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New Electrochemical and Optical Detection Methods for Biological and Environmental Applications

A Dissertation Presented for

The Doctor of Philosophy

Degree

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Royce Nicholas Dansby-Sparks

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DEDICATION

This dissertation is dedicated to my wife Casey and to my family, who have supported me emotionally and financially throughout this process. I am indebted to all of you for the encouragement you have given to me.

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ABSTRACT

Detection of chromium and vanadium is of interest for biomedical and environmental applications. The two metals have narrow limits between being essential and toxic for humans. Ultra-sensitive techniques have been studied to measure Cr and V at low concentrations found in human blood samples ($\sim 3\text{-}10\ \mu\text{g L}^{-1}$ Cr and $<1\ \mu\text{g L}^{-1}$ V) and environmental samples. Bismuth film and mercury-alloy electrodes have been developed as alternatives to traditional Hg-based electrodes for the Cr and V detection. While catalytic adsorptive stripping voltammetry (CAAdSV) has been used to detect Cr and V, little is known about the process. The mechanisms of CAAdSV have been probed to provide a better understanding of its exceptional sensitivity and selectivity.

Near-real time monitoring of plume gas constituents is desired as a diagnostic tool for combustion efficiency, ensuring safe testing conditions and observing releases of green house gasses. Ground testing rockets is a crucial preliminary step that ensures their performance during critical space missions. Optical sol-gel sensors for carbon dioxide have been developed for remote sensing applications. They are inexpensive and are compatible with the harsh environments encountered during rocket plume tests. The sensors are a viable approach to compliment current infrared (IR) measurements for real-time CO_2 detection. Additional work on kerosene and isopropyl alcohol sensing has been explored for incorporation into a multi-analyte sensing platform.

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NOMENCALTURE AND ABBREVIATIONS

<i>A</i>	absorbance
A	amps
AAS	atomic absorption spectroscopy
AOP	Advanced Oxidation Process
<i>b</i>	pathlength
BiFE	bismuth film electrode
<i>c</i>	concentration
°C	degrees Celcius
CAA	chloranillic acid
CAdSV	catalytic adsorptive stripping voltammetry
C_f	collective constant term for quartz crystal properties
CV	cyclic voltammetry
DI	deionized
DPV	differential pulse voltammetry
DTPA	diethylenetriaminepentaacetic acid
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
EPA	Environmental Protection Agency
EQCM	electrochemical quartz crystal microbalance
EtOH	ethanol
ϵ	molar absorptivity

f_0	resonant frequency of the fundamental mode of the crystal
g	gram
GA	gallic acid
GCE	glassy carbon electrode
h	hour
HPTS	1-hydroxyprene-3,6,8-trisulfonate or pyranine
$h\nu$	incident photon energy
Hz	hertz
ICP-OES	inductively coupled plasma optical emission spectrometer
IPA	isopropyl alcohol
L	liter
LOX	liquid oxygen
m	meter
MeOH	methanol
MFE	mercury film electrode
mM	milli molar
M	Molar
MOSRT	Multi-Analyte Optical Sensor for Rocket Engine Testing
M Ω	megaohm
mA	milliamp
min	minutes
mg	milligram
MHz	megahertz

mL	milliliter
MTEOS	methyltriethoxysilane
MTMOS	methyltrimethoxysilane
MWE	microwire electrode
NaOAc	sodium acetate
NDIR	nondispersive infrared
nm	nanometer
ORMOSIL	Organically Modified Silica
ppb/ $\mu\text{g L}^{-1}$	parts per billion
ppm/ mg L^{-1}	parts per million
ppt/ ng L^{-1}	parts per trillion
QCM	quartz crystal microbalance
R^2	square of correlation coefficient
rpm	rotations per minute
s	second
SEM	scanning electron microscopy
SERS	surface enhanced Raman spectroscopy
SWV	square wave voltammetry
t	time
TMOS	trimethoxysilane
UV-vis	ultraviolet-visible
V	volts
Δf	measured frequency shift

μ	shear modulus of quartz
μA	microamps
μg	microgram
μL	microliter
μm	micrometer
ρ	density of quartz

Part 1

Introduction and Background

1.1. Foreword

Chemical sensors have found applications in a variety of applications. The work presented in this dissertation focuses on the development of chemical sensors and new analytic detection methods for medical and environmental applications. New electrochemical methods have been explored for trace chromium and vanadium detection in biological fluids and environmental samples. Optical sol-gel and polymer thin film sensors have been developed to monitor gaseous analytes found in rocket engine test environments.

Diabetes affects more than 23.6 million people in the US, or nearly 8% of the total population. Of the total number of cases, 5.7 million remain undiagnosed. The total direct and indirect costs of the disease in 2007 were approximately \$174 billion, and the numbers are steadily increasing.¹ Chromium has been used as a low-cost dietary supplement for the management and treatment of diabetes and its complications.²⁻⁵ Vanadium compounds also provide various insulin-like effects and are capable of improving glucose homeostasis (metabolic equilibrium) and insulin in Type I & II diabetes.⁶⁻⁸ An understanding of the efficacy and monitoring of the safety of chromium and vanadium for long-term use is desired. Our research in this area is focused on the detection of these metals at ng L⁻¹ levels in complex sample matrices.⁹⁻¹² This involves the use of the Advanced Oxidation Process (AOP) to pretreat biological samples and release metals from complexes, e.g., peptide-Cr complexes.¹³ The AOP process involves the use of UV light and hydrogen peroxide to decompose organic matter and metal complexes that might

otherwise interfere with electrochemical measurements. This dissertation outlines a new method for the determination of V(V) using Catalytic Adsorptive Stripping Voltammetry (CAdSV) techniques and discusses studies to elucidate the detection mechanism using electrochemical and spectroscopic techniques.

Spectroscopic methods are ideal for monitoring exhaust-plumes for the development of rocket engine–health monitoring and failure detection systems.¹⁴ The space launch vehicle ground testing facilities have a critical need for near-real-time, miniaturized, and remote sensing systems for the detection of constituents of rocket engine effluents. The characterization of plume constituents can provide valuable information about engine performance as well as address safety concerns for ground personnel. Additionally, many constituents need to be monitored to ascertain the environmental impact of their release. This portion of the thesis involves the development of optical sensor based on sol-gel chemistry and thin polymer films for the detection of carbon dioxide (CO₂), kerosene vapors, and isopropyl alcohol (IPA).

1.2. Analysis Techniques Used in the Research Studies

1.2.1. Electrochemical Techniques

Electrochemistry is the process of measuring electrical quantities with the intent of extracting chemical information from them. From measurements of voltage, current, or charge, different information such as analyte concentration, thermodynamics, or reaction kinetics can be inferred.¹⁵ In general, electroanalytical techniques are heterogeneous, meaning the reactions of

interest only occur at the interface of the electrode and solution in what is known as the double layer. The two general types of electrochemical measurements are potentiometry and amperometry. Potentiometry is a static technique involving the measurement of non-faradaic processes. No charge transfer occurs across the interface, but potentials change due to surface changes. The classic example of a potentiometric sensor is the pH meter which is a H^+ ion selective electrode. When faradaic processes are measured, a current is produced as electrons are being transferred to or from the electrode and solution. Typically, a three-electrode system is used consisting of a working, counter and reference electrode. The working electrode is where the half reaction of interest actually occurs. The counter electrode completes the circuit and the reference electrode (typically Ag/AgCl, 3 M KCl) maintains a constant potential. The resistance to the reference electrode is set arbitrarily high in order to maintain as little current as possible, thus ensuring that the composition of that half cell stays more or less constant. In such an arrangement, a potential is measured as the difference between the working and reference electrodes.

The electrochemical techniques used in this work are generally scanning or pulsed waveforms. In cyclic voltammetry (CV), a high and low potential are set and a starting potential picked. The potential is swept linearly to the maximum or minimum point, termed the switching potential, and then reversed. Typically, the technique is performed in an unstirred solution so the redox species will not leave the double layer. The technique is particularly useful for obtaining reaction kinetics and redox reversibility. Pulsed techniques refer to

methods in which the potential is not swept in a linear fashion but is pulsed in an effort to minimize background signals. These techniques are generally more sensitive because they measure current when the difference between the desired faradaic curve and the interfering charging is large.¹⁶ The square wave voltammetry waveform is obtained by superimposing a pulse sequence onto a staircase (Figure 1.1). The potential step is large enough so that oxidation or reduction can occur during the forward and reverse step. The difference in these two currents is plotted to give a peak rather than the usual voltammetric wave.¹⁵ The difference only accounts for the faradaic response, which greatly reduces the charging currents effect on the response and nearly eliminates background charging currents.

1.2.2. Absorption-Emission Spectroscopy

The two types of absorption spectroscopy used in this work are atomic and molecular absorption. Both rely on Beer's law, which states that for

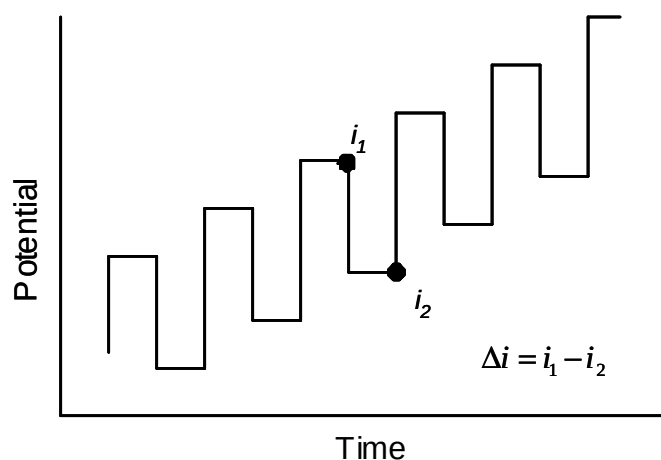


Figure 1.1. Waveform of square wave voltammetry.

monochromatic radiation, absorbance (A) is directly proportional to the pathlength (b) and concentration (c) by:

$$A = \epsilon bc \quad (1.1)$$

Where ϵ is the molar absorptivity constant with units of $\text{M}^{-1} \text{cm}^{-1}$ to make the product unitless.¹⁷ In UV-vis experiments, incident light is absorbed by molecules in the path of the light. When a molecule absorbs the energy from a photon, it is promoted to a higher energy excited state. The absorbed energy is then transferred through a radiationless transition by transferring energy to nearby solvent molecules or through vibrational relaxation.¹⁷ For atomic absorption measurements, the sample is first atomized by a high temperature flame in an atomic absorption spectrometer (AAS), which replaces the cuvette in conventional spectrophotometry. A hollow cathode lamp is placed so that atomic lines, specific to the metal of interest, are emitted from the lamp and pass through the flame. There, the atomized sample can absorb the light and produce an analytical signal. One advantage is that the absorption lines are extremely narrow (0.002 to 0.005 nm) and are specific to each element, making these techniques highly selective.¹⁶ For atomic emission measurements, an inductively coupled plasma–optical emission spectrometer was used. In contrast to AAS, no lamp is needed as the plasma reaches temperatures high enough to promote some atomic species directly to an excited state which can spontaneously emit photons and return to the ground state.

1.2.3. Fluorescence Spectroscopy

Fluorescence spectroscopy is a technique which monitors the emission of light from a molecule which is in an excited state. Molecules then emit radiation at wavelengths longer than that of the excitation source in all directions. The excitation wavelength is selected by a monochromator while luminescence is measured at another monochromator placed at a 90° angle from the incident light to avoid any contribution from the excitation source. An emission spectrum is obtained by holding the excitation light at a certain wavelength while scanning the emission wavelength. An excitation scan is obtained by the reverse process.¹⁷ The emission at a single wavelength is then proportional to the concentration of the analyte.

1.2.4. Fourier Transform Infrared and Raman Spectroscopy

As with other types of absorption based measurements, molecules can be excited to higher energy states by exposing them to infrared radiation. Since infrared radiation has lower energy, energy changes on absorption are in the range of 8 to 40 kJ mol⁻¹.¹⁸ Energies in this range correspond to the stretching and vibrational frequencies of most covalent bonds. Additionally, only bonds that have a dipole moment that changes as a function of time are capable of absorbing infrared radiation. Thus symmetric bonds such as H₂ or Cl₂ do not absorb. A typical Fourier transform infrared spectrometer uses a beam splitter to split the source light into two equal beams. One passes through the beamsplitter and to an adjustable mirror. The other is reflected to a stationary mirror and

reflected back where the two split beams are superimposed before going through the sample and on to a detector. The distance between the stationary and moving mirror is different. Thus, the two waves are not in phase when they reach the detector. Fourier analysis decomposes an interferogram from the time to frequency domain to obtain the spectrum. Because the sample absorbs certain spectra, the interferogram contains the spectrum of the source minus the spectrum of the sample.¹⁷ The spectra presented in this work were collected with a special technique typically used for powder samples called diffuse reflectance infrared Fourier transform spectrometry (DRIFTS). In this technique, the sample is placed inside a sample holder and incident light strikes the top of the sample cell. Radiation, scattered in all directions from the sample, is collected by an ellipsoidal mirror and refocused onto the detector.¹⁶ This technique makes it possible to take DRIFTS spectra from sol-gel films deposited on otherwise non-IR transparent substrates.

Raman scattering and surface enhanced Raman spectroscopy (SERS) have also been used in this work. For Raman spectroscopy, irradiation of the sample is accomplished with a powerful visible or near-infrared laser.¹⁶ The spectrum of the scattered radiation is measured with a suitable spectrometer. However, the intensities of the Raman scattered lines are generally very weak, around 0.001% of the incident energy.¹⁶ Scattering can be elastic or inelastic, referred to as Rayleigh and Raman scattering respectively. When the irradiated light interacts with the sample, the analyte molecule is excited to one of an infinite number of virtual states of energy corresponding to that of the interacting

photon. Raman scattering can be classified as either Stokes or anti-Stokes, depending on if the energy is greater or less than that of the incident radiation.¹⁶ Surface enhanced Raman spectroscopy (SERS) involves obtaining Raman spectra on samples that are adsorbed on the surface of metal particles (usually gold, silver or copper) or roughened surface of metal.¹⁶ Though not fully understood, SERS can provide signal enhancements of up to 10^9 .

1.2.5. The Quartz Crystal Microbalance Electrode

The quartz crystal microbalance (QCM) is a device that is able to measure very minute changes in mass at its surface.¹⁹ When simultaneous monitoring of the electrochemical response and the mass change at the electrode is desired, electrochemical quartz crystal microbalance (EQCM) techniques have proven useful.¹⁵ The piezoelectric properties of the thin piece of quartz forms the basis for measuring the mass changes and two electrodes deposited on opposing sides of the crystal can deliver an alternating current to drive oscillation.²⁰ The frequency of oscillation is sensitive to mass changes on the crystal surface according to the Sauerbrey equation:

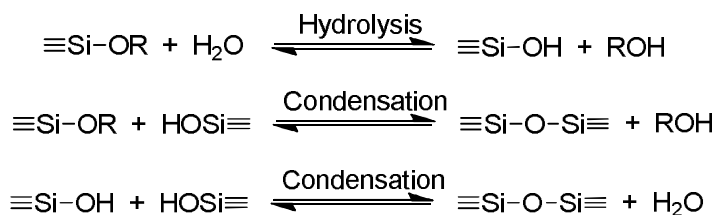
$$\Delta f = \frac{-2 f_0^2 m n}{(\rho \mu)^{1/2}} = -C_f m \quad (1.2)$$

Where Δf is the frequency change caused by addition of mass per unit area, m , to the crystal surface, n is the harmonic number of the oscillation, μ is the shear

modulus of quartz, and ρ is the density of quartz. The constants are generally lumped into a single constant, C_f , the value of which greatly depends on the medium which the crystal is oscillating.¹⁵ For electrochemical measurements, the crystal is sealed in a Teflon cell allowing one of the frequency driving electrodes to be exposed to the analysis solution for electrochemical detection.

1.2.6. Overview of Sol-gel for Sensing Applications

Sol-gels refer to a number of reactions involving the use of alkoxide precursors to prepare solid glass and ceramic oxide materials and were first reported over 150 years ago²¹. The initial motivation for the use of sol-gels was primarily their potentially high purity and homogeneity and the lower processing temperatures required as compared to traditional glass melting and ceramic powder methods.²² The process generally involves the hydrolysis of an alkoxide precursor such as $\text{Si}(\text{OR})_4$ or $\text{R}'\text{Si}(\text{OR}'')_3$ (R = alkyl) followed by a condensation reaction to produce an inorganic cross-linked polymer with a three dimensional porous structure. The sol-gel reactions (Scheme 1.1) can be adjusted to tailor the physical properties of the resulting gel. Properties such as the size of the alkoxide ligand, solution pH, organic substitutions for one or more of the alkoxide groups, solvents, temperature, and catalyst selection can all be adjusted to give different products.²¹⁻²⁹ As a result, sol-gels have been used in many applications including electronics, optics, separations, catalysis, and sensing.^{21,30-32}



Scheme 1.1. The reactions in the sol-gel process.

Chemical sensing has been the focus of our research using sol-gels.³³⁻³⁵ Many unique physical properties of sol-gels make them appealing for sensing applications. Sol-gels are extremely inert and compatible with numerous chemical agents, making their use as sensor matrix supports desirable. Sol-gels offer glass-like properties without the need to heat to extreme temperatures, allowing for the incorporation of temperature sensitive organic molecules as sensing transducers. Encapsulation of sensing materials is usually accomplished by doping them inside the sol-gel or by grafting them to the backbone of the matrix. Doping is more easily accomplished, but leaching of physically entrapped molecules can be problematic. Organofunctionalized sol-gel materials offer more rigidity because the functional groups are attached by covalent bonds. However, the process can be tedious and there are a limited number of materials available that contain the necessary $-\text{Si}(\text{OR})_3$ groups. Sol-gels contain pores that allow for the delivery of analytes to the encapsulated interior sensing materials. One of the most important features for optical sensing is that they are transparent in the visible region.³⁶ Sol-gels have found applications in the optical monitoring of pH,^{23,25,28,29,37-45} metal ions,^{9,46-49} and

various other analytes.⁵⁰⁻⁵² Sol-gels have also found use in electrochemical^{53,10,54-59} and spectroelectrochemical⁶⁰ sensing applications.

1.3. Summary of Dissertation Parts

1.3.1. Part Two

Part 2 of the dissertation describes the use of thick bismuth film electrodes as a mercury free alternative for the determination of ultra-trace vanadium by CAdSV. The fragile Bi films were stabilized with protective polystyrene over-coatings. Highly sensitive ng L^{-1} level detection was attainable with extended (10 min) deposition times.

1.3.2. Part Three

An electrochemical technique is described in Part 3 for ultra-trace (ng L^{-1}) vanadium (V) measurement.¹² CAdSV for V(V) analysis was developed at mercury-coated gold micro-wire electrodes (MWEs, 100 μm) in the presence of gallic acid (GA) and bromate ion. A potential of -0.275 V (vs Ag/AgCl) was used to accumulate the complex in acetate buffer (pH 5.0) at the electrode surface followed by a differential pulse voltammetric scan. Parameters affecting the electrochemical response, including pH, concentration of GA and bromate, and deposition potential and time have been optimized. Linear response was obtained in the $0\text{--}1000\text{ ng L}^{-1}$ range (2 min deposition), with a detection limit of 0.88 ng L^{-1} . The method was validated by comparison of results for an unknown solution of V(V) by atomic absorption measurement. The protocol was evaluated

in a real sample by measuring the amount of V(V) in river water samples. The proposed use of MWEs for the detection of V(V) is sensitive enough for future use to test V(V) concentration in biological fluids treated by the advanced oxidation process (AOP).¹¹

1.3.3. Part Four

Studies to explore the CAdSV mechanism for detection of Cr(VI) and V(V) are discussed in Part 4. The Cr detection mechanism was probed with electrochemical quartz crystal microbalance (EQCM) measurements of mass changes as the surface of both bismuth and mercury modified gold QCM crystals. Spectroelectrochemical measurements of diethylenetriaminepentaacetic acid (DTPA) adsorption on silver electrodes were collected under potential control with *in-situ* surface enhanced Raman spectroscopy. The mechanism of V(V) detection with gallic acid complexing ligand was also studied with EQCM.

1.3.4. Part Five

Part 5 describes optical fluorescence sol-gel sensors that have been developed for the detection of carbon dioxide gas in the 0.03–30% range with a detection limit of 0.008% (or 80 ppm) and a quantitation limit of 0.02% (or 200 ppm) CO₂. Sol-gels were spin-coated on glass slides to create an organically modified silica-doped matrix with the 1-hydroxypyrene-3,6,8-trisulfonate (HPTS) fluorescent indicator. The luminescence intensity of the HPTS indicator (513 nm)

is quenched by CO₂, which protonates the anionic form of HPTS. An ion pair technique was used to incorporate the lipophilic dye into the hydrophilic sol-gel matrix. TiO₂ particles (<5 µm diameter) were added to induce Mie scattering and increase the incident light interaction with the sensing film, thus increasing the signal-to-noise ratio. Moisture-proof overcoatings have been used to maintain a constant level of water inside the sensor films. The optical sensors are inexpensive to prepare and can be easily coupled to fiber optics for remote sensing capabilities. A fiber-optic bundle was used for the gas detection and shown to work as part of a multianalyte platform for simultaneous detection of multiple analytes. The studies reported here resulted in the development of sol-gel optical fluorescent sensors for CO₂ gas with sensitivity below that in the atmosphere (ca. 387 ppm). These sensors are a complementary approach to current FT-IR measurements for real-time carbon dioxide detection in environmental applications.

1.3.5. Part Six

Initial studies to evaluate optical sensing strategies for gas phase kerosene and isopropyl alcohol detection are discussed in Part 6. Several sensing dyes for both analytes were tested in both sol-gel and polymer film matrices. Sensitive fluorescence based measurements of gas phase isopropyl alcohol were made using Chromoionophore IX dye in ethyl cellulose matrix. Preliminary tests of these sensors are shown in a custom-designed, multi-

channel portable sensing device for remote simultaneous multi-analyte sensing of rocket plume constituents.

Part 2

Detection of Vanadium at Bismuth Film Electrodes

2.1. Introduction

Vanadium is the 21st most abundant element in the earth's crust,⁶ and it is released in large quantities into the environment by the burning of fossil fuels and industrial processes.⁶¹ Vanadium concentrations in natural waters can range from 10 to 40 nM and are a good indicator of urban pollution levels.^{62,63} It is an element of considerable environmental interest because of its wide use in a variety of industrial applications and because of its narrow thresholds between essential and toxic levels in living organisms.⁶⁴ Due to the low concentrations present in these samples, highly sensitive and field portable methods of analysis are desirable.

The impact of vanadium on human health has also been noted. Vanadium is thought to be an essential trace element but toxic at elevated levels. The use of vanadium supplements to treat diabetes remains controversial as its efficacy has not been definitely proven in humans.⁶ The supplements provide various insulin-like effects in *in-vitro* and *in-vivo* systems, and have shown the ability to improve glucose homeostasis (metabolic equilibrium) and insulin resistance in Type 1 and Type 2 diabetes.^{6-8,61,65} An understanding of the efficacy and monitoring of the safety of vanadium for long-term use is desired. The levels of vanadium in human blood and urine have been reported to be ca. 50 and 510 ng L⁻¹, respectively.⁶¹ The analysis of blood and urine samples often requires pretreatment which tends to increase their volumes.¹¹ Therefore, a sensitive method, at the low ng L⁻¹ level, is needed for the detection of V in biological fluids.

Reliable measures for assessing V status in humans and environmental samples are very limited. Three analytical techniques, neutron activation, inductively coupled plasma mass spectrometry [(ICP-MS) such as (high resolution) HR-ICP-MS or (dynamic reaction cell) DRC-ICP-MS], and graphite furnace atomic absorption spectroscopy (GF-AAS), have the required sensitivity for V measurement in biological samples from humans and low-level environmental samples.⁶⁶ However, these techniques are very specialized, bulky, and expensive, making their use for routine analysis difficult.

Sensitive electrochemical techniques have been developed for trace V analysis. Electrochemical methods are far less expensive and are more portable than the three aforementioned techniques. Specifically, catalytic adsorptive stripping voltammetry (CA_{AdSV}) has proven useful for trace V(V) detection. These techniques use complexing ligands such as chloranilic acid,^{66,67} cupferron,⁶⁸ catechol,⁶² or gallic acid⁶⁹ to absorb the target metal ions on the surface of the electrode. The electrode reduces the absorbed complex, after which a chemical oxidant re-oxidizes the complex making it available for direct electrode reduction many times during the scan. This cyclic reaction in combination with the preconcentration of the complex on the electrode surface increases the faradaic current response and results in a highly sensitive technique.^{70,71} Traditionally, mercury-based electrodes have been used with sub-ng L⁻¹ detection limits.^{67,68} More recently, Wang and coworkers have demonstrated the use of non-toxic bismuth film electrodes as an alternative to mercury based electrodes.⁶⁶ However, the limit of detection of bismuth film

electrodes was three orders of magnitude higher than those of mercury-based electrodes. Therefore, an alternative to mercury-drop and film electrodes that maintains the required sensitivity for ultra trace vanadium detection is highly desired.

In this work, the development of an aqueous V(V) analysis by CAdSV using gallic acid as the ligand is described. The use of mercury-free thick bismuth film electrodes was explored first followed by mercury-coated gold microwire electrodes (MWEs) described in Part 3. An additional polystyrene coating was applied to increase the stability of the film on the glassy carbon electrode substrate.

2.2. Experimental

2.2.1. Reagents

All reagents were purchased from Fisher Scientific unless stated otherwise. Sodium acetate trihydrate (NaOAc) was dissolved and the pH adjusted (pH 5.0 unless stated otherwise) with acetic acid to make 0.1 M NaOAc buffer. The buffer contained appropriate amounts of gallic acid (0.2 mM unless stated otherwise) and vanadium standard solution. Stock solutions of 0.356 M potassium bromate (Mallinckrodt) in 0.1 M NaOAc buffer were prepared by dissolving the appropriate amounts of each in deionized (DI) water and adjusting pH to 5.0. Stock solutions of vanadium (5000 mg L^{-1}) were prepared by dissolving sodium metavanadate in a small amount of water and nitric acid (HNO_3) and diluting the solution to the final concentration with 5% HNO_3 or

obtained from commercially available AA standards (1000 mg L⁻¹, Ricca). Vanadium standards were made by adding the appropriate volume of stock solution to prepared buffer solutions. Buffer solutions were used for a maximum of one week and stored at 4 °C when not in use. The bismuth plating solution, containing 20 mM Bi(III), 0.5 M potassium bromide (KBr) and 1 M hydrochloric acid (HCl), was prepared by dissolving bismuth needles (99.998%, Alfa Aesar) in 500 µL of concentrated nitric acid (HNO₃) and adding this to a solution of potassium bromide (KBr) and HCl. Polystyrene solution (1% w/w) was made by dissolving polystyrene pellets (Scientific Polymer Products, Inc., approx Mw = 235,000) in toluene or hexanes with stirring.

2.2.2. Instrumentation and Set-up

Electrochemical measurements were conducted using an Electrochemical Workstation (650A/440A, CH Instruments, Austin, TX) connected to a computer and using the corresponding software. The working electrode was a bismuth modified glassy carbon electrode (3 mm diameter, Cypress Systems, 66-EE047) described below. Ag/AgCl (model CHI111, CH Instruments) and a platinum wire were used as reference and counter electrodes, respectively. The electrodes were placed in a 25 mL electrochemical cell for voltammetric detection. All glassware was first cleaned in a base bath followed by soaking in 1 M nitric acid and was rinsed numerous times with DI water before use.

2.2.3. Analysis Procedures

Acetate buffer (19 mL) with gallic acid (0.2 mM) was pipetted into a 25 mL voltammetric cell. All solutions were deoxygenated by bubbling with nitrogen gas for 5 min before analysis. Potassium bromate solution (1 mL) was added at the time of measurement. Preconcentration times were also built into the scan using the CHI software and stirring was applied followed by a 15 s period with no stirring before the scan. Differential pulse voltammetry (DPV) scans were then obtained (0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period).

Bismuth film electrodes were prepared by electrodepositing bismuth on a polished glassy carbon electrode (Cypress Systems, Lawrence, KS) in the Bi plating solution. A potential of -0.25 V was applied for 300 s without stirring to reduce Bi(III) ions and form a visible thick film on the electrode surface. Polystyrene coatings were put on top of the Bi, to protect the fragile film, by pipetting 5 μ L of 1% polystyrene solution and 5 μ L dimethylformaldehyde, similar to previous reports for Nafion films.⁷² Once dry, the film was cured with a heat gun for approximately 1 min and allowed to cool before use. Electrochemical detection was accomplished by DPV. Potassium bromate solution (1 mL) was added to standard solutions (19 mL) directly before measurement. The electrode was held at a potential of -0.35 V with stirring to deposit the V-GA complex on the surface of the working electrode. To accomplish this, the stripping mode in the CHI software was utilized with a set time of 600 s. The stirring was turned off 15 s before the start of the potential scan. The DPV scanned from -0.35 to -0.85 V

(0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period) to generate the voltammetric scans. The electrode was cleaned in buffer solution by applying a potential of -1.2 V for 40 s with stirring. The resulting plots were background fitted and subtracted using CHI software.

2.3. Results and Discussion

2.3.1. Thick Film Bismuth Electrodes for CAdSV of Vanadium

Bismuth film electrodes were first used in an attempt to eliminate the need for mercury-based electrodes. They exhibit similar properties of mercury-based electrodes, such as the high overpotentials for hydrogen evolution needed for CAdSV. A variety of CAdSV techniques for V(V) detection using several ligands at mercury-based electrodes have been reported with detection limits as low as 4.9×10^{-12} M.^{62,68,69,73,74} There are a number of recent papers and reviews describing the use of thin film bismuth electrodes, including CAdSV techniques for detection of chromium and vanadium.^{66,75-78} We studied the use of Bi thick film electrodes for CAdSV analysis of V(V) using both CAA and GA with a hope to achieve a lower detection limit than that previously reported at bismuth thin films.⁶⁶ In addition, we are interested in making more reproducible and robust Bi films on glassy carbon electrode (GCE) substrates.

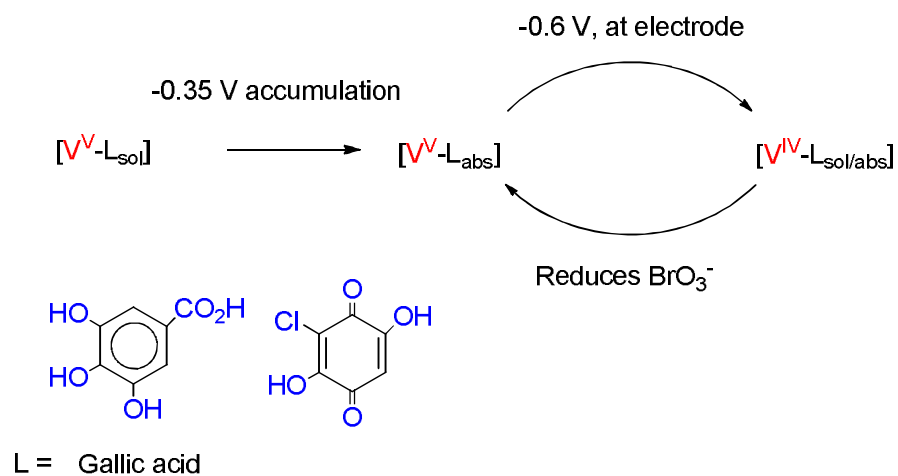
2.3.1.1. CAdSV for Vanadium Detection

Gallic acid and chloranillic acid have both been previously used as complexing ligands for the determination of V(V) by CAdSV techniques. In this

system the ligand first binds to V(V) in the bulk solution to form the complex (Scheme 2.1). The electrode is then held at an accumulation potential to preconcentrate the complex on the surface of the electrode. The preconcentration step leads to the first level of signal enhancement as the concentration is now considerably higher in the diffusion layer of the electrode than in the bulk of the solution. Once the accumulation is complete, the electrode is scanned in the negative direction using either differential pulse or square wave voltammetry techniques. The absorbed complex is then reduced at the electrode to V(IV) at which point the chemical oxidant bromate quickly oxidizes the complex back to the V(V) state making it available for reduction. This cyclic reaction greatly amplifies the signal and is the basis for the high sensitivity obtainable from CADSV techniques.

2.3.1.2. Use of Chloranilic Acid as the Complexing Ligand

Thick Bi films were plated using more concentrated Bi(III) (0.02 M) solutions to produce visible films on the electrode surface. The thicker films were found to be more reproducible than thin films. However, when directly used, the films were found to be fragile and had a tendency to degrade (Figures 2.1). In addition, when using CAA as the complexing ligand, the complex was difficult to remove from the electrode surface to regenerate the electrode for subsequent scans. When buffer solution without V(V) was run first, there were no catalytic peaks. After exposing the electrode to CAA-V complex and following a cleaning



Scheme 2.1. Proposed mechanism for CADSV analysis of V(V) at film electrodes.



Figure 2.1. (A) Bi film electrode on GCE, 60 s deposition, -0.25 V , 0.02 M Bi(III) ; (B) The Bi electrode after exposure to a solution containing residual H_2O_2 .

step, the buffer produced a response (Figure 2.2). Only after repeating the cleaning step numerous times could the complex be removed. The calibration plot using CAA ligand displayed a non-zero intercept due to the irreversible adsorption, and the buffer response was only used after exposure to V(V) containing samples (Figure 2.3).

2.3.1.3. *Protective Polymer Films for Added Stability*

The pretreatment of biological samples often requires harsh conditions and the use of chemicals such as hydrogen peroxide, a strong oxidant that is known to oxidize Bi. We were interested in robust electrodes that can tolerate residual H_2O_2 ¹¹ and resist fouling of the Bi surface by biological materials that might be present in the pretreated samples. We have thus investigated the use of a protective layer on the Bi surface to reduce degradation and fouling. Polymer films have been widely used as protective coatings on film electrodes. Nafion films provide several important advantages including added mechanical stability, increases in sensitivity, and resistance to fouling.⁷² Nafion is a linear polymer with sulfonic acid and carboxylic acid groups developed by DuPont in 1962.⁷⁹ The films are chemically and thermally inert and can form thin membranes, and the sulfonate and carboxylate groups can interact with cations by partial or total exchange. However, the anionic polymer will adversely influence the adsorption of the anionic vanadate ion. Indeed, a Nafion film coated from a 1% Nafion solution on a Bi film electrode caused a dramatic decrease in the catalytic reduction peak for V(V)-V(IV).

