  
Contaminant: (o) - Xylene  
Concentration: 175 ppm  
Soil: Ticino Sand  
Grain Size Range: Natural Soil
Appendix I

RESULTS OF LASER INDUCED FLUORESCENCE TESTS
PERFORMED ON SINGLE - COMPOUND AQUEOUS SOLUTIONS TO
CALIBRATE SECOND GENERATION PROBE
**Test Name:** MCBEQ1  
**Contaminant:** Benzene  
**Concentration:** 1780 ppm

**Wavelength - Time - Intensity Curve**

Concentration Indicator: 0.638 a.u.

Maximum Emission  
*Intensity:* $4.03 \times 10^{-3}$ a.u.  
*Wavelength:* 296 nm  
*Lifetime:* 2.9 ns

**Intensity Contour Plot**

Contour Spacing: $4.0 \times 10^{-4}$ a.u.  
Contour Origin: $4.0 \times 10^{-4}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: MCBEQ2
Contaminant: Benzene
Concentration: 1780 ppm

Date Performed: June 6, 1997

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.657 a.u.
Maximum Emission
Intensity: $4.06 \times 10^{-3}$ a.u.
Wavelength: 296 nm
Lifetime: 3.2 ns

☐ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-4}$ a.u.
Contour Origin: $4.0 \times 10^{-4}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: MCBEQ3
Contaminant: Benzene
Concentration: 1780 ppm

Date Performed: June 6, 1997

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 0.699 a.u.
Maximum Emission
Intensity: $4.32 \times 10^{-3}$ e.u.
Wavelength: 296 nm
Lifetime: 3.2 ns

☐ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-4}$ a.u.
Contour Origin: $4.0 \times 10^{-4}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: MCB7501
Contaminant: Benzene
Concentration: 750 ppm

Date Performed: June 6, 1997

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.265 a.u.
Maximum Emission
Intensity: $1.64 \times 10^{-3}$ a.u.
Wavelength: 300 nm
Lifetime: 3.3 ns

Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-4}$ a.u.
Contour Origin: $4.0 \times 10^{-4}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
Test Name: MCB7502  
Contaminant: Benzene  
Concentration: 750 ppm

☐ Wavelength - Time - Intensity Curve

Concentration In 'icator: 0.278 a.u.
Maximum Emission:  
Intensity: \( \times 10^{-3} \) a.u.
Wavelength: \( \lambda \) 8 nm
Lifetime: 3.0 ns

☐ Intensity Contour Plot

Contour Spacing: \( 4.0 \times 10^{-4} \) a.u.
Contour Origin: \( 4.0 \times 10^{-4} \) a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile
Test Name: MCB7503
Contaminant: Benzene
Concentration: 750 ppm

Date Performed: June 7, 1997

Wavelength - Time - Intensity Curve

Concentration Indicator: 0.212 a.u.
Maximum Emission
Intensity: $1.49 \times 10^{-3}$ a.u.
Wavelength: 296 nm
Lifetime: 2.7 ns

Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-4}$ a.u.
Contour Origin: $4.0 \times 10^{-4}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
**Test Name:** MCXEQ1

**Contaminant:** (o) - Xylene  
**Concentration:** 175 ppm

**Wavelength - Time - Intensity Curve**

Concentration Indicator: 10.810 a.u.  
Maximum Emission  
Intensity: $3.95 \times 10^{-2}$ a.u.  
Wavelength: 296 nm  
Lifetime: 6.6 ns

**Intensity Contour Plot**

Contour Spacing: $4.0 \times 10^{-3}$ a.u.  
Contour Origin: $4.0 \times 10^{-3}$ a.u.

**Intensity - Time Signature**

**Emission - Wavelength Profile**
Test Name: MCXEQ2

Contaminant: (o) - Xylene
Concentration: 175 ppm

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 10.391 a.u.
Maximum Emission
Intensity: $3.85 \times 10^{-2}$ a.u.
Wavelength: 296 nm
Lifetime: 6.5 ns

☐ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-3}$ a.u.
Contour Origin: $4.0 \times 10^{-3}$ a.u.

