

**Development of a Field-Portable Near-Infrared Water-Cement Ratio Meter
Phase I: Investigation of Spectral Feasibility**

Final Report

Principal Investigator, Professor William G. Fateley
Co-Principal Investigator, Dr. Nathan Chaffin

Presented to
Kansas Department of Transportation
Materials Research Center
Research Unit
2300 S.W. Van Buren Street
Topeka, Kansas 66611

June 25, 1999

1. Report No. KS-99-3		2. Government Accession No.		3. Recipient Catalog No.	
4 Title and Subtitle DEVELOPMENT OF A FIELD-PORTABLE NEAR-INFRARED WATER CEMENT RATIO METER PHASE I: INVESTIGATION OF SPECTRAL FEASIBILITY				5 Report Date June 1999	
				6 Performing Organization Code	
7. Author(s) Hani G. Melhem				8 Performing Organization Report No. 282 KS-99-3	
9 Performing Organization Name and Address Kansas State University Department of Civil Engineering Manhattan, Kansas 66506				10 Work Unit No. (TRAIS)	
				11 Contract or Grant No. C1074	
12 Sponsoring Agency Name and Address Kansas Department of Transportation Docking State Office Bldg. Topeka, Kansas 66612				13 Type of Report and Period Covered Final Report June 1998 to July 1999	
				14 Sponsoring Agency Code	
15 Supplementary Notes					
16 Abstract <p>In this work near-infrared reflection spectroscopy has been applied to the analysis of freshly mixed cement and concrete. This work shows that it is feasible to determine the water-cement ratio of a batch of cement or concrete provided that the temperature and hardening time (i.e., amount of time passed since mixing) of the mixture is known. In the case of cement, 14 out of 15 cases showed a positive correlation between water-cement ratio and the analyte band. In the case of concrete five out of five cases showed a positive correlation between water-cement ratio and the analyte band. The admixture agents Daravair and Daracem were undetectable when mixed at levels at three and 16 fluid ounces per 100 pounds of cement, respectively. The near-infrared spectra of concrete were not strongly affected by the presence of coarse aggregates. The effect of coarse aggregates on near-infrared spectra was to increase scattering which, in turn, increased baseline tilt at shorter wavelength. This effect can be overcome by baseline correction and does not necessitate the use of a probetip sheath.</p>					
17 Key Words Analyte Band, Cement, Concrete, Reflection Spectroscopy, Water-Cement Ratio			18 Distribution Statement No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161		
19 Security Classification (of this report) Unclassified	20 Security Classification (of this page) Unclassified	21 No. of pages 43	22 Price		

ABSTRACT

In this work near-infrared reflection spectroscopy has been applied to the analysis of freshly mixed cement and concrete. This work shows that it is feasible to determine the water-cement ratio of a batch of cement or concrete provided that the temperature and hardening time (i.e., amount of time passed since mixing) of the mixture is known. In the case of cement, 14 out of 15 cases showed a positive correlation between water-cement ratio and the analyte band. In the case of concrete five out of five cases showed a positive correlation between water-cement ratio and the analyte band. The admixture agents Daravair and Daracem were undetectable when mixed at levels at three and 16 fluid ounces per 100 pounds of cement, respectively. The near-infrared spectra of concrete were not strongly affected by the presence of coarse aggregates. The effect of coarse aggregates on near-infrared spectra was to increase scattering which, in turn, increased baseline tilt at shorter wavelength. This effect can be overcome by baseline correction and does not necessitate the use of a probetip sheath.

TABLE OF CONTENTS

	Page
Abstract	i
List of Figures	iii
List of Tables	iv
Main Report	1
Appendix A: Beer's Law Plots of Cements	20
Appendix B: Beer's Law Plots of Concretes	31

LIST OF FIGURES

		Page
Figure 1	Schematic of Instrumental Configuration	4
Figure 2	Near-Infrared Reflection Spectra of Ashgrove Cement (with Daravair) with Water to Cement Ratios of a) 0.36 b) 0.40 c) 0.44 7500 to 4600 cm^{-1}	6
Figure 3	Near-Infrared Reflection Spectra of Ashgrove Cement (with Daravair) with Water to Cement Ratios of a) 0.36 b) 0.40 c) 0.44 5600 to 4650 cm^{-1}	7
Figure 4	Near-Infrared Reflection Spectra of Concrete Mix 5 (320 kg/m^3 , 50% CA and FA, Daravair and Daracem) with Water to Cement Ratios of a) 0.35 b) 0.42 c) 0.49 7500 to 4500 cm^{-1}	9
Figure 5	Near-Infrared Reflection Spectra of Concrete Mix 5 (320 kg/m^3 , 50% CA and FA, Daravair and Daracem) with Water to Cement Ratios of a) 0.35 b) 0.42 c) 0.49 5600 to 4600 cm^{-1}	10
Figure 6	A Time Series of Near-Infrared Reflection Spectra of Ashgrove Cement, W/C = 0.40 5600 to 4600 cm^{-1}	11
Figure 7	Mid-Infrared Spectra of Pure Daravair (top) and Pure Water (bottom) 400 to 4000 cm^{-1}	13
Figure 8	Mid-Infrared Spectra of Pure Daracem (top) and Pure Water (bottom) 400 to 4000 cm^{-1}	14
Figure 9	Near-Infrared Spectra of Ashgrove Cement with Daravair (a) and without Daravair (b) The Bottom Spectrum (c) is the result of subtracting (b) from (a)	15
Figure 10	Near-Infared Reflection Spectra of Concrete Mix #3 with Normal Mixture (top two spectra, red and gray) and with 10% of Cement Substituted with Sand (bottom two spectra, green and blue)	17

LIST OF TABLES

		Page
Table 1	Cement Mix Design	2
Table 2	Concrete Mix Design	2
Table 3	Comparison of Percent Standard Deviation (for identical water-cement ratios) for Monarch Cement, with and without Daravair, and Concrete Mix #2	16

Introduction

In order to accurately predict the strength and durability of an adequately mixed and compacted concrete mix it is useful, if not necessary, to know the water-cement ratio of the fresh concrete mix. While this fact has been known for sometime, no reliable, commercially-available instrument for measuring the water-cement ratio of concretes in the field is known to exist by the author. Dr. Mustaque Hossain and coworkers (Department of Civil Engineering, Kansas State University) have developed a prototype device which is capable of determining the water-cement ratio of a fresh concrete mix by first separating the cement from the aggregates and then measuring the turbidity of the water-cement slurry. This technology is promising, but it is not well-suited for field measurements due to its size (~32 ft³) and weight (several hundred pounds). The time required to perform a measurement with their system is approximately five minutes. While this amount of time is not inordinate, it is clearly desirable to minimize the time required to measure water-cement ratio in the field. In our proposal to the Kansas Department of Transportation (KDOT) we proposed to perform Phase I of a multiphase project.

The overall goal of the project is to design, fabricate, and test a portable (less than two ft³ and 20 pounds), real-time, water-cement ratio meter. The instrument will be backpack-mounted with a hand-held fiber-optic probe that can be immersed in any sample. Data acquisition will be initiated by pressing a probe-mounted trigger after the probe has been dipped into the concrete mixture in question. Measurement of the concrete will take less than 10 seconds and the water-cement ratio will be displayed less than five seconds after completion of the measurement.

The goal of Phase I of the project is to investigate spectral feasibility. Understanding the nature of the correlation between any given concrete or cement mix's near-infrared reflection spectrum and its water-cement ratio is a logical and invaluable first step toward the success of the overall project.

Approach

Cement

In order to avoid any spectral effects arising from the presence of aggregates found in concrete, early research focussed on cements. The near-infrared reflection spectra of 30 different cement samples (five cements x two admixtures [one with Daravair, one with no admixture] x three water-cement ratios) were measured. In all, 30 unique cement mixes were mixed and measured. Table 1 illustrates the mix design.

W/C	Ash grove	Dura pozz	Lone Star	Medusa	Monarch	Ash Grove Daravair	Dura Pozz Daravair	Lone Star Daravair	Medusa Daravair	Monarch Daravair
0.36										
0.40										
0.44										

Table 1 Cement Mix Design

Spectral measurement began five minutes after mixing. Spectra were then measured every three minutes for 90 minutes of the hardening process (30 spectra per sample). Three replicates of each sample were mixed and measured in an effort to prevent anomalous data from being included in the data set. Thus, a total of 2700 spectra (30 unique mixes x 30 spectra per mix x three replicates) were measured.

Concrete

The next stage of Phase I research involved the measurement of near-infrared reflection spectra of concretes. Fifteen unique concrete mixes were analyzed (five mix designs x three water-cement ratios). The mix designs were provided by John Wojakowski at KDOT. Table 2 illustrates the concrete mix designs. Again, three replicates of each sample were mixed and measured every three minutes beginning either seven or eight minutes after mixing. Beginning with mix #3 an extra minute was added to the normal seven minute time in an effort to achieve better mixing. Thus, a total of 1350 near-infrared spectra (15 unique mixes x 30 spectra per mix x three replicates) of concrete were measured.

Mix	Cement (kg/m ³)	Water-Cement Ratio	% Coarse Aggregate	% Fine Aggregate	Daravair?	Daracem?
1	357	0.44, 0.48, 0.52	50	50	No	No
2	379	0.36, 0.40, 0.44	50	50	No	Yes
3	357	0.40, 0.46, 0.52	50	50	Yes	No
4	357	0.30, 0.35, 0.40	50	50	Yes	Yes
5	320	0.35, 0.42, 0.49	40	60	Yes	Yes

Table 2 Concrete Mix Design

The analytical band in this study (see discussion on page six of this report) arises from stretching and bending of water molecules in the cement or concrete. It is well known that temperature has a profound effect on the nature of near-infrared spectra of water molecules. Any increase in temperature increases the amount of random molecular motion that works against the formation of hydrogen bonds. Therefore, the temperature of each mixture at the time of measurement was recorded.

Experimental

Figure 1 shows a schematic of the instrumental configuration used to measure near-infrared spectra in this study. Near-infrared radiation emitted by a standard glo-bar source was modulated by a Midac Fourier Transform Infrared Spectrometer Model M2402-C (on loan from AeroSurvey, Inc., Manhattan, Kansas, made by Midac Corporation, Costa Mesa, California) equipped with a calcium fluoride beamsplitter. The radiation was then focussed onto a fiber optic bundle by a quartz optic mounted on the side of the spectrometer. The radiation was then internally reflected down a 1.5 meter bundle of six 150 micron low-hydroxyl silica fibers. This fiber bundle led to the Visionex Enviva Reflection Probe (Visionex, Inc., Atlanta, Georgia). Radiation exited the fiber bundle, impinged on the sample, and was then collected by a central 150 micron low hydroxyl silica fiber, which delivered the radiation to the detector. The one mm diameter photovoltaic indium gallium arsenide detector (Fermionics *Opto-Technology*, Simi Valley, California), converted the encoded radiation signal to an electrical signal. This signal was then amplified by an InGaAs-1000 Preamplifier (Infrared Systems Development, Corporation, Orlando, Florida) and was sent to the 233 MHz Pentium II processor-based data control computer (Gateway 2000, North Sioux City, South Dakota). Data collection was controlled by Midac Grams/32 version 4.02 software (Galactic Industries Corporation, Irvine, California). All near-infrared spectra shown within this work were measured at a spectral resolution of eight cm^{-1} .

The five cements used in this research, Ash Grove Type I, DuraPozz Grab 972656R, Lone Star Type III, Medusa High Alkali 86-3554, and Monarch Type I/II 98-4016, were obtained from KDOT. Water used in the cement research was obtained from the in-house distilled water source at the Kansas State University Department of Chemistry. It was maintained at approximately 25 C in a water bath prior to mixing. Cements were mixed by hand according to a modified ASTM method C305 supplied by John Wojakowski at KDOT. Spectral collection began five minutes after introduction of water to the cement.

The mix design for the concretes is outlined in Table 2. In all, all concrete mixes Monarch Type I cement supplied by the Kansas State University Department of Civil Engineering (KSUDCE) was used. Water used in the concrete research was obtained from the in-house water supply at KSUDCE. Concrete sand and three-quarters minus gravel were also obtained from KSUDCE. Concretes were mixed using a pan-style mechanical mixer according to a method found in the literature¹. In this method all aggregate was introduced to the pan along with approximately two-thirds of the total water. This combination was then mixed for one minute. Then, the cement and remaining water were introduced and mixed for either five or six more minutes (the extra minute mixing time was added for mixes 3, 4, and 5. Spectral collection began either seven or eight minutes after mixing began.

