Estimation of Gypsum- Calcite Percentages Using a Fourier Transform Infrared Spectrophotometer (FTIR), in Alexandria Gypsiferous Soil -Iraq

Moutaz Al Dabbas*[1], Mohammed Y. Eisa[1], Weam H. Kadhim[2]
[1]Central Environmental Laboratory, College of Science, University of Baghdad.
[2]Department of Geology, College of Science, University of Baghdad

Abstract

In this study the Fourier Transform Infrared Spectrophotometry (FTIR) provides a quick, efficient and relatively inexpensive method for identifying and quantifying gypsum concentrations in the samples taken from different sites from different localities from Alexandria district southwest Baghdad. A comprehensive spectroscopic study of gypsum-calcite system was reported to give good results for the first time by using IR for analytical grades of gypsum ($CaSO_4.2H_2O$) and calcite ($CaCO_3$) pure crystals. The spectral results were used to create a calibration curve relates the two minerals concentrations to the intensity (peaks) of FTIR absorbance and applies this calibration to specify gypsum and calcite concentrations in Iraqi gypsiferous soil samples, which were collected from different quarries at Alexandria district-Babylon Governorate , southwest of Baghdad city. The peaks were assigned to the fundamental vibrational modes of $(SO_4)^{-2}$ in gypsum and $(CO_3)^{-2}$ in calcite. Thus FTIR appears to provide fast and reliable method for identifying gypsum and calcite concentrations in the gypsiferous soils or any sediments or rocks that have different concentrations of these two minerals.

Keywords FTIR Analysis, gypsum, calcite, concentration prediction.

تقدير تراكيز الجبسوم والكالسايت باستخدام جهاز طيف الاشعة تحت الحمراء (FTIR) للترب الجبسية في الاسكندرية – العراق

معتز الدباس*[1]، محمد يعقوب عيسى[1]، وئام حسن كاظم[2]
[1]المختبر البيئي المركزي، كلية العلوم، جامعة بغداد، بغداد، العراق
[2]قسم الجيولوجي، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة:

ثبت في هذه الدراسة أن استخدام جهاز طيف الأشعة تحت الحمراء (FTIR) يوفر طريقة سريعة وفعالة وغير مكلفة نسبيا لتحديد وقياس تراكيز الجبسوم والكالسايت لعينات أخذت من مواقع مختلفة في منطقة الاسكندرية جنوب غرب بغداد. وقد أفادت الدراسة الطيفية الشاملة لنظام بلورات الجبسوم – الكالسيت النقية في أطياف الأشعة باستخدام جهاز تحت الحمراء ولاول مرة بانها اعطت نتائج جيدة للنظم التحليلية لبلورات الجبسوم ($CaSO_4.2H_2O$) والكالسيت (كربونات الكالسيوم $CaCO_3$) النقية . ثم باستخدام نتائج أطياف هذين المعدنين النقيين تم التوصل إلى إنشاء منحنى المعايرة الذي يشير الى تراكيز المعدنين من خلال شدة التراكيز الظاهرة من ارتفاع قمم منحنى FTIR الامتصاصية وتنطبق هذه المعايرة لتحديد تراكيز الجبسوم

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*Email: profaldabbas@yahoo.com

والكالسايت في عينات جمعت من الترب الجبسية التي اخذت من مقالع مختلفة من منطقة الإسكندرية في محافظة بابل إلى الجنوب الغربي من مدينة بغداد . ومن خلال مطابقة قمم النماذج المجهولة التراكيز من الترب الجبسية التي تحتوي على المعدنين وبنسب مختلفة وشدتها (اي ارتفاع قمة منحنيات كل معدن) ومقارنتها بالمنحنى القياسي تم تعيين تراكيز الجبسوم والكالسيت في الترب الجبسية. وبالتالي فان FTIR يمكن ان يعطي وسيلة سريعة وموثوق بها لتحديد تراكيز الجبسوم والكالسايت في الترب الجبسية او اية رواسب او صخور لهذين المعدنين.

Introduction

Calcium Sulfate ($CaSO_4$), in mineral form is commonly called gypsum and occurs abundantly in many areas of the world. In natural deposits, the main form is the dihydrate. Some anhydrite is also present in most areas, although to a lesser extent. Mineral composition can be found in table-1[1].

The hemihydrates (plaster of Paris), is normally produced by heat conversion of the dihydrate from which $3/2H_2O$ is removed as vapor after combustion. The resulting powder is also known as plaster of Paris which represents the greatest commercial significance as building materials. It is used in fabricated building materials, Portland cement and agricultural soil conditioning.

The natural or mineral form of gypsum is most widely extracted by mining or quarrying and used commercially. Natural gypsum is rarely found in a pure form. The dihydrate and anhydrous forms are commonly found together. Impurities in gypsum deposits typically include calcium and magnesium carbonates, silica oxides, clays and small amounts of various soluble salts. In some cases, the crude ore is beneficiated to provide a commercial feedstock in which the percentage of functional dihydrate has been increased to a level 80% or higher [2-4].

Gypsum is also obtained as a byproduct of various chemical processes. The main sources are from processes involving scrubbing gases evolved in burning fuels that contain sulfur such as coal used in electrical power generating plants, and the chemical synthesis of chemicals such as sulfuric acid, phosphoric acid, titanium dioxide, citric acid and organic polymers [1].

The aim of this study is to measure the concentration of gypsum and/or calcite by using Shimadzu Fourier Transform Infrared Spectrophotometry (FTIR) to construct a calibration curve of gypsum ($CaSO_4.2H_2O$) and calcite ($CaCO_3$) pure crystals to indicate these two minerals concentrations in unknown mixture such as gypsiferous soils from Alexandria district southwest Baghdad, figure-1.

Materials and Methods

Shimadzu Fourier Transform Infrared Spectrophotometry (FTIR) instrument used to analyze pure crystals of calcium carbonate (calcite) $CaCO_3$ (98%) and calcium sulfate dihydrate (gypsum) $CaSO_4.2H_2O$ (98.5%) that were supplied by the Department of Geology, College of Science, University of Baghdad from Fatha formation near Baiji city, Salahdin Governorate in the north of Baghdad. These two pure minerals are used to predict calibration curve represent the intensity (absorbance) of vibrational modes of the characteristic bonds of SO_4^{-2} and CO_3^{-2}.