☐ Intensity - Time Signature

☐ Emission - Wavelength Profile

Date Performed: June 7, 1997

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Test Name: MCXEQ3

Date Performed: June 7, 1997

Contaminant: (o) - Xylene
Concentration: 175 ppm

- Wavelength - Time - Intensity Curve

Concentration Indicator: 9.232 a.u.
Maximum Emission
  Intensity: $3.52 \times 10^{-2}$ a.u.
  Wavelength: 296 nm
  Lifetime: 6.6 ns

- Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-3}$ a.u.
Contour Origin: $4.0 \times 10^{-3}$ a.u.

- Intensity - Time Signature

- Emission - Wavelength Profile
Test Name: MCXTM1
Contaminant: (o) - Xylene
Concentration: 10 ppm

Date Performed: June 7, 1997

□ Wavelength - Time - Intensity Curve

Concentration Indicator: .499 a.u.
Maximum Emission
Intensity: $2.08 \times 10^{-3}$ a.u.
Wavelength: 294 nm
Lifetime: 6.5 ns

□ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-4}$ a.u.
Contour Origin: $2.0 \times 10^{-5}$ a.u.

□ Intensity - Time Signature

□ Emission - Wavelength Profile
**Test Name:** MCXTM2

**Contaminant:** (o) - Xylene

**Concentration:** 10 ppm

- **Wavelength - Time - Intensity Curve**

  - **Concentration Indicator:** .603 a.u.
  - **Maximum Emission**
    - **Intensity:** $2.90 \times 10^{-3}$ a.u.
    - **Wavelength:** 294 nm
  - **Lifetime:** 6.5 ns

- **Intensity Contour Plot**

  - **Contour Spacing:** $2.0 \times 10^{-4}$ a.u.
  - **Contour Origin:** $2.0 \times 10^{-4}$ a.u.

- **Intensity - Time Signature**

- **Emission - Wavelength Profile**
Test Name: MCNEQ1
Contaminant: Naphthalene
Concentration: 33 ppm

Date Performed: June 7, 1997

△ Wavelength - Time - Intensity Curve

Concentration Indicator: 46.891 a.u.
Maximum Emission
Intensity: $4.42 \times 10^{-2}$ a.u.
Wavelength: 322 nm
Lifetime: 43.4 ns

△ Intensity Contour Plot

Contour Spacing: $4.0 \times 10^{-3}$ a.u.
Contour Origin: $4.0 \times 10^{-3}$ a.u.

△ Intensity - Time Signature

△ Emission - Wavelength Profile

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**Test Name:** MCNEQ2  
**Date Performed:** June 7, 1997

- **Contaminant:** Naphthalene  
- **Concentration:** 33 ppm

### Wavelength - Time - Intensity Curve

- **Concentration Indicator:** 44.466 a.u.  
- **Maximum Emission:**  
  - **Intensity:** $4.23 \times 10^{-2}$ a.u.  
  - **Wavelength:** 320 nm  
- **Lifetime:** 43.6 ns

### Intensity Contour Plot

- **Contour Spacing:** $4.0 \times 10^{-3}$ a.u.  
- **Contour Origin:** $4.0 \times 10^{-3}$ a.u.

### Intensity - Time Signature

### Emission - Wavelength Profile
Test Name: MCN5M1
Contaminant: Naphthalene
Concentration: 5 ppm

Date Performed: June 7, 1997

Wavelength - Time - Intensity Curve

Concentration Indicator: 8.307 a.u.
Maximum Emission
Intensity: $8.88 \times 10^{-3}$ a.u.
Wavelength: 322 nm
Lifetime: 41.2 ns

Intensity Contour Plot

Contour Spacing: $1.0 \times 10^{-3}$ a.u.
Contour Origin: $1.0 \times 10^{-3}$ a.u.

Intensity - Time Signature

Emission - Wavelength Profile
**Test Name:** MCN5M2  
**Contaminant:** Naphthalene  
**Concentration:** 5 ppm

**Date Performed:** June 7, 1997

- **Wavelength - Time - Intensity Curve**

Concentration Indicator: 5.083 a.u.

Maximum Emission
- Intensity: $5.68 \times 10^{-3}$ a.u.
- Wavelength: 320 nm
- Lifetime: 40.8 ns

- **Intensity Contour Plot**

Contour Spacing: $1 \times 10^{-3}$ a.u.
Contour Origin: $1.6 \times 10^{-3}$ a.u.

