

# UNIVERSITY OF NORTH★TEXAS™

## **Application of FTIR for Quantitative Lime Analysis**

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16. Abstract  <p>TxDOT currently uses the titration method for the quantitative analysis of lime samples. The titration method is time consuming (hours if not an entire day is spent for each analysis) and it is not an accurate test due to chemical interferences and sample preparation variances. In addition, the titration method consumes chemicals that are costly and add to hazardous waste inventory. On the other hand, lime and its related materials absorb Infrared rays and exhibit their fingerprint spectra that are free of spectral interferences. In this implementation project, application of Fourier Transform Infrared spectroscopy (FTIR) was investigated for rapid and accurate quantitative analysis of lime from three forms including quick lime, hydrated lime and slurry lime. Calibration curves relating absorption relative intensities of lime to lime concentrations (for both quicklime and slurry lime samples) were generated that showed <math>R^2 = 0.88</math>, and will be utilized to quantify lime content of an unknown sample. Sample preparation method for different forms of lime is discussed and precautions to consider for interference avoidance are discussed. Results indicated that FTIR is a safe and straightforward method that requires minimal operator training and expertise. Finally, a testing protocol for lime quantification using FTIR was developed.</p>			
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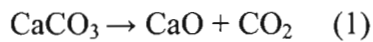
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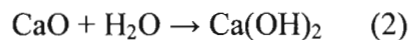
## 1.0 Background and Significance of Work

Lime or calcium oxide (CaO) is produced through the calcinations process of lime kiln at high temperatures. Lime also refers to calcium hydroxide, Ca(OH)<sub>2</sub> and magnesium hydroxide, Mg(OH)<sub>2</sub>, which are the hydroxides produced from this reaction of the oxide and water. In the case of calcium oxide, CaO the reaction occurs readily and is highly exothermic. Both Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> are chemical bases. Lime is an important chemical widely used for neutralization of acidic solutions as a cheap alkali and has numerous applications in building and construction, where it can be utilized in masonry cement. In brick-laying applications it is well known that addition of a small amount of lime to the mortar improves elasticity, workability, and water-retention to the mixture. Lime is produced through heating of limestone (CaCO<sub>3</sub>) at elevated temperatures ranging from 1850 °C to 2450 °C as shown in reaction 1.



According to reaction 1, the main source of lime is limestone, which itself has a natural source in some cases from oyster shells [1]. Therefore, depending on the purity of the natural source, the amount of “available lime” varies from one source to another. Nature does create predominantly limestone deposits composed of predominantly calcium carbonate; however, these locations are considerably fewer than those of dolomitic limestone (high Calcium limestone). Calcium oxide will react readily with water at normal temperatures to produce calcium hydroxide and an excess of heat; this is an exothermic process.

Three common types of lime used in pavement industry include quicklime, hydrated lime, and slurry lime. Quicklime (CaO) is a powder with the highest available lime (about 100%) among the three forms. Hydrated lime (Ca(OH)<sub>2</sub>) is produced by the hydration of quicklime according to reaction 2.



Based on reaction 2, it takes 56 lbs of lime and 18 lbs of water to make 74 lbs of hydrated lime. In its simplest form, 56 lbs of quicklime is equivalent to 74 lbs of hydrated lime. Therefore, quicklime has 1.32 times more available lime compared to hydrated lime, as it is the molar weight ratio of Ca(OH)<sub>2</sub>/ CaO. Slurry lime contains the least amount of available lime, but is

suitable for some applications. Table 1 presents Standard Transportation Commodity Code (STCC), Chemical Abstract Service (CAS), and the Environmental Protection Agency (EPA) reference identifications for different lime forms.

**Table 1: Reference identifications for lime samples[1].**

<b>Reference</b>	<b>Quicklime</b>	<b>Hydrated Lime</b>
<b>STCC</b>	32-741-10	32-741-11
<b>CAS#</b>	1305-78-8	1305-62-0
<b>EPA#</b>	A350-2789	S349-3522
<b>Chemical Name</b>	calcium oxide	calcium hydroxide
<b>Formula</b>	CaO	Ca(OH) <sub>2</sub>
<b>Molecular Wgt</b>	56.08	74.09
<b>Mol. Wgt. Ratio</b>	1	1.32

### **1.1 Existing standard methods for lime quantification and their drawbacks**

ASTM C25 (American Society for Testing and Materials standard) and AWWA B202 (American Water Works Association) tests are two commonly used standard test procedures for lime quality control. In these methods, available lime in a given sample is determined by solubilization of the calcium through the use of a concentrated sugar solution to form calcium succrate. The laboratory steps in the two tests are very similar. The sample of quicklime or hydrated lime is pulverized, weighed, and mixed with a specified amount of water in a flask. The flask is heated and a specified amount of additional boiling water is added to compensate for evaporation. The flask is swirled and boiled for a minute, then placed in a cold water bath to cool it to room temperature. It is noteworthy that the solubility of lime is inversely proportional to temperature. Sugar is added, and then the flask is swirled and allowed to stand for 15 minutes, with periodic additional swirling to allow the sugar and lime reaction to take place. Phenolphthalein solution serving as a pH change indicator is added, and the sample is titrated until the first disappearance of the pink color that lasts for at least three seconds. The burette is then read to determine the available calcium oxide percentage (CaO%). Both tests require a specified sample weight and a specified acid normality such that 1 ml of the volume of acid used

equals 1% CaO. This way laboratory personnel simply read the volume of the acid in number of milliliters used that equates the percentage of available lime in the sample.

Precise knowledge of lime sample weight, incomplete solubility of lime in solution, poor end point detection in the titration process, prolonged time requirement for the complete analysis, and sample weight change due to air slaking (described below) are among the drawbacks to these procedures that warrant the need for development of a rapid and reliable method for lime quantification.

All forms of quicklime immediately begin to undergo *air slaking* when exposed to any moisture in the air [1]. This simply means that the moisture in the air reacts with the quicklime to form calcium hydroxide. This process occurs all the time, but has its greatest effect when the sample has been pulverized to a powder. The surface area of the quicklime is increased dramatically, which increases the rate of air slaking. Weighing the sample to a very specific, designated weight requires the laboratory personnel to take extra time in weighing at which point air slaking of the sample is occurring. Depending upon the extra time required, the sample weight can change to varying degrees. Although modifications to these procedures have been proposed [2], results obtained in such tests are not error-free due to experimental and chemical interferences in the titration process. In addition, these test procedures are slow and tedious.

## **1.2 Application of FTIR for lime quantification**

Fourier Transform Infrared Spectroscopy is a well-established analytical technique used for analysis of solids, liquids and gases. This technique is routinely used for research and development, as well as quality control/quality assurance in many industries including pharmaceutical, paper and pulp, and polymers and plastics. FTIR was primarily developed for analysis of organic matters based on their chemical bonding characteristics, but more and more, this technique is finding its applications in the analysis of inorganic matters like oxides, nitrides, etc. Relatively weaker chemical bonds in organic matters excite easier than stronger bonds between a metallic element like iron and oxygen; however, chemical bonding in many oxides including CaO and oxide-hydroxide such as  $\text{Ca}(\text{OH})_2$  are weak enough to generate a vibration spectrum that could be used for analytical purposes. The fact that lime and its derivatives

produce an interferometer spectrum will be utilized in this project to quantitatively analyze lime samples.

**1.2.1 Working Principle:** FTIR involves the twisting, rotating, bending, and vibration of the chemical bonding (Figure 1). Let incident infrared radiation intensity be  $I_0$  and  $I$  be the intensity of the beam after it interacts with the sample. The ratio of intensities  $I/I_0$  as a function of frequency of light gives a spectrum, which can be in three formats: as transmittance, reflectance, and absorbance. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum, which is a unique characteristic of the functional groups comprising the molecule, and also the configuration of the atoms. A detector is used to read out the intensity of light after it interacts with the sample. The typical setup of a FTIR is as shown in the Figure 2. The author has successfully applied this technique for the identification and characterization of iron oxides [3-6]. Specifically, magnetite and maghemite that are not differentiable with popular x-ray diffraction technique were successfully identified by FTIR [5].

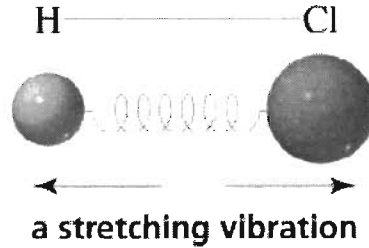
Advantages of applying this technique for quantification of lime include:

- Minimal sample preparation
- Fast, reliable, and robust analysis
- No need of messy chemicals
- No spectra interferences
- Fully computerized analysis
- Ease of operation and minimal operator training and expertise

## The IR Experiment

### Stretching Vibrations

Atom positions with respect to each other are not fixed !!  
There are relative movements to each other, which can be described by a spring-model.  
Considering two atoms results in the following model



Energy-uptake can be accomplished by electromagnetic radiation

### Stretching and Bending Vibrations of three atoms

a) stretching:

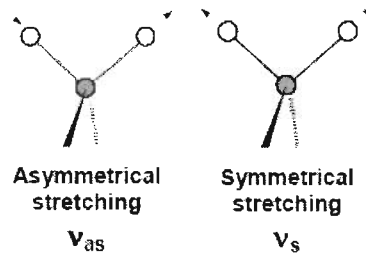


Figure 1: Stretching and bending vibrations of atoms due to absorption of IR radiation.

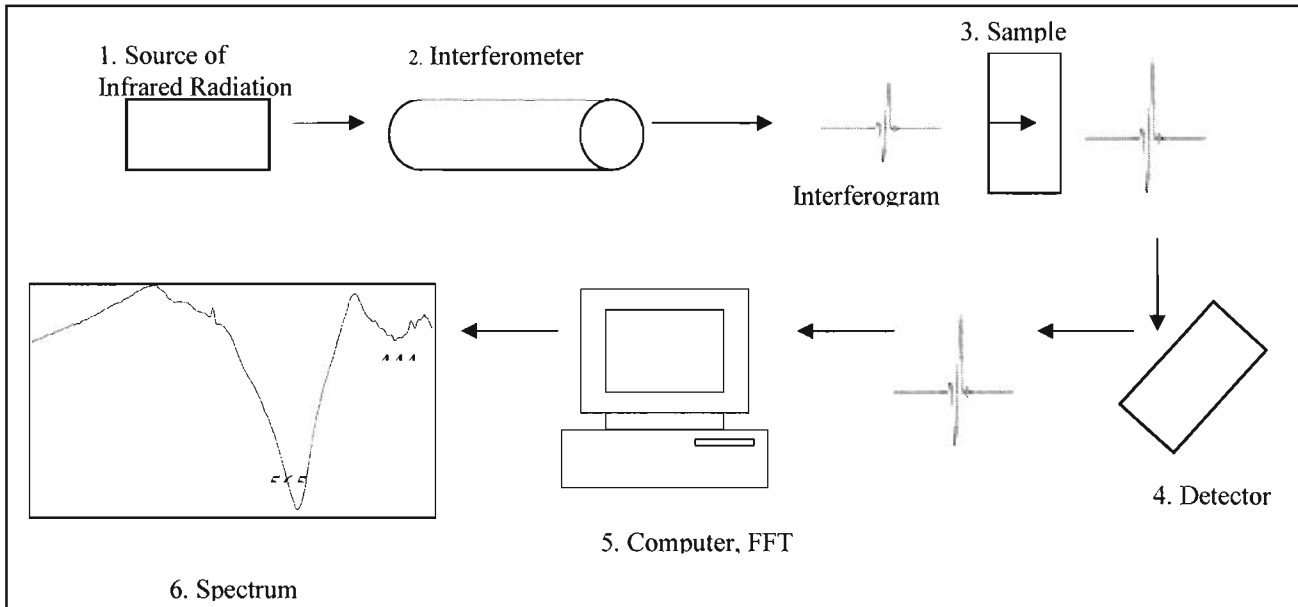
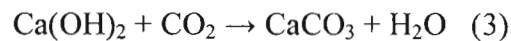


Figure 2: Experimental set-up for Fourier Transform Infrared Spectroscopy.

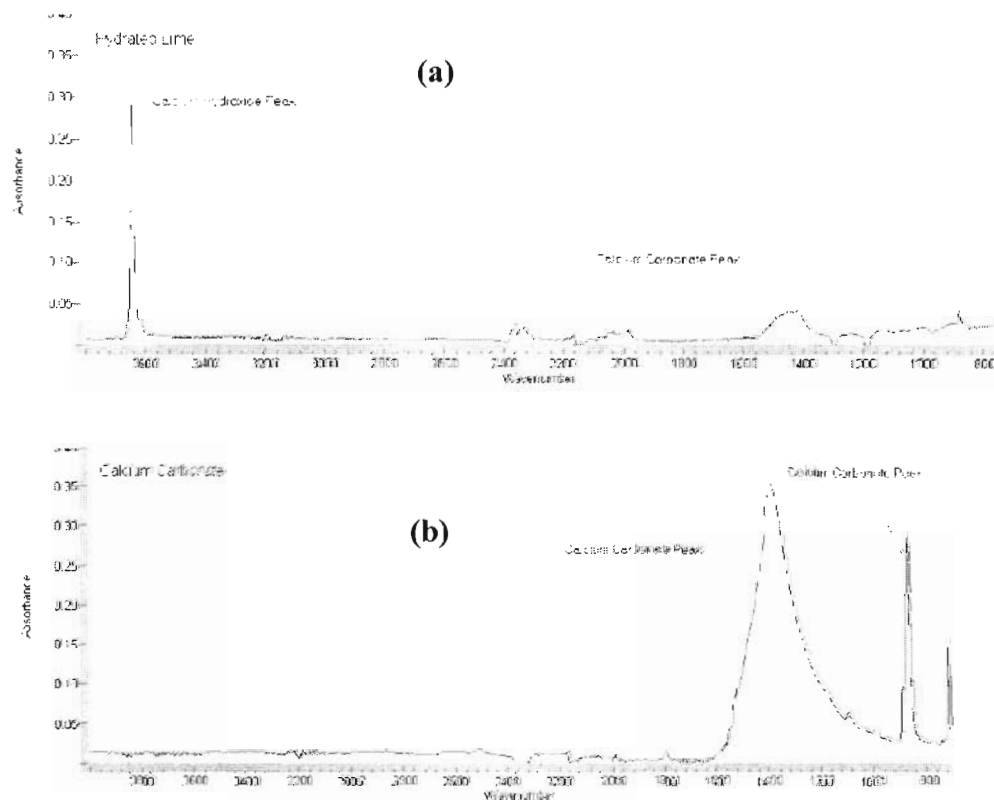
(Adapted from Richard Brundle et al, 1992)

## 2.0 Literature review

T. Arnold et al [7] used FTIR for quantitative determination of lime in hot-mix asphalt. Their results show hydrated lime exhibited a sharp peak at a wave number of  $3640\text{ cm}^{-1}$  due to the presence of the hydroxyl group in  $\text{Ca}(\text{OH})_2$  (Figure 3.a). They suggested that this sharp peak could be used to demonstrate the presence and quantify the amount of lime. They assigned a peak at about  $1390\text{ cm}^{-1}$  to C-O stretching that they related to a calcium carbonate impurity. The presence of calcium carbonate could be explained by reaction 3.

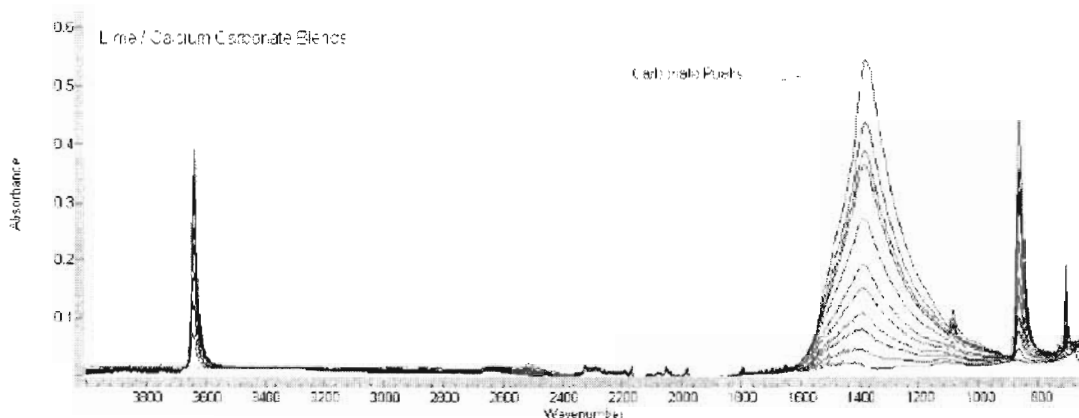


They clearly showed that the FTIR spectrum of calcium carbonate does not show one peak at  $3640\text{ cm}^{-1}$ , but rather shows two peaks: one at  $1390\text{ cm}^{-1}$ , and the other at  $866\text{ cm}^{-1}$  (Figure 3.b). Their analysis based on the linearity of the relationship between the  $3640\text{ cm}^{-1}$  peak area and the lime concentration showed a correlation factor,  $R^2$ , of 0.968 and based on peak height yielded an  $R^2$  of 0.977. They did similar analysis for calcium carbonate based on  $1390\text{ cm}^{-1}$  and  $866\text{ cm}^{-1}$  peaks, and obtained an  $R^2$  of roughly 0.97, irrespective of the peak used, peak area, or height.