Samples of Iraqi gypsiferous soil from various quarries were taken from Alexandria district-Babylon Governorate to the south west of Baghdad city, figure.-1. These quarries were used as row materials for local factories to produce plaster of Paris. The gypsiferous soil samples were collected at 50 cm intervals from the surface to about 150 cm deep and from different sampling locations (quarries), figure-1.

Fourier Transform Infra Red (FTIR) is the preferred method that used in this study. In infrared spectroscopy, IR radiation is passed through the sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum [2].

Fourier Transform Infrared Spectrophotometry (FTIR) spectra of minerals display characteristic features, usually absorption features, which can be related qualitatively to variations in the constituent minerals. Absorption features result from the detection of vibrational modes, i.e. lattice vibrations and/or molecular group vibrational modes. Qualitative mineral identification is possible because minerals have characteristic absorption bands in the midrange of the infrared, wave numbers 4000 to 400 cm^{-1}. Quantitative analysis with an FTIR is also possible because in simple two component mixtures, absorbance feature sizes are proportional to the concentration of each component as given by Beer's Law [3, 4].

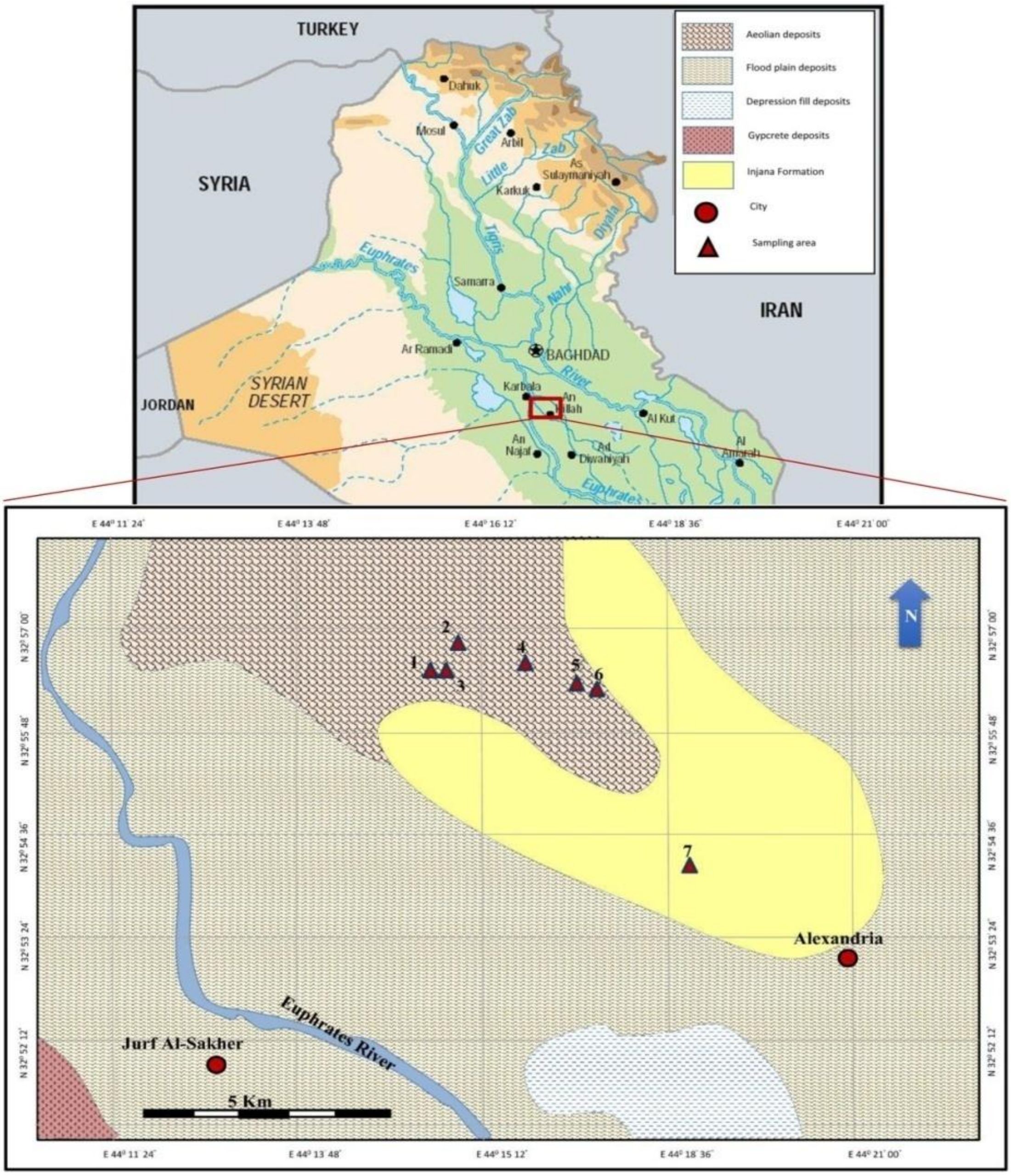

Figure 1- Location map of studied area (Alexandria).

Table 1- Mineral compositions of Gypsum types [1]

Common Name	Molecular Formula	Composition Wt.%		
		CaO	SO_3	Combined H_2O
Anhydrite	$CaSO_4$	41.2	58.8	---------------
Gypsum	$CaSO_4.2H_2O$	32.6	46.5	20.9
Plaster of Paris	$CaSO_4.1/2H_2O$	38.6	55.2	6.2

A recent detailed study [5] of the ternary mixture of calcium carbonate ($CaCO_3$), calcium sulfate hemihydrates ($CaSO_3.1/2H_2O$) and gypsum ($CaSO_4.2H_2O$) by FTIR spectroscopy is developed, figure-2. The method involves the FTIR analysis of powder mixtures of several concentrations of three components and shows the absorbance peaks of the pure phase for each component alone, figure-2.