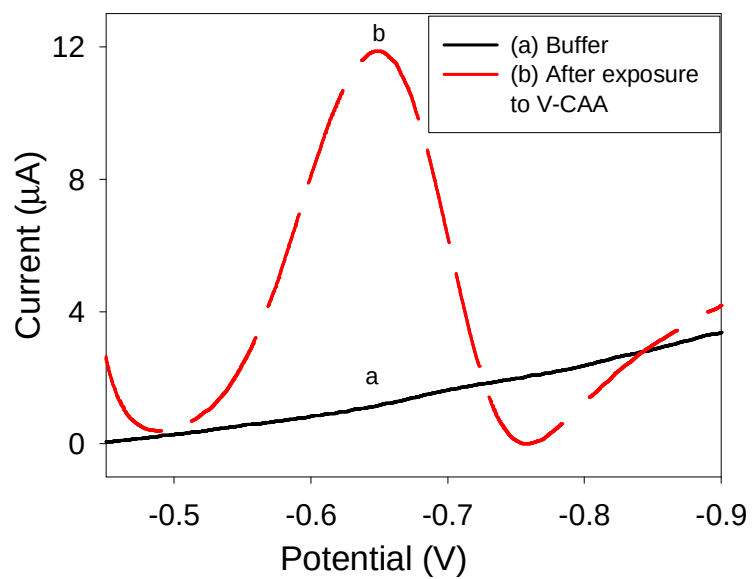


Figure 2.2. Comparison of buffer DPV response (-0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period) at a freshly prepared electrode and buffer response after exposure to V-CAA containing solutions, showing the extent of irreversible adsorption.

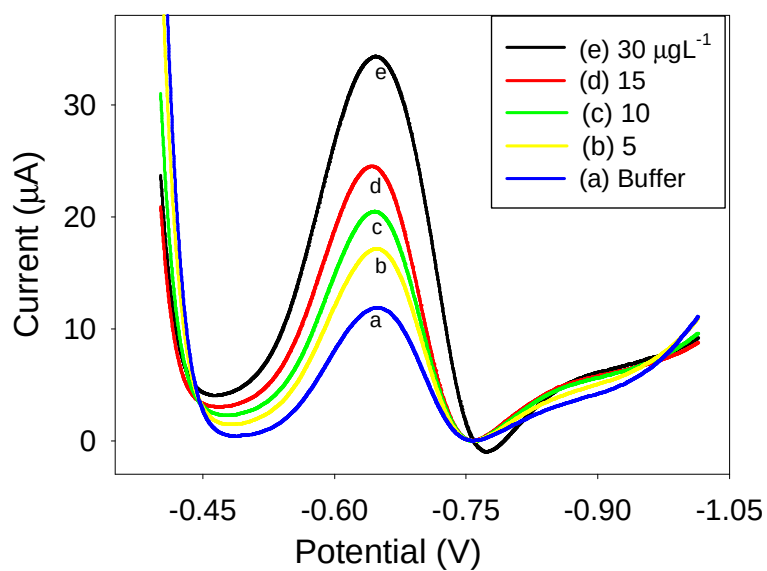


Figure 2.3. CAdSV detection of V-CAA complex accumulation at -0.35 V showing the irreversible adsorption response for the buffer.

Polystyrene films were investigated as a non-ionic alternative to Nafion films. A bare GCE was compared to one coated with a thin polystyrene film to determine what effect the film would have on the electrochemical properties (Figure 2.4). There was a slight decrease in sensitivity in the cyclic voltammetry of a standard solution of potassium ferrocyanide, due to the decrease in the effective area of the GCE from polystyrene coverage. Thick Bi film electrodes coated with polymer showed consistent and reproducible results.

2.3.1.4. Use of Gallic Acid as the Complexing Ligand for Quantitative Analysis

The use of gallic acid (GA) and thick Bi film electrodes gave reproducible results for V(V) concentrations at $\mu\text{g L}^{-1}$ levels with accumulations times of 120 s (Figure 2.5). These results are comparable to results obtained from the CAA complexing ligand at Bi-based thin film electrodes. However, irreversible adsorption of the GA-V complex was not observed at our thick Bi films electrodes as was observed with the CAA-V complex (Figure 2.2). However, detection at ng L^{-1} level was only possible with extended accumulations times (10 min). The DPV scans were background fitted and subtracted to obtain the six point calibration plot (Figure 2.5) with a linear response: peak current (μA) = $0.0 (0.1) + 3.6(0.2) \times 10^{-3} C_{\text{V(V)}} (R^2 = 0.990)$. While using GA as the complexing ligand solved the problem of irreversible adsorption seen with CAA at thick film electrodes, detection of ng L^{-1} levels required extended accumulation times. In comparison, mercury-coated microwire electrodes require a much shorter (120 s)

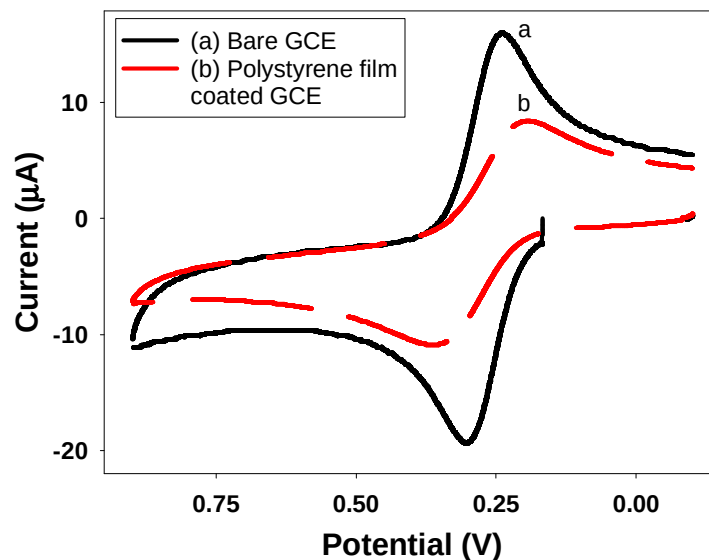


Figure 2.4. Comparison of current response of $[\text{Fe}(\text{CN})_6]^{3-}$ at bare glassy carbon and polystyrene-coated electrodes (0.1 V/s scan rate, 0.001 V sample interval).

accumulation times to achieve similar sensitivity (Part 3).

2.4. Conclusions

While Bi based electrodes are attractive due to the low toxicity of the material, they leave much to be desired when compared to traditional mercury based electrodes. Bi thick films, however, did show a response for CAdSV detection of V(V) using GA as a ligand. The determination of ultra trace levels (ng L^{-1}) required extended preconcentration times to accumulate enough of the complex to generate a usable signal. The thicker films required to obtain the required sensitivity seem to be very fragile and are not ideal for use in systems

that require harsh conditions or reagents such as hydrogen peroxide that might be leftover from the AOP treatment of biological samples. The development of safer alternatives to traditional mercury drop or film electrodes that maintain the required sensitivity is a challenging task, and bismuth based electrodes have proven to partially fill this need. Hopefully the development of more stable Bi films or substrates for the Bi films will advance to the point where they could be a viable technique for clinical based detection of ultra-trace metals in biological fluids.

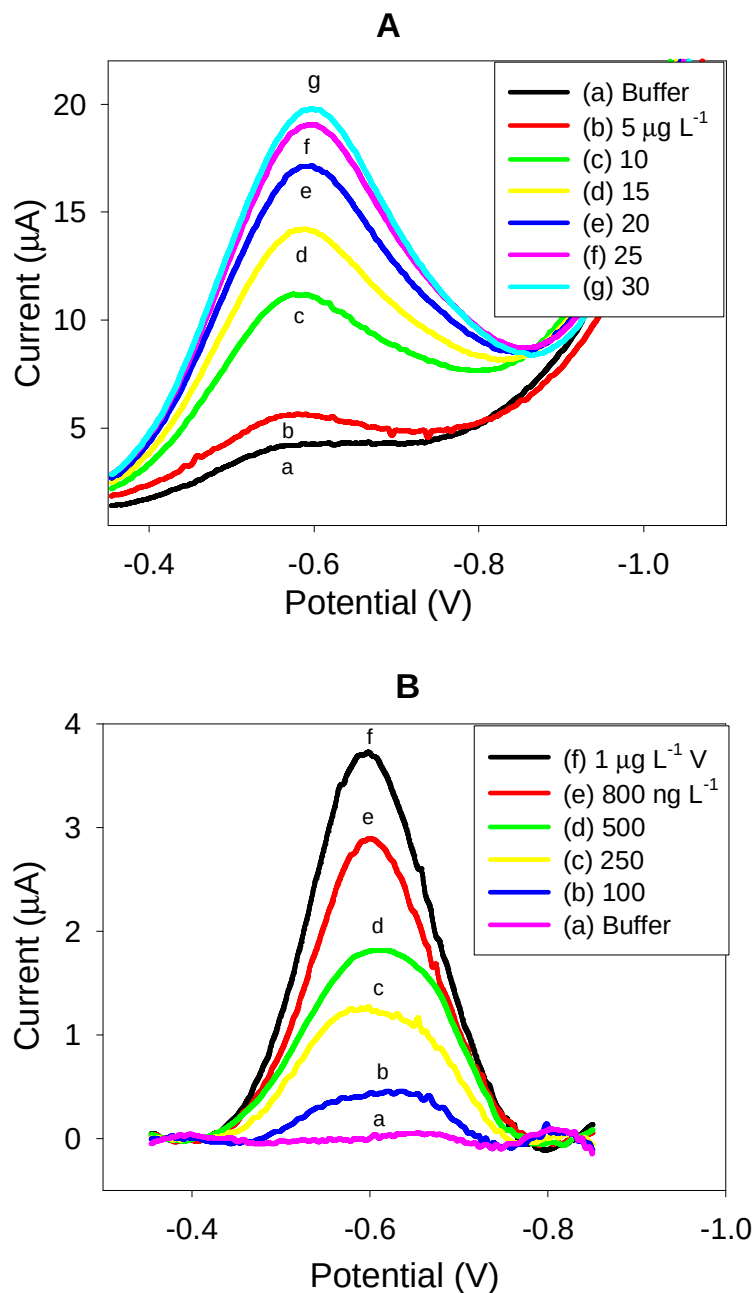


Figure 2.5. (A) V-GA CAdSV detection at polymer-coated Bi film electrode, 120 s accumulation; (B) V-GA CAdSV detection, 600 s accumulation with background fitting and subtraction (-0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period).

Part 3

Gold-Mercury-Alloy Microwire Electrodes for the Detection of Vanadium

3.1. Introduction

While BiFE can be used for trace V(V) detection, the sensitivity of these methods is orders of magnitude higher than mercury drop or film based electrodes.⁸⁰ Mercury drop and film electrodes, while highly advantageous for detection, are not viable approaches for clinical based systems. Therefore, an alternative to mercury-drop and film electrodes that maintains the required sensitivity for ultra trace vanadium detection is highly desired. MWEs have recently been developed for CAdSV detection of iron-dihydroxynaphthalene complex using bromate as an oxidant.⁸¹ Gold forms amalgams with mercury, immobilizing it on the electrode and thus lowers the risks of toxicity. The alloys are more stable and are more sensitive electrodes upon multiple amalgamations.⁸² This section reports our work in the development of aqueous V(V) analysis by CAdSV using gallic acid as the ligand. MWEs have been demonstrated for use in CAdSV detection of V(V) for the first time with a detection limit of 0.88 ng L^{-1} . An electroanalytical protocol has been optimized and characterized to develop an effective CAdSV technique for V(V) analysis. The use of microwire electrodes produces less mercury waste than purely mercury-based electrodes while maintaining a high degree of sensitivity needed for demanding applications. MWEs are also shown to be effective for detection of V(V) in untreated river water by the standard addition method and the method has been validated by quantification of a V(V) standard of unknown concentration.

3.2. Experimental

3.2.1. Reagents

All reagents were purchased from Fisher Scientific unless stated otherwise. Sodium acetate trihydrate (NaOAc) was dissolved and the pH adjusted (pH 5.0 unless stated otherwise) with acetic acid to make 0.1 M NaOAc buffer. The buffer contained appropriate amounts of gallic acid (0.2 mM unless stated otherwise) and vanadium standard solution. Stock solutions of 0.356 M potassium bromate (Mallinckrodt) in 0.1 M NaOAc buffer were prepared by dissolving the appropriate amounts of each in DI water and adjusting pH to 5.0. Stock solutions of vanadium (5000 mg L^{-1}) were prepared by dissolving sodium metavanadate in a small amount of water and nitric acid (HNO_3) and diluting the solution to the final concentration with 5% HNO_3 or obtained from commercially available AA standards (1000 mg L^{-1} , Ricca). Vanadium standards were made by adding the appropriate volume of stock solution to prepared buffer solutions. Buffer solutions were used for a maximum of one week and stored at 4°C when not in use. Mercury plating solutions (400 mg L^{-1}) were made by dilution of a 1000 mg L^{-1} AA standard solution (in HNO_3 , Fisher).

3.2.2. Instrumentation

Electrochemical measurements were conducted using an Electrochemical Workstation (650A/440A, CH Instruments, Austin, TX) connected to a computer. The working electrode was an in-house fabricated mercury-coated gold micro-wire working electrode. Ag/AgCl (model CHI111, CH Instruments) and platinum

wire were used as reference and counter electrodes, respectively. The counter electrode was torched in a flame prior to each use. The electrodes were placed in a 25 mL electrochemical cell for voltammetric detection. All glassware was first cleaned in a base bath followed by soaking in 1 M nitric acid and was rinsed numerous times with DI water before use.

3.2.3. Electrode Fabrication

Mercury-coated gold micro-wire electrodes (MWEs) were produced based on previously published procedures.^{81,82} Briefly, 100 μm diameter gold wire (99.99%, Aldrich) was cut into approximately 2 cm lengths and inserted into the end of a disposable 200 μL pipette tip. A small amount of silver conducting epoxy was placed on the end of a copper wire (Fisher) and inserted into the top of the pipette tip until it nearly reached the end of the tip. The copper wire was turned until the gold wire also rotated to ensure electrical connection. The tip was then passed through a flame to melt and seal the plastic to the gold wire. The exposed gold wire was then cut before use to approximately 2-3 mm in length (Figure 2.1). Mercury was coated from a solution of 400 mg L^{-1} Hg by applying a potential of -0.4 V for 600 s. The electrodes were then activated several times by applying a -3 V potential for 3 s. Electrodes could be used for several days without significant losses in sensitivity and mercury could be re-deposited several times on Au wire.



Figure 3.1. Disposable mercury-gold–microwire electrode with a 100 μM diameter gold wire inserted into a 200 μL disposable pipette tip.

3.2.4. Analysis Procedure

Acetate buffer (19 mL) with gallic acid (0.2 mM) was pipetted into a voltammetric cell. All solutions were deoxygenated by bubbling with nitrogen gas for 5 min before analysis. Potassium bromate solution (1 mL) was added at the time of measurement. The micro-wire electrode was activated inside the analyte solution at -3 V for 3 s by adding a preconditioning step in the CHI software. Preconcentration times were also built into the scan using the CHI software and stirring was applied followed by a 15 s period with no stirring before the scan. Differential pulse voltammetry (DPV) scans were then obtained (0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period).

The electrode was held at a potential of -0.35 V with stirring to deposit the V-GA complex on the surface of the working electrode. To do this, the stripping mode in the CHI software and a time of 600 s were set. The stirring was turned

off 15 s before the start of the potential scan. The DPV scanned from -0.35 to -0.85 V (0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period) to generate the voltammetric scans. The electrode was cleaned in buffer solution by applying a potential of -1.2 V for 40 s with stirring. The resulting plots were background fitted and subtracted using CHI software.

3.3. Results and Discussion

3.3.1. Mercury-Coated Gold Microwire Electrodes for Use in CAdSV

Detection of V

MWEs were used until there was a notable decrease in sensitivity after which they could be redeposited and used again many times. It is essential to calibrate the electrode each time it is used as the sensitivity does change between days or Hg depositions. These electrodes are easier to make than labor-intensive micro-disc electrodes and offer better sensitivity due to the larger area of the electrode.⁸² MWEs have an overpotential for the direct reduction of bromate, which allows for catalytic detection of complexes at more positive potentials than the potential of direct bromate reduction. Additionally, the small size of the electrode produces a steady-state mass transport condition and resulting constant current with little or no stirring during the deposition step. A further advantage of MWEs is that they have been demonstrated to work in flow injection systems for CAdSV detection of Fe.⁸¹ This method could be easily adapted to flow analysis of V(V) for increased automation, and perhaps an on-line preconcentration technique could be coupled if higher sensitivity were

needed.^{74,83} Initial experiments at a 100 μm diameter electrode showed a CAdSV catalytic V(V)-GA peak in the presence of bromate at -0.55 V similar to that reported on a hanging mercury drop electrode.⁶⁹ The response increased linearly with added concentration of V(V) in the 50-1000 ngL^{-1} range.

3.3.2. Optimization of the Catalytic Signal

The experimental conditions were optimized by changing various parameters of the detection method. The standard conditions of pH 5.0 (acetate buffer), 100 μM GA, 10 mM BrO_3^- , a 120 s deposition at -0.3 V were kept constant while each parameter was optimized. A 3 s activation at -3 V was used immediately prior to DPV scans.

3.3.2.1. Optimization of pH

Variation of pH showed that the peak current was most sensitive at pH 5 (Figure 3.2). This is consistent with the reported work at mercury drop electrodes. The pK_a of GA is 4.45, and thus at $\text{pH} > 4.5$, an increase in pH leads to an increase in gallate anion concentration which in turn increases the formation of the V(V)-GA complex. However, at $\text{pH} > 5$ the dissociation of metavanadate increases as well, and thus it is expected that less V(V)-GA complex would form.⁶⁹ The peak potential also shifts in a more negative direction with increase in pH. Therefore, it is reasonable that pH of 5 in 0.1 M acetate buffer was found to be optimum.

3.3.2.2. Effect of Ligand Concentration

Next, the concentration of gallic acid was optimized (Figure 3.3). Increase in the concentration of GA from 0 to 1 mM showed a large increase at first, which leveled off at higher concentrations. For further results, 200 μ M GA was used as there was no significant gain in peak current at higher concentrations.

3.3.2.3. Effect of Oxidant Concentration

The sensitivity increased with increased concentration of bromate (Figure 3.4). There was little change between 0 and 7 mM. Between 7 and 15 mM, the increase was more dramatic, followed by a smaller change after that. Thus, 15 mM was chosen as the optimum concentration of bromate. It is important that

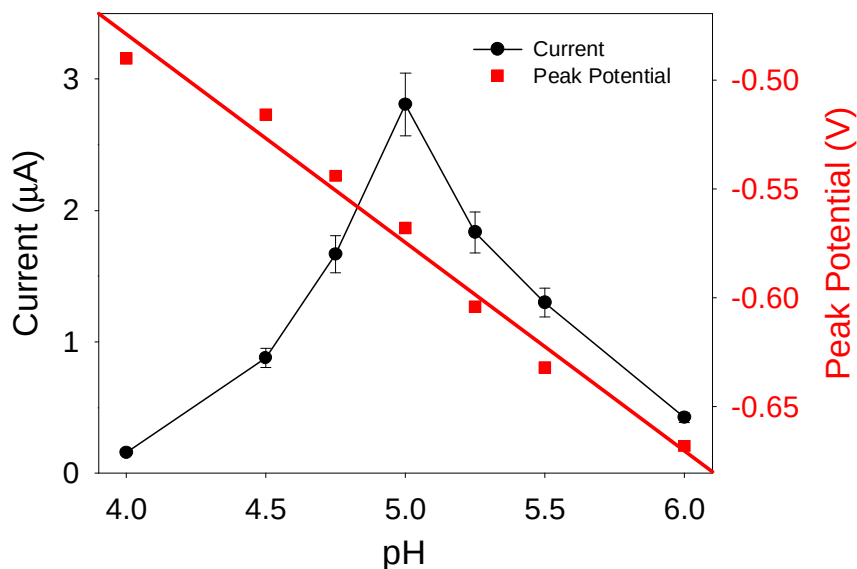


Figure 3.2. Signal optimization for buffer pH, 0.1 M sodium acetate buffer, pH 5.0, 100 μ M GA, 10 mM bromate, -0.3 V accumulation potential, and 120 s deposition time.

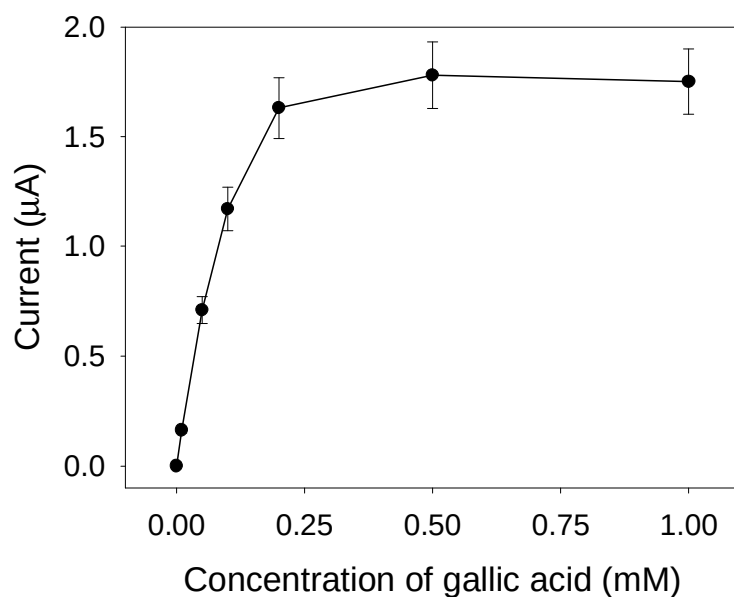


Figure 3.3. Optimization of concentration of GA ligand for vanadium detection by CAdSV.

bromate be added to the solution only at the time of measurement. Buffer solutions containing GA change color from clear to a slight yellow color after the addition of bromate. The solutions were only stable for a short time after the addition of the oxidant. Therefore, the bromate solution was added to each sample individually before measurement and the measurement was completed within 3 min of the addition. New solutions are required for each measurement.

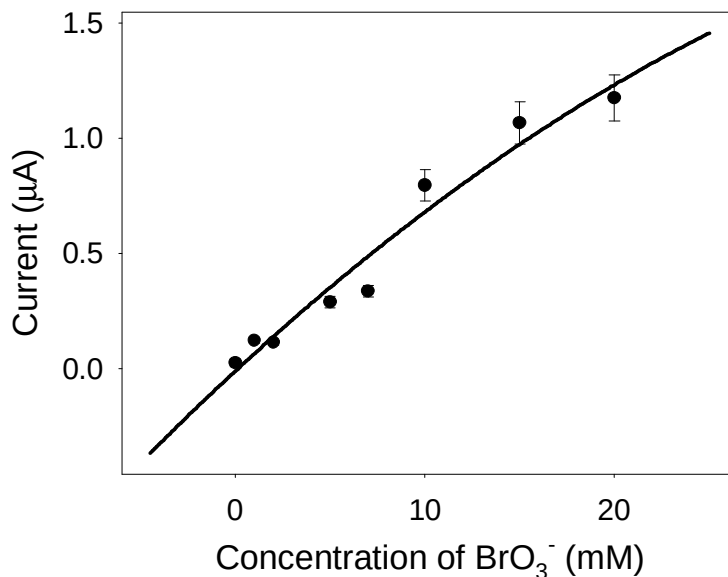


Figure 3.4. Optimization of bromate oxidant concentration for vanadium detection by CAdSV.

3.3.2.4. Selection of Deposition Potential and Time

The deposition potential was optimized by varying it from -0.2 to -0.4 V. Peak current remained statistically constant producing a satisfactory stripping wave from -0.2 V to -0.325 V. At potentials >-0.3 V, the deposition potential was closer to the start of the peak and in the case of -0.4 V, the peak started immediately at the onset of the scan reducing the effect peak height and peak area. All accumulations after this point were at -0.275 V. The deposition time was also investigated (Figure 3.5B). The accumulation time was increased from 10-420 s at -0.275 V. The peak current increases linearly from 10-100 s and

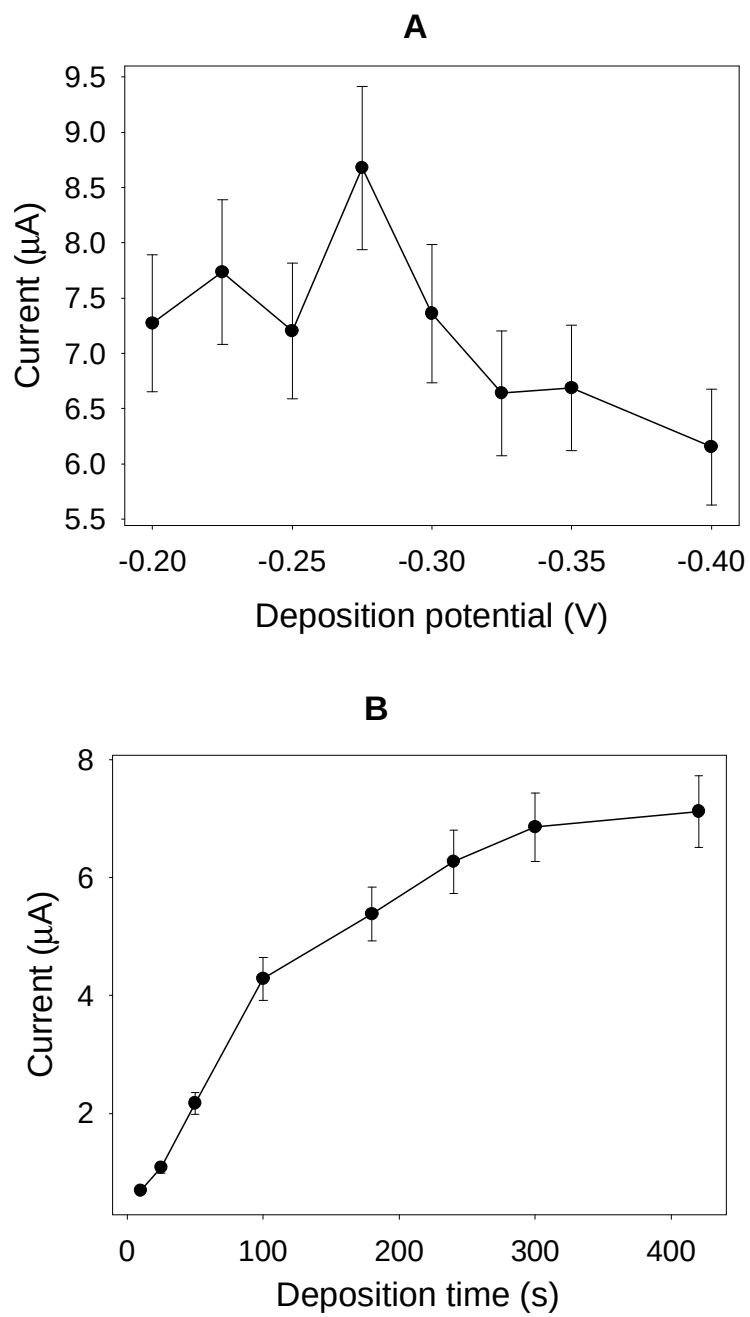


Figure 3.5. Optimization of deposition potential (A) and time (B) for vanadium detection by CAdSV

begins to level off afterwards. Accumulation times of >300 s appear to make little difference.

3.3.3. Performance of the Electrode

3.3.3.1. *Postwave Adsorption Peak*

MWEs were used to generate calibration plots using the optimized parameters. Figure 3.6 A shows the calibration in the 0-1000 ng L⁻¹ range. At low concentrations two peaks are evident, one at -0.55 V and the other at -0.65 V. At higher concentrations, the first peak dominates. While the reason for this phenomenon is unknown, one possible explanation is that the more negative peak is a postwave adsorption peak, first studied by Brdicka and later by Wopschall.^{84,85} Two forms of the complex could exist, one from a strongly absorbed monolayer directly on the surface of the electrode and the other from weakly absorbed multi-layers. At low concentrations, the relative amount of both species is evidently more or less equal and thus two peaks are evident. At higher concentrations, the surface of the electrode is saturated with the complex and the more positive peak from the multi-layer absorption dominates. Given that this system is catalytic, the chemical reaction of the oxidant with the monolayer complex might also be limited when the multilayer species is more prevalent. The multilayer complex would consume the oxidant in the diffusion layer, leading to selective catalytic peak enhancement for that complex. With no oxidant, there would be only non-catalytic reduction current for the monolayer species. Accordingly, it was found that the area of both peaks was best for

generating calibration plots when two peaks were present. A similar response phenomenon was seen at a HMDE with CAA as the ligand for V(V) detection. In this study, two peaks were observed when the concentration of CAA was lower than that of V(V). As the concentration of ligand was increased, the more positive peak disappears and the negative peak gets stronger.⁶⁷ While this could have some implications about the ratio of GA-V(V) in the current study, it is unlikely due to the fact that GA is present in great excess (10^4 M).

3.3.3.2. Reproducibility and Limit of Detection

The calibration data were fit using both linear and hyperbola equations (Figure 3.6B). The calibration in Figure 3.6 yielded the following linear plot: peak area ($V \cdot \mu A$) = $0.5(0.2) + 1 \times 10^{-2} (0.04 \times 10^{-2}) C_{V(V)}$ ($R^2 = 0.9927$). Repetitive scans of a 50 ng L^{-1} standard produced reproducible reduction peaks after two min accumulation times with a limit of detection of 0.88 ng L^{-1} based on 3 times the standard deviation. Even with extended accumulation times (10 min), bismuth electrodes could not produce the sensitivity of mercury-based counterparts.⁶⁶ As noted earlier, MWEs offer comparable detection limits to mercury-drop electrodes while using much less mercury.⁶⁷ Furthermore, mercury forms an alloy with gold making the mercury films more stable and safer than mercury drop or films electrodes. For these reasons we believe that mercury-coated microwire electrodes are superior for applications where lower detection limits are required.

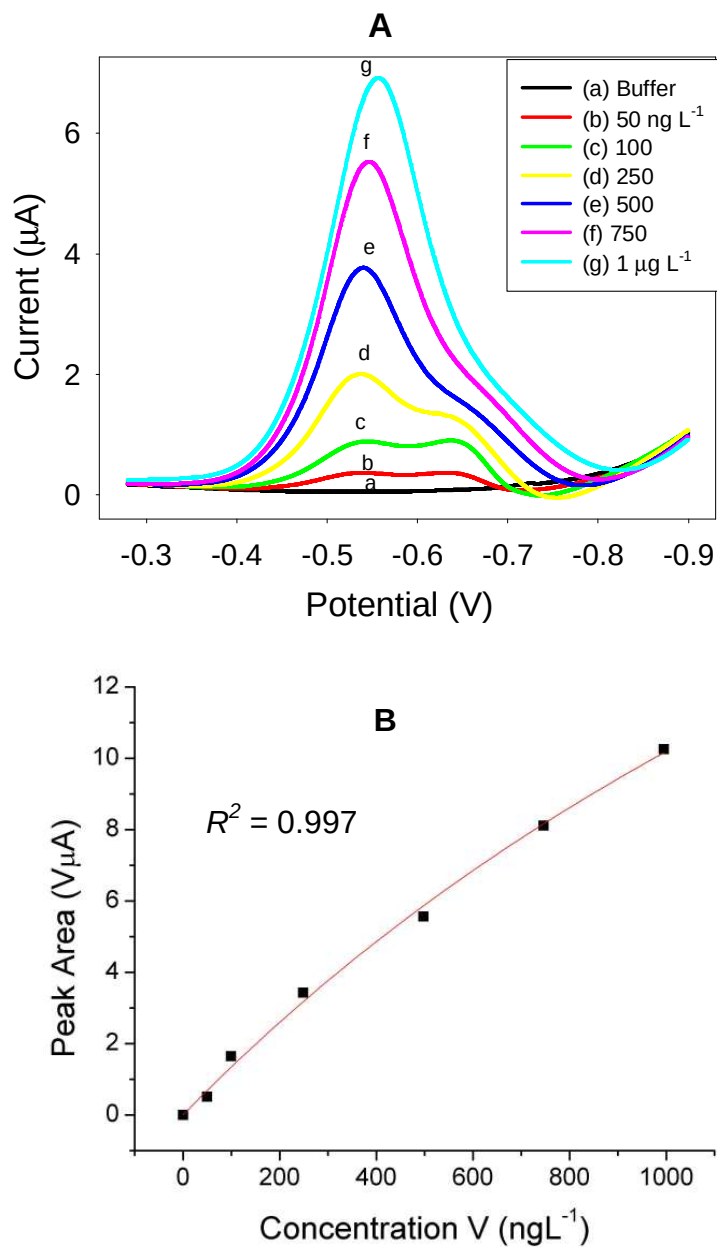


Figure 3.6. (A) Differential pulse voltammograms for increasing levels of vanadium(V), -0.275 V accumulations for 120 s; (B) Hyperbola fit.

3.3.3.3. Interference Study

Several common inorganic anions were tested for their interference on V(V) CAdSV detection. The effect of various metal ions at concentrations 20 times that of a 500 ngL^{-1} V(V) sample is shown in Table 3.1. While most metal ions did decrease the overall current of the V(V) CAdSV peak, the peak was, however, still present in all cases. Mo(VI) showed the most significant change to the background response with what appears to be two small non-catalytic peaks (-0.28 and -0.7 V). As is expected, the model surfactant Triton X-100 produced a significant decrease in the peak current due to the fact that it absorbs at negative potentials.⁸⁶ An in-depth interference study at HMDE for the same GA-V(V) CAdSV system tested 28 inorganic species and showed that organic acids such as citric acid and oxalic acid caused the stripping wave to disappear (Table 3.2.).⁶⁹ Because of the matrix effect on the overall sensitivity of the measurement, it is suggested that the sensitivity of each sample be ascertained separately by means of the standard addition method.