**Figure 3: FTIR spectra of hydrated lime (a) and calcium carbonate (b) [7].**

The T. Arnold group further suggested that visual examination of the FTIR spectrum provides an instant indication of lime quality. To demonstrate this, they used the existence of the peak at  $1390\text{ cm}^{-1}$  to indicate the presence of calcium carbonate impurity as shown in Figure 4. Figure 4 shows a series of superimposed spectra from samples with different carbonate amounts.



**Figure 4: Superimposed FTIR spectra of lime-calcium carbonate blends.**

Legodi et al [8] recommended FTIR as a rapid analytical tool for quantitative determination of  $\text{CaCO}_3$  in mixtures containing  $\text{Ca}(\text{OH})_2$ . In their analysis, they integrated carbonate bands between  $2646\text{--}2423\text{ cm}^{-1}$ ,  $1833\text{--}782\text{ cm}^{-1}$ ,  $954\text{--}724\text{ cm}^{-1}$ , and  $930\text{--}730\text{ cm}^{-1}$ . They calculated the fraction of  $\text{CaCO}_3$  present by integrating the bands at various wave numbers relative to the intensity in the same region of the spectrum of the 100%  $\text{CaCO}_3$  sample. Their results show a correlation coefficient of 0.993 and 0.987 when they used absorption bands around  $2646\text{--}2423\text{ cm}^{-1}$  and  $1833\text{--}1782\text{ cm}^{-1}$ , respectively. Zaki et al [9] show a spectrum of  $\text{CaO}$  that displays a sharp band at  $3656\text{ cm}^{-1}$ , two broad weak bands centered around  $3822$  and  $3388\text{ cm}^{-1}$ , a medium doublet centered around  $1444\text{ cm}^{-1}$ , and a very strong absorption below  $600\text{ cm}^{-1}$ . Figure 5 shows Zaki's IR spectra of  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{CaCO}_3$ . According to Zaki, Figure 5 reveals that all of the absorptions displayed for  $\text{CaO}$  are rather similar to those exhibited by the pure  $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$ . McDevitt and Baun [10] were quoted by Zaki that there are two IR absorption bands characteristics of  $\text{Ca-O}$  lattice vibrations of pure  $\text{CaO}$ , a broad, strong absorption band centered around  $400\text{ cm}^{-1}$ , and a medium strong band at  $290\text{ cm}^{-1}$ . Zaki further suggested that rehydration of  $\text{CaO}$  by means of ambient water molecules converts  $\text{CaO}$  into  $\text{Ca}(\text{OH})_2$ . Gonzalez et al [11] indicated that Calcium oxide has a broad band between  $250$  and  $600\text{ cm}^{-1}$  corresponding to a stretching vibration of the  $\text{Ca-O}$  group.

According to F. Bosch Reig and his colleagues [12], in constant ratio method “the standard compound must be chemically and spectrally compatible with the sample, in other words, homogenous, stable sample-standard mixtures must be obtained. Furthermore, the standard must have a measurable absorbance signal in an area free of absorbance bands from the sample itself.” Table 2 shows peaks and baselines used for calcium carbonate and silica quantification, using the potassium ferricyanide standard.

**Table 2: Peaks and baselines used for calcium carbonate and silica quantification, using the potassium ferricyanide standard [12].**

Compound	Peak height	$\nu_{\max}$ (cm <sup>-1</sup> )	Base line (cm <sup>-1</sup> )
Potassium ferricyanide	F	2115	2082 – 2163
Calcium carbonate	C <sub>1</sub>	875	728 <sup>a</sup>
	C <sub>2</sub>	712	630 <sup>a</sup>
Silica	S <sub>1</sub>	796	831 – 709
	S <sub>2</sub>	779	831 – 709

<sup>a</sup> Horizontal base line tangent at wavenumber indicated.

In the constant ratio method, the concentration of analyte in the sample is directly proportional to the analyte/standard absorbances and the concentration of the standard. The proportionality constant  $K_{M,p}$  given in Equation (1) is the characteristic parameter of the system:

$$C_M = K_{M,p}(\nu_1, \nu_2) \cdot C_p [A_M(\nu_1) / A_p(\nu_2)] \quad (1)$$

where  $C_M$  is the concentration of analyte,  $K_{M,p}(\nu_1, \nu_2)$  is the proportionality constant,  $C_p$  is the concentration of the internal standard,  $A_M(\nu_1)$  is the absorbance of the analyte at the wavenumber  $\nu_1$ , and  $A_p(\nu_2)$  is the absorbance of internal standard at the wavenumber  $\nu_2$ . In this method, the proportionality constant is determined experimentally. Furthermore, Reig et al. emphasized the importance of solid inorganic particle size their distribution that must be kept under control to obtain a reproducible proportionality constant. X-ray diffraction is another technique used for the quantitative analysis of lime [13-17].



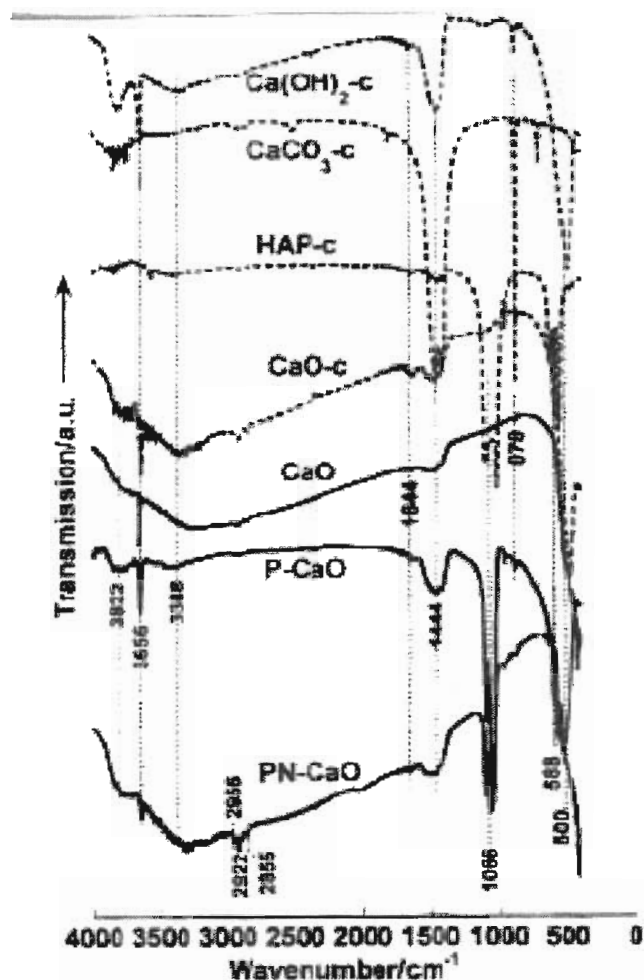


Figure 5: IR spectra of calcium oxide and calcium hydroxide shown by Zaki et al [9].

Based on available literature information gathered so far, a list of candidate FTIR peaks that could possibly be used is given in Table 3.

**Table 3: Infrared absorption bands for lime and its derivatives.**

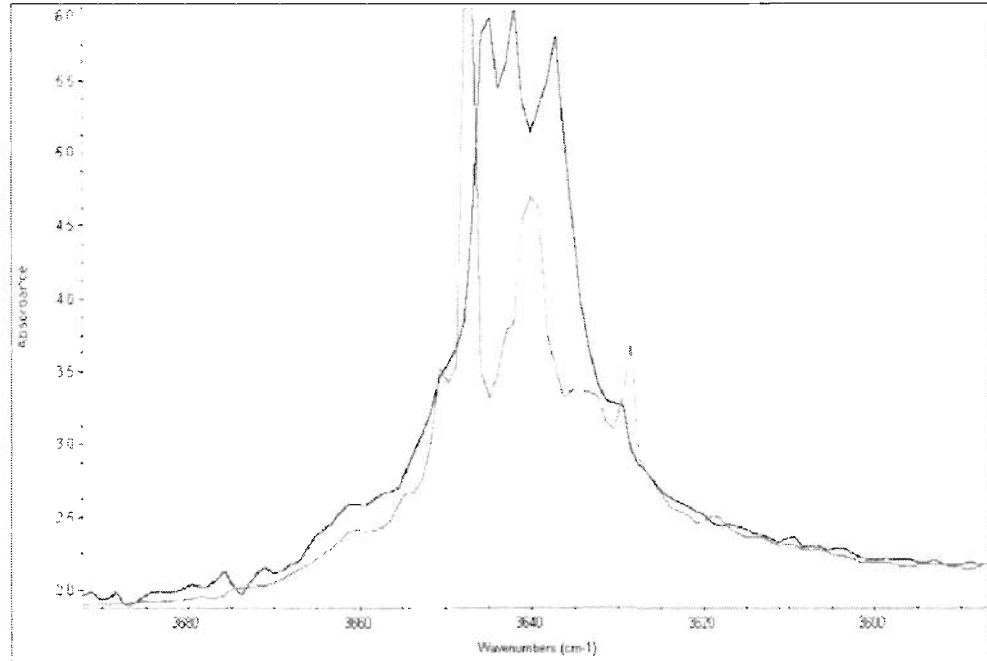
Phase	FTIR Absorption Band	Reference	Comments
Quicklime (Calcium oxide, CaO)	3640 cm <sup>-1</sup>	7	Sharp peak
	*3656cm <sup>-1</sup> , **3822 cm <sup>-1</sup> ,	9	*Sharp band,
	**3388cm <sup>-1</sup> ,	9	**Broad and Weak
	*1444 cm <sup>-1</sup> , **<600 cm <sup>-1</sup>	9	*Medium, *v.Strong
	*400 cm <sup>-1</sup> , **290 cm <sup>-1</sup>	10	*Broad & Strong,
	250-600 cm <sup>-1</sup>	11	**Medium-Strong Broad band
Hydrated lime (Calcium Hydroxide Ca(OH) <sub>2</sub> )	Overlapping bands with Quicklime	9	
Calcium Carbonate (CaCO <sub>3</sub> )	1390 cm <sup>-1</sup> , 866 cm <sup>-1</sup>	7	
	2646-2423 cm <sup>-1</sup> , 1833-782cm <sup>-1</sup> ,	8	
	954-724 cm <sup>-1</sup> , 930-730 cm <sup>-1</sup>		

The literature search will be conducted to compile a large collection of FTIR spectra from different sources for phases of interest including spectra of high purity standards acquired from reliable sources like NIST etc. This process will identify common sources of impurities and their FTIR spectra so that peak/band assignment to a given spectrum is done reliably.

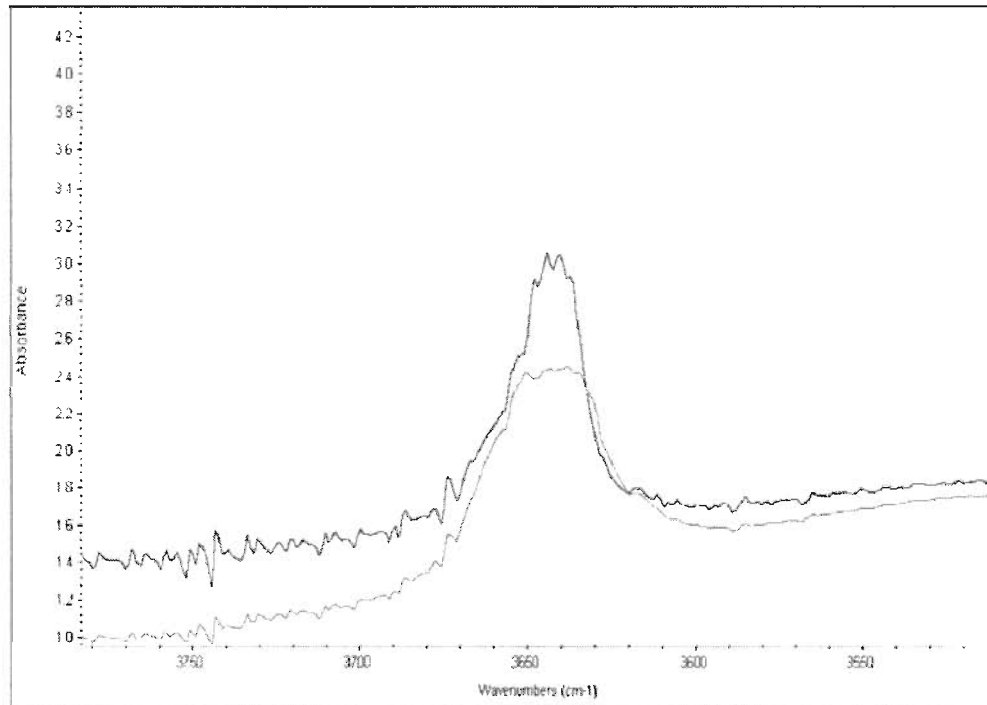
### **3.0 Research Method**

The Research Method for this study is experimental. The Nicolet Avatar 370 was used to collect all FTIR spectra and the accompanying E-Z Omnic software was used to analysis the collected spectra. Experiments were performed with the ATR attachment and the standard transmission setup, it was decided that the standard transmission setup was easier to manage sample amounts.

Several experiments were performed to identify what factors affected the results of FTIR test. Some of the factors that were experimented with were compression strength, sample sizes, atmosphere exposure, and type of FTIR test (transmission or reflection). Figure 6 shows how the variation in compression strength affects the FTIR spectra, the variation demonstrates an inconsistent peak profile. Another factor that was identified from the literature review as a potential factor was exposure to humidity in the atmosphere. Time trials were performed that exposed samples to the atmosphere, Figure 7 shows the profiles of samples exposed to the atmosphere for different amounts of time. Sample sizes are also important; too much sample in the pellet could lead to peaks that max out the FTIR scale for absorbance. It was also determined that transmission is superior to reflectance test for quantitative purposes. With these factors in mind a protocol was developed which will maximize repeatability, precision, and accuracy. A complete protocol was developed and is given in Appendix A.



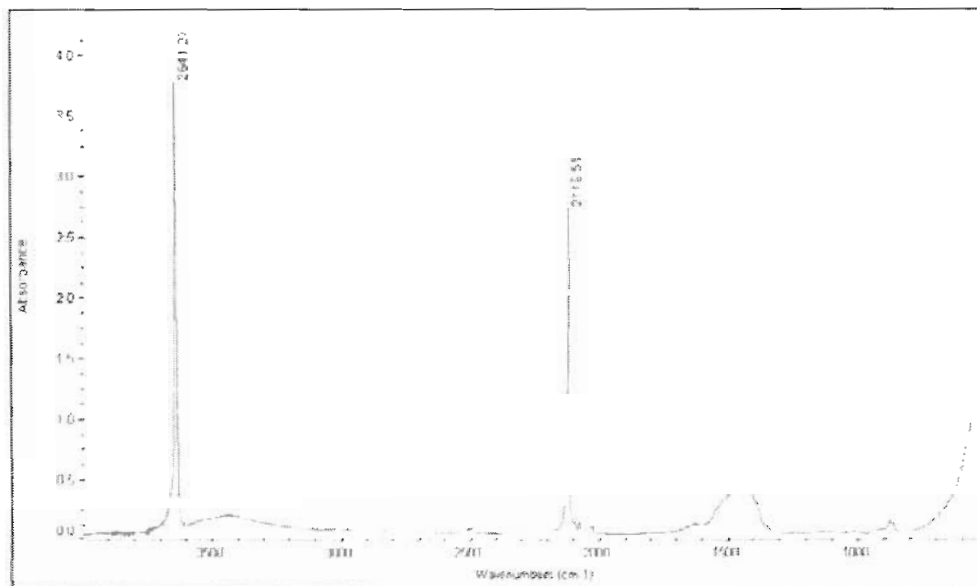
**Figure 6: Variation in Pressure in Pellet Die.  
Light Blue-5kpsi; Dark Blue-10kpsi; Red-15kpsi.**



**Figure 7: Variation in Atmosphere Exposure.  
Green-24hrs; Blue-48 hrs; Red-72 hrs.**

Using the principle of relative intensity ratios this research developed a method for lime quantification. The method involves using an internal standard to eliminate variation in peak

height from the same sample from run to run. The internal standard that was chosen for this method was Potassium Ferricyanide. This standard was chosen because of its limited featured spectra which will not interfere with the peaks that are to be analyzed from the calcium oxide. Figure 8 shows the spectra of calcium oxide with the standard, notice the only peak that is a result of the standard is the 2115 $\text{cm}^{-1}$  peak.