- **Intensity - Time Signature**

- **Emission - Wavelength Profile**
Appendix J

RESULTS OF LASER INDUCED FLUORESCENCE TESTS
PERFORMED ON MULTI-COMPOUND AQUEOUS SOLUTIONS
Test Name: BX551  
Date Performed: June 7, 1997

Contaminants: Benzene, (o) - Xylene (Aqueous Equilibrium Solutions)
Composition by Volume: 50% Benzene Solution / 50% (o) - Xylene Solution

- **Wavelength - Time - Intensity Curve**

![3D Graph](image1)

- **Concentration Indicator:** 5.152 a.u.
- **Maximum Emission**
  - **Intensity:** $2.12 \times 10^{-2}$ a.u.
  - **Wavelength:** 296 nm

- **Intensity Contour Plot**

![Intensity Contour](image2)

- **Contour Spacing:** $2.0 \times 10^{-3}$ a.u.
- **Contour Origin:** $2.0 \times 10^{-3}$ a.u.

- **Emission - Wavelength Profile**

![Intensity vs. Wavelength](image3)

- **Intensity (a.u.):**
  - 0.4
  - 0.3
  - 0.2
  - 0.1
  - 0.0

- **Wavelength (nm):**
  - 275
  - 290
  - 305
  - 320
  - 335
  - 350
Test Name: BX552

Date Performed: June 7, 1997

Contaminants: Benzene, (o) - Xylene (Aqueous Equilibrium Solutions)

Composition by Volume: 50% Benzene Solution / 50% (o) - Xylene Solution

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 5.851 a.u.

Maximum Emission
- Intensity: $2.32 \times 10^{-2}$ a.u.
- Wavelength: 294 nm

☐ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.
Contour Origin: $2.0 \times 10^{-3}$ a.u.

☐ Emission - Wavelength Profile
Test Name: BX721

Date Performed: June 7, 1997

Contaminants: Benzene, (o) - Xylene (Aqueous Equilibrium Solutions)
Composition by Volume: 75% Benzene Solution / 25% (o) - Xylene Solution

- Wavelength - Time - Intensity Curve

Concentration Indicator: 3.634 a.u.

Maximum Emission
Intensity: $1.55 \times 10^{-2}$ a.u.
Wavelength: 296 nm

- Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.
Contour Origin: $2.0 \times 10^{-4}$ a.u.

- Emission - Wavelength Profile
Test Name: BX722

Date Performed: June 7, 1997

Contaminants: Benzene, (o) - Xylene (Aqueous Equilibrium Solutions)
Composition by Volume: 75% Benzene Solution / 25% (o) - Xylene Solution

- Wavelength - Time - Intensity Curve

Concentration Indicator: 3.359 a.u.
Maximum Emission
Intensity: $1.48 \times 10^{-2}$ a.u.
Wavelength: 296 nm

- Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.
Contour Origin: $2.0 \times 10^{-3}$ a.u.

- Emission - Wavelength Profile

Intensity (a.u.)

Wavelength (nm)
Test Name: BX271  
Date Performed: June 7, 1997

Contaminants: Benzene, (o) - Xylene (Aqueous Equilibrium Solutions)  
Composition by Volume: 25% Benzene Solution / 75% (o) - Xylene Solution

- Wavelength - Time - Intensity Curve

Concentration Indicator: 8.968 a.u.  
Maximum Emission  
Intensity: $3.49 \times 10^{-2}$ a.u.  
Wavelength: 296 nm

- Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.  
Contour Origin: $2.0 \times 10^{-3}$ a.u.

- Emission - Wavelength Profile

Intensity (a.u.)

0.4 0.3 0.2 0.1 0.0  

275 290 305 320 335 350  

Wavelength (nm)
Test Name: BX272  Date Performed: June 7, 1997

Contaminants: Benzene, (o) - Xylene (Aqueous Equilibrium Solutions)
Composition by Volume: 25% Benzene Solution / 75% (o) - Xylene Solution

**Wavelength - Time - Intensity Curve**

Concentration Indicator: 8.653 a.u.
Maximum Emission
Intensity: $3.39 \times 10^{-2}$ a.u.
Wavelength: 296 nm

**Intensity Contour Plot**

Contour Spacing: $2.0 \times 10^{-3}$ a.u.
Contour Origin: $2.0 \times 10^{-3}$ a.u.