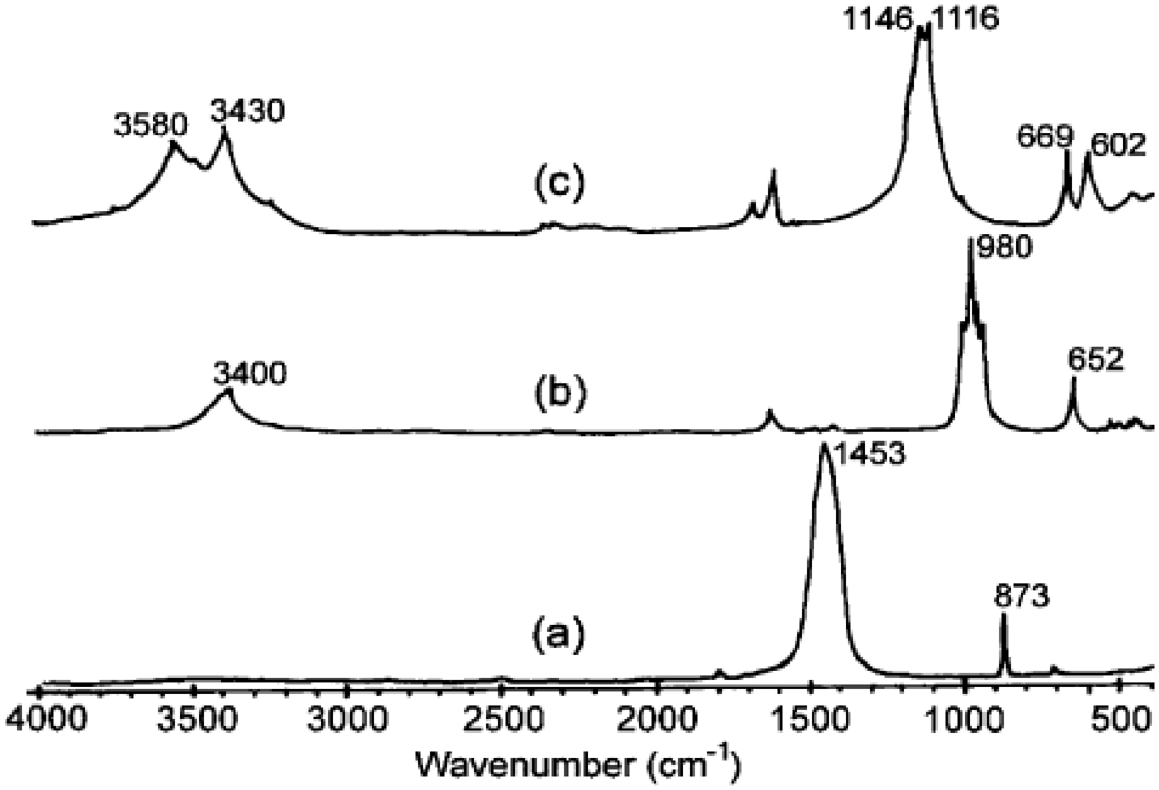

Figure 2- Standards FTIR spectra of (a) pure calcium carbonate; (b) pure calcium sulphite hemihydrates; (c) pure gypsum after Böke ,et al., [5]

Böke ,et al., [5], shows the presence of a strong band at 1453 cm^{-1}, concerning the C–O stretching mode of carbonate together with a band at 873 cm^{-1} of the bending mode figure-2. The observed bands at 980 and 652 cm^{-1} concerning those reported in the literature for sulfate ion [6]. The broad absorption at 980 cm^{-1} is assigned to the symmetric and asymmetric S–O stretching modes. The narrow peak at 652 cm^{-1} concerned to the symmetric bending mode. The strong band centered at 1140 cm^{-1} and the small peaks at 669 and 602 cm^{-1} are assigned to the stretching and bending modes of sulfate as seen in the pure gypsum spectrum.

However, in the spectrum of a natural sample contains many components, it is significantly more difficult to extract quantitative results. Although still based on Beer's law, the absorbance at a specific wavelength is the sum of the absorbance of all sample components that absorb at that wavelength [5].

In this research and for FTIR analysis, 0.01 g of each sample mixture (i.e. Calcite and gypsum) were mixed with 0.5 gm of spectral grade KBr, and finely ground in an agate mortar to 40 μm, thoroughly dried at 105 °C, and pressed into pellets under about 10 $tons/cm^2$ pressure. Spectral measurements were carried out on an FTIR spectrophotometer (Shimadzu, IR Affinity-1) that was operated in the absorbance mode, in the Central Environmental Laboratory,College of Science-University of Baghdad. Spectra were normally acquired with the use of 4 cm^{-1} resolution yielding IR traces over the range of 400–4000 cm^{-1}. All data were corrected for background spectrum. The sample chamber of the FTIR was kept desiccated, but was not evacuated and the background was corrected to remove the effect of any remaining H_2O. Each analysis takes about 30 sec; most of the time is spent gathering 22 spectra that are co-added to reduce noise. Theoretically, noise should be reduced as the number of co-added spectra increases. However, our experiments showed a practical limit to the noise reduction with co-added spectra. Data were recorded as percent reflectance relative to KBr, which was used as a standard to calibrate the machine as many studies on FTIR [7] and the record diffuse reflectance rather than absorbance was considered in this study.

Results and Data Analysis

The FTIR spectrum of pure calcium carbonate shows the presence of a strong band centered around 1425.4 cm^{-1}, characteristics of the C–O stretching mode of carbonate together with a narrow band around 875.68 cm^{-1} of the bending mode, figure-3.

The strong band centered around 1128 cm^{-1} which splits into two components at around 1141.95 and 1116.78 cm^{-1} and the small peaks at 669.3 and 601.79 cm^{-1} are assigned to the stretching and bending modes of sulfate as seen in the pure gypsum spectrum, figure-3.

