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UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

A STUDY OF THE OPTICAL TRANSMISSION PROPERTIES OF THE POLYMER

HPG

A Dissertation

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

Doctor of Philosophy

By

SONJA RENAE WILKINSON

Norman, Oklahoma 2000 UMI Number: 9964764

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A STUDY OF THE OPTICAL TRANSMISSION PROPERTIES OF THE POLYMER HPG

A Dissertation APPROVED FOR THE SCHOOL OF ELECTRICAL AND COMPUTER ENGINEERING

BY



To: Mom and Dad

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Anybody who has been seriously engaged in scientific work of any kind realizes that over the entrance to the gates of the temple of science are written the words: *Ye must have faith*. It is a quality which the scientist cannot dispense with. Max Planck "Where is Science Going?"

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS	vi
LIST OF TABLES	vi
LIST OF ACRONYMS	
ACKNOWLEDGMENTS	x
ABSTRACT	xi

Chapter

1 Introduction	.1
1.1 Purpose of Research	1
1.2 Related Research	3
1.3 Hydroxypropyl Guar	5
1.4 Contributions to Research Area	7
1.5 Summary of Content	8
2 Theoretical Background	10
2.1 Principles of Spectroscopy by Region	10
2.1.1 Ultraviolet-Visible Spectroscopy	14
2.1.2 Near-Infrared Spectroscopy	15
2.2 Optical Transmission Theory	.16
2.3 Equation for Determination of Extinction Coefficients	.26
3 Statistics Overview	29
3.1 Applied Statistical Formulas	29
3.2 Precision of Repeated Measurements	.35
4 Initial Spectral Investigation in the UV to NIR	40
4.1 Spectral Properties of Water	40
4.2 Spectral Properties of Cuvets	42
4.3 Spectral Properties of HPG and Silica Flour Components	44
4.4 Transmission Window of HPG in UV to NIR	49

5	Extinction Coefficients for HPG Fracturing Fluid	52
	5.1 Coefficients for HPG in VIS Region	53
	5.2 Coefficients for HPG in NIR Region	61
	5.3 Comparison of Transmission Properties in VIS-NIR	70
6	Extinction Coefficients for HPG with Silica Flour Added	73
	6.1 Coefficients for Silica Flour in VIS Region	73
	6.2 Coefficients for Silica Flour in NIR Region	81
	6.3 Comparison of Transmission Properties in VIS-NIR	94
7	Calibration of Optical Density vs. HPG Concentration	97
	7.1 Calibration of HPG in VIS Region	97
	7.2 Calibration of HPG in NIR Region	105
	7.3 Comparison of Calibration Methods for HPG	114
8	Calibration of Optical Density vs. Silica Flour Concentration	121
	8.1 Calibration of Silica Flour Concentration in VIS Region	121
	8.2 Calibration of Silica Flour Concentration in NIR Region	129
	8.3 Comparison of Calibration Methods for Silica Flour	138
9	Conclusions and Recommendations	144
	9.1 Contributions	144
	9.2 Summary of Results	145
	9.3 Implications for Sensor Development	151

APPENDIX: CD-ROM

1	Concentration Dependence of Optical Transmission in HPG Fluids
	for the Near-Infrared Spectrum

- 2 Histograms of Repeated Measurements at Various Wavelengths
- 3 Raw RSD Data for 5 Samples Measured 5 Times Each in the VIS
- 4 Raw HPG Optical Density Data in the VIS Region
- 5 Plots of HPG Optical Density Data and Corresponding Calibration Curves in the VIS Region

- 6 Extinction Coefficients for HPG in the VIS Region
- 7 Plots of Transmitted Intensity vs. Pathlength for HPG in the VIS Region
- 8 Raw HPG Optical Density Data in the NIR Region
- 9 Plots of HPG Optical Density Data and Corresponding Calibration Curves in the NIR Region
- 10 Extinction Coefficients for HPG in the NIR Region
- 11 Raw Optical Density Data for HPG with Silica Flour Added in the VIS
- 12 Extinction Coefficients for HPG with Silica Flour Added in the VIS
- 13 Raw Optical Density Data for HPG with Silica Flour Added in the NIR
- 14 Extinction Coefficients for HPG with Silica Flour Added in the NIR.
- 15 Confidence Intervals for HPG Using Exponentially Transformed Data in the VIS Region
- 16 Smoothed Optical Density Data and Polynomial Calibration Curves for HPG with Silica Flour Added in the VIS Region
- 17 Optical Density Data and Calibration Curves for HPG with Silica Flour Added in the NIR Region

REFERENCES	153
------------	-----

ILLUSTRATIONS

Figure 1.1	Illustration of Different Concentrations of Guar from Dilute to	
	Highly Concentrated Guar Solutions	. 6
Figure 2.1	Block Diagram of a Typical Spectrophotometer	. 12
Figure 2.2	Transmittance of a Liquid Sample	. 13
Figure 2.3	Scattering Process of an Obstacle	. 22
Figure 2.4	Scattering and Absorption in a HPG Sample	23
Figure 3.1	Histogram of 20 Repeated Measurements for a 25 lb/Mgal	
	HPG Fluid	. 30
Figure 3.2	Optical Density Spectra for 5 Samples, Measured 5 Times Each	
	In the Visible Spectrum	. 36
Figure 3.3	RSD for 5 Samples Measured 5 Times Each in the Visible	
	Spectrum	. 36
Figure 3.4	RSD for 2 Samples Measured at 0 and 180 Degrees	. 37
Figure 3.5	Comparison of RSD for 12 Samples from 2 Different Batches	39
Figure 3.6	Comparison of Precision for Multiple Measurements in the	
	Visible and NIR Regions	. 39
Figure 4.1	Spectra of Tap Water in the Visible Region	. 41
Figure 4.2	Near-Infrared Spectra of Water	42
Figure 4.3	Percent Transmission of Sample Cuvets Used in the	
	Visible Spectrum	43
Figure 4.4	Spectra of Blank Cuvets Used in the Ultraviolet-Visible Region,	
	Average of Three Scans	44
Figure 4.5	Ultraviolet-Visible Spectra for Various Components of HPG	
	Fracturing Fluid, Average of 12 Samples	46
Figure 4.6	5 lb/Mgal Silica Flour and Tap Water Mixture Averaged Over	
	10 Scans	48

Figure 4.7	Optical Density Spectra of 40 lb/Mgal HPG in NIR Region49
Figure 4.8	Spectra of Various Concentrations of HPG Fracturing Fluid Over
	the Entire Spectral Range 100 nm to 3100 nm 50
Figure 5.1	Raw HPG Spectra in Visible Region, Average of 4 Scans53
Figure 5.2	Coefficient of Determination for Linear Regression of Various HPG
	Concentration Ranges and Optical Density in the Visible Region 54
Figure 5.3	HPG Optical Density Data and Corresponding Calibration
	Curve at 658 nm
Figure 5.4	Extinction Coefficients for HPG in Visible Region
Figure 5.5	Percent Transmitted Intensity vs. Pathlength for HPG in the
	Visible Region
Figure 5.6	Transmitted Intensity vs. Pathlength for a 30 lb/Mgal HPG Fluid
	At Various Wavelengths in the Visible Spectrum
Figure 5.7	Transmitted Intensity vs. Concentration at 1 cm, 5 cm, and 10 cm
	For 400 nm and 820 nm
Figure 5.8	Percentage Increase in Transmitted Intensity for 800 nm vs.
	400 nm at a Depth of 1 cm 60
Figure 5.9	Percentage Increase in Transmitted Intensity for 800 nm vs.
	400 nm at a Depth of 5 cm 60
Figure 5.10	Raw HPG Spectra in NIR, Average of 3 Scans
Figure 5.11	Coefficient of Determination for Linear Regression of Various HPG
	Concentration Ranges and Optical Density in the NIR
Figure 5.12	HPG Optical Density Data and Calibration Curve at 865 nm63
Figure 5.13	Extinction Coefficients for HPG in the NIR Region65
Figure 5.14	Transmitted Intensity vs. Pathlength for HPG at 865 nm65
Figure 5.15	Transmitted Intensity vs. Pathlength for a 20 lb/Mgal HPG at
	Various Wavelengths in the NIR Spectrum
Figure 5.16	Transmitted Intensity vs. Concentration at 1 cm, 5 cm, and 10 cm
	For 865 nm and 1300 nm

.

Figure 5.17	Percentage Increase in Transmitted Intensity for 865 nm vs.	
	1300 nm at a Depth of 1 cm	69
Figure 5.18	Percentage Increase in Transmitted Intensity for 865 nm vs.	
	1300 nm at a Depth of 5 cm	69
Figure 5.19	Comparison of Transmitted Intensity for 820 nm and 865 nm	71
Figure 5.20	Percentage Change in Transmitted Intensity for 865 nm vs.	
	820 nm	71
Figure 6.1	Average Spectra for 5 Scans of a 40 lb/Mgal HPG with Various	
	Amounts of Silica Flour	73
Figure 6.2	Coefficients of Determination for Linear Regression of a	
	40 lb/Mgal HPG with Various Concentration Ranges of Silica	
	Flour in the Visible Region	74
Figure 6.3	Optical Density vs. Silica Flour Concentration at 814 nm	75
Figure 6.4	Optical Density vs. Silica Flour Concentration at 520 nm	76
Figure 6.5	Extinction Coefficients for a 40 lb/Mgal HPG with Silica	
	Flour Added in the Visible Region	77
Figure 6.6	Transmitted Intensity vs. Pathlength for HPG with Silica Flour	
	Added at 800 nm	78
Figure 6.7	Transmitted Intensity vs. Pathlength for a 40 lb/Mgal HPG Fluid	
	With 25 lb/Mgal of Silica Flour Added in the Visible Region	79
Figure 6.8	Comparison of Transmitted Intensity vs. Concentration for HPG	
	With Silica Flour Added at 820 nm and 400 nm	80
Figure 6.9	Comparison of Percent Improvement in Transmission Intensity at	
	Various Depths for 800 nm and 400 nm in HPG with Silica	
	Flour Added	80
Figure 6.10	Raw Spectra for 40 lb/Mgal HPG with Various Amounts of Silica	
	Flour Added in the NIR Region	82
Figure 6.11	Coefficients of Determination for Linear Regression of 40 lb/Mgal	
	HPG with Various Concentrations of Silica Flour in the NIR	8 3
Figure 6.12	Average Spectra Over 4 Scans for 40 lb/Mgal HPG with Various	

	Amounts of Silica Flour in the NIR at Wavelengths 1125 nm to	
	1140 nm	84
Figure 6.13	Coefficients of Determination for 40 lb/Mgal HPG with Silica Flour	
	Added in the Wavelength Range 1125 nm to 1140 nm	85
Figure 6.14	Calibration Curve and Raw Data for a 40 lb/Mgal HPG with	
•	Various Amounts of Silica Flour Added at 1131 nm	85
Figure 6.15	Calibration Curve and Raw Data for a 40 lb/Mgal HPG with	
•	Various Amounts of Silica Flour Added at 1129 nm	86
Figure 6.16	Extinction Coefficients for 40 lb/Mgal HPG with Silica Flour	
i	in the NIR	88
Figure 6.17	Extinction Coefficients for 40 lb/Mgal HPG with Silica Flour	
]	In the Wavelength Range 1130 nm to 1132 nm	88
Figure 6.18	Transmitted Intensity vs. Pathlength for 40 lb/Mgal HPG with	
:	Silica Flour Added at 1078 nm	89
Figure 6.19	Transmitted Intensity vs. Pathlength for a 10 lb/Mgal HPG with	
\$	Silica Flour Added at Various Wavelengths in the NIR Spectrum	90
Figure 6.20	Transmitted Intensity vs. Silica Flour Concentration at 0.5 cm,	
- - -	1.0 cm, and 1.5 cm for 1078 nm and 1300 nm	91
Figure 6.21	Comparison of Percent Improvement in Transmission Intensity at	
•	Various Depths for 1078 nm and 1300 nm in HPG with Silica	
]	Flour Added	92
Figure 6.22	Transmitted Intensity for 40 lb/Mgal HPG with Various Amounts	
(of Silica Flour Added at 1131 nm	93
Figure 6.23	Comparison of Transmitted Intensity for HPG with Silica Flour	
4	Added at 820 nm and 1078 nm	95
Figure 6.24	Percentage Improvement in Transmitted Intensity in HPG with	
Ś	Silica Flour Added at 1078 nm vs. 820 nm	96
Figure 7.1	Comparison of Coefficients of Determination for HPG in the Visible	
1	Region for Raw and Exponentially Transformed Data	98
Figure 7.2	Comparison of SER for Raw Data and Exponentially Transformed	

	Data with Regard to Calibration of HPG Concentration in the
	Visible Region
Figure 7.3	Percent Improvement in SER for the Case of Exponentially
	Transformed Data vs. Raw Data for HPG in the Visible Region 100
Figure 7.4	Comparison of SEP for Raw Data and Exponentially Transformed
	Data with Regard to Calibration of HPG Concentration in the
	Visible Region
Figure 7.5	Percent Improvement in SEP for the Case of Exponentially
	Transformed Data vs. Raw Data for HPG in the Visible Region 101
Figure 7.6	Confidence Intervals for HPG in the Visible Region Using
	Exponentially Transformed Data102
Figure 7.7	Percent Average REP for HPG Using Exponential Data
	Transformation in the Visible Region 103
Figure 7.8	Percent RSD for 4 Scans of HPG in the Visible Region 104
Figure 7.9	Sensitivity of Exponentially Transformed Method of Linear
	Regression for HPG in the Visible Region105
Figure 7.10	Comparison of Coefficients of Determination for HPG in NIR
	Region for Linear and Polynomial Regression106
Figure 7.11	Comparison of SER for Linear and Polynomial Regression with
	Regard to Calibration of HPG Concentration in the NIR Region 107
Figure 7.12	Percent Improvement in SER for the Case of Polynomial Regression
	vs. Linear Regression for HPG in the NIR Region 108
Figure 7.13	Comparison of SEP for Linear and Polynomial Regression with
	Regard to Calibration of HPG Concentration in the NIR Region 109
Figure 7.14	Percent Change in SEP for Polynomial vs. Linear Regression for
	HPG in the NIR Region
Figure 7.15	Confidence Intervals for HPG in the NIR Region at 1100 nm111
Figure 7.16	Confidence Interval for HPG in the NIR at 985 nm112
Figure 7.17	Percent Average REP for HPG using Linear and Polynomial

	Regression in the NIR Region	112
Figure 7.18	Percent RSD for 3 Scans of HPG in the NIR Region	113
Figure 7.19	Sensitivity of Linear Regression for HPG in the NIR Region	114
Figure 7.20	Comparison of Calibration Methods According to Coefficients of	
	Determination for HPG in the VIS and NIR Regions	115
Figure 7.21	Comparison of SER for Various Calibration Methods of HPG in	
	the VIS and NIR Regions	116
Figure 7.22	Comparison of SEP for Various Calibration Methods of HPG in the	
	VIS and NIR Regions	117
Figure 7.23	Comparison of Percent REP for Different Calibration Methods of	
	HPG in the VIS and NIR Regions	117
Figure 7.24	Comparison of Percent RSD for HPG in the VIS and NIR Regions	118
Figure 7.25	Comparison of Sensitivity for Various Calibration Methods of HPG	
	in the VIS and NIR Regions	119
Figure 8.1	Comparison of Coefficients of Determination for Various	
	Calibration Methods for Silica Flour in the Visible Region	122
Figure 8.2	Comparison of SER for Various Calibration Methods of Silica	
	Flour in the Visible Region	123
Figure 8.3	Comparison of SEP for Various Calibration Methods on Silica	
	Flour in the Visible Region	124
Figure 8.4	Smoothed Calibration, Prediction Data Along with Polynomial	
	Calibration Curve for HPG with Silica Flour Added at 600 nm	125
Figure 8.5	%REP for Polynomial Regression of HPG with Silica Flour	
	Added in the Visible Region	126
Figure 8.6	Percent Average RSD for 40 lb/Mgal HPG with Silica Flour Added	
	In the Visible Region of the Spectrum	127
Figure 8.7	Sensitivity for Polynomial Regression of 40 lb/Mgal HPG with	
	Silica Flour Added in the Visible Region	128
Figure 8.8	Coefficients of Determination for Various Calibration Methods	
	For Silica Flour in the NIR Region	130

Figure 8.9	SER for Various Calibration Methods for Silica Flour in the	
	NIR Region	131
Figure 8.10	SER for Silica Flour Calibration in the NIR Region	132
Figure 8.11	SEP for Various Calibration Methods for Silica Flour in the	
	NIR Region	132
Figure 8.12	SEP for Silica Flour Calibration in the NIR Region	133
Figure 8.13	Linear Calibration of Raw Data Along with Prediction Data for	
	Silica Flour in the NIR at 1131 nm	135
Figure 8.14	Polynomial Calibration of Silica Flour Concentration in the NIR	
	at 950 nm	135
Figure 8.15	Percent Average REP for Polynomial Regression of Silica Flour	
	in the NIR	136
Figure 8.16	Percent RSD for Silica Flour Concentration in a 40 lb/Mgal HPG	
	In the NIR	136
Figure 8.17	Sensitivity of Polynomial Calibration Method for Silica Flour	
	in the NIR	137
Figure 8.18	Coefficients of Determination for Polynomial Regression of Silica	
	Flour Concentration in the Visible and NIR Regions	139
Figure 8.19	SER for Polynomial Regression of Silica Flour Concentration	
	In the Visible and NIR Regions	139
Figure 8.20	SEP for Polynomial Regression of Silica Flour Concentration	
	in the Visible and NIR Regions	140
Figure 8.21	Comparison of Percent REP for Polynomial Regression of Silica	
	Flour Concentration in the Visible and NIR Regions	141
Figure 8.22	Comparison of Precision for Polynomial Regression of Silica	
	Flour Concentration in the Visible and NIR Regions	142
Figure 8.23	Comparison of Sensitivity for Polynomial Regression of Silica	
	Flour Concentration in the Visible and NIR Regions	143

TABLES

Table 4.1	Components of HPG Fracturing Fluids in This Study	45
Table 4.2	Band Assignments for Components of HPG Fracturing Fluid	. 47
Table 5.1	Percent Transmitted Intensity Values for 865 nm and 1300 nm	. 68
Table 6.1	Depth in 40 lb/Mgal with Silica Flour Added, at Which 50% of	
	Initial Intensity Remains for 0 lb/Mgal to 55 lb/Mgal Silica Flour	
	at 1131 nm	. 94

.