3.3.4. Validation of Method

3.3.4.1. V(V) Analysis of Standards

To validate the accuracy of the new technique, an expired vanadium AA (exp. date 1987) standard was quantified by both flame AA and the proposed protocol using standard addition of a certified AA standard (Table 3.3.). The AA analysis resulted in a concentration of $1078 \pm 2 \text{ mg L}^{-1}$. After a 10^6 times dilution

Table 3.1. Effect of interferences on CdSV determination of V(V) with GA

Interference	Peak influence	Recovery of 0.5 $\mu\text{g L}^{-1}$ V(V) together with 10 $\mu\text{g L}^{-1}$ interference
Ni(II) ^a	Increase peak current	<1 σ of 0.5 $\mu\text{g L}^{-1}$ mean
Cr(VI) ^a	Decrease	
Mo(VI) ^a	New peak at -0.7 V and baseline shift at -0.3 to -0.4 V	
Fe(III) ^a	Decrease	
Al(III) ^a	Decrease	
Se(IV) ^a	Decrease	
As(III) ^a	Decrease	
Sn(II) ^a	Decrease	
Triton X-100 (50 mg L ⁻¹) ^b	Completely suppressed	

^a Reference standard solutions for atomic absorption of these elements (1000 mg L⁻¹, Fisher Chemical) were used.

^b Triton X-100 = Polyethylene glycol mono [4-(1,1,3,3-tetramethylbutyl)phenyl] ether (Acros)

to ng L^{-1} level, the MWE technique resulted in a concentration of $1098.6 \pm 0.05 \text{ ngL}^{-1}$, a difference of 1.9%.

3.3.4.2. Analysis of Emory River Water

River water samples were collected from the Emory River near Harriman, Tennessee. River water was acidified with nitric acid, filtered, and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and the new CAdSV method for V(V) content. For the electrochemical analysis, river water was diluted to ng L^{-1} concentrations to make solutions containing buffer components. All conditions were the same as those reported in the optimization procedure. A vanadium level of $31.13 \pm 0.05 \mu\text{g L}^{-1}$ was found in the original water sample by use of the standard addition method [4 additions of 25-100 ng L^{-1} V(V) to diluted ($\sim 50 \text{ ng L}^{-1}$) river water] resulting in a linear response: peak height (μA) = $-0.18(0.01) + 3.5(0.2) \times 10^{-3} C_{\text{V(V)}} (R^2 = 0.9934)$ (Figure 3.7). This result was validated by the ICP-OES (309.31 nm) concentration of $29.1 \pm 4.6 \mu\text{g L}^{-1}$ by standard addition method (Table 3.2). These results are promising for the feasibility of use for these electrodes in possible field-testing applications.

3.4. Conclusions

The detection of ultra-trace vanadium(V) was successful using both mercury-coated gold micro-wire and bismuth film electrodes. The parameters for detection at MWEs were optimized for pH, concentration of ligand and oxidant, deposition potential and deposition time. MWEs offer detection limits that rival

that of pure mercury-based electrodes. However, these electrodes eliminate mercury waste and stabilize it by amalgamation with gold. They have been demonstrated for use in river samples without pretreatment and were validated by comparison of AA results. Bismuth-based electrodes have limited lifecycles, insufficient detection limits for vanadium, and are not easily automated for clinical based trials of the detection of metals in biological samples. MWEs are robust, have low detection limits, and have been demonstrated to be compatible with flow injection analysis.⁸¹ We are investigating pretreatment of biological samples for V(V) analysis and the use of the electrochemical methods here to determine vanadium concentrations in these samples.

Table 3.2. Interferences of CAdSV detection of V(V) at HMDE⁶⁹

Interferant	Effect on stripping wave/Concentration where no interference was observed
citric acid and oxalic acid	Wave disappears
tartaric acid	Reduces the sensitivity
Sn(II)	1x concentration of V(V)
Ge(IV), Mo(VI), Nb(V), Ti(IV), W(VI)	10x
Re(VII), Sb(II)	20x
Ta(V), Bi(III), Cu(II)	50x
Cr(III), Ga(III), Pb(II)	100x
Ag(I), Al(III), As(III), Au(III), Cd(II), Co(II), Fe(III), Hg(II), In(III), Mn(II), Ni(II), Se(IV), Te(IV), Tl(I)	1000x

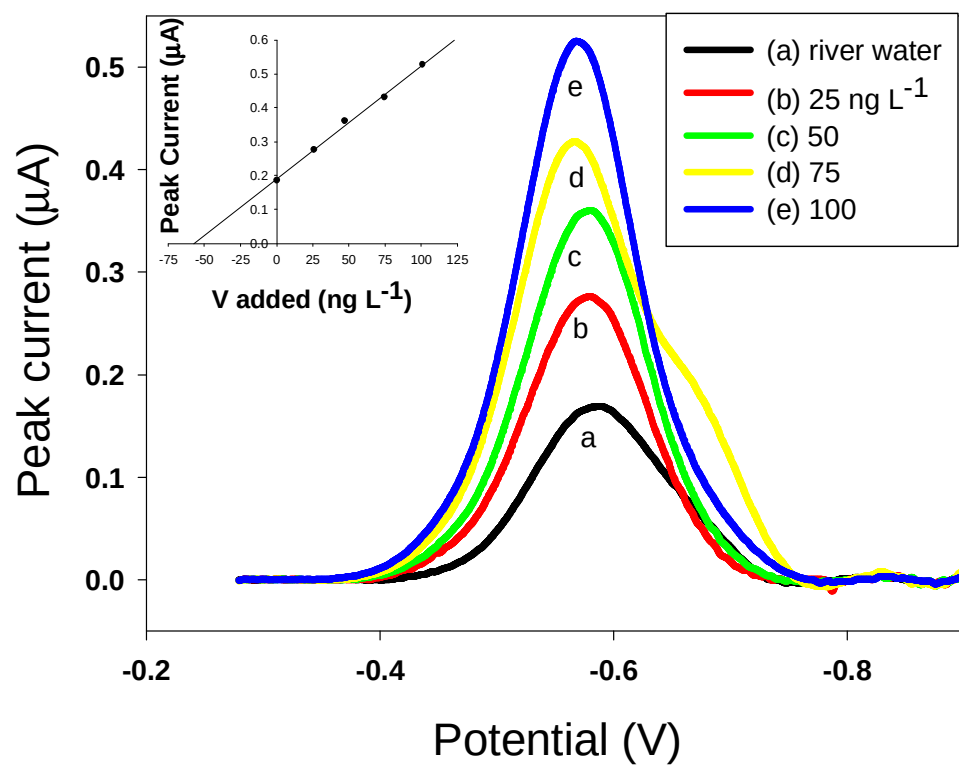


Figure 3.7. Standard addition of V(V) to Emory River water samples. Conditions as in Figure 3.6A with background fitting and subtraction.

Table 3.3. Determination of vanadium by standard addition

MWE CAdSV				AAS / ICP-OES			
Sample	Slope		Intercept	R^2	[V]		
	($\mu\text{A ng}^{-1} \text{L} \times 10^{-3}$)	(ng L^{-1})			(mg L^{-1}) ^a	($\mu\text{g L}^{-1}$) ^b	(mg L^{-1}) ^a ($\mu\text{g L}^{-1}$) ^b
AA							
Standard ^a			-110.36		$3.86 \pm 0.05 \times$	$-5.393 \pm$	1078 ± 2
	5.8 ± 0.1	± 0.03		0.9988	10^{-3}	0.009	
Emory River			$-52.52 \pm$		8.58 ± 0.05	-29.1 ± 4.6	29 ± 5
water ^b	3.5 ± 0.2	0.09		0.9985	$\times 10^2$		

^a concentration unit in mg L^{-1}

^b concentration unit in $\mu\text{g L}^{-1}$

Part 4

Studies of the CAdSV Process for Trace Vanadium and Chromium Analysis

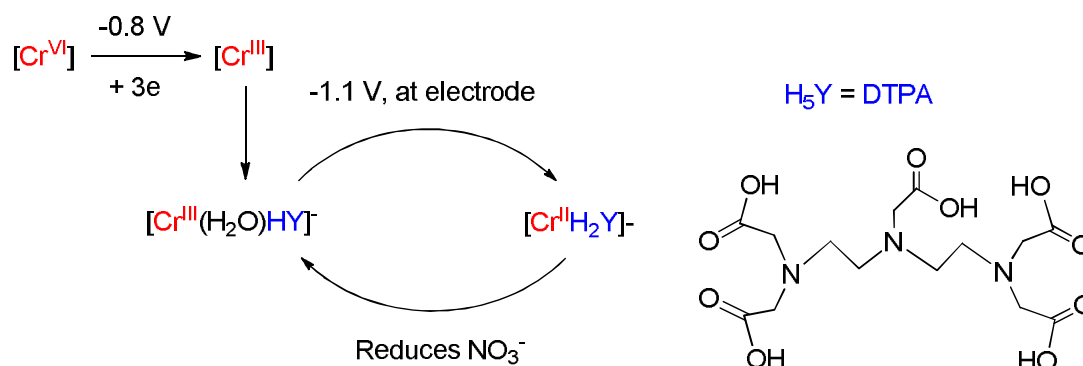
4.1. Introduction

Improvements in sensitivity for standard voltammetric detection methods are achieved by increasing the faradaic signal current to noise current ratio, i_f/i_{noise} . This is typically accomplished by increasing the faradaic current using techniques like square wave and differential pulse voltammetry to reduce capacitive currents or by using methods or electrodes to increase current.⁷⁰ One such method is to accumulate a metal or electroactive complex on the surface of the working electrode. In this technique, a potential is applied which accumulates the analyte on the surface of the electrode, effectively enhancing the reduction/oxidation current by increasing the concentration of the species in the diffusion layer relative to that of the bulk solution. Alternatively, catalytic methods rely on cyclic reactions at the surface of the electrode to regenerate an electroactive species, making it available for multiple cycles between redox states. Catalytic techniques represent a departure from simple nernstian controlled behavior as the current is proportional only to the concentration of the species at the electrode and not directly to the number of electrons consumed or produced as the turnover rate is unknown. The two techniques can be utilized simultaneously to achieve two levels of signal enhancement, termed catalytic adsorptive stripping voltammetry (CAAdSV).

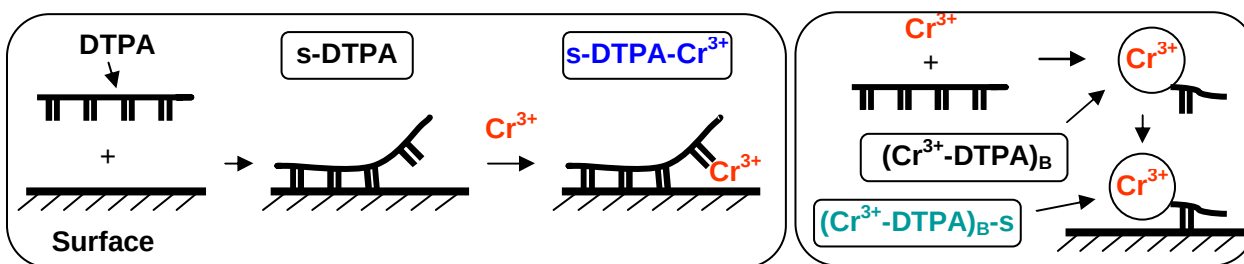
CAAdSV techniques readily achieve high sensitivity and selectivity for ultra-trace metal analysis.^{70,87} The CAAdSV process for Cr(VI) detection (Scheme 4.1) has been used to achieve high sensitive detection of sub-ppt levels of Cr(VI) at mercury based electrodes and ppt levels at bismuth based electrodes.^{11,75,88,89}

These techniques use accumulation potentials to adsorb Cr(VI)-ligand complexes on the electrode while chemical oxidants are used to reoxidize the complex after reduction scan to regenerate the electroactive species. In the CAdSV process for Cr(VI), diethylenetriaminepentaacetic acid (DTPA) is often used to complex Cr(III) produced by the reduction of Cr(VI) at the electrode, forming a complex that is absorbed to the surface of the electrode.⁹⁰ The technique is selective for Cr(VI) because Cr(III) eventually forms an inactive hexaqua complex, thus only freshly reduced Cr(III) will form the active DTPA complex.⁹⁰ Once the complex is accumulated on the surface of the electrode, the potential is swept in the negative direction to reduce the Cr(III) complex to Cr(II) at approximately -1.1 V (vs. Ag/AgCl). Potassium nitrate (NO_3^-) is added to the solution to chemically reoxidize the complex back to the reduced form, forming the basis of the catalytic reaction according to Scheme 4.1.

CAdSV is typically carried out at Hg drop or film electrodes due to their superior accumulation of complexes and negative potential window.^{75,88,91} More recently, Wang and co-workers have pioneered the use of Bi based alternatives as a non-toxic substrate for replacement of Hg based electrodes.^{66,75,92} While CAdSV techniques are widely used for ultra-trace detection, little is actually known about the detection mechanism. Sanders et al. probed the method extensively with electrochemical techniques to develop the proposed mechanism (Scheme 4.1).⁹⁰ A better understanding of how the ligands bind to the metals or how the resulting complexes are absorbed could lead to better developed techniques and designed ligands.



Scheme 4.1. Proposed mechanism for CAdSV detection of Cr(VI).



Scheme 4.2. Schematic showing the formation of s-DTPA- Cr^{3+} and $(\text{Cr}^{3+}\text{-DTPA})_{\text{B-s}}$.

The aim of this work was to attain some basic qualitative measure of the CAdSV process using in-situ techniques to ascertain more information about the process for both Cr determination with DTPA and NO_3^- and V(V) with GA/CAA and BrO_3^- at both Bi and Hg based electrodes. For example, it is not clear if Cr(III)-DTPA first forms in the diffusion layer of the electrode, followed by absorption of the complex, or if the DTPA first binds to the electrode and then subsequently binds Cr(III) (Scheme 4.2). The mechanisms have been probed by the in-situ monitoring of mass changes during the CAdSV process using

electrochemical quartz crystal microbalance (EQCM) for both Cr(VI) and V(V) analysis and surface enhanced Raman spectroscopy (SERS) for Cr(III)-DTPA.

4.2. Experimental

4.2.1. Chemical Reagents and Materials

Potassium bromide (KBr, Mallinckrodt Chemicals), hydrochloric acid (HCl, ACS certified, Fisher), nitric acid (HNO₃, trace metal grade, Fisher), acetic acid (CH₃COOH, glacial, Fisher), sodium acetate (CH₃COONa, ACS certified, Fisher) diethylenetriaminepentaacetic acid (DTPA, ≥99%, Fluka), and gallic acid (anhydrous, 99%, Alfa Aesar) were used as received. The bismuth plating solution, containing 140 mg L⁻¹ Bi, 0.5 M potassium bromide (KBr) and 1 M hydrochloric acid (HCl), was prepared by dissolving bismuth needles (99.998%, Alfa Aesar) in 500 µL of concentrated nitric acid (HNO₃) and adding this to a solution of potassium bromide (KBr) and HCl. Stock solutions of V(V) and Cr(VI) were made by dilution of a 1000 mg L⁻¹ AA standard (Sigma Aldrich) in DI water (DI, 18 MΩ-cm) from a Barnstead International E-pure 4-holder deionization system.

4.2.2. Instrumentation and Analysis

For the EQCM experiments, a Teflon cell was used to house the crystals. Polished, mounted, and bonded gold-coated quartz crystals (International Crystal Manufacturing Company, Inc.) were used as received. The crystals have a fundamental frequency of approximately 7.995 MHz and working electrode

diameter of 0.546 cm. Electrochemical measurements were taken on a CH instruments model 440a potentiostat with EQCM capabilities. In-Situ SERS measurements were obtained from a Horiba Jobin-Yvon T64000 Raman spectrometer inside a specially designed spectroelectrochemical Raman cell. A Ag electrode (3 mm diameter) was made by fixing a rod of Ag inside a rod of polyoxymethylene with a hole drilled just smaller than 3 mm in diameter. A copper lead wire was attached to the reverse side of the disk with conducting silver epoxy.

4.3. Results and Discussion

4.3.1. Studies of CAdSV Processes by Electrochemical Quartz Crystal Microbalance

4.3.1.1. CAdSV of Cr(III)-DTPA System at Bi-Coated Au-QCM Electrodes

In order to gain a deeper understanding of the interaction of DTPA and Cr with the electrode surface during CAdSV detection, studies have been conducted using both Bi- and Hg-coated Au electrochemical quartz crystal microbalances. For the Bi film studies, Au-EQCM electrodes were first exposed to Bi plating solution (3 mL) containing 140 mg L⁻¹ Bi, 0.5 M KBr and 1 M HCl. A deposition potential of -0.25 V was used to reduce Bi(III) to metallic Bi on the surface of the electrode. The resulting current response and frequency shift (Δf) are shown in Figure 4.1. The Δf decreases due to the additional mass of deposited Bi. The current response is typical of diffusion-based deposition¹⁵ with an increase in current at ~200 s, perhaps due to nucleated growth. Assuming completely

uniform growth, an approximate mass of the Bi deposited can be calculated according to the Sauerbrey equation (Eq. 1.2) to be 1.696×10^{-6} g. The total volume of Bi deposited was estimated as 1.73×10^{-7} cm³, based on the density of Bi (9.808 g/cm³). Taking the area of the QCM electrode (0.234 cm²) into account and assuming a uniform cylindrical deposition, the height of the Bi can be estimated as 74 Å. As the distance between bi atoms in the metal is approximately 3.30 Å,⁹³ it can be assumed that the film is multiple layers of Bi thick and covers nearly the entire electrode surface.

Several differences between deposition of Bi on glassy carbon electrodes (GCE) and Au-EQCM should be noted. GC is a superior substrate for Bi deposition at negative potentials due to its extended negative overpotential for hydrogen evolution. There are, however, no commercially available carbon based EQCM manufacturers. Thus we used an adapted procedure for Au-based electrodes. The potential window for Au electrodes is shifted considerably more positive than that of GCE, with the onset of hydrogen evolution appearing around -1.0 V (Figure 4.2). For GCE Bi Film electrodes, the surface of the electrode is coated with a very thin Bi film which appears to isolated islands of Bi (Figure 4.3). This is not desirable when using Au based electrodes as the exposed areas of Au will generate hydrogen bubbles on the surface of the electrode and cause unwanted current and frequency responses. Thus, high concentrations of Bi (140 mg L⁻¹) and more positive deposition potentials (-0.25 V) were used to deposit visibly thick films on the Au surface.

After the deposition of Bi on the QCM, the cell was rinsed with water and a Cr(VI) analysis buffer (3 mL, 0.98 mg L^{-1} Cr, 0.1 M NaOAc, and 0.25 M KNO_3 , pH 6.0) was added to the cell along with $120 \text{ }\mu\text{L}$ DTPA solution (0.1 M in pH 6.0 NaOAc buffer). A deposition potential of -0.8 V was applied to reduce Cr(VI) to Cr(III) and accumulate the electroactive $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})\text{HY}]^-$ complex on the surface of the crystal (Figure 4.4). A drop in frequency was expected during the accumulation step from the addition of mass from the adsorption of the complex. An increase in frequency was, however, observed. This is most likely because bismuth had been oxidized during the cleaning of the electrochemical cell

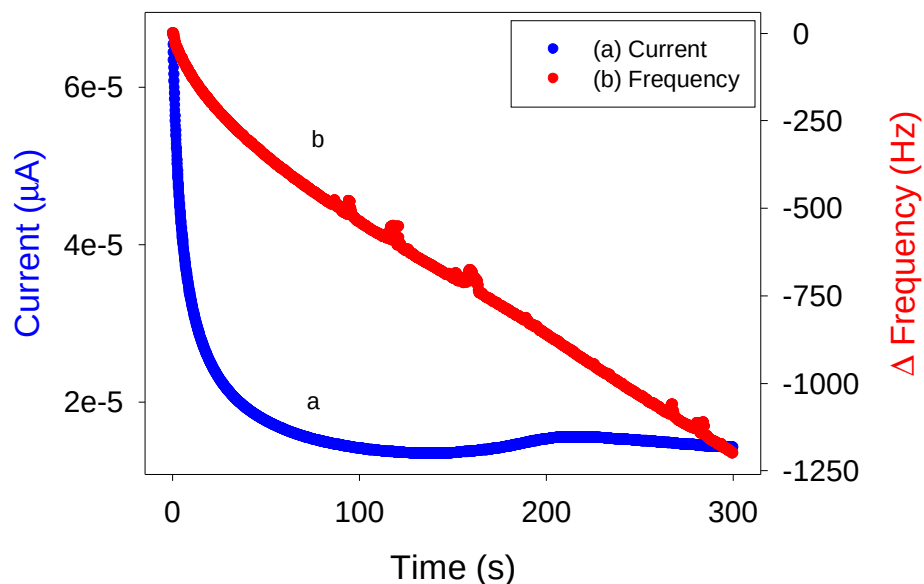


Figure 4.1. Deposition curve (blue) and frequency shift (red) on deposition of Bi film on Au EQCM -0.25 V vs Ag/AgCl, 140 mg L^{-1} Bi, 0.5 M KBr, and 1 M HCl.

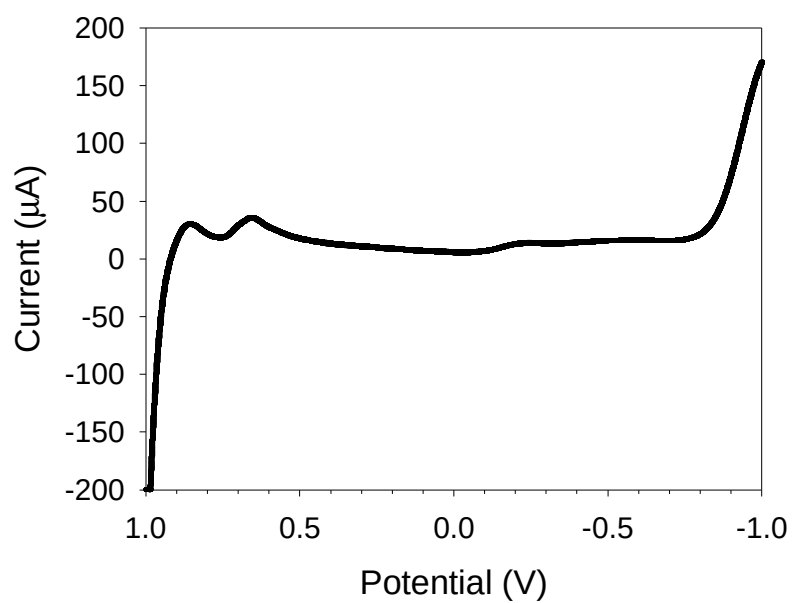


Figure 4.2. Potential window of Au EQCM electrode in 1 M HCl.

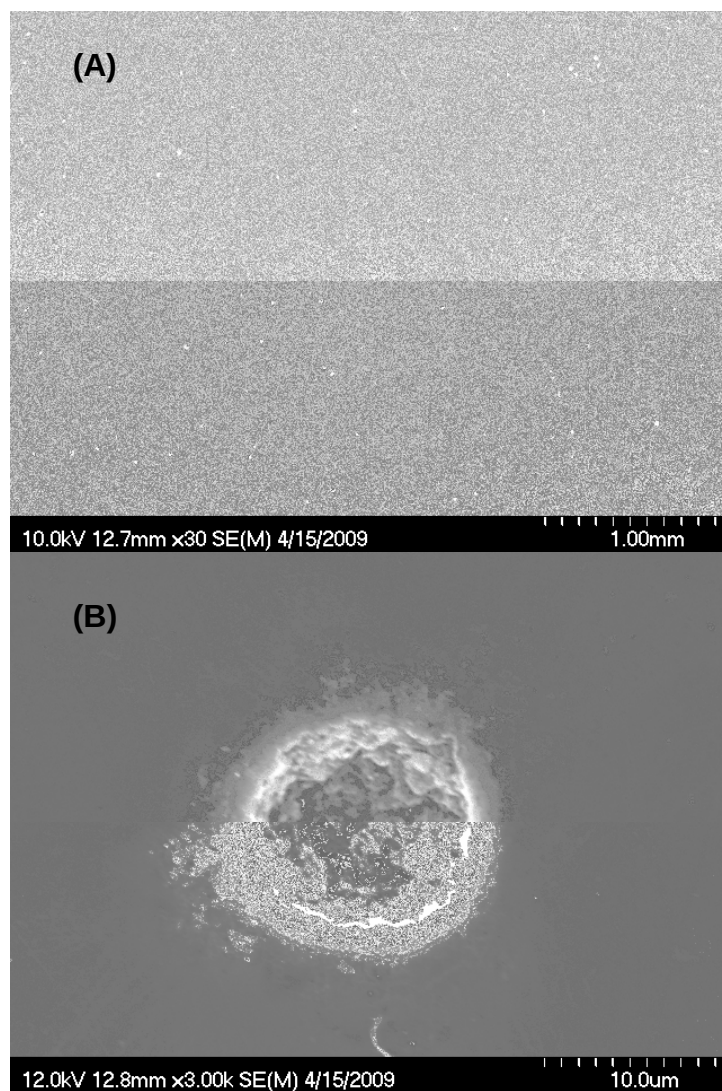


Figure 4.3. SEM images of Bi films on a plate GCE showing nucleated growth of Bi with remaining exposed GC (A) and approximate dimensions of individual islands of Bi (B).

between the Bi deposition and Cr(III)-DTPA accumulation steps.⁹⁴ During this cleaning step the surface of the electrode is exposed to air which could easily oxidize the Bi on the surface of the QCM. The resulting positive shift in frequency could then be the combination of both a smaller frequency drop due to complex deposition and a larger positive shift due to the reduction of Bi oxides (Bi reduction at -0.4 V in pH 6.0 NaOAc buffer) or physical loss of bismuth during the process by hydrogen evolution, with the net effect of an overall positive frequency shift. The Δf due to Cr(III)-DTPA absorption is likely masked as the concentration of Bi/Bi-oxide on the surface is high relative to the amount of

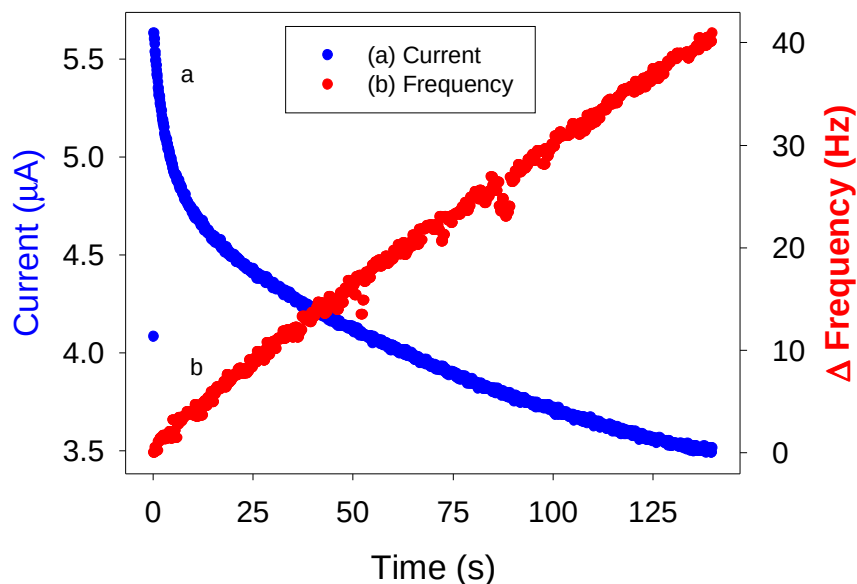


Figure 4.4. Current response and frequency shift during potentiometric Cr(III)-DTPA accumulation at Bi-Au-EQCM electrode, 1 mg L⁻¹ Cr(VI), 120 μL of 0.1 M DTPA, -0.80 V deposition potential for 140 s.

complex expected to absorb during the deposition step. Indeed, some of our work at Bi bulk electrodes was done in a glove box under a nitrogen environment to avoid oxygen all together.

After the accumulation of $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})\text{HY}]^-$ on the electrode (according to Scheme 4.1), a CV scan was initiated to reduce the complex to $[\text{Cr}^{\text{II}}\text{H}_2\text{Y}]^-$ electrochemically at -1.1 V. According to the proposed mechanism, the complex should then be partially stripped from the surface inducing a positive Δf . The CV (Figure 4.5A) produced a reduction peak around -1.2 V, consistent with direct nitrate reduction observations at bulk Bi and thick film electrodes. What is not entirely clear is if the corresponding Δf is due to the stripping of Cr(III)-DTPA from the surface of the electrode or some other potential induced process (direct nitrate reduction or hydrogen evolution). The relatively large shift in frequency during the negative and flat response on the reverse scan seems to be consistent with the proposed mechanism. However, after the experiment, bubbles were visible on the surface of the Bi film. Thus hydrogen evolution continues to occur even at thick film electrodes. It is interesting to note the magnitude of the Δf during the stripping step here is only about 10% of the positive shift observed during the deposition step.

4.3.1.2. CAdSV of Cr(III)-DTPA System at Hg-Au-Alloy QCM Electrodes

Hg-Au EQCM was explored as a possible alternative to the Bi-Au EQCM. As described in Chapter 3, Hg forms alloys with Au and could be used to probe the Cr(III)-DTPA mechanism, as the underlying process is the same for both Hg

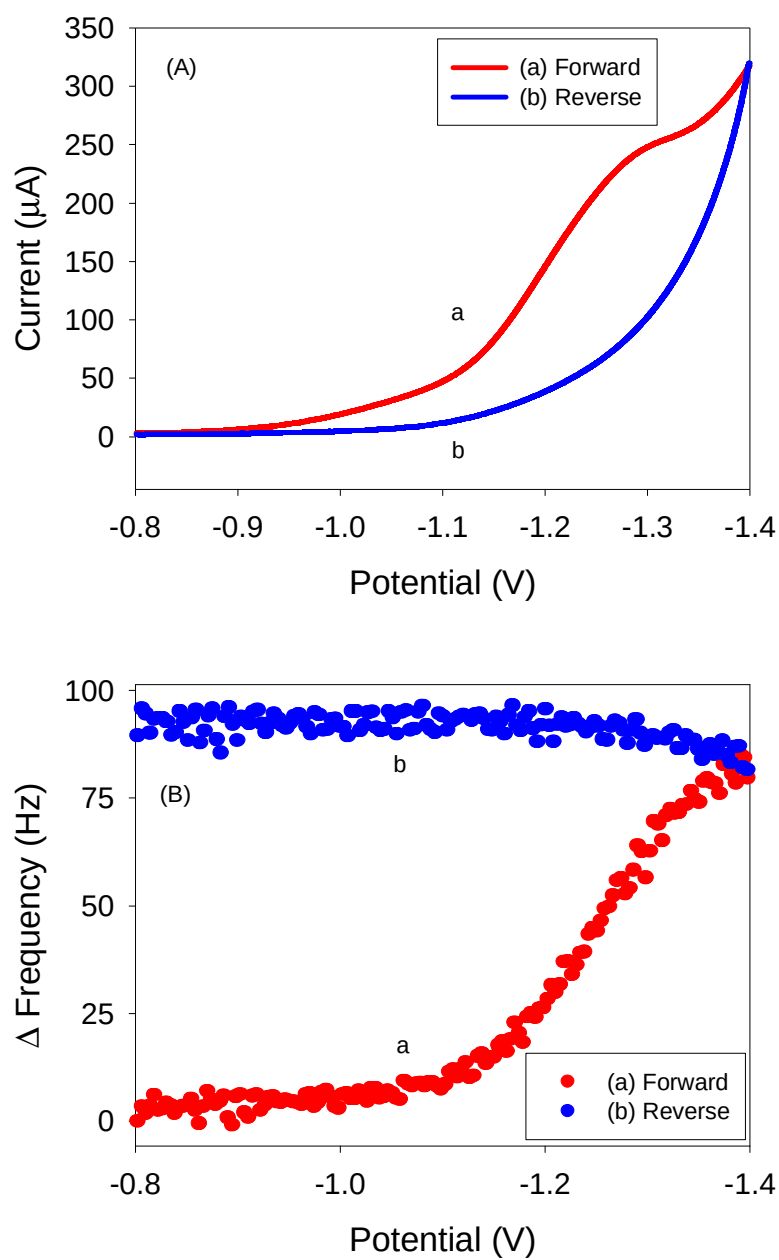


Figure 4.5. Cyclic voltammogram of Cr(III)-DTPA at Hg-Au alloy EQCM electrode (A) and corresponding frequency change (B).

and Bi electrodes. Films were deposited on clean Au EQCM electrodes from a Hg plating solution (3 mL, 10 mg L⁻¹ Hg) at -1.2 V for 300 s (Figure 4.6). During the initial 150 s of deposition, the Δf was very noisy as the deposition potential is well into the hydrogen evolution range of the pure Au electrode (Figure 4.2). As more Hg was deposited and an alloy was formed the noise began to decrease and the electrode behaved more like a traditional Hg electrode. It is known that Hg is not as easily oxidized as Bi. Thus mercury oxides should not have such a marked effect on the frequency response during the Cr(III)-DTPA accumulation step. Again the Sauerbrey equation was used to calculate the volume of Hg deposited as $8.9 \times 10^{-8} \text{ cm}^3$, based on a density of 13.534 g/cm³. If you assume that Hg is deposited on the Au without forming an alloy, this volume would produce a film of approximately 12 Å in thickness.

A decrease in frequency was indeed observed at Hg modified Au-QCM. The decrease is most likely from the accumulation of the complex at the electrode (Figure 4.7), unlike what was observed during the same process at thick BiFEs on QCM electrodes. To ensure that Cr(III)-DTPA accumulation was responsible for the frequency drop during the deposition step, a control test was conducted in a buffer solution to compare the relative frequency change in solutions containing DTPA and Cr(III)-DTPA. As seen in Figure 4.8, Cr(VI) has a dramatic effect on the negative shift in frequency, indicating that the frequency shift is due to Cr(III)-DTPA complex deposition.

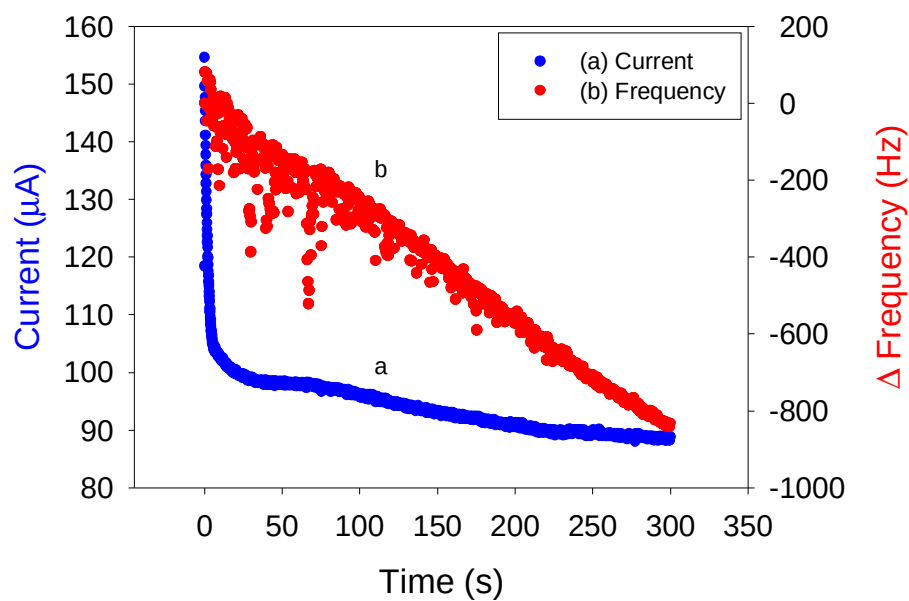


Figure 4.6. Deposition curve (blue) and frequency shift (red) on deposition of a Hg film on Au EQCM -1.2 V vs Ag/AgCl, 10 mg L⁻¹ Hg.