The stretching vibrations of the H_2O molecules in the gypsum occur at 3547.09 and 3404.36 cm^{-1} as shown in figure-4.

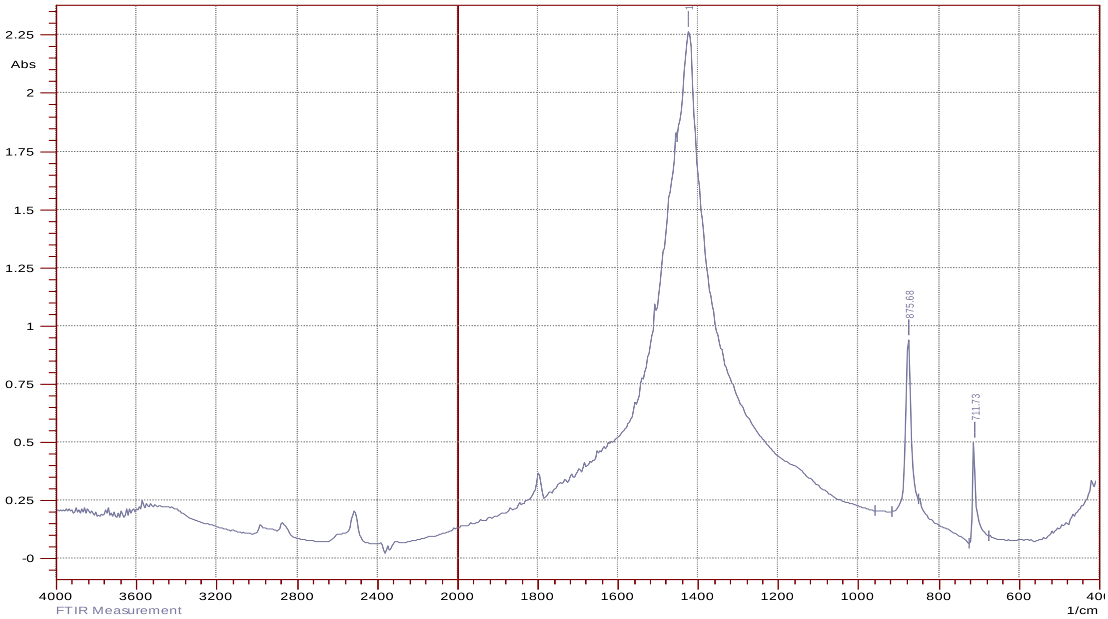

Figure 3- FTIR spectrum of pure calcite

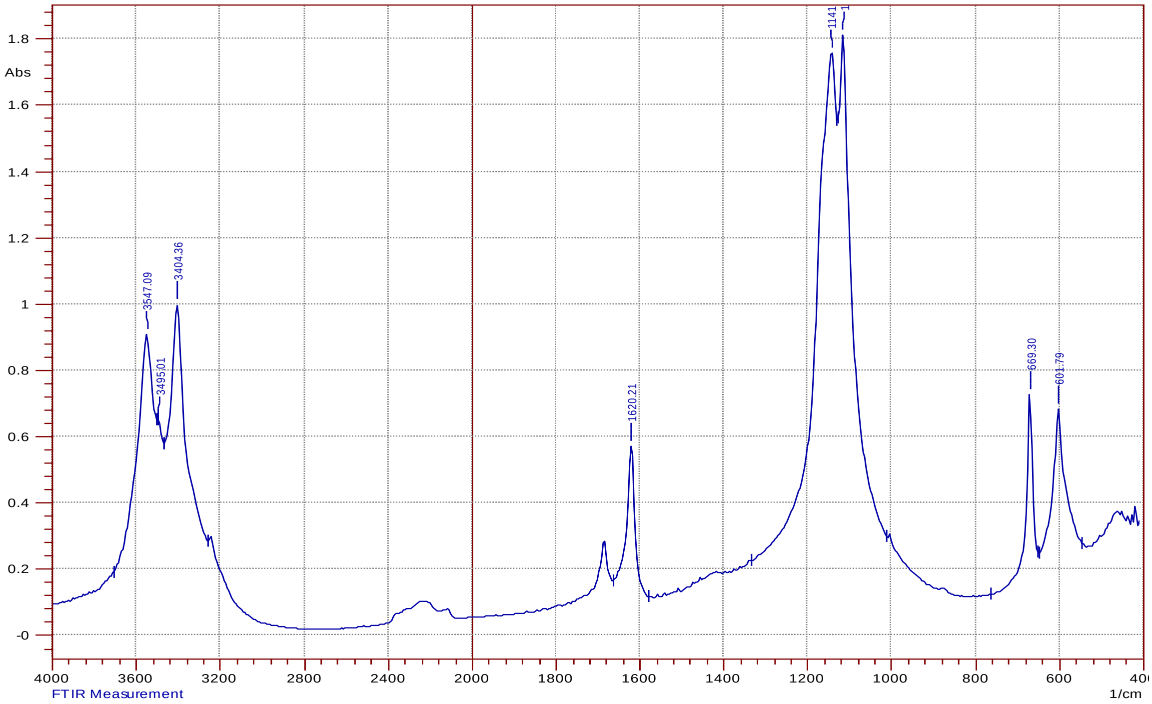

Figure 4- FTIR spectrum of pure gypsum

In this work, among those bands described, the strong absorption band of carbonate at 1425.4 cm^{-1}, the band centered around 1128 cm^{-1} of sulfate were used as analyze peaks for the analysis of the related components. The FTIR spectrum of the examined mixture shows that there is no significant interference between the analyzed peaks of the components in the mixture. Thus the chosen analyzed peaks, can be safely used for analysis of the individual components in the mixtures.

According to the collected data, quantification of the mixtures were used to create a calibration curve that can be further used to predict the compositions of unknown mixtures based on the intensity of the absorbance peak. The FTIR analysis of a binary mixture of calcite-gypsum system consists of 50 weight percent of each compounds and 40% calcite - 60% gypsum mixture, using analytical grades of the components are shown in figure-5 and figure-6, respectively.