ACRONYMS

D	Optical Density
EM	Electromagnetic
HPG	Hydroxypropyl Guar
Mgal	Thousand Gallons
NIR	Near-Infrared
REP	Relative Error of Prediction
RSD	Relative Standard Deviation
SEP	Standard Error of Prediction
SER	Standard Error of Regression
UV	Ultraviolet
VIS	Visible

ABSTRACT

Hydroxypropyl Guar (HPG) is a polymer used extensively in the petroleum industry for fracturing oil and gas wells. Understanding the transmission of electromagnetic (EM) radiation in these fluids plays an essential role in the design, development, and improvement of optical sensing devices used to monitor and characterize these polymers. This investigation has resulted in the first comprehensive study of the transmission characteristics of HPG in the visible and near-infrared regions of the electromagnetic spectrum. Optical density data was collected for HPG fluids of various concentrations. Mixtures containing silica flour, a fluid loss additive, were also examined. Based upon optical transmission theory, a method was developed to determine the validity of calculating extinction coefficients at various fluid concentrations throughout the visible and near-infrared region of the spectrum. These coefficients were used to model the depth of penetration of EM radiation into HPG fluids. Calibration methods for optical density and concentration were also evaluated throughout the visible and near-infrared regions. Key results indicate that the best overall penetration into HPG fluids with no silica flour added occurs at wavelengths centered around 865 nm. In the case of fluids containing silica flour, the best penetration occurs at wavelengths centered around 1078 nm. These results, all with many others presented in this dissertation, will be of great utility in the design and development of in situ optical sensors for the characterization of HPG.

Chapter 1

Introduction

1.1 Purpose of Research

One of the most powerful tools available today for studying the various properties of molecules, compounds, and complex mixtures is based on the interaction of molecules with electromagnetic radiation. Spectroscopic methods are commonly used to study these interactions to gain knowledge about the physical and chemical properties of a substance, and applications in this area range from the determination of concentration to molecular structure. Determinations like these can be based not only on the absorption of radiation, but also from scattering of radiation traversing a given media. In most cases, absorption of radiation is used to monitor concentration, temperature, and various other parameters of a given substance along with transmission characteristics when scattering is negligible. On the other hand, scattering of radiation is also used to study a variety of other properties including molecular size, shape, and orientation, as well as particle size. When measuring the transmission characteristics of a substance, it is usually necessary to separate the effects of absorption and scattering to provide accurate information about the sample being measured.

Unlike most applications in chemistry, it is not the purpose of this research to discern the relative importance of absorption and scattering in producing attenuation of radiation as it traverses a medium. Rather, the fundamental theory of absorption is examined in terms of the electromagnetic theory on which it is based. Since this theory holds for single scattering events, this dissertation treats absorption and scattering as a combination of events that lead to the optical extinction of radiation as it traverses a polymer and are not differentiated in terms of individual contributions.

Very little optical transmission data is available on Hydroxypropyl Guar (HPG) as easily accessible published work in this area, and manufacturers furnish only a very select amount of information in the infrared region. Therefore, the intent of this dissertation is to develop an understanding of the transmission properties of these fluids by (1) determining the depth of penetration for various wavelengths and concentrations and (2) determining the empirical relationship between concentration of HPG, or silica flour, and optical density as a function of wavelength in the visible (VIS) and near-infrared (NIR) regions of the spectrum. The main advantage is that once these relationships are established, it is possible to model the transmission of electromagnetic (EM) radiation in HPG at these wavelengths. The ability to model the transmission properties of HPG is very important in terms of optoelectronic sensor design since these properties of HPG can be used in the petroleum industry to develop and improve a variety of monitoring and analysis based sensors. The optical density of HPG fracturing fluid, as well as HPG fracturing fluid with silica flour added, is, for the first time to our knowledge, modeled over the entire visible and NIR spectral range. Interest in the optical density of these fluids has been stimulated by the need for information about their optical transmission characteristics, since all optoelectronic sensor design starts with the determination of an optimal wavelength(s) and initial power requirements. It is very important to determine optimal values for these

parameters which are dependent on the application, as trade-offs in sensor performance are inevitable.

1.2 Related Research

Several applications have been reported in the literature where optical sensors have been used to investigate various fluids in the petroleum industry. For example, in order to develop a better model of filter cake formation, experiments were conducted using an optical fiber fluorescence probe to determine filter cake concentration. An argon laser was used to excite fluorescent tags mixed into the HPG fluid as it flowed through a Plexiglass slot. These measurements were made on dilute HPG solutions.¹

A wireline tool was developed that used optical principles for continuous analysis of formation fluids such as water and oil mixtures and gas. It estimated the volume fraction of water and oil in the sensor's flowline and the presence of gas as well. The principles of optical absorption in the visible and near-infrared region and the change in index of refraction between oil, gas, and water were the basis on which the sensor was developed. Therefore, the transmittance of these fluids as a function of wavelength, measured as the optical density of the fluids, was the first step in the design of this sensor even though this data was not included in the published results. By providing real time information on the formation fluids being produced, the sensor monitors the transition of produced fluids from filtrate to oil in the formation.²

The relative contributions of absorption and scattering in crude oils were investigated using near-infrared spectroscopy to aid in chemical analysis of these

3

fluids. Both absorption and scattering are present in crude oils in the near-infrared region and result in a broad extinction profile in this spectral region. ³ In other work, optical absorption was utilized to determine sand density profiles for varying concentrations of sand-laden fluids flowing through a lucite slot. Incandescent light sources and photodiode arrays were used to evaluate the sand concentration of the water and polymer fluids. ⁴ Similar work was done in analyzing oil sand slurries using near-infrared spectroscopy. ⁵ In addition, a procedure using luminesence spectroscopy was developed to characterize particular mixtures of crude oil and drilling mud so that information relevant to the drilling operation was provided rapidly at the well site. ⁶

In all these areas of optical sensor development in the petroleum industry, there has been no mention, to our knowledge, of the optical properties of HPG fracturing fluids with and without silica flour. In fact, the closest reference to using optical sensing in conjunction with HPG fracturing fluids was in the case of the flourescent probe used to determine filter cake concentration.¹ Even here, the source wavelength of the sensor was selected on the basis of which wavelength was needed to excite the flourescent tags added to the fracturing fluid. Therefore, this constraint precluded the need to determine the optimum source wavelength. However, in most sensor development, depth of penetration or optical transmission characteristics of the fluid versus wavelength, is a fundamental part of the information required to develop an optimum sensing device. As an example, this approach has been used as described earlier to investigate the transmission properties of various crude oils and oil sand slurries in the visible and near-infrared regions, but no information has been found on these properties for HPG fracturing fluids with and without silica flour in these regions.

1.3 Hydroxypropyl Guar

Hydraulic fracturing is a method patented by R. F. Farris in 1953 and used in the petroleum industry to increase the productivity of a well by fracturing the production formation, thereby increasing the well drainage area. ⁷ To fracture a formation, energy is generated by injecting highly viscous fluids down a well and into the formation. Water based polymers are the most widely used polymers due to their relatively low cost, high performance and ease in handling, and generally consist of adding water-soluble polymers to water.⁸

Hydroxypropyl guar is a galactomannan polysaccharide derived from guar gum, a naturally occurring polymer which is processed from the endosperm of guar beans. Here, the polysaccharide is comprised of the simple sugars mannose and galactose. In its powder form, guar molecules are tightly coiled like used nylon fishing line. When Guar is mixed with water, it associates with water molecules in solution; the molecules relax and straighten to a degree forming a viscous liquid. It is considered a random-coil polymer, not a rigid rod. The chemical structure of guar allows it to be modified chemically to form HPG. HPG behaves as a semiflexible molecule when present in aqueous solutions under elongational flow situations. In the absence of an applied electric field, a dilute macromolecular solution will exhibit all possible orientations of macromolecular axis systems with equal probability.

Therefore, these dilute solutions are considered optically isotropic.⁹ Since the degree to which molecular scattering in a solution void of suspended matter occurs depends on the optical anisotropy of the fluid, it is reasonable to assume that molecular scattering will not be a major contributor to transmission losses for these fluids.

5

Optical anisotropy describes a material whose optical properties vary with direction. It is important to note that guar from different sources varies in many ways including molecular weight and mannose to galactose ratio. Additionally, it is difficult to obtain complete molecular dispersion of guar in solution. This results in a certain amount of supermolecular particles being present in the solution along with individual macromolecules which will provide some level of scattering. In low weight, dilute, linear guar fluids, individual polymer coils are spatially separated and as the concentration of guar increases, the individual molecules begin to interact as shown in Figure 1.¹⁰



Figure 1.1 Illustration of Different Concentrations of Guar from Dilute to Highly Concentrated Guar Solutions.¹⁰

Since HPG is a derivative of guar, it can be regarded in the same manner as guar in terms of its variance in molecular weight, mannose to galactose ratio, lack of complete dissolution in solution, and its spatial separation versus concentration characteristics. Due to the fact that HPG is a polymer, which includes millions of molecules in a tiny drop, statistical methods must be used in making generalizations about characteristics of the polymer. For example, a bulk polymer sample of HPG has a molecular weight that is given as a distribution or average.

The HPG fracturing fluids used in this research consisted of water, HPG, sodium bicarbonate, fumeric acid, a bactericide, and in some cases silica flour. Sodium bicarbonate was added to water in order to raise the pH, which aids in the dispersion of the powdered HPG when it was added. Fumeric acid is then added to lower the pH and promote hydration of the polymer. A small amount of bactericide was then added before leaving the sample to hydrate. Silica flour is used as a fluid loss additive in HPG fracturing fluids.

1.4 Contributions to Research Area

As stated earlier, there is very little data available on the optical density of HPG, and HPG with silica flour added, in the VIS (Visible) and NIR (Near-Infrared) regions of the electromagnetic spectrum. This work provides the first attempt, to our knowledge, at gathering optical density data in these regions and comparing these wavelengths to determine which areas are best suited for optical sensor development. The data and corresponding conclusions resulted in a peer-review journal paper which is reprinted in Appendix 1. In addition, a novel method was developed to determine the validity of calculating extinction coefficients at various concentrations for both HPG and HPG with silica flour added. Depth of penetration into these fluids is modeled using the extinction coefficients derived from the optical density data. The

correlation between concentration of HPG or silica flour and optical density is also modeled and evaluated for statistical significance. This work uses spectrophotometry in a unique way to measure the extinction of radiation in these fluids. This is accomplished by combining the fundamental principles of spectrophotometry and optical transmission theory to develop a method of modeling the desired optical transmission characteristics using optical density data.

1.5 Summary of Content

The work presented in this dissertation begins with coverage of the principles of spectroscopy and the theoretical background of optical transmission through a liquid medium based on electromagnetic theory as presented in Chapter 2. This theoretical basis is then used to determine the relationship between intensity, distance traveled, and the corresponding extinction coefficient at a given wavelength and fluid concentration. Chapter 3 follows with an overview of the statistical formulas used in the evaluation of the data. In addition, statistical results for the precision of repeated measurements are presented.

An overview of the spectral characteristics of all the individual components that make up HPG fluids, including silica flour, is presented in Chapter 4. Chapter 5 involves the determination of extinction coefficients for HPG in both the visible and NIR regions. Once a suitable concentration range has been determined, the coefficients are calculated and values for the percent transmitted intensity at various wavelengths and concentrations are calculated. In Chapter 6 the same evaluation is provided for the case of a 40 lb/Mgal HPG with silica flour added, where lb/Mgal refers to the concentration in pounds per thousand gallons of water. Chapter 7 and Chapter 8 provide results on the calibration process of optical density and fluid concentration for HPG and HPG with silica flour added, respectively. These chapters use statistical methods to evaluate the best wavelengths and methods for calibration of both fluid types in the visible and NIR regions. Finally, Chapter 9 presents the conclusions and recommendations resulting from this body of work. Appendices for this dissertation are in electronic format and can be found on CD-ROM with each appendix represented by its own file.

Chapter 2

Theoretical Background

In characterizing the transmission of radiation though various concentrations of the polymer HPG, the theory underlying optical transmission through a liquid medium and the principles of spectrophotometry must be considered. Therefore, a brief description of these theories and principles are covered in this chapter.

2.1 Principles of Spectroscopy

In a general sense, spectroscopy is the use of the absorption, emission, or scattering, of EM radiation by atoms or molecules to qualitatively or quantitatively study the atoms or molecules, or to study physical processes. Atoms or molecules can absorb or scatter radiation of different wavelengths throughout the EM spectrum. This effort focuses on the interaction of radiation with atoms or molecules in the visible and NIR spectral regions.

In the present work, spectrophotometry is not used to identify fluid components, measure particle size, or measure any of a variety of parameters that it is normally used to measure. While the basic measurement is the same, the application of the resulting data is different. The measurements involve the ratio of the intensity of transmitted radiation, I, to that of the incident radiation, I_0 . The result is a measurement of the energy lost due to absorption by the sample, as well as energy lost due to baseline errors such as scattering. Generally, chemists will use spectroscopy for quantitative measurements of an analyte in solution and, in doing so, are only interested in the absorbance information in the spectra. An analyte is a component of a test sample, the content of which, has to be measured. Consequently, the presence of scattering is a complication that must be eliminated prior to measurement or modeled to provide an accurate quantitative method, as it contributes to a statistical variation in quantitative measurements. The processes of absorption and scattering physically modify the direction and penetration of electromagnetic radiation as it passes through media. Absorption corresponds to a loss of incident radiation, whereas scattering results in a redirection of radiation. With that in mind, this body of work views scattering as a process that contributes to the extinction of light as it traverses a medium and is, therefore, part of the overall process under investigation. As long as multiple scattering is not prevalent, the theory for making quantitative measurements still holds. So, in this work, the spectrophotometer was not only used to determine HPG concentration in the presence of scattering, it was also used to develop an understanding of the transmission characteristics of these fluids in the VIS and NIR regions. In principle, spectrophotometers can measure the extinction of a liquid sample with particulates, since light scattered in directions other than the forward direction is not detected.¹¹

All UV-VIS (Ultra-Violet-Visible) and NIR spectrophotometers consist of the same basic components: (1) a source of electromagnetic energy, (2) wavelength selection from the spectral output of the source, (3) an optically transparent sample holder located in the path of the light beam, (4) detection of resulting intensity, and (5) a means of recording/displaying the results as shown in Figure 2.1. In both the visible

and near-infrared regions, a spectrophotometer was used to collect data from the samples. The transmittance of a sample, as measured by a spectrophotometer, is the ratio of the radiant power transmitted by a sample to the radiant power incident upon it,



Figure 2.1 Block Diagram of a Typical Spectrophotometer.

as given by:

$$T = \frac{I}{I_0} \tag{2.1}$$

This relationship is illustrated in Figure 2.2 for a sample of fluid in a cuvet, which is a rectangular cell used to hold liquid samples. If absorption is the only process involved in removing radiant energy from the path, then absorbance, A, as defined by the International Union of Pure and Applied Chemistry, is defined by Equation (2.2) and is the quantity being measured.¹²
$$A = -\log_{10}(T)$$
 (2.2)



Figure 2.2 Transmittance of a Liquid Sample.

Absorptions in a spectrum have two components: continuum and individual features. The continuum is the "background absorption" onto which other absorption features are superimposed. However, if scattering in the fluid is to be accounted for along with absorption, then the spectrophotometer measures the Optical Density, D, of the sample according to Equation (2.3).

$$D = -\log_{10}(T) \tag{2.3}$$

It is clear from equations (2.2) and (2.3) that the difference is one of nomenclature to help identify which processes are being measured even though the quantities measured are the same in both cases - optical transmission through the sample.¹³ In the strictest sense, Equation (2.3) describes cases involving single scattering events where multiple scattering is neglected. When the concentration of a substance reaches a certain limit to be determined, the correct description of light transmission through the media includes multiple scattering which complicates the derivation of Equation (2.3) significantly. Nevertheless, this relationship based on single scattering events is often used as a good approximation in cases of multiple scattering.³

2.1.1 Ultraviolet-Visible Spectroscopy

UV-VIS spectroscopy is generally considered the measurement of the wavelength and intensity of absorption of UV and visible light by a sample since, in this region from 190 nm to 750 nm, radiation is energetic enough to promote electronic transitions of the outer electrons in the bonds of the molecules to higher energy levels. It is usually applied to molecules and complexes in solution in order to make quantitative measurements about the sample. This region is rarely used for qualitative measurements, as the absorption in this region results in broadband absorption peaks due to the large number of solvent interactions with the analyte. Visible spectroscopy is used to monitor concentration, pH, and temperature since these factors can affect the position and intensity of absorption bands of molecules. In the visible region of the spectrum, all optical density spectra were obtained on an HP 8452A Diode Array UV-

VIS Spectrophotometer located in the Chemistry department at the University of Oklahoma. All visible spectra were originally scanned over a range of 190 nm to 820 nm with a resolution of 2 nm. The spectrophotometer's software stored a reference spectra that was subtracted from each subsequent spectra measured. Unless otherwise noted, all samples were measured at room temperature.