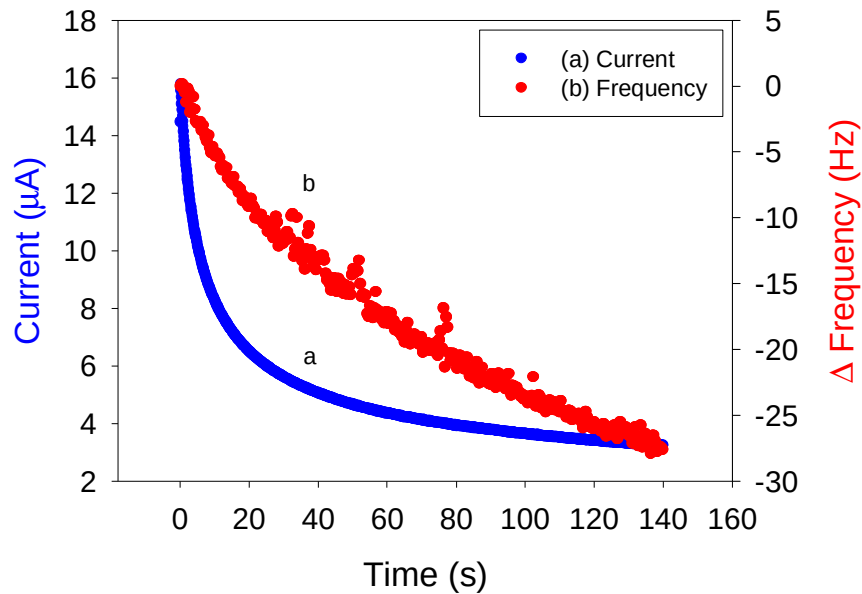


Figure 4.7. Current and frequency shift during potentiometric Cr(III)-DTPA accumulation at Hg-Au-EQCM electrode, 1 mg L⁻¹ Cr(VI), 120 μL of 0.1 M DTPA, -0.80 V deposition potential for 140 s.

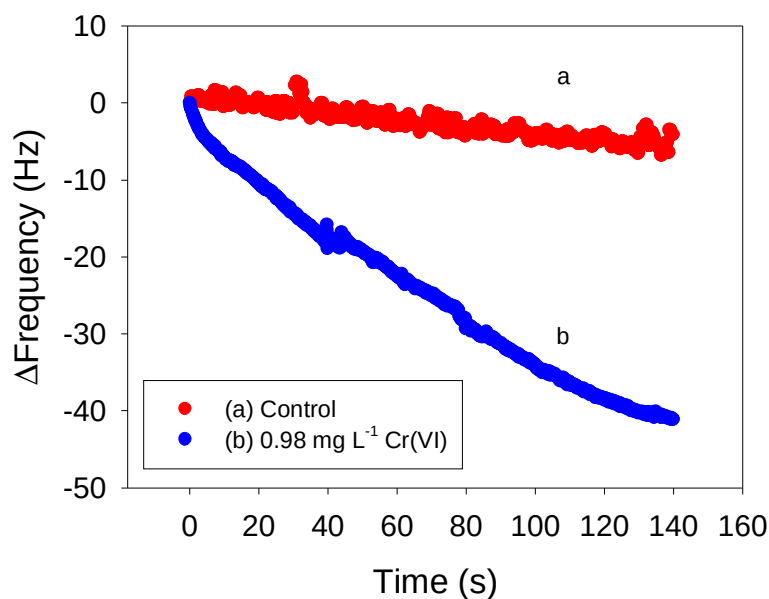


Figure 4.8. Frequency shift for control test (red), 0.1 M NaOAc, 0.25 M KNO₃, 3.8 mM DTPA, no Cr(VI) and identical solution with 0.98 mg L⁻¹ Cr(VI) (blue)

After the accumulation step, a CV scan was obtained in the QCM mode (Figure 4.9). The voltammogram shows the presence of a peak at ca. -1.0 V, which might be the catalytic Cr(III)-DTPA peak. The shift in reduction potential vs BiFEs is expected as the reported peak at GCE-MFE is -1.0 V vs Ag/AgCl.⁷⁵ The lack of a frequency response during the CV scan, however, does not seem to suggest any mass change during this process. This result conflicts with the proposed mechanism and makes any meaningful analysis of mass changes during the actual catalytic stripping response doubtful. Interestingly, when Hg-Au-microwire electrodes were tested for Cr(III)-DTPA detection, direct nitrate reduction was noted at -0.98 V, which is significantly positive shifted from the direct reduction observed at ~-1.4 V at BiFE and BiBEs. This leads to the

conclusion that Hg-Au alloy electrodes are not suitable for use in Cr(III)-DTPA analyses as the direct reduction of nitrate is shifted to potentials more positive than the reduction potential of the Cr(III)-DTPA complex that is needed using nitrate as the oxidant to produce a catalytic response. It is, however, not clear that the voltammetric response observed in Figure 4.9 is due to the Cr(III)-DTPA complex reduction or direct reduction of nitrate.

4.3.1.3. *CAdSV of V(V)-GA System at Hg-Au-Alloy-QCM Electrodes*

For the EQCM study of the V(V)-GA system, Hg alloy deposition parameters used previously in the microwire studies were used for consistency. Thus, Hg solutions (400 mg L^{-1}) were used to deposit Hg for 600 s in a static solution at -0.4 V. Due to the considerably more positive potential and higher concentration of Hg, there is little noise in the frequency shift (Figure 4.10) of the electrode during the formation of the alloy as was seen for the Cr(III)-DTPA studies (Figure 4.6). As expected, the magnitude of the frequency shift is also significantly increased due to the fact that more Hg is deposited and thus the alloy will contain a higher percentage of Hg.

After the deposition of Hg and formation of the alloy, the cell was rinsed with water and a V(V) analysis buffer (3 mL, 0.1 M NaOAc, and 0.2 mM GA, at pH 5.0) was added to the cell along with KBrO₃ solution (160 μL , 0.356 M in pH 5.0 NaOAc buffer) and V(V) stock solutions where needed [150 μL , 1 mg L^{-1} V(V)]. A deposition potential of -0.35 V was applied to deposit the V(V)-GA complex on the surface of the crystal. After the accumulation step a CV scan

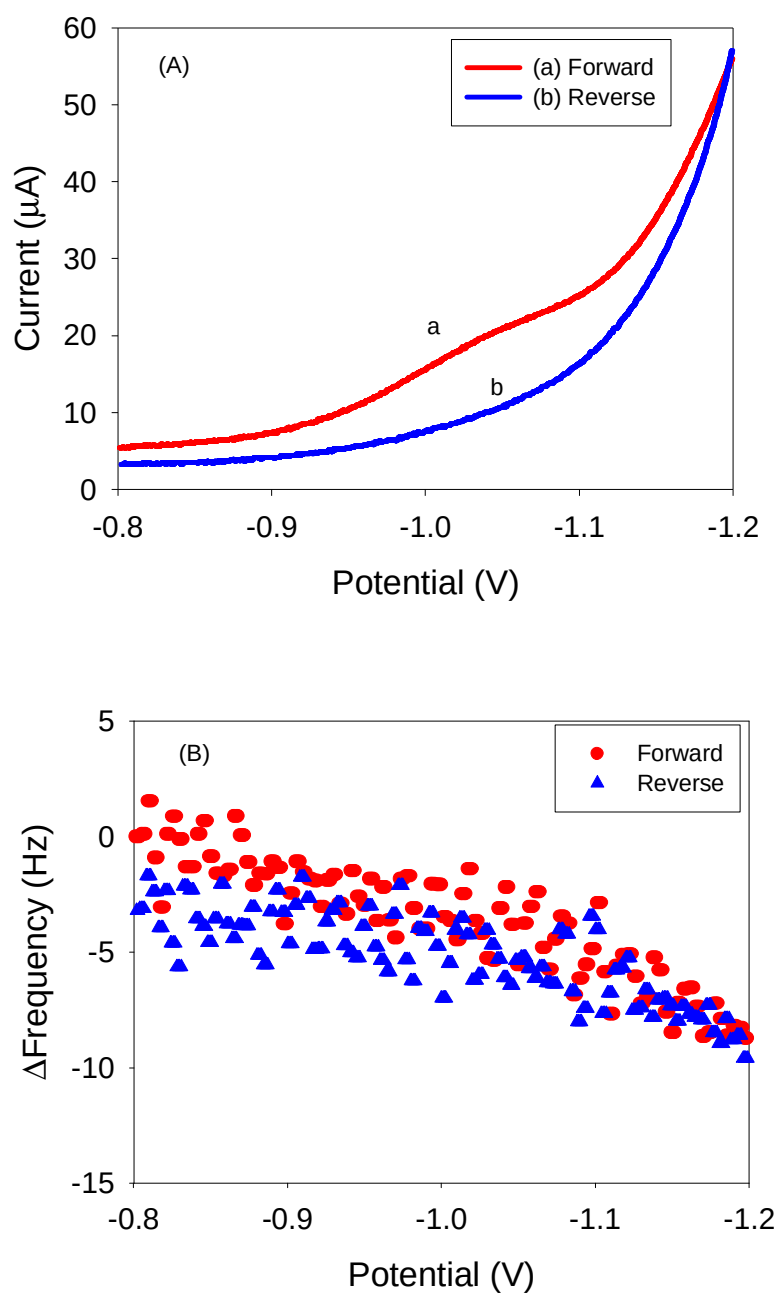


Figure 4.9. Cyclic voltammogram of a Cr(III)-DTPA at Hg-Au alloy EQCM electrode (A) and corresponding frequency change (B).

was run in QCM mode to get the current and frequency response in both buffer with and without V. The buffer response shows slight electroactivity of an unknown species around -0.45 V, but no significant response in the absence of V(V) (Figure 4.11A). The frequency response shows virtually no shift. Thus no mass is being added or stripped from the surface of the electrode (Figure 4.11B). This suggests that gallic acid alone does not absorb significantly to the surface of the electrode. With the addition of $50 \mu\text{g L}^{-1}$ V(V) to the solutions, there is a significant difference observed in the CV response (Figure 4.12A) with the addition of a peak around -0.7 V. The corresponding frequency shift correlates nicely with the proposed mechanism for V(V) detection (Scheme 2.1). In CV mode, the reduction peak is negatively shifted to -0.7 V vs. differential pulse techniques where the V(V)-GA reduction peak appears around -0.6 V. However, QCM is only compatible with linear sweep techniques such as CV. Thus it is not possible to get simultaneous differential pulse or square wave voltammograms and frequency shifts. To prove that the current response is indeed due to V(V)-GA reduction and not some other possible electrochemical reduction such as direct bromate reduction, a DPV scan was obtained (Figure 4.13) from the same QCM electrode while not running in QCM mode (no frequency results obtained). It is clear from this differential pulse voltammogram that, though shifted to -0.7 V, the peak observed in the CV in Figure 4.12A is indeed the same CAdSV V(V)-GA reduction peak as seen at the microwire electrode using DPV.

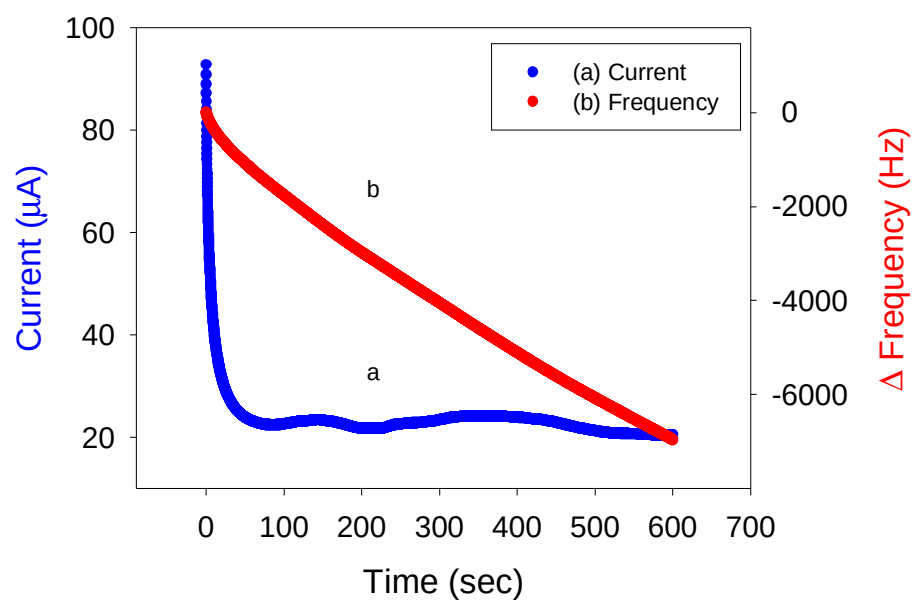


Figure 4.10. Deposition curve (blue) and frequency shift (red) on deposition of Hg film on Au EQCM, -0.4 V vs Ag/AgCl, 400 mg L⁻¹ Hg.

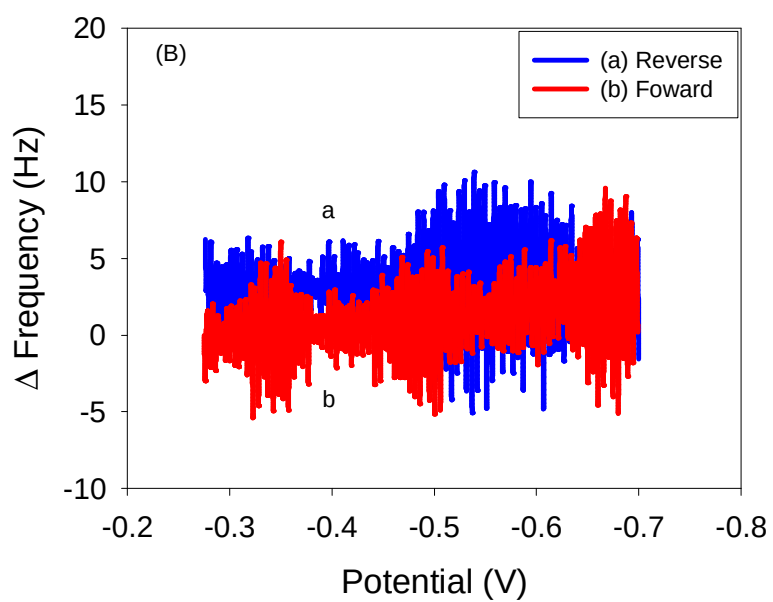
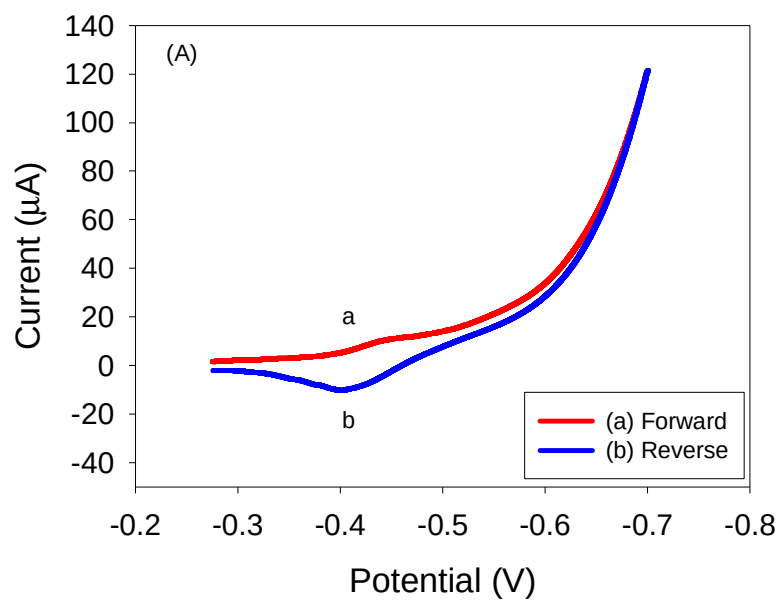


Figure 4.11. EQCM Cyclic voltammogram of a buffer solution at Hg-Au alloy EQCM electrode (A) and corresponding frequency change (B).

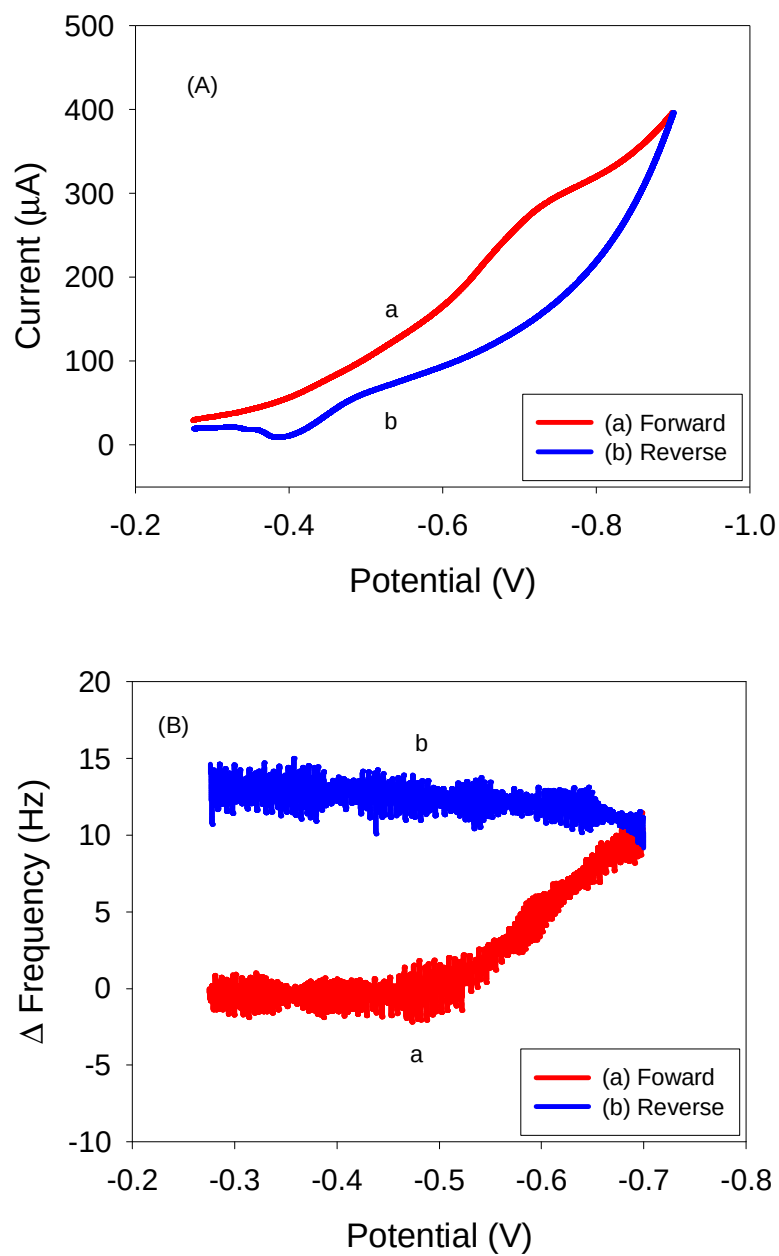


Figure 4.12. EQCM cyclic voltammogram of V(V)-GA at Hg-Au alloy EQCM electrode (A) and corresponding frequency change (B).

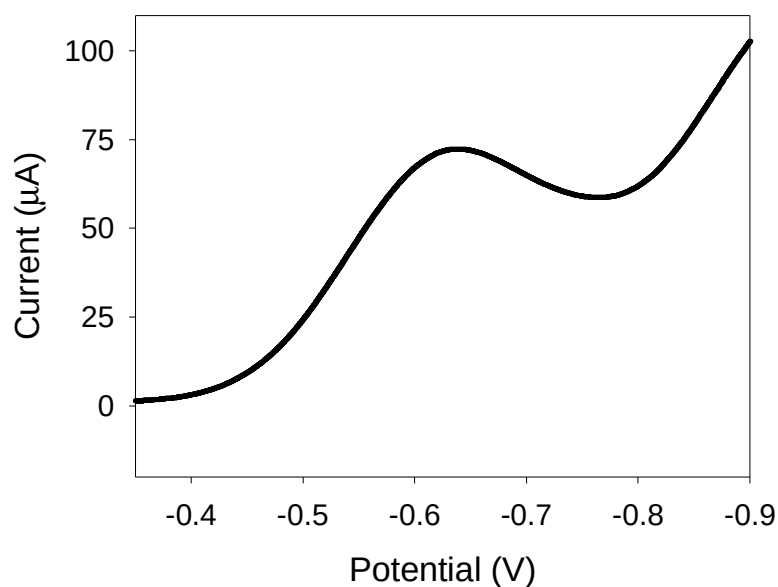


Figure 4.13. CAdSV differential pulse voltammogram at the QCM electrode from buffer solution containing $50 \mu\text{g L}^{-1}$ V(V).

4.3.2. Raman Spectroscopy

There are few spectroscopic techniques with the sensitivity required to detect sub-monolayers deposited on solid substrates. Therefore there is a limitation to the kinds of analytical techniques with the required sensitivity to detect Cr(III)-DTPA complexes on the surfaces of electrodes either in-situ or ex-situ. In-situ vibrational spectroscopy can provide a valuable insight into the interaction of molecules with metal electrode surfaces.⁹⁵ Surface enhanced Raman spectroscopy (SERS) is one such technique. Raman spectroscopy alone is not extremely sensitive, especially in the low-frequency region below 800 cm^{-1} where metal-oxide interactions are often observed.⁹⁵ When surface molecules

are absorbed on certain metal species (i.e., gold, silver or copper), drastic enhancement in the resulting signal can result.⁹⁶ The reasons for this enhancement are not entirely understood, but the Raman lines of adsorbed molecules are often enhanced by factors of 10^3 to 10^9 .¹⁶

The mechanism of electroreduction of several species on Bi-submonolayer-modified Au(111) has been explored through surface enhanced Raman scattering techniques.^{95,97,98} In this work, underpotentially deposited Bi on Au(III) was used to enhance reduction kinetics for both peroxide and oxygen species and observe SERS signals for reactants and products. What is not entirely clear is whether or not the deposited Bi layer only plays the role of a catalyst or if it also contributes to the SERS response. In-situ SERS was explored as a means of monitoring reactions of Cr(III)-DTPA at electrodes surfaces under potential control as a possible technique to determine the nature of DTPA and Cr(III)-DPTA binding during the CAdSV process.

4.3.2.1. In-Situ Raman of Cr(III)-DTPA Process

Solution Raman spectra were first obtained to determine which spectral characteristics of the Cr(III)-DTPA system could be exploited to monitor SERS at the surface of electrodes. Solutions of the inactive form of Cr(III)-DTPA complex were made by the reaction of CrCl_3 with DTPA in aqueous solution at pH 6.0. Deep purple crystalline powders were formed, but a single crystal has not yet been obtained. However, the solution does contain a Cr(III)-DTPA complex from which a solution Raman spectra were obtained and compared to that of DTPA,

pH 6.0 adjusted with NaOH (Figure 4.14). A previous study of adsorbed ethylenediaminetetraacetic acid SERS at Ag electrodes reports Raman peaks at 920, 1344, 1390 and 1633 cm^{-1} for the CH_2 of acetate, $\text{N}^+\text{-H}$ band, COO^- symmetric stretch and COO^- asymmetric stretch respectively.⁹⁹ The solution Raman spectra of free DTPA and Cr(III)-DTPA complex have corresponding peaks at approximately 1640 cm^{-1} . This peak is most likely the asymmetric stretch of the acetate functionality of DTPA. Interestingly, the intensity of the peak does not appear to change once the ligand is complexed with Cr(III). The peaks appearing in the range starting at approximately 1250 cm^{-1} to 1450 cm^{-1} and the peak around 920 cm^{-1} appear to be suppressed on binding to Cr(III).

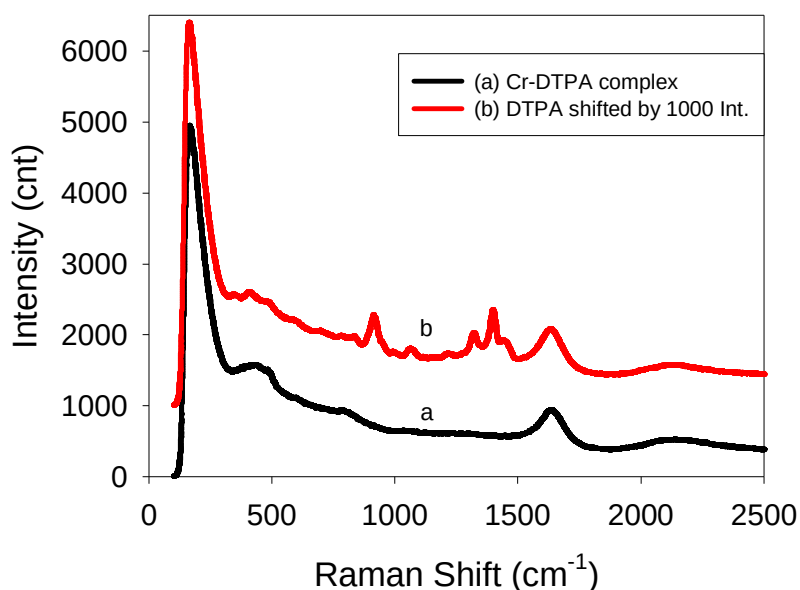


Figure 4.14. Solution Raman spectra of Cr(III)-DTPA complex and free DTPA at pH 6.0.

A specialized spectroelectrochemical cell (Figure 4.15) was used to obtain in-situ spectroelectro-Raman measurements in which the working surface of the electrode can be positioned close to the optical window where a SERS microscope can be focused and the signal collected. The working electrode cell has two outlet ports which allow the introduction of analyte solutions to the electrode by peristaltic pumping. The working electrode compartment is positioned perpendicular to the other two electrode compartments. The reference electrode (Ag/AgCl) was connected to the flow cell compartment by a capillary tube directly adjacent to the working electrode surface. A fine glass frit separates the counter electrode compartment from the working electrode compartment, minimizing solution transfer between the two compartments.



Figure 4.15. Spectroelectrochemical cell with three separated compartments for working (center), counter (bottom) and reference (top) electrodes. Flow introduced through the glass tubes on either side of the center compartment.

Bismuth-modified glassy carbon electrodes (GCE) were first explored to see if any SERS activity could be obtained. Bismuth films were electrodeposited on a GCE prior to placing the electrode in the electrochemical cell as discussed previously. Once in the cell, analyte solution was pumped through the cell and a potential of -0.8 V was applied to reduce Cr(VI), form the Cr(III)-DTPA complex, and adsorb the complex to the surface of the electrode. At Bi modified GCEs, three Raman peaks were observed during the entire process with no spectral changes observed during the accumulation or stripping steps. The three peaks were identified as the disorder-induced D ($\sim 1350\text{ cm}^{-1}$) and the intrinsic graphite G ($\sim 1590\text{ cm}^{-1}$) bands of carbon as expected for GC¹⁰⁰ and a sharp peak due to nitrate in the buffer solution.¹⁰¹ No spectral activity was observed when using Bi-GCE substrates for SERS enhancement. CAdSV peaks for Cr(III)-DTPA were observed during the in-situ measurements, thus Cr(III)-DTPA was present at the surface of the electrode.

4.3.2.2. *In-Situ SERS of DTPA and Nitrate Adsorption on Silver Electrodes*

Silver is widely used as a SERS substrate. Previously, Wetzal et al. showed that ethylenediaminetetraacetic-disodium salt (EDTA) adsorbed on silver electrodes as monitored by SERS.¹⁰¹ Later, Bunding et al. repeated similar experiments and showed that SERS from EDTA and N,N,N',N'-tetramethylethylenediamine (TMEDA) contained many similar bands. This work claimed that EDTA could be decarboxylating to form TMEDA on the surface of the electrode. EDTA and DTPA are both polyamine carboxylic acid chelating

ligands, which contain multiple nitrogen and carboxylic acid binding sites. The structure of EDTA is similar to that of DTPA in that EDTA contains one less nitrogen and carboxylic acid group (Figure 4.16). Wetzel was able to show that EDTA forms complexes with oxidized Ag from the surface of the electrode. Once in solution, the complex forms and is redeposited on silver electrodes under potentiostatic control. By observing differences in the solution Raman and SERS spectra of EDTA, they were able to provide evidence of structural or compositional changes of the surface species vs. those in solution. Interestingly, when NaNO_3 was used as the electrolyte, Wetzel observed a newly enhanced peak at 1050 cm^{-1} which was attributed to nitrate. It was proposed that EDTA was coadsorbing nitrate during the process since solutions of nitrate alone could not produce SERS enhancements.

Recently Bhandari et al. developed a silver-coated polypropylene filter as a highly sensitive SERS substrate.¹⁰² In this work High Performance Extraction Disc Cartridges (HPEDC) from 3M were modified with Ag by physical vapor deposition. This technique concentrates analytes by passing solutions through

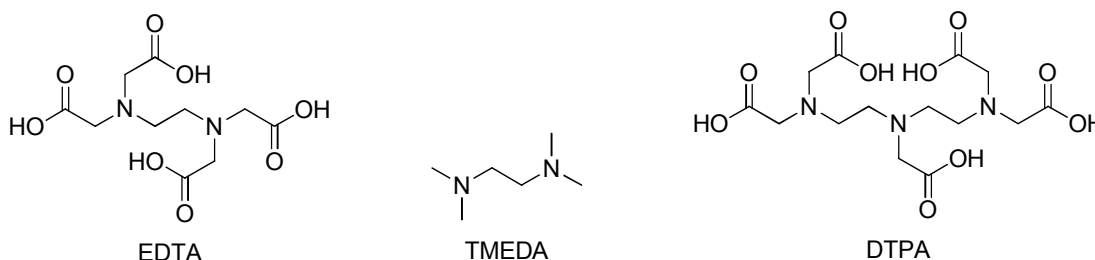


Figure 4.16. Molecular structures of EDTA, TMEDA, and DTPA

the HPEDCs followed by SERS analysis of the filter surface, leading to sensitivities at the $\mu\text{g L}^{-1}$ level for endocrine disrupting chemicals. The substrate was extensively optimized for SERS enhancement. Thus it was used to determine if Ag substrates would be adequate for the SERS detection of the Cr(III)-DTPA complex. Solutions of 1 mM Cr(III)-DTPA were detected using this technique and the SERS response is shown in Figure 4.17.

Due to the similarities between EDTA and DTPA and the fact that nitrate is involved in the catalytic process for Cr detection by CAdSV, in-situ electrochemical experiments at Ag electrodes were conducted substituting DTPA for EDTA. A Ag electrode (3 mm diameter) was first polished on polishing pads using 1.0, 0.5 and 0.03 μm alumina oxide slurry and rinsed and sonicated prior to use. Once in the cell, NaOAc buffer containing 0.1 M DTPA was pumped through the cell by peristaltic pump to simulate stirring conditions. The Ag electrode was scanned through successive anodic oxidation and reduction cycles, with an initial and final potential of -53 mV and an anodic potential of 497 to 647 mV in 50 mV intervals at a scan rate of 20 mV/s. After each CV, a SERS spectrum was obtained from the surface of the Ag electrode (Figure 4.18). The purpose of the anodic scans is to induce dissolution and re-deposition of silver which roughens the surface of the Ag, making it a better SERS substrate and to form silver-DTPA complexes on the surface of the electrode.

Initially, two peaks were present at approximately 1340 and 1595 cm^{-1} . After the first anodic scan to 497 mV a new peak at 920 cm^{-1} appears, the peak at 1340 cm^{-1} shifts to 1400 cm^{-1} and the peak at 1595 cm^{-1} is nearly suppressed.

It has been reported that SERS spectra of carboxylates have strong symmetric stretches around 1380 cm^{-1} and very limited or non-existent asymmetric stretches on silver substrates.¹⁰³ The new peaks at 920 and 1400 cm^{-1} are consistent with what was reported by Wetzel for EDTA at Ag electrodes.¹⁰¹ The peak at 920 cm^{-1} continues to increase in intensity until at more anodic scans the Ag surface becomes irreversibly oxidized and the SERS activity starts to diminish for all peaks (Figure 4.18). At this point, the Ag electrode needed to be polished to regenerate a fresh Ag substrate. The experiment was repeated with the addition of 0.25 M nitrate to observe if DTPA could co-adsorb nitrate at the surface of the electrode. The Raman spectra do show an additional peak at 1040 cm^{-1} corresponding to the addition of nitrate (Figure 4.19). However, an increase in response was not observed as was seen by Wetzel. It is thus believed that the peak was observed from the solution species in the cell between the optical window and the electrode surface and not from any SERS enhanced adsorbed species.

4.4. Conclusions

Studies were conducted to explore the CAdSV mechanism for detection of Cr(VI) and V(V). The Cr(VI) detection mechanism was probed with electrochemical quartz crystal microbalance (EQCM) measurements of mass changes as the surface of both bismuth and mercury modified gold QCM crystals. These experiments are complicated by the fact that a commercial source of carbon based EQCM could not be obtained. Therefore detection at

gold based electrodes is limited in the negative potential window required for CAdSV Cr(VI) detection. However, for the V(V)-GA system, the EQCM results at Hg-Au-alloyed electrodes correlate nicely with the expected catalytic mechanism. Mass changes were noted for both deposition of the complex during the potential controlled adsorption step and during the stripping step. Spectroelectrochemical measurements of diethylenetriaminepentaacetic acid adsorption on silver electrodes were collected under potential control with *in-situ* surface enhanced Raman spectroscopy. These results seem to suggest that DTPA does form complexes on the surface of Ag electrodes. However, it could not be concluded that DTPA coadsorbs nitrate as was seen for EDTA over 20 years ago. The mechanism of V(V) detection with gallic acid complexing ligand was also studied with EQCM. These studies seem to support the proposed electrochemical mechanism when using Hg-modified Au-EQCM.