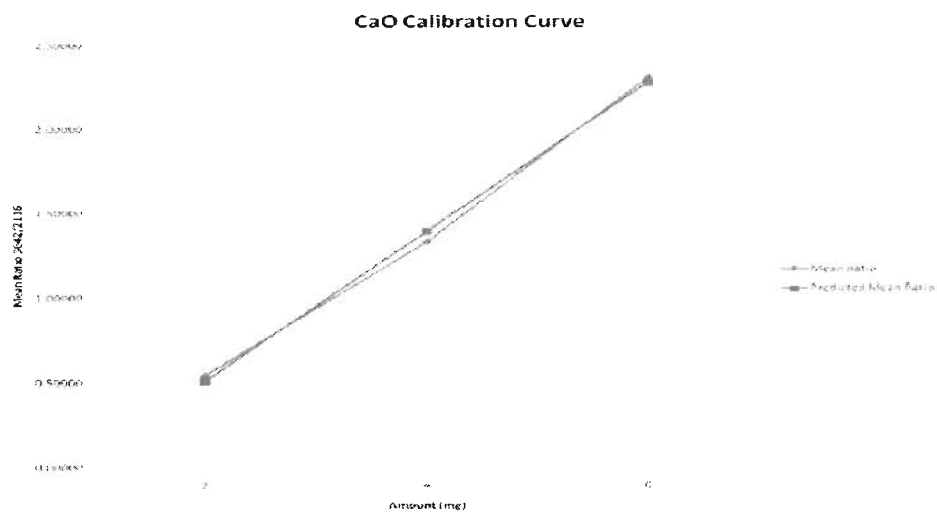


**Figure 8: Calcium Oxide (3640 peak) and Potassium Ferricyanide (2115 peak).**

#### **4.0 Results and Discussions:**

##### **4.1 FTIR Analysis of commercial Calcium Oxide:**

Figure 9 shows incremental amount of a commercial high purity CaO. With larger concentrations of CaO the peak height ratio with the internal standard increases. The linear regression used, generated an  $R^2$  value of 0.99.



**Figure 9: CaO Calibration Curve.**

#### 4.2 FTIR Analysis of Field Quicklime Samples:

Four Quicklime samples with known compositions were provided to researchers and 8 samples of each quicklime batches were prepared for FTIR transmittance measurements. Results of characteristics absorption band for CaO (absorption band at  $878\text{ cm}^{-1}$ ) in reference to absorption band of Potassium Ferricyanide ( $2116\text{ cm}^{-1}$ ) were measured and results were tabulated in Table 4. Appendix B contains FTIR spectra of all samples analyzed.

**Table 4: FTIR absorption band ratio of CaO/Potassium Ferricyanide for four Quicklime field samples.**

	Quicklime			
	878/2116			
	J06482349	J06482398	J07481649	J07481648
1	0.0259	0.0356	0.0054	0.0084
2	0.0302	0.0368	0.0062	0.0080
3	0.0282	0.0384	0.0050	0.0088
4	0.0273	0.0350	0.0058	0.0081
5	0.0262	0.0372	0.0060	0.0092
6	0.0280	0.0400	0.0064	0.0085
7	0.0230	0.0370	0.0051	0.0080
8	0.0273	0.0355	0.0056	0.0078
AVG	0.02700	0.03694	0.00569	0.00835
STD	0.00210	0.00166	0.00050	0.00047
%STD	8%	4%	9%	6%

Variation in absorption intensities ratios measured for different samples are shown in Table 4.

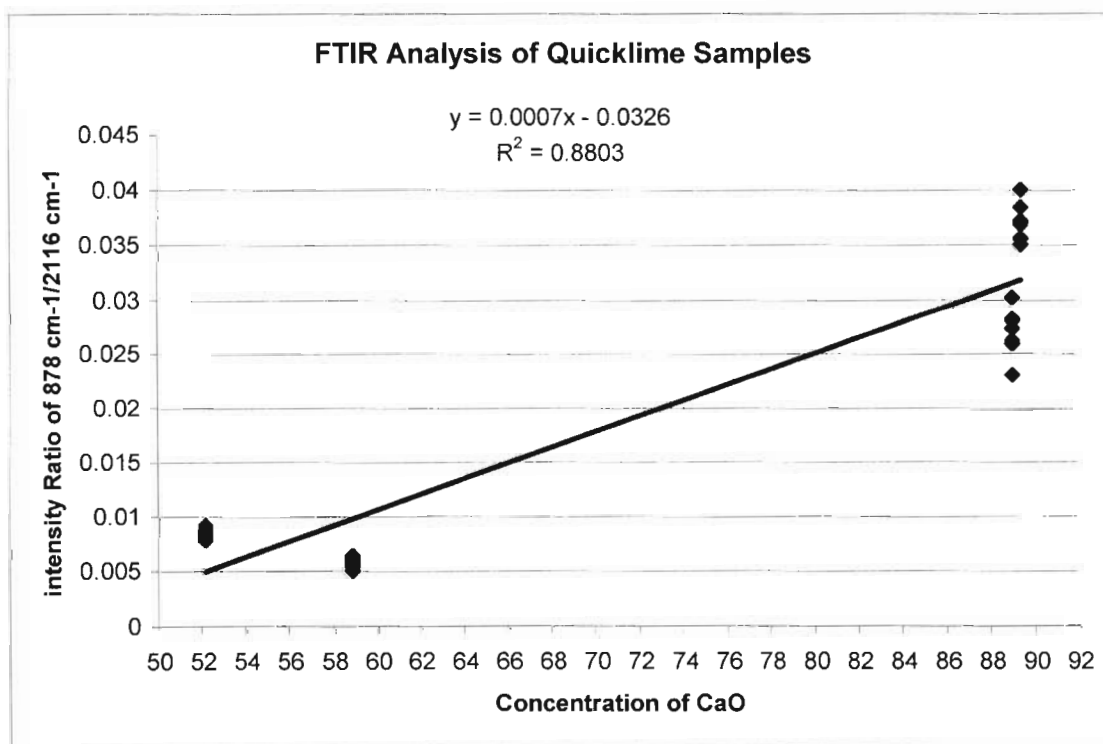
Sample J0642349, J06482398, J07481649, and J07481648 showed 8,4,9, and 6 percent variations

with respect to their standard deviations respectively. Summary of known composition and measured FTIR intensity ratio for 878 cm<sup>-1</sup>/2116 cm<sup>-1</sup> is shown in Table 5.

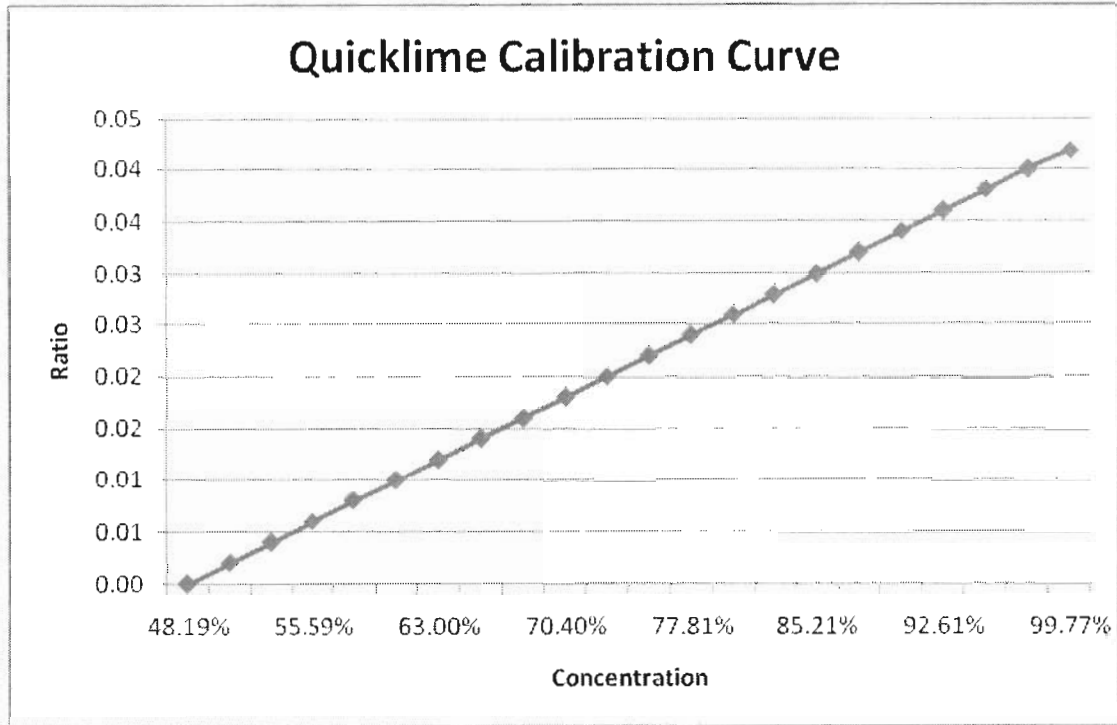
**Table 5: CaO Concentration and FTIR intensity ratio for 878 cm<sup>-1</sup>/2116 cm<sup>-1</sup> absorption bands for four known field samples.**

Sample	Quicklime	
	Concentration	Ratio
J06482349	88.9%	0.02700
J06482398	89.3%	0.03694
J07481649	58.8%	0.00569
J07481648	52.1%	0.00835

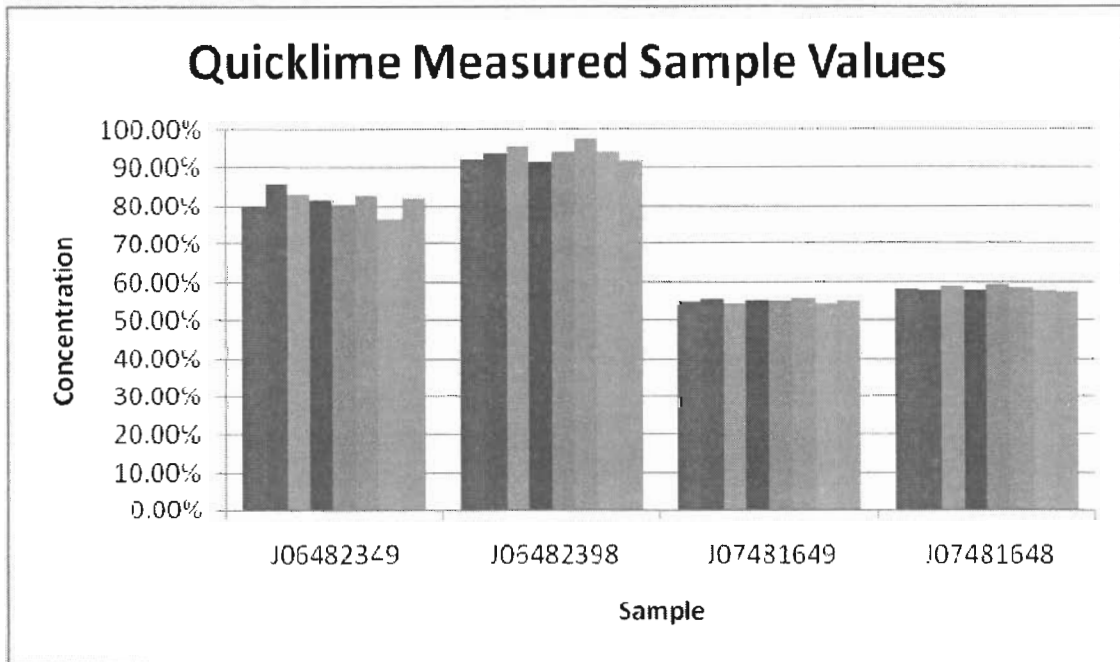
A linear regression analysis was done based on complete data given in Table 4 and Figure 10 presents a intensity ratio vs CaO concentration showing an R<sup>2</sup> of 0.88. A generalized trend based on data provided in Table 4 shows R<sup>2</sup> of 0.88. Figure 11 shows calibration curve for Quiclime based on the mathematical model developed and Figure 12 represent variation of Quicklime concentration for each measurement based on the developed model.



**Figure 10: Intensity ratio vs CaO concentration for known field Quicklime samples.**



**Figure 11: Quicklime calibration curve based on the mathematical model.**



**Figure 12: Variations of CaO concentration based on the mathematical model.**

#### 4.3 FTIR Analysis of Field Slurry Samples:

Three field slurry samples were received and analyzed using FTIR. FTIR absorption band at  $3641\text{ cm}^{-1}$  that is the characteristic band for hydrated and slurry calcium hydroxide was used in

reference to absorption band at 878 cm<sup>-1</sup>. Measured values of the absorption band ratios for 8 separate measurements from 8 samples are given in Table 6. Average ratio, standard deviation and percent standard deviation for these measurements are included in Table 6. Summary of known composition and measured FTIR intensity ratio for 3641 cm<sup>-1</sup>/878 cm<sup>-1</sup> is shown in Table 7.

**Table 6: FTIR absorption band ratio of Ca(OH)<sub>2</sub> (3641 cm<sup>-1</sup>)/CaO (878 cm<sup>-1</sup>) for three slurry lime field samples.**

	Slurry		
	3641/878		
	J06482741	J06482720	J06482697
1	16.4392	18.2713	21.9898
2	15.2039	15.1377	21.2871
3	14.8921	15.3941	20.4529
4	15.4573	17.4382	21.7584
5	14.2391	18.0112	22.7122
6	16.0205	16.8375	20.1728
7	15.1739	15.9728	21.2834
8	14.7824	14.7639	22.5382
AVG	15.2760	16.4783	21.5244
STD	0.6992	1.3513	0.9102
%STD	5%	8%	4%

**Table 7: Ca(OH)<sub>2</sub> Concentration and FTIR intensity ratio for 3641 cm<sup>-1</sup> /878cm<sup>-1</sup> absorption bands for three known field samples.**

Sample	Slurry	
	Concentration	Ratio
J06482741	91.4%	15.27605
J06482720	91.6%	16.47834
J06482697	93.6%	21.52435

A linear regression analysis was done based on complete data given in Table 6 and Figure 13 presents a intensity ratio vs Ca(OH)<sub>2</sub> concentration showing an R<sup>2</sup> of 0.88. A generalized trend based on data provided in Table 5 shows R<sup>2</sup> of 0.88. Figure 14 shows calibration curve for slurry lime based on the mathematical model developed and Figure 15 represent variation of slurry lime concentration for each measurement based on the developed model.

For each of the seven samples that were analyzed, eight runs were performed on each. To be 95% confident of the concentration of any sample within 3% purity it was required to run



each sample eight times when developing the calibration curve. TxDOT will be using these calibration curves primarily for a pass/fail or comparison, for these purposes readings within 3% of the actual concentration is reasonable. Depending of the precission of the FTIR machine, running more samples may narrow the confidence interval. If running more samples does not narrow the confidence interval, then the FTIR's maximum precission has been reached.