In all cases, materials were weighed on digital balances with a resolution of 0.1 grams. The probe was immersed approximately five mm into all samples prior to the beginning of spectral collection. Reflection reference spectra were obtained by placing InfragoldTM (Labsphere, North Sutton, New Hampshire), a piece of aluminum electrochemically coated with gold, beneath the probe tip. The distance from the tip to the reference material was then adjusted as to provide a detector signal in the analytical region ($\sim 5200 \text{ cm}^{-1}$) similar to that obtained when measuring the sample. Sample

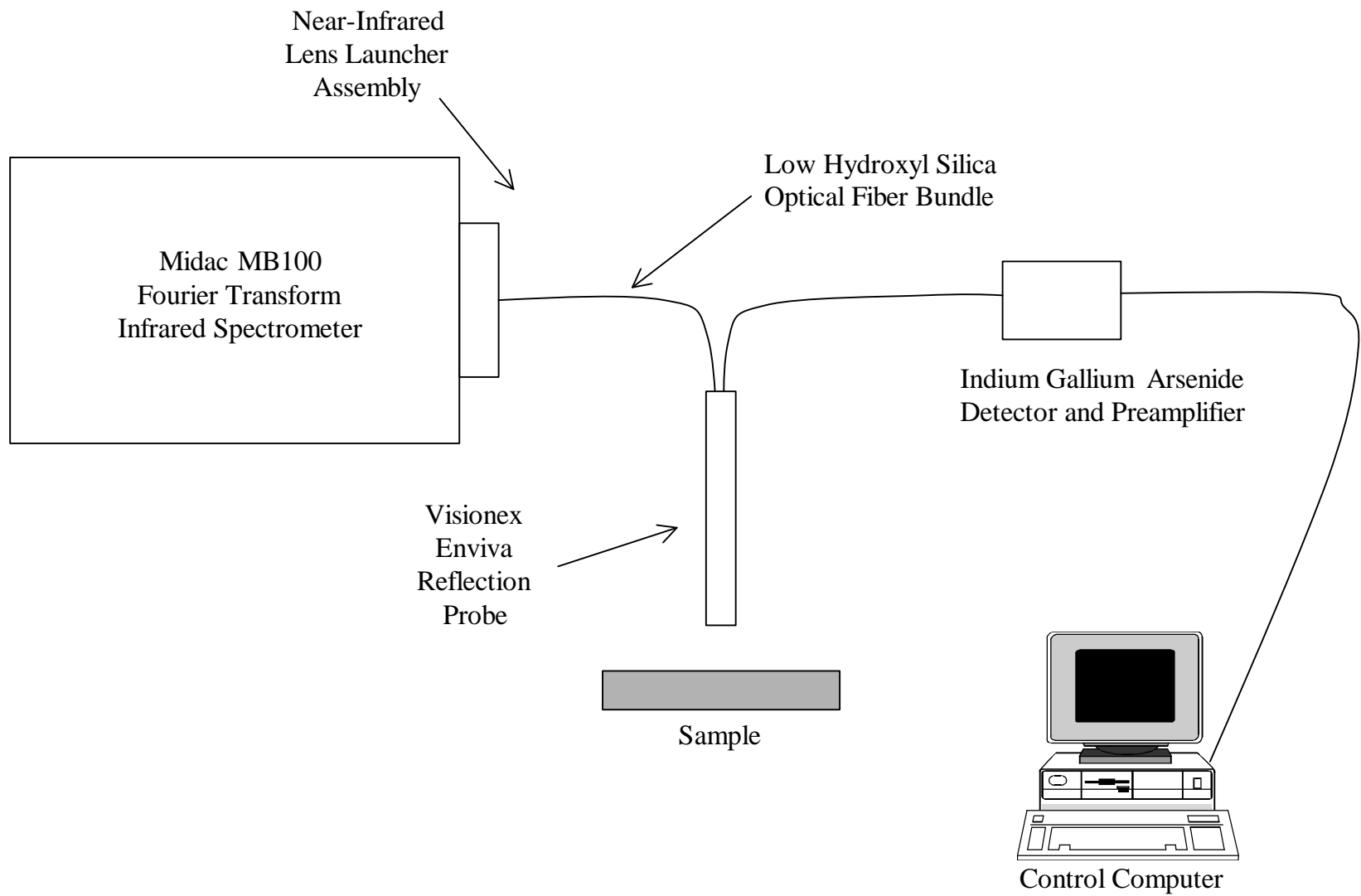


Figure 1 Schematic of Instrumental Configuration

temperatures were measured using a Type J thermocouple connected to a Campbell Scientific CR-10X data logger. When added (see Tables 1 and 2) Daravair 1000 and Daracem 19 were added at a rate of three fluid ounces and 16 fluid ounces per 100 lb of cement, respectively.

The mid-infrared spectra shown in this report were measured at a resolution of eight cm^{-1} using a Mattson Genesis II Fourier Transform Spectrometer with a Specac Golden Gate attenuated total reflection accessory with KRS-5 lenses.

Results and Discussion

The main goal of Phase I of this research is to gain an understanding of the nature of the correlation between any given concrete or cement mix's near-infrared reflection spectrum and its water-cement ratio. Figure 2 shows the near-infrared reflection spectra of Ashgrove cement (with Daravair) with water-cement ratios of 0.36, 0.40, and 0.44. These spectra are typical of any such trio of cements measured in this study. The peak at approximately 5170 cm^{-1} in each spectrum is due to the stretch/bend combination band of water. The broader peak centered at approximately 6900 cm^{-1} is due to the first overtone of the oxygen-hydrogen stretching fundamental at approximately 3500 cm^{-1} . The tilt in the baseline that begins at around 6000 cm^{-1} is due to differences in the scattering coefficient of the sample and reference materials.

To the naked eye, spectral differences are minor. The most obvious differences are in the signal-to-noise ratio in the high wavenumber region. However, when the 5600 to 4650 cm^{-1} region of these spectra is expanded, and the spectra are overlaid on the same ordinate scale, differences between the three spectra become clear (see Figure 3). For samples with relatively high water-cement ratios, the peak at 5170 cm^{-1} is higher and wider. From a spectroscopy standpoint this is logical. Increased water concentration should lead to increased absorption by water-related bands.

The area beneath the band at 5170 cm^{-1} should be, according to Beer's Law, linearly proportional to the concentration of water measured by the illumination cone of the fiber optic probe. If this law holds for the measurements made in this study then it is reasonable to assume that with proper calibration this method could be used to measure water-cement ratio of cements and concretes. Plots of band area between 5280 and 4625 cm^{-1} versus water-cement ratio for cement can be found in Appendix A. This spectral region was chosen by subtracting an Ashgrove cement spectrum with water-cement ratio of 0.36 from an Ashgrove cement spectrum with water-cement ratio of 0.44. By doing this, the region within the 5170 cm^{-1} -centered band most sensitive to changes in water-cement ratio became clear. Each point in the plots in Appendix A (and B) represents the average of three replicate measurements. The R^2 value for the trendline determined by Microsoft Excel software is shown on each plot. The standard deviation of each set of three measurements was determined using the standard "n-1" non-biased algorithm within Microsoft Excel.

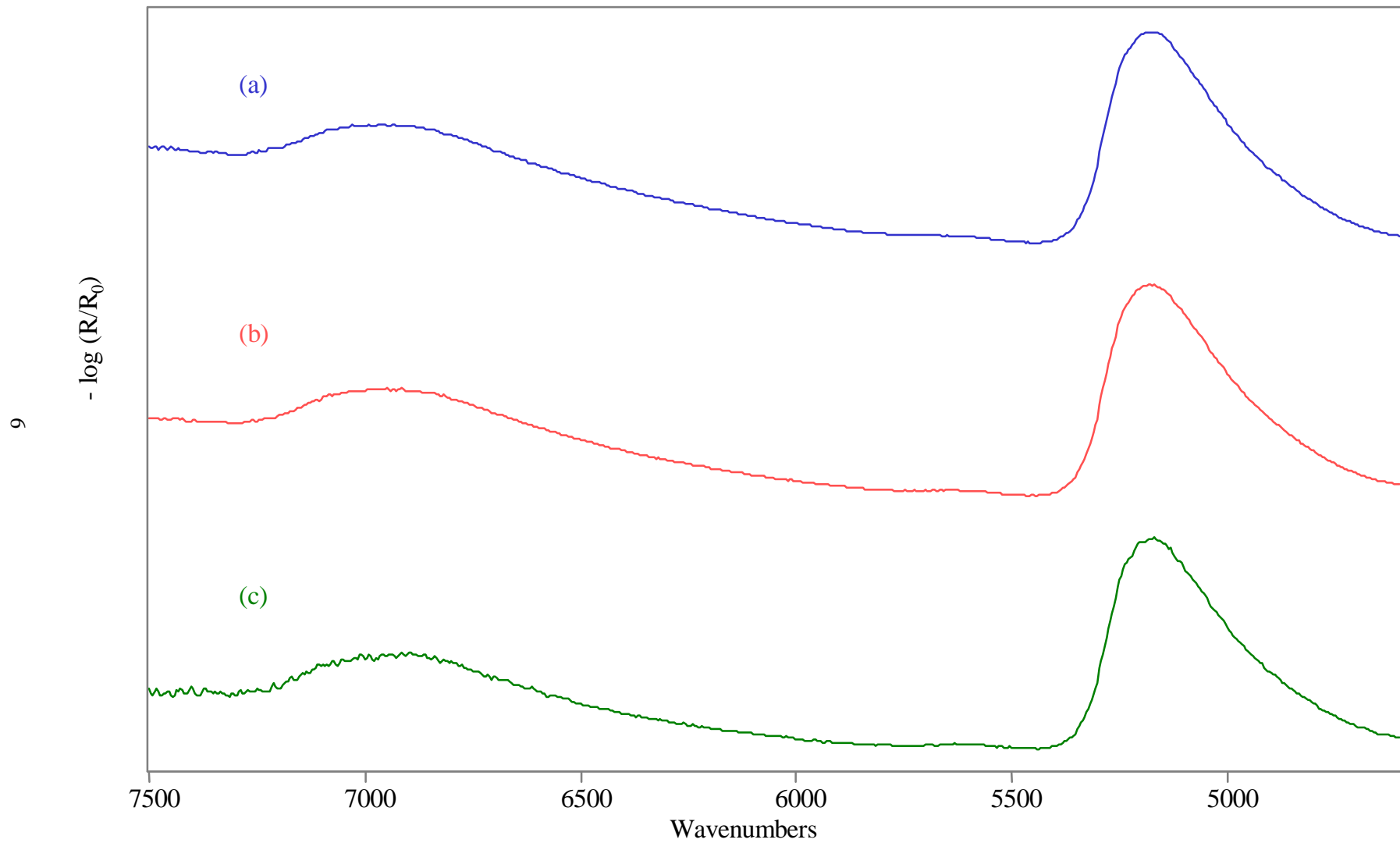


Figure 2 Near-Infrared Reflection Spectra of Ashgrove Cement (with DaraVair) with Water to Cement Ratios of a) 0.36 b) 0.40 c) 0.44 7500 to 4600 cm^{-1}

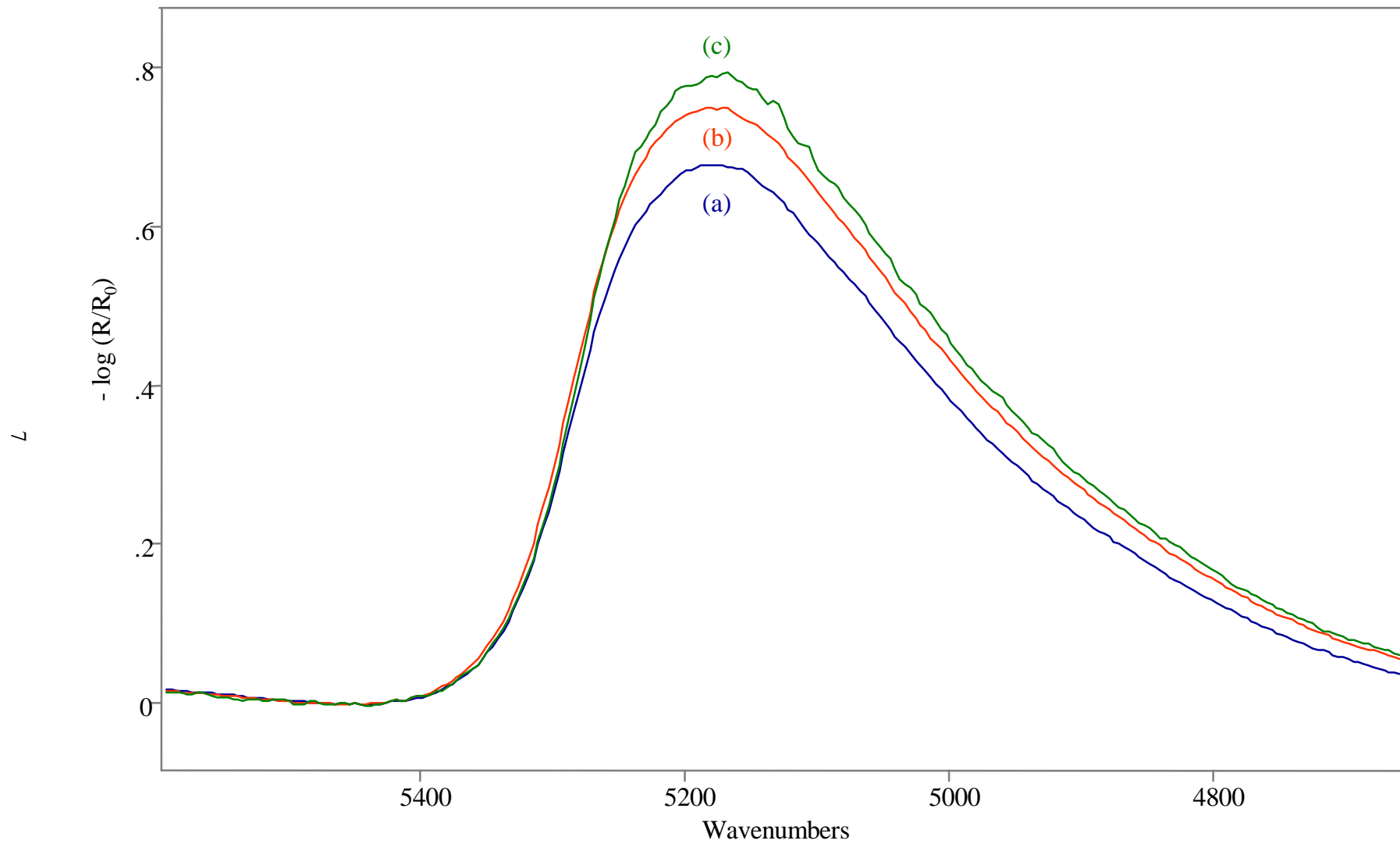


Figure 3 Near-Infrared Reflection Spectra of Ashgrove Cement (with DaraVair) with Water to Cement Ratios of a) 0.36 b) 0.40 c) 0.44 5600 to 4650 cm^{-1}

Determination of Water-Cement Ratios of Cements by Near-Infrared Spectroscopy

Within the proposal submitted to KDOT by the author a number of questions were poised. The first was “Is it feasible to determine the water-cement ratio of a batch of cement by analysis of its near-infrared spectrum, provided that the temperature and hardening time (i.e., amount of time passed since mixing) of the mixture are known?” Based on the Beer’s Law plots in Appendix A, the author feels the answer to this question is yes. With one exception (Medusa cement with Daravair), each of the plots shows a positive correlation between band area between 5280 cm^{-1} and 4625 cm^{-1} and water-cement ratio. The standard deviations of the points are, in many cases, quite large. But, considering that the samples were mixed manually, this is not too surprising. R^2 values of the trendlines are poor compared to more traditional, controlled research. The fact remains, though, that in 14 of 15 cases a positive correlation between water-cement ratio and the chosen analytical band area exists. This leads the author to believe that *with more controlled mixing, and perhaps more replicate measurements*, this method could be used to measure the water-cement ratio of cements.