2.1.2 Near-Infrared Spectroscopy

NIR spectroscopy uses radiation that spans the 750 nm to 2500 nm spectral region. In this region, the radiation is energetic enough to excite overtones and combinations of molecular vibrations to higher energy levels. In the purest sense, overtones and combinations are not allowed, but appear as weak bands due to anharmonicity or Fermi resonance. Three phenomena are primarily responsible for the characteristics of these absorption spectra: (1) molecular vibrational absorption, (2) electronic absorption, and (3) scattering. A majority of all the absorption bands in this region are due to vibrations involving hydrogen.

NIR spectroscopy has the ability to predict many optical, physical, and chemical properties including thermal capacity, refractive index, compressibility, chemical composition, electrical conductivity, and viscosity.¹⁴ It has also been used to characterize the dynamics of polymerization and the effect of thermal processing on polymer structures.¹⁵ In addition, NIR spectroscopy is well-suited to applications involving optical fibers. The use of optical fibers for remote monitoring and sampling for process or quality control is very advantageous. Therefore, the use of NIR

spectroscopy and optical fibers show great promise in the development of a number of optical sensors for use in the petroleum industry. The effective sampling depth for any optical sensor in this situation depends on both the fluid under study and the wavelength of radiation used by the sensor. Since NIR bands have lower absorptivities than IR bands, thicker and more highly scattering media can be monitored by NIR spectroscopy. In order to determine the effect on the transmission window of the various additives used when mixing HPG fracturing fluids, spectra were taken using a Perkin Elmer UV/VIS/NIR Spectrometer, model Lambda 19, spanning the entire range of 100 nm to 3100 nm. The remaining optical density spectra were scanned from 865 nm to 1350 nm at a resolution of 1 nm. The lower wavelength cuttoff in this case was determined by the fact that at 864 nm the spectrophotometer had to switch light sources in order to span the entire UV-VIS-NIR region. As a result the values measured at 864 nm did not correspond very well with those at 865 nm and above. Therefore, the decision was made to start at 865 nm instead of 821 nm, where the measurements from the visible region ended. This instrumentation was located at the National Institute of Standards and Technology in Boulder, Colorado.

2.2 Optical Transmission Theory

The transmission properties of electromagnetic radiation are ultimately dependent on the type of media involved which can be categorized as absorbing, scattering, or a combination of absorbing and scattering media. For media that are considered absorbing only, the derivation of the exponential law of absorption begins with Faraday who was the first to show experimental results connecting light with magnetism and suggested that light was electromagnetic in nature. The quantitative theory supporting this claim was derived later by James Maxwell. He summarized the existing laws of electromagnetism into a set of equations now known as Maxwell's equations.¹⁶

This electromagnetic theory provides a mechanism for describing the transmission of light in a transparent, isotropic, absorbing medium. For the work considered here, birefringence and consequently anisotropy should not be a concern due to the lack of flow induced strain on the polymer.¹⁷ Birefringence occurs when a beam of radiation separates as it penetrates a refracting object and the two emerging beams are polarized in opposite directions. Consequently, describing the propagation of electromagnetic energy through an arbitrary, absorbing medium begins with Maxwell's equations. These equations can be combined to form the well-known wave equation which describes the propagation of an electric field as:

$$\left(\frac{\partial^2}{\partial x^2} - \frac{\varepsilon(\omega)}{c^2} \frac{\partial^2}{\partial t^2}\right) \vec{E}(\vec{x}, t) = 0$$
(2.4)

where

 $\vec{E}(\vec{x},t)$ = amplitude of the electric field at position x and time t. $\varepsilon(\omega)$ = dielectric constant of the medium at a frequency ω c = speed of light in a vacuum Solving the wave equation results in:

$$\vec{E}(\vec{x},t) = \vec{E}_0 e^{j\vec{k}'\vec{x}-j\omega t}$$
(2.5)

where

- \vec{E}_0 = amplitude of the electric field at position $\vec{x} = 0$ and time t = 0
- \vec{k}' = wave vector that points in the direction of propagation of the electromagnetic field.

Substituting equation (2.5) into (2.4) results in the magnitude of the wave vector:

$$\left|k'\right|^{2} = \frac{\varepsilon(\omega)\omega^{2}}{c^{2}}$$
(2.6)

and

$$\sqrt{\varepsilon(\omega)} = n_c(\omega) = n(\omega) + ik(\omega)$$
(2.7)

where

 $n_c(\omega) = complex refractive index.$

- $n(\omega)$ = real part of the complex refractive index and is related to the phase velocity of plane waves in matter
- $k(\omega)$ = the imaginary part of the complex refractive index and is called the absorption index. It is related to the attenuation of plane waves in matter.

So, we can rewrite equation (2.5) in terms of equations (2.6) and (2.7).

$$\vec{E}(\vec{x},t) = \vec{E}_0 e^{\frac{-k(\omega)\omega\,\vec{x}}{c}} e^{i\left(\frac{n(\omega)\omega\,\vec{x}}{c} - \omega t\right)}$$
(2.8)

The amount of energy transported by an electromagnetic wave that flows per second across unit area, perpendicular to the direction of travel is the intensity of the wave. The intensity of the resulting electric field is proportional to the square of its absolute value:

$$I(\bar{x}) = I(0)e^{\frac{-2k(\omega)\omega\bar{x}}{c}}$$
(2.9)

For the case when \bar{x} is chosen to be the same direction as propagation, the vector \bar{x} becomes the scalar x and equation (2.9) can be rewritten as

$$I(x) = I_0 e^{\frac{-2k(\omega)\omega x}{c}}$$
(2.10)

Equation (2.10) describes how radiation is absorbed as it propagates in a medium, showing that the intensity decreases along the direction of propagation.¹⁸ We can also use the following relationship to rewrite equation (2.10)

$$\omega = \frac{2\pi c}{\lambda} \tag{2.11}$$

so it looks like this

$$I(x) = I_0 e^{\frac{-4\pi k(\omega)x}{\lambda}}$$
(2.12)

The relationship between absorption index, k, and the absorption coefficient, α_{abs} is

$$k(\omega) = \frac{\alpha_{abs}}{4\pi \overline{\nu}} = \frac{\alpha_{abs}\lambda}{4\pi}$$
(2.13)

Equation (2.13) allows us to rewrite equation (2.12) in terms of the absorption coefficient, α_{abs} .¹⁹

$$I(x) = I_0 e^{-\alpha_{abs} x}$$
(2.14)

Equation (2.14), known as the exponential law of absorption, has been attributed to both Pierre Bouguer and Johann Lambert. This relationship is sometimes erroneously referred to as Lambert's law which, actually refers to another law developed by this German physicist and mathematician that explains the variation with angle of the radiation from a surface.²⁰

To this point, we have considered only electromagnetic wave propagation in a strictly homogeneous medium, therefore, only the process of absorption must be considered. Heterogeneity of a sample occurs when volume elements differ in composition and optical properties. In a heterogeneous medium, the attenuation of EM energy is partially the result of scattering. The relationship for radiation traversing a scattering medium as shown in Figure 2.3, in the absence of any absorption, can be described by

$$I = I_0 e^{-\alpha_{\rm sc} x} \tag{2.15}$$

In equation (2.15), α_{sc} is the scattering coefficient. Generally, scattering and absorption occur together, thereby complicating the theory and measurement of either process independent of the other. Therefore, it is not sufficient to address only the absorption process or the scattering process. To understand the basic phenomena of absorption and scattering, matter must be thought of as a composition of discrete electric charges better known as electrons and protons. In this sense, a single electron, atom, molecule, liquid particle or solid particle can be thought of as an obstacle in the transmission of certain types of electromagnetic radiation. If such an obstacle were struck by an electromagnetic wave, its electrons and protons would be set into oscillatory motion by the electric field of the wave. These excited electrons and protons can re-radiate electromagnetic energy, referred to as scattering, or they may transform part of the incident energy into other forms, referred to as absorption.¹¹



Figure 2.3 Scattering Process of an Obstacle.¹¹

In the strictest sense, only a vacuum is homogeneous. Therefore, even in media that we usually consider homogeneous, such as a pure liquid, it is still possible to show heterogeneties with a sufficiently fine probe. As mentioned previously, there will generally be a certain degree of inhomogeneity involved with these fluids due to their lack of complete dispersion in solution. Therefore, in the case of HPG, it is assumed that both absorption and scattering remove energy from a beam of EM radiation propagating through a sample, as shown in Figure 2.4. While scattering changes the direction of propagation, it doesn't directly alter the amount of energy in the beam. Absorption requires a decrease in radiant energy which occurs when radiant energy is converted to thermal energy.



Figure 2.4 Scattering and Absorption in a HPG Sample.

So we consider the term "extinction" to encompass the attenuation of EM waves due to scattering and absorption as the wave traverses a heterogeneous medium, as both processes contribute to the attenuation of the beam of radiation as it traverses the medium. If multiple scattering in the medium can be neglected, the intensity of an EM wave as it propagates a distance x through medium can be described by the following equation.

$$I = I_0 e^{-(\alpha_{abs} + \alpha_{scat})x}$$
(2.16)

Here, the absorption coefficient, α_{abs} , and the scattering coefficient, α_{scat} , both add to the extinction of electromagnetic radiation as it traverses a medium. In the presence of multiple scattering, the relationship between the absorption coefficient and the scattering coefficient becomes more complicated than the sum of the two.^{20,21} Since several types of measurements are required to determine the relative contributions of the absorption and scattering coefficients and since the individual contributions are not required for this work, the following equation will be used to determine the ratio of incident to transmitted radiation.

$$I(x) = I_0 e^{-\alpha_{ext}x} \tag{2.17}$$

In Equation (2.17), α_{ext} is the extinction coefficient that represents attenuation due to a combination of absorption by the solution and particulates, as well as scattering. This relationship assumes that all light that is scattered is excluded from detection, which is generally the case for single scattering events for particles which are smaller than or on the order of the wavelength. It is not possible to determine the magnitudes of absorption and scattering independently using transmission measurements. Additional measurements must be made to obtain this information.

Equation (2.17) is referred to in several ways throughout the literature including Bouguer's law, Lambert's law of absorption, the exponential law of absorption, and the Bouguer-Lambert law.^{19,21,22,23} This equation is hereto referred to as the exponential law of extinction due to the contributions of both absorption and scattering. It is based on the principle that each layer of equal thickness of a medium will attenuate an equal fraction of the electromagnetic energy traversing it. It holds for absorption and single scattering events in an isotropic medium with constant temperature and pressure and for a beam of monochromatic radiation. Consequently, in a solution, the attenuation of radiation depends on both the concentration of the solution and its thickness. No exceptions have ever been found to this law that could not be traced to experimental error.²⁴ Extinction of electromagnetic radiation as it propagates through a medium can be measured as the ratio of transmitted to incident intensity, as shown in Equation (2.17).¹¹ Spectrophotometers can measure this ratio very quickly and efficiently for liquid samples.

2.3 Equation for the Determination of Extinction Coefficients

To calculate the extinction coefficients for these fluids, we need to determine that multiple scattering is not a contributing factor so that the theory on which the transmission intensity was based is valid. One way to determine if multiple scattering is present during spectroscopic measurements involving the transmission of radiation is to examine the relationship between optical density and concentration. It is an established fact that the presence of multiple scattering is evident when the relationship between optical density and concentration becomes nonlinear at higher concentrations. This nonlinearity is seen as a decrease in the change in optical density with changing concentration and graphically appears as a "flattening" of the calibration curve at higher intensities. This is mainly because of the fact that multiple scattering increases the probability that radiation is scattered back into the path of the detector, increasing the amount of light transmitted over the single scattering case for the same number of particles.

Note that nonlinearity at higher concentrations can be caused by several factors other than multiple scattering. For our work, we are content to conclude that if the relationship becomes nonlinear at higher concentrations, there is a high probability that multiple scattering is occurring and the given concentration range cannot be used to determine the extinction coefficients of the fluid. This is sufficient reason since even if the cause of the nonlinearity were due to nonlinearity of the instrument at that range, the results would still be incorrectly biased at that range and therefore inaccurate for the determination of extinction coefficients.

26

Once a suitable concentration range has been determined for the evaluation of extinction coefficients, the coefficients are calculated using the optical density data as described below. Equation (2.3) describing the measurement of optical density, D, as measured by the spectrophotometer, can be rewritten in terms of intensity by substituting Equation (2.1) for transmittance:

$$D = -\log_{10}\left(\frac{I}{I_0}\right) \tag{2.18}$$

Equation (2.17) related the intensity of radiation passing through a medium to its extinction coefficient, α_{ext} . Combining Equations (2.14) and (2.18) results in:

$$D = -\log_{10}\left(e^{-\alpha_{ex}x}\right) \tag{2.19}$$

Converting base ten logarithm to natural logarithm, yields the following relationship between the extinction coefficient and optical density at a particular wavelength and concentration of HPG:

$$\alpha_{ext} = \frac{2.303D}{x} \tag{2.20}$$

Equation (2.20) can be used to calculate the extinction coefficients for all concentrations which do not show a nonlinear response in their correlation between concentration and optical density. The pathlength of the cuvets used in measuring optical density was 1 cm for both the VIS and NIR cases. Therefore, the extinction coefficients are simply a constant multiplied by the optical density value at a particular wavelength and concentration. Once the coefficients have been calculated, Equation (2.17) can be used to determine the percentage of intensity that is transmitted at any distance, x, given the extinction coefficient.

Chapter 3 Statistical Overview

One of the guiding principles in the area of regression analysis is that quantitative results from regression models are of little value unless they are accompanied by some estimate of the errors inherent in them. Along these lines, the calibration model that is the best predictor is not necessarily the one that best fits the calibration data. Therefore, statistics are used to determine the fitness of a particular calibration, as well as indicate the ability of a particular calibration to accurately predict concentrations in samples not used in the development of the model. In this research, calibration curves were used not only to establish a relationship between concentration and optical density, but also to determine the concentrations at which multiple scattering could be neglected, and thereby define the range over which transmission characteristics could be calculated. In assessing the validity of these calibration models, various statistical methods were used to determine the accuracy, precision, detection limit, sensitivity, fit, and predictive ability of the model. A discussion of these statistics follows, as well as a look at the repeatability of the spectrophotometric methods used.

3.1 Applied Statistical Formulas

To apply most statistical tests, including hypothesis testing and interval estimation, to a given set of data, the assumption must be made that the data is drawn from a normal population. Although it hasn't been proven that repeated measurements like those made here are always normally distributed, there is considerable evidence that this is true in most cases. In addition, a slight departure from normality is not usually important in the evaluation of the most commonly applied statistical tests.²⁵ To confirm this, 20 repeated measurements were made on a 25 lb/Mgal sample of HPG and the frequency distributions were plotted from 300 nm to 800 nm every 50 nm. These distributions approximated the normal distribution, as shown in Figure 3.1, for a wavelength of 550 nm. The remainder of the distributions at different wavelengths are located in Appendix 2.



Figure 3.1 Histogram of 20 Repeated Measurements for a 25 lb/Mgal HPG Fluid.

For every data set, several different calibration curves were investigated based on the concentration range, data pretreatments, and linear vs. nonlinear models. Initially, the question for each fluid at a given wavelength is which calibration curve best represents the relationship between optical density and concentration. In this sense we must ask the following questions: which curve provides the best fit to the calibration data, which curve provides the best predictive ability for future data, and which curve has the least amount of error associated with it? Additional statistics, such as confidence limits, accuracy, precision, limit of detection, sensitivity, etc., were measured to aid in the evaluation of a regression model as well.

One measure of a model's ability to explain the relationship between variables is the coefficient of determination, R^2 . This statistic allows us to determine the amount of variation in the data, which is adequately modeled by the calibration curve. It is a measure of the degree to which the calibration fits the data. However, the coefficient of determination does not measure the appropriateness of the model, as it can't imply that the model will be an accurate predictor for future samples.

The statistics termed standard error of regression (SER) and standard error of prediction (SEP) can be used along with the coefficient of determination to evaluate the best model for a given data set.²⁶ SER is the standard deviation of the residuals due to differences between the data and resulting values, as calculated by the calibration equation for samples within the calibration data set. It is an indication of the total residual error due to the particular regression equation to which it applies. The following equation was used to calculate the SER:

$$SER = \sqrt{\frac{\sum_{i} (y_i - \hat{y}_i)^2}{n-2}}$$
 (3.1)

where

 y_i = each optical density value at a given concentration \hat{y}_i = the predicted optical density at a given concentration n = number of concentration samples used

SEP is similar to SER, but it is the standard deviation for the residuals due to differences in the data and the predicted values using samples outside the calibration data set, using instead the prediction data set. The equation for SEP follows:

$$SEP = \sqrt{\frac{\sum_{i} (y_i - \hat{y}_i)^2}{n - 1}}$$
(3.2)

Calculating SER is a way of evaluating how well the calibration equation fits the data while SEP is a way of evaluating how well the equation will predict future observations. The units for SEP and SER are the same as those for optical density.