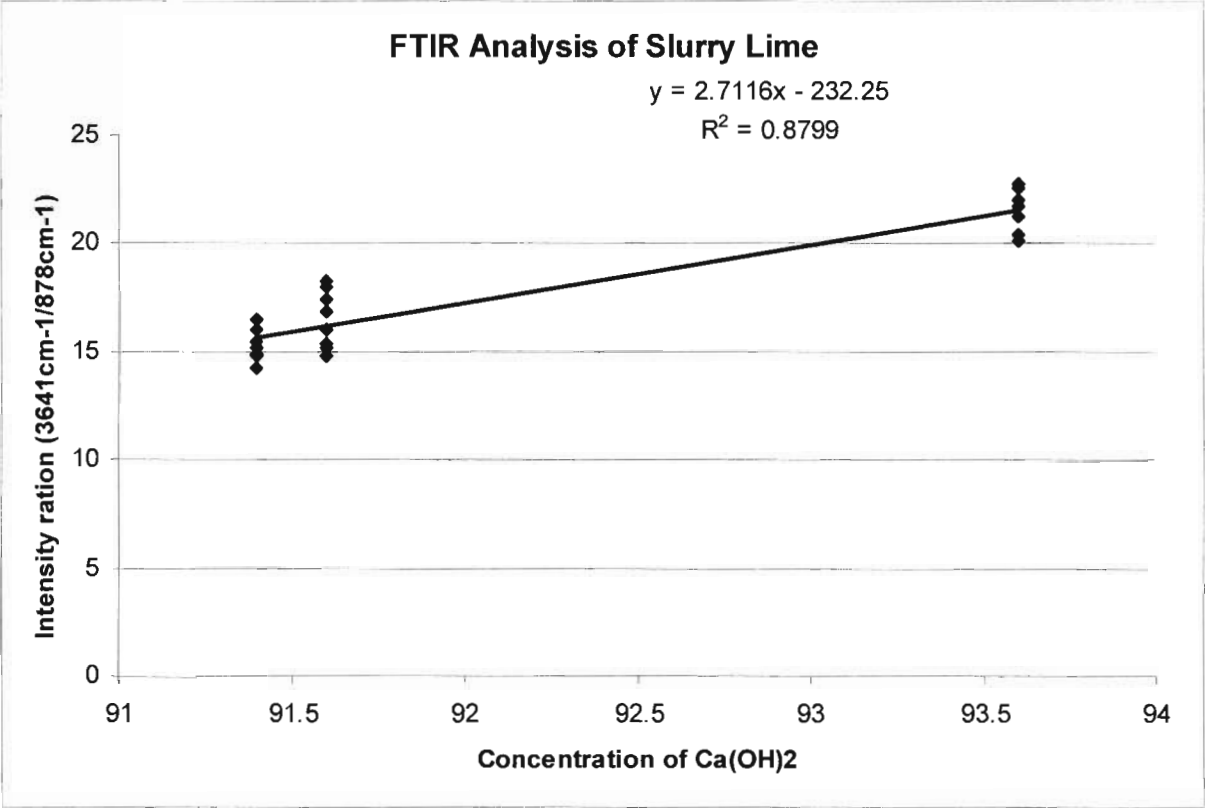
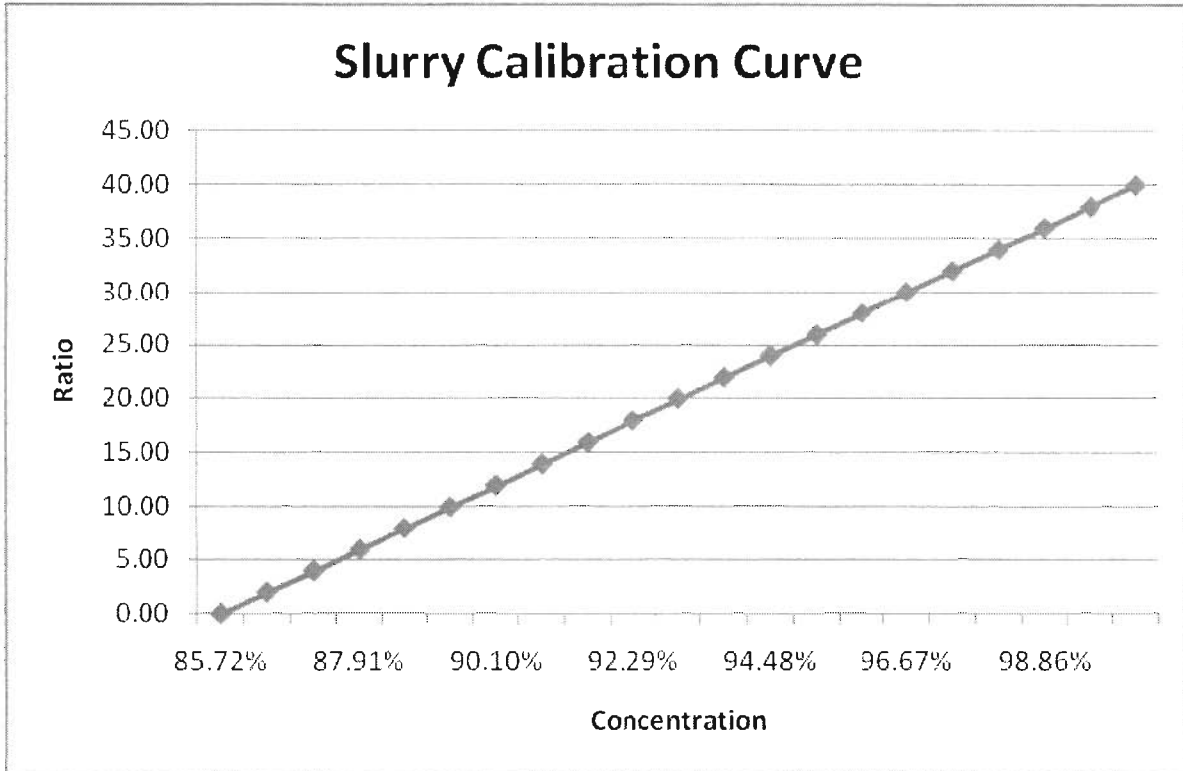
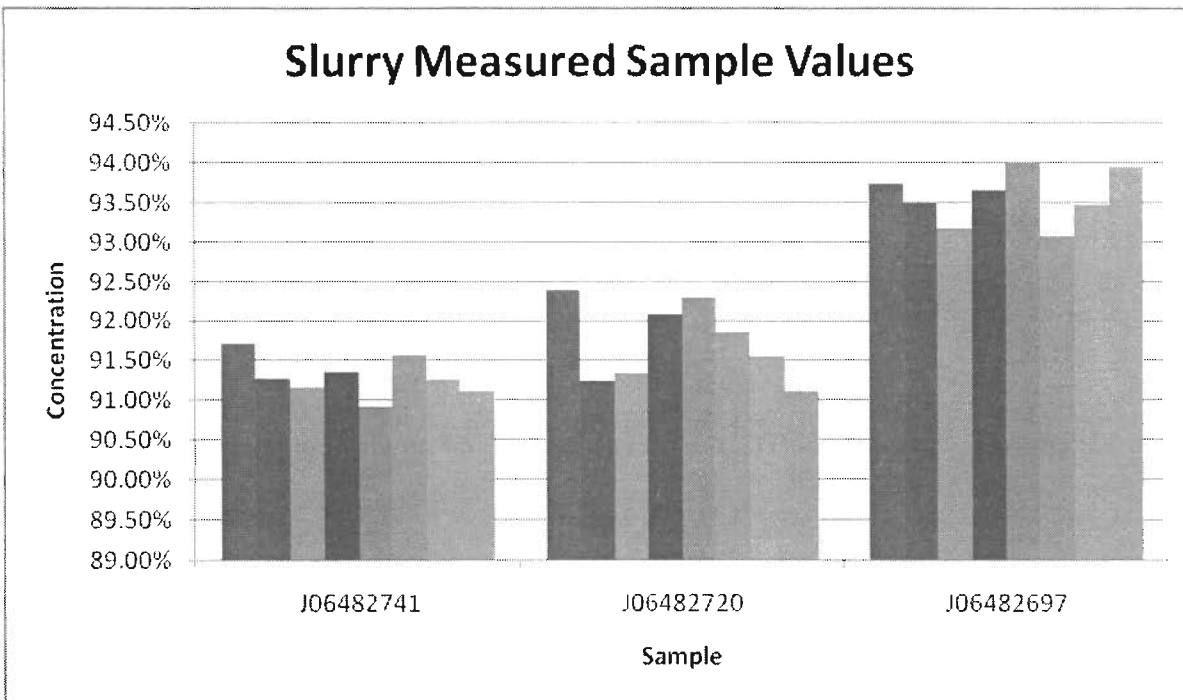


Figure 13: Intensity ratio vs Ca(OH)<sub>2</sub> concentration for known field slurry lime samples.



**Figure 14: Slurry lime calibration curve based on the mathematical model.**



**Figure 15: Variations of  $\text{Ca(OH)}_2$  concentration based on the mathematical model.**

#### 4.4 X-ray Diffraction Analysis:

Experiments were also conducted using Ragaku Ultra III with  $\text{CuK}\alpha$  ( $\lambda=1.54 \text{ \AA}$ ) X-Ray Diffraction (XRD) system. Experimental parameters used to run the XRD experiments are as follows: start angle ( $2\theta$ ) = 10 degrees; end angle ( $2\theta$ ) = 90 degrees; scan rate 2 degrees per minute; step size 0.05 degrees. Figure 16 shows detected diffracted peaks that were identified in a typical XRD pattern for a lime sample.

A similar calibration curve was developed using the peak height ratio of calcium oxide and magnesium oxide, although the correlation factors were not nearly as high as the FTIR correlation factors. The highest  $R^2$  value that was obtained from XRD regressions is 0.76. Figures 17 and 18 show calibration curves developed based on XRD analysis for quicklime and slurry lime samples respectively. The  $R^2$  value for the quicklime XRD data was 0.928. The  $R^2$  value for the slurry XRD data was 0.763. A side by side comparison of the concentrations obtained from FTIR and XRD is given in Table 8.

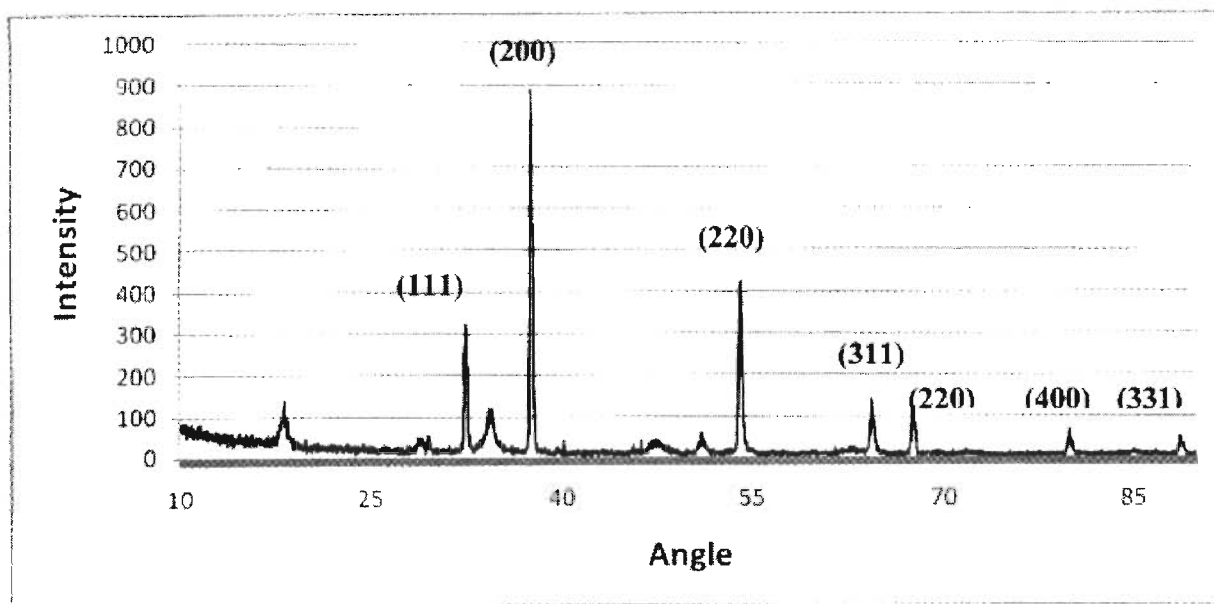
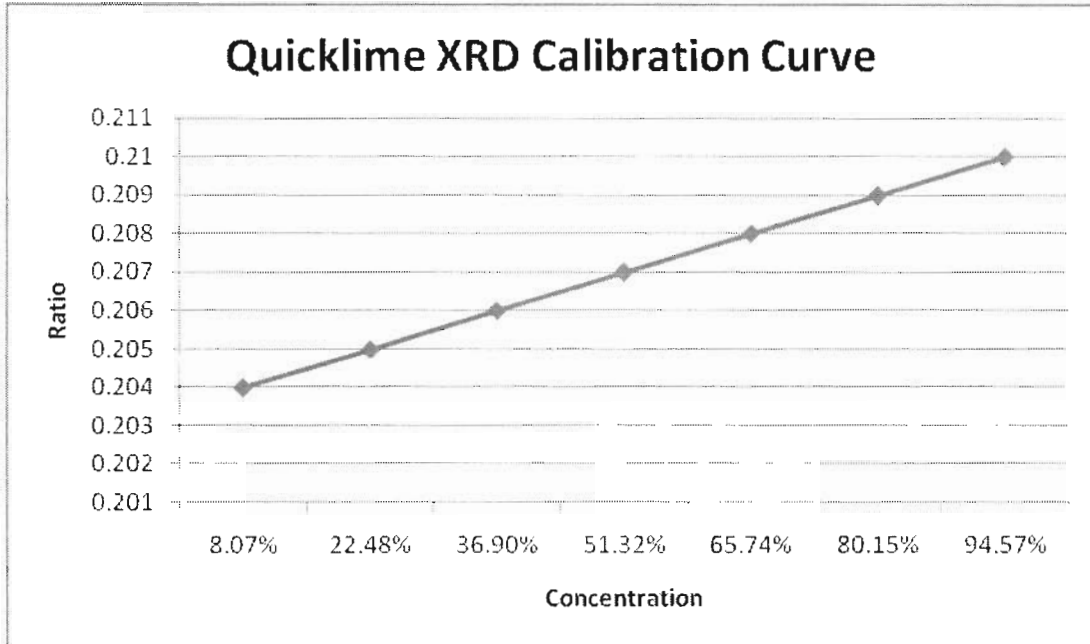
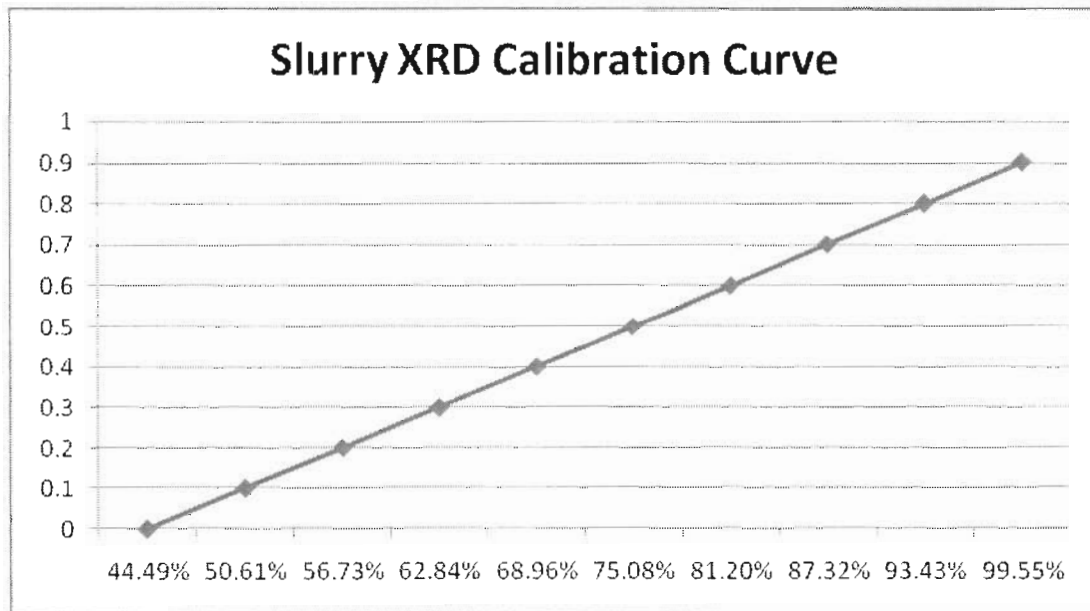


Figure 16: XRD pattern of a typical lime sample with identified CaO diffraction peaks.



**Figure 17: Calibration curve for Quicklime analysis using XRD.**



**Figure 18: Calibration curve for slurry lime analysis using XRD.**

**Table 8: Comparison of FTIR and XRD concentration measurements. Data sheets for all samples analyzed are given in Appendix C.**

	<b>Titration</b>	<b>FTIR</b>	<b>XRD</b>
<b>Sample</b>	<b>Concentration</b>		
<b>J06482349</b>	<b>88.9%</b>	<b>88.91%</b>	<b>87.32%</b>
<b>J06482398</b>	<b>89.3%</b>	<b>89.30%</b>	<b>92.45%</b>
<b>J07481649</b>	<b>58.8%</b>	<b>58.77%</b>	<b>62.94%</b>
<b>J07481648</b>	<b>52.1%</b>	<b>52.05%</b>	<b>49.97%</b>
<b>J06482741</b>	<b>91.4%</b>	<b>91.40%</b>	<b>88.62%</b>
<b>J06482720</b>	<b>91.6%</b>	<b>91.60%</b>	<b>93.74%</b>
<b>J06482697</b>	<b>93.6%</b>	<b>93.60%</b>	<b>90.13%</b>

**5.0 Summary:**

The goal of this study was to develop a protocol for the quantification of lime samples using an FTIR system. In the new procedure minimal sample preparation, minimal uses of chemicals, and adequate accuracy have been achieved. Using the FTIR quantification method developed in this research lime sample concentrations can be quickly and accurately determined.

**5.1 Recommendations:**

FTIR has been proven to accurately classify different grades of lime. It is the recommendation of the project to integrate this new quantification method into TXDOT’s quality assurance program. Although the results obtained from XRD are not as strong as FTIR regressions, this project’s results as a whole support the use of FTIR. To ensure a smooth transition from the old titration method to the new FTIR method it is highly recommended that this technique be integrated and that all additional tests be used to fine-tune the results obtained thus far. It is also recommended that when using the FTIR method the instructions developed in

this research should be followed precisely. As noted in the user manual all measurements should be highly precise and all instruments should be properly calibrated.

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## Appendix A: Protocol

### Application of FTIR for Quantitative Lime Analysis Testing Procedure

#### SCOPE

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This test method is used to determine the percent concentration of Lime (CaO). Lime is a compound that is infrared active. By using infrared spectrum of Lime sample and the given calibration curve the concentration of Lime in a given sample can be determined.

This test method implies that the equipment used for the analysis is operated by experienced personnel according to the manufacturer's directions for optimum performance. A thorough understanding of infrared spectral analysis is recommended.

This method involves hazardous material, operations, or equipment. This standard does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

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#### **Part I, Sampling Lime Products**

(Content of part I is completely adopted from TXDOT website:  
<ftp://ftp.dot.state.tx.us/pub/txdot-info/cst/TMS/600-J series/pdf/chm600.pdf>)

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This part covers the sampling of lime in powdered form as:

- ◆ Bulk Hydrate, discharged from tank trucks.
- ◆ Hydrated Lime, as bagged hydrate from bag trucks being loaded, or from bagged shipments after delivery to warehouse or job site.
- ◆ Quicklime in crushed or pebble form, discharged from tank trucks.
- ◆ Commercial Lime Slurry, a mixture of hydrated lime solids in water, from sampling port at the plant site or in the distributor truck.