Determination of Water-Cement Ratios of Concretes by Near-Infrared Spectroscopy

Another question poised in the proposal was, “Is it feasible to determine the water-cement ratio of a batch of concrete by analysis of its near-infrared spectrum, provided that the temperature and hardening time (i.e., amount of time passed since mixing) of the mixture are known?” Figure 4 shows the near-infrared reflection spectra of concrete mix #5 with water-cement ratios of 0.36, 0.40, and 0.44. These spectra are typical of any such trio of concretes measured in this study. The explanation of spectral features in Figure 2 also holds for these spectra. Again, to the naked eye, spectral differences are minor. An interesting observation is that the baseline tilt of these three spectra is greater than that of the spectra in Figure 2. This is most likely due to increased scattering by both coarse and fine aggregate and addresses the question poised in the proposal regarding the effect of aggregate on the appearance of near-infrared spectra of concrete. Assuming proper mixing, this effect will be reproducible.

When the 5600 to 4650 cm^{-1} region of these spectra is expanded, and the spectra are overlaid on the same ordinate scale, differences between the three spectra become clear. Such a spectral overlay is shown in Figure 5. At first glance it appears as if the spectrum of concrete with water-cement ratio of 0.42 is in violation Beer’s Law. However, it must be noted that it is the *area* between 5280 and 4625 cm^{-1} that is important in this study. The relatively rapid tailing off of Spectrum B at lower wavenumber decreases its area such that it does, indeed, obey Beer’s Law. All five of the Beer’s Law plots for the concrete measurements (see Appendix B) show a positive correlation between band area between 5280 cm^{-1} and 4625 cm^{-1} and water-cement ratio. Therefore, the author answers yes to the question discussed at the beginning of this paragraph; based on the findings of the author it *is* feasible to determine the water-cement ratio of a batch of concrete by analysis of its near-infrared spectrum, provided that the temperature and hardening time (i.e., amount of time passed since mixing) are known.

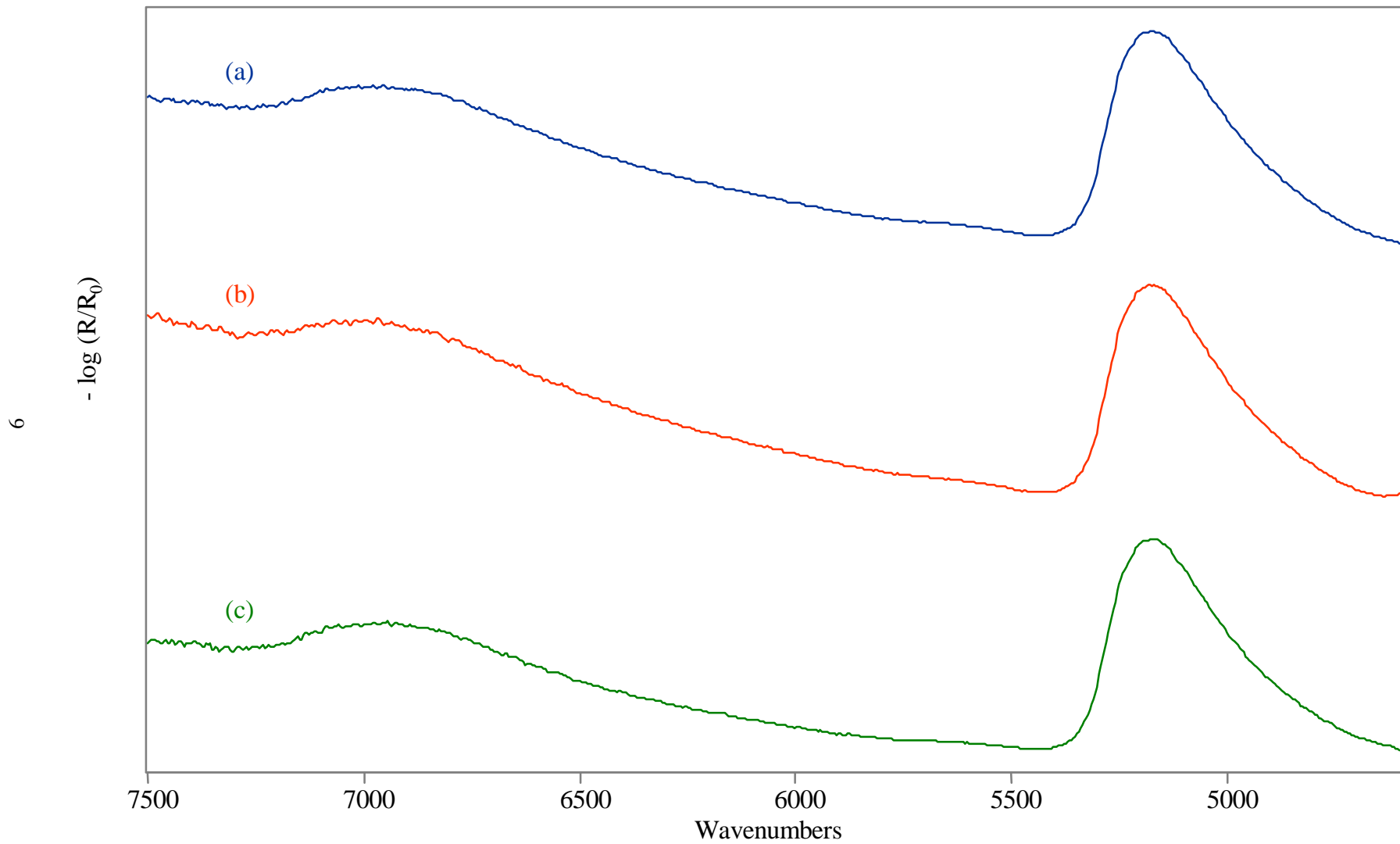


Figure 4 Near-Infrared Reflection Spectra of Concrete Mix 5 (320 kg/m^3 , 50% CA and FA, AEA and HRWRA) with Water to Cement Ratios of a) 0.36 b) 0.40 c) 0.44 7500 to 4500 cm^{-1}

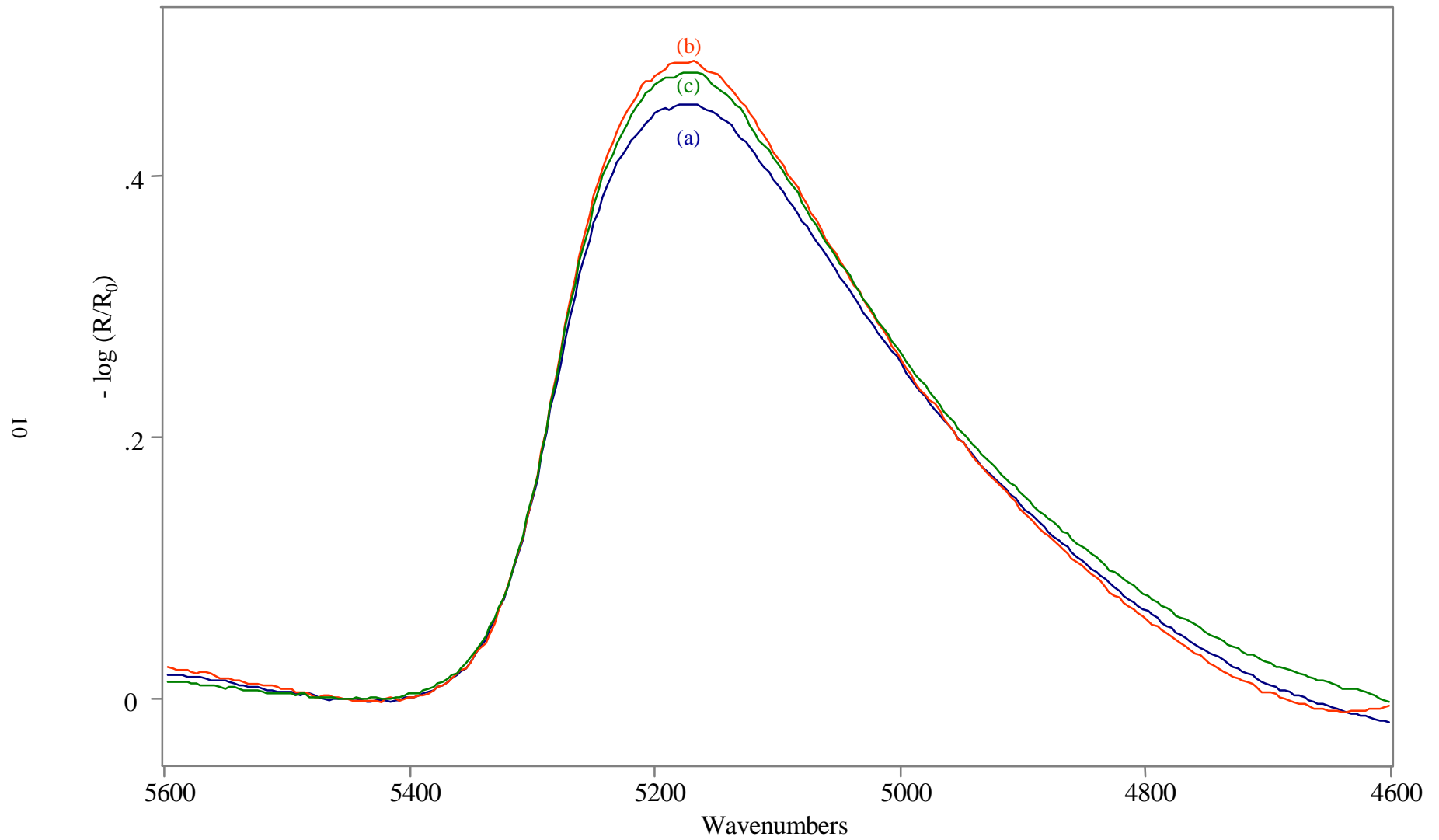


Figure 5 Near-Infrared Reflection Spectra of Concrete Mix 5 (320 kg/m^3 , 50% CA and FA, AEA and HRWRA) with Water to Cement Ratios of a) 0.35 b) 0.42 c) 0.49 5600 to 4600 cm^{-1}

The Effect of Hardening Time

As stated earlier, a spectrum was measured once every three minutes soon after the mixing of the cement or concrete. Performed 30 times, this produced a 90 minute time series of spectra for each sample. These spectra were measured to observe the nature of time-dependent band changes during hardening. Figure 6 shows a typical spectral time series for Ashgrove cement with a water-cement ratio of 0.40. As time increases, both the height and width of the analytical band increase. This effect was observed for the majority of cement and concrete spectra. There were some cases in which the band height and width increase was not as profound. The author believes this is due to contraction or shifting of the sample during hardening. If intimate contact between the probetip and the sample is broken, the water absorption will change, most likely decreasing. In either case this finding validates the caveat regarding hardening time made in the questions poised in the proposal. It will, indeed, be necessary to know the amount of time passed since mixing in order to accurately determine water-cement ratio of cements and concretes by this method. If hardening time is *not* taken into account during calibration its effect could easily be confused with that of changing water-cement ratio.

Detection of Admixtures

Within the proposal for this research the following question was asked: “Is the presence of the admixture agents used in cement/concrete research detectable by near-infrared reflection spectrometry?” The best method of answering this question necessitates a brief discussion of near-infrared spectrometry. Molecular vibrational absorptions in the near-infrared region of the electromagnetic spectrum arise from overtones and combinations of fundamental molecular vibrational absorptions in the mid-infrared (relatively longer wavelengths compared to the near-infrared region). These overtones and combinations are much weaker than the fundamental absorptions from which they rise. Also, the location of the combination or overtone band within the near-infrared can be easily approximated with knowledge of the location of the appropriate fundamental absorption band. The shorter the wavelength of the fundamental absorption, the better the chance that its overtones and combinations will be detectable in the near-infrared region. Figure 7 shows the mid-infrared spectrum of pure Daravair and pure water. The spectral differences below 1000 cm^{-1} are instrumental in nature and should be disregarded. Above 1000 cm^{-1} , the spectra are quite similar. The contour of the oxygen-hydrogen stretching and bending fundamentals of water centered at 3270 cm^{-1} and 1630 , respectively, *does* differ from the contour of the corresponding bands in the spectrum of Daravair. It is doubtful, however, that the combinations and overtones bands of Daravair will be noticeably different from those of pure water added to cement or concrete. Figure 8 shows a similar spectral comparison of pure Daracem and pure water. Daracem does exhibit non-aqueous absorption slightly above 1000 cm^{-1} . However, these absorptions occur at quite long wavelength and would therefore most likely be undetectable by near-infrared spectrometry of the cements and concretes measured in this study.

Further proof of the lack of ability to detect Daravair and Daracem by this near-infrared method is shown in Figure 9. The top and middle spectra are near-infrared

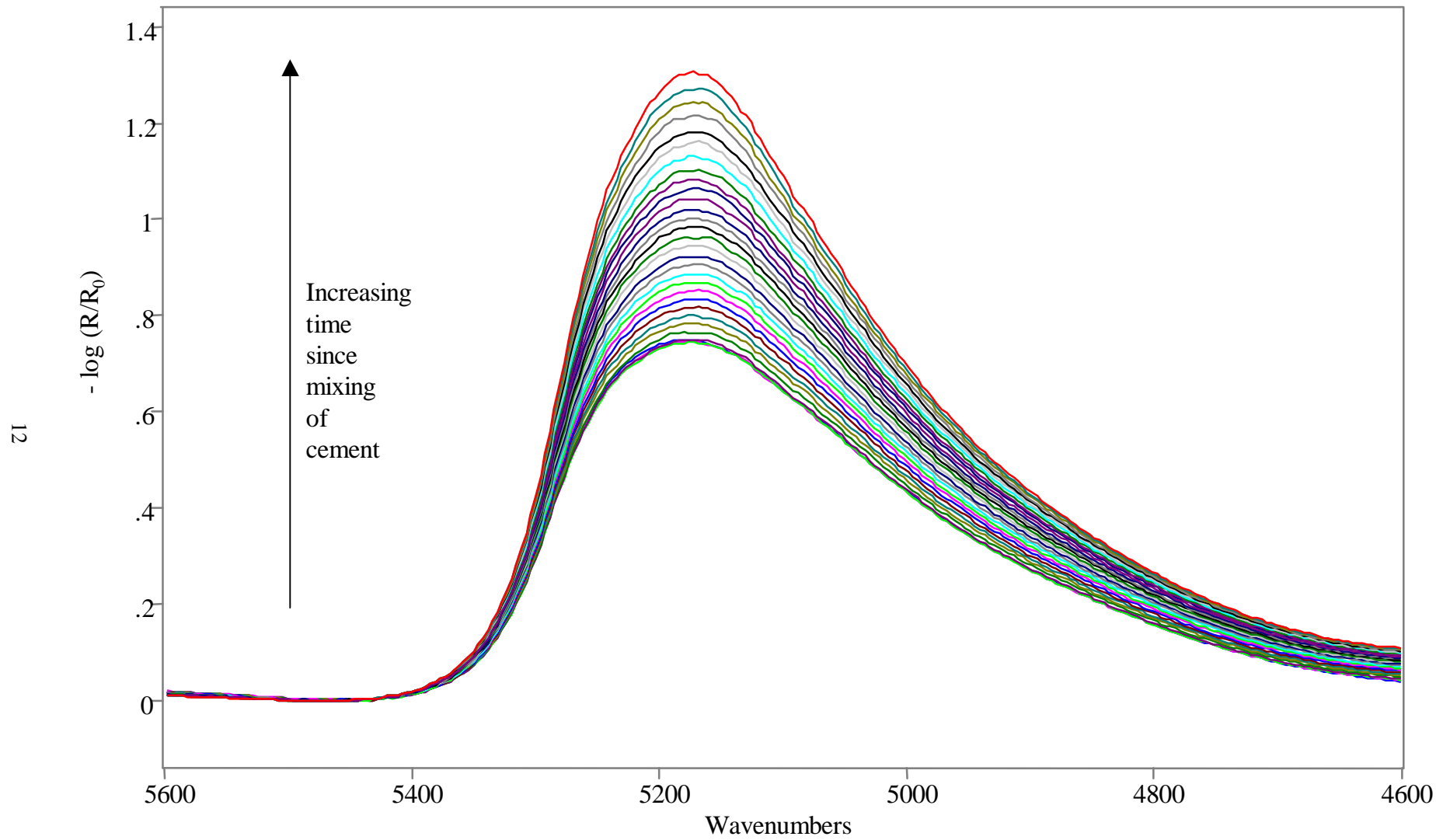


Figure 6 A Time Series of Near-Infrared Reflection Spectra of Ashgrove Cement, W/C = 0.40
5600 to 4600 cm^{-1}