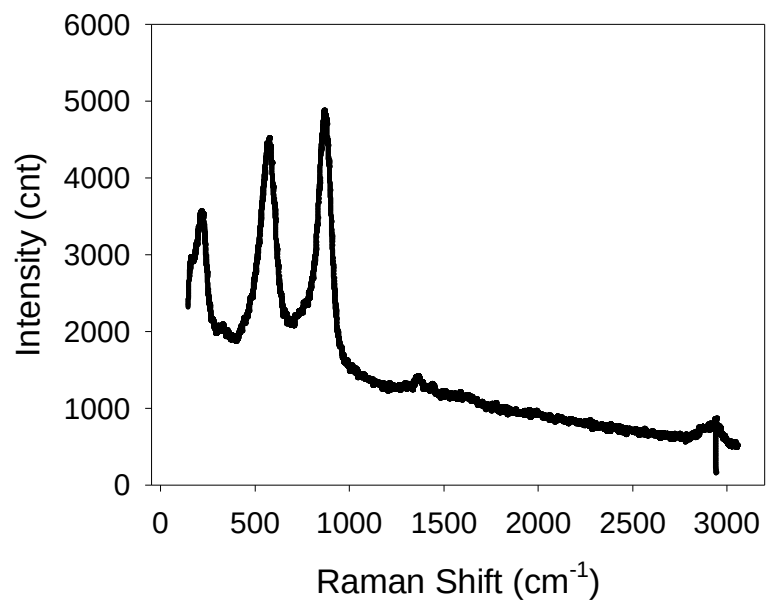


Figure 4.17. SERS response of 1 mM Cr(III)-DTPA solution at HPEDC.

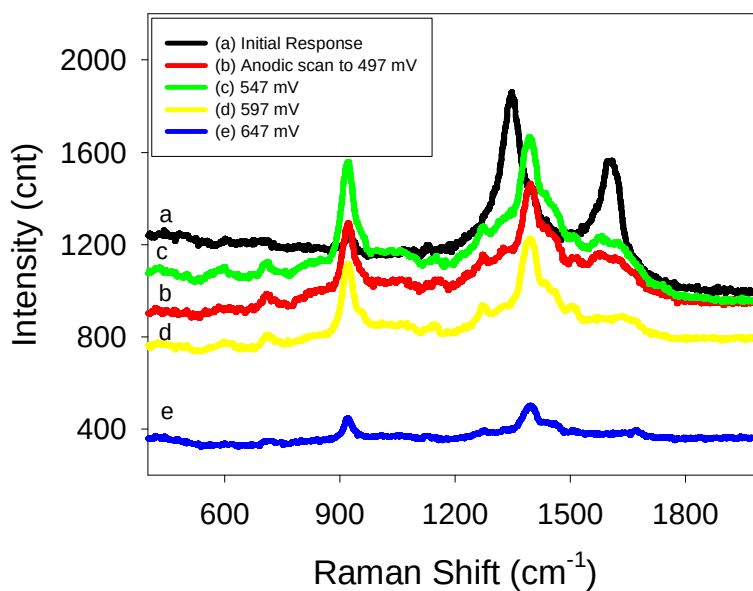


Figure 4.18. In-situ electrochemically induced SERS spectra of DTPA at a Ag electrode under successively more anodic oxidation/reduction scans.

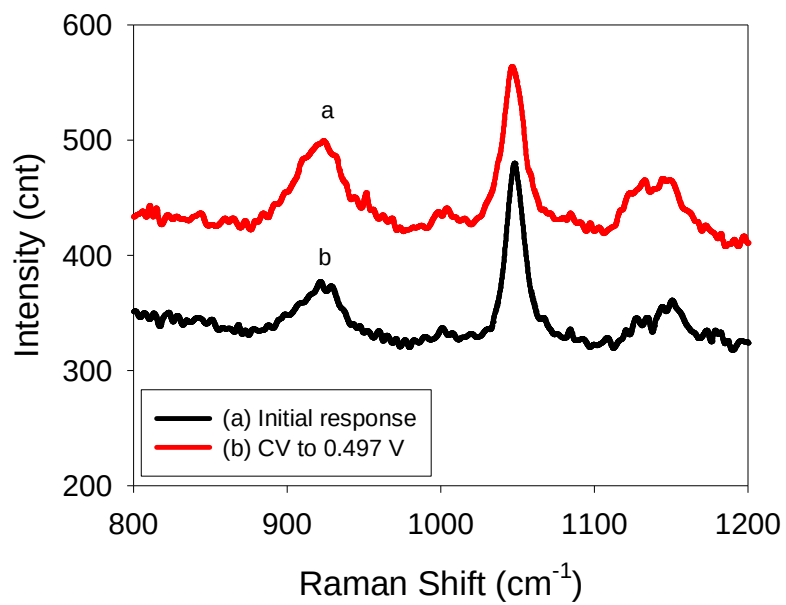


Figure 4.19. In-situ electrochemically induced SERS spectra of DTPA in the presence of nitrate at a Ag electrode.

Part 5

Sol-gel Sensors for the Detection of Carbon Dioxide below Atmospheric Levels

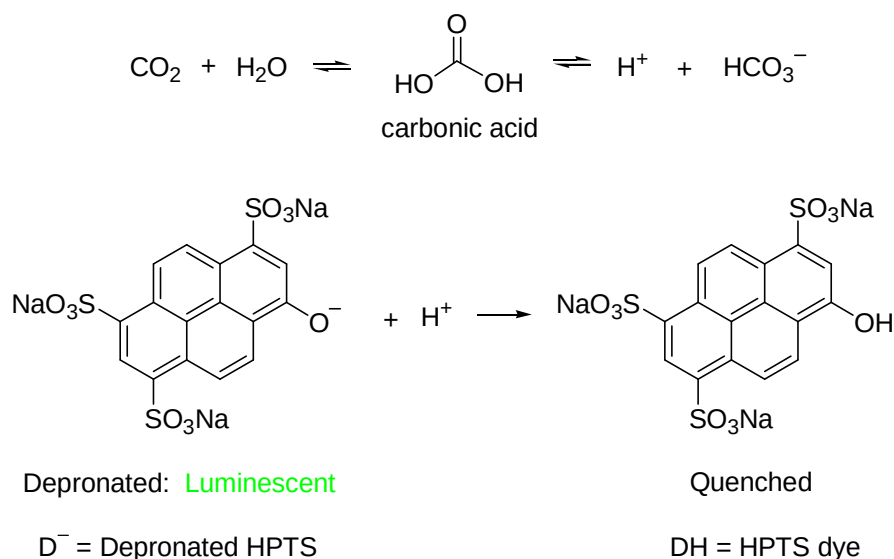
5.1. Introduction

Carbon dioxide gas detection is of interest to the food, beverage and health industries.¹⁰⁴ Quantification of environmental release of carbon dioxide is also significant because of its role in global climate change. The monitoring of green houses gases, as mandated by the US Environmental Protection Agency (EPA), is expected to become more significant in the near future. Analysis of CO₂ in the gas phase is commonly accomplished by infra-red spectroscopy.¹⁰⁵ This technique is prone to interferences from water vapor, and usually requires long pathlengths and expensive equipment.¹⁰⁴ Nondispersive infrared (NDIR) sensors are an inexpensive alternative to traditional FTIR and have been demonstrated for detection of various gases including CO₂.¹⁰⁶ Gas chromatography coupled to a suitable detector such as a thermal conductivity detector can also be used to monitor gas composition. However, this technique is not capable of measuring in real time and is not easily automated. Additionally, the measurement of aqueous CO₂ cannot be accomplished by either of the previously mentioned techniques. For measurements of dissolved CO₂, the Severinghaus electrode has become the standard.^{107,108} Even though the electrode, or modified versions, is still used, it is expensive, bulky, susceptible to interference, and has slow response times.¹⁰⁴

Recently, optical sensors have proved useful for many analytes because of their inherent ease of production and use. They are often inexpensive and can be mass-produced as disposable chemical sensors. Coupling these optical sensors to fiber optics for remote sensing applications is simple. The two basic

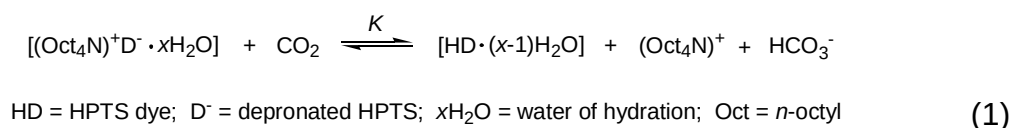
types of optical sensors employ colorimetric or luminescent (intensity or lifetime) for signal transduction. There have been numerous reports of optical sensors for CO₂ detection.¹⁰⁹⁻¹¹⁷ The majority of studies utilize the luminescent dye 1-hydroxypyrene-3,6,8-trisulfonate (HPTS or pyranine) and can be classified as either wet or dry sensors depending on whether they require an aqueous buffer for CO₂ detection. A wet sensor usually contains the deprotonated dye in an aqueous sodium bicarbonate buffer covered by a gas permeable membrane. CO₂ dissolves in water to produce carbonic acid which protonates the dye according to Scheme 5.1., thus changing its fluorescence response.^{118,119}

To overcome the need for an aqueous environment, Mills,^{113,120-122} Wolfbeis^{123,124} and coworkers used an ion-pairing approach to incorporate the polar dye into hydrophobic polymer matrices. Water of hydration associated with



Scheme 5.1. Operation of the dry HPTS sensor for carbon dioxide.

the ion-pair makes it possible for the sensors to maintain their sensitivity to CO₂ while eliminating the need for aqueous buffers. The quenching of HPTS fluorescence relies on the protonation of the dye-counter ion (D⁻) by carbonic acid formed by the interaction of CO₂ with the water of hydration according to the equilibrium in Eq. 1, where [(Oct₄N)⁺D⁻•xH₂O] is an example of a hydrated ion-paired dye using tetra-*n*-octylammonium cation and *K* is the equilibrium constant for the process:¹²⁰



Sol-gels offer many advantages as a sensor matrix material such as high stability, tolerance to harsh conditions (heat, pH, etc.), a microporous environment for improved gas diffusion, ease of use and production of thin films, and excellent film uniformity. The choice of precursors, solvents, organic modifier, catalysts, or coating procedure can greatly influence the properties of the resultant sol-gel matrices making them easy to tailor for specific detection needs. Malins et al. first demonstrated the ion-pair phase transfer reagent approach to integrate the hydrophilic dye into a hydrophobic organically modified silica (ORMOSIL) glass matrix.^{116,117,125} In that work, sol-gels were deposited on glass substrates by means of dip-coating to produce 650-1700 nm thick films. The influence of humidity was investigated and it was shown that the matrix was significantly permeable to water vapor making the sensor best suited to

environments with controlled humidity levels. Additionally, the production of the ion-paired ORMOSIL was complex and required large amounts of material in order to have sufficient material for dip-coating the films.

In the current research work, studies were performed to evaluate sol-gels for optical CO₂ sensors. A simple sol-gel procedure has been developed to produce and optimize sensors with thin films and higher sensitivity (limit of detection: 80 ppm; in comparison, the current atmospheric CO₂ concentration is ~387 ppm).¹²⁶ The ion-pair dye is incorporated into the ORMOSIL precursor solution prior to the hydrolysis and condensation reactions to form the sol-gel sensors. The ion-pair containing alkoxide precursor has a long shelf life (>6 months), improving the efficiency of the technique by eliminating complex and wasteful fabrication steps. Film deposition by the spin-coating method reduces the amount of sol-gel needed and can generate films with a range of thicknesses (~8-30 nm to >1 μm).¹²⁷ Storage conditions during curing were shown to greatly influence the sensor response and diffusion of gas through the films. The addition of TiO₂ particles into the sol-gel sensor films to induce Mie scattering is demonstrated to enhance the interaction of incident light with the film, thus increasing sensitivity. Additionally, moisture proof over-coatings were investigated for their use in retaining water vapor from the sensing material. The use of pin-printing technique has also been explored to demonstrate mass fabrication.

5.2. Experimental

5.2.1. Chemical Reagents

Tetra-*n*-octylammonium bromide ($\text{Oct}_4\text{N}^+\text{Br}^-$, 98%, Alfa Aesar), 1-hydroxypyrene 3,6,8-trisulfonate (HPTS or pyranine, Alfa Aesar), methyltriethoxysilane [$\text{MeSi}(\text{OEt})_3$, 98+%, Acros], TiO_2 powder (99.9%, <5 micron, Sigma Aldrich), tetraphenylmethyldisilazane (Gelest), and Ag_2O (98%, Acros) were used as received. All other chemicals were purchased from Fisher Scientific. Aqueous solutions were prepared using DI water (18 M Ω cm) from a Barnstead International e-pure 4-holder deionization system. Glass slides were cut to 1 cm² squares from standard microscope slides. Custom mixed gases (30.00%, 0.9900%, and 0.1000% CO_2 with N_2 balance) were acquired from Airgas.

5.2.2. Instrumentation

A Perkin Elmer LS55 luminescence spectrometer with a pulsed Xe source was used for fluorescence measurements of the sol-gel films. Films were coated using a custom-built spin coater. The films were placed in a brass flow cell constructed to be compatible with a front surface sample cell holder purchased from Perkin Elmer. The brass flow cell has a gas flow volume of approximately 0.5 x 10 x 10 mm (Figure 5.1). The sliding mechanism was removed from the accessory to make room for the flow cell and gas tubing. Gas was mixed to the appropriate concentration by two separate flow rotameters (Thermo Barnant Gilmont) with precision valves. The flow meters were calibrated for gas flow

using a 100 mL glass bubble meter. Temperature and humidity were measured by a remote probe sensor (Fisher Scientific). A Thermo Fisher Evolution-600 ultraviolet–visible spectrophotometer was used to acquire absorbance spectra of the sensing films. A Varian 4100 Fourier transform infrared spectrophotometer equipped with a Bio-rad diffuse reflectance accessory was used to monitor the formation of moisture proof over-coatings. Scanning electron microscope (SEM) images were obtained for sensing films on glass substrates on a Hitachi S-4700 SEM. An Xact II compact microarray pin printing system (LabNext) was used to produce the pin-printed sensor array elements for use with fiber optic detection.

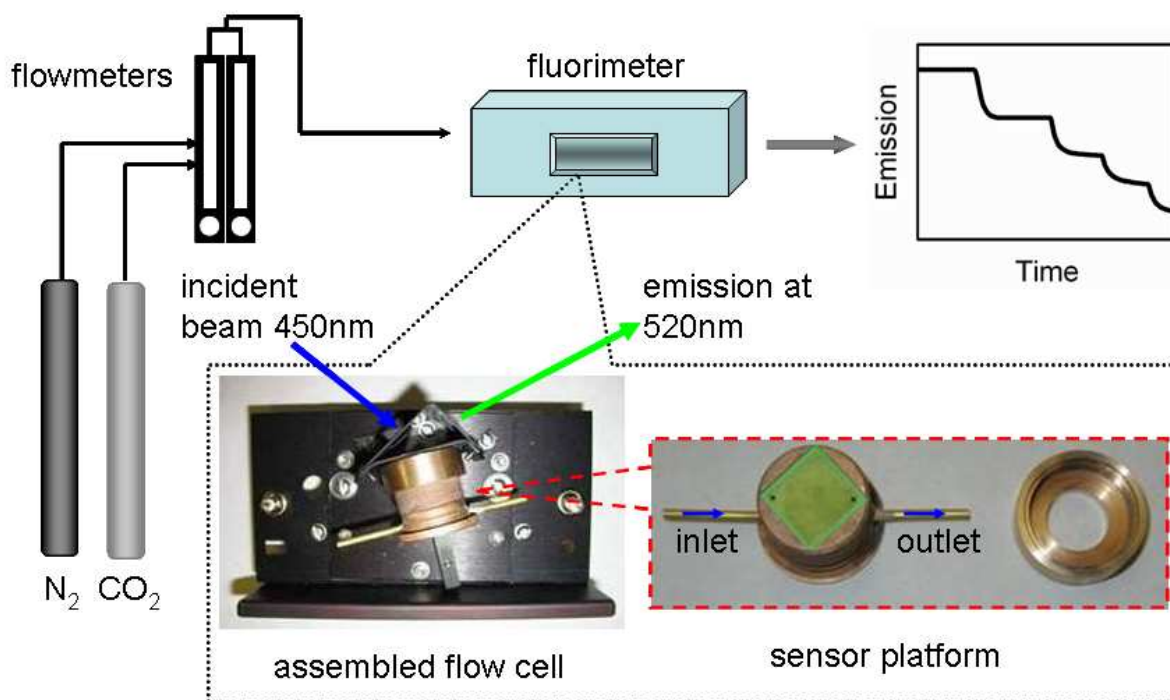
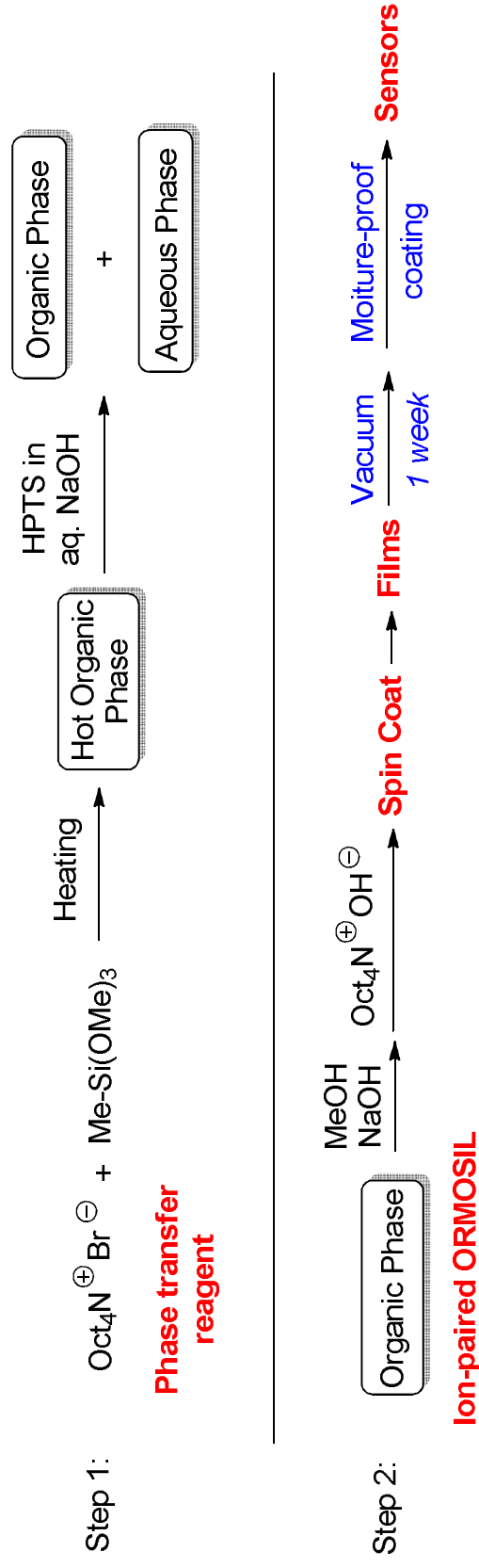


Figure 5.1. Schematic diagram of instrumental set-up and flow cell design

5.2.3. Sensor Preparation

A modified coating procedure was developed based on the work of Malins et al.¹¹⁶ Tetra-*n*-octylammonium hydroxide ($\text{Oct}_4\text{N}^+\text{OH}^-$) free base was made by combining Ag_2O (0.58 g) and $\text{Oct}_4\text{N}^+\text{Br}^-$ (1.4 g) in MeOH (10 mL) and stirring at high speed for 4 h. The solids were allowed to settle and the solution was decanted and refrigerated in a tightly capped vial. The sol-gel and resulting thin films were made according to Scheme 5.2. First, HPTS dye (5 mg) was added to aqueous NaOH (5 mL, 0.1 M) and stirred to dissolve. $\text{Oct}_4\text{N}^+\text{Br}^-$ (0.15 g) was then added to the $\text{MeSi}(\text{OEt})_3$ precursor (2.8 mL) and gently heated with stirring until $\text{Oct}_4\text{N}^+\text{Br}^-$ solid was dissolved. The basic dye solution was added to $\text{MeSi}(\text{OEt})_3$ after heating was stopped, but while $\text{Oct}_4\text{N}^+\text{Br}^-$ was still dissolved in the ORMOSIL precursor. The mixture was gently stirred to ensure the two layers remained immiscible and until it was apparent that the majority of dye had been transferred from the aqueous phase into the organic phase. Once the phase-transfer was complete, the precursor was separated from the aqueous phase to ensure that sol-gel hydrolysis and condensation reactions did not occur. The ion-pair remains solubilized in the ORMOSIL precursor at room temperature (Step 1, Scheme 5.2). This solution is stable for long periods of time (>1 year, for use in Step 2, Scheme 5.2). All sensors presented for direct comparison were made from a single solution of ion-paired ORMOSIL to ensure consistent concentrations of dye between batches of sensors.



Scheme 5.2. Sol-gel formulation and film coating procedures. Step 1: Preparation of bulk ion-paired ORMOSIL precursor (one time). Step 2: Sol-gel reaction and fabrication of sensors.

The sol-gel was formed by mixing ORMOSIL (200 μL), MeOH (100 μL), and NaOH (50 μL , 0.01 M) with stirring. After 1 h, $\text{Oct}_4\text{N}^+\text{OH}^-$ solution (50 μL) was added and stirred for two min or until the sol-gel viscosity was reasonable for spin coating. To utilize the principle of Mie scattering, TiO_2 powders were added to the sol-gel coating solutions and applied in the form of coatings. Typically, oven-dried TiO_2 powder (~ 3.7 mg) was added to MeOH (5 mL) and sonicated. Sol-gels were made as described above, but with 50 μL of pure MeOH and 50 μL of TiO_2 -MeOH (added after 1 h of stirring). The sol was coated on cleaned glass slides (~ 1 cm^2). Prior to the coating, the slides were cleaned in piranha solution (1:3 = 30% H_2O_2 :conc. H_2SO_4) for 10 min followed by sonication in water and subsequent rinses in acetone, ethanol, methanol, and DI water and dried under compressed nitrogen to prevent water spotting. This ensured adhesion of the sol-gel to the glass substrate by covalent reaction with freshly hydrolyzed silanol groups on the glass surface. Sol-gel (50 μL) was pipetted onto the slide and drawn to the edges of the slide with a plastic pipette tip. The spin coater was set to 1770 or 2660 rpm for approximately 10 s. The finished films were stored in Schlenk tubes under nitrogen atmosphere or vacuum for 1 week prior to use.¹²⁸ In the case where moisture proof over-coatings were used, the films cured as above under vacuum followed by spin coating an additional layer or by dipping the film in a solution of coating material followed by rinsing in solvent and additional curing under vacuum. To make the SurfaSil™ overcoat, the sensor was dipped into a dilute solution of SurfaSil (2 wt%) in acetone for several minutes (Sensor 6). Ethylcellulose coatings were made from a solution of

dissolved ethylcellulose (4 wt%) in a 4:1 mixture of toluene and ethanol, and the solution was spin-coated on top of a cured HPTS sensor (Sensor 7). To make the disilazne coatings, 2% (Sensor 8a) or 4% (Sensor 8b) solutions of 1,3-dimethyl-1,1,3,3-tetraphenyl-disilazanesolution were prepared in hexane. The cured films were placed in the solution for 2 min with agitation. The sensor was then removed and washed briefly with hexane and then returned to an air-tight container to cure again under vacuum. A summary of fabrication and storage conditions is shown in Table 5.1.

5.2.4. Preparation of a Pin-Printed Working Model

Sol solutions with the ion-paired indicator were printed onto clean, glass slides. Prior to printing the glass slides were cleaned by soaking in 1 M NaOH for 4 h, followed by rinsing with copious amounts of DI water and drying at 80 °C. The HPTS doped ORMOSIL formulations were printed directly on to the slides by using the Xact III™ Microarrayer system with Xtend pins (LabNext). The relative humidity of the print chamber was maintained between 30 and 40% during printing. The individual sensing elements were of the order of 500 µm in diameter with column-to-column center spacing and row-to-row center spacing set to 600 µm. The printed sensor arrays were aged at 80 °C for 18 h to ensure complete cure of the matrix. To quantify the analyte concentrations using *in-situ* optical methods, a trifurcated fiber optic bundle was used to bring light from an optoelectronic unit to the sensing region and to guide photons to the detector inside the optoelectronic unit. Incorporation of the sensor chip on the tip of the

Table 5.1. Summary of the CO₂ sensor fabrication conditions

Sensor	Preparation notes	Storage	Spin Speed (rpm)	Moisture-proof Coating	Figure(s)
1	100 % ion-paired ORMOSIL	N ₂	1770	n/a	5.3
2	Ion-paired ORMOSIL : MeSi(OEt) ₃ 1:3	N ₂	1770	n/a	5.4
3	100% ion-paired ORMOSIL	N ₂	2660	n/a	5.5A
4	Same as 3	vacuum	2660	n/a	5.5B, 5.7 & 5.9
5	TiO ₂ addition	vacuum	1770	n/a	5.9
6	Same as 3	vacuum	2660	SurfaSil	n/a
7	Same as 3	vacuum	2660	Ethylcellulose	5.12A
8a	Same as 3	vacuum	2660	2% disilazane	5.12B
8b	Same as 3	vacuum	2660	4% disilazane	5.12C

fiber bundle was achieved using optically transparent adhesive, with the coated side facing outward. A working model of the sensor was tested using an automated setup for detecting gaseous analytes. The sensors were placed in a test chamber connected to a mass flow controller (MFC) to introduce gases at the desired composition consisting of ultra high purity nitrogen and carbon dioxide mixed at various proportions. The gases were cycled between these two mixtures at least two to three times. The sensor response was monitored using the optoelectronic readout unit, which was controlled by LabView VI for automated data acquisition. The sensor was evaluated based on the absorption changes of the sensor thin film at 460 nm, utilizing a test set-up with a band-pass filter at 460 nm placed in front of the detector. Similarly the sensor response based on the fluorescence quenching of the HPTS indicator in the presence of CO₂ gas was evaluated by using an emission cut-off filter at 497 nm. The absorption/fluorescence characteristics of indicator-doped pin-printed coatings were measured using a custom optoelectronic unit produced by InnoSense LLC.

5.2.5. Analysis Procedures

The sol-gel-coated films were fit into a custom designed flow cell (Figure 5.1). The inlet was connected to two gas flow meters to control the ratio of CO₂ to N₂ and in the case of humidity tests the gas stream was allowed to flow over a solution of water. Quantitative tests to measure response to various CO₂ concentrations were made by mixing CO₂ and N₂ gas while keeping the total flow rate constant. The outlet was connected to a sealed vial containing a

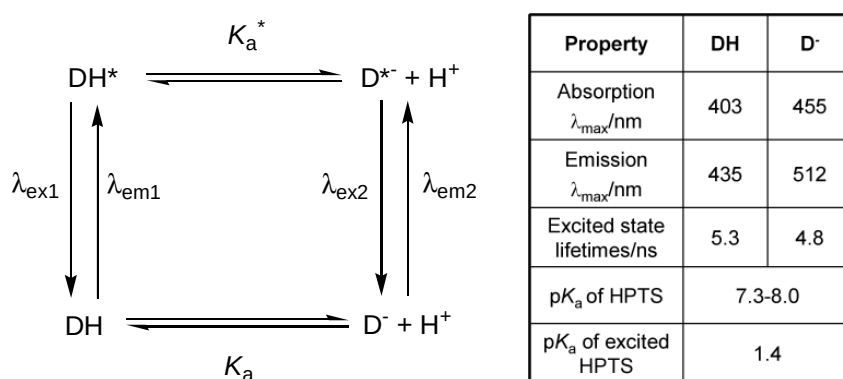
temperature/humidity probe and then to a bubbler to prevent backflow of gases. HPTS dye is reported to have absorption and emission characteristics according to Scheme 5.3.¹⁰⁴ The following are the nominal parameters used to collect fluorescent sensor response: λ_{ex} 455 nm, λ_{em} 522 nm, 10 nm slits, ~800 V PMT detector voltage (adjusted to get max sensitivity for each sensor), 1 s integration time, and an emission cut-off filter of 515 nm. The time based emission was collected and the sensor was calibrated after an initial sensor equilibration time (~25 min) or when baseline drift was satisfactory.

5.3. Results and Discussion

5.3.1. Sol-gel Sensor for Carbon Dioxide Gas Detection

5.3.1.1. Sensor Fabrication and Characterization

Malins et al.¹¹⁶ reported an organically modified silica (ORMOSIL) sol-gel sensor doped with the fluorescent pH-sensitive HPTS dye. When following the procedure outlined in the paper, several problematic steps were noted. The most



Scheme 5.3. Absorption and emission characteristics of HPTS dye.¹⁰⁴

significant problem was that $\text{Oct}_4\text{N}^+\text{Br}^-$, used for ion pairing, would not easily dissolve in the alkoxide precursor $\text{MeSi}(\text{OEt})_3$. It was reported that using a few drops of CCl_2H_2 would dissolve $\text{Oct}_4\text{N}^+\text{Br}^-$, but several mL were required to fully solubilize it. The additional solvent prevented the sol from gelling properly. Later, the same authors reported using HCCl_3 to dissolve $\text{Oct}_4\text{N}^+\text{Br}^-$.¹²⁵ In this approach, the incorporation of the dye by ion-pairing happens at the time of the sol-gel reaction to produce the sensing film, requiring the need for the ion-pairing process during the preparation of each batch of sensors. Additionally, the procedure used dip coating to produce the films, placing limitations on the film thickness. A modified procedure (Scheme 5.2) was developed to prepare the films in the current work. The modified procedure allows for more control over the preparation process and produces consistent and sensitive sensors with easy fabrication techniques.

By heating the precursor while adding $\text{Oct}_4\text{N}^+\text{Br}^-$, the ion-paired dye was incorporated into the sol-gel precursor prior to any significant sol-gel reaction (Step 1, Scheme 5.2). This forms a shelf stable precursor that can be used many times with just one preparation, eliminating the need for the first steps in the original process. The original report used HCl to catalyze the hydrolysis and condensation reactions to form the sol-gel. After the sol-gel reaction was complete, $\text{Oct}_4\text{N}^+\text{OH}^-$ was added to change to a basic pH, ensuring that the sensor would be responsive to CO_2 . In our approach, NaOH is used to catalyze the sol-gel reaction. This maintains a basic environment during the entire preparation procedure. An additional benefit is that base catalyzed sol-gels tend

to have greater porosity due to the formation of highly condensed particulate sols and thus have greater diffusion rates and response times.¹²⁹ The thickness of the thinnest, TiO₂-free films produced by spin coating, as measured by ellipsometric methods, were found to range from ca. 8-30 nm. This is similar to other reported thin sol-gel films (~20 nm) produced by spin-coating techniques.¹²⁷ In comparison, 650 nm is the thinnest reported film by a dip coating method.¹¹⁶ Our spin-coating method has also produced TiO₂-free films with thickness of 0.5-1.5 μm , as measured by non-contact profilometry. SEM images of the films on glass substrates show fairly uniform coating of the surface with some structural defects, possibly due to contraction of the films during the curing process (Figure 5.2). The combination of higher active dye content (improved ion-pair and basic environment), thinner films (spin coating) and larger pore sizes (base hydrolysis),

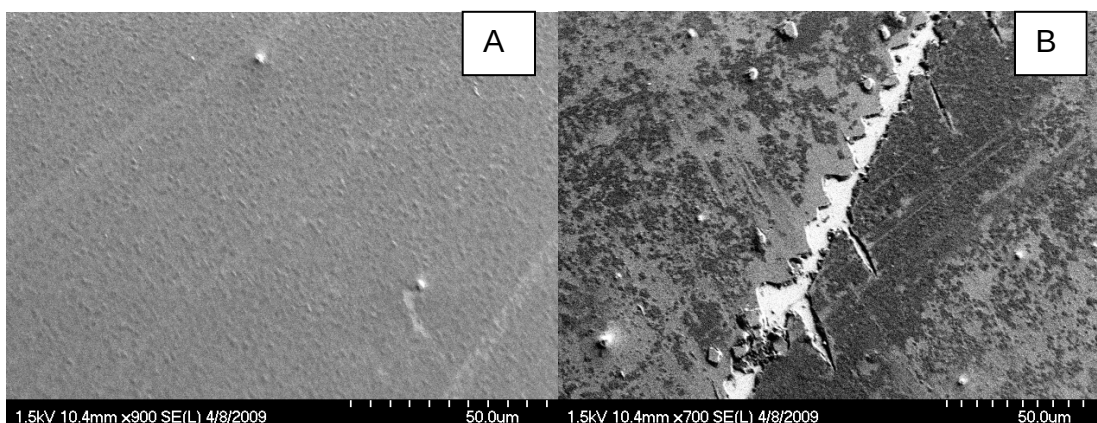


Figure 5.2. SEM images of dye-doped sol-gel sensors showing: (A) uniform coverage of the sol-gel; (B) surface defects due to contraction of the films during curing.

likely contributes to the overall better sensitivity of the sol-gel films in the current work (previous work reported as below 0.1%).¹¹⁶

5.3.1.2. CO₂ Analysis and Optimization of Sensor Performance

Sensor 1 was tested for response to high (0-30%, Figure 5.3) and low concentrations of CO₂ using the modified flow-cell with the fluorimeter. While the response to high concentrations was satisfactory, it was found that they were not sensitive to 0.1% CO₂. At very high dye concentrations, the equilibrium involving CO₂ and the dye has little effect on the cumulative fluorescence signal. The concentration of dye is therefore a critical parameter for control of sensitivity. Films with lower dye contents were produced by mixing different ratios of precursors with and without the ion pair dye to control the amount of HPTS present in the film (Sensor 2). This is facilitated by the new fabrication technique, which allows one to ratio precursors to form the final ORMOSIL with various

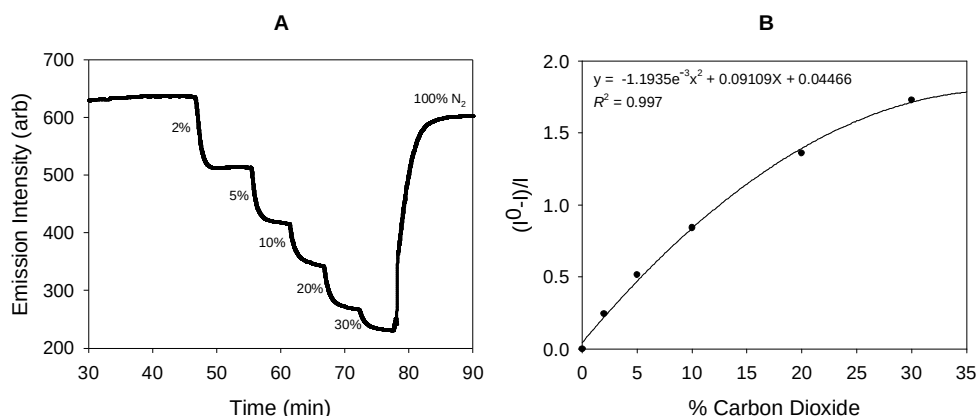


Figure 5.3. Sensor 1: (A) Response to 2-30% CO₂; (B) Resulting calibration plot.

concentrations of dye. Mixing dye containing ORMOSIL with MeSi(OEt)₃ helped to achieve sensors with sensitivity to 0.1% CO₂ (Figure 5.4). However, the long response times are indicative of limited CO₂ diffusion in the sensor matrix.