#### **Apparatus**

The following apparatus is required:

#### ***Bulk Hydrate***



- ◆ paint brush, 51 mm (2 in.) wide
- ◆ 4 L (1 gal.) bucket with double friction type lid and bail
- ◆ top hatch sampling device consisting of a 2.8 m (9 ft.) length of 38 mm (1.5 in.) IPS PVC 1120 plastic pipe of SDR 1.10 MPa (26,160 psi), to meet ASTM D 2241-94, "Specification for Poly (Vinyl Chloride) (PVC) Pressure-Rated Pipe (SDR Series)."
  - This pipe is fitted at one end with a rubber stopper drilled with a 6.4 mm (0.25 in.) diameter hole.
  - The stopper may be cemented in place, using a standard adhesive epoxy.
  - A 76 mm x 51 mm (3 in. x 2 in.) half-round plate of 12-gauge steel, to which a hook is spot-welded, should be riveted and cemented with epoxy to the rubber stopper end of the pipe.
  - The 76 mm (3 in.) long metal hook should be 13 mm x 19 mm (0.5 in. x 0.75 in.), doubled over section, with a 6.4 mm (0.25 in.) slot.
  - The opening of the hook should face away from the rubber stopper.
  - The hook will catch the bucket bail, so the bucket and pipe can be lowered to the ground. This allows the sampler to alight from the truck safely.
- ◆ bottom sampling tube consisting of two concentric plastic pipes:
  - The outer pipe is a 3.2 m (115 in.) long, 38 mm (1.5 in.) inside diameter IPS PVC plastic pipe fitted at one end with a tip made from a 191 mm (7.5 in.) length of solid aluminum round stock 41 mm (1 5/8 in.) in diameter tapered to a point along 165 mm (6.5 in.) of its length, inserted 25 mm (1 in.) into the tube and fastened with two screws through the wall of the pipe into tapped holes on either side of the tip.
  - The point of the tip should be rounded to a 13 mm (0.5 in.) diameter point for safety.
  - An adhesive epoxy may be used to mold an epoxy tip in a metal, foil or cardboard mold.
  - The inner pipe is a 32 mm (1.25 in.) IPS PVC plastic pipe 3.0 m (10 ft.) long.
  - Slip this pipe inside the outer pipe. It will extend beyond the outer pipe at the upper end, forming a handle to allow the sampler to rotate the inner tube within the outer tube.
  - Cut a 32 mm (1.25 in.) wide by 305 mm (12 in.) long sampling port through both

pipes 38 mm (1.5 in.) from the lower, plugged, end.

- Create index marks on the outside of the outer and inner pipes at the upper end labeled "open" and "closed," to indicate the relative position of the opening in the inner pipe to that of the outer.

### ***Bagged Lime***

- ◆ paint brush, 51 mm (2 in.) wide
- ◆ 4 L (1 gal.) bucket with double friction type lid and bail
- ◆ bag sampling tube made from 19 mm (0.75 in.) diameter steel electrical conduit 1 m (3 ft.) long. The opening at one end shall be tapered with a 102 mm (4 in.) diagonal cut.

### ***Quicklime***

- ◆ safety goggles
- ◆ respirator
- ◆ rubber gloves
- ◆ paint brush, 51 mm (2 in.) wide
- ◆ 4 L (1 gal.) bucket with double friction type lid and bail
- ◆ device designed to hold a sample bucket between the wheel path of a bulk transport discharging quicklime without allowing the bucket to turn over, but permitting safe, easy removal of the container from the windrow with the sample intact. One suggested design:
  - From 19 mm (0.75 in.) plywood, cut three pieces, one 457 mm (18 in.) square, another 356 mm (14 in.) square and the third 254 mm (10 in.) square.
  - Cut holes to closely fit the 4 L (1 gal.) sample bucket in the centers of the smaller two plywood squares.
  - Center the 254 mm (10 in.) board on the 356 mm (14 in.) board and fasten them together.
  - Center these two on top of the 457 mm (18 in.) board and fastened together.
  - To a corner of this unit fasten a 2.4 m (8 ft.) length of 3.2 mm (1/8 in.) diameter flexible steel cable.
  - To the other end of the cable attach a 254 mm (10 in.) length of steel conduit or wooden dowel as a "T" handle, used to slide the filled bucket from wind-rowed quicklime.
- ◆ plastic sample bag 457 mm x 241 mm (18 in. x 9.5 in.)

### ***Commercial Lime Slurry***

- ◆ safety goggles
- ◆ 2 L (1/2 gal.) large-mouth (89 mm [3.5 in.] diameter) polyethylene bottle and a polypropylene or phenolic screw cap – Nalge Company No. 2234-0020
- ◆ plastic electrical tape, PVC 19 mm (0.75 in.) wide
- ◆ cloth rag or shop towel.

### **Sampling Procedures**

- ◆ Hydrated Lime
  - from loaded tank trucks

*CAUTION:* These trucks are pressurized for unloading, and attempts to open a pressurized top hatch could be fatal. Therefore, the contractor should make the load available for sampling prior to pressurization, with top hatches open. If the truck is offered for sampling pressurized, it shall be the responsibility of the contractor to bleed off the pressure and open the top hatches.

The following describes the sampling procedure for hydrated lime in powdered form as bulk hydrate.

### **Sampling Hydrated Lime from Loaded Tank Trucks**

#### **Step Action**

1 Collect a 2 L (1/2 gal.) sample for analysis. To avoid contamination by moisture or other materials, take samples from the truck prior to unloading.

*CAUTION:* These trucks are pressurized for unloading, and attempts to open a pressurized top hatch could be fatal. Therefore, the contractor should make the load available for sampling prior to pressurization, with top hatches open. If the truck is offered for sampling pressurized, it shall be the responsibility of the contractor to bleed off the pressure and open the top hatches.

2 The preferred sampling method is rodding material from the top of the truck through open hatches.

3 If the material in the truck cannot be sampled prior to unloading, then various optional sampling methods may be used, provided the sample is representative, and is not allowed

to become contaminated by moisture or mixing with base or other road material. Less desirable methods include:

- ◆ scoop samples obtained through open top hatches
- ◆ as discharged from tank trucks
- ◆ hose discharge
- ◆ dry application "catch-pan" method.

4 Do not scoop samples from material applied on roadway due to likelihood of contamination. Bulk hydrated lime should be sampled at the rate of one sample per 181.44 Mg (200 tons), unless otherwise directed. This represents roughly one trailer of every ten shipped. The trailer to be sampled should be selected at random and identified on the sample ticket by seal number, name of producer and date sampled. The seal numbers of the other nine loads need not be listed. Samples shall not be combined. Lime becomes contaminated by exposure to the atmosphere. To preserve the quality of samples, use the paintbrush to clear the sample bucket rim of lime collected during sampling, so an effective seal is obtained. Two bulk samplers are listed. The top hatch device samples the upper portion of the load through the top hatches of a bulk transport. The unit is inserted with the air hole in the rubber stopper open. When withdrawing the tube, hold the hole shut with a thumb. The bottom sampler is designed to obtain bottom samples, but may be used to take samples at various levels within the truck, or for other sampling tasks. The device is inserted at the sampling level desired with its port closed. Then the port is opened, the tube is slid back and forth, the port is closed, and the tube is removed. Lime is released from the tube by tapping the device and allowing the lime to exit from the top end into a sample bucket.

- from bag trucks

The following procedure describes sampling for hydrated lime in powdered form as bagged hydrate from bag trucks being loaded.

### **Sampling Hydrated Lime from Bag Trucks**

#### **Step Action**

- 1 Sample at least six sacks to represent each truck being shipped.
- 2 Sample at least four to six sacks from each lot being inspected and combine the material

to form a composite sample representing that lot.

- 3 Samples may be taken from the separate lots that comprise the whole if the entire lot consigned for an individual truck is from several different warehouse lots.
- 4 Insert the bag sampling tube through the sack loading spout and take sufficient diagonal roddings to insure a representative portion from each sack, without significantly reducing the volume.
  - ◆ Take care not to puncture the sack with the sampling tube.
    - from bagged shipments after delivery to warehouse or job site

The following procedure describes the sampling of hydrated lime in powdered form as bagged hydrate from warehouse or job site.

### **Sampling Hydrated Lime from Bagged Shipments after Delivery to Warehouse or Job Site**

#### **Step Action**

- 1 Use the bag sampling tube described in the equipment list to obtain a 2 L (1/2 gal.) sample from at least six sacks of material.
- 2 Select sacks for sampling from various points in the load or shipment, to collect a representative sample.
- 3 ◆ Insert the bag sampling tube through the sack loading spout and take sufficient diagonal roddings to insure a representative portion from each sack, without materially reducing the poundage.
  - ◆ Take care not to puncture the bottom or sides of the sack with the sampling tube.
  - ◆ Quicklime in Crushed or Pebble Form

*CAUTION:* Quicklime is extremely hazardous and capable of inflicting severe caustic burns to skin, lung damage, and/or eye injury and blindness, if handled improperly. Personnel handling, sampling or testing quicklime should wear proper protective clothing, respirators, dust-proof goggles and waterproof gloves.

- discharged from tank trucks

The following procedure describes sampling of quicklime in crushed or pebble form as discharged from tank trucks.

## **Sampling Quicklime (in Crushed or Pebble Form) as Discharged from Tank Trucks**

### **Step Action**

1 Instruct the truck to pass over a collection device while unloading.

CAUTION: Quicklime generates fines in transit. Since air-blown quicklime fines are hazardous, quicklime is usually unloaded at the job site by gravity feed through ports at the bottom of each compartment on the truck. Most trucks will be equipped with 3 or 4 such compartments, which are usually opened to discharge simultaneously.

2 Collect samples from the midpoint of the unloading of the truck.

NOTE: Specifications limit the amount of fines in the sample and include sizing requirements. The sizing and gradation of the sample taken shall be representative of the load. Quicklime fines tend to settle to the bottom of the compartments and the initial discharge usually contains a higher percentage than the remainder of the load. The top of the load tends to contain the coarsest material. The center of the discharge run represents the entire load.

3 ♦ The sampler should pick up the collection device and carefully transfer the entire sample to a plastic sample bag.

♦ Close and seal the bag with tape or rubber band and place in a sample bucket for transport.

♦ The bucket should be marked "caustic" and "quicklime."

4 Ship samples by motor freight *only*.

NOTE: Do not ship by bus, parcel post, air, or rail. This is hazardous material, which, upon contact with water and combustibles, can cause fires. For this and other safety-related reasons, the carriers listed have refused to accept the material for shipment.

• from tank trucks

The following procedure describes the sampling of quicklime in crushed or pebble form from tank trucks.

## **Sampling Quicklime (in Crushed or Pebble Form) from Tank Truck**

### **Step Action**

1 ♦ Collect samples from the top of the trucks.

- ◆ Dig below the surface of the pebble quicklime at least 203 mm (8 in.) and dip a sample with a 4 L (1 gal.) bucket.

### **Sampling Quicklime (in Crushed or Pebble Form) from Tank Truck**

#### **Step Action**

- ◆ A sample should be a minimum of 3 L (3/4 gal.).
- 2 ◆ Carefully transfer the entire sample to a plastic sample bag.
  - ◆ Close and seal the bag with tape or rubber band and place in a sample bucket for transport.
  - ◆ The bucket should be marked "caustic" and "quicklime."

3 Ship samples by motor freight only.

NOTE: Do not ship by bus, parcel post, air, or rail. This is hazardous material, which, upon contact with water and combustibles, can cause fires. For this and other safety related reasons, the carriers listed have refused to accept the material for shipment.

- ◆ Commercial Lime Slurry
  - from the truck

The following procedure describes the sampling of commercial lime slurry from the truck.

### **Sampling Commercial Lime Slurry from the Truck**

#### **Step Action**

1. Draw the sample from the permanent sampling port located concentrically at the rear of the truck.

NOTE: The sampling port shall consist of a 13 mm (0.5 in.) minimum, quick acting valve fitted to a 19 mm (0.75 in.) diameter pipe and outlet spout.

2. Open the sampling valve quickly and completely during sampling.
3. Half fill the plastic sample jug, to permit agitation and testing.
4. Tightly seal the jug and tape the cap to avoid leakage during transport.

NOTE: The sampling, capping and sealing of the slurry sample shall be the sole responsibility of the truck driver by direct request from a TxDOT representative.

- from the plant

The following procedure describes the sampling of commercial lime slurry from the plant.

### **Sampling Commercial Lime Slurry from the Plant**

#### **Step Action**

- 1 Collect sample from the sampling valve in the vertical riser from the slurry tank to the loading spout.
- 2 Observe the same consistency and sampling precautions as outlined above, in 'Sampling Commercial Lime Slurry from the Truck.'
- 3 Take a sample (1 per truckload) to represent a truckload.
- 4 Sampling must be witnessed by a TxDOT representative.



## Part II, Testing Slurry & Hydrated Lime

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### 2.1.0 APPARATUS

- 2.1.1 Digital Scale (precision >0.1 mg)
  - 2.1.2 Hydraulic Press Capable of >12 ksi
  - 2.1.3 13 mm Pellet Die Set with Vacuum Attachment
  - 2.1.4 Vacuum Pump with a Compatible Pellet Die Connection
  - 2.1.5 Pestle and Mortar Set
  - 2.1.6 Tweezers
  - 2.1.7 Weighting Papers
  - 2.1.8 Desiccator
  - 2.1.9 Spatula
  - 2.1.10 Fourier Transform Infrared Spectrometer (capable of recording spectrum between 400-4000  $\text{cm}^{-1}$ )
  - 2.1.11 IR Grade Potassium Bromide
  - 2.1.12 Reagent Grade Potassium Ferricyanide
- 

### 2.2.0 PREPARATION OF SAMPLES

- 2.2.1 About 20 mg of slurry should be placed into a desiccator to allow for drying for 25 minutes. For Hydrated Lime in solid form skip this step and continue with the step 2.2.2.
- 2.2.2 Prepare a mixture of 2 mg of sample, 2 mg of Potassium Ferricyanide, and 100 mg of Potassium Bromide.

- 2.2.3 Grind the mixture for approximately 3 minutes with a pestle in a mortar, so that the mixture is a uniform fine powder. It is highly recommended that the pestle and mortar set be kept in an oven when not in use to keep moisture from accumulating. It is also important that the set is at room temperature when used.
- 2.2.4 Then deposit the mixture in a 13 mm pellet die. By hand lightly tap the die to spread the mixture as evenly as possible across the bottom anvil, then insert the plunger and slowly rotate it 1-1.5 turns making sure not to apply pressure. Then remove plunger and proceed with the top anvil and compress with the plunger. Compress the mixture with 12 ksi for 4 minutes under vacuum. As with the grinding set the die should be kept in an oven when not in use, but should be allowed to cool to room temperature before use.
- 2.2.5 Carefully remove the pellet from the die with tweezers and place the pellet in the spectrometer's sample holder or an IR pellet sample holder card. Often the sample is not fully uniformly compressed, so white spots may appear, in which case avoid placing the white spot in the center of the holder window. If the sample is composed predominantly of the white spots preparation of another sample is recommended.

---

2.3.0 **TESTING PARAMETERS**

- 2.3.1 KBr Beam Splitter FTIR
- 2.3.2 Collection of spectrum from 4000-400  $\text{cm}^{-1}$
- 2.3.3 Transmission Mode
- 2.3.4 32 Scans
- 2.3.5 Resolution of 2  $\text{cm}^{-1}$
- 2.3.6 Gain 1.0
- 2.3.7 Aperture 100
- 2.3.8 Mirror Velocity at 0.6329

---

2.4.0 **TESTING PROCEDURE**

2.4.1 With the above testing parameters run the FTIR scan, it is recommended that the background be measured before taking the measurement. Figure 1 is an example of what the spectra of Lime should look like.

2.4.2 Use the standard baseline subtraction tool to eliminate tilt of the baseline. When the baseline is severely tilted the most likely cause is that the mixture was not ground finely enough, in that case the pellet should be remade and retested.