Accuracy of a method refers to the degree of agreement between a test result generated by a particular model and the true value. Since noise can bias the accuracy of any individual measurement, the average of several measurements on each sample was used as the optical density at each concentration. A statistic known as the relative error of prediction (REP) was used to measure the accuracy of each calibration model and is defined in Equation (3.3).¹⁴

$$\% REP = \frac{1}{n} \sum_{i} \left| \frac{y_i - \hat{y}_i}{y_i} \right| * 100$$
(3.3)

The precision of a method is a measure of the degree of agreement among individual test results when a procedure is applied repeatedly to multiple samplings. To determine the precision of these methods, a set of samples, all having the same concentration, were measured and the relative standard deviation (RSD) was calculated.²⁵ This statistic was used to measure precision, because it provides a comparison of random errors for different concentrations since it is an indication of the magnitude of the standard deviation as a portion of the mean value.

$$\% RSD = \frac{s}{\bar{x}} * 100 \tag{3.4}$$

where

s = standard deviation of samples

 \overline{x} = average value of samples

The detection limit for a calibration method is defined here as the lowest concentration that can be detected and is not to be confused with sensitivity. A detection limit for each method was determined by taking the average value of several scans of the baseline fluid and adding two standard deviations. The baseline fluid for HPG was water and for HPG with silica flour was HPG.^{25,27} In addition, the sensitivity was described in each linear regression case by a graph of the slope of the calibration curve which provided a measure of the change in optical density given a change in concentration.

In statistical analysis, samples are measured in an effort to make predictions about the corresponding population from which the samples were taken. One way of evaluating the expected values based on the sample measurements is to define a range within which the true value should reasonably lie. This method of analysis is referred to as confidence intervals and implies that we can assert, with a given degree of confidence, or probability, that the confidence intervals include the true value. Confidence intervals for the mean response can be calculated to show the expected range, at a certain level of confidence, of optical density values that will occur around the calibration curve based on the data used to form the calibration curve. The equation used to calculate confidence intervals is given in Equation (3.5).²⁸

$$E(y|x_0) = \hat{y}_0 \pm t \left(\frac{\alpha}{2}, n-2\right) \left[\sqrt{\frac{\sum_{i} (y_i - \hat{y}_i)^2}{n-2}} \left(\frac{1}{n} + \frac{(x_0 - \bar{x})^2}{\sum_{i} (x_i - \bar{x})^2}\right) \right]$$
(3.5)

where

 x_i = each concentration value

 \overline{x} = average concentration of samples

t = students t test for a given confidence level, α , and degrees of freedom (n-2)

n = number of samples

3.2 Precision of Repeated Measurements

Before multiple samples were measured at each concentration for averaging, several experiments were preformed to indicate the precision and repeatability of these methods. In the visible spectrum, five different samples were drawn from the same batch of a 40 lb/Mgal HPG fluid. Each sample was measured five times, removing and repositioning the sample after each measurement. This resulted in 25 measured spectra, shown in Figure 3.2. The resulting spectra are tightly grouped, showing good signs of repeatability of optical density measurements for multiple samples of the same batch. It also shows that the error due to repositioning of the sample between measurements is relatively small.

As a quantitative measure of the precision in this case, the relative standard deviation was calculated for these 25 spectra at each wavelength resulting in the graph of Figure 3.3. For wavelengths of 252 nm to 820 nm, excluding 654 nm and 658 nm, the RSD is less than 3% with a majority of the values in the 1.5% to 2% range. The raw data for this experiment can be found in Appendix 3.



Figure 3.2 Optical Density Spectra for 5 Samples, Measured 5 Times Each in the Visible Spectrum.



Figure 3.3 RSD for 5 Samples Measured 5 Times Each in the Visible Spectrum.

In another experiment, two samples from the same batch were measured twice at 0 degrees and also twice at 180 degrees, for a total of eight measurements. The resulting RSD is given in Figure 3.4. In this case, the values of RSD are lower, generally less than 1%, than in the previous case where more samples were involved and repositioning occurred between every measurement.



Figure 3.4 RSD for 2 Samples Measured at 0 and 180 Degrees.

As a final experiment in the visible region, two separate batches of 40 lb/Mgal HPG were mixed and 12 samples were measured from each batch. The RSD for the 12 samples of each batch as well as the RSD for all 24 samples combined are shown in

Figure 3.5. When two separate batches were mixed, and the RSD was measured for 12 samples from each batch, the RSD increased significantly to values greater than 4% at all wavelengths. Figure 3.5 also shows the individual results for precision with regard to each batch and this shows that the second batch had higher values of RSD than the first batch. Comparison to Figure 3.3 reveals that the RSD values for 5 samples measured 5 times, each were lower than either of the cases in Figure 3.5. This would lead to the conclusion that the majority of the error occurring in repeated measurements of samples occurs when the samples are from different batches, or mixtures, which implies that the majority of the error is due to weighing or volumetric inaccuracies incurred during the mixing process.

As a comparison to the visible region, an experiment was conducted in the NIR where two samples were measured twice at 0 and 180 degrees. A plot of the results versus those found in the visible region for the same type of experiment is provided in Figure 3.6. Comparing the two wavelength regions shows that the visible region results in better precision than the NIR. This is a result of the standard deviation values across all wavelengths in the NIR being an order of magnitude larger than those found in the visible region for the same type of measurements. The wavelengths in the NIR region where the RSD values were zero are due to the optical density values being at the maximum allowed level of 6 for all measurements. This maximum value was defined during the setup of the spectrophotometer and at this maximum value only 0.0001% of the incident radiation is being transmitted through the sample.



Figure 3.5 Comparison of RSD for 12 Samples from 2 Different Batches.



Figure 3.6 Comparison of Precision for Multiple Measurements in the Visible and NIR Regions.

Chapter 4

Initial Spectral Investigation in the UV to NIR

Several factors contributed to the selection of the spectral regions to be investigated using spectroscopy. Since the overall goal is to aid in the development of optical sensor design for use with HPG fracturing fluids, the cost of sources and detectors, as well as their availability, was a factor. Performance in the regions that complied with the above restraints was the next criteria. It was found that most manufacturers of HPG have spectra for fracturing fluids based on HPG in the midinfrared region of the spectra where they are used as "fingerprints" of the fluids for identification purposes. However, not only are these spectra hard to obtain due to their proprietary nature, but they are also of limited use in the context of this research since the absorption of water in the mid-infrared region is too high to achieve adequate penetration depths, thereby rendering this region of the spectrum inadequate for the development of most optical sensors in conjunction with HPG fluids. However, the near-infrared region, as well as the visible region, do not show the same degree of absorption in water. Since HPG is made up largely of water, both the visible and nearinfrared regions were investigated as possible areas for sensor development.

4.1 Spectral Properties of Water

It is well documented in the literature that water shows no appreciable absorption in the visible region of the spectrum.^{11,29} Figure 4.1 shows the visible

spectrum of tap water. There is only one large peak for optical density in this region and it occurs at 656 nm. Two other peaks occur at 486 nm and 580 nm, but are still very low optical densities. Therefore, the visible region shows good transmission characteristics for tap water over its entire region.



Figure 4.1 Spectra of Tap Water in the Visible Region.

However, there are areas in the NIR that show small and appreciable amounts of absorption. This is illustrated in Figure 4.2.³⁰ In the spectral region from 1100 nm to 2500 nm, there are two absorption bands, whereas the spectral region from 800 nm to 1300 nm shows only small amounts of absorption for water.³⁰ There are two large absorption bands for water located at 1450 nm and 1950 nm where the OH bonds



Figure 4.2 Near-Infrared Spectra of Water.³⁰

show natural resonances. In this region, the absorbance of water for a sample with a pathlength of 1 mm exceeds 3 absorbance units for wavelengths greater than 1900 nm, which translates into 0.1% transmitted radiation.³¹ Therefore, the region 650 nm to 1300 nm is particularly suited to the study of samples containing a high concentration of water, such as HPG fracturing fluids.

4.2 Spectral Properties of Cuvets

In the visible region of the spectrum, sample measurements were made using ultraviolet-visible grade optical methacrylate cuvets. These cuvets had a pathlength of 1 cm and transmission characteristics shown in Figure 4.3.



Figure 4.3 Percent Transmission of Sample Cuvets Used in the Visible Spectrum.

In the ultraviolet region of the spectrum, there is a considerable reduction in transmission of radiation through the cuvets, but at wavelengths greater than 350 nm the transmission is greater than 88%. Blank cuvets were placed in the spectrophotometer and spectra were taken to quantify the cuvets contribution to the HPG fracturing fluid sample's spectra. Figure 4.4 shows the resulting spectra, which is an average of three scans. There are significant amounts of attenuation in the ultraviolet region below about 300 nm due to interactions between the radiation and the methacrylate of the cuvets. In the NIR region, samples of these fluids were placed in cuvets with SUPRASIL 300[®] quartz windows, which had a pathlength of 1 cm. These cuvets were usable at wavelengths of 190 nm to 3600 nm with at least 80 percent transmission over this entire wavelength range.



Figure 4.4 Spectra of Blank Cuvets Used in the Ultraviolet-Visible Region, Average of Three Scans.

4.3 Spectral Properties of HPG and Silica Flour Components

To determine the spectral contribution of each additive in these fluids, optical density spectra was taken in the UV-VIS region on each individual additive as represented in the fracturing fluid. The relative amounts of each additive used to prepare the different batches of HPG fracturing fluid are given in Table 4.1. Two categories of fracturing fluids were tested: 1) plain HPG fracturing fluid, and 2) HPG fracturing fluid with silica flour added. In order to determine the contribution of each additive in these fluids, spectra was taken on each individual additive as represented in the fracturing fluid. These spectra included samples of tap water, 0.3 g of sodium

bicarbonate in 1000 mL of water, and 0.3 g of fumeric acid in 1000 mL of water, and 0.24 mL of bactericide in 1000 mL of water.

Component	Amount	
Water	1000 mL	
Sodium Bicarbonate	0.3 g	
HPG	0.119 g/lb	
Fumeric Acid	0.3 g	
Bactericide	0.24 mL	
Silica Flour	0.12 g Mgal/lb	

Table 4.1 Components of HPG Fracturing Fluids in This Study

Figure 4.5 displays the results of these measured spectra where each of the given spectra is the average of 12 samples from the same batch. Fumeric acid exhibits a large absorption band in the ultraviolet region of the spectrum, peaking at 262 nm and extending from 250 nm to 300 nm, while the bactericide shows a similar, although much smaller, band with a peak at 256 nm and also ranging from 250 nm to 300 nm. Sodium bicarbonate has a small band centered at 285 nm that ranges from 250 nm to 325 nm. In Figure 4.5, the tap water samples showed very little attenuation in the entire region except for a small, narrow band at 656 nm. However, there are two other

narrow, weak bands that are not noticeable for water in Figure 4.5 because of the scale being used. Consequently, Figure 4.1 shows the spectra for water alone and these weaker features become more apparent.



Figure 4.5 Ultraviolet-Visible Spectra for Various Components of HPG Fracturing Fluid, Average of 12 Samples.

The UV-VIS spectral contributions of each component used to form HPG fracturing fluids are summarized in Table 4.2. This data shows that, in the ultraviolet region of approximately 250 nm to 325 nm, there are several factors contributing to the attenuation of radiation at these wavelengths. With that in mind, this region of the

spectrum is not optimal for general optical sensor development if depth of penetration into the fluid is critical.

Component	Band Range (nm)	Band Peak (nm)	Optical Density at Peak
Tap Water		656	0.052
Distilled Water		656	0.048
Bactericide	250-300	256	0.206
Fumeric Acid	250-300	262	1.740
Sodium Bicarbonate	250-325	285	0.006

Table 4.2 Band Assignments for Components of HPG Fracturing Fluid.

However, if analysis in regard to the amounts of bactericide, fumeric acid or sodium bicarbonate present in a fracturing fluid were of interest, the region 250 nm to 325 nm would be optimal for sensor development. In addition, a sample of 1000 mL of tap water was mixed with silica flour to form a concentration of 5 lb/Mgal silica flour in water. Ten samples of this mixture were measured to provide information on the silica flour's optical density spectra. The average of these ten spectra is shown in Figure 4.6. It is clear from Figure 4.6 that other than the contributions due to tap water at 486 nm, 580 nm, and 656 nm, the only contribution of silica flour to the visible spectrum is one of a baseline shift over all wavelengths from 400 nm to 820 nm.



Figure 4.6 5 lb/Mgal Silica Flour and Tap Water Mixture Averaged over Ten Scans.

This shift does show a decreasing trend with increasing wavelength which would indicate the possibility that scattering was the major contributor in this case, as its contribution to optical density decreases with increasing wavelength. However, the possibility of background absorption is not ruled out as an additional contributor in this case although silica flour shows no absorption peaks in the visible range of 400 nm to 820 nm.

In the NIR region of the spectrum, a spectrum for a 40 lb/Mgal HPG fluid was measured and showed no appreciable features other than the two broad absorption bands associated with the water. This comparison can be seen by comparing Figure
4.7 to Figure 4.2. This comparison shows that the HPG components only add a baseline shift to the shape of the optical density spectra for water. Therefore, each individual component was not measured as it was in the UV-VIS region.



Figure 4.7 Optical Density Spectra of 40 lb/Mgal HPG in NIR Region.

4.4 Transmission Windows of HPG in the UV to NIR

The first step in determining the range of wavelengths to be considered for this study was to determine the wavelengths at which water was highly absorbent as discussed in Section 4.1. This led to wavelengths greater than 1350 nm being excluded from the NIR range. Then, the individual contributions of the HPG components were taken into consideration, and wavelengths below 400 nm were excluded because of extinction attributed to the components of HPG, as well as the spectral response of the cuvets in that region. To confirm that the region 400 nm to 1350 nm was an appropriate window in the UV-VIS-NIR region for this optical characterization, a full scan over these regions was recorded using the Perkin Elmer UV-VIS-NIR spectrophotometer for three fluids: 20 lb/Mgal, 40 lb/Mgal, and 60 lb/Mgal. Figure 4.8 shows the result of these measurements.



Figure 4.8 Spectra of Various Concentrations of HPG Fracturing Fluid Over the Entire Spectral Range 100 nm to 3100 nm with the Spectrophotometer Set for an Optical Density Range 0 to 6.

The two absorption peaks in the near-infrared region are visible in Figure 4.8, along with the large absorbencies due to water beyond about 1300 nm. A definite transmission window is evident in the spectral region of approximately 400 nm to about 1300 nm and this is where the majority of all the remaining research is focused. When looking at this region, more detail is clear due to the increased amplitude of the y-axis. The optical density is shown to flat-line at a value of six. This characteristic is due to the setup of the spectrophotometer, which was set for an optical density range of 0 to 6.

Chapter 5

Extinction Coefficients for HPG Fracturing Fluid

For both the cases of HPG and HPG with silica flour added, the method detailed in Chapter 2 was used to calculate extinction coefficients. However, before these calculations could be made, the concentration range over which the underlying theory applied must be determined. As discussed earlier, the main assumption in question was that of single versus multiple scattering. Therefore, the concentration range over which only single scattering events occurred must be determined before the coefficients could be calculated. This was achieved by plotting the raw optical density data versus concentration and identifying nonlinearities, which could be attributed to multiple scattering events. Once the appropriate concentration range was selected, the extinction coefficients were measured and examples given for transmitted intensity versus distance. Extinction coefficients were investigated for HPG fluids ranging from 5 lb/Mgal to 55 lb/Mgal in the VIS and NIR regions. Appropriate concentrations were selected from this concentration range, for both spectral regions, and the resulting coefficients are presented. Additionally, a comparison is made of the transmission properties of HPG in the VIS and NIR regions.

5.1 Coefficients for HPG in VIS Region

As stated previously, spectra were measured for different concentrations of HPG in the range 5lb/Mgal to 60 lb/Mgal. An average of 4 scans for 4 different samples was used to determine the appropriate concentration range over which extinction coefficients would be calculated for HPG in the visible region of the spectrum. Figure 5.1 shows the resulting spectra at each concentration, and the raw data is located in Appendix 4. Concentration ranges of 5 lb/Mgal to 60 lb/Mgal, 5 lb/Mgal to 50 lb/Mgal, and 5 lb/Mgal to 45 lb/Mgal were investigated for linearity in terms of the coefficient of determination, for each of these ranges and all wavelengths.



Figure 5.1 Raw HPG Spectra in Visible Region, Average of 4 Scans.

Figure 5.2 shows the results for linear regression analysis of the raw optical density data versus concentration of HPG at different concentration ranges.



Figure 5.2 Coefficient of Determination for Linear Regression of Various HPG Concentration Ranges and Optical Density in the Visible Region.

The best values for the coefficient of determination, over all wavelengths, occurs for the concentration range 5lb/Mgal to 60 lb/Mgal where the values range from a low of 0.977 to a high of 0.992. Only one wavelength resulted in a value less than 0.985, and that wavelength was 656 nm where the low value of 0.977 occurred. Most of the values for coefficient of determination centered on 0.988 with over 20 wavelengths having values of 0.99 or higher. A value for the coefficient of determination that is close to unity implies that the data fits a linear relationship well. However, the data could still have a trend that would suggest the presence, to a small degree, of multiple scattering. As discussed in Chapter 2, the presence of multiple scattering would appear in a scatter plot of optical density data versus concentration as a leveling off of the values of optical density with increasing concentration, deviating from linearity at higher concentrations. To assess the current case, plots were made of the raw data and resulting calibration curve as derived from linear regression at various wavelengths throughout the region. The curve associated with a wavelength of 658 nm is shown in Figure 5.3. Additional plots are located in Appendix 5 and include wavelengths from 400 nm to 800 nm, taken every 50 nm. These figures show that the small deviations from linearity do not show the form expected to be present in the case of multiple scattering, as deviations from the calibration curve occur in both the positive and negative direction as concentration values increase.

As a result of this investigation, extinction coefficients for the entire concentration range were calculated in the visible region from 400 nm to 820 nm according to Equation (2.20). The resulting coefficients are shown graphically in Figure 5.4 while the raw data is located in Appendix 6. This graph illustrates that at each wavelength, the extinction coefficient increases with increasing concentration. It also shows that at each concentration, the coefficients decrease with increasing wavelength except at wavelengths where water showed absorption peaks or bands: 484 nm – 486 nm, 564 nm – 590 nm, and 656 nm. This implies that, in general, better



Figure 5.3 HPG Optical Density Data and Corresponding Calibration Curve at 658 nm.