It is clearly found from figure-5 and figure-6 that there are two main bands as discussed. The strong band centered around 1138 cm^{-1} which splits into two components at around 1120.64 and 1151.5 cm^{-1} and the small peaks at 669.3 and 603.72 cm^{-1} are assigned to the stretching and bending modes of sulfate of gypsum spectrum. The presence of a strong band centered around 1425.4 cm^{-1}, which are characteristics of the C–O stretching mode of carbonate together with a narrow band around 875.68 cm^{-1} of the bending mode of the carbonate of calcite. Two other mixtures of calcite-gypsum system of (75-25wt. %) and (25-75wt. %) weight percent system is shown in figure-7 and figure-8, respectively. From the results of the FTIR spectroscopy, it was found that the main absorbance peaks are strongly affected by the components concentration. So, two mixtures of the same studied system with various compositions of (60-40), (40-60) weight percent and the main absorbance peaks are recorded in table-2 for the whole studied set of experiments.

Table-2, the column 2 shows the composition of the system in weight percent, while the columns 3 and 4 shows the intensity of the main peaks absorbance which are recorded in respect to the FTIR spectrum.

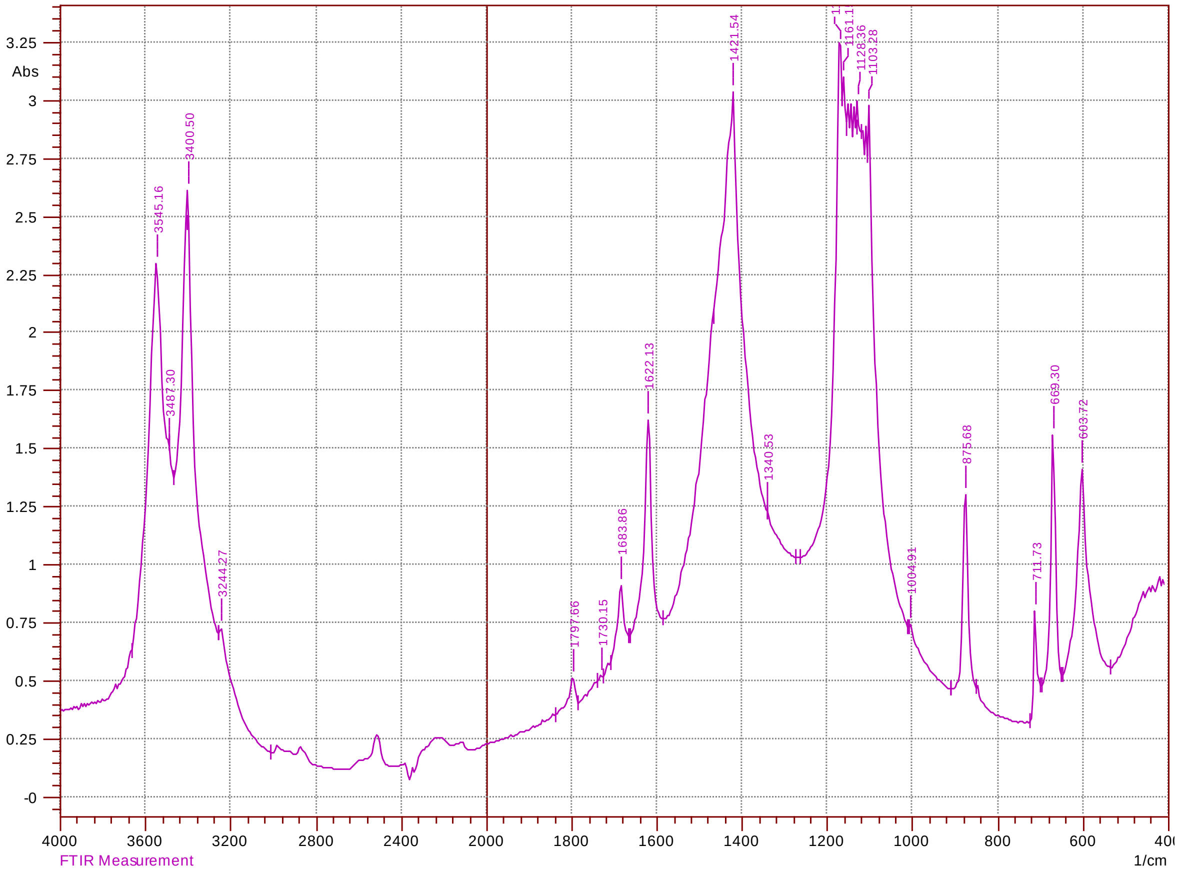

Figure 5- FTIR spectrum of calcite-gypsum 50 wt.% mixture

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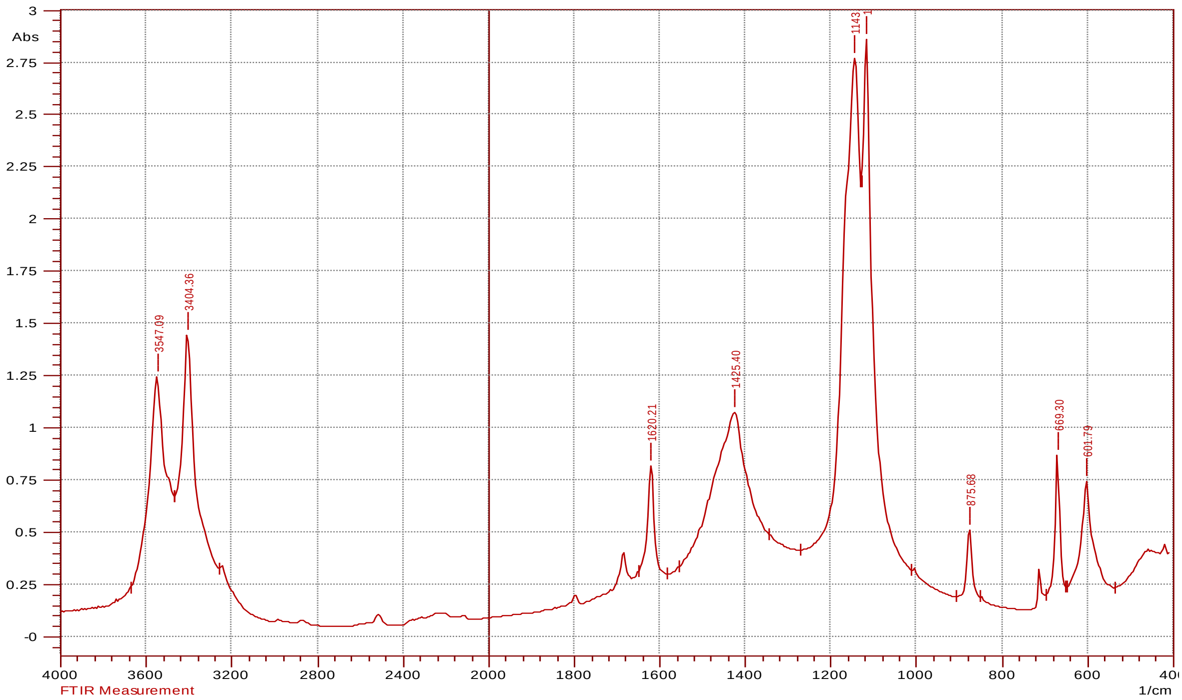