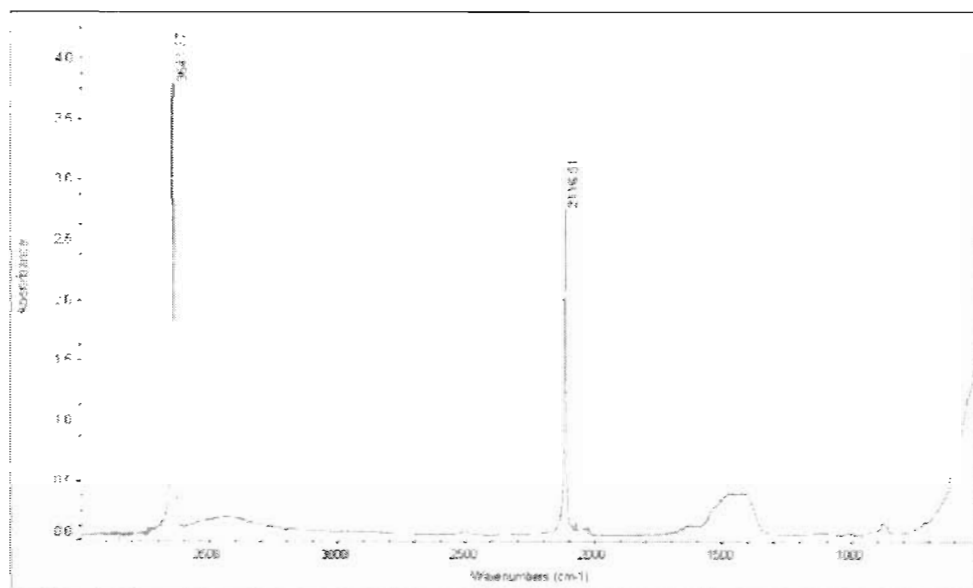


Figure 1: Typical Lime Spectra

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## 2.5.0 ANALYSIS

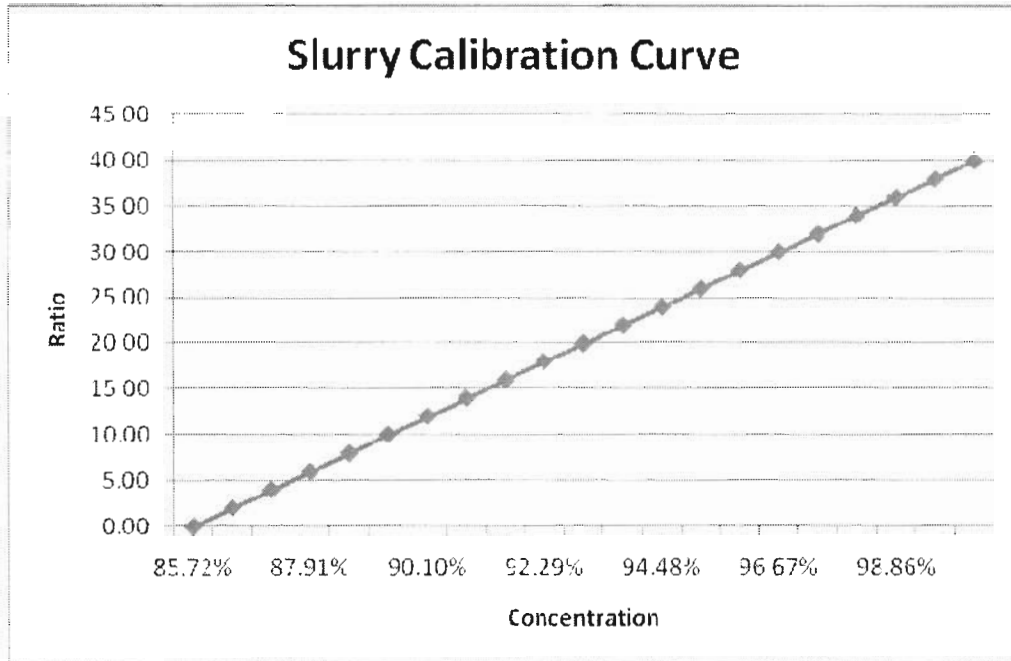
2.5.1 Zoom in so that the peaks that are to be measured can be viewed clearly, but are not large to hinder baseline point identification. Use the peak height measurement tool to calculate the peak height of interest:

- 3640 peak
- 878 peak

2.5.2 Calculate the ratio of the two peak heights:

- $\text{Slurry Ratio} = \frac{\text{Height of 3640 peak}}{\text{Height of 878 peak}}$

2.5.3 Using the calibration curve and the intensity ratio determine the concentration of lime (Figure 2).



**Figure 2: Slurry Calibration Curve**

### Part III, Testing Quicklime

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3.1.0 **APPARATUS**

3.1.1 Digital Scale (precision >0.1 mg)

3.1.2 Hydraulic Press Capable of >12 ksi

3.1.3 13 mm Pellet Die Set with Vacuum Attachment

3.1.4 Vacuum Pump with a Compatible Pellet Die Connection

3.1.5 Pestle and Mortar Set

3.1.6 Tweezers

3.1.7 Weighting Papers

3.1.8 Desiccator

3.1.9 Spatula

- 3.1.10 Fourier Transform Infrared Spectrometer( capable of recording spectrum between 400-4000  $\text{cm}^{-1}$ )
  - 3.1.11 IR Grade Potassium Bromide
  - 3.1.12 Reagent Grade Potassium Ferricyanide
- 

### 3.2.0 **PREPARATION OF SAMPLES**

- 3.2.1 Prepare a mixture of 2 mg of sample, 2 mg of Potassium Ferricyanide, and 100 mg of Potassium Bromide.
  - 3.2.2 Grind the mixture for approximately 3 minutes with a pestle in a mortar, so that the mixture is a uniform fine powder. It is highly recommended that the pestle and mortar set be kept in an oven when not in use to keep moisture from accumulating. It is also important that the set is at room temperature when used.
  - 3.2.3 Then deposit the mixture in a 13 mm pellet die. By hand lightly tap the die to spread the mixture as evenly as possible across the bottom anvil, then insert the plunger and slowly rotate it 1-1.5 turns making sure not to apply pressure. Then remove plunger and proceed with the top anvil and compress with the plunger. Compress the mixture with 12 ksi for 4 minutes under vacuum. As with the grinding set the die should be kept in an oven when not in use, but should be allowed to cool to room temperature before use.
  - 3.2.4 Carefully remove the pellet from the die with tweezers and place the pellet in the spectrometer's sample holder or an IR pellet sample holder card. Often the sample is not fully uniformly compressed, so white spots may appear, in which case avoid placing the white spot in the center of the holder window. If the sample is composed predominantly of the white spots preparation of another sample is recommended.
- 

### 3.3.0 **TESTING PARAMETERS**

- 3.3.1 KBr Beam Splitter FTIR
- 3.3.2 Collection of spectrum from 4000-400  $\text{cm}^{-1}$

- 3.3.3 Transmission Mode
  - 3.3.4 32 Scans
  - 3.3.5 Resolution of 2  $\text{cm}^{-1}$
  - 3.3.6 Gain 1.0
  - 3.3.7 Aperture 100
  - 3.3.8 Mirror Velocity at 0.6329
- 

### 3.4.0 TESTING PROCEDURE

3.4.1 With the above testing parameters run the FTIR scan, it is recommended that the background be measured before taking the measurement. Figure 1 is an example of what the spectra of Lime should look like.

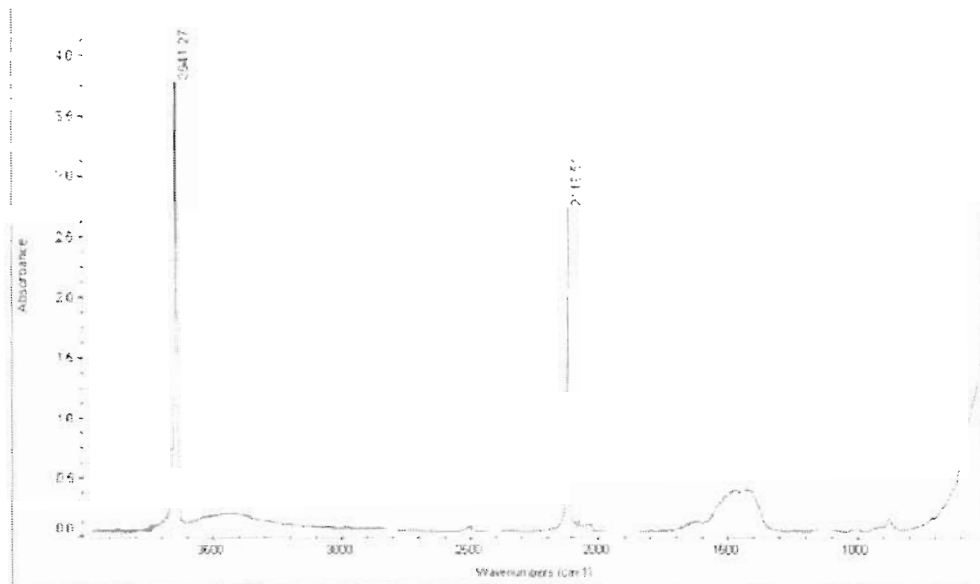


Figure 1: Typical Lime Spectra

3.4.2 Use the standard baseline subtraction tool to eliminate tilt of the baseline. When the baseline is severely tilted the most likely cause is that the mixture was not ground finely enough, in that case the pellet should be remade and retested.

---

3.5.0 ANALYSIS

3.5.1 Zoom in so that the peaks that are to be measured can be viewed clearly, but are not large to hinder baseline point identification. Use the peak height measurement tool to calculate the peak height of interest:

- 2115 peak
- 878 peak

3.5.2 Calculate the ratio of the two peak heights:

- Quicklime Ratio=Height of 878 peak/Height of 2116 peak

3.5.3 Using the calibration curve and the intensity ratio determine the concentration of lime (Figure 3).

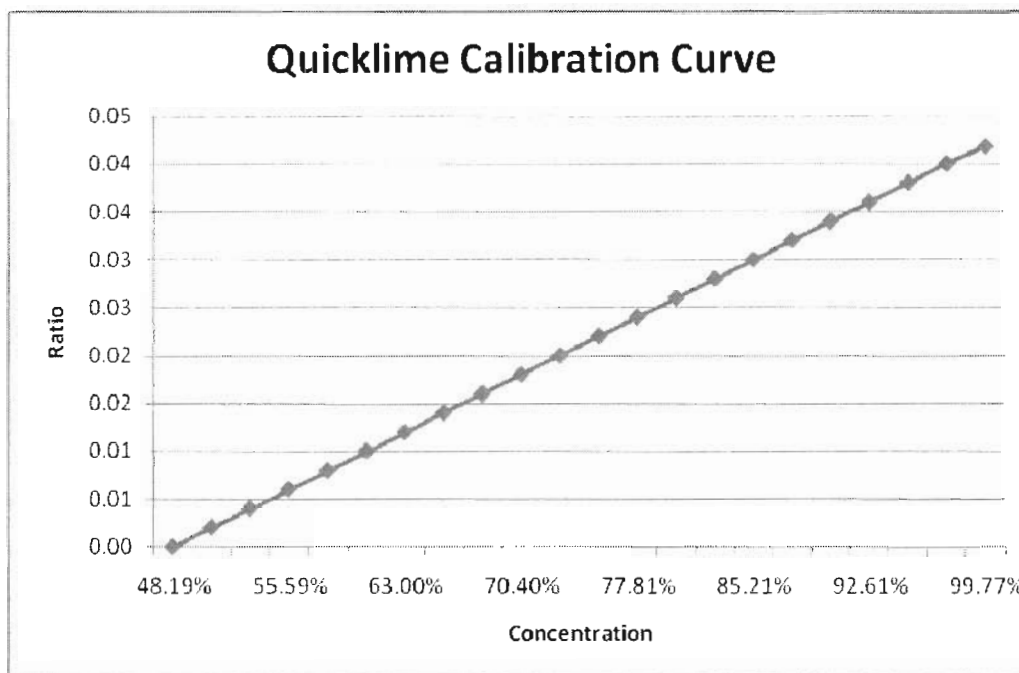
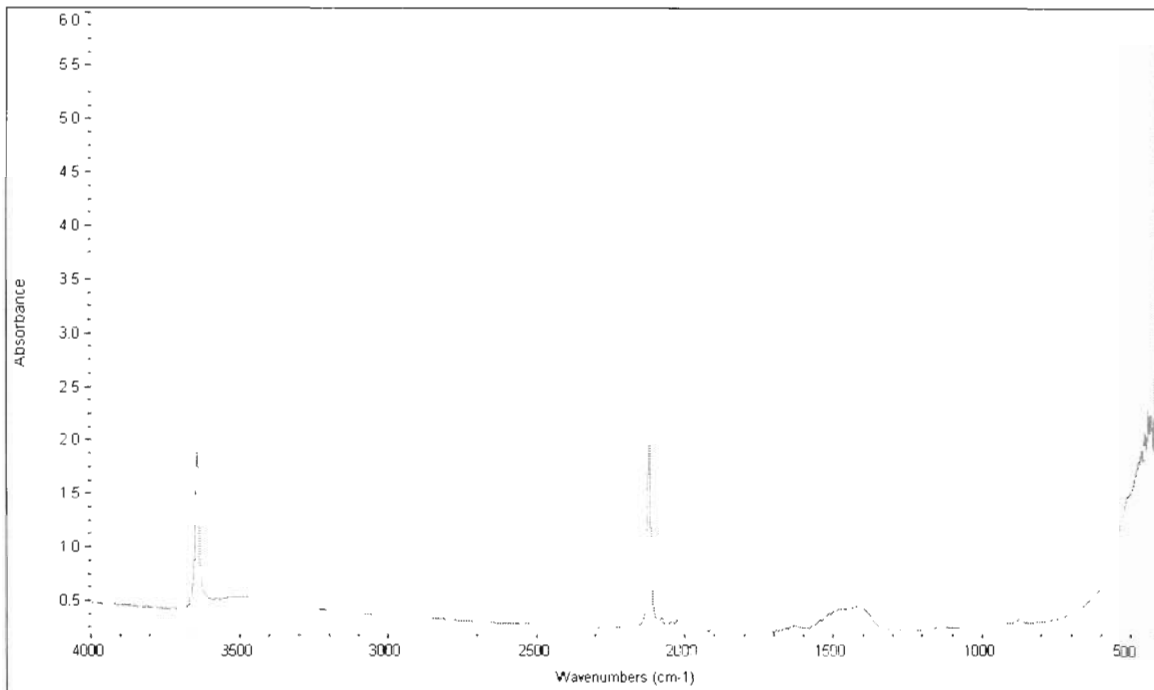
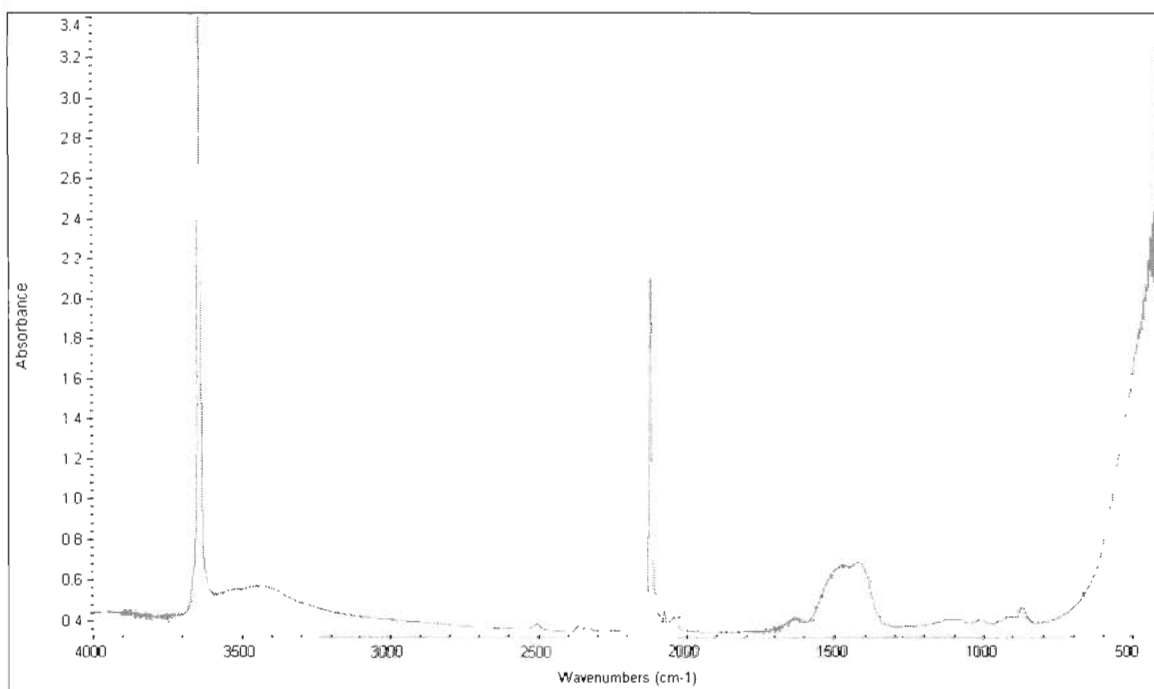