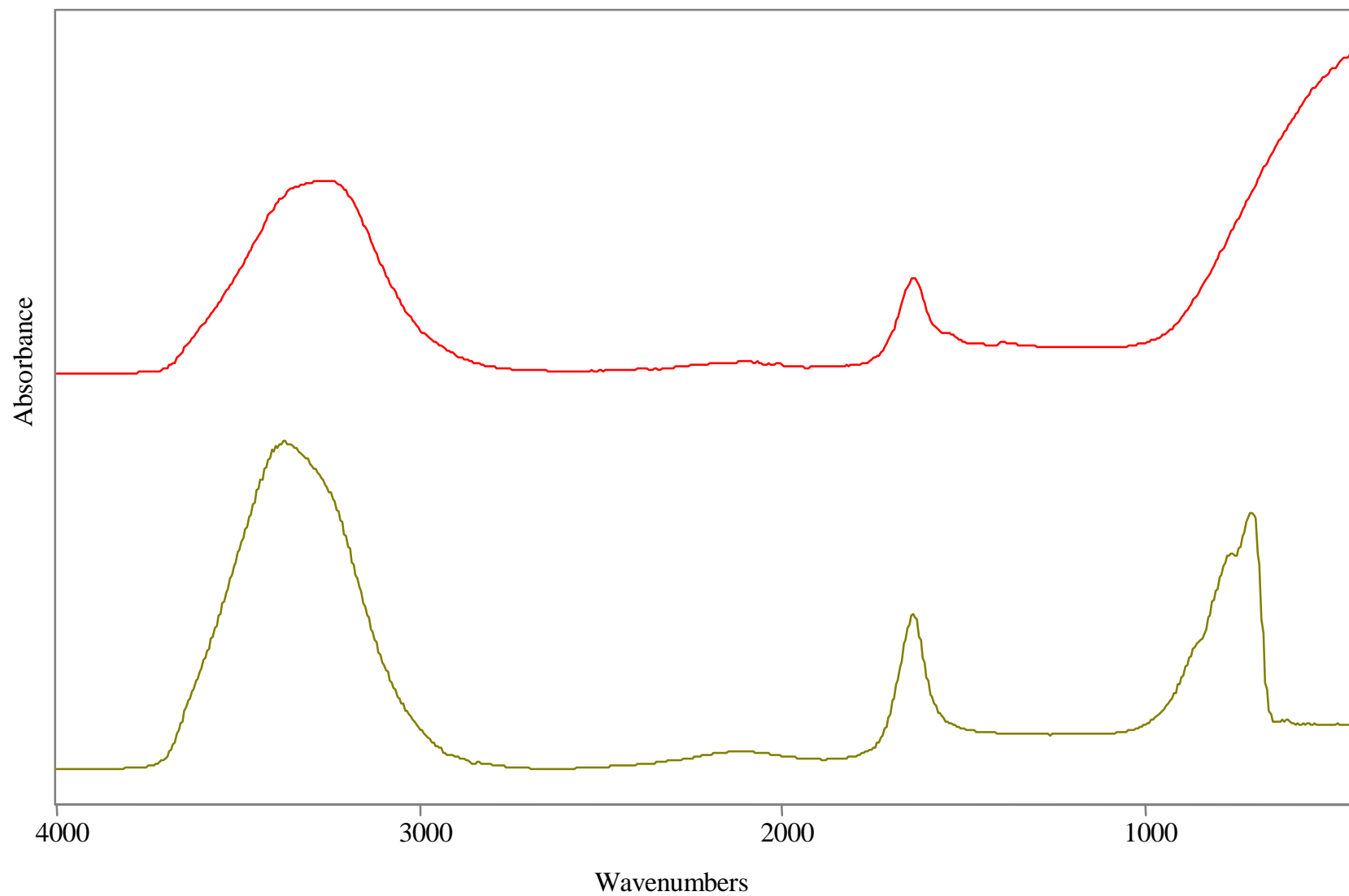


Figure 7 Mid-Infrared Spectra of Pure Daravair (top) and Pure Water (bottom)
400 to 4000 cm⁻¹

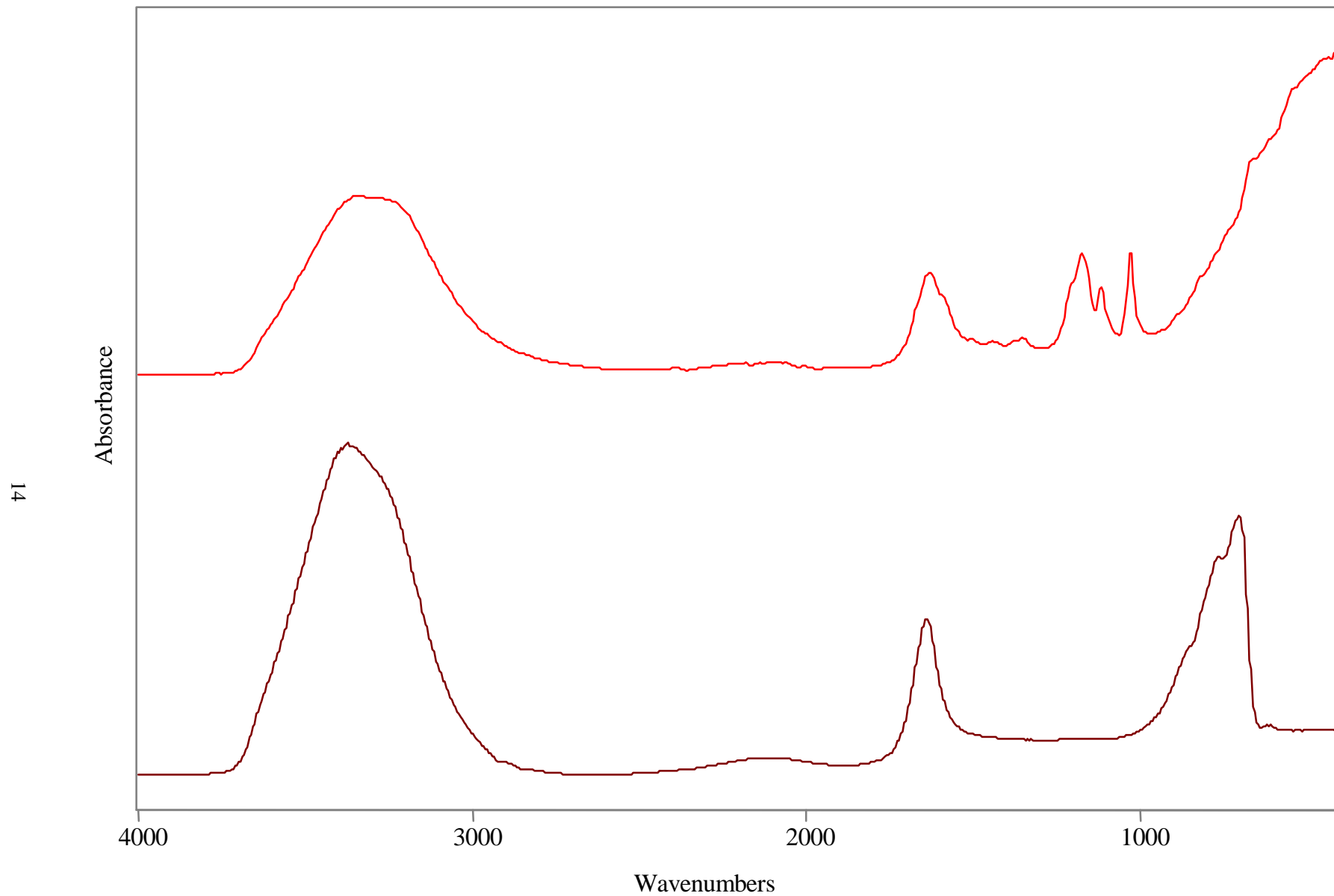


Figure 8 Mid-Infrared Spectra of Pure Daracem (top) and Pure Water (bottom)
400 to 4000 cm^{-1}

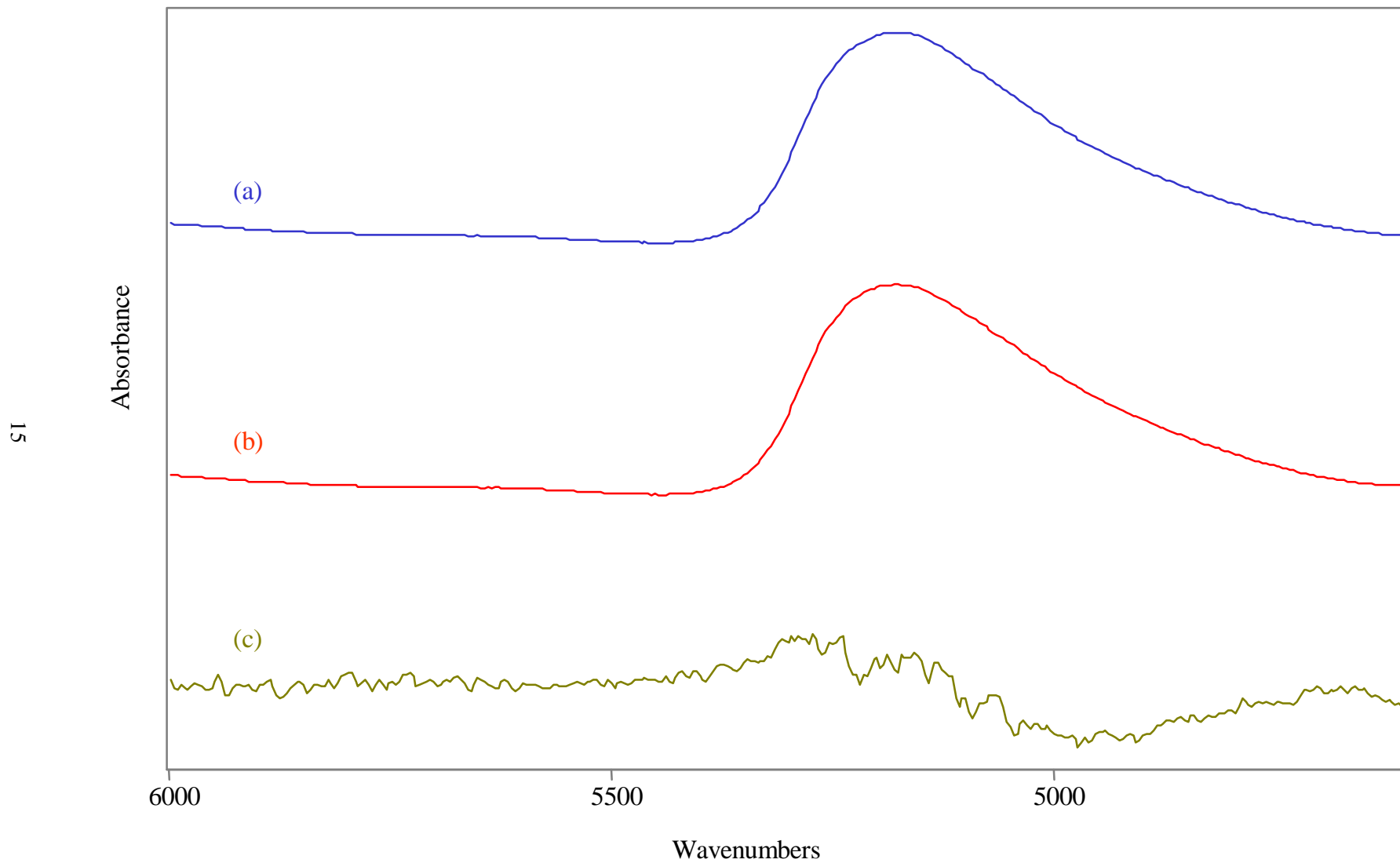


Figure 9 Near-Infrared Spectra of Ashgrove Cement with Daravair (a) and without Daravair (b)
The bottom spectrum (c) is the result of subtracting (b) from (a)

spectra of Ashgrove cement (W/C = 0.40) with and without Daracem. The bottom spectrum is the result of subtracting Spectrum B from Spectrum A (note: Spectrum B was multiplied by 0.97 in order to make the resultant ordinate zero at 5182 cm⁻¹). If Daravair is not detectable, this spectrum should be a flat line. A slight negative residual is noted around 4900 cm⁻¹. However, the small magnitude of this residual, coupled with earlier conclusions regarding the nature of the mid-infrared absorptions of Daravair, lead the author to attribute this residual to other causes (such as mixing error). Therefore, the author concludes that admixtures at the concentrations used in this work are undetectable by the method used in this work.