In an effort to make the dye concentration lower and increase diffusion simultaneously, thinner films were made by increasing the spin coating speed (Sensor 3). This produced notably thinner films (as low as 8.2 ± 0.2 nm) which contained less dye due to the decrease in the overall volume of the sensing film. Different ratios of ORMOSIL to MeSi(OEt)₃ were tested, but for thinner films 100% ORMOSIL was found to have the best sensitivity. The initial tests for response to 0.1% CO₂ showed that this method did improve the response toward lower levels of CO₂ gas (Figure 5.5A). However, because diffusion was again limited in the film, response times were still long for low concentrations of CO₂.

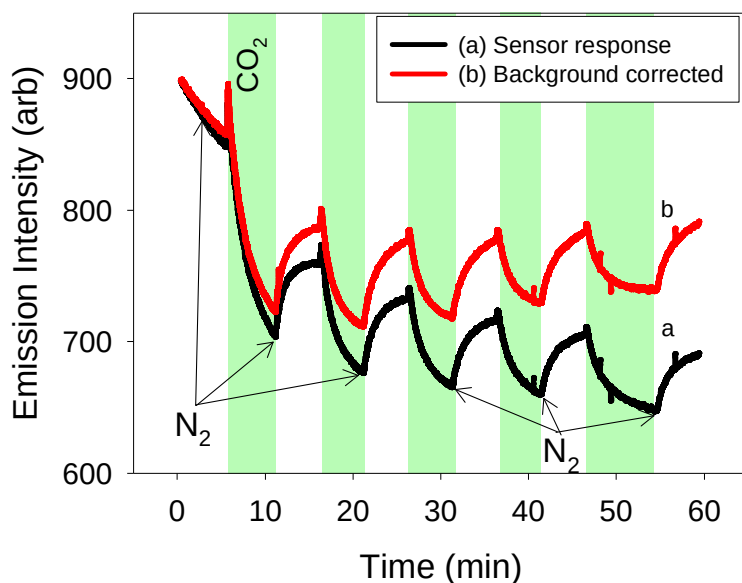


Figure 5.4. Response of Sensor 2 with low dye content to 0.1% CO₂.

5.3.1.3. *Effect of Sensor Storage Conditions*

The storage environment of the sensors was found to have a direct effect on the sensitivity of the sensor. Sensors stored in air lost their sensitivity (Figure 5.6) over time (<1 week). The reasons for loss of fluorescence are not entirely clear, but it is thought that acidic gasses found in lab environments and the atmosphere (NO_x and SO_x) could irreversibly protonate the dye and make it insensitive to changes in pH.¹⁰⁴ Attempts were made to regenerate a basic environment by soaking the sensors in basic buffers, but the sensing properties could not be regenerated. To minimize this effect, the sensors were cured and stored under nitrogen when not in use. Additionally, it was found that storing the sensors under a static vacuum in a Schlenk tube¹²⁸ during the curing process (Sensor 4) dramatically improved the response times (Figure 5.5B) while maintaining sufficient water levels necessary to retain sensitivity towards CO_2 . The residual water and solvent blocking the pores can be successfully removed by this technique. This also supports literature reports that the water of hydration on the ion-pair is tightly bound and is not easily removed.^{104,116,117} The sensors can also be used under very dry conditions and stored under vacuum for at least one month without adverse affects. These sensors (Sensor 4) were used to generate a calibration for 0-1% CO_2 (Figure 5.7). The response and recovery times (90%) of the sensor are usually ca. 30 and 75 s, respectively. The limit of detection (3σ) was found to be 0.008% or 80 ppm and the limit of quantification 0.02% or 200 ppm, below atmospheric CO_2 concentrations (~ 380 ppm).¹³⁰⁻¹³²

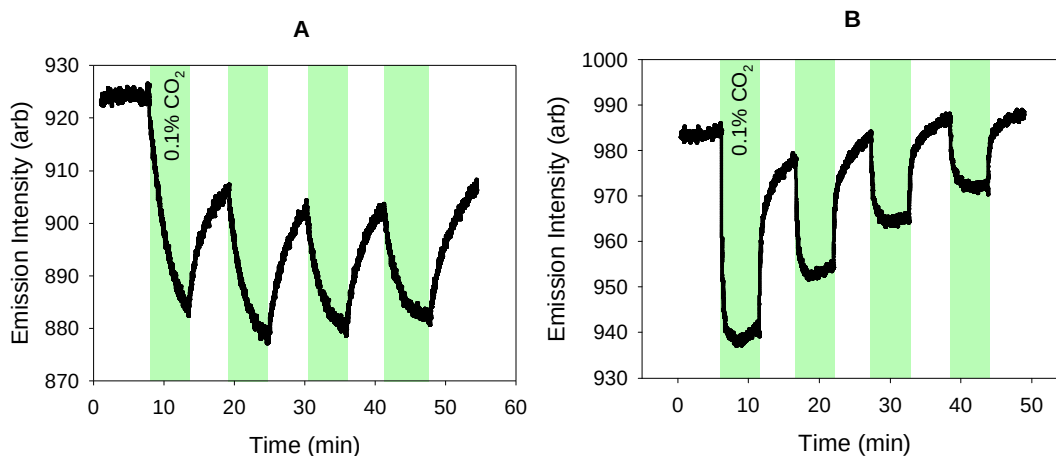


Figure 5.5. Response to pulses of 0.1% CO₂: (A) Cured under N₂ (Sensor 3); (B) Cured under vacuum (Sensor 4).

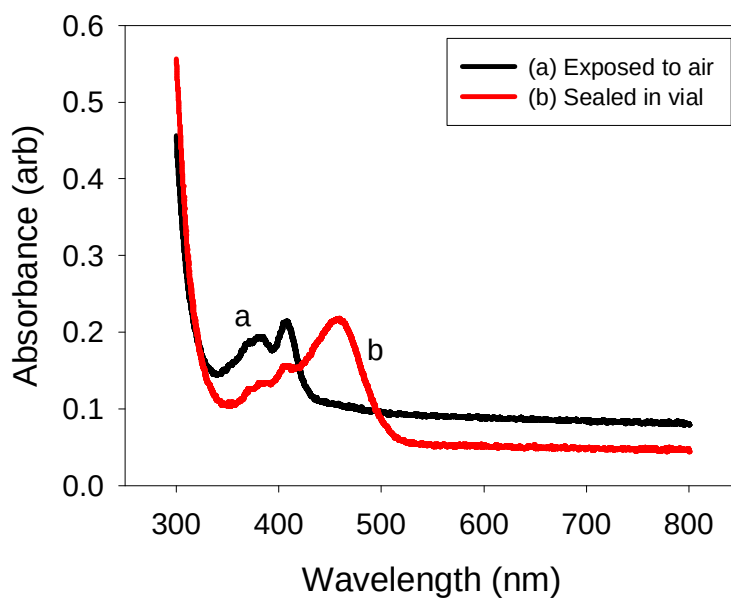


Figure 5.6. Comparison of absorbance of HPTS sol-gel sensors: (a) Exposed to air; (b) Sealed in a vial.

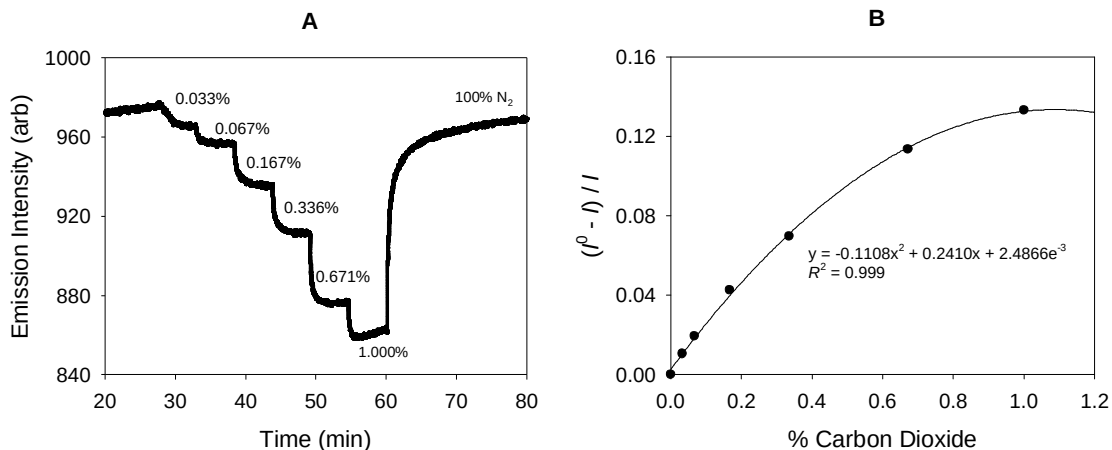


Figure 5.7. Sensor 4: (A) Response to 0-1% CO₂; (B) Resulting calibration plot.

5.3.1.4. Use of Titanium Oxide Particles to Induce Mie Scattering

To increase the signal to noise ratio, TiO₂ particles were incorporated into the film.¹³³ Mie scattering phenomena caused by the isotropic titania sphere within an otherwise homogenous sensing matrix was harnessed to enhance signal collection (Figure 5.8). TiO₂ particles scatter all visible wavelengths more or less equally. Scattering of light by the TiO₂ particles within the sensing matrix allows for more effective interaction of light with the indicator material in the sensing layer, effectively increasing the path length and exposed area of the sensor without increasing gas diffusion rates from thicker sensing layers. The optimum scattering comes from particles that are 0.5 times the wavelength of interest. In the case of HPTS sensors, the optimum particle size would be approximately 200-300 nm in diameter. A source of particles in this specific size range was not readily available at the time the study was conducted, hence TiO₂ particles of <5 μm were used. The addition of TiO₂ particles in the sensing film

(Sensor 5) did cause an increase in the excitation and emission intensity, but it is unclear if the enhancement is solely from TiO_2 incorporation, or from a combination of factors including that the films were noticeably thicker than other films (Figure 5.9).

5.3.1.5. Moisture Proof Coatings

Because water is involved in the equilibrium process that governs the response of the sensor, it is important to maintain a constant water percentage within the sensing film. To accomplish this, several options for moisture proof coatings were evaluated. First, commercially available SurfaSil™ siliconizing fluids were used. SurfaSil is a siloxane primarily used to treat glassware and prevent non-specific binding to surface silanol groups (Figure 5.10A). Surfasil reduces the number of unreacted hydrophilic silanol groups on the surface of the sensor and functionalizes the outer layer of the film with hydrophobic groups. However, after exposure to the solution (by both dip and spin coating), the sensor lost most of its characteristic yellow-green fluorescent color and was no longer responsive to CO_2 . During the reaction of SurfaSil with Si-OH , a small amount of HCl is released which effectively protonates the HPTS dye rendering it insensitive to CO_2 . The sensor could not be regenerated by soaking it in a basic buffer like NaHCO_3 , because the resulting films were highly impermeable to liquid water.

Ethylcellulose was also tested as a potential moisture proof over-coating. However, toluene in the solution also caused the films to lose their CO_2

sensitivity. An alternative coating, 1,3-dimethyl-1,1,3,3-tetraphenyl-disilazane (Figure 5.10B) releases basic NH_3 during its reaction with the excess silanol groups on the outer surface of the sensor. The basic by-product maintains the required pH environment and allows for the application of the coating without adversely affecting the sensing layer. Absorption spectra of the sensor films before and after coating (Sensor 8a) showed no change to the HPTS absorption after coating (Figure 5.11A). The sensors were monitored by DRIFTS before and after coating to confirm changes to the surface. Two new features, at ~ 3300 and $3000\text{--}3100\text{ cm}^{-1}$ range (Figure 5.11B) were visible after coating, consistent with the addition of unreacted amine groups and aromatic rings respectively. This was confirmed by repeating with silica gel powders instead of a sensing film which were run as powder DRIFTS samples and showed similar spectral changes (results not shown).

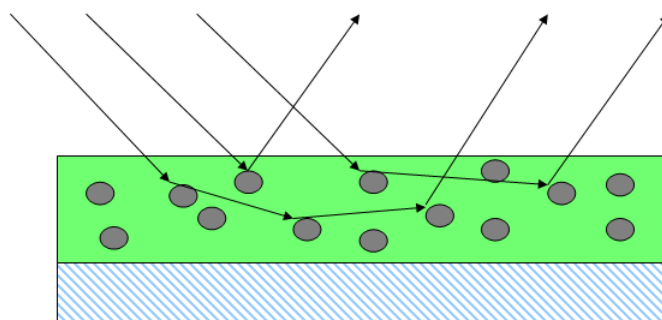


Figure 5.8. Illustration of the Mie scattering effect of TiO_2 particles incorporated into a sol-gel matrix.

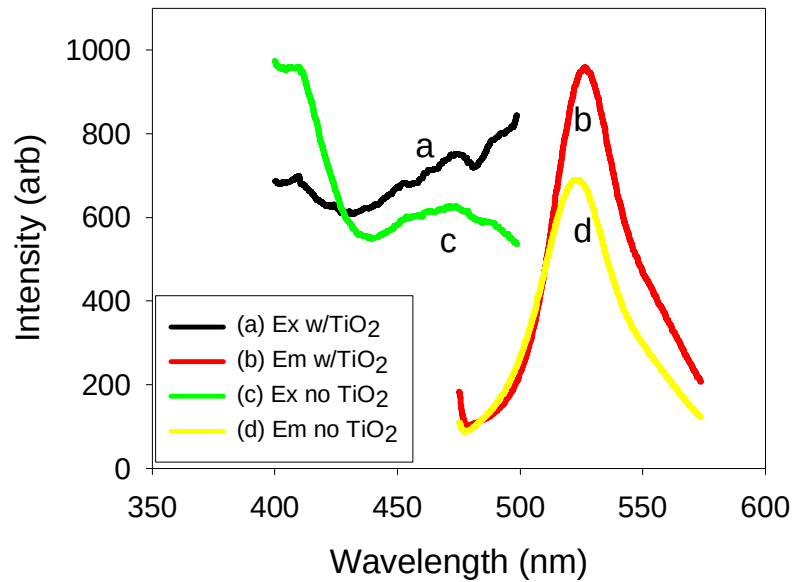


Figure 5.9. Comparison of Sensors 4 (without TiO₂) and 5 (with TiO₂).

Excitation and emission spectra (excitation at 450 nm and emission at 515 nm).

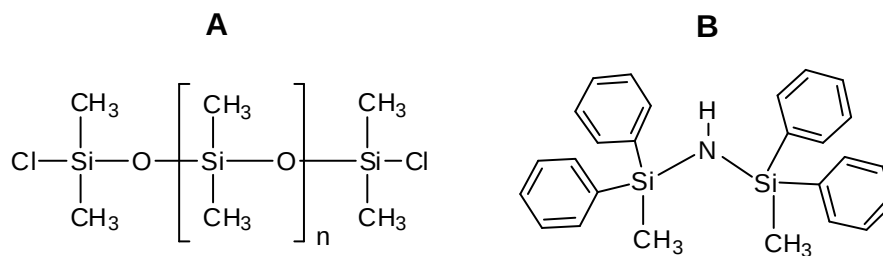


Figure 5.10. Chemical structures of (A) SurfaSil and (B) 1,3-dimethyl-1,1,3,3-tetraphenyl-disilazane.

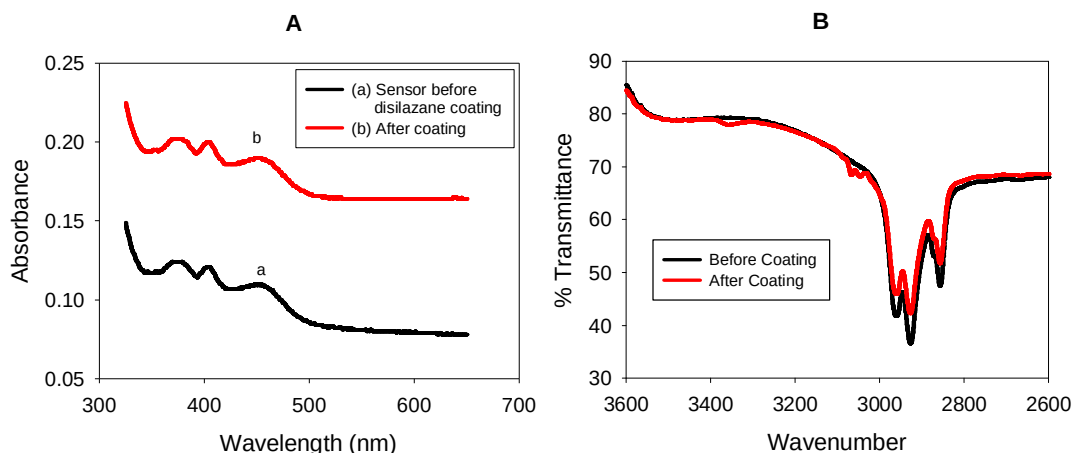


Figure 5.11. Sensor 8a: (A) Absorbance spectra before and after disilazane coating; (B) DRIFTS spectra before and after disilazane coating.

After coating, the sensors (Sensors 8a-b) were tested for their response to humid gases. The introduction of humid nitrogen caused an instantaneous increase in the overall fluorescence signal for all sensors (with and without moisture-proof coatings). The sensors without moisture-proof coatings showed as much as a 47% increase in intensity when gas with 85% relative humidity was introduced vs. dry gas (Sensor 4). The intensity of the ethylcellulose-coated sensor increased by 26% (Sensor 7) and those for disilazane-coated films increased by 4.7% (Sensor 8b) and 18% (Sensor 8a) respectively, depending on the concentration of disilazane in the coating solution (Figure 5.12). While neither coating totally prevents the effect of humidity changes, the decrease in both cases indicates that ethylcellulose and disilazane coatings restrict the diffusion of water vapor into the sensing film. Films with disilazane coatings (Sensors 8a-b) were shown to retain their sensitivity to CO₂.

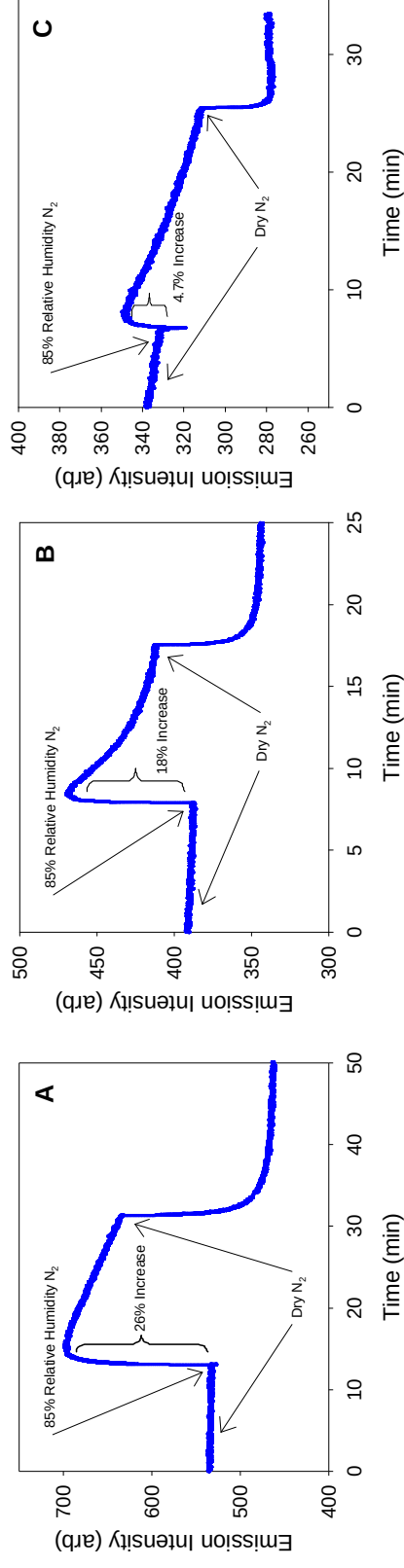


Figure 5.12. Effect of moisture-proof coating on the change of sensor response when switching between dry and 85% humidity nitrogen with (A) coatings of ethylcellulose and coatings of 1,3-dimethyl-1,1,3,3-tetraphenyl-disilazane from 2% (B) and 4% (C) solutions. The response to 85% humidified N_2 from sensors without coatings was as high as 47%.

5.3.1.6. *Pin-Printed Fiber Optic Sensor Arrays*

The motivation for producing pin-printed sensors was to develop low-cost, multi-analyte compatible and disposable sensors, which could significantly reduce operational costs over the lifetime of the detection system compared to competing technologies. Data acquisition and data analysis would also be simplified in the new approach. Specific indicators can be incorporated on a single sensing chip platform where multi-analyte sensing would be beneficial/required. The sensor platform developed through the direct-write pin-printing technology allows integration of multiple measurements with a single fiber optic sensor head.

Pin-printing methods were used to incorporate the sensor indicators for CO₂ and on a chip. Direct-write pin-printing technology makes high-volume fabrication of the sensor chip possible, ultimately eliminating the individual calibration of each sensor by producing many identical sensors in one batch. An Xact™ Microarrayer system was used for contact printing the sensor indicator onto a substrate, offering excellent spotting uniformity of the printed sensor and allows printing up to 1500 spots per 20 x 70 mm chip area (Figure 5.13). Another feature of the microarray printer is the minimal amount of indicator required for the sensor fabrication. Typically, the deposition volume ranges between 5-25 nL. Chemically resistant Xtend™ composite pins take up the “inks or sols” by capillary action and deposit circular dots (0.5 mm).

The response of the sensor at CO₂ gas concentrations of 5000, 1000 and 650 ppm (Figure 5.14) clearly reveals the temporal response of the sensor and

its fast recovery while introducing pure N_2 gas as was seen for the bulk spin-coated sensor. The pin-printed sensors have been shown to respond well to CO_2 (~387 ppm) in the presence of other atmospheric gasses in compressed air samples (Figure 5.15). While the film thickness of pin-printed sensors (typically 6 μm) is thicker than those produced by spin-coating, the results show that transferring such optical sol-gel techniques to multi-analyte sensing applications is possible.

5.3.2. Capnography – CO_2 Monitoring in Human Breath

Exhaled carbon dioxide (CO_2) is monitored in medical settings to assess patient health status. The field of study devoted to monitoring breathing is generally referred to as capnography. Commercially available capnography equipment often utilizes infrared detection of CO_2 . However, commercial

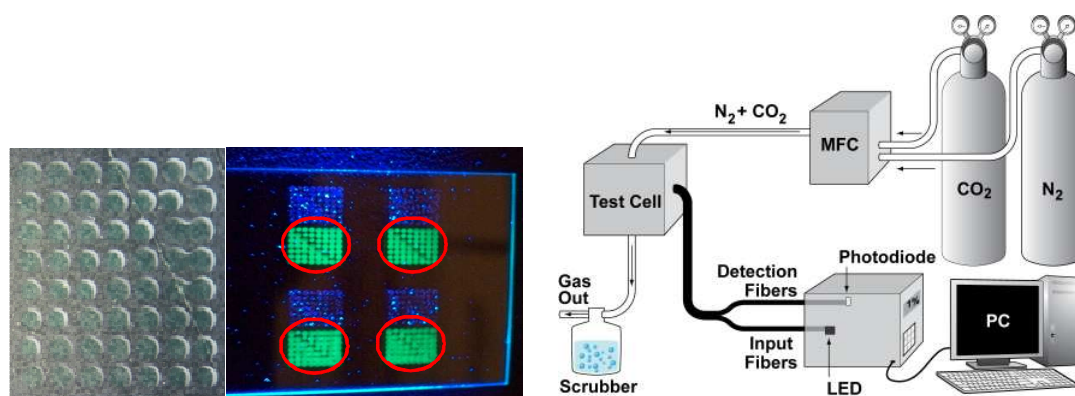


Figure 5.13. Pin-printed sensors for CO_2 (left) and fluorescence of HPTS sensors on excitation from a 470 nm LED light source (middle) and experimental set-up for pin-printed arrays with fiber optic detection (right).

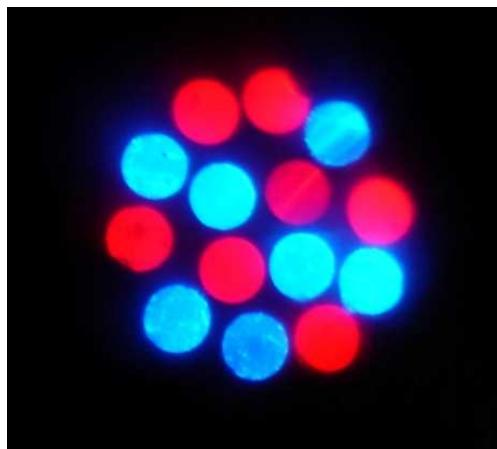
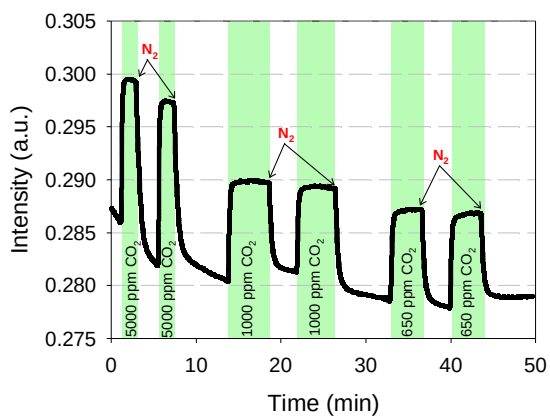


Figure 5.14. Fiber optic mounted sensor response to 5000, 1000, and 650 ppm CO_2 (left) and illumination/detection bundle (right) used for transporting the illuminating light from a blue LED to the sensor head and the resulting change in photon intensity to the detection photodiode.

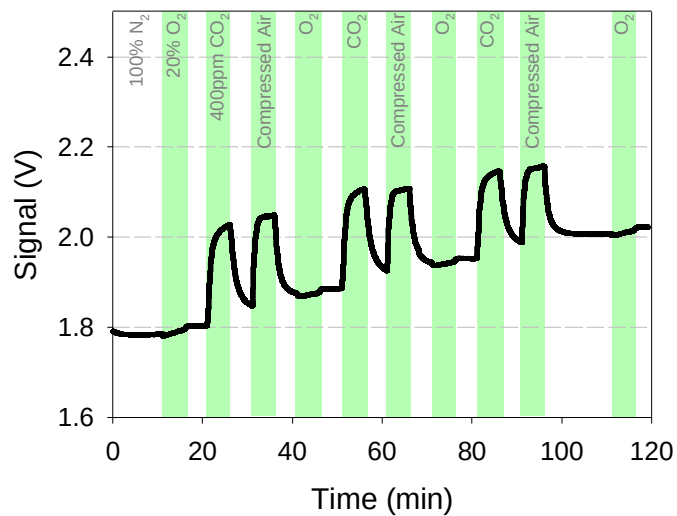


Figure 5.15. Pin-printed array response to 400 ppm CO_2 , 20% O_2 , and compressed air ($\sim 20\% \text{O}_2$, 380 ppm CO_2).

technologies are available employing photoacoustic, Raman, and colorimetric detection for real-time monitoring of CO₂ in exhaled breath. Preliminary tests were conducted to establish the feasibility of the current CO₂ sensor for monitoring exhaled CO₂ levels and breathing intervals. Sensors were mounted in the flow cell with a nitrogen (N₂, ~85% humidity) gas flow of 2 mL min⁻¹. Exhaled breath was introduced from a tee connection to a breathing mask equipped with a one-way flow valve. The quenching response due to the introduction of exhaled breath (typically >6% CO₂) and recovery during the inhale cycle of breathing is clearly shown in Figure 5.16. The use of colorimetric

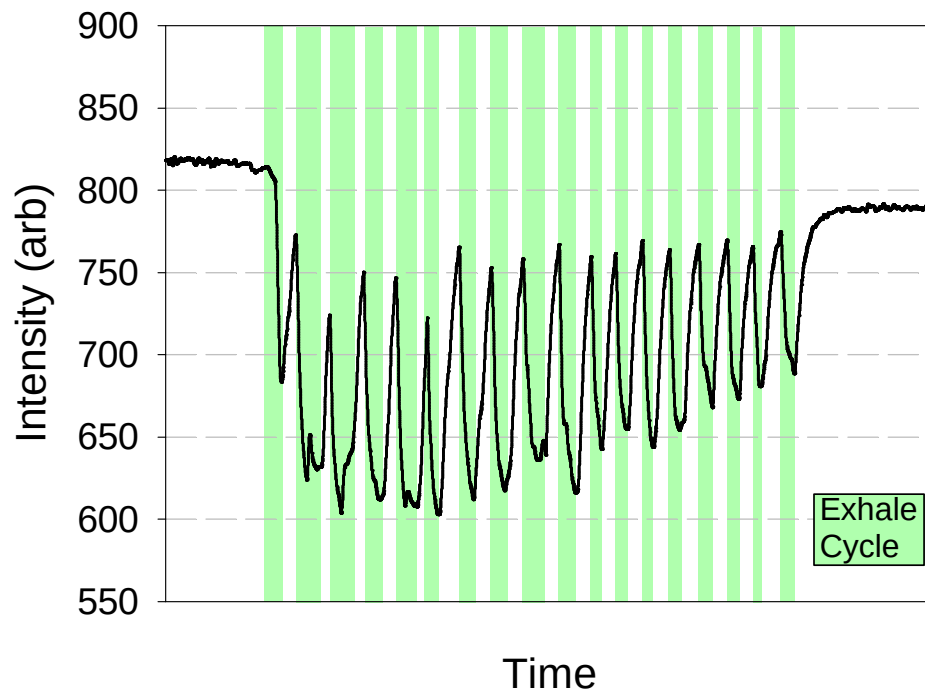


Figure 5.16. The quenching and recovery response of a sol-gel HPTS sensor for real-time CO₂ analysis in exhaled breath.

detection in commercial applications has to date been for disposable sensors based on color changes of the pH dye metacresol purple. The sensor color is observed by eye and compared to a color chart.¹³⁴

5.4. Conclusions

In the current work, organically modified sol-gel films containing HPTS⁻-Oct₄N⁺ ion pair were coated on glass slides to create CO₂ quenching fluorescent sensors. The ion-pair technique has been altered to yield highly sensitive, versatile sensors with simplified fabrication steps. Curing of the films under vacuum in a Schlenk tube was shown to increase the rate of diffusion of the analyte gas. The sensor was shown to be sensitive to concentrations of CO₂ in the 0.03-30% range with a limit of detection of 0.008% (or 80 ppm) and a limit of quantitation of 0.02% (or 200 ppm) CO₂, both well below atmospheric levels. The effect of humidity on the sensor was partially mitigated by applying moisture-proof coatings on top of the sensing film. TiO₂ particles (<5 μm diameter) were added to induce Mie scattering and increase the incident light interaction with the sensing film thus increasing the signal to noise ratio. A pin-printed array of sensors was coupled to a bifurcated fiber optic cable that can direct the excitation and emission light connected to a light source and detection unit. Preliminary experiments show that the sensor could have applications in the medical field of capnography and this sensing method is currently being investigated for use in monitoring combustion gas composition.

Part 6

Alcohol and Kerosene Detection Using Thin-Film Optical Sensors

6.1. Introduction

Hydrocarbons fuel many of the rockets used by the National Aeronautics and Space Administration (NASA) and are expected to play a major role in the future of the space program.¹³⁵ The John C. Stennis Space Center (SSC) in Mississippi is the leading NASA testing facility for liquid fuel rocket testing and certification.¹³⁶ There are a variety of ground-test sensing needs including chemical sensors for CO₂, CO, hydrocarbons, and isopropyl alcohol (IPA). In the 1960s, two test stands, the A-1 and A-2, were built to ground-test shuttle engines prior to launching. In anticipation of testing the new J-2X rockets for use in the Constellation program, construction of the A-3 test stand was started in 2007. The A-3 test stand is unique in that it will be able to simulate atmospheric conditions at altitudes of approximately 30,480 m.¹³⁶ To simulate these conditions, a vacuum must be generated by chemical steam generators. Steam is generated by the combustion of IPA, liquid oxygen (LOX), and water to generate approximately 2096 kg/s of steam.¹³⁶ The main combustion products of IPA are H₂O, CO₂, O₂, CO, and N₂. However, several hydrocarbons might also be produced, including methane, ethylene, acetylene, ethane, propylene, propane, and IPA.¹³⁶ The presence of these components in the line of sight of current optical emission/absorption measurements will complicate analysis. There is a need at the space launch vehicle ground-testing facilities for near-real-time detection methods that are miniaturized and are suitable for remote chemical detection in rocket plume testing conditions. Initial work on optical sol-gel and polymer sensors for the detection two rocket plume components, IPA

and kerosene are briefly discussed in this chapter. The ultimate goal is to develop sensors for various plume constituents which can be incorporated into a miniaturized multi-analyte testing device for simultaneous detection of multiple plume constituents. These sensors could then be placed in different locations around the plume for spatial and temporal responses, from which valuable information on environmental impact and rocket efficiency can be obtained.