Figure 3: Quicklime Calibration Curve

**Appendix B: FTIR spectra of all samples**

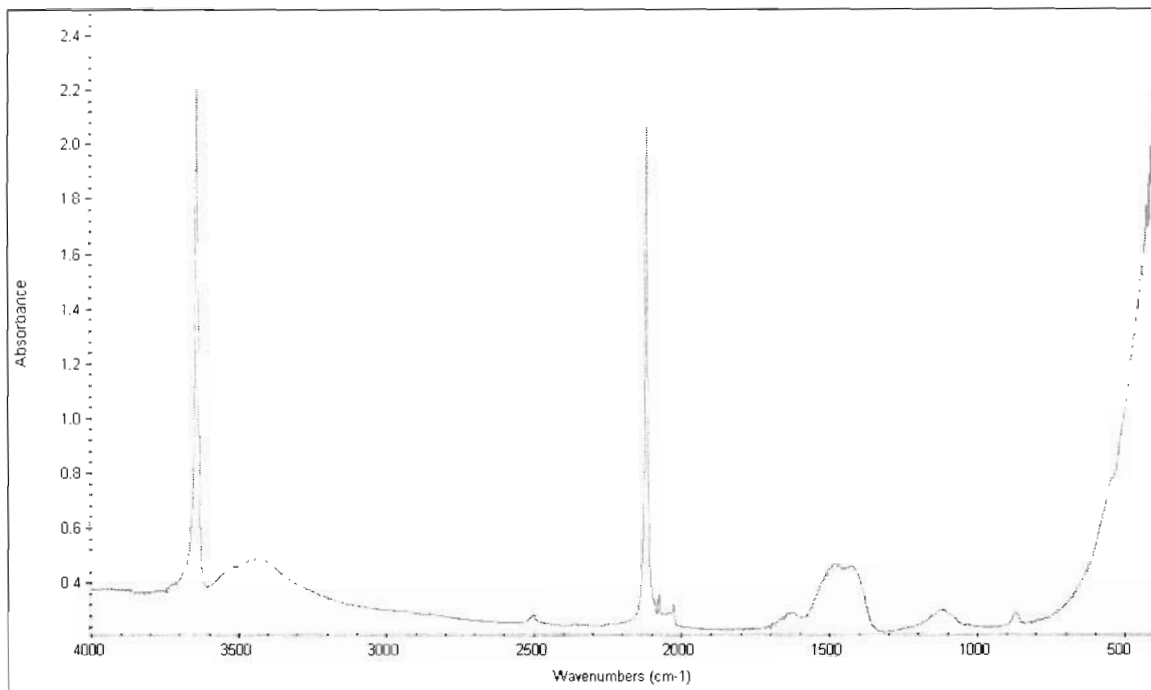


**J06482349**

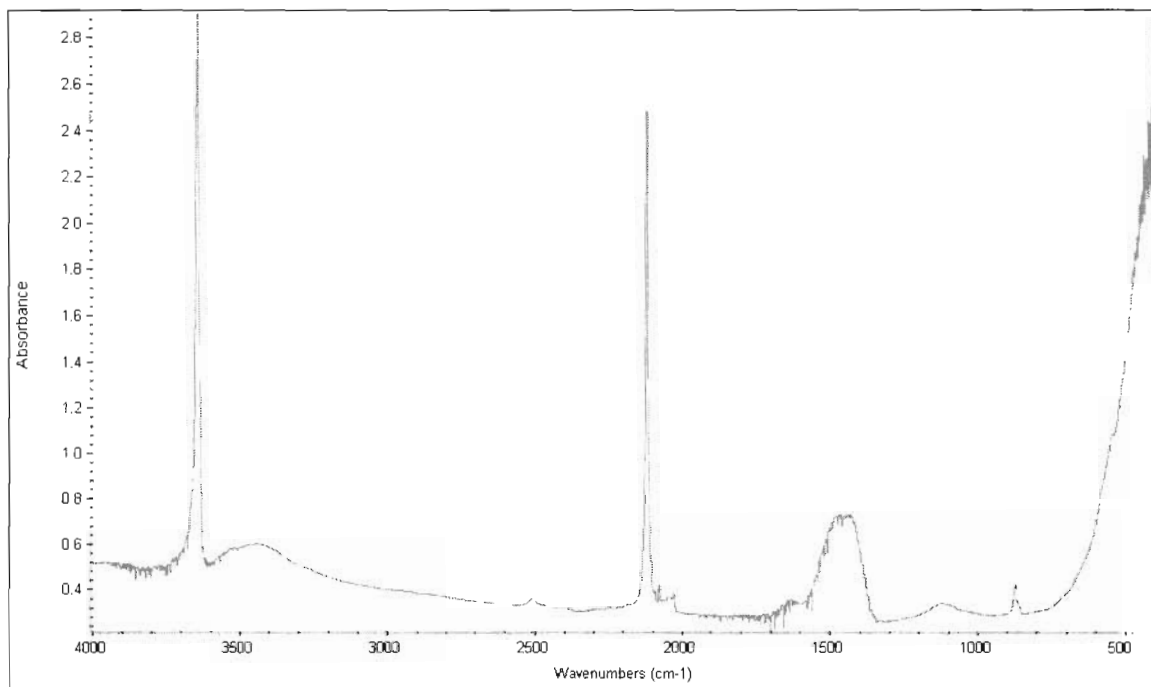


**J06482398**

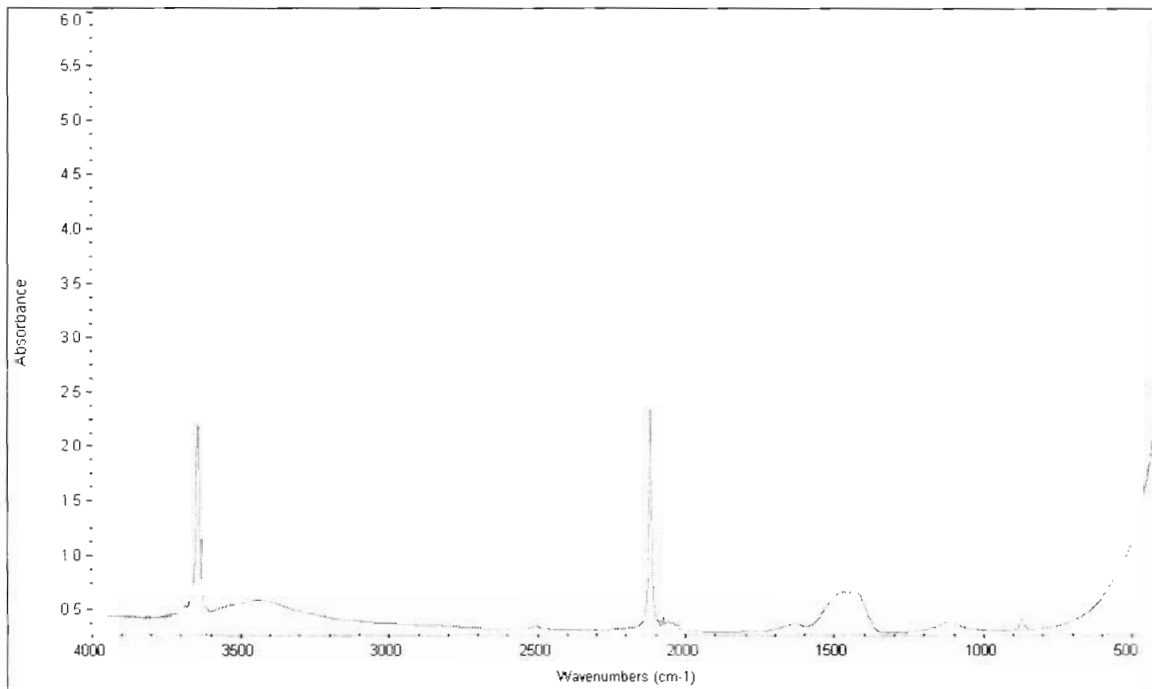




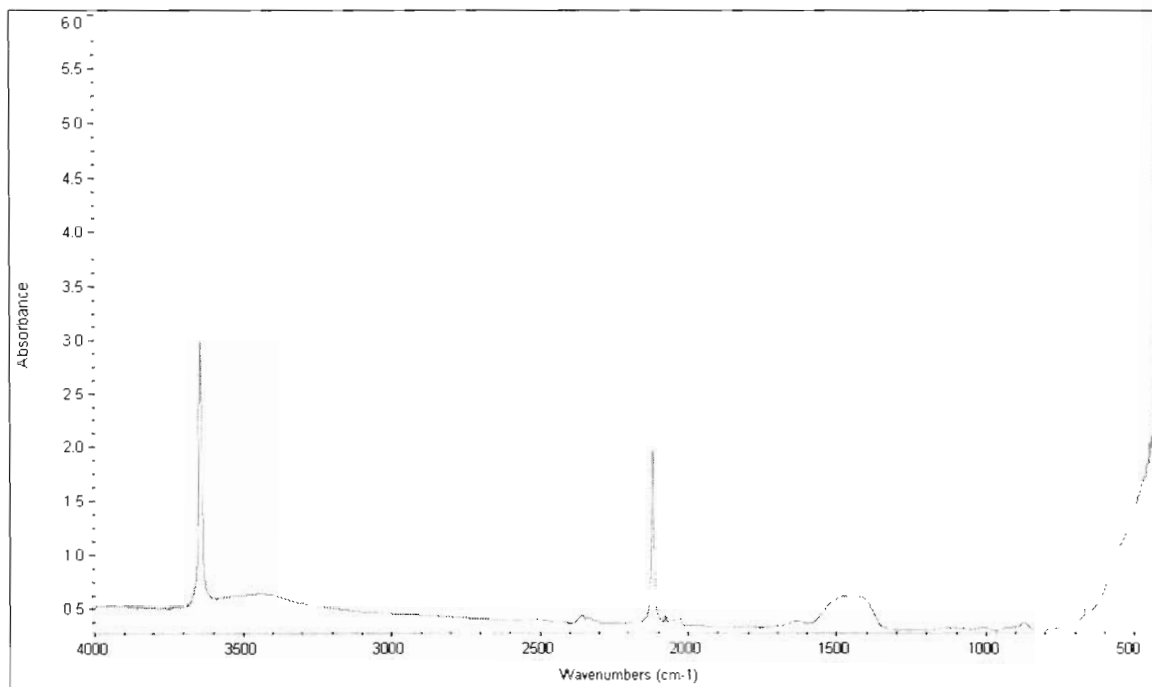
**J06482697**



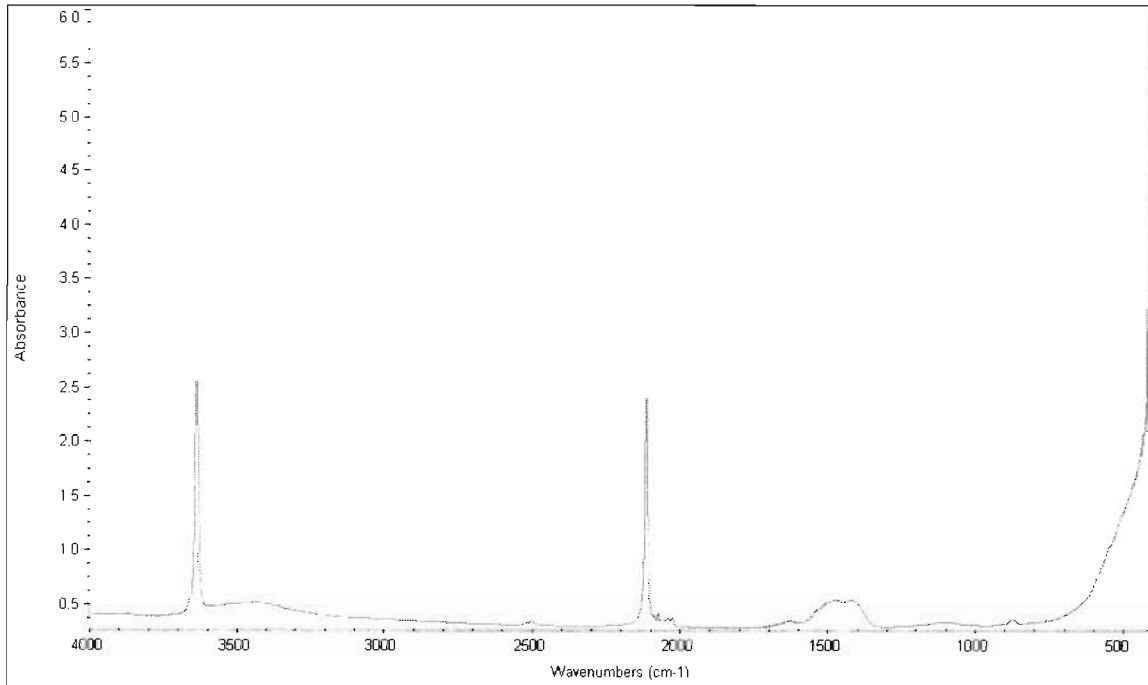
**J06482720**



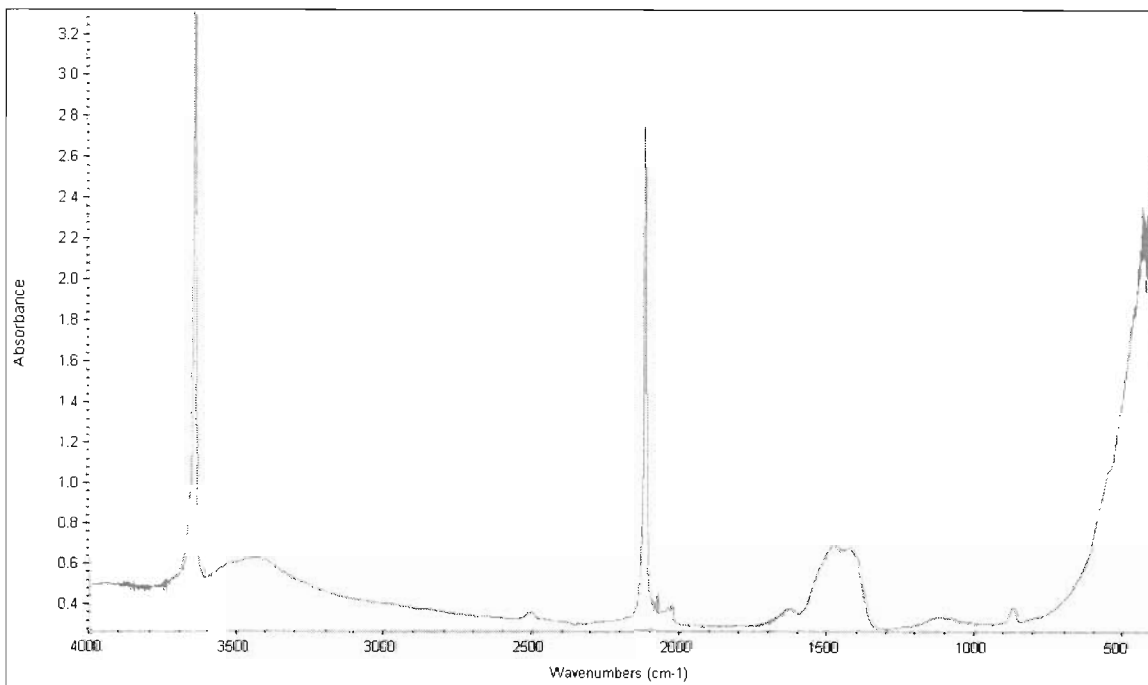
**J06482741**



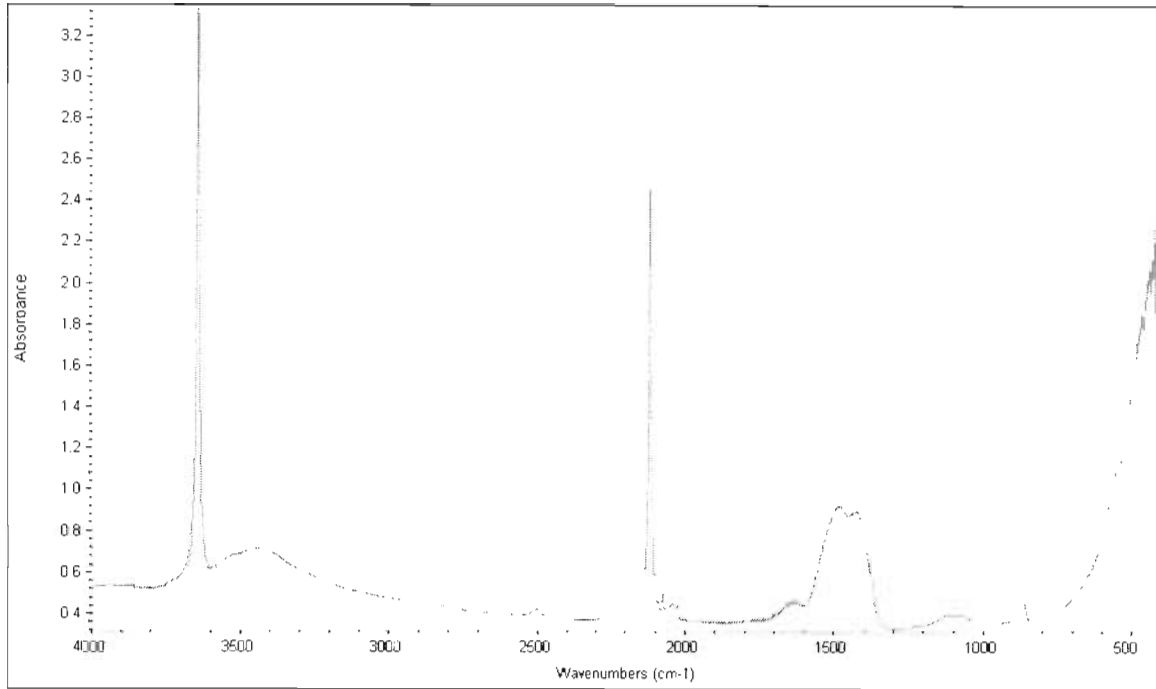
**J07480271**



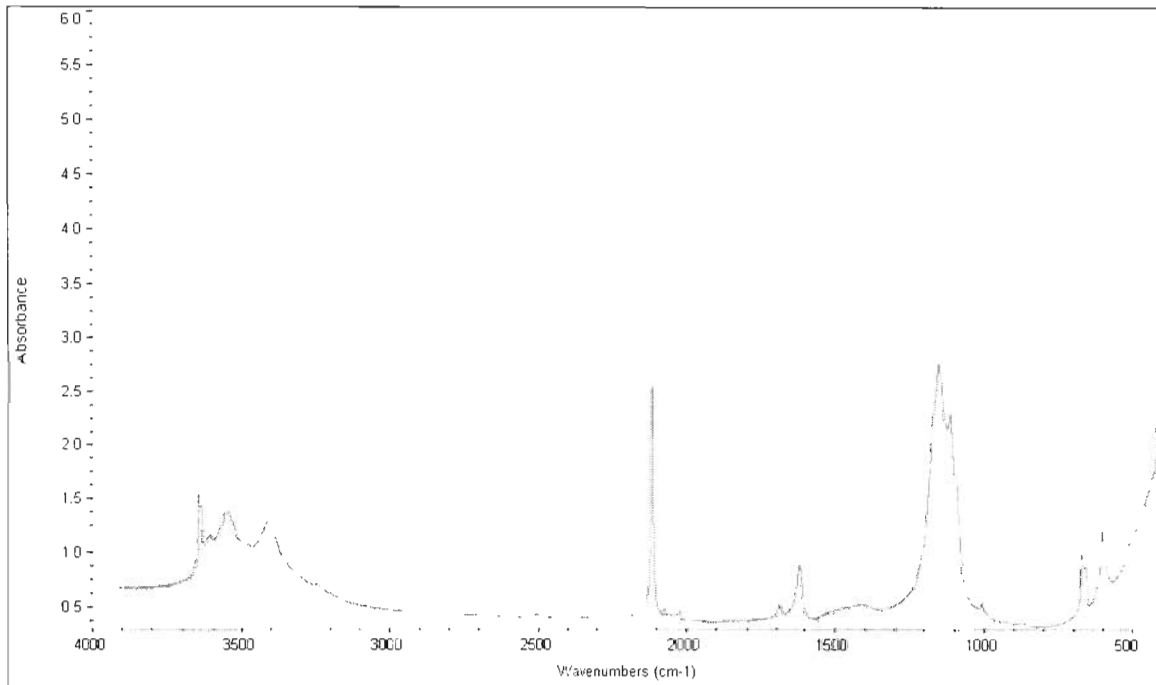
**J07480295**



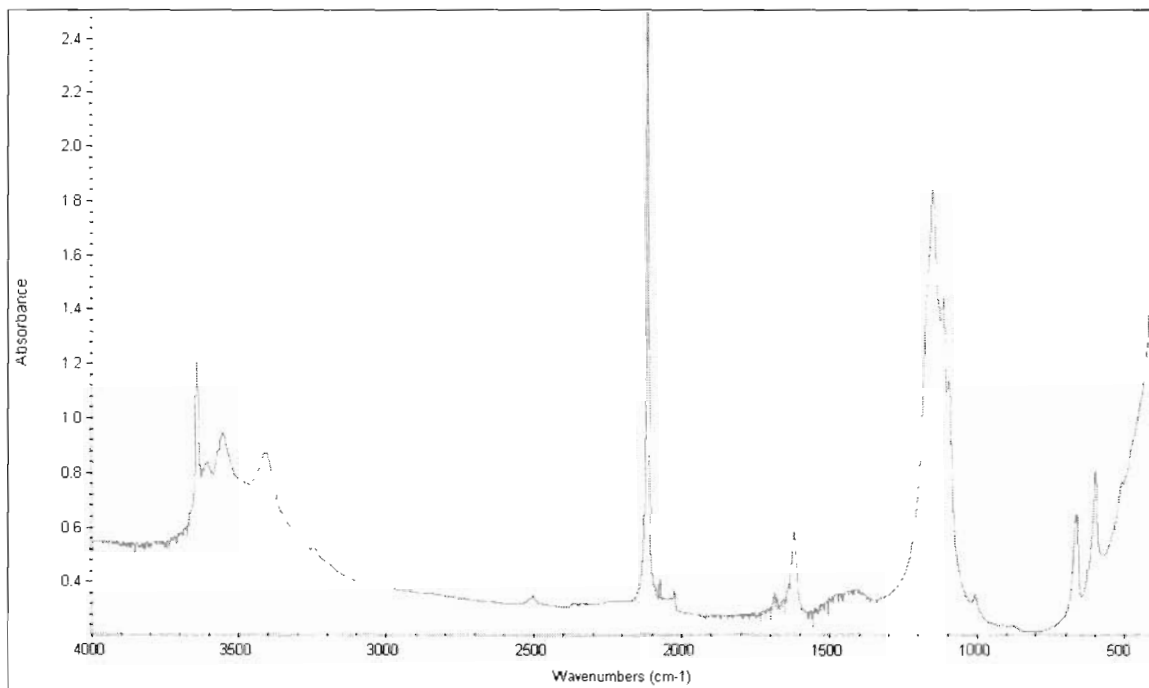
**J07480356**



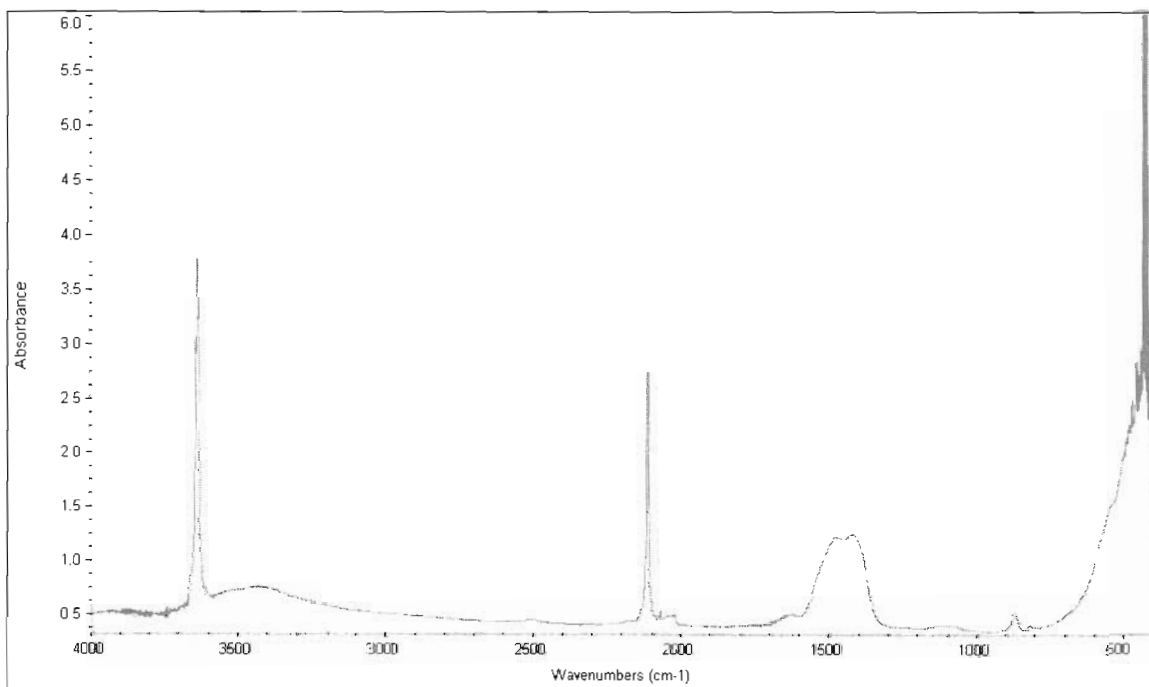
**J07480357**



**J07481648**



**J07481649**



**J07481891**

### Appendix C: Field Samples Data Sheets

Sample Number: J06482349

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#### Sample Identification :

Lab Number : J06482349      CSJ # : 055002032      Site Manager No. : 02510008060090  
Date Received : 11/3/2006      Date Sampled :      Date Completed : 11/17/2006  
Material Code : 349 - Lime      Fabricator :  
Producer Code : 353      Producer Name : Chemical Lime (Clifton)  
District : 02 - Fort Worth      County : Erath      ID Marks : 56  
Requisition No. :      Reference No. :  
Quantity : 1      Units : TON      Spec Item:      Seal ID :  
Stamp Code : 1 - Meets Specifications  
Remarks :

---

#### Test Results:

Tex 600j\_03: Lime: Quicklime

#### Titration

N HCl      1  
Sample wt. (g)      2.504  
HCl (mL)      79.4

#### Results

	Min	Max
CaO (%)	88.91	87%
Retained on 1" Sieve (%)	-	-
Retained on 3/4" Sieve (%)	-	-
Retained on No.6 Sieve (%)	-	-

#### Comments

Tested By MSEPULV      Entered By MSEPULV  
Date Rec'd 11/3/2006      Completed ✓ 11/10/06

---

Sample Number: J06482398

---

**Sample Identification :**

Lab Number : J06482398      CSJ # : 013810018      Site Manager No. : 1905006RBORGAN\*\*003  
Date Received : 11/8/2006      Date Sampled :      Date Completed : 11/17/2006  
Material Code : 349 - Lime      Fabricator :  
Producer Code : 356      Producer Name : Texas Lime Co.  
District : 19 - Atlanta      County :      ID Marks :  
Requisition No. :      Reference No. :  
Quantity .      Units :      Spec Item:      Seal ID :  
Stamp Code : 1 - Meets Specifications  
Remarks :

---

**Test Results:**

Tex 600j\_03: Lime: Quicklime

**Titration**

N HCl      1  
Sample wt. (g)      2.5998  
HCl (mL)      82.8

**Results**

	Min	Max
CaO (%)	89.30	87%
Retained on 1" Sieve (%)	-	-
Retained on 3/4" Sieve (%)	-	-
Retained on No.6 Sieve (%)	-	-

**Comments**

Tested By MSEPULV  
Date Rec'd 11/8/2006

Entered By CKERN  
Completed  11/17/06

---

Sample Number: J07481649

**Sample Identification :**

Lab Number : J07481649      CSJ # : 038504037      Site Manager No. : 0251007TCUNNI\*218  
Date Received : 9/11/2007      Date Sampled : 8/28/2007      Date Completed : 9/12/2007  
Material Code : 349 - Lime      Fabricator :  
Producer Code : 353      Producer Name : Chemical Lime (Clifton)  
District : 02 - Fort Worth      County : Hood      ID Marks :  
Requisition No. :      Reference No. :  
Quantity :      Units :      Spec Item:      Seal ID : 261350  
Stamp Code : 5 - Does Not Meet Specifications  
Remarks :

**Test Results:**

Tex 600j\_03: Lime: Quicklime

**Titration**

N HCl      1  
Sample wt. (g)      2.6052  
HCl (mL)      54.6

**Results**

	Min	Max
CaO (%)	58.77	87% - LOW
Retained on 1" Sieve (%)	-	-
Retained on 3/4" Sieve (%)	-	-
Retained on No.6 Sieve (%)	-	-

Warning: Test result is outside of the specification limits.

Comments Split sample and re-ran

Tested By PWOODRU

Entered By PWOODRU

Date Rec'd 9/11/2007

Completed  09/12/07



Sample Number: J07481648

**Sample Identification :**

Lab Number : J07481648      CSJ # : 017104067      Site Manager No. : 0205207THOMSO\*067  
Date Received : 9/11/2007      Date Sampled : 8/30/2007      Date Completed : 9/12/2007  
Material Code : 349 - Lime      Fabricator :  
Producer Code : 353      Producer Name : Chemical Lime (Clifton)  
District : 02 - Fort Worth      County : Tarrant      ID Marks :  
Requisition No. :      Reference No. :  
Quantity :      Units :      Spec Item:      Seal ID : 26765  
Stamp Code : 5 - Does Not Meet Specifications  
Remarks :

**Test Results:**

Tex 600j\_03: Lime: Quicklime

**Titration**

N HCl      1  