The Effect of Mixing Errors

Upon the request of Dick McReynolds, this project’s monitor at KDOT, the effect of substituting fine aggregate (sand) for cement was investigated. The result of this study is shown in Figure 10. Substitution of 10% of cement with sand in Concrete mix #3 (W/C = 0.46) resulted in decreasing the height and area of the water combination band at 5170 cm⁻¹. This area would, in the field, be used to determine the water-cement ratio of the mix and would result in an erroneously low value. Therefore, a mixing error such as this will clearly be problematic to accurate determination of water-cement ratio by this method.

Probe tip sheathing

As discussed in the proposal the necessity of creating a sheath for the probe tip was considered. Because the presence of aggregate does not seem to drastically alter the quality of the Beer’s Law plots, the author feels it is not necessary to construct a sheath. A more statistical approach to verifying this is to compare the percent standard deviations for cements and concretes. Each of the five concrete mixes contained Monarch cement. Therefore, it is only valid to compare these with the cement analyses that used Monarch cement. Further, it is most valid to compare only mix #2 as its water-cement ratios (0.36, 0.40, 0.44) were the same as those used in the cement analyses. Table 3 shows a comparison of these standard deviations.

Material	Point at W/C = 0.36 % Standard Deviation	Point at W/C = 0.40 % Standard Deviation	Point at W/C = 0.44 % Standard Deviation
Monarch Cement	9.35	11.40	19.35
Monarch Cement with Daravair	2.37	8.67	8.83
Concrete Mix #2	17.52	5.87	3.65

Table 3 Comparison of Percent Standard Deviation (for identical water-cement ratios) For Monarch Cement, with and without Daravair, and Concrete Mix #2

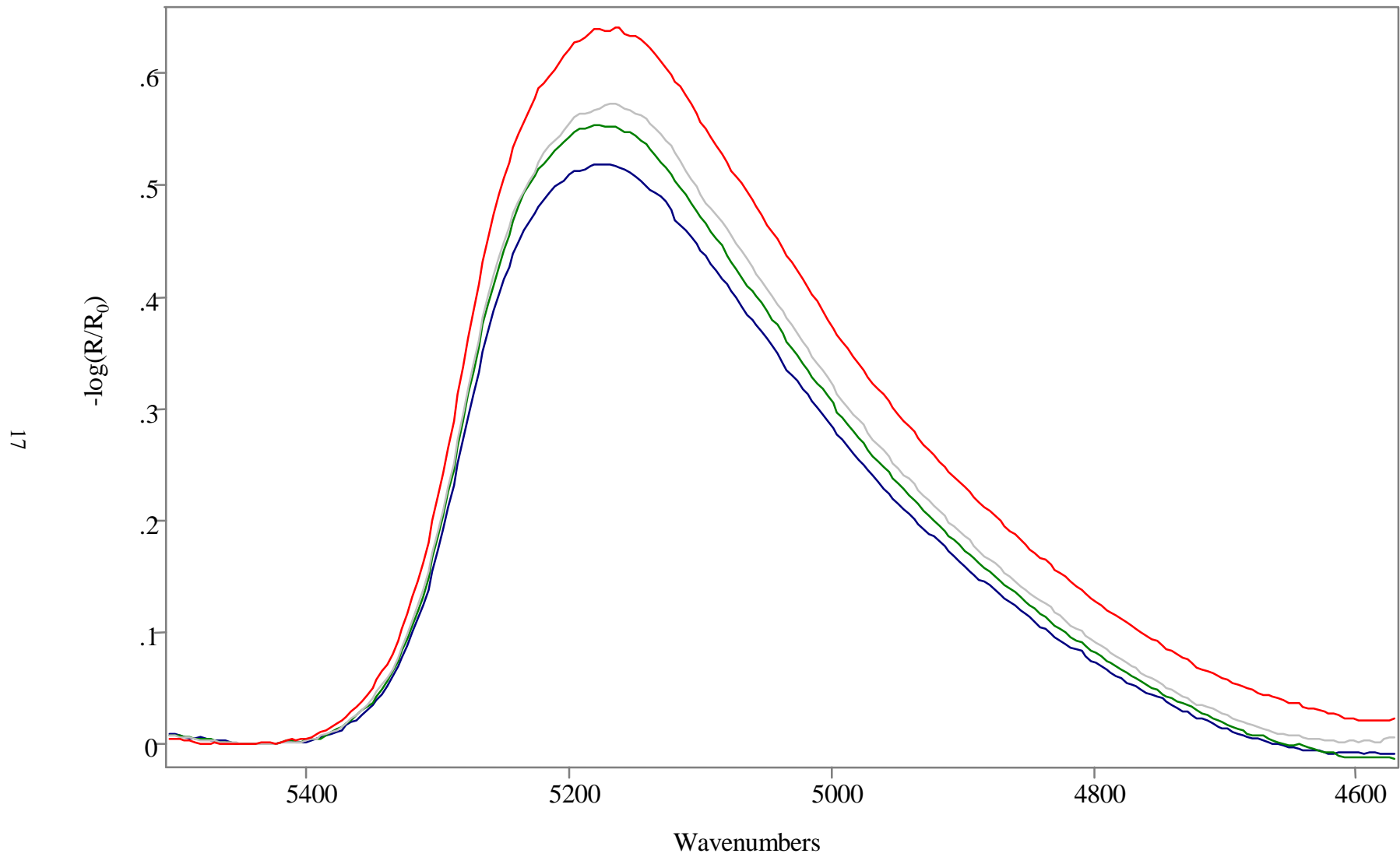


Figure 10 Near-Infrared Reflection Spectra of Concrete Mix #3 with normal mixture (top two spectra, red and gray) and with 10% of cement substituted with sand (bottom two spectra, green and blue)

If the percent standard deviations of concrete mix #2 were higher than those of the Monarch cement analyses, it would be logical to construct a sheath to prohibit the aggregate in concrete from reaching the area around the probetip. The values in Table 3 show that this is not the case. However, in the interest of *protecting* the fiber optic probetip, the construction of a sheath was investigated. In order to allow only cement and water to intimately contact the tip of the probe a sheath of 200 mesh wire cloth must be used. However, this fine of a wire filter prohibited even the most aqueous of mixes to pass through to contact the probetip. Based on this finding, and the lack of a serious problem created by the presence of aggregate near the probetip, the idea of creating a sheath for the probetip was abandoned.

Conclusions

Listed below are condensed answers to the questions poised in the proposal of this research.

- Is it feasible to determine the water-cement ratio of a batch of cement by analysis of its near-infrared spectrum, provided that the temperature and hardening time (i.e., amount of time passed since mixing) of the mixture are known?

Yes, in 14 of 15 cases a positive correlation between water-cement ratio and the analytical band exists. Future calibration samples should be mixed with a mechanical mixer and an unmodified ASTM method.

- Is the presence of admixture agents used in this cement research detectable by near-infrared spectrometry?

No, Daravair and Daracem, added at three fluid ounces and 16 fluid ounces per 100 pounds of cement, respectively, are not detectable by this method.

- Is it feasible to determine the water-cement ratio of a batch of concrete by analysis of its near-infrared spectrum, provided that the temperature and hardening time (i.e., amount of time passed since mixing) of the mixture are known?

Yes, in five of five cases a positive correlation exists between water-cement ratio and the analytical band. Future calibration should involve more replicates.

- Is the presence of admixture agents used in this cement research detectable by near-infrared spectrometry?

No, Daravair and Daracem, added at three fluid ounces and 16 fluid ounces per 100 pounds of cement, respectively, are not detectable by this method.

- Does the presence of coarse aggregate in concrete strongly affect the appearance of the near-infrared reflection spectra of concrete?

No, the only noticeable effect of the aggregate is to increase scattering, which, in turn, increases baseline tilt at higher wavenumbers.

- Is this effect reproducible?

Yes, it is reproducible. Slight variation in the degree and nature of the baseline tilt does exist, though, due to the nonhomogeneous nature of even well-mixed concrete.

- If the effect of the presence of aggregate is not reproducible, can the problem be overcome by using a screening sheath on the probetip?

If the percent standard deviations of concrete mix #2 were higher than those of the Monarch cement analyses, it would be logical to construct a sheath to prohibit the aggregate in concrete from reaching the area around the probetip. The values in Table 3 show that this is not the case.

- What effect does substitution of 10% of cement by sand have on the near-infrared spectra of concrete samples?

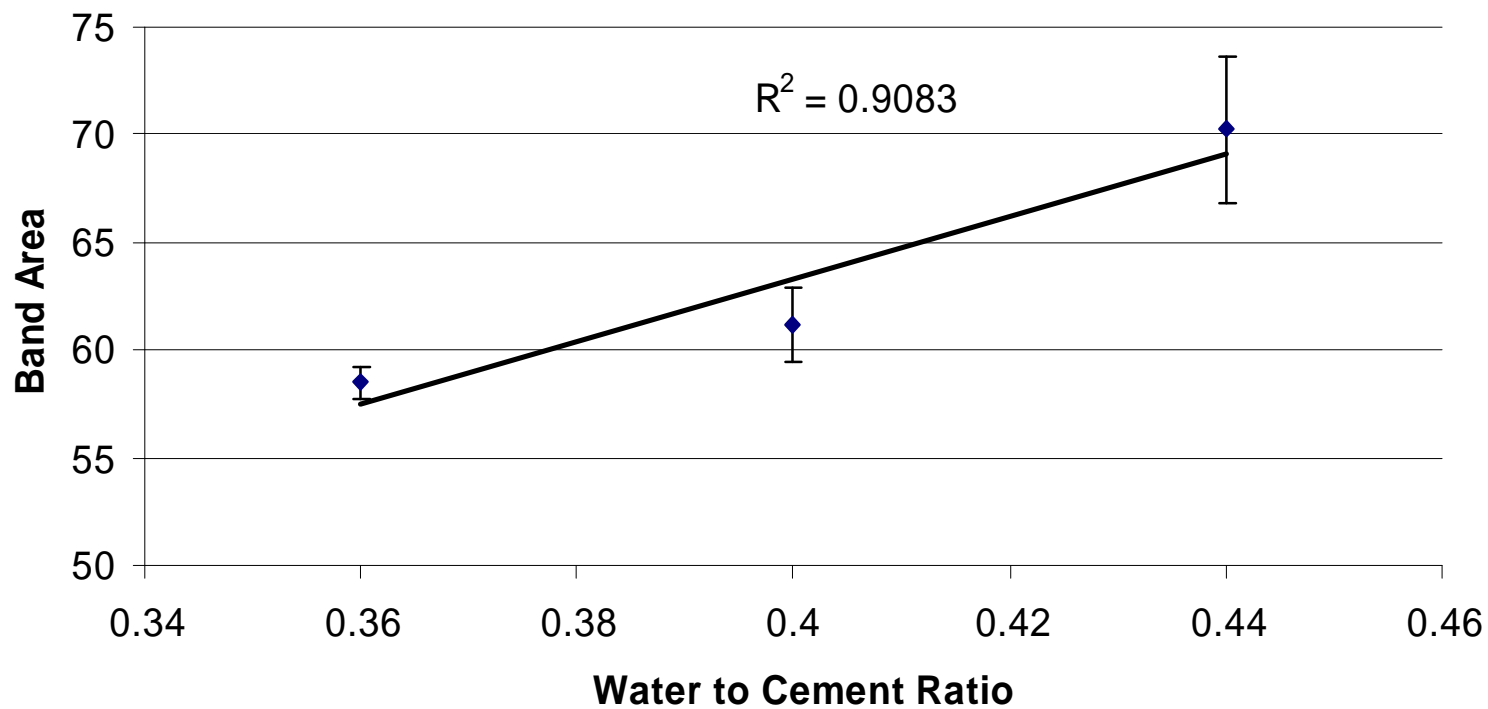
Substitution of 10% of cement with sand in concrete mix #3 ($W/C = 0.46$) resulted in decreasing the height and area of the water combination band at 5170 cm^{-1} (see Figure 10). This area would, in the field, be used to determine the water-cement ratio of the mix and would result in an erroneously low value. Therefore, a mixing error such as this will clearly be problematic to accurate determination of water-cement ratio by this method.

References

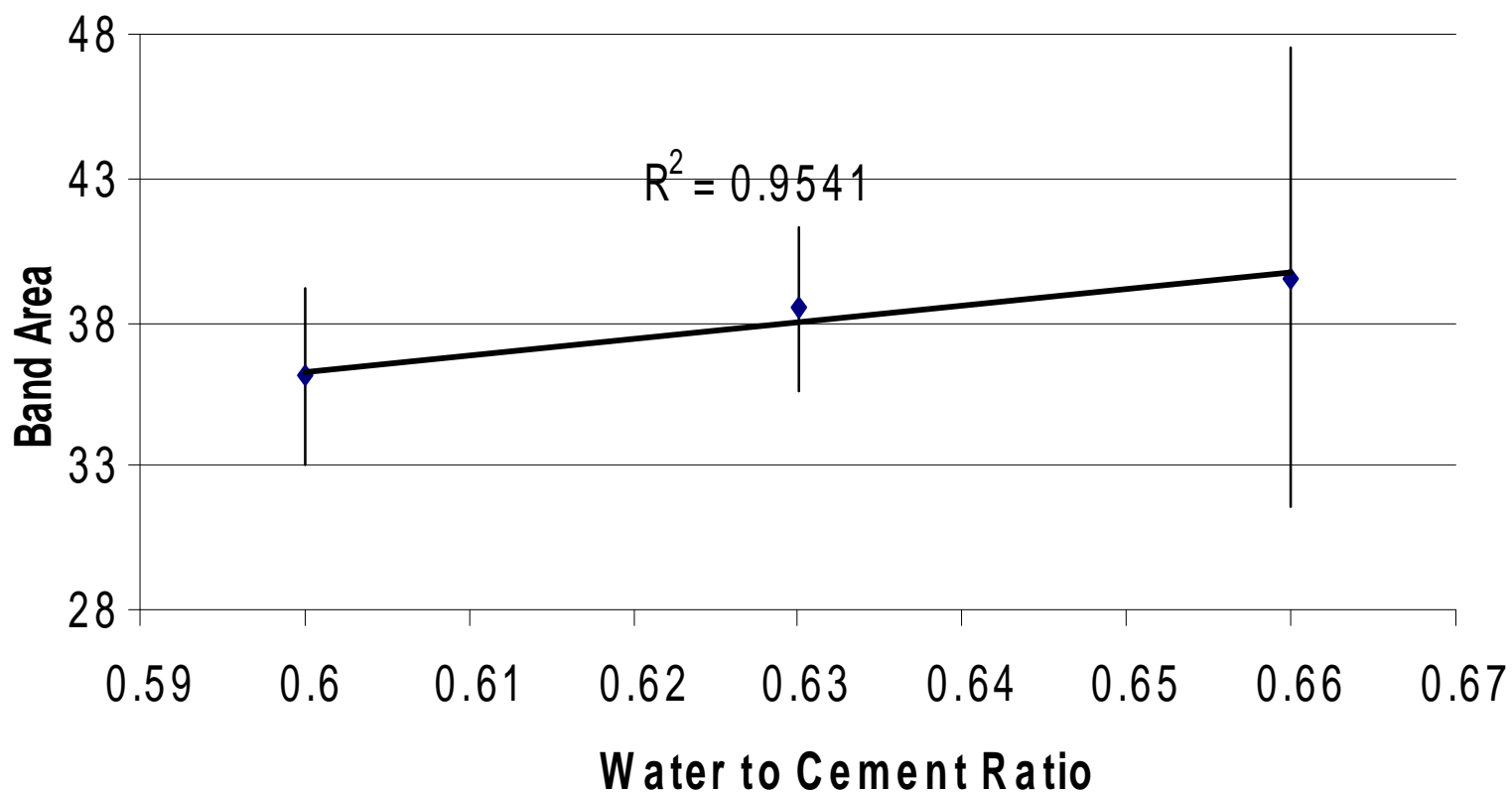
1. "Design and Control of Concrete Mixtures," Portland Cement Association, Eleventh Edition, July 1968.