Figure 6- FTIR spectrum of 40% calcite - 60% gypsum mixture

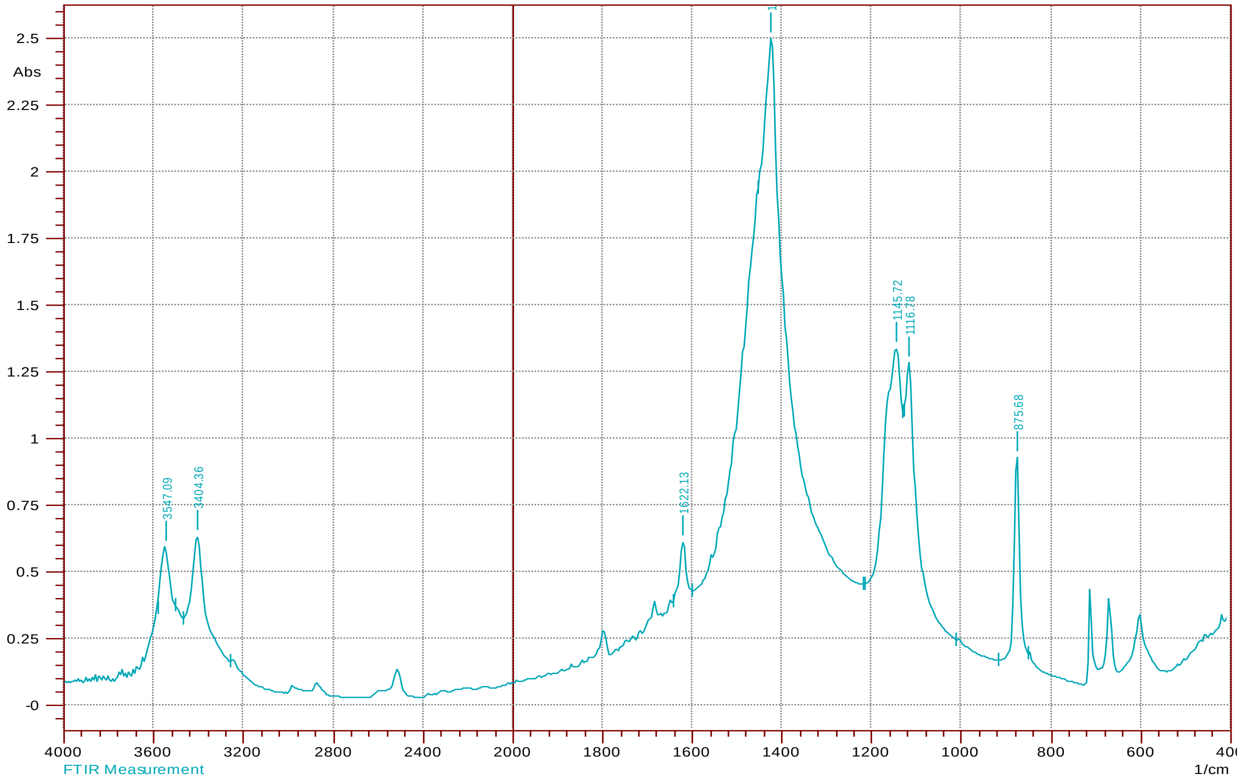

Figure 7- FTIR spectroscopy of calcite-gypsum system (75-25wt. %)