6.2. Experimental

6.2.1. Chemical Reagents and Materials

Methyltriethoxysilane (MTEOS, 98% Acros), methyl trimethoxy-silane (MTMOS, 97% Acros), Methyl Red (MR, ACS certified, Acros), Rhodamine B (Allied Chemical), Phenol Blue (PB, 92% Acros), Nile Blue chloride (NB, Aldrich), Reichardt's dye (Aldrich), sodium hydroxide (NaOH, ACS certified, Fisher), hydrochloric acid (12.1 M, ACS certified, Fisher), isopropanol (IPA, ACS certified, Fisher), methanol (MeOH, ACS certified, Fisher), ethanol (EtOH, ACS certified, Fisher), toluene (ACS certified, Fisher), ethylcellulose (EC, 49% ethoxy content, MP Biomedicals, Inc.), Chromoionophore IX (Fluka), tridodecylmethylammonium chloride (TDMACl, 98%, Sigma Aldrich), bis(2-ethylhexyl) sebacate (DOS, Sigma Aldrich), bis(trimethoxysilylpropyl)amine (ATMOS, Gelest), N¹-[3-(trimethoxysilyl)propyl]ethane-1,2-diamine (ethylenediamine precursor, 97% Aldrich) were used as received. Tetrahydrofuran (ACS certified, Fisher) was dried over potassium/benzophenone, distilled, and stored under N₂ before use. Aqueous solutions were prepared using DI water (18 MΩ cm) from a Barnstead

International e-pure 4-holder deionization system. Glass slides were cut from standard microscope slides. Vapor phase analytes were introduced in nitrogen flow from a standard high purity N₂ tank (Airgas) or bleed off from a liquid N₂ tank as described below.

6.2.2. Instrumentation

A Perkin Elmer LS55 luminescence spectrometer with a pulsed Xe source was used for fluorescence measurements of the sensing films. Films were coated using a custom-built spin coater. For fluorescence measurements, the films were placed in the brass flow cell described in Section 5.2.2. Absorbance-based measurements were made using either a Thermo Evolution 600 scanning UV-vis spectrophotometer or Agilent 8453 photodiode array UV-vis spectrophotometer with a peltier thermostatted cell holder for temperature control. The sensors were placed inside a 2 mm pathlength quartz cell with plastic gas inlet and outlet tubes placed at the top and bottom. The top of the cuvette was sealed tightly with parafilm to create a gas-tight flow cell.

6.2.3. Experimental Procedures

Solutions of MR (0.5 mM) were prepared in aqueous phase by adjusting pH to 4.0 with HCl and organic phase by mixing the appropriate amount of dye in isopropanol (not pH adjusted). Generally, MR sol-gel films were produced by mixing 200 μ L of either methyl triethoxy-silane (MTEOS) or methyl trimethoxy-silane (MTMOS) precursors with 100 μ L of EtOH or MeOH, respectively, 25 μ L of

0.1 M NaOH, and 3-4 mg of dye. The solutions were stirred for 1 h followed by spin coating on clean glass slides at ~2620 rpm. For EC-MR films, initially 1 g of a 10% (w/w) EC solution in 1:4 (v/v) toluene:EtOH was combined with 7 mg of MR dye and stirred for several hours until a homogenous mixture was achieved. This optimized procedure from phase I of the project was later modified to use a 2.5% EC solution to create a less viscous coating solution and thinner, more uniform films. To produce the sensing films containing the fluorescent dye Rhodamine B, 1 mg of Rhodamine B was combined with 200 μ L of MTMOS, 50 μ L of EtOH, and 25 μ L of 10 mM NaOH and stirred for 1 h. The gels were spin-coated on glass slides and stored under static vacuum for 52 h before testing.

PVC films of Chromoionophore IX were first made according to previously published methods.^{137,138} Briefly, 1 mg of dye was dissolved in 88 μ L of THF along with 40 mg of PVC, 80 mg of DOS plasticizer, and 0.28 mg of TDMACl catalyst. Films were spin-coated on glass slides at 2620 rpm and stored under ambient conditions to produce fluorescent orange films. Sol-gel based films of Chromoionophore IX were fabricated by an adaptation of work by Korent et al.¹³⁹ Briefly, 2 mg of dye and 0.28 mg of TDMACl were mixed with 100 μ L of MTEOS, 100 μ L of TMOS, 100 μ L of EtOH, and 25 μ L of 0.1 M NH_4OH catalyst. The solution was stirred at high speed for 1 h before coating. Glass slides were coated by spin-coating 50 μ L of the sol solution at 3850 rpm. Ethyl cellulose based sensors were made similarly to other EC sensors described earlier. EC solution (2.5% w/w) was made by dissolving 0.25 g of EC in 8 mL of toluene and 2 mL of EtOH with sonication for 10 min followed by stirring until dissolved. To

make the sensing films, either 1 or 2 mg of Chomoionophore IX dye and 0.28 mg of TDMACl were dissolved in 1 g of 2.5% EC solution with stirring. The dye containing EC solution was spin-coated on glass slides at a variety of spin rates. The films were cured under static vacuum for 24 h prior to testing and between uses.

Sol-gel films for kerosene detection (Sol-A and Sol-B Table 6.1) were produced based on a previously published procedure.¹⁴⁰ Bis(trimethoxysilylpropyl)amine (ATMOS), N¹-[3-(trimethoxysilyl)propyl]ethane-1,2-diamine, and methyltrimethoxysilane (MTEOS) were used for sol-gel precursors. The appropriate precursor (25 μ L) was mixed with 45 μ L of methanol, 30 μ L of water, 30 μ L of MTMOS precursor along with 30 μ L of dye solution (10 mM in methanol), stirring for 1 h until the viscosity of the sol was adequate for spin coating.

6.2.4. Analysis Procedures

Several potential indicator dyes were selected and tested for response to IPA and interference from kerosene and temperature. A UV-vis (photodiode array detector) equipped with a peltier temperature controller/magnetic stirrer was used to monitor changes in the absorbance spectra of the indicator dyes with changing concentrations of analytes and varying temperatures. In order to achieve high sensitivity for IPA and kerosene, aqueous or organic solutions of the dye were used, respectively. Aliquots of either IPA or kerosene were then added and the final percentage calculated. For temperature based studies, the

temperature controller was used to adjust the cell temperature from 10 to 100 °C. The controller is equipped with a thermocouple probe that is inserted in the top of the cell to monitor the actual temperature of the analyte solution. The dye solutions were placed in a sealed cell with thermocouple inserted and the temperature was ramped up and down to get the spectra. It should be noted that the return temperature ramps were not completely reversible, most likely due to structural changes/decomposition at higher temperatures. Fluorescence based tests of the dyes and sensing films were conducted in solution/solid phase in a Perkin Elmer LS55 luminescence spectrometer utilizing a standard 1 cm quartz cuvette or front surface accessory fitted with a custom flow cell as described earlier for CO₂ sensors.³³ For time-based signal measurements, a signal reading was usually integrated over 1 s. When signal averaging was used to improve signal noise, each data point was averaged with the two data points preceding and following it.

Gas phase kerosene and IPA was generated by flowing N₂ gas over the headspace of a 500 mL Erlenmeyer flask containing a small amount of either analyte. When quantitative amounts of IPA were needed for calibration data, a gas saturator/bubbler was used to saturate the gas stream with analyte at various temperatures. Calculations of vapor pressure at various temperatures were made using Antoine equation (6.1), where A, B, and C are constants over a defined temperature range.¹⁴¹

$$\log p = A - \frac{B}{t + C} \quad (6.1)$$

The gas saturator consisted of a double walled glass vessel in which the analyte solution is kept (Figure 6.1). The lid contained a fine glass frit gas diffuser which extended into the analyte solution allowing N₂ to flow into the solution. The lid has a both a gas inlet and outlet for N₂ and anayte saturated N₂ respectively and is gas sealed by an O-ring and clamp. The analyte vessel was then connected to a thermostatted recirculating temperature controller and the temperature set to 0 °C to obtain approximately 1.08% IPA (10,000 ppm). This could be further diluted by mixed the various amounts of N₂ make up flow and 1% IPA in N₂ to the desired concentration of IPA.

6.3. Results and Discussion

6.3.1. Dye Selection/Testing and Sensor Preparation for the Measurement of Isopropyl Alcohol

In previous collaborations with Innosense LLC, Neutral Red was shown to respond to changes in IPA vapor concentrations. Neutral Red belongs to the class of dyes known as quinone-imines.¹⁴² When exposed to solvents of different polarities, the absorbance spectrum of the dye solution shifts. These types of dye are more generally named solvatochromatic dyes, and optical vapor sensors have been developed for a variety of dyes including Reichardt's betaine dye and Phenol Blue immobilized in sol-gels.¹⁴³ While Neutral Red did show

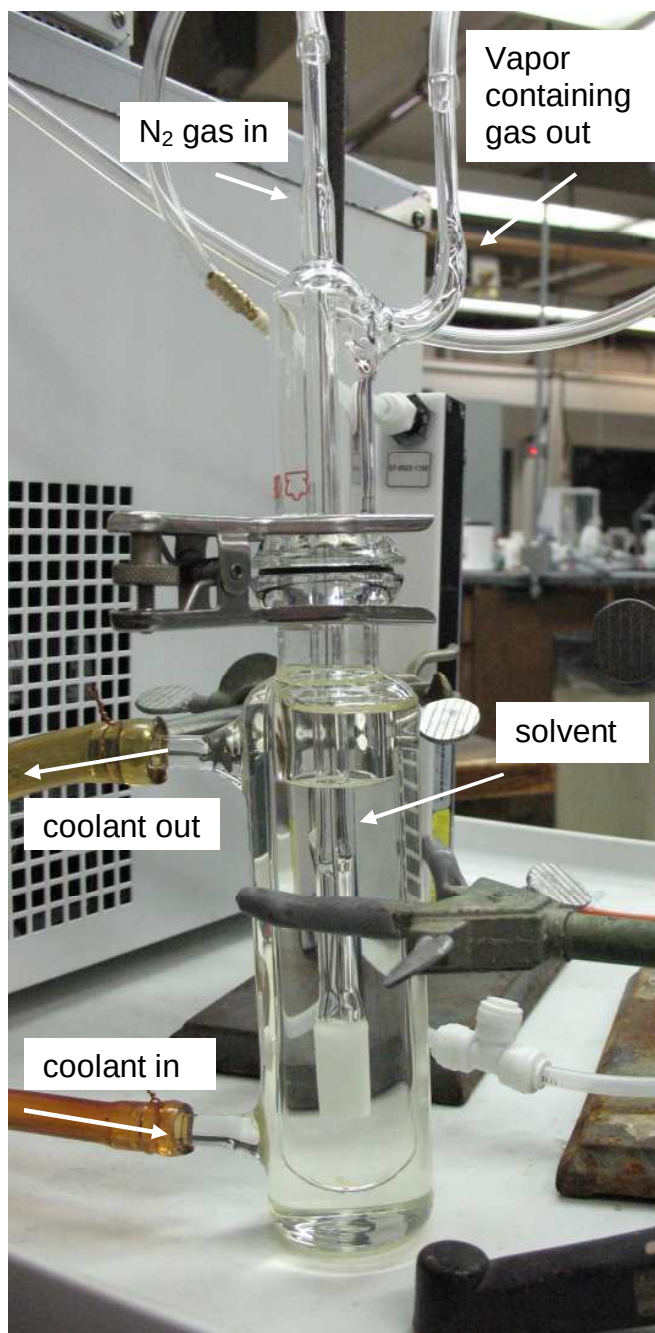


Figure 6.1. Gas saturator/bubbler for generating analytical quantities of VOCs in N₂ gas streams.

changes in absorption spectra on exposure to IPA, evaluating alternate optical dyes and sensing strategies was thought to be valuable for the project. Outlined below are some of the alternative sensing mechanisms that our group has been investigating. Four additional solvatochromatic dyes, Methyl Red, Rhodamine B, Phenol Blue, and Nile Blue have been evaluated. In the case of Methyl Red, the absorbance of the dye is changed on exposure to alcohols. This section will also describe the use of a chemically selective Chromoionophore IX dye for IPA detection.

6.3.1.1. *Methyl Red Indicator*

Methyl Red dye (MR) is a commonly used pH indicator dye, with a pK_a of 5.1, which also exhibits solvatochromatic responses due to polarity changes in its immediate environment (Figure 6.2). In the case of Methyl Red (MR), the absorbance of the dye is changed on exposure to alcohols. In solution phase, Methyl Red is blue-shifted in the presence of IPA and we observed a slight decrease in peak intensity. The dye has previously been incorporated into sol-gel sensors for liquid phase measurements of IPA, but response times were >24 h and the sensors were not highly sensitive.¹⁴⁴ To our knowledge, the dye has not been used for detection of IPA in the gas phase or at low concentrations. While the sensor responds to other alcohols, IPA was shown to have the largest effect on the dye.

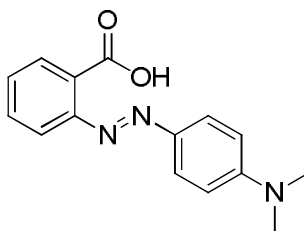


Figure 6.2. Chemical structure of Methyl Red indicator dye.

The dye was first tested for aqueous phase response to both temperature and % volume of added IPA (Figure 6.3). For temperatures between 20 and 80 °C, the absorbance peak at 550 nm remains essentially unchanged. A very small new peak in the near IR range appears at high temperatures at ~940 nm and disappears on return to lower temperatures (Figure 6.3A). For response to IPA, aliquots of IPA-dye solution were added to ensure the total dye concentration did not change. Over the range of 0-18%(v/v), the absorbance peak blue shifts from 550 nm to ~440 nm with a decrease in intensity (Figure 6.3B).

MR indicator dye was immobilized in various sol-gel matrices for use as a sensor for gas phase IPA detection. First, organically modified silica sol-gel precursors were evaluated for producing MR immobilized gas sensors. For MTEOS sensors, the sol solution was found to be biphasic and not ideal for spin coating sensors. For MTMOS sols, the use of 0.1 M NaOH for base catalysis caused the sol-gel reaction to proceed too quickly and the sols gelled before 1 h. Changing to 25 μ L of 10 mM NaOH resulted in a reduction of the sol-gel formation kinetics and successful sensor fabrication. Additionally, 1:1 mixed films of ORMOSIL : TMOS were prepared using similar formulations. The spin-

coated films were cured in an oven for 12 h at 60 °C followed by curing under vacuum to remove residual solvents. Comparison of the solution phase response of MR to the MTEOS films under N₂ gas flow demonstrates that the polarity of the ORMOSIL substrate falls somewhere between that of aqueous and mixed aqueous/IPA solutions (Figure 6.4A). The decrease in peak height is attributed to the thickness of the sensing thin film, in accordance with Beer's Law. Upon exposure to pulses of IPA containing N₂ gas, the broad absorbance peak from 400-500 nm increases and returns back to the original response in 100% N₂ flow (Figure 6.4B).

Gas phase sensor response was tested using the gas saturator system described in Section 6.2.3. Pulses of 1% IPA were introduced (Figure 6.5A) to the MTMOS and mixed MTMOS/TMOS sensors, and the effects on the absorbance were monitored (Figure 6.5B). The MTMOS sensor showed a reversible response to 1% IPA with a very flat baseline. MTMOS/TMOS sensors also showed reversible response, but had considerable baseline drift on exposure to IPA. These spectra were collected using the glass substrate as the reference. When used in the opto-electronic unit design by Innosense LLC (see Section 6.3.3.), a blank sol-gel or polymer film will be used for dynamic baseline correction which should mitigate signal drift.

Preliminary studies of MR in EC matrix were completed in an attempt to limit the number of references needed in the final opto-electronic unit set-up. The optimized procedure developed in phase I was initially used to create the

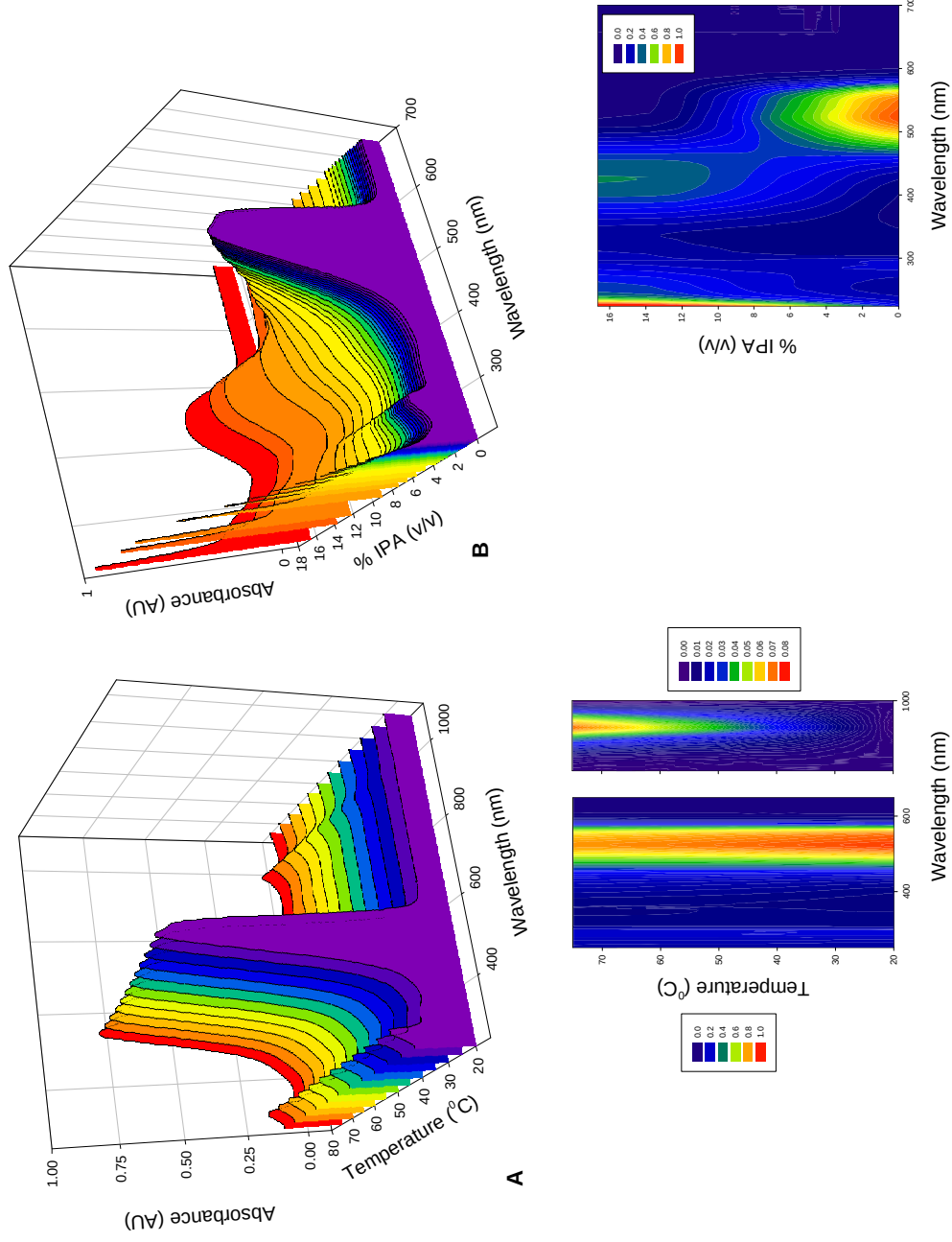


Figure 6.3. (A) Response of Methyl Red to temperature; (B) Response of Methyl Red to changes in IPA concentrations.

EC-MR solution. The solutions appeared to be extremely thick and too viscous for spin coating. For the first two trials that were conducted, the solutions contained 4 and 8 times the original ratio of toluene:ethanol solvent, respectively, in order to make the solution less viscous. EC formulations gave extremely uniform and transparent looking films after spin coating onto slides. It was noted that the films could be peeled off easily in one piece, which may indicate that a surface pretreatment is needed to increase film adhesion. Absorbance spectra were obtained during pulses of 1% IPA and N₂, and it was noted that the response signal at 415 nm was somewhat small with noticeable drift (Figure 6.6). Still, samples showed quick response times (<1 min) when the gases were being switched from the N₂ baseline to 1% IPA. Future trials may include diluting the EC solution with greater excesses of 4:1 toluene:ethanol ratios in hopes of achieving thinner films or adding a porogen to increase gas diffusion through the sensing films.

6.3.1.2. Rhodamine B Fluorescent Indicator

Rhodamine B (Figure 6.7) is a fluorescent dye that is commonly used for staining and a flow and transport tracer in biological and hydrology studies, respectively. It is well known that the intensity of the emission peak is enhanced when the dye is solvated by alcohols. In aqueous phase, the expected emission peak at 575 nm was observed which increased linearly upon the addition of aliquots of IPA (Figure 6.8A). Thus, Rhodamine B was selected as a possible indicator for incorporation into sol-gels for the optical of sensing alcohols.

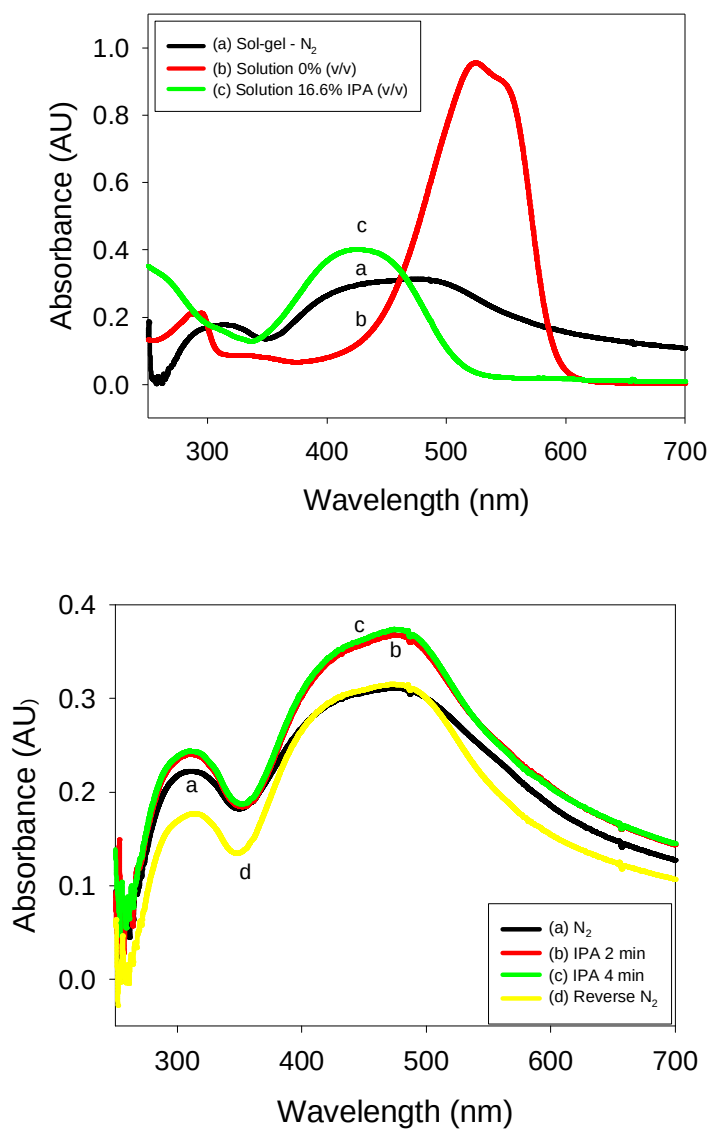


Figure 6.4. (A) Comparison of solution phase response to MR immobilized in MTEOS ORMOSIL; (B) Spectral response to pulses of IPA vapors in N_2 gas.

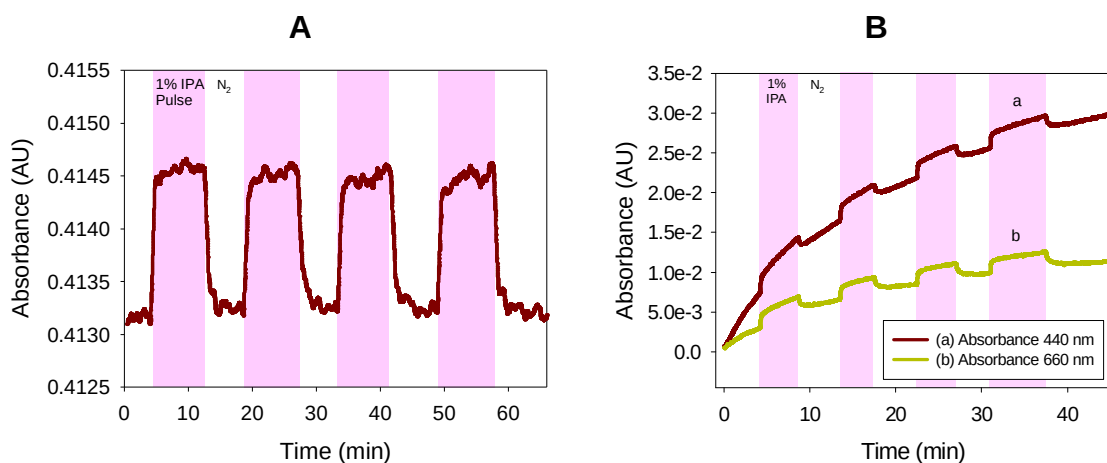


Figure 6.5. (A) MR-MTMOS film absorbance response (420 nm) every 0.5 s to pulses of 1% IPA in N₂, 0.5 s signal interval averaged over five points; (B) 1:1 MTMOS:TMOS film absorbance response to pulses of 1% IPA in N₂, 0.5 s signal interval without averaging.

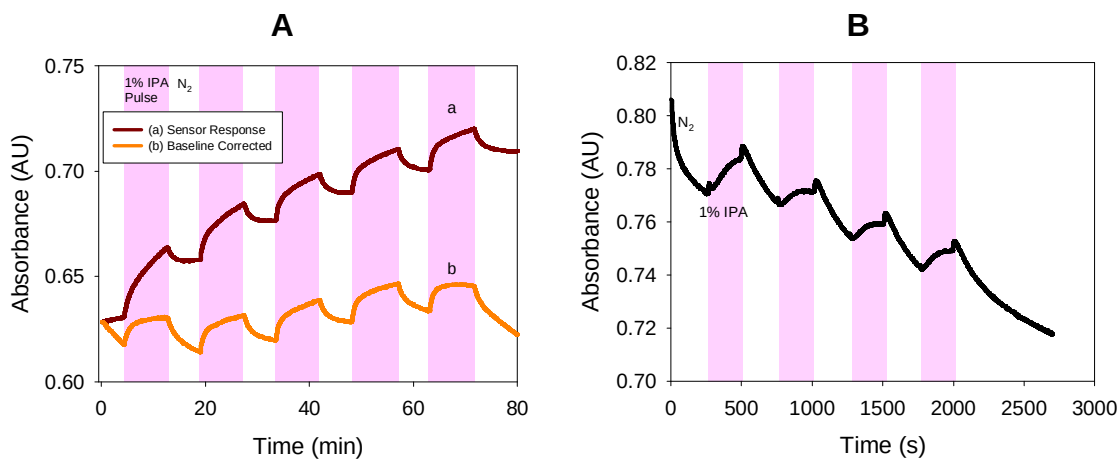


Figure 6.6. (A) Trial 1 – Thicker film MR-EC response at 415 nm to pulses of 1% IPA in N₂; (B) Trial 2 - Thinner film MR-EC response.

Rhodamine B was immobilized in a MTMOS sol-gel matrix as a potential sensor for IPA vapors. The emission response of the indicator in the sol-gel matrix was red shifted to 590 nm from 575 nm in aqueous phase (Figures 6.8A and 6.9A). The intensity of the emission peak increased upon exposure to IPA vapors. However, the original N₂ response could only be obtained after storage under dynamic vacuum for several hours. The time based fluorescence measurements on exposure to IPA are shown below (Figure 6.9B).

6.3.1.3. *Phenol Blue Indicator*

Phenol Blue is a positive solvatochromic dye with a quinineimine (Figure 6.10A) form that predominately contributes to the electronic structure in ground state.¹⁴⁵ The dye red-shifts from 552 nm in hexane to 684 nm in water due to the increase in polarity and formation of the excited state zwitterionic form (Figure 6.10B). Because the indicator is a thermosolvatochromatic dye, its solution phase response to temperature, % IPA, and % kerosene were all explored (Figure 6.11). For the temperature tests, the peaks at 360 and 570 nm decrease slightly with increasing temperature, however no peak shift was observed. An

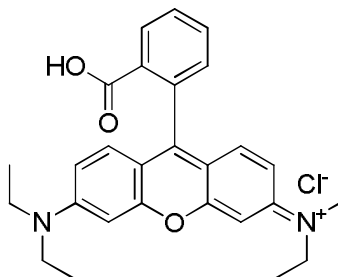


Figure 6.7. Chemical structure of Rhodamine B

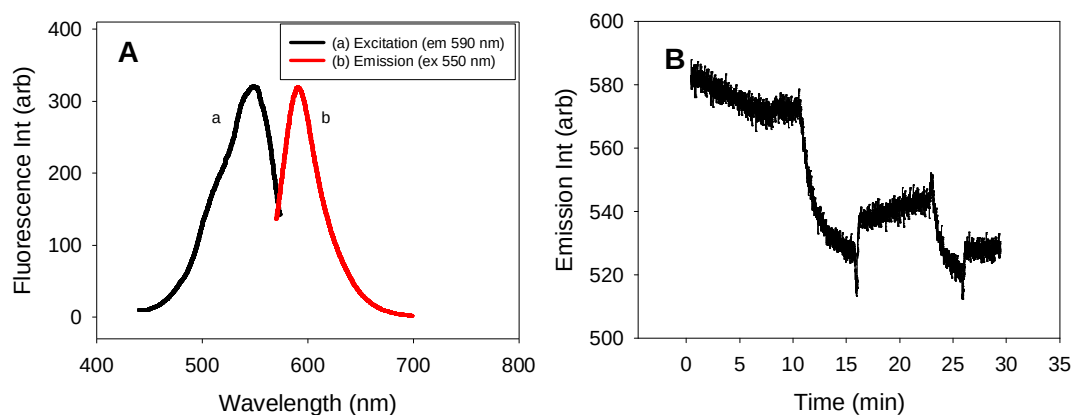


Figure 6.9. (A) Excitation/Emission scan of Rhodamine B immobilized in a MTMOS sol-gel matrix. (B) Emission time-based response to pulses of N_2 saturated with IPA at room temperature.

increase was observed for the reverse temperature ramp back to 20 °C but the response was not completely reversible. On exposure to IPA, the peak at 650 nm blue shifts to 570 nm with a decrease in peak intensity and a new feature was observed at 360 nm. For sensitivity to kerosene, ethyl alcohol (EtOH) was used for the baseline response as water is not miscible with kerosene. Upon the addition of aliquots of kerosene, the peak at 615 nm decreased slightly due to the addition of non-polar kerosene. An additional peak at ~250 nm was observed in the region where virtually all organic compounds absorb.

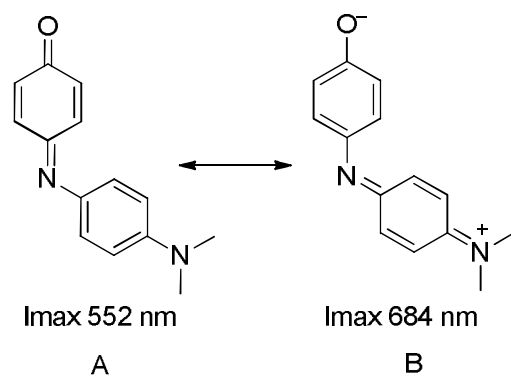


Figure 6.10. The zwitterionic forms of Phenol Blue.

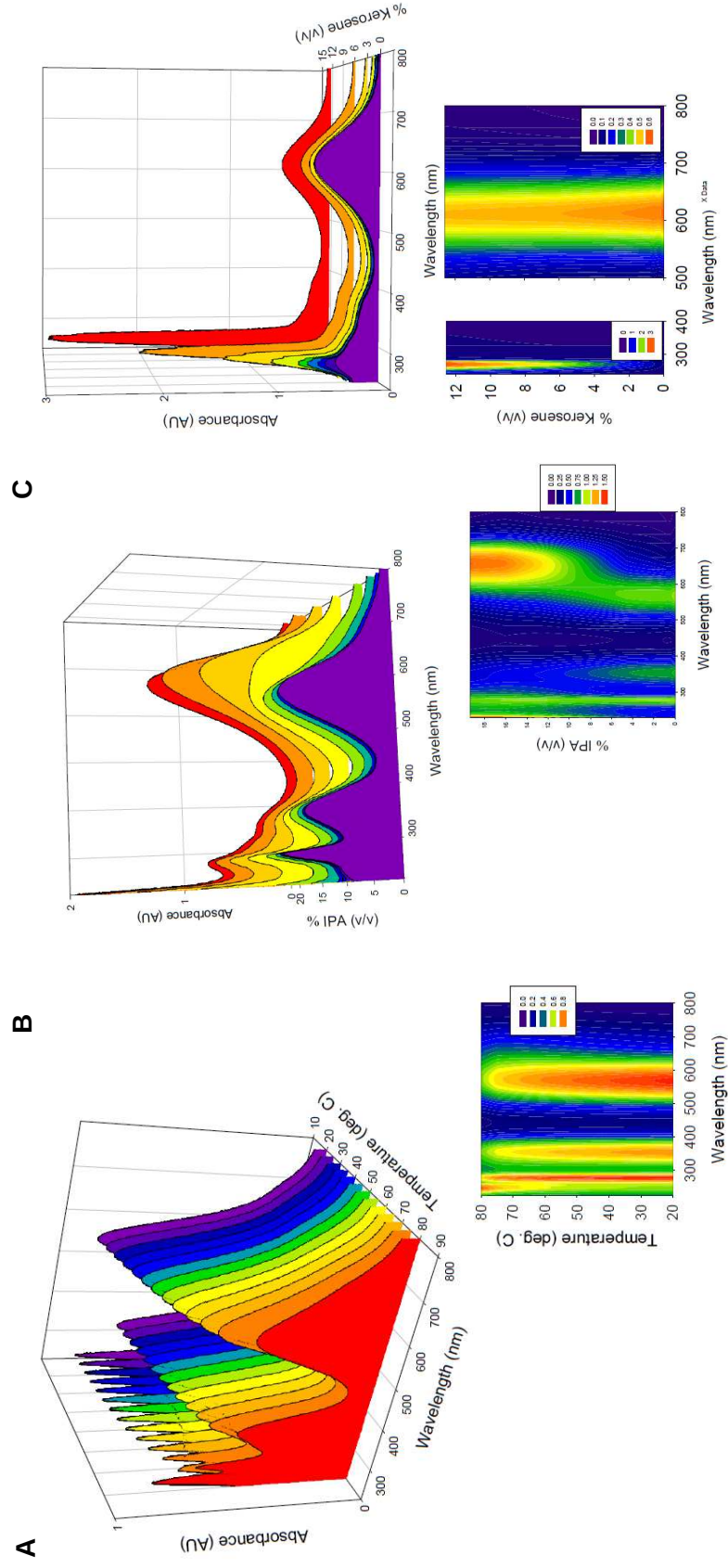


Figure 6.11 (A) Temperature Response of 1 mM aqueous Phenol Blue (20% IPA) from 20-80 °C; (B) Spectral changes of aqueous Phenol Blue solution with addition of IPA to 20% (v/v); (C) Phenol Blue dissolved in EtOH, spectral changes with addition of kerosene to 15% (v/v).