Appendix A: Beer's Law Plots of Cements

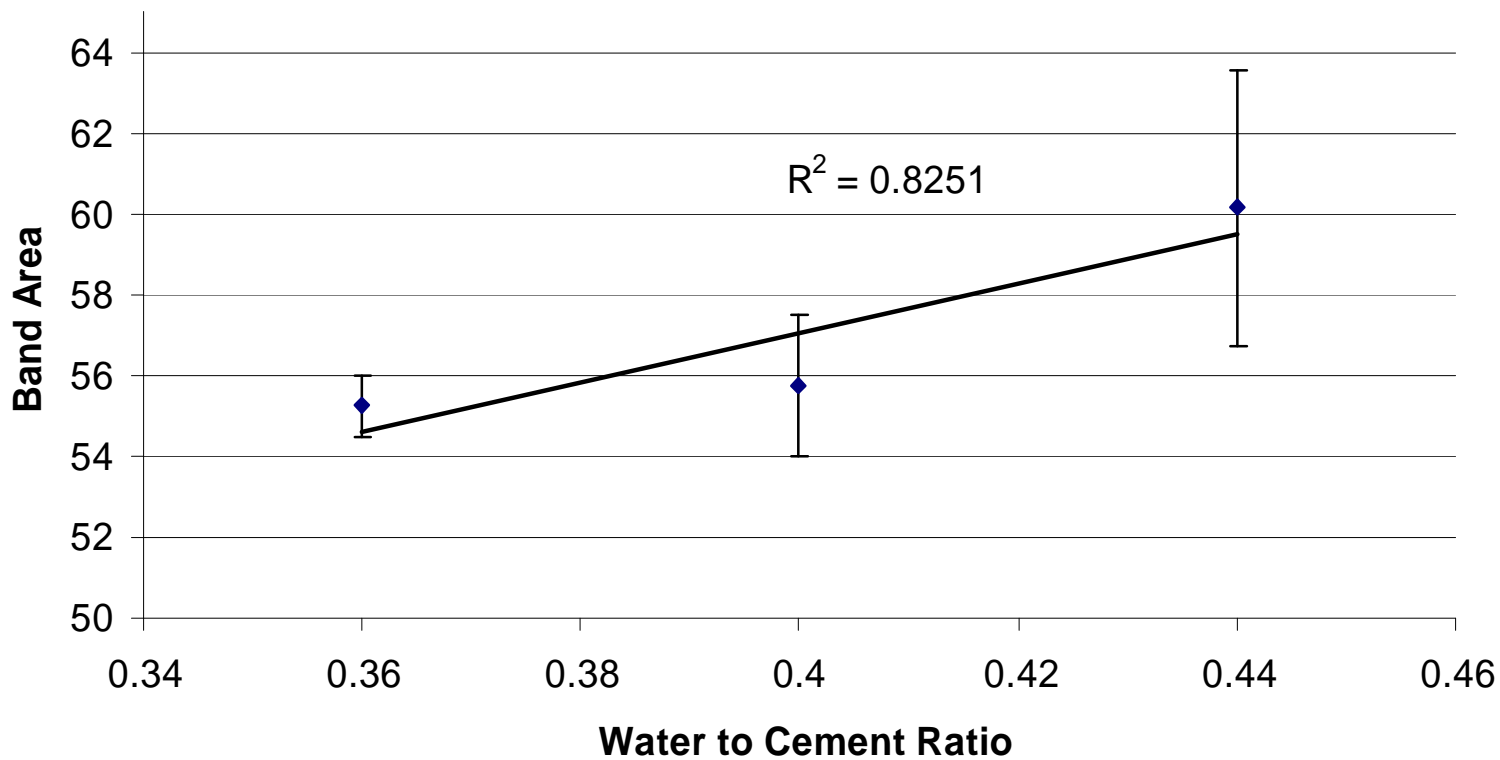
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio Ashgrove Cement**



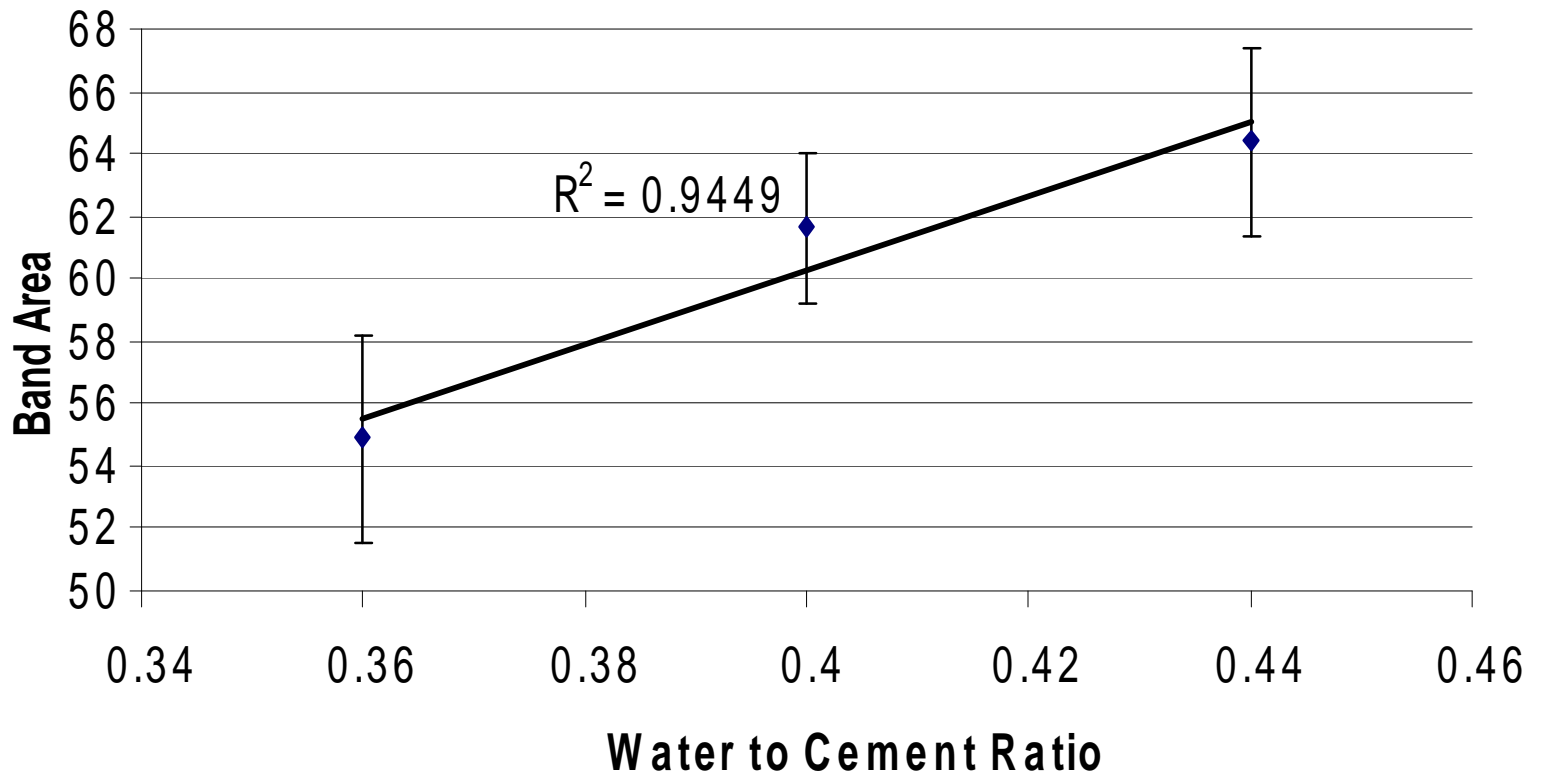
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio DuraPozz Cement**



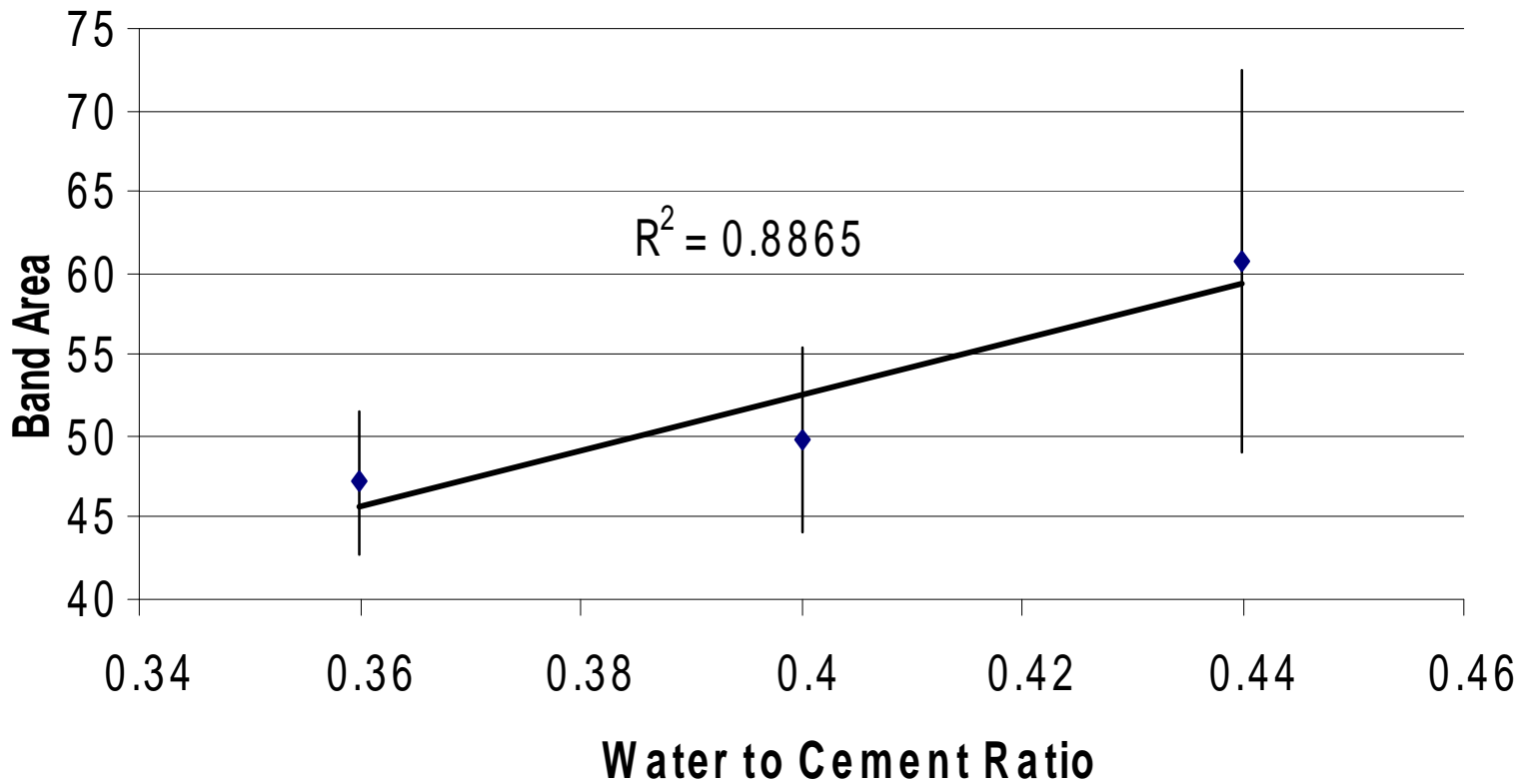
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio Lone Star Cement**