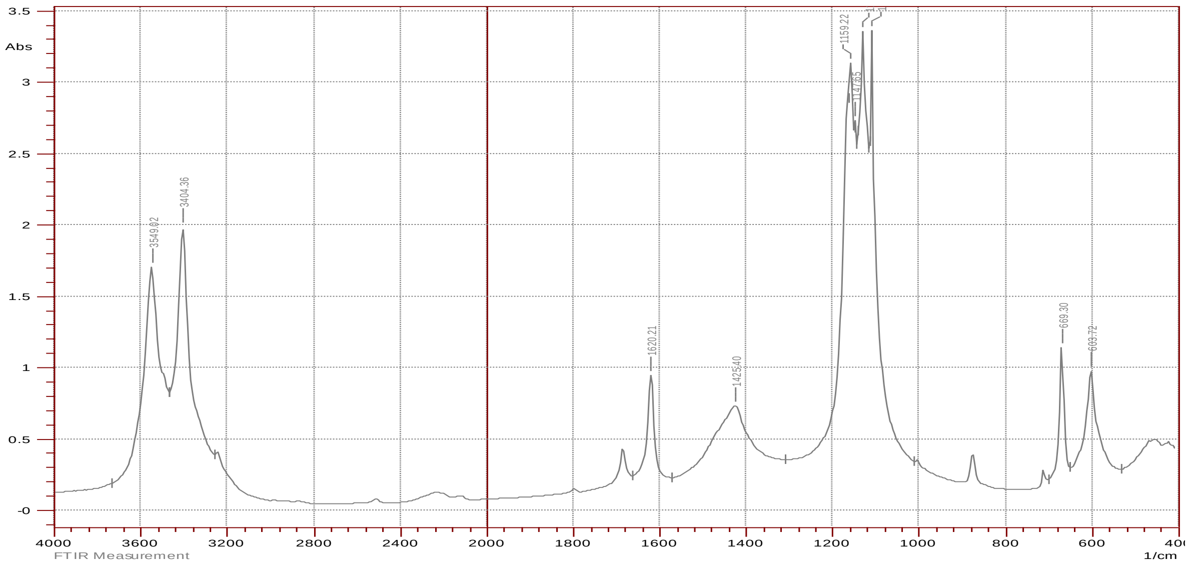

Figure 8- FTIR spectroscopy of calcite-gypsum system (25-75wt. %)

Table 2- Intensity of absorbance of calcite-gypsum system at various compositions.

No.	Ca-Gy wt.%	Cal. Abs.	Gyp. Abs.	Total Abs.	Gyp.Int. Ratio	Gyp. Conc.
1	100-0	2.267	0	2.267	0	0
2	75-25	2.5	1.337	3.837	34.84	25
3	60-40	1.571	2.003	3.574	56.04	40
4	50-50	1.743	2.863	4.606	62.15	50
5	40-60	1.073	2.863	3.936	72.73	60
6	25-75	0.733	3.365	4.098	82.11	75
7	0-100	0	1.813	1.813	100	100

In order to discuss the concentration of any component in the mixture, a calibration curve is constructed based on the ratio of the absorbance of this component to the summation of the two components as calculated in column 6 [5]. Figure-9 shows two calibration curves of the two components according to the data in table -2.

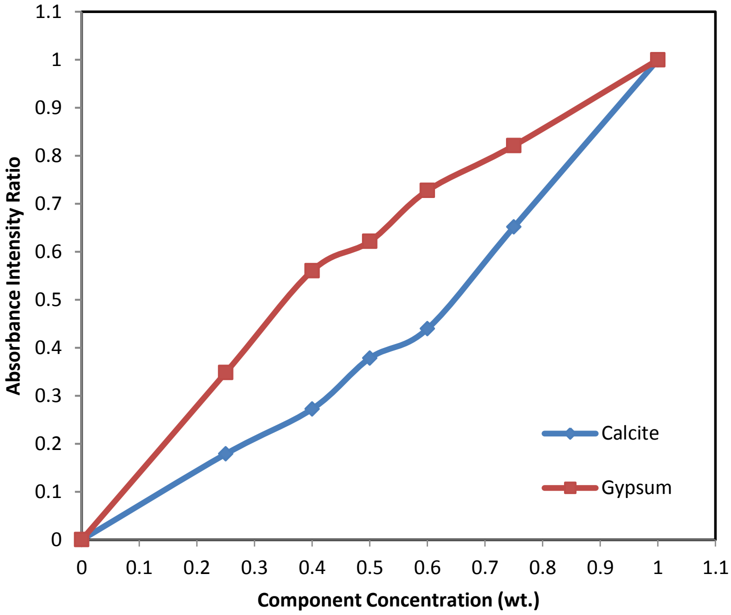

Figure 9- Calibration curve of calcite-gypsum system concentration prediction.

In this study, the collected representative samples from various depths of Alexandria quarries figure-1 taken to specify gypsum content based on the resulted calibration curve. Figure-10, figure-11 and figure-12 show the FTIR spectrum of the three selected samples of gypsiferous soils from Alexandria.

Using the resulted calibration curve shown in figure-9, the prediction of the gypsum concentration in the three representatives samples of gypsiferous soils from Alexandria were done with respect to the absorption ratios, as shown in table -3.

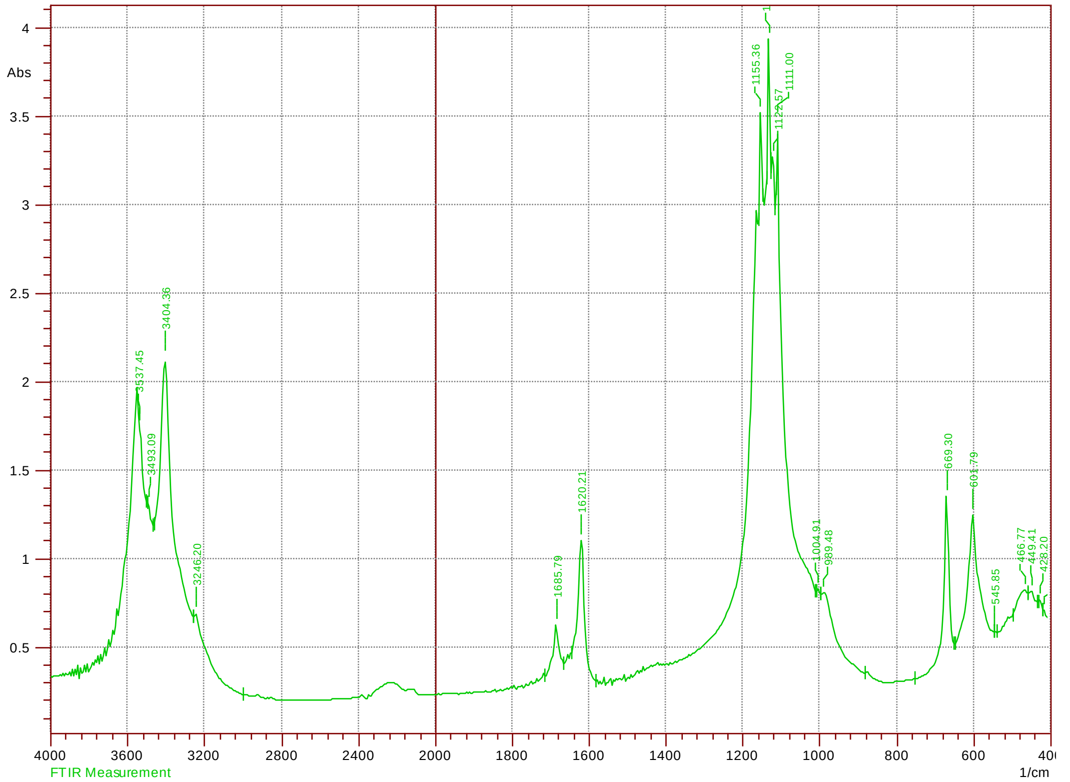

Figure 10- FTIR spectroscopy of sample 1, gypsiferous soil from Alexandria.