Figure 5.4 Extinction Coefficients for HPG in Visible Region.

transmission in HPG will be achieved at the longer wavelengths of the visible region. To quantify this conclusion, Equation (2.17) was used to calculate the percent of transmitted intensity that remains after traversing a given pathlength in HPG for various wavelengths and concentrations. As an example, Figure 5.5 shows the results at 820 nm for transmitted intensity versus pathlength at each concentration from 5 lb/Mgal to 60 lb/Mgal. Additional graphs of transmitted intensity versus pathlength are given in Appendix 7.



Figure 5.5 Percent Transmitted Intensity vs. Pathlength for HPG in the Visible Region.

Another way to look at these results is by wavelength, which is shown in Figure 5.6.



Figure 5.6 Transmitted Intensity vs. Pathlength for a 30 lb/Mgal HPG Fluid at Various Wavelengths in the Visible Spectrum.

Both Figure 5.5 and Figure 5.6 show better penetration into a given fluid is achieved at longer wavelengths in the visible region. To determine the significance of selecting the optimum wavelength, values of transmitted intensity at depths of 1 cm, 5 cm, and 10 cm, are compared for wavelengths of 820 nm and 400 nm in Figure 5.7. At all three depths, the percentage of transmitted intensity is greater for the case of 820 nm.



Figure 5.7 Transmitted Intensity vs. Concentration at 1 cm, 5 cm, and 10 cm for 400 nm and 820 nm.

The improvement in fluid penetration at 820 nm as opposed to 400 nm is evaluated as a percentage increase in transmission of 820 nm over 400 nm at 1 cm and 5 cm in Figure 5.8 and Figure 5.9, respectively. At a depth of 1 cm, the percent improvement in using a wavelength of 800 nm over a wavelength of 400 nm increases monotonically from a value of 5.5% improvement at 5 lb/Mgal to 117% improvement at 60 lb/Mgal. In comparison, at a depth of 5 cm, the percent improvement increases from a value of 31% at 5 lb/Mgal to 4677% at 60 lb/Mgal. Therefore, the impact of selecting a longer versus shorter wavelength in the visible region is greater for larger depths of penetration.



Figure 5.8 Percentage Increase in Transmitted Intensity for 800 nm vs. 400 nm at a Depth of 1 cm.



Figure 5.9 Percentage Increase in Transmitted Intensity for 800 nm vs. 400 nm at a Depth of 5 cm.

5.2 Coefficients for HPG in NIR Region

To determine the extinction coefficients for various concentrations of HPG in the NIR, three samples were scanned every 5 lb/Mgal in the concentration range 5 lb/Mgal to 60 lb/Mgal. The resulting averages at each concentration in the NIR are displayed in Figure 5.10, and the raw data is given in Appendix 8.



Figure 5.10 Raw HPG Spectra in NIR, Average of 3 Scans.

In the NIR region, concentration ranges of 5 lb/Mgal to 60 lb/Mgal, 5 lb/Mgal to 55 lb/Mgal, 5 lb/Mgal to 50 lb/Mgal, and 5 lb/Mgal to 45 lb/Mgal were evaluated for

linearity as was the case in the visible region in the previous section. Linear regression analysis was performed on the data for each of these concentration ranges and the resulting coefficients of determination are given in Figure 5.11.



Figure 5.11 Coefficients of Determination for Linear Regression of Various HPG Concentration Ranges and Optical Density in the NIR.

Resulting values for the coefficients of determination show good linearity is in two of the concentration ranges, namely 5 lb/Mgal to 50 lb/Mgal and 5 lb/Mgal to 45 lb/Mgal. In both of these cases, the values are very close to 0.99 or higher. It would be preferable to select the larger range of 5lb/Mgal to 50 lb/Mgal as the appropriate range

for the determination of extinction coefficients, since it would provide transmission information for a 50 lb/Mgal HPG fluid. However, the data must also be evaluated graphically for an indication of nonlinearity. A graph of the raw data along with a calibration curve for the range 5 lb/Mgal to 45 lb/Mgal is found in Figure 5.12 at a wavelength of 865 nm.



Figure 5.12 HPG Optical Density Data and Calibration Curve at 865 nm.

It is apparent after studying the graph, that the last three concentrations show a nonlinear trend at high concentrations. A second order polynomial was fitted to the entire range of optical density data and shows the relative decrease in optical density

with increasing concentration at concentrations greater than 45 lb/Mgal. Therefore, even though the coefficients of determination are relatively high for the range 5 lb/Mgal to 50 lb/Mgal, Figure 5.12 shows that the trend at concentrations higher than 45 lb/Mgal could indicate the presence of multiple scattering. As a result, the determination of extinction coefficients in the NIR will be limited to the concentration range: 5 lb/Mgal to 45 lb/Mgal. Additional graphs of the optical density data in the NIR were evaluated which included wavelengths at every 50 nm in the range 900 nm to 1350 nm, to determine the linearity across the entire NIR. These graphs are found in Appendix 9.

Extinction coefficients were calculated according to Equation (2.20) for the NIR region at concentrations of HPG ranging from 5 lb/Mgal to 45 lb/Mgal. A graphical display of the results is given in Figure 5.13, and the actual values are located in Appendix 10. This graph illustrates an overall increase in extinction coefficient values for increasing wavelengths, with two disturbances due to the two absorption bands of water in this region. These bands are centered around 975 nm and 1190 nm. Consequently, the best transmission, in terms of the depth of penetration into the fluid, is found at the lower wavelengths around 865 nm. Additionally, values for the extinction coefficient at wavelengths between the two absorption peaks, 1050 nm to 1115 nm, should also provide good transmission into HPG. To assess the validity of these conclusions, the percent transmitted intensity versus pathlength at each concentration from 5 lb/Mgal to 45 lb/Mgal and various wavelengths was graphed as in Figure 5.14 for the case of 865 nm. At a wavelength of 865 nm, the percentage of



Figure 5.13 Extinction Coefficients for HPG in the NIR Region.



Figure 5.14 Transmitted Intensity vs. Pathlength for HPG at 865 nm.

initial intensity that is transmitted at a given distance decreses with increasing concentration. A more interesting look at transmission in HPG in the NIR is taken in Figure 5.15. In this example, the percent transmitted intensity versus pathlength is shown for a 20 lb/Mgal HPG fluid.



Figure 5.15 Transmitted Intensity vs. Pathlength for a 20 lb/Mgal HPG at Various Wavelengths in the NIR Spectrum.

The results indicate that an increase in wavelength does not always result in a decrease in transmitted intensity at a given distance. Wavelengths exhibited in the graph encompass the entire wavelength range of 865 nm to 1350 nm, with points taken every 50 nm. Consequently, the best wavelengths for transmission are 865 nm followed by 900 nm. These two wavelengths are followed by 1050 nm and 1100 nm, which happen to be located in the region between the two absorption bands of water as mentioned earlier. To assess the impact of wavelength selection in the NIR, values of transmitted intensity at depths of 1 cm, 5 cm, and 10 cm, are compared for wavelengths of 865 nm and 1300 nm in Figure 5.16. At all three transmission depths, the percentage of transmitted intensity is greater for the case of 865 nm. Values for transmitted intensity at depths of 5 cm and 10 cm for the case of 1300 nm are not visible in Figure 5.16 due to their small values. Hence, the resulting values were placed in Table 5.1 for



Figure 5.16 Transmitted Intensity vs. Concentration at 1 cm, 5 cm, and 10 cm for 865 nm and 1300 nm.

clarification. The table reveals how the percentage of transmitted intensity decreases to

values approximating zero for distances of 5 cm and 10 cm at 1300 nm.

Depth	Concentration of HPG in lb/Mgal				
Wavelength	5 lb/Mgal	10 lb/Mgal	15 lb/Mgal	20 lb/Mgal	25 lb/Mgal
1 cm, 865 nm	86.5632	81.8025	78.0249	75.5092	69.0558
5 cm, 865 nm	48.6034	36.6297	28.9179	24.5471	15.7036
10 cm, 865 nm	23.6229	13.4173	8.3624	6.0256	2.4660
1 cm, 1300 nm	24.1157	23.1775	22.5165	21.9213	20.3892
5 cm, 1300 nm	0.0816	0.0669	0.0579	0.0506	0.0352
10 cm, 1300 nm	6.65E-05	4.47E-05	3.35E-05	2.56E-05	1.24E-05
				1	
Depth		Concentra	tion of HPG i	n lb/Mgal	
Depth Wavelength	30 lb/Mgal	Concentra 10 lb/Mgal	ation of HPG i 40 lb/Mgal	n lb/Mgal 45 lb/Mgal	
Depth Wavelength 1 cm, 865 nm	30 lb/Mgal 65.0379	Concentra 10 lb/Mgal 61.0145	ation of HPG i 40 lb/Mgal 57.7786	n lb/Mgal 45 lb/Mgal 54.8782	
Depth Wavelength 1 cm, 865 nm 5 cm, 865 nm	30 lb/Mgal 65.0379 11.6368	Concentra 10 lb/Mgal 61.0145 8.4560	ation of HPG i 40 lb/Mgal 57.7786 6.4392	n lb/Mgal 45 lb/Mgal 54.8782 4.9774	
Depth Wavelength 1 cm, 865 nm 5 cm, 865 nm 10 cm, 865 nm	30 lb/Mgal 65.0379 11.6368 1.3541	Concentra 10 lb/Mgal 61.0145 8.4560 0.7150	ation of HPG i 40 lb/Mgal 57.7786 6.4392 0.4146	n lb/Mgal 45 lb/Mgal 54.8782 4.9774 0.2477	
Depth Wavelength 1 cm, 865 nm 5 cm, 865 nm 10 cm, 865 nm 1 cm, 1300 nm	30 lb/Mgal 65.0379 11.6368 1.3541 19.5314	Concentra 10 lb/Mgal 61.0145 8.4560 0.7150 18.6380	ation of HPG i 40 lb/Mgal 57.7786 6.4392 0.4146 17.9721	n lb/Mgal 45 lb/Mgal 54.8782 4.9774 0.2477 17.3527	
Depth Wavelength 1 cm, 865 nm 5 cm, 865 nm 10 cm, 865 nm 1 cm, 1300 nm 5 cm, 1300 nm	30 lb/Mgal 65.0379 11.6368 1.3541 19.5314 0.0284	Concentra 10 lb/Mgal 61.0145 8.4560 0.7150 18.6380 0.0225	ation of HPG i 40 lb/Mgal 57.7786 6.4392 0.4146 17.9721 0.0187	n lb/Mgal 45 lb/Mgal 54.8782 4.9774 0.2477 17.3527 0.0157	

Table 5.1 Percent Transmitted Intensity Values for 865 nm and 1300 nm.

At depths of 1 cm and 5 cm the percentage improvement in transmitted intensity for 865 nm over 1300 nm was calculated and exhibited in Figure 5.17 and Figure 5.18, respectively. At 1 cm, the percentage improvement in transmitted intensity at 865 nm versus 1300 nm decreases with increasing concentration and values range from 259% at 5 lb/Mgal to 216% at 45 lb/Mgal. The same trend is true at a depth of 5 cm,



Figure 5.17 Percentage Increase in Transmitted Intensity for 865 nm vs. 1300 nm at a Depth of 1 cm.



Figure 5.18 Percentage Increase in Transmitted Intensity for 865 nm vs. 1300 nm at a Depth of 5 cm.

although the percentage improvement in using 865 nm versus 1300 nm is much greater with values ranging from 59,489% at 5 lb/Mgal to 31,535% at 45 lb/Mgal. A much larger percentage improvement at 5 cm is a result of the drastic reduction in transmitted intensity for 1300 nm as seen in Table 5.1. As was the case in the visible region, wavelength selection has a larger impact on transmission at greater depths of penetration.

5.3 Comparison of Transmission Properties in VIS-NIR

Now a comparison of the two spectral ranges investigated above will reveal which wavelengths provide the best transmission in HPG fluids over the entire VIS-NIR region. Comparing transmitted intensity at 1 cm, 5 cm, and 10 cm for wavelengths of 865 nm and 820 nm, as shown in Figure 5.19, reveals that one wavelength does not always provide better transmission through all concentrations of HPG. In fact, the graph illustrates that a wavelength of 820 nm will provide a higher percentage of transmitted intensity for concentrations up to 15 lb/Mgal. However, at HPG concentrations of 20 lb/Mgal to 45 lb/Mgal, a wavelength of 865 nm provides much better transmission. At a concentration of 15 lb/Mgal the two wavelengths perform very similarly with an improvement in transmitted intensity of only 6.8% at a depth of 5 cm for 820 nm over 865 nm. The percentage improvement of transmitted intensity for 865 nm versus 820 nm is displayed in Figure 5.20 with negative values representing those cases in which 820 nm exhibited an improvement in transmitted intensity over 865 nm. For a depth of 5 cm, the percentage increase in transmitted



Figure 5.19 Comparison of Transmitted Intensity for 820 nm and 865 nm.



Figure 5.20 Percentage Change in Transmitted Intensity for 865 nm vs. 820 nm.

intensity at concentrations above 15 lb/Mgal, increases from 90.3% at 20 lb/Mgal to 482% at 45 lb/Mgal.

In summary, it was demonstrated that to maximize the depth of penetration of radiation into HPG fluids at concentrations ranging from 5 lb/Mgal to 45 lb/Mgal, selecting the correct wavelength becomes critical. In general, it is sufficient to say that wavelengths in the NIR region of 750 nm to 900 nm will provide the best overall transmission into these fluids. If, however, the amount of intensity transmitted is critical, then a closer look needs to be taken at this NIR range. One important fact to determine is what concentrations will be studied, since it was shown that concentration does have an effect on which wavelength provides the best transmission characteristics. If low weight concentrations of 5 lb/Mgal to 20 lb/Mgal are of interest then a shorter wavelength around 820 nm would be optimum. If on the other hand, higher concentrations were of more interest, then a longer wavelength of 865 nm would be optimum. If the entire range of concentrations 5 lb/Mgal to 45 lb/Mgal were of equal interest, the longer wavelength of 865 nm would still be preferable as it would add more benefit at more concentrations as mentioned earlier.

Chapter 6

Extinction Coefficients for HPG with Silica Flour Added

6.1 Coefficients for Silica Flour in the VIS Region

Extinction coefficients were investigated in the visible region of the spectrum for a 40 lb/Mgal HPG fluid, with silica flour added, in concentrations of 0 lb/Mgal to 55 lb/Mgal. An average of 5 scans was used to determine the silica flour concentration range over which extinction coefficients could reliably be determined. These raw, averaged spectra are displayed in Figure 6.1 and the corresponding raw optical density data is located in Appendix 11.



Figure 6.1 Average Spectra for 5 Scans of a 40 lb/Mgal HPG with Various Amounts of Silica Flour.

Concentration ranges of (1) 0 lb/Mgal to 55 lb/Mgal, (2) 0 lb/Mgal to 50 lb/Mgal, (3) 0 lb/Mgal to 45 lb/Mgal, (4) 0 lb/Mgal to 40 lb/Mgal, and (5) 0 lb/Mgal to 35 lb/Mgal were evaluated using the corresponding coefficient of determination for a linear regression in that concentration range. Results of these linear regression methods are given in Figure 6.2 for each silica flour concentration range. For each range, the values for the coefficient of determination display an increasing trend with increasing wavelength, except for a few wavelengths where the values drop: 436 nm, 546 nm, 612 nm, and 632 nm.



Figure 6.2 Coefficients of Determination for Linear Regression of a 40 lb/Mgal HPG with Various Concentration Ranges of Silica Flour in the Visible Region.

The silica flour concentration range of 0 lb/Mgal to 40 lb/Mgal shows values increasing towards 0.99 at longer wavelengths. At wavelengths greater than 652 nm, the coefficient of determination is greater than 0.985 for the concentration range 0 lb/Mgal to 40 lb/Mgal. The concentration range 0 lb/Mgal to 35 lb/Mgal has coefficients of determination greater than 0.988 except in the range 540 nm to 550 nm. Therefore, scatter plots of optical density versus concentration were made at wavelengths above 652 nm for the concentration range 0 lb/Mgal to 40 lb/Mgal and at various wavelengths throughout the entire range for the concentration range 0 lb/Mgal to 35 lb/Mgal and at wavelengths throughout the entire range for the concentration range 0 lb/Mgal to 35 lb/Mgal. Figure 6.3 presents a resulting graph at a wavelength of 814 nm for the range 0 lb/Mgal to 40 lb/Mgal while Figure 6.4 shows the same type of graph at a wavelength of 520 nm.



Figure 6.3 Optical Density vs. Silica Flour Concentration at 814 nm.



Figure 6.4 Optical Density vs. Silica Flour Concentration at 520 nm.

Figure 6.3 reveals that all optical density data points have a linear relationship to concentration in the range 0 lb/Mgal to 40 lb/Mgal at 814 nm. However, Figure 6.4 shows that at 520 nm the trend of the scatter plot at higher concentrations resembles that due to multiple scattering. Therefore, for wavelengths greater than 652 nm, extinction coefficients will be calculated for a silica flour concentration range of 0 lb/Mgal to 40 lb/Mgal while at wavelengths less than 654 nm, coefficients will be calculated for a concentration range of 0 lb/Mgal to 35 lb/Mgal. The resulting coefficients are presented in Figure 6.5 while the actual values are included in

Appendix 12. Resulting extinction coefficients show a decreasing trend with increasing wavelength other than at the wavelengths associated with absorption peaks for water: 486 nm, 580 nm, and 656 nm. As a result, better transmission is expected at longer wavelengths in the visible region of the spectrum.



Figure 6.5 Extinction Coefficients for a 40 lb/Mgal HPG with Silica Flour Added in the Visible Region.