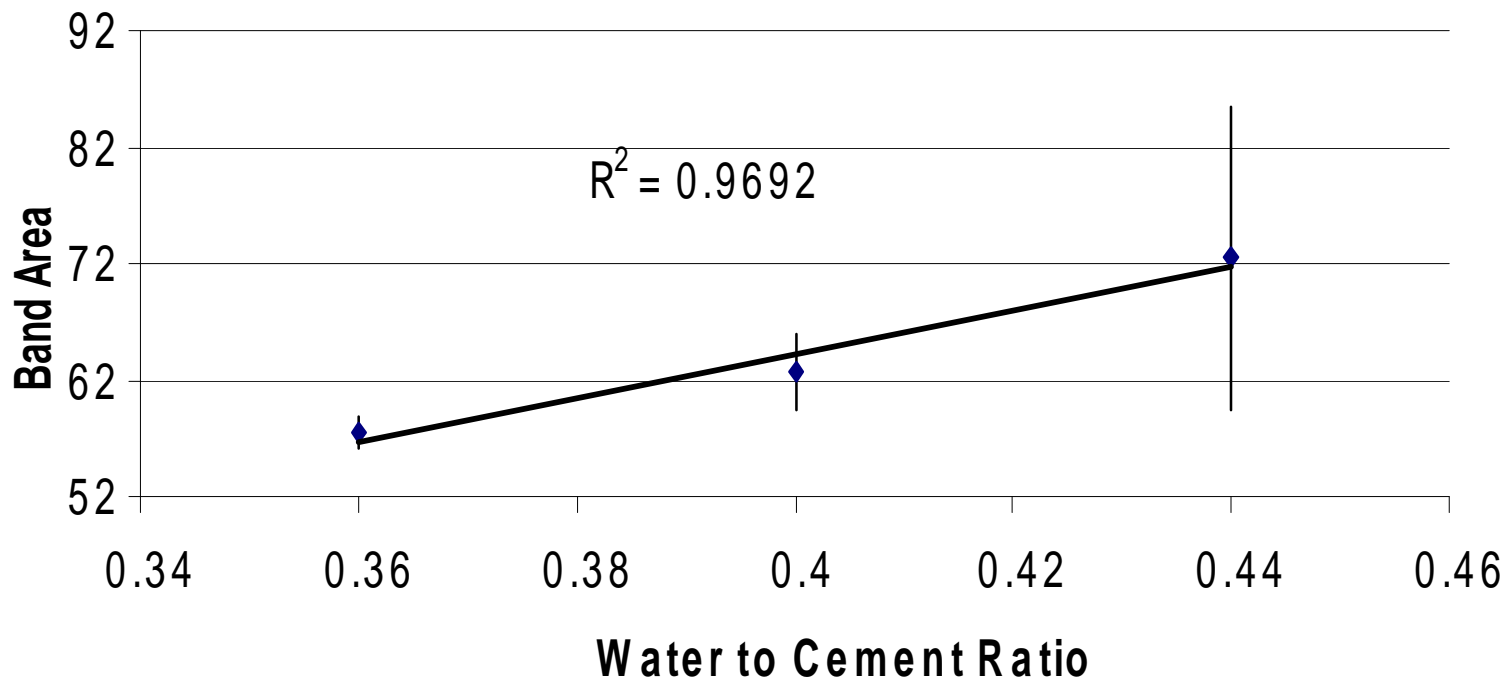
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio Medusa Cement**



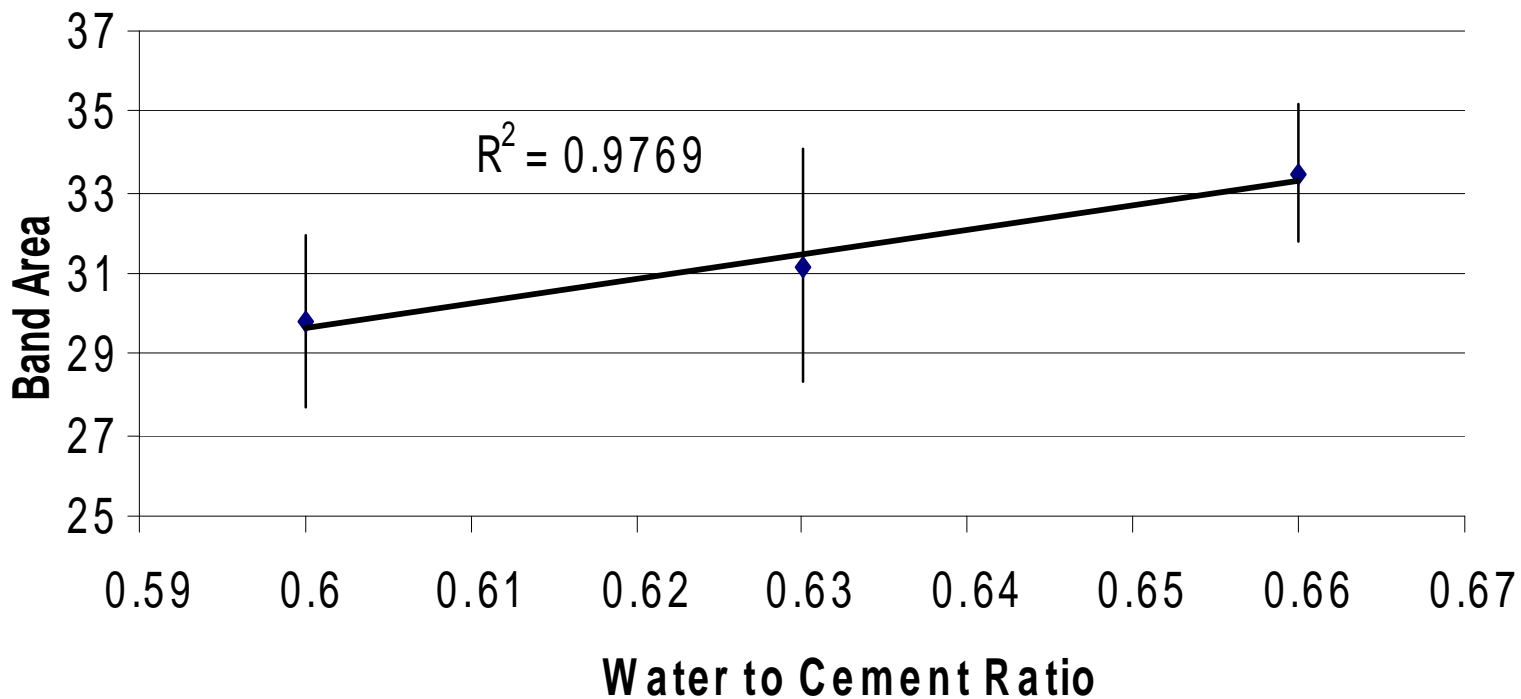
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio Monarch Cement**



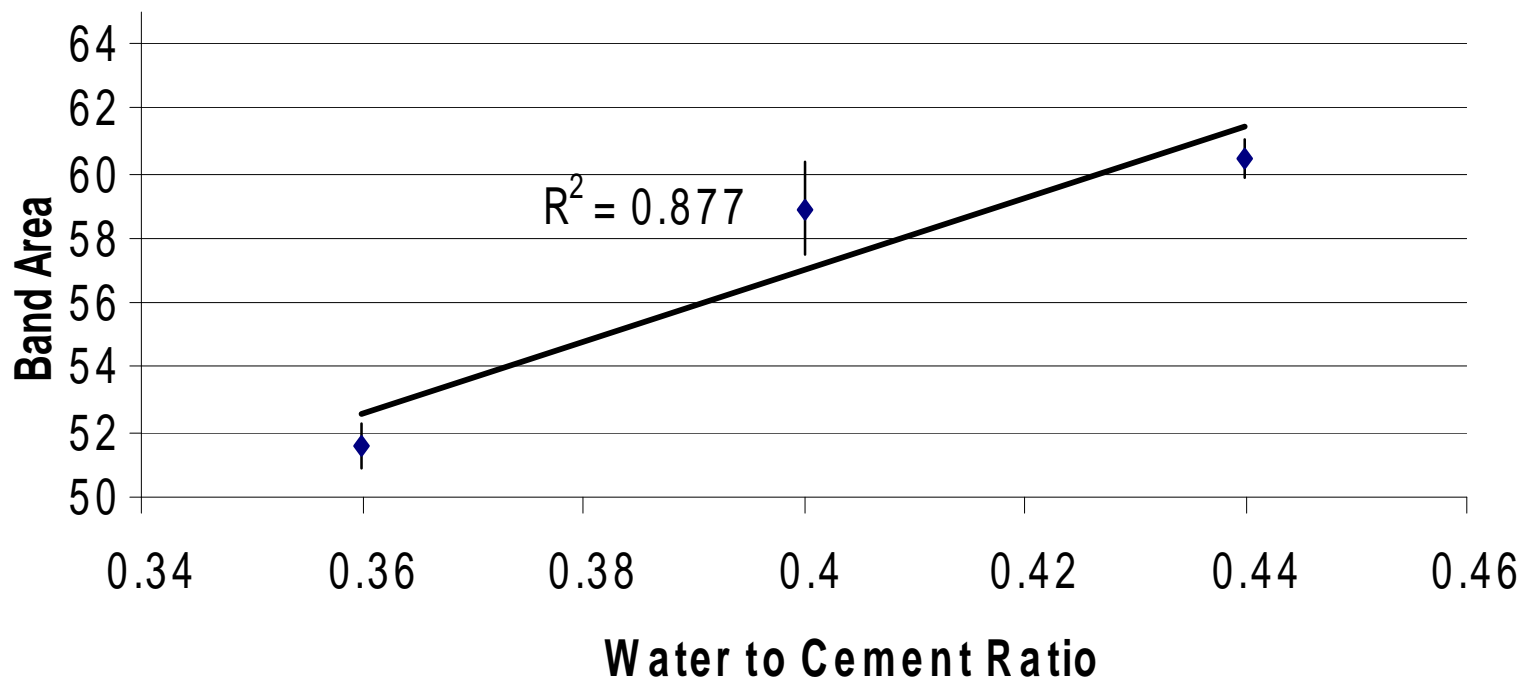
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Ashgrove Cement with Daravair**



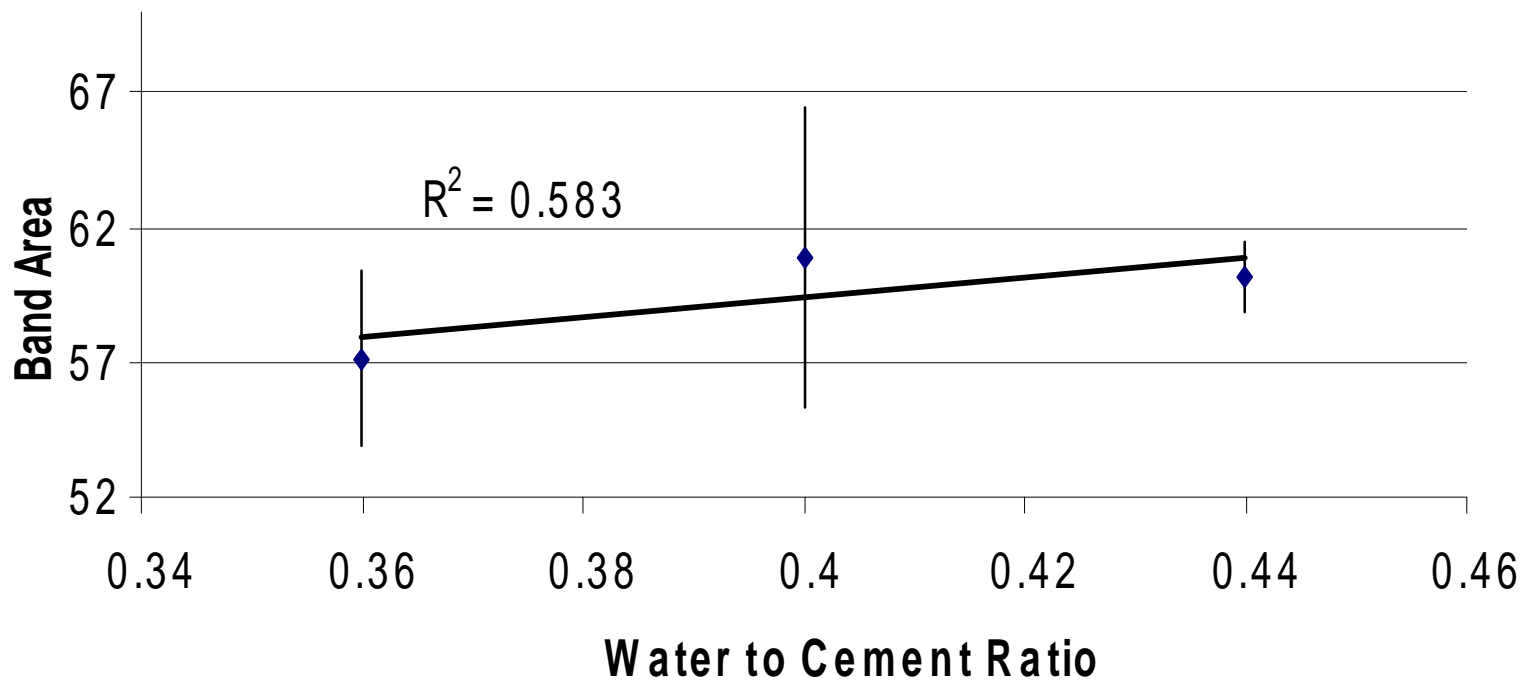
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Durapozz Cement with Daravair**



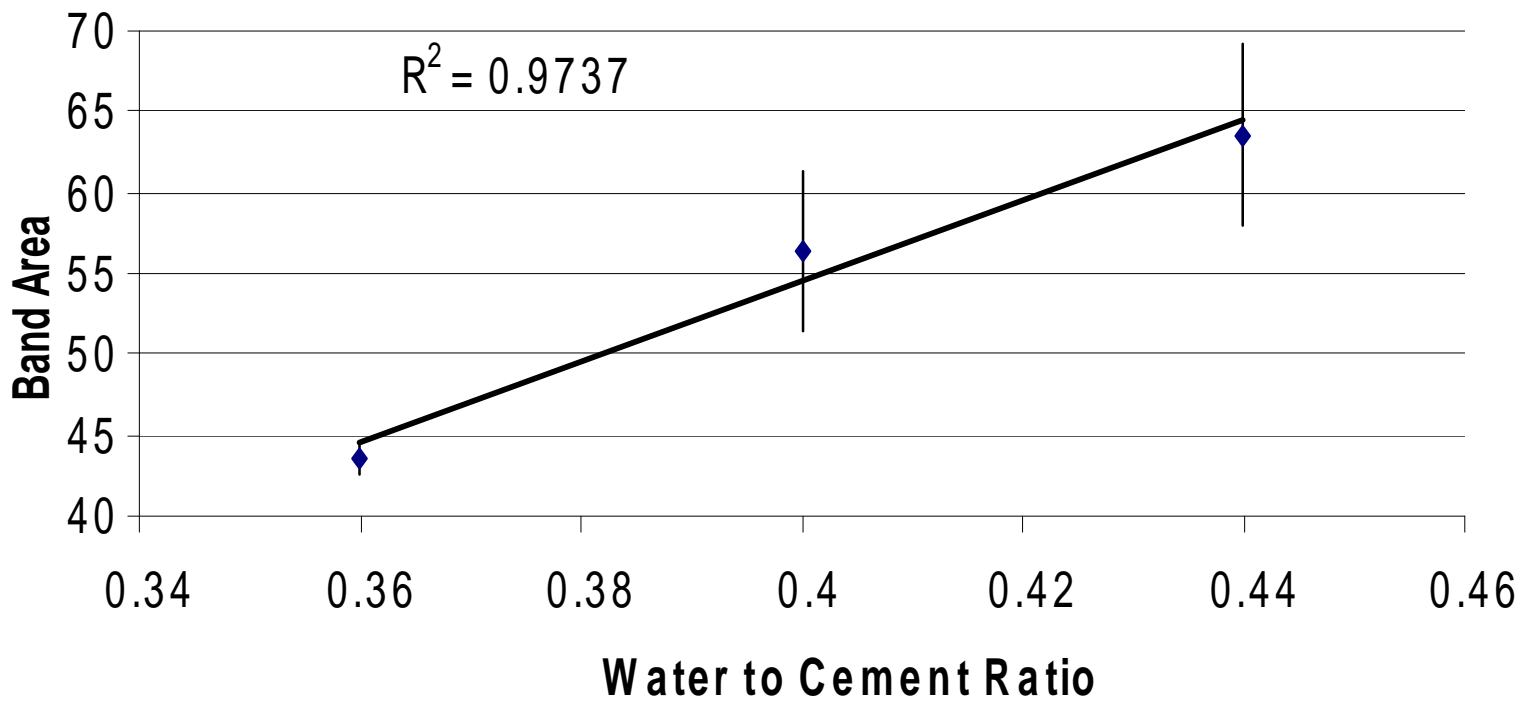
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Lonestar Cement with Daravair**