Sample wt. (g)      2.7908  
HCl (mL)      51.8

**Results**

	Min	-	Max
CaO (%)	52.05	87%	LOW
Retained on 1" Sieve (%)		-	
Retained on 3/4" Sieve (%)		-	
Retained on No.6 Sieve (%)		-	

Warning: Test result is outside of the specification limits.

Comments Split sample initially

Tested By PWOODRU

Entered By PWOODRU

Date Rec'd 9/11/2007

Completed  09/12/07

Sample Number: J06482741

**Sample Identification :**

Lab Number : J06482741      CSJ # : 050602086      Site Manager No. : 2005406KMOORE5\*031  
Date Received : 12/20/2006      Date Sampled : 11/14/2006      Date Completed :  
Material Code : 348 - Lime      Fabricator :  
Producer Code : 358      Producer Name : Chemical Lime (LaPorte)  
District : 20 - Beaumont      County : Chambers      ID Marks :  
Requisition No. :      Reference No. :  
Quantity :      Units :      Spec Item:      Seal ID :  
Stamp Code : 0 - Not Completed  
Remarks :

**Test Results:**

Tex 600j\_02:Lime: Slurry

Bulk Density    11.73

Titration		Muffle	
N HCl	1	Sample wt. (g)	6.8114
N NaOH	1	Cruc. Wt. (g)	26.7094
Sample wt. (g)	7.4975	Cruc. Wt. + Res. (g)	29.3923
HCl 8.3 (mL)	96		
HCl Total (mL)	109		
NaOH 4.4 (mL)	9.7		

**Results**

		Min	Max
Solids (%)	51.9	**	-
Ca(OH) <sub>2</sub> (%)	91.4	87%	-
LOI (%)	60.61		-
Retained on No. 6 Sieve (%)		0.2%	-
Retained on No. 30 Sieve (%)		4%	-

\*\* 28% minimum for Bealls, 38% minimum for CLI-La Feria, 35% minimum for CLI-New Braunfels  
38% minimum for CLI-LaPorte, 38% minimum for CLI-NW Houston, 38% minimum for CLI-Arcola  
All other producers: 40% minimum solids

**Comments:**

Tested By: PWOODRU      Entered By: PWOODRU  
Date Rec'd: 12/20/2006      Completed :  12/28/06

Sample Number: J06482720

**Sample Identification :**

Lab Number : J06482720      CSJ # : 003919042      Site Manager No. : 2151006JMORENO1164  
Date Received : 12/18/2006      Date Sampled : 12/14/2006      Date Completed : 12/21/2006  
Material Code : 348 - Lime      Fabricator :  
Producer Code : 272      Producer Name : Chemical Lime (La Feria)  
District : 21 - Pharr      County : Cameron      ID Marks :  
Requisition No. :      Reference No. :  
Quantity :      Units :      Spec Item:      Seal ID :  
Stamp Code : 1 - Meets Specifications  
Remarks :

**Test Results:**

Tex 600j\_02:Lime: Slurry

Bulk Density    10.65

Titration		Muffle	
N HCl	1	Sample wt. (g)	6.7837
N NaOH	1	Cruc. Wt. (g)	27.0805
Sample wt. (g)	4.0426	Cruc. Wt. + Res. (g)	29.0806
HCl 8.3 (mL)	38.9		
HCl Total (mL)	51		
NaOH 4.4 (mL)	10.7		

**Results**

		Min	Max
Solids (%)	38.9	**	-
Ca(OH) <sub>2</sub> (%)	91.6	87%	-
LOI (%)	70.52		-
Retained on No. 6 Sieve (%)		0.2%	-
Retained on No. 30 Sieve (%)		4%	-

\*\* 28% minimum for Bealls, 38% minimum for CLI-La Feria, 35% minimum for CLI-New Braunfels  
38% minimum for CLI-LaPorte, 38% minimum for CLI-NW Houston, 38% minimum for CLI-Arcola  
All other producers: 40% minimum solids

**Comments:**

Tested By: LISELT      Entered By: LISELT  
Date Rec'd: 12/18/2006      Completed :  12/18/06

Sample Number: J06482697

**Sample Identification :**

Lab Number : J06482697      CSJ # : 350810002      Site Manager No. : 2005406JFELAN\*\*022  
Date Received : 12/15/2006      Date Sampled : 12/6/2006      Date Completed : 12/21/2006  
Material Code : 348 - Lime      Fabricator :  
Producer Code : 358      Producer Name : Chemical Lime (LaPorte)  
District : 20 - Beaumont      County : Chambers      ID Marks :  
Requisition No. :      Reference No. :  
Quantity :      Units :      Spec Item:      Seal ID :  
Stamp Code : 1 - Meets Specifications  
Remarks :

**Test Results:**

Tex 600j\_02:Lime: Slurry

Bulk Density    11.41

Titration		Muffle	
N HCl	1	Sample wt. (g)	6.8728
N NaOH	1	Cruc. Wt. (g)	30.6874
Sample wt. (g)	4.4209	Cruc. Wt. + Res. (g)	33.1835
HCl 8.3 (mL)	53.6		
HCl Total (mL)	66		
NaOH 4.4 (mL)	10.9		

**Results**

		Min	Max
Solids (%)	48.0	**	-
Ca(OH)2 (%)	93.6	87%	-
LOI (%)	63.68	-	-
Retained on No. 6 Sieve (%)		0.2%	-
Retained on No. 30 Sieve (%)		4%	-

\*\* 28% minimum for Bealls, 38% minimum for CLI-La Feria, 35% minimum for CLI-New Braunfels  
38% minimum for CLI-LaPorte, 38% minimum for CLI-NW Houston, 38% minimum for CLI-Arcola  
All other producers: 40% minimum solids

**Comments:**

Tested By: LISELT

Entered By: LISELT

Date Rec'd: 12/15/2006

Completed : ✓ 12/18/06