Investigating the validity of these conclusions requires calculating the transmitted intensity at various concentrations and wavelengths. A plot of transmitted intensity

versus pathlength is shown in Figure 6.6 for a wavelength of 800 nm for each concentration, 0 lb/Mgal to 40 lb/Mgal, of silica flour.



Figure 6.6 Transmitted Intensity vs. Pathlength for HPG with Silica Flour Added at 800 nm.

An additional graph of transmitted intensity versus wavelength is shown in Figure 6.7 for a 40 lb/Mgal HPG fluid with 25 lb/Mgal of silica flour. Figure 6.7 reveals that penetration is better in HPG with silica flour added at longer wavelengths in the visible region. Both graphs illustrate the small pathlength of transmission in HPG with silica flour added versus plain HPG.



Figure 6.7 Transmitted Intensity vs. Pathlength for a 40 lb/Mgal HPG Fluid with 25 lb/Mgal of Silica Flour Added in the Visible Region.

To confirm the improvements seen at longer wavelengths in this region, a comparison of two wavelengths, 400 nm and 820 nm, was made at 0.5 cm, 1.0 cm and 1.5 cm pathlengths into the fluid as illustrated in Figure 6.8. At each depth, a wavelength of 820 nm provided better penetration into the fluid than 400 nm. The differences between the two wavelengths are not as drastic as in the previous case of plain HPG in the visible region, but an improvement in 820 nm over 400 nm is evident. The improvement in percent transmitted intensity at each depth, for 800 nm versus 400 nm, was calculated as a percent increase in transmitted intensity of the 800 nm case over the 400 nm case. Results for these calculations are provided graphically in Figure 6.9.



Figure 6.8 Comparison of Transmitted Intensity vs. Concentration for HPG with Silica Flour Added at 820 nm and 400 nm.



Figure 6.9 Comparison of Percent Improvement in Transmission Intensity at Various Depths for 800 nm and 400 nm in HPG with Silica Flour Added.

At each transmission depth in Figure 6.9, the percent improvement in transmission when using a wavelength of 820 nm versus 400 nm, shows an increase up to a silica flour concentration of 20 lb/Mgal, then starts to decrease slightly up to a concentration of 35 lb/Mgal. For the case of penetration depth equal to 0.5 cm, the improvement in using the longer wavelength is equal to 126 % at 0 lb/Mgal of silica flour, rises to a level of 252 % at 25 lb/Mgal and decreases to a final value of 191 % at 35 lb/Mgal. Similar, but smaller values are encountered for depths of 1.0 cm and 1.5 cm as shown in Figure 6.9. Hence the majority of improvement that is obtained when using a longer wavelength of 820 nm, is encountered at smaller depths of penetration and the impact decreases as the depth of penetration into the fluid increases. This graph also shows that at all three depths, the most improvement is gained at a silica flour concentration of 20 lb/Mgal.

6.2 Coefficients for Silica Flour in the NIR Region

Coefficients for a 40 lb/Mgal HPG with silica flour added in concentrations of 0 lb/Mgal to 55 lb/Mgal were determined from the average of 4 scans at each concentration. These averaged optical density values are graphed versus wavelength in Figure 6.10 and raw values are found in Appendix 13. One obvious difference between HPG and HPG with silica flour added is the amount of "spectral noise" found in the latter case. For the NIR region, silica flour concentration ranges of (1) 0 lb/Mgal to 55 lb/Mgal, (2) 0 lb/Mgal to 50 lb/Mgal, (3) 0 lb/Mgal to 45 lb/Mgal, (4) 0 lb/Mgal to 40 lb/Mgal, (5) 0 lb/Mgal to 35 lb/Mgal, and (6) 0 lb/Mgal to 30 lb/Mgal were investigated to determine which range was appropriate for calculating extinction coefficients. Linear regression analysis was applied to the data of Figure 6.10 in these ranges and the resulting values for the coefficient of determination are provided in Figure 6.11. Results for the entire silica flour range of 0 lb/Mgal to 55 lb/Mgal do not, in general,



Figure 6.10 Raw Spectra for 40 lb/Mgal HPG with Various Amounts of Silica Flour Added in the NIR Region.

show good linearity by virtue of the resulting coefficients of determination. However, if a closer look is taken of the coefficients of determination for the full range of silica

flour concentration, a small region off wavelengths do indicate good linearity for the regression analysis. This wavelength region includes 1130 nm to 1132 nm and appears



Figure 6.11 Coefficients of Determination for Linear Regression of 40 lb/Mgal HPG with Various Concentrations of Silica Flour in the NIR.

to be an absorption band that occurs at higher concentrations of silica flour. A smaller region of the entire spectrum is plotted in Figure 6.12 so that these features are easily observed. In looking at the values for the coefficient of determination in this area of the NIR, three wavelengths show good linearity: 1130 nm, 1131 nm, and 1132 nm, as

shown in Figure 6.13. This phenomenon has to do with the presence of absorption at these wavelengths, which could mask weak scattering effects occurring at these and neighboring wavelengths. The calibration curve and corresponding raw data in Figure 6.14, for a wavelength of 1131 nm, illustrates the linearity of the raw data over the entire region of silica flour concentrations. Examining a wavelength on the edge of the absorption band shows a different relationship between optical density and concentration, as illustrated in Figure 6.15 for a wavelength of 1129 nm.



Figure 6.12 Average Spectra Over 4 Scans for 40 lb/Mgal HPG with Various Amounts of Silica Flour in the NIR at Wavelengths 1125 nm to 1140 nm.


Figure 6.13 Coefficients of Determination for 40 lb/Mgal HPG with Silica Flour Added in the Wavelength Range 1125 nm to 1140 nm.



Figure 6.14 Calibration Curve and Raw Data for a 40 lb/Mgal HPG with Various Amounts of Silica Flour Added at 1131 nm.



Figure 6.15 Calibration Curve and Raw Data for a 40 lb/Mgal HPG with Various Amounts of Silica Flour Added at 1129 nm.

The nonlinearity that is seen as the silica flour concentration increases is much more pronounced at 1129 nm than it was in Figure 6.14 at 1131 nm. Therefore, extinction coefficients were calculated for all silica flour concentrations, 0 lb/Mgal to 55 lb/Mgal, in the wavelength range 1130 nm to 1132 nm. However, three wavelengths are not very representative of the entire NIR region. Consequently, extinction coefficients were also calculated at the remaining wavelengths in the NIR region for silica flour concentrations of 0 lb/Mgal to 30 lb/Mgal. Selection of this concentration range is supported by the coefficient of determination results for this range as well as Figure 6.14 and Figure 6.15, which show the degree of linearity for raw optical density data in this concentration range.

Extinction coefficients were calculated for these wavelengths and concentration regions and are graphically displayed in Figure 6.16, while raw values for the coefficients in the concentration range 0 lb/Mgal to 30 lb/Mgal are found in Appendix 14. For the special case of wavelengths 1130 nm to 1132 nm, Figure 6.17 shows the resulting extinction coefficients as calculated for the entire silica flour concentration range. Figure 6.16 indicates that the extinction coefficients in this case are somewhat flat across the entire wavelength range except at wavelengths close to 1190 nm and beyond 1315 nm where the coefficients peak. The lowest values are found in the wavelength region 1054 nm to 1100 nm. A graph of transmitted intensity versus pathlength is provided in Figure 6.18 for a wavelength of 1078 nm. Transmitted intensity values decrease with increasing silica flour concentration, with the largest change occurring at the lowest concentrations.

There is a very large difference in transmitted intensity for the case of HPG and HPG with 5 lb/Mgal silica flour, which grows with increasing pathlength into the fluid. In addition, Figure 6.19 presents the relationship between transmitted intensity and pathlength at a silica flour concentration of 10 lb/Mgal for various wavelengths in the NIR.



Figure 6.16 Extinction Coefficients for 40 lb/Mgal HPG with Silica Flour in the NIR.



Figure 6.17 Extinction Coefficients for 40 lb/Mgal HPG with Silica Flour in the Wavelength Range 1130 nm to 1132 nm.



Figure 6.18 Transmitted Intensity vs. Pathlength for 40 lb/Mgal HPG with Silica Flour Added at 1078 nm.

These wavelengths were taken from the entire range, 900 nm to 1300 nm, with calculations made every 50 nm. From these wavelengths, the best transmission was achieved at 900 nm, 1050 nm, and 1100 nm. Showing slightly less transmission depths were wavelengths of 1000 nm and 950 nm. The remaining wavelengths showed significant degradation in transmission.

For comparison purposes, extinction coefficients at wavelengths of 1078 nm and 1300 nm will be used to evaluate transmission performance of radiation in a 40 lb/Mgal HPG with silica flour added. A wavelength of 1078 nm should provide the best possible transmission, while 1300 nm is one of the worst wavelengths outside of



Figure 6.19 Transmitted Intensity vs. Pathlength for a 10 lb/Mgal HPG with Silica Flour Added at Various Wavelengths in the NIR Spectrum.

the peak ranges mentioned earlier. Figure 6.20 shows the results of this comparison at pathlengths of 0.5 cm, 1.0 cm, and 1.5 cm. At all three transmission depths, the percentage of transmitted intensity is greater for the wavelength 1078 nm. A transmission depth of 0.5 cm results in a percent transmitted intensity ranging from 99% at 0 lb/Mgal to 66 % at 30 lb/Mgal for a wavelength of 1078 nm. In regards to a wavelength of 1300 nm, the percent-transmitted intensity is lower and ranges from 89% at 0 lb/Mgal to 60 % at 30 lb/Mgal. The difference in transmitted intensity for these two wavelengths, at this distance, is much greater at 0 lb/Mgal than at 30 lb/Mgal. This phenomenon is illustrated for all three pathlengths in Figure 6.21.



Figure 6.20 Transmitted Intensity vs. Silica Flour Concentration at 0.5 cm, 1.0 cm, and 1.5 cm, for 1078 nm and 1300 nm.

At all three transmission depths, the percentage improvement in transmitted intensity due to a wavelength of 1078 nm versus 1300 nm, shows a small decrease up to a silica flour concentration of 25 lb/Mgal, then increases at a concentration of 30 lb/Mgal. At a depth of 0.5 cm, the percent improvement between the two wavelengths ranges from 11.3% at 0 lb/Mgal to a low of 9.2% at 25 lb/Mgal and back up to 11.5% at 30 lb/Mgal



Figure 6.21 Comparison of Percent Improvement in Transmission Intensity at Various Depths for 1078 nm and 1300 nm in HPG with Silica Flour Added.

Similar results are obtained at 1.0 cm and 1.5 cm transmission depths, but the overall improvement increases with increasing depth into the fluid. The conclusion is that selecting 1078 nm over 1300 nm provides better penetration into the fluid and the improvement is largest at greater depths.

If evaluation of the transmission of radiation through all silica flour concentrations, 0 lb/Mgal to 55 lb/Mgal, is of interest, a wavelength in the range 1130 nm to 1132 nm should be used as demonstrated earlier. Figure 6.22 exhibits the transmitted intensity of radiation at a wavelength of 1131 nm for the entire

concentration range. To quantify the effect of increased silica flour concentration over the entire concentration range, Table 6.1 provides the distance traveled in the fluid at which the remaining intensity is half its original value. At 5 lb/Mgal, the radiation will travel 0.565 cm before losing half its original intensity whereas, at 55 lb/Mgal, it only travels 0.092 cm before doing so. Penetration into HPG is significantly reduced by adding silica flour to the fluid.



Figure 6.22 Transmitted Intensity for 40 lb/Mgal HPG with Various Amounts of Silica Flour Added at 1131 nm.

Table 6.1 Depth in 40 lb/Mgal HPG with Silica Flour Added, at Which 50%

Concentration of Silica Flour	% Transmitted Intensity = 50
(lb/Mgal)	(cm)
0	2.175
5	0.565
10	0.330
15	0.2415
20	0.195
25	0.164
30	0.1465
35	0.129
40	0.1155
45	0.103
50	0.097
55	0.092

of Initial Intensity Remains for 0 lb/Mgal to 55 lb/Mgal Silica Flour at 1131 nm.

6.3 Comparison of Transmission Properties in VIS-NIR

Comparing transmission properties for both spectral ranges will determine which wavelengths provide the best transmission in HPG fluids with silica flour added throughout the entire visible and NIR region. As in the case of HPG, the extinction coefficients for HPG with silica flour added reveal that at wavelengths less than 821 nm the range of coefficients over the concentration range 0 lb/Mgal to 30 lb/Mgal is slightly larger than the range for coefficients at wavelengths larger than 864 nm. A comparison is made for transmitted intensity at the best wavelengths from each region: 820 nm and 1078 nm. Figure 6.23 presents this data at depths of 0.5 cm, 1.0 cm, and 1.5 cm for each wavelength.



Figure 6.23 Comparison of Transmitted Intensity for HPG with Silica Flour Added at 820 nm and 1078 nm.

Figure 6.23 indicates that a wavelength of 1078 nm will provide better fluid penetration at all silica flour concentrations in the range 0 lb/Mgal to 30 lb/Mgal than a wavelength of 820 nm. Therefore, wavelengths in the NIR region surrounding 1078 nm should be selected as a source if maximum fluid penetration is to be achieved. The amount of improvement attained in utilizing a wavelength of 1078 nm versus 820 nm is presented in Figure 6.24. Resulting values for the percent improvement in the 1078 nm case versus 820 nm, reveal that at 0.5 cm into the fluid the percent improvement ranges from 48% at 0 lb/Mgal silica flour to 131% at 30 lb/Mgal silica flour.



Figure 6.24 Percentage Improvement in Transmitted Intensity in HPG with Silica Flour Added at 1078 nm vs. 820 nm.

In addition, at 1.5 cm the improvement increases at each concentration over that of the 0.5 cm case to values of 227% at 0 lb/Mgal silica flour to 1134% at 30 lb/Mgal silica flour. The conclusion from this set of data is that the percentage improvement in selecting a wavelength of 1078 nm over 820 nm gets higher in two cases (1) for an increase in concentration at a given depth, and (2) for an increase in depth at a given concentration.

Chapter 7

Calibration of Optical Density vs. HPG Concentration

7.1 Calibration of HPG in VIS Region

In order to study the concentration dependence of HPG fracturing fluids in the visible spectrum, the 4 scans analyzed in Chapter 5, for HPG in the visible region, were separated into two sets. The first set contains the first three runs, the average of which is considered the calibration data set, while the remaining scan is considered the prediction data set. It was demonstrated in Chapter 5 that a linear regression between the raw optical density data and concentration, for concentrations in the range 5 lb/Mgal to 60 lb/Mgal, did not show a high degree of linearity, as demonstrated in Figure 5.2. Therefore, in order to improve the calibration of optical density data and HPG concentration over this range, a transformation of the optical density data was made.

In cases such as this, where a slightly nonlinear function is expressed as a linear function after a suitable transformation, the model is considered transformably linear. When this type of transformation occurs, the least squares estimators of slope and intercept have least squares properties with respect to the transformed data, not the original data. The transformation made here was performed by taking the exponential value of the optical density data such that x = Exp(x). Resulting values for the coefficient of determination in this case, as calculated by least squares linear regression, are compared to those resulting in the linear regression of the raw data in Figure 7.1. This graph shows the improvement in the linear fit of optical density data

and HPG concentration with the use of data transformation. Coefficients of determination for the exponentially transformed case show a slightly decreasing trend with increasing wavelength where values range from 0.997 at 400 nm to 0.994 at 820 nm. These values show that the exponentially transformed data results in a very good linear calibration over the entire concentration range. However, the coefficient of determination is not the only metric by which a calibration should be judged, as it gives no indication of how well the data will predict future observations. Consequently, the statistics for SER and



Figure 7.1 Comparison of Coefficients of Determination for HPG in Visible Region for Raw and Exponentially Transformed Data.

SEP as described in Equation (3.1) and Equation (3.2), respectively, are calculated to help evaluate the best method of calibration. Results for the statistic SER are shown in Figure 7.2 for both cases.



Figure 7.2 Comparison of SER for Raw Data and Exponentially Transformed Data with Regard to Calibration of HPG Concentration in the Visible Region.

Figure 7.2 reveals a much higher value for errors resulting from the regression in the case of using raw data. The amount of improvement is quantified in Figure 7.3 and

shows that a slight decline in improvement takes place as the wavelength increases. In this case, the percent improvement ranges from 89.8% at 400 nm to 88% at 820 nm with a drop in value to 83.7% at 656 nm. This implies a significant improvement in the regression method for the exponentially transformed data.



Figure 7.3 Percent Improvement in SER for the Case of Exponentially Transformed Data vs. Raw Data for HPG in the Visible Region.

In addition to looking at the resulting values for SER, values of SEP are also examined with results provided in Figure 7.4. These results also show that the case of exponentially transformed data has less error with regard to the prediction of future observations. The amount of improvement for SEP is shown in Figure 7.5.



Figure 7.4 Comparison of SEP for Raw Data and Exponentially Transformed Data with Regard to Calibration of HPG Concentration in the Visible Region.



Figure 7.5 Percent Improvement in SEP for the Case of Exponentially Transformed Data vs. Raw Data for HPG in the Visible Region.

Improvements in SEP for the exponentially transformed case are not as dramatic as they were for SER, however, both statistics show that this method results in a better calibration than in the case of using raw data. Confidence intervals were constructed at various points throughout the entire visible wavelength region, making calculations every 50 nm. Figure 7.6 displays the results for these calculations at 450 nm; the remaining graphs can be found in Appendix 15. All confidence intervals were calculated at a 95% confidence level.



Figure 7.6 Confidence Intervals for HPG in the Visible Region Using Exponentially Transformed Data

Additionally, the percent REP is calculated at each concentration of HPG in the range 5 lb/Mgal to 60 lb/Mgal and an average value of REP is then calculated across all concentrations. Results for this average value of REP are given in Figure 7.7.