6.3.1.4. Nile Blue Indicator

Fluorescent dye Nile Blue (Figure 6.12) has been previously reported for use as an indicator for alcohols when used in poly(ethylene glycol) (PEG) dimethacrylate hydrogels.¹⁴⁶ Nile Blue has also been shown to be viable sensing dye for alcohol detection. When Nile Blue is immobilized in a hydrogel polymer film, two emission bands are observed at 630 and 700 nm.¹⁴⁶ This allows for the ratiometric detection of fluorescence changes induced by alcohols. The pore size of the sensing films could also be tailored to prevent larger molecules from diffusing into the film and affecting the signal. The main advantage of Nile Blue is that the sensor response is not highly affected by high temperatures. The hydrogel sensors were autoclavable without significant changes in signal output. EtOH solutions were tested with an intention to measure alcohol concentration in wines. The mechanism underlying the change seems to be similar to that of other solvatochromatic dyes such as Reichardt's dye and Phenol Blue. We observed the fluorescence emission response to increasing IPA concentration up to 4% (v/v) (Figure 6.13). The peak at 670 nm decreases slightly with the addition of aliquots of IPA to the cuvette.

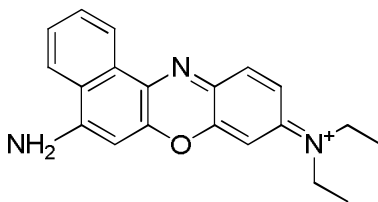


Figure 6.12. Chemical Structure of Nile Blue (NB).

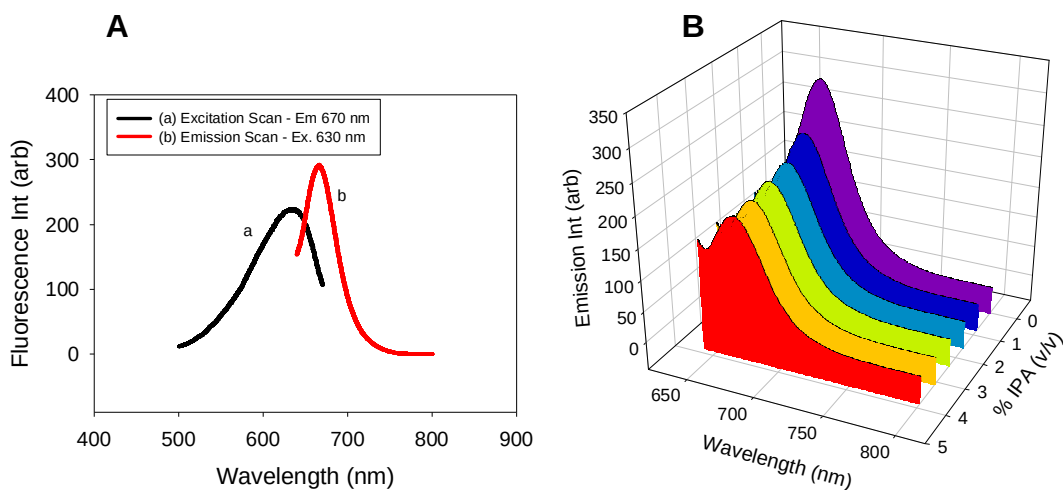


Figure 6.13. (A) Fluorescence excitation/emission scan for NB in aqueous phase; (B) Emission peak at 670 nm response to increasing IPA up to 4% (v/v).

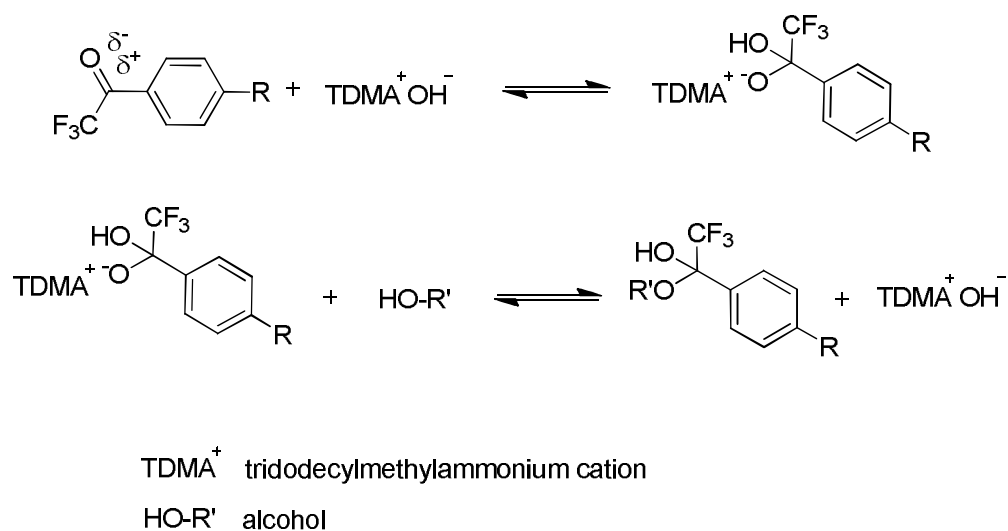
6.3.1.5. *Chomroionophore IX*

One of the only classification of dyes that have been shown to be chemically selective for alcohol detection are trifluoroacetophone-based stilbene dyes (Scheme 6.1).^{137,147-150} The sensing mechanism relies on the reaction of the trifluoroacetyl group of the dye with an alcohol to form a hemiacetal. Here the dye is composed of a stilbene moiety terminated by electron donor and acceptor groups. The trifluoroacetyl group serves as the electron acceptor due to the strong electron withdrawing capacity of both the carbonyl group and the trifluormethyl group. At the same time, the alkylamino group serves as both the electron donor group and makes the dye lipophilic so it can be incorporated into a polymer matrix. Reaction with alcohols (Scheme 6.1) changes the electron

acceptor capabilities of the trifluoroacetyl group and thus causes the emission spectra to blue shift.

In solution, it was shown that different alcohols blue-shift the fluorescence emission to different extents. In purely organic solutions, i.e., cyclohexane, the dye was reported to emit at 476 nm. On exposure of IPA, the emission peak is shifted to 439 nm with a very small quantum yield.¹³⁷ The fluorescence quenching mechanism forms the basis for detection of the alcohol. In cases where multiple alcohols are present, the quantum yield of the hemiacetal formation from IPA could be enhanced with light harvesting dyes to enhance the selectivity.¹⁵¹ The reaction of the alcohol with the trifluoroacetyl group is quite slow, requiring several hours to reach equilibrium. To overcome this, Mohr et al. demonstrated that the addition of a quaternary ammonium hydroxide, tetradecylammonium chloride (TDMACl), as a catalyst could significantly speed the reaction and make the dye viable for alcohol sensing. To our knowledge, the dyes have not been demonstrated for use in sol-gel matrices or for gas phase detection of alcohols.^{137-139,147,149,150,152-154}

Sensing films were initially produced according to Mohr et al.^{137,138} After exposure to air for several days, the films lost most of their visible color. However, they were still responsive to 1% IPA pulses (Figure 6.14B). An emission peak at 540 nm (cutoff filter at 515 nm, PMT 900 mv) was observed when the films were excited at 450 nm (Figure 6.14A). The emission peak was monitored during pulses of N₂ and N₂ containing 1% IPA vapors, and a decrease in emission intensity was observed due to hemiacetal formation. The response



Scheme 6.1. Trifluoroacetophenone-stilbene based dyes with selectivity for alcohol detection. The proposed mechanism of the catalysis by the trifluoroacetyl group with an alcohol is shown.¹³⁸

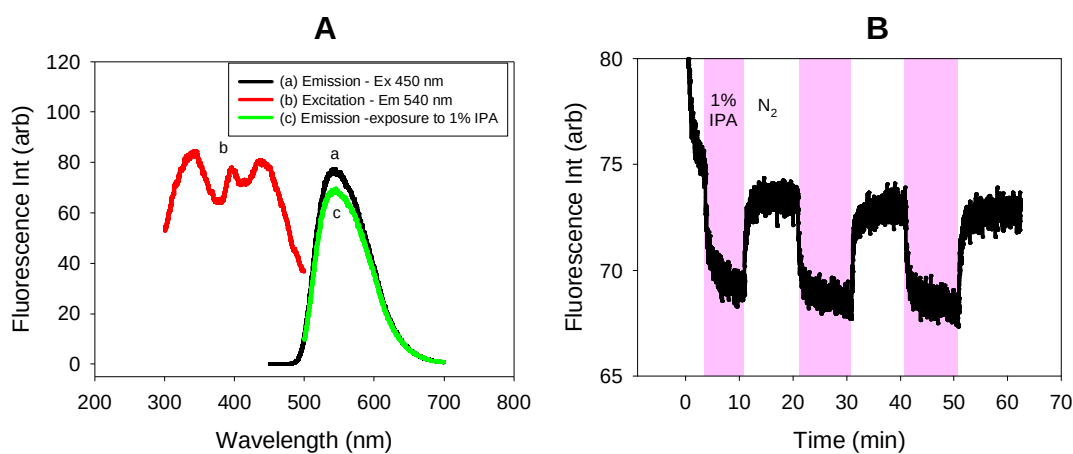


Figure 6.14. (A) Excitation/Emission scans of PVC sensing film and emission showing signal quenching on exposure of 1% IPA; (B) Time based emission at 540 nm showing signal response to pulses of 1% IPA in N₂ without signal averaging or background correction.

shows that the reaction is reversible in the time scale required for sensing.

These results are promising as they represent a clear advantage over sensing strategies that rely on physical changes (i.e., polarity) for chemical selectivity.

A second set of sensing films were made with twice the dye content, a spin rate of 6600 rpm, and storage under nitrogen in order to obtain higher sensitivity for 1% IPA. The results from these sensors (Figure 6.15) showed better sensitivity and a 0.5% pulse of IPA produced roughly one half the response of a 1% pulse. The sensors were then tested for quantitative response to IPA in the 0.033-1% range (Figure 6.16). While the PVC sensors appear to

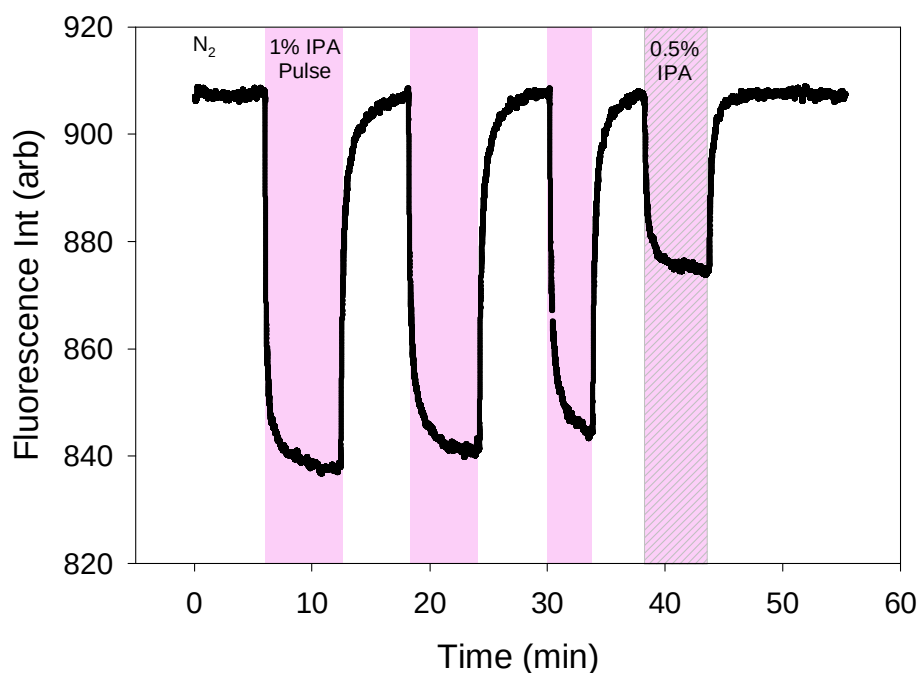


Figure 6.15. PVC sensor with twice the dye content and stored under N₂ response to both 1% and 0.5% IPA pulses.

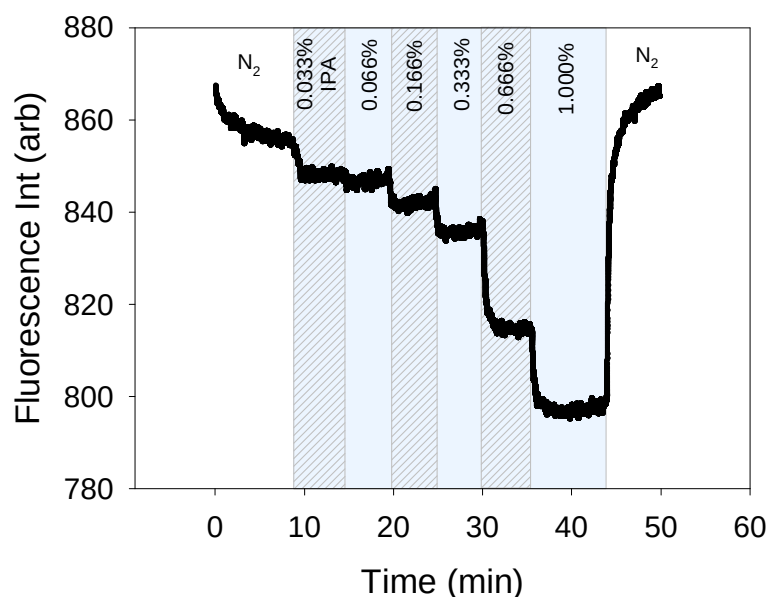


Figure 6.16. PVC sensors calibration response to 0.033-1.00% IPA with signal averaging and baseline correction.

respond nicely to various concentrations of IPA, the signal is quite noisy and requires signal averaging. The baseline is also corrected for baseline drift.

Both sol-gel and ethylcellulose (EC) were explored as possible alternative sensor matrices for Chromoionophore IX alcohol sensors. Sol-gel based sensors were fabricated by an adaptation of work by Korent et al.¹³⁹ As the sol-gel reaction uses alcohols as a solvent and alcohols are a by-product of the reaction, it was imperative to store the sensors under vacuum to remove residual solvents. The sol-gel sensor response to pulses of 1% IPA is shown in Figure 6.17. While the sensor does show a somewhat reversible response, the response times were somewhat variable. Initially the response to IPA was quick,

but after switching back to N₂, the background response was higher than the initial baseline and the second pulse of IPA showed slow response. One reason for this behavior could be that the sol-gel matrix has an affinity for alcohols, and once exposed regeneration of baseline conditions might be difficult.

The motivation for using EC as a sensing matrix stems from the ultimate goal of designing a multi-analyte sensing platform. The multi-channel device needs at least one channel devoted to a background sensor with an identical formulation as the sensing matrix minus the incorporation of the sensing dye. Innosense LLC has developed numerous sensors using EC as the matrix. Figure 6.18 shows the calibration response of an EC sensor made with 1 mg of dye and a spin rate of 3850 rpm. Using an EC matrix stabilized the baseline

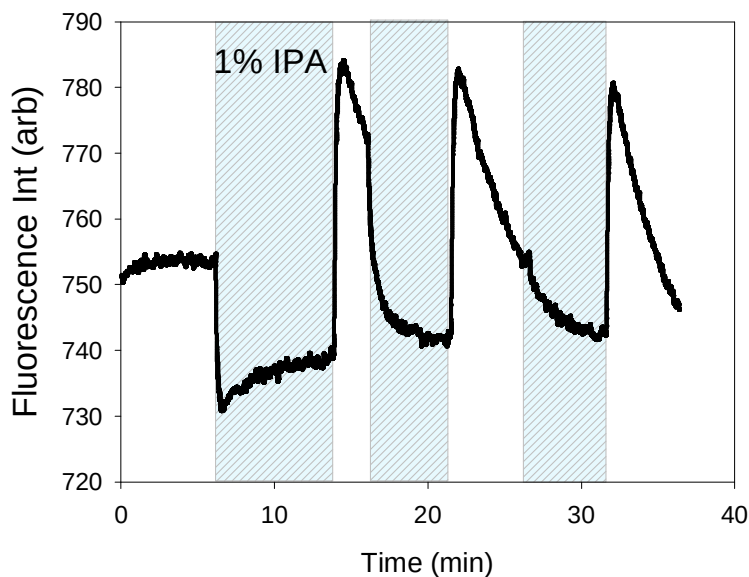


Figure 6.17. Response behavior of Chromoionophore IX sol-gel sensor on exposure to 1% pulses of IPA; Emission detected at 580 nm.

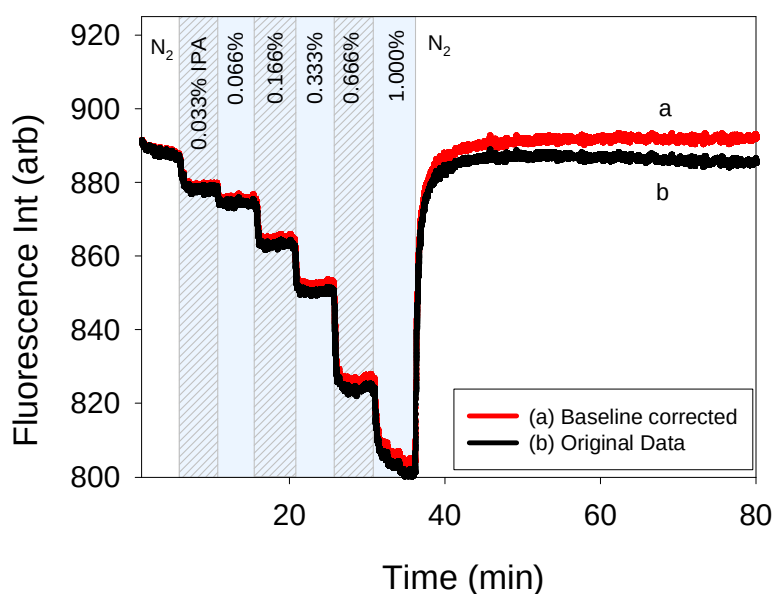


Figure 6.18. Response of a Chromoionophore IX IPA sensor in EC to 0-1% IPA calibration vapors.

response as can be seen by the small difference between the original (black) and baseline corrected response (red).

6.3.2. Dye Selection for Kerosene Sensor

The optical detection of kerosene will be achieved by using indicators that change their absorbance or fluorescence emission characteristics in the presence of kerosene vapors. Reichardt's betaine dye (Figure 6.19A) and resorufin dye (Figure 6.19B) were selected for their potential sensitivity towards kerosene vapors. Reichardt's dye is a solvatochromic dye with an electronic transition of approximately 350 nm when changing the solvent from tetrahydrofuran to methanol.¹⁵⁵ Two different sol-gel formulations were used to

immobilize the indicator in the sol-gel matrix. Due to the hydrophobic nature of the dye, a non-polar media is required. When using pure alkoxide precursors, such as tetramethyl orthosilicate (TMOS), the dye precipitates. Additionally, acid catalyzed sol-gel reactions can adversely protonate the phenolate group of the dye. Successful encapsulation of the dye requires slightly basic non-polar conditions. Two separate formulations were used as outlined in Table 6.1.

In Sol-A, bis(trimethoxysilyl)propylamine (ATMOS) and methyltrimethoxysilane (MTEOS) were used for sol-gel precursors according to a previously published procedure.¹⁴⁰ The kerosene sensors prepared by Sol-A formulation were wine red in color (Table 6.1). ATMOS is advantageous because its long chain spacer unit contains both hydrophobic and hydrophilic groups, providing a good mixture of polar and non-polar environment for the dye. Additionally, the amino-containing precursors provide the slightly basic sol-gel conditions needed to prevent protonation of the dye.¹⁴⁰ In Sol-B formulations, the ethylenediamine functionalized precursor N¹-[3-(trimethoxysilyl)propyl]ethane-1,2-diamine was used. The optical properties of Reichardt's dye are strongly influenced by non-covalent properties as can be seen in the color difference between the sensors prepared with different precursors. Figure 6.12 shows the UV-vis absorption properties of both kerosene sensors. Sol-A sensors show an absorption peak at ~520 nm while in Sol-B sensors the dye absorption peak is shifted to ~650 nm. On exposure of kerosene, the absorption peak red shifts by approximately 80 nm.

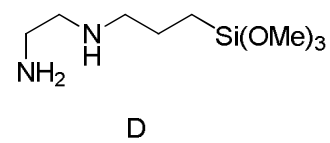
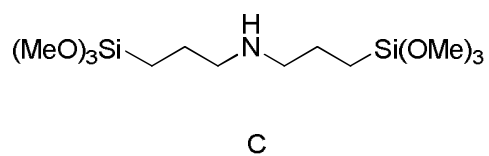
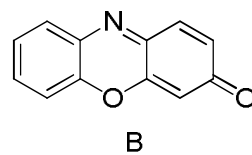
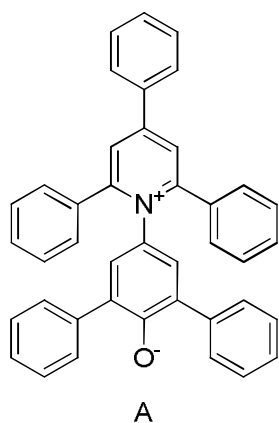
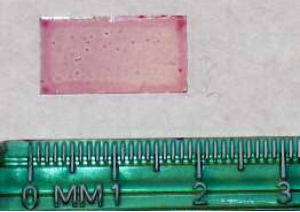
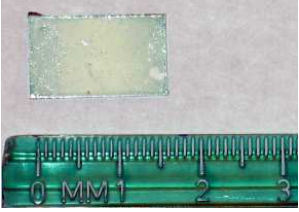


Figure 6.19. Chemical structure of Reichardt's dye (A), Resorufin dye (B), Bis(trimethoxysilylpropyl)amine (C), and ethylenediamine N¹-(3-(trimethoxysilyl)propyl)ethane-1,2-diamineprecursors (D).

Table 6.1. Kerosene sol-gel sensor formulations using Reichardt's dye

<i>Sol-A</i> <i>Precursors</i>	<i>Sol-B</i> <i>Precursors</i>	<i>Kerosene sensor</i> <i>prepared with Sol-A</i>	<i>Kerosene sensor</i> <i>prepared with Sol-B</i>
25 μ L of ATMOS	200 μ L of Ethylenediamine precursor		
45 μ L of MeOH	250 μ L of MeOH		
30 μ L of 10 mM dye/MeOH	7.5 mg of dye		
30 μ L of H ₂ O	60 μ L of H ₂ O		
30 μ L of MTEOS	100 μ L of MTEOS		

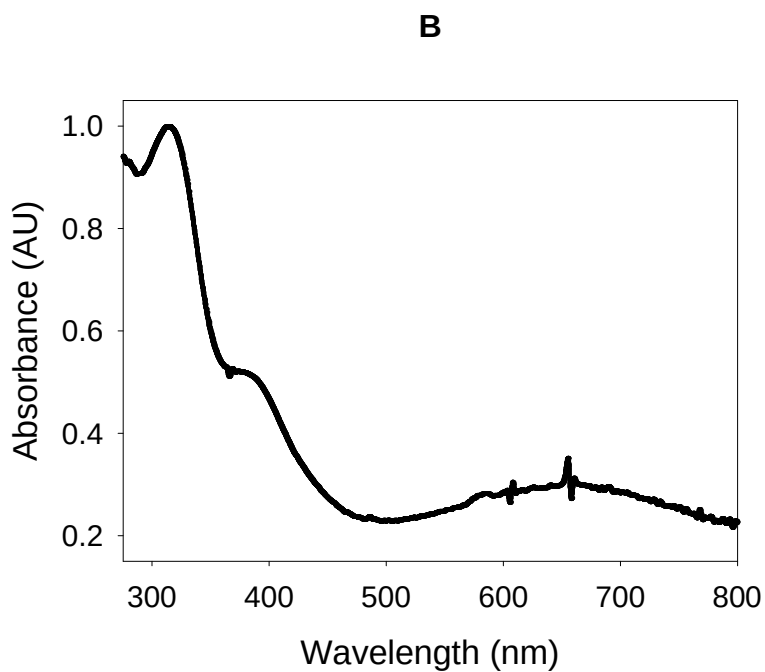
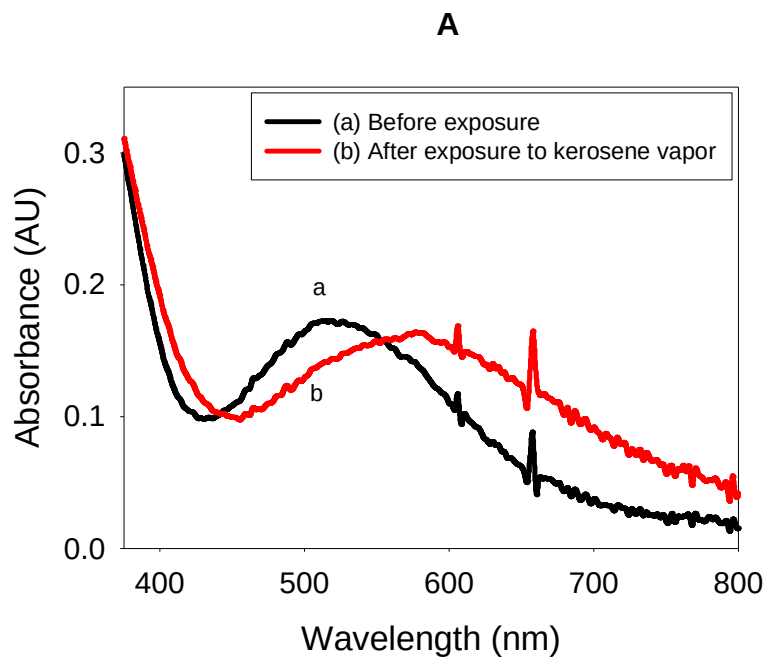


Figure 6.20. (A) Sol-A ATMOS sol-gel sensor absorbance before and after exposure to kerosene vapor. (B) Sol-B ethylenediamine sol-gel sensor absorbance showing matrix induced peak shift.

The disadvantage of this approach is that many factors can cause the absorbance peak to shift, making selectivity a major issue. The Sol-A formulation was adapted from a report that used Reichardt's dye as a temperature sensor.¹⁴⁰ When our sensors were exposed to N₂ at various temperatures, the absorbance peaks were red- and blue-shifted for increases and decreases in temperature, respectively.

6.3.3. Multi-analyte Optical Sensor for Rocket Engine Testing – MORST

The ultimate goal is to develop a multi-analyte sensing platform that is capable of simultaneously monitoring various plume constituents in near-real-time. The device under development by InnoSense LLC. for use with this project is termed a multi-analyte optical sensor for rocket engine testing (MOSRT). The current generation MOSRT consists of a four channel miniaturized sensing platform in which four optical signals can be obtained simultaneously from a single interchangeable LED light source. Each channel has a slot for an optical filter to enable absorbance based measurements (notch filter) or fluorescence (cut-off filters) measurements. Temperature is monitored during the duration of the test with a built-in temperature probe. The unit is interfaced to PC by a National Instruments USB controller and controlled with LabView software.

During initial tests, simple disposable plastic filters (#89 Moss Green & #389 Chroma Green, Roscolux filters) were utilized for proof of concept using similar sensors for IPA and testing response at each of the four channels. Four EC IPA sensors as described in Section 6.3.1.5 were used to detect repetitive

pulses of 1% IPA (Figure 6.21). All four channels responded nearly identically. However, there was a considerable baseline drift. Additional tests were conducted by Innosense LLC to demonstrate the ability to test multiple analytes simultaneously from pin-printed sensor arrays. A humidity, CO₂, O₂ and reference sensor was each placed in one of the four channels. The response to individual components of air and compressed air was tested with the MOSRT set-up (Figure 6.22).

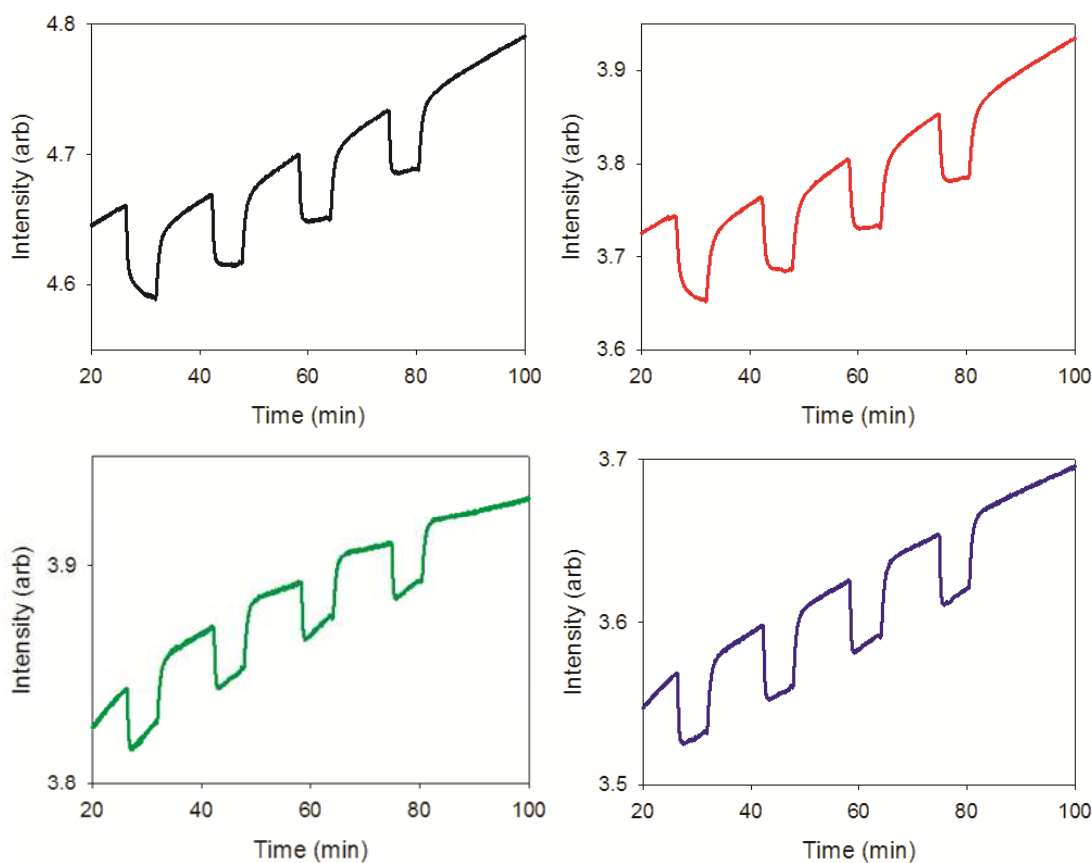


Figure 6.21. MOSRT response for four EC-IPA sensors.

6.4. Conclusions

Initial studies have been conducted to evaluate optical sensing strategies for gas phase kerosene and isopropyl alcohol. Several solvatochromatic dyes have been investigated for sensitivity towards both IPA and kerosene.

Chromoionophore IX, one of the few chemically selective dyes for alcohol sensing, has been demonstrated for gas phase IPA detection for the first time in several sensing matrices. Preliminary tests of these sensors are shown in a custom-designed multi-channel portable sensing device for remote simultaneous multi-analyte sensing of rocket plume constituents.

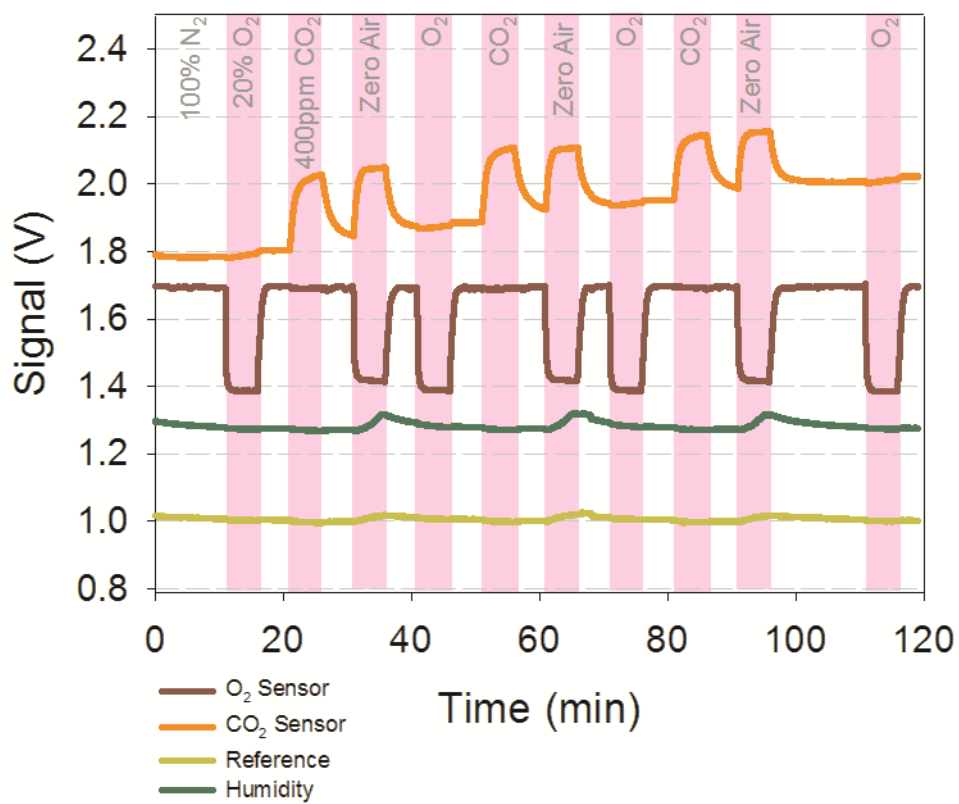


Figure 6.22. MOSRT CO₂, O₂, humidity and reference sensor response to 20% O₂, 400 ppm CO₂, and compressed air.

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Vita

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