**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Medusa Cement with Daravair**

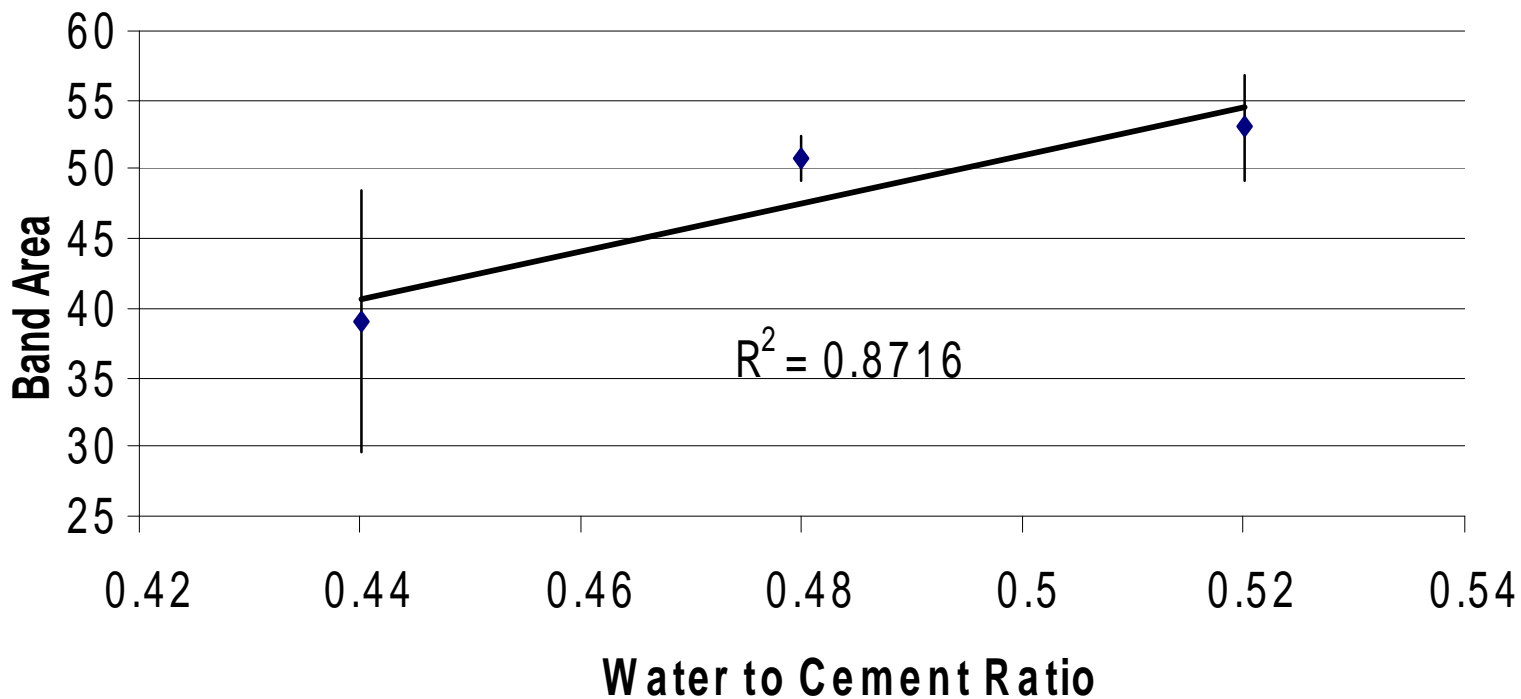


**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Monarch Cement with Daravair**

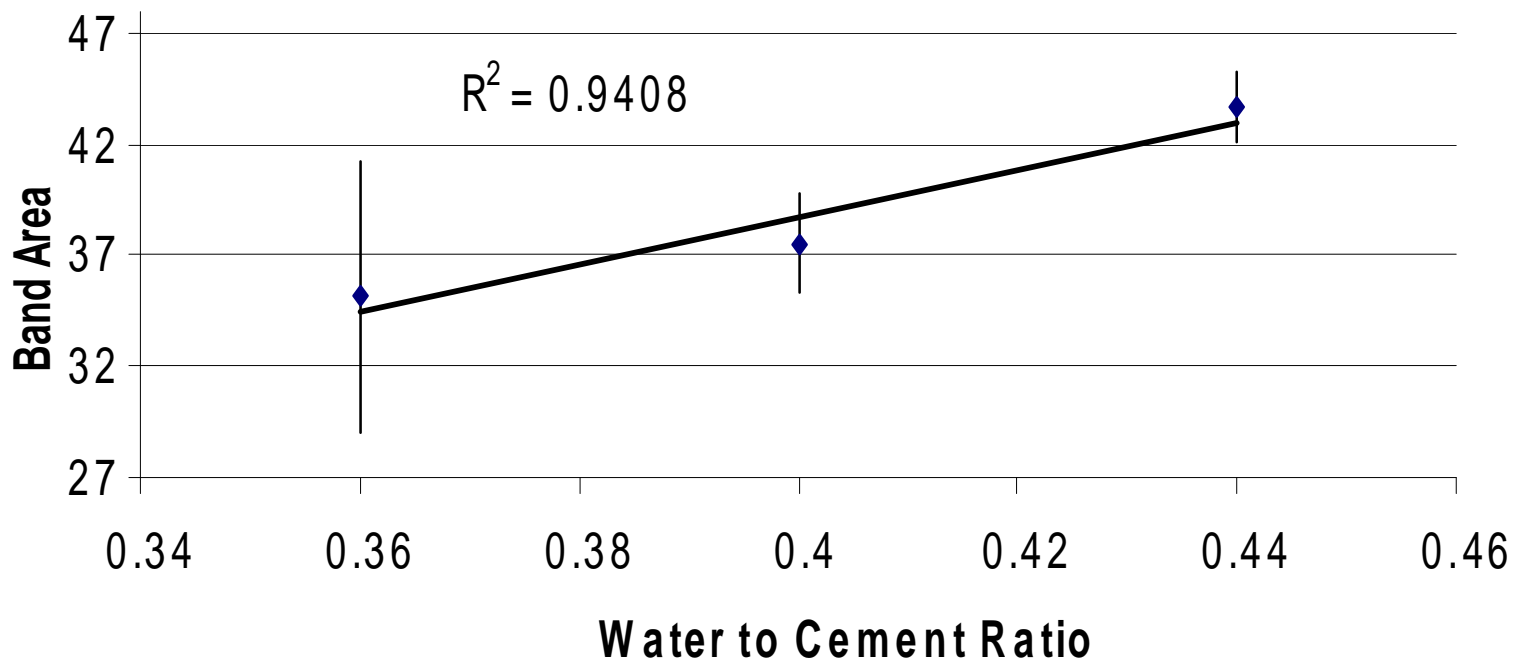


Appendix B: Beer's Law Plots of Concretes

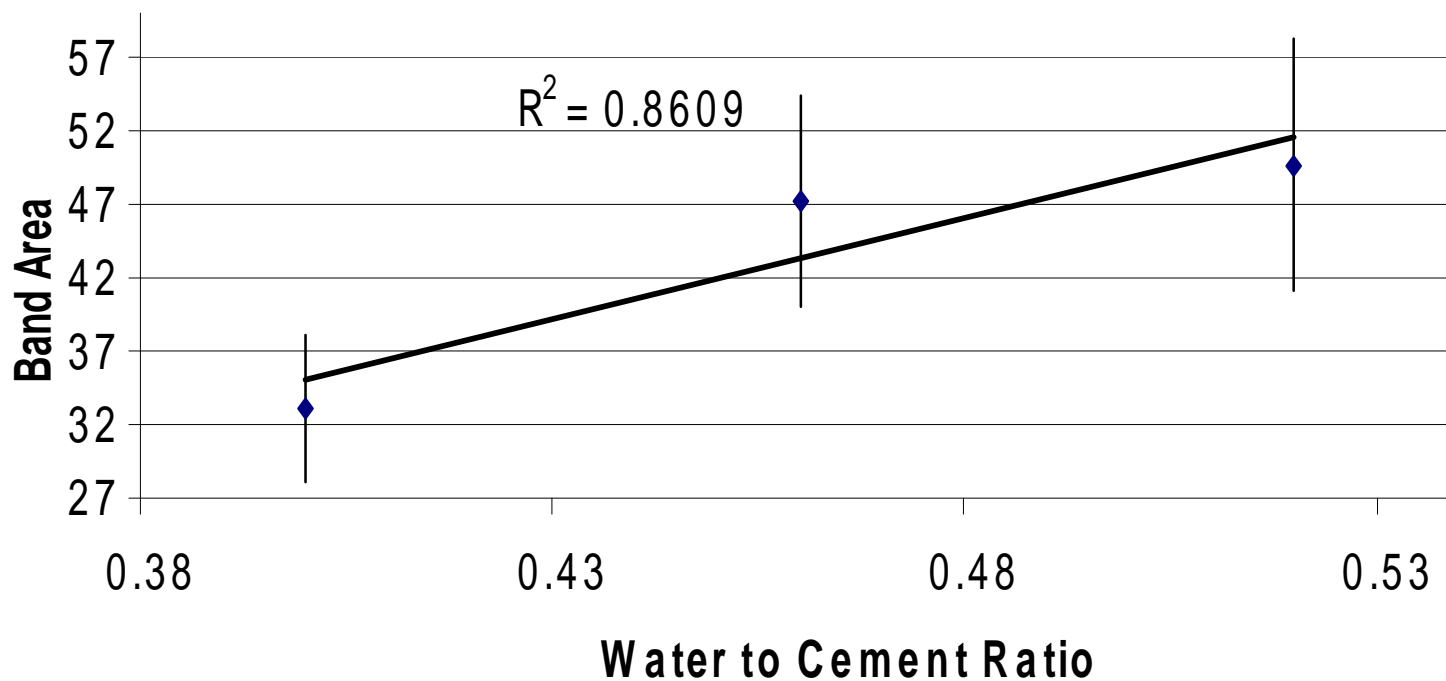
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Concrete Mix #1**



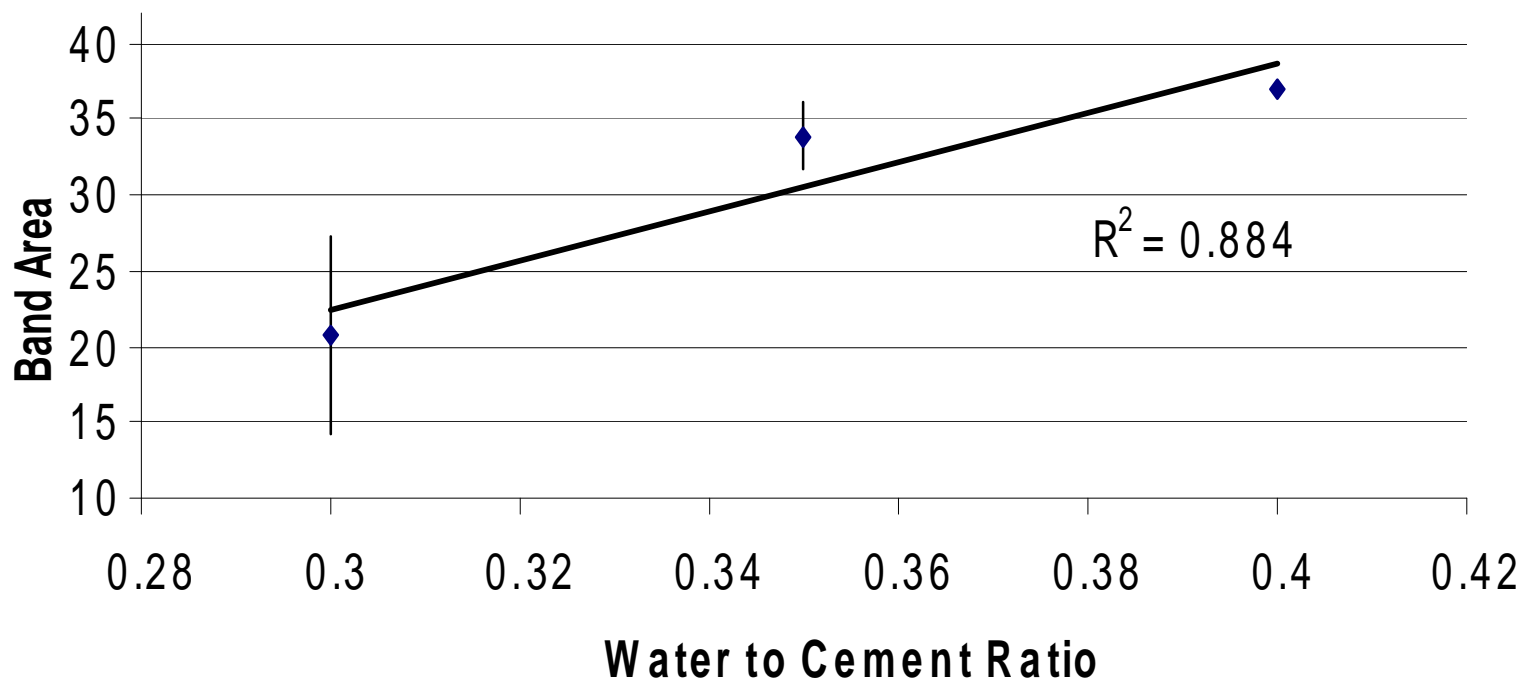
**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Concrete Mix #2**



**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Concrete Mix #3**



**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Concrete Mix #4**



**Band Area (5280 to 4625 wavenumbers)
vs. Water to Cement Ratio
Concrete Mix #5**