Figure 7.7 Percent Average REP for HPG Using Exponential Data Transformation in the Visible Region.

The data in Figure 7.7 suggests that the accuracy of this method is good since values of average REP are less than 1.5%. To judge the precision of this method, the percent

RSD was calculated at each concentration over all 4 scans; the average value over all concentrations is given in Figure 7.8.



Figure 7.8 Percent RSD for 4 Scans of HPG in the Visible Region.

Values for RSD range from around 2% at 400 nm to just over 3.5% at 820 nm. Other than the peak at 656 nm, the overall trend of RSD increases with an increase in wavelength. Sensitivity of this method was gauged by looking at the slope of the resulting calibration for the exponentially transformed case. Figure 7.9 presents a graphical representation of the resulting slope.



Figure 7.9 Sensitivity of Exponentially Transformed Method of Linear Regression for HPG in the Visible Region.

Figure 7.9 shows that the sensitivity of this method is best at lower wavelengths and degrades with increasing wavelength notwithstanding points 486 nm, 568 nm to 592 nm, and 656 nm.

7.2 Calibration of HPG in NIR Region

The evaluation of concentration dependence of HPG in the NIR to optical density was based on the four scans at each concentration as presented in Chapter 5. These three scans were broken out into two sets. Set number one consisted of scans

one and two, averaged together and designated as the calibration data set, while set two consisted of scan three, comprising the prediction data set. Chapter 5 showed that the linear relationship between optical density and HPG concentration over the range 5 lb/Mgal to 60 lb/Mgal was not very good, with coefficients of determination averaging around 0.96 for all wavelengths. As in the case of HPG in the visible region, a data transformation was evaluated using an exponential transformation. This method resulted in coefficients of determination only slightly higher than those for the case of the data and values for the coefficient of determination were calculated. The resulting values for coefficients of determination in all three cases are presented in Figure 7.10.



Figure 7.10 Comparison of Coefficients of Determination for HPG in NIR Region for Linear and Polynomial Regression.

The coefficients of determination for the polynomial regression were the highest of the three methods, exceeding 0.99 for the wavelength range 1020 nm to 1230 nm. As in the case for HPG in the visible region, values were calculated for the SER in the case of linear regression using raw data and polynomial regression using raw data. The resulting values of SER are presented in Figure 7.11 which shows that the error involved in the regression of the calibration data is greatest for the linear case, although both cases show relatively small amounts of error. The percent improvement in the polynomial calibration versus the linear calibration is shown in Figure 7.12.



Figure 7.11 Comparison of SER for Linear and Polynomial Regression with Regard to Calibration of HPG Concentration in the NIR Region.

The improvement in SER is greatest for the shorter and longer wavelengths in this region and is smallest in the middle part of the NIR spectrum, around 990 nm to 1225 nm. In addition to the SER for these two methods, the SEP was also calculated, the results of which are exhibited in Figure 7.13. In this instance, the results are not as clear since one method does not perform better than the other at all wavelengths. At the shorter wavelengths, up to 1063 nm, the polynomial regression method provides the least amount of error. Then there is a band of wavelengths at which the linear regression method results in the least amount of error due to prediction, 1063 nm to 1137 nm. Following this, the polynomial regression again shows the least amount of



Figure 7.12 Percent Improvement in SER for the Case of Polynomial Regression vs. Linear Regression for HPG in the NIR Region.

error in the range of 1138 nm to 1168 nm. Finally, at the longest wavelengths, both methods show comparable results.



Figure 7.13 Comparison of SEP for Linear and Polynomial Regression with Regard to Calibration of HPG Concentration in the NIR Region.

Therefore, the graph of percent improvement is designated percent change and has positive and negative values depending on whether the polynomial regression or linear regression has the lowest value of SEP at a particular wavelength. Figure 7.14 displays these results.



Figure 7.14 Percent Change in SEP for Polynomial vs. Linear Regression for HPG in the NIR Region.

The percent change values swing equally in the positive and negative direction, indicating that, in terms of SEP, polynomial regression outperforms linear regression at 950 nm to the same magnitude that linear regression outperforms polynomial at 1115 nm. These results are a classic case of the raw calibration data fitting the calibration curve better than the prediction data at some wavelengths.

To graphically view the fit of the data, confidence intervals were calculated for the linear regression case, at a wavelength of 1100 nm, and presented in Figure 7.15 along with the corresponding prediction data. Figure 7.15 illustrates that the prediction data follows a more linear trend than does the calibration data, especially at higher concentrations of HPG.



Figure 7.15 Confidence Intervals for HPG in the NIR Region at 1100 nm.

This accounts for the fact that the SER is lower for the polynomial regression at this wavelength, while the SEP is higher for the same case at this wavelength. Now, calculations for confidence intervals at a shorter wavelength, say 985 nm, are made and the results are given in Figure 7.16. It is apparent after viewing Figure 7.16 that both the calibration data and prediction data fit a polynomial curve more so than a linear curve. All confidence intervals were calculated at a 95% confidence level.

The accuracy of both methods was calculated as the average REP over all HPG concentrations and is shown in Figure 7.17. In terms of accuracy, the polynomial regression method shows a lower value of relative prediction error over most wavelengths.



Figure 7.16 Confidence Interval for HPG in the NIR at 985 nm.



Figure 7.17 Percent Average REP for HPG using Linear and Polynomial Regression in the NIR Region.

For the polynomial regression case, the values of REP range from a high of 5.25% at 1080 nm to a low of only 0.47% at 1350 nm. Precision is measured in terms of %RSD, as shown in Figure 7.18.



Figure 7.18 Percent RSD for 3 Scans of HPG in the NIR Region.

Values for the percent average RSD range from a high of approximately 1.5% to a low of 0.247%, with the lower values occurring at the longer wavelengths. Sensitivity of the linear regression is determined by the slope of the calibration curve as shown in Figure 7.19.



Figure 7.19 Sensitivity of Linear Regression for HPG in the NIR Region.

Sensitivity of the linear regression method decreases monotonically with increasing wavelength in the NIR.

7.3 Comparison of Calibration Methods for HPG

Now, comparisons are made between methods used in the visible and NIR region for HPG fluids. The first comparison is for coefficients of determination. Values used for the coefficient of determination in the visible region are a result of the exponentially transformed linear regression, while those used in the NIR region are from the polynomial regression. Results of this comparison are displayed in Figure 7.20.



Figure 7.20 Comparison of Calibration Methods According to Coefficients of Determination for HPG in the VIS and NIR Regions.

According to Figure 7.20, the best fit of the optical density data to a calibration curve over the entire concentration range for HPG occurs for the exponentially transformed data used in a linear regression in the visible region. Overall, the best wavelengths in terms of fit are going to be the shortest wavelengths occurring around 400 nm.

A comparison of SER values in the visible and NIR Regions is presented in Figure 7.21. This graph shows that the lowest values for the SER are a result of the polynomial regression in the NIR at around 1265 nm. A similar comparison is made for the case of SEP, exhibited in Figure 7.22. Here, the results show that the lowest values obtained for SEP, over the entire wavelength region, occurred in several areas of the



Figure 7.21 Comparison of SER for Various Calibration Methods of HPG in the VIS and NIR Regions.

NIR for the case of polynomial regression. The lowest value of SEP occurred at a wavelength of 1158 nm, but wavelengths around 985 nm and 1265 nm provided low values as well. Another way to compare the different methods is to compare the values of REP in both regions as shown in Figure 7.23. Results from this comparison indicate that percent REP is more stable in the visible region for the case of exponentially transformed data using linear regression, but that the very lowest values occur at the longest wavelengths of the NIR for the case of polynomial regression.

Precision is evaluated by looking at the percent RSD values in both regions, as presented in Figure 7.24. While values for RSD are increasing with increasing wavelength in the visible region, they tend to decrease with increasing wavelength



Figure 7.22 Comparison of SEP for Various Calibration Methods of HPG in the VIS and NIR Regions.



Figure 7.23 Comparison of Percent REP for Different Calibration Methods of HPG in the VIS and NIR Regions.

in the NIR. The lowest values for percent RSD are found at the longer wavelengths in the NIR region.



Figure 7.24 Comparison of Percent RSD for HPG in the VIS and NIR Regions.

Sensitivity of each linear regression method is just a measure of its slope, which provides the change in optical density divided by the corresponding change in concentration. For the polynomial regression case, the sensitivity was measured by taking the difference in optical density between each concentration point, dividing by the change in concentration, and finding the average of all the points at each wavelength. We thereby determine an average change in optical density with unit change in concentration. These results are given in Figure 7.25.



Figure 7.25 Comparison of Sensitivity for Various Calibration Methods of HPG in the VIS and NIR Regions.

The results in Figure 7.25 show that the sensitivity for both the linear and polynomial regression in the NIR region are very similar and both are lower than the sensitivity of the linear regression of transformed data in the visible region. Therefore, the best

sensitivity is achieved at the lowest wavelengths in the visible region, namely wavelengths around 400 nm.
Chapter 8

Calibration of Optical Density vs. Silica Flour Concentration

8.1 Calibration of Silica Flour Concentration in VIS Region

The calibration of a 40 lb/Mgal HPG, with various amounts of silica flour added, in the visible region, was based on five spectral scans of optical density at each concentration of silica flour. Silica flour concentrations ranged from 0 lb/Mgal to 55 lb/Mgal with scans being made every 5 lb/Mgal. As was the case for HPG, the five different data sets covering the entire visible region were divided into a calibration set, which consisted of the average of scans one through three, and the prediction set which consisted of the average of scans four and five.

The calibration data set was used in a variety of regression methods to determine the best calibration method in the visible region. One of the methods tried was to smooth the data using a 15 point binomial smoothing algorithm. In addition to smoothing the data, an exponential transformation was applied to the smoothed data and, finally, a polynomial regression was applied to the smoothed calibration data. Coefficient of determination data was gathered in each case to help evaluate the fit of that calibration method to the data; results for these values are given in Figure 8.1. This shows that the best values for the coefficient of determination, over all wavelengths in the visible region, is for the case of a polynomial regression on smoothed calibration data. The case of linear regression on the raw optical density data had the lowest values



Figure 8.1 Comparison of Coefficients of Determination for Various Calibration Methods for Silica Flour in the Visible Region.

for coefficient of determination, while the cases for linear regression of smoothed data and of exponentially transformed smoothed data were somewhat higher than the raw data, but substantially lower than the smoothed polynomial regression.

To continue the evaluation of these methods, the focus will shift to the three best cases as evaluated by the coefficients of determination: linear regression of smoothed calibration data, linear regression of exponentially transformed and smoothed data, and polynomial regression of smoothed data. Another measure of how well a calibration performs is the amount of error associated with that particular regression, and can be quantified by calculating the SER as shown in Figure 8.2 for each of the three methods.



Figure 8.2 Comparison of SER for Various Calibration Methods of Silica Flour in the Visible Region.

Calculating values for SER indicates that the calibration method with the least amount of error due to the regression is the polynomial regression of smoothed calibration data. Smoothed linear regression was somewhat higher overall and the case of exponentially transformed smoothed data in a linear regression showed the poorest results in terms of SER. Now, evaluation of the error due to predicting new observations is determined by



Figure 8.3 Comparison of SEP for Various Calibration Methods on Silica Flour in the Visible Region.

calculating the values of SEP in these three cases, as presented in Figure 8.3. The results for SEP are very similar to those found for SER, in that the best performance was achieved by the polynomial regression of smoothed calibration data. A slightly higher error of prediction was found for the linear regression of smoothed data and much higher values of SEP were found for the case of exponentially transformed and smoothed data using a linear regression. All statistical analysis to this point indicates that the polynomial regression is the optimum calibration method for calibrating silica flour concentration and optical density in the visible region of the spectrum. With this in mind, graphs were constructed every 50 nm, from 450 nm to 750 nm, including the

end points of 430 nm and 790 nm, which include the smoothed optical density data, the smoothed prediction data, and the polynomial calibration curve at that wavelength. One of these graphs is exhibited here in Figure 8.4 and the remaining graphs are located in Appendix 16.



Figure 8.4 Smoothed Calibration, Prediction Data Along with Polynomial Calibration Curve for HPG with Silica Flour Added at 600 nm.

Another way to gauge the relative error involved in the prediction of new observations is by calculating the percent REP at each silica flour concentration and averaging these values over the entire concentration range, the result of which is presented in Figure 8.5 for the polynomial regression.



Figure 8.5 %REP for Polynomial Regression of HPG with Silica Flour Added in the Visible Region.

The results for accuracy in the polynomial regression case show that percent REP values range from 1.98% to 3.48%, with no clear trend across all wavelengths. Precision for this method is judged by the percent average RSD as presented in Figure 8.6. These values of RSD are averaged over the results of all silica flour concentrations.



Figure 8.6 Percent Average RSD for 40 lb/Mgal HPG with Silica Flour Added in the Visible Region of the Spectrum.

The results for precision show that the values for percent RSD fall between 2.5% and 0.84%, except at a wavelength of 546 nm where the value jumps to 4.86%. Lastly, the sensitivity of this method needs to be evaluated. Since the polynomial regression has shown the best performance in this situation, values are calculated between each two adjacent concentration values for the difference in optical density, divided by the change in concentration. Due to the fact that this is not a linear calibration and therefore a slope cannot be calculated across all concentrations, the difference values calculated at each change in concentration were averaged over all concentrations to

give an average change in optical density with concentration over the entire concentration range. These values are displayed graphically in Figure 8.7.



Figure 8.7 Sensitivity for Polynomial Regression of 40 lb/Mgal HPG with Silica Flour Added in the Visible Region.

Wavelengths which provide the highest sensitivity include the region 674 nm to 724 nm, where the best value results in an average change of 0.0586 optical density units per lb/Mgal of silica flour. Areas that provide the worst level of sensitivity include 482 nm to 492 nm, and 536 nm to 554 nm.

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8.2 Calibration of Silica Flour Concentration in NIR Region

In the study of calibrating silica flour concentration in a 40 lb/Mgal HPG fluid with optical density in the NIR, three scans were made at every 5 lb/Mgal in the range 0 lb/Mgal to 55 lb/Mgal. The first two scans were averaged together and are considered the calibration data set, while the last scan is considered the prediction data set. For the NIR region, the same types of calibrations were evaluated as for the case of silica flour concentration in the visible region. Namely, four different methods of calibration were considered at these wavelengths: raw data using a linear regression method, smoothed data using a linear regression method, exponentially transformed optical density data using a linear regression method, and smoothed data using a polynomial regression method. Figure 8.8 presents the coefficients of determination for these four cases.

Coefficients for these methods show that the polynomial regression method provides a superior fit to the calibration data with values approaching one except at wavelengths 1175 nm to 1197 nm and wavelengths greater than 1302 nm. The case for exponentially transformed data using a linear regression was the second best method with coefficients averaging around 0.985. Lowest in the area of coefficients of determination, were the raw data and smoothed data using linear regression. However, there is a small band of wavelengths for the raw data case in which the coefficients of determination approach 0.99 for the entire concentration range. This phenomenon was discussed in Chapter 6 and graphically demonstrated in Figure 6.12 and Figure 6.13. Values for the coefficient of determination at these three wavelengths for the case of



Figure 8.8 Coefficients of Determination for Various Calibration Methods for Silica Flour in the NIR Region.

raw data and linear regression are: 0.989 at 1130 nm, 0.990 at 1131 nm, and 0.988 at 1132 nm. Therefore, only three of the cases will be evaluated further: exponentially transformed and smoothed data using linear regression, smoothed data using polynomial regression, and raw data using linear regression in the range 1130 m to 1132 nm.

Values for the SER for each of the three methods are given in Figure 8.9 from which it is immediately obvious that the case of exponentially transformed data has a large amount of error, with respect to the regression, compared to the other two cases.



Figure 8.9 SER for Various Calibration Methods for Silica Flour in the NIR Region.

In fact, the values for that case are so large that the other two cases are indistinguishable. Consequently, the graph's y-axis scale is modified and the resulting graph is given in Figure 8.10. Now, the values for the other two cases are apparent in Figure 8.10. Note the small group of points with the label "Raw data" represents the three wavelengths used for evaluation of raw data and linear regression.

The polynomial regression method provides the smallest amount of error due to the regression itself and the case of raw data exhibits fairly low values at the three designated wavelengths as well. SEP was also calculated for each case and results are provided in Figure 8.11. Here again, the values for the exponentially transformed data



Figure 8.10 SER for Silica Flour Calibration in the NIR Region.



Figure 8.11 SEP for Various Calibration Methods for Silica Flour in the NIR Region.

are so large that the other methods are indistinguishable so the graph in Figure 8.11 is modified in terms of scale and displayed in Figure 8.12. These results are very similar to the SER case above. The values of SEP in Figure 8.12 show that the lowest error in the regression cases is for the polynomial regression, followed by the raw data linear regression at specified wavelengths.



Figure 8.12 SEP for Silica Flour Calibration in the NIR Region.

The conclusion drawn from the data generated thus far is that the case of exponentially transformed data exhibits too much error in terms of the regression and future predictions and will be removed from further consideration in this region. So, there are two methods still under evaluation: polynomial regression of smoothed data and linear regression of raw data at 1130 nm to 1132 nm. Charts including the calibration data, prediction data, and corresponding calibration curve were constructed; one of each type of graph is shown below in Figure 8.13 and Figure 8.14 with the remaining graphs being placed in Appendix 17. Both graphs show good agreement between the calibration data, prediction data, and calibration curve. These two graphs also show the difference in curvature of the scatterplots for the data at different wavelengths and for raw data versus smoothed data.