**Emission - Wavelength Profile**
Contaminants: Naphthalene, (o) - Xylene (Aqueous Equilibrium Solutions)
Composition by Volume: 50% Naphthalene Solution / 50% (o) - Xylene Solution

- **Wavelength - Time - Intensity Curve**
  - Concentration Indicator: 23.593 a.u.
  - Maximum Emission
    - Intensity: $2.30 \times 10^{-2}$ a.u.
    - Wavelength: 296 nm

- **Intensity Contour Plot**
  - Contour Spacing: $2.0 \times 10^{-3}$ a.u.
  - Contour Origin: $2.0 \times 10^{-3}$ a.u.

- **Emission - Wavelength Profile**
Test Name: NX552

Contaminants: Naphthalene, (o) - Xylene (Aqueous Equilibrium Solutions)
Composition by Volume: 50% Naphthalene Solution / 50% (o) - Xylene Solution

☐ Wavelength - Time - Intensity Curve

Maximum Emission
Intensity: $2.19 \times 10^{-2}$ a.u.
Wavelength: 320 nm

☐ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.
Contour Origin: $2.0 \times 10^{-3}$ a.u.

☐ Emission - Wavelength Profile
Test Name: NX721  
Date Performed: June 7, 1997

Contaminants: Naphthalene, (o) - Xylene (Aqueous Equilibrium Solutions)  
Composition by Volume: 75% Naphthalene Solution / 25% (o) - Xylene Solution

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 31.328 a.u.

Maximum Emission

Intensity: $3.17 \times 10^{-2}$ a.u.
Wavelength: 320 nm

☐ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.
Contour Origin: $2.0 \times 10^{-3}$ a.u.

☐ Emission - Wavelength Profile
**Test Name:** NX722

**Date Performed:** June 7, 1997

**Contaminants:** Naphthalene, (o) - Xylene (Aqueous Equilibrium Solutions)

**Composition by Volume:** 75% Naphthalene Solution / 25% (o) - Xylene Solution

☐ **Wavelength - Time - Intensity Curve**

![3D plot showing intensity over time and wavelength](image)

- **Concentration Indicator:** 31.029 a.u.
- **Maximum Emission**
  - **Intensity:** $3.20 \times 10^{-2}$ a.u.
  - **Wavelength:** 322 nm

☐ **Intensity Contour Plot**

![Contour plot showing wavelength vs time](image)

- **Contour Spacing:** $2.0 \times 10^{-3}$ a.u.
- **Contour Origin:** $2.0 \times 10^{-3}$ a.u.

☐ **Emission - Wavelength Profile**

![Profile plot showing intensity vs wavelength](image)

- **Intensity (a.u.):**
  - 0.0 to 1.5
- **Wavelength (nm):**
  - 275 to 350
Test Name: NX271  
Date Performed: June 7, 1997

Contaminants: Naphthalene, (o) - Xylene (Aqueous Equilibrium Solutions)
Composition by Volume: 25% Naphthalene Solution / 75% (o) - Xylene Solution

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 14.901 a.u.

Maximum Emission
- Intensity: $2.20 \times 10^{-2}$ a.u.
- Wavelength: 296 nm

☐ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.
Contour Origin: $2.0 \times 10^{-3}$ a.u.

☐ Emission - Wavelength Profile
Test Name: NX272  
Date Performed: June 7, 1997

Contaminants: Naphthalene, (o) - Xylene (Aqueous Equilibrium Solutions)  
Composition by Volume: 25% Naphthalene Solution / 75% (o) - Xylene Solution

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 15.834 a.u.

Maximum Emission  
Intensity: $2.67 \times 10^{-2}$ a.u.  
Wavelength: 296 nm

☐ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.  
Contour Origin: $2.0 \times 10^{-3}$ a.u.

☐ Emission - Wavelength Profile
Test Name: BXN252

Date Performed: June 7, 1997

Contaminants: Benzene, (o) - Xylene, Naphthalene (Aqueous Equilibrium Solutions)
Composition by Volume: 25% Benzene Solution / 50% (o) - Xylene Solution / 25% Naphthalene Solution

☐ Wavelength - Time - Intensity Curve

Concentration Indicator: 12.095 a.u.

Maximum Emission
Intensity: $2.00 \times 10^{-2}$ a.u.
Wavelength: 320 nm

☐ Intensity Contour Plot

Contour Spacing: $2.0 \times 10^{-3}$ a.u.
Contour Origin: $20 \times 10^{-3}$ a.u.

☐ Emission - Wavelength Profile