Relative error in the prediction of new observations is evaluated by calculating the percent REP at each concentration and averaging over all the concentrations for each method. Figure 8.15 illustrates the results of these calculations. Relative error due to prediction of future observations averages just under 4% over all wavelengths in the NIR, excluding the region 1177 nm to 1193 nm, where a large peak in standard error appears. As a comparison, percent REP values for the raw data case is: 16.65% at 1331 nm, 14.07% at 1131 nm, and 15.82% at 1132 nm. These values are much higher than in the polynomial regression case, leading to the conclusion that the polynomial regression case offers more accuracy at all wavelengths in the NIR for silica flour calibration. In terms of precision, values for the RSD were calculated and are given in Figure 8.16. Data for the percent RSD shows that the precision in this area of the spectrum is fairly stable at the shorter wavelengths, from 850 nm to approximately 1125 nm. As the wavelength of the source increases beyond this point, the precision tends to degrade for a majority of the wavelengths above 1125 nm. Sensitivity is



Figure 8.13 Linear Calibration of Raw Data Along with Prediction Data for Silica Flour in the NIR at 1131 nm.



Figure 8.14 Polynomial Calibration of Silica Flour Concentration in the NIR at 950 nm.



Figure 8.15 Percent Average REP for Polynomial Regression of Silica Flour in NIR.



Figure 8.16 Percent RSD for Silica Flour Concentration in a 40 lb/Mgal HPG in the NIR.

calculated as in the previous case for polynomial regression, as a change in optical density divided by the change in concentration at each change in concentration and averaged over all corresponding points. Results for sensitivity in the case of polynomial regression are given in Figure 8.17.



Figure 8.17 Sensitivity of Polynomial Calibration Method for Silica Flour in the NIR.

Figure 8.17 shows that sensitivity is fairly flat across the region except in the area of 1175 nm to 1193 nm and at wavelengths beyond 1324 nm. These wavelengths will provide the largest amount of sensitivity, whereas the remaining wavelengths have

sensitivity values of around 0.05 on average. The case of raw data and linear regression results in sensitivity values as determined by the slope of the linear regression, of 0.055 to 0.057 at the wavelengths 1130 nm to 1132 nm.

8.3 Comparison of Calibration Methods for Silica Flour

Comparisons between the visible and NIR regions begin with an assessment of the fit of the data to a calibration curve, or the deviation of the error about a given curve as implied by the coefficient of determination. In both the visible and NIR regions, the polynomial calibration curve resulted in the best fit of the data with values approaching one. Therefore, a comparison was made of these methods in the visible and NIR regions, as shown in Figure 8.18. The coefficients of determination are slightly higher for the NIR case, but only for wavelengths which are not in the range of 1173 nm to 1200 nm or greater than 1265 nm, where the values drop significantly. However, in either case the values are high enough, greater than 0.99, that the overall fit of the data is very good in both regions of the spectrum, except as previously noted.

In terms of SER, the resulting values for the respective polynomial regressions are displayed in Figure 8.19, where the lowest amount of error due to the regression is found at wavelengths around 925 nm. For the visible region, the lowest value of SER is found at a wavelength of around 600 nm. This value is only slightly higher than that found in the NIR at 925 nm. As long as the wavelength regions of 1177 nm to 1196 nm and wavelengths greater than 1284 nm are avoided, the remaining spectrum



Figure 8.18 Coefficients of Determination for Polynomial Regression of Silica Flour Concentration in the Visible and NIR Regions.



Figure 8.19 SER for Polynomial Regression of Silica Flour Concentration in the Visible and NIR Regions.

produced standard errors of regression of less than 0.1. Very similar results were achieved when values for SEP, shown in Figure 8.20, were calculated in these two cases. Here again, the values over much of the region are less than 0.1 with larger values occurring in areas similar to those for the case of SER and the lowest value of SER occurring at a wavelength of approximately 928 nm. Both the SER and SEP measurements for these two polynomial calibrations show only small amounts of error over most of the visible and NIR spectrum.



Figure 8.20 SEP for Polynomial Regression of Silica Flour Concentration in the Visible and NIR Regions.

The accuracy of both polynomial calibrations is compared in Figure 8.21. Average percent REP for the visible case of polynomial regression varies between values of 2% and 4%, while the values in the NIR region have more variance. However, the smallest relative error due to prediction is found in the NIR at 1261 nm, and several other bands of wavelengths provide values for percent REP less than 2%. So, as long as the wavelength band 1175 nm to 1196 nm, the peak at 1017 nm, and wavelengths beyond 1321 nm are avoided, the NIR provides many wavelengths which result in small errors due to prediction.

Comparing the relative standard deviations of the scans in the two spectral regions will determine which wavelengths provide greater precision when making repeated measurements. Figure 8.22 presents the values for percent RSD in the visible and NIR regions. Overall, slightly better precision was achieved for the measurements in the visible region over those made in the NIR. In the NIR region, the precision begins to degrade at longer wavelengths as illustrated in Figure 8.22.



Figure 8.21 Comparison of Percent REP for Polynomial Regression of Silica Flour Concentration in the Visible and NIR Regions.



Figure 8.22 Comparison of Precision for Polynomial Regression of Silica Flour Concentration in the Visible and NIR Regions.

Sensitivity is also compared for these two cases, as presented in Figure 8.23. The wavelengths providing the largest amount of sensitivity occur in the NIR region at around 1186 nm and wavelengths greater than 1320 nm. However, these are the same wavelengths that performed poorly in terms of errors for prediction, calibration, and even goodness of fit as noted earlier in this chapter. Consequently, the best sensitivity would be found in the visible region of the spectrum.



Figure 8.23 Comparison of Sensitivity for Polynomial Regression of Silica Flour Concentration in the Visible and NIR Regions.

Chapter 9

Conclusions and Recommendations

9.1 Contributions

In reviewing the relevant literature in the area of optical characterization of HPG polymers in the visible and NIR regions, it was found that very little data has been published in this area. This dissertation presents for the first time, to the best of our knowledge, the optical density data and resulting conclusions for optical transmission in HPG and HPG with silica flour added in the visible and NIR regions. Some of these results were published in a peer-review journal and a copy of this article is located in Appendix 1. The work reflected in this dissertation is the result of a unique application of spectrophotometry to measure the extinction of radiation in HPG in the presence of scattering.

In this dissertation, the theoretical background for the extinction of radiation when traveling through a given medium was examined. Relationships were determined, based upon this theory, for the resulting intensity of the radiation as a function of distance traveled into the fluid and for the corresponding extinction coefficients at various wavelengths and concentrations. The relationship between optical density and concentration helped to provide the concentration range over which the theoretical derivation of extinction coefficients would hold. This was a novel approach to determine the percent transmitted intensity through these fluids. In addition to determining the extinction coefficients for HPG fluids and HPG with silica flour added at various concentrations throughout the visible and NIR regions, the empirical relationship between optical density and fluid concentration at each wavelength in these regions was measured. From these measurements, the best methods of calibration were determined. From the development of extinction coefficients transmission in HPG can be determined at various wavelengths and fluid concentrations and through the use of calibration models the concentration of a fluid can be determined from its optical density. The ability to model these types of fluid properties is of primary importance in the development or improvement of optoelectronic sensors designed to monitor or analyze these fluids.

9.2 Summary of Results

Since measuring optical density of these fluids requires averaging of repeated measurements for the best statistical evaluation of the results, the amount of error involved in making repeated measurements was examined. It was found, in the visible region, that the largest source of error came from measuring samples from different batches of the fluid. RSD values for measurements between different batches were higher than those for different samples from the same batch, or multiple measurements of a single sample. Even repositioning of the samples between measurements did not cause as much error as the case for different batches of a fluid. This led to the conclusion that in the visible region, the majority of error due to repeated measurements could most likely be attributed to weighing and volumetric precision. In the NIR, the amount of error inherent in measuring multiple samples with repositioning between measurements was greater than that found in the visible region as shown in Figure 3.6.

To define a range of wavelengths in the visible and NIR, over which the transmission characteristics of these fluids should be studied, the transmission properties properties of all the fluid components were studied individually. Since HPG is comprised largely of water, the absorption characteristics of water in the visible and NIR regions were considered. In the visible region, 200 nm to 820 nm, water showed little absorption with only a few characteristic peaks present at low values of optical density. However, the NIR region shows large absorption bands at wavelengths beyond 1300 nm. Therefore, the region 200 nm to 1300 nm provided sufficient transmission of visible and NIR radiation in water.

In addition to examining the spectral contributions of water, all the remaining components of the HPG fluid were tested individually. It was found that fumeric acid exhibits a large absorption band in the UV region, 250 nm to 300 nm. Other bands were distinguished for the remaining components but these individual bands did not possess significant values of optical density. On the other hand, once the contributions of each component were combined, the ultraviolet region of the spectrum generally showed a high degree of extinction. Consequently, the overall wavelength range for this study was defined as 400 nm to 1300 nm. This transmission window is very evident in Figure 4.8, which shows the spectra of various concentrations of HPG fracturing fluid over the range 100 nm to 3100 nm.

146

In determining extinction coefficients for HPG, the raw optical density data was plotted versus fluid concentration and any nonlinearities present were evaluated in terms of the coefficient of determination and graphical inspection as it relates to multiple scattering. Once appropriate concentration ranges were determined, the coefficients were calculated and transmitted intensities at various concentrations and wavelengths were calculated as a function of pathlength into the fluid. For HPG in the visible region, a concentration range of 5 lb/Mgal to 60 lb/Mgal was used to calculate extinction coefficients. Only a wavelength of 656 nm showed poor linearity and so is not recommended for evaluation. Extinction coefficients were calculated for the wavelength range 400 nm to 820 nm in the visible region. The results of percent transmitted intensity calculations determined that better penetration into HPG was achieved as the wavelength of the radiation increased. In this case, 820 nm showed the best transmission properties. The percentage improvement in transmitted intensity resulting from selecting a wavelength of 820 nm versus 400 nm ranges from 5.5% at 5 lb/Mgal 117% at 60 lb/Mgal at a depth of 1 cm. These numbers increase to 31% at 5 lb/Mgal to 4677% at 60 lb/Mgal at a depth of 5 cm.

For HPG in the NIR, determination of extinction coefficients was limited to concentrations of 5 lb/Mgal to 45 lb/Mgal. Here, the best wavelengths for transmission were found to be the lower wavelengths of the NIR around 865 nm followed by the region 1050 nm to 1100 nm. In the NIR, an increase in wavelength does not necessarily imply better transmission in HPG. This is due to the presence of absorption bands attributed to water in this region. The percentage improvement between the best wavelength, 865 nm, and the worst, 1300 nm, was found to range from 259% at 5

lb/Mgal to 216% at 45 lb/Mgal at a depth of 1 cm. At 5 cm, these values increase to 59,489% at 5 lb/Mgal to 31,535% at 45 lb/Mgal. The impact here on transmission is very large as the depth of penetration increases. Comparing the best wavelengths in each region, 820 nm and 865 nm, shows that a wavelength of 820 nm provides a higher percentage of transmitted intensity for HPG concentrations up to 15 lb/Mgal while 865 nm does for concentrations of 20 lb/Mgal to 45 lb/Mgal as seen in Figure 5.20. For a depth of 5 cm, the percentage increase in transmitted intensity at concentrations greater than 15 lb/Mgal ranges from 90% at 20 lb/Mgal to 482% at 45 lb/Mgal. The wavelength range of 750 nm to 900 nm provides the best transmission of radiation in HPG, where 865 nm is the best wavelength for transmission in concentrations of 5 lb/Mgal to 45 lb/Mgal.

Silica flour added to a 40 lb/Mgal HPG fluid was also tested over the silica flour concentration range 0 lb/Mgal to 55 lb/Mgal in the visible region. It was concluded that silica flour concentrations of 0 lb/Mgal to 35 lb/Mgal were appropriate for calculations of extinction coefficients at all wavelengths 400 nm to 820 nm and that an extended range of 0 lb/Mgal to 40 lb/Mgal was appropriate for wavelengths 654 nm to 820 nm. As in the case of HPG in the visible region, the best transmission was obtained at the longest wavelength, 820 nm. A comparison of percent improvement in transmitted intensity for a wavelength of 820 nm versus 400 nm resulted in values ranging from 126% at 0 lb/Mgal and rises to 252% at 25 lb/Mgal then decreasing to 190% at 35 lb/Mgal. In addition, the majority of improvement in transmitted intensity is obtained at smaller depths of penetration, unlike the case of HPG in the visible region. In the NIR region, extinction coefficients were calculated for concentration ranges 0 lb/Mgal to 55 lb/Mgal at wavelengths 1130 nm to 1132 nm and over all wavelengths, 865 nm to 1300 nm, in the concentration range of 0 lb/Mgal to 30 lb/Mgal. The best transmission properties in the NIR were observed in the range 1054 nm to 1100 nm with a value of 1078 nm providing the best penetration. A comparison of 1078 nm versus 1300 nm shows percentage improvement in transmitted intensity at 1078 nm is 11% at 0 lb/Mgal to 9% at 25 lb/Mgal and back up to 11.55 at 30 lb/Mgal at 0.5 cm. This improvement increases with increasing depth into the fluid. It was also shown that penetration into HPG was significantly reduced by the addition of silica flour into the HPG. Evaluation of transmission over the visible and NIR range is accomplished by comparing the percent improvement in transmitted intensity at 1078 nm versus 820 nm. Results show that at 0.5 cm into the fluid, the percent improvement ranges from 48% at 0 lb/Mgal to 131% at 30 lb/Mgal.

Calibration of optical density data and concentration of HPG was compared for the best-case calibration methods in the visible and NIR regions. The visible region demonstrated the best calibration for a linear regression of exponentially transformed optical density data, while in the NIR, the best method was for a second order polynomial regression. Higher coefficients of determination were found in the linear regression case implying that the data "fit" the linear calibration curve better at the lowest wavelengths, around 400 nm. However, values that quantify the error in the regression and in prediction of new observations showed that the polynomial regression in the NIR produced smaller amounts of these types of errors. A wavelength of 1265 nm provided the best values overall for SER, SEP, and % REP over the visible and NIR regions. In addition, the precision was shown to be the best at wavelengths greater than 1150 nm. However, comparison of the sensitivity of the two methods provided a different outcome where the greatest sensitivity was achieved at wavelengths around 400 nm.

For silica flour calibration, a 40 lb/Mgal HPG was tested in the visible and NIR regions with varying concentrations of silica flour. The results for calibration of optical density with silica flour concentration are a bit clearer than in the case of HPG. In both spectral areas, polynomial calibration was found to be the best calibration method. Only the RSD values, which measure the precision of a measurement method, were better in the visible region, and all other statistical evaluations showed that the NIR provided a better calibration. Values for the coefficient of determination were slightly higher for the NIR region, but not by much. Resulting values for the errors SER and SEP were smallest at wavelengths around 925 nm. Meanwhile, the accuracy as measured by the average percent REP was the lowest at a wavelength of 1261 nm, but still showed good accuracy at a wavelength of 925 nm where percent REP was less than 2%. Lastly, the sensitivity of the two methods was compared and it was determined that the best method in term of sensitivity was the polynomial regression at 1186 nm or at wavelengths greater than 1300 nm. Sensitivity values for a wavelength of 925 nm is about average for the NIR and slightly less than the average in this visible region.

9.3 Implications for Sensor Development

HPG in the visible and NIR regions did not have one wavelength that produced the best depth of penetration at all concentrations of HPG in the range 5 lb/Mgal to 45 lb/Mgal. However, wavelengths centered on 865 nm will provide the best over all transmission for the concentrations considered. It was also shown that the best wavelength region for transmission was not the best region for calibration of optical density and HPG concentration. For minimal error in the regression and prediction of future observations as well as the best accuracy and good precision, wavelengths centered around 1265 nm should be used. Nevertheless, if sensitivity is the most important aspect of a sensor based on this type of measurement method, a wavelength in the visible region close to 400 nm should be used. The important thing to note is that neither of these wavelengths, 1265 nm or 400 nm, provide the best penetration into HPG fluids, as that wavelength was determined to be around 865 nm. Consequently, a compromise would have to be made, as they always are in sensor design, to accommodate the most important aspects of a particular application.

Silica flour added to a 40 lb/Mgal HPG resulted in the best transmission at wavelengths in the NIR around 1078 nm although the distance traveled into the fluid decreased sharply from that of plain HPG. In this case, wavelength selection becomes even more crucial to get substantial fluid penetration. Errors due to the regression and future prediction of observations were at a minimum for wavelengths centered around 925 nm. The accuracy of this method and the sensitivity were also best in the NIR though not at wavelengths centered around 925 nm. However, values for accuracy and

sensitivity were still comparatively good at 925 nm. Here again, if sensitivity is the most important performance criteria for a sensor based on this method, then a wavelength in the visible region should be used provided it can meet the transmission requirements of the application. Therefore, wavelength selection for the calibration of HPG with silica flour added will depend on the relative importance of depth of penetration into the fluid, regression and prediction error, accuracy, and sensitivity. As in the case of HPG, one wavelength will not perform the best in all areas.

It should be noted that availability of sources at a specified wavelength as well as the cost of these devices also play a large role in optical sensor development. Even though this work focused on evaluating the results in terms of the best wavelengths for calibration of concentration and transmission through HPG, the raw optical density data and relevant statistics for the remaining wavelengths were also provided so that any wavelength of interest could be evaluated.

In summary, the optical transmission characteristics of HPG and HPG with silica flour added were investigated in the visible and NIR regions. The result is that a sensor's application and corresponding specifications will determine which wavelength is best for a given design since each wavelength offers different advantages and disadvantages as illustrated throughout this dissertation. Therefore, depending on the most critical performance criteria of an optical sensor developed to monitor or analyze HPG polymers, the data provided will determine the best wavelength choice for the sensor's source.

152

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