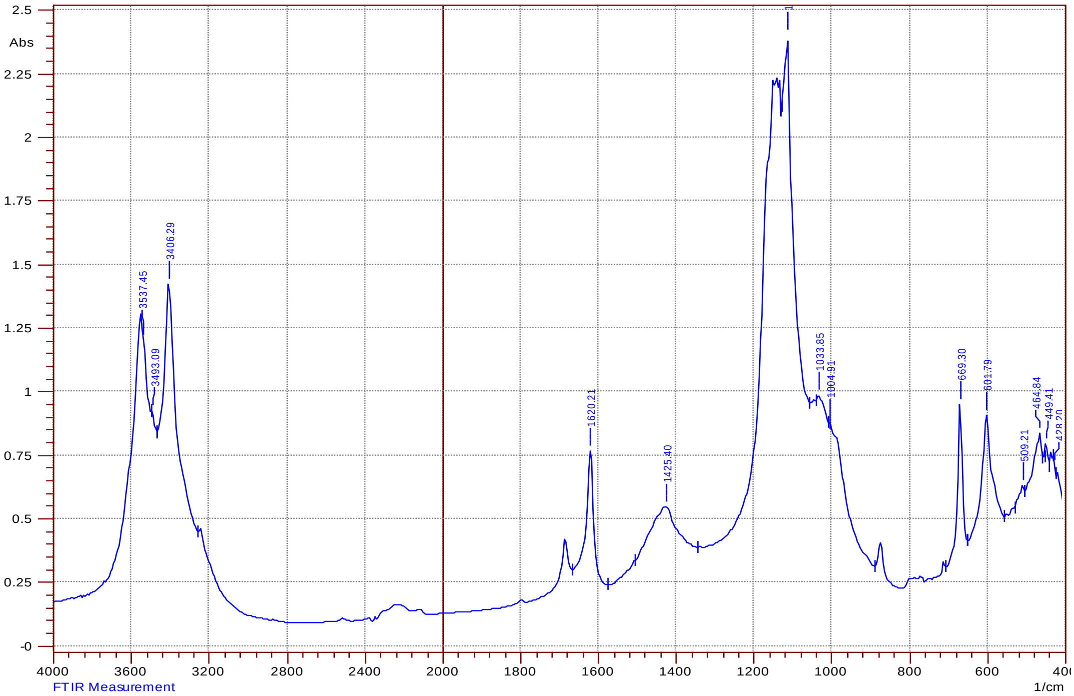

Figure 11- FTIR spectroscopy of sample 2, gypsiferous soil from Alexandria.

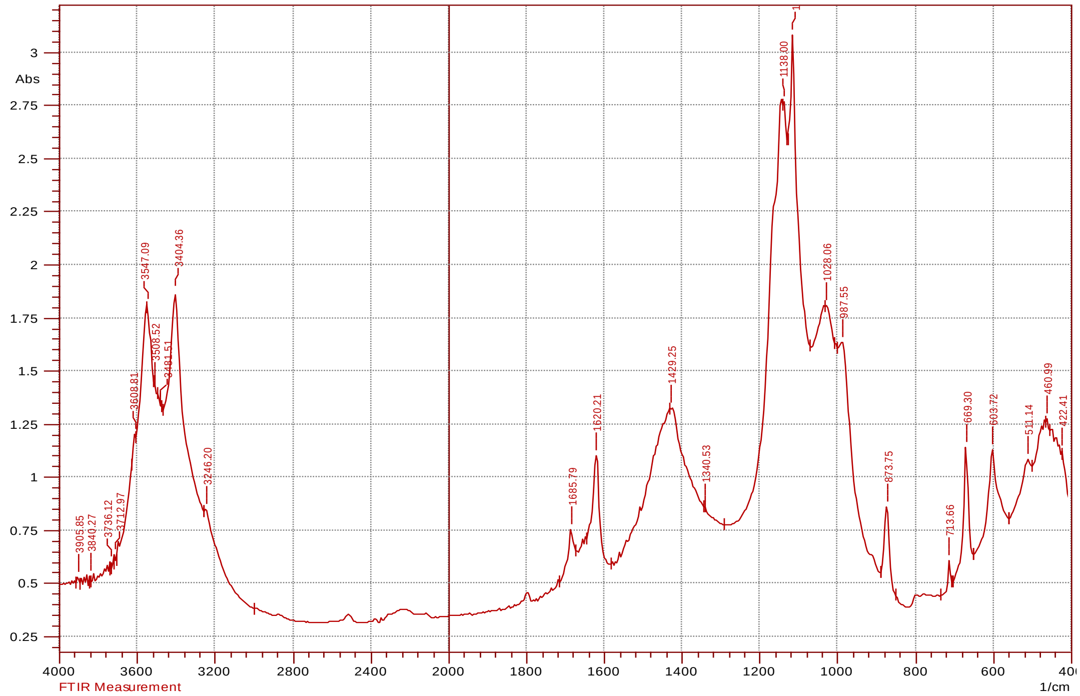

Figure 12- FTIR spectroscopy of sample 3, gypsiferous soil from Alexandria.

Table 3- Predicted gypsum concentrations

Sample No.	Gyp.Abs. Intensity	Cal.Abs. Intensity	Gyp.Abs. Ratio	Gyp.Conc. Wt.%
1	3.9	0.9	0.8125	77
2	2.3	0.6	0.7931	73
3	3.1	1.35	0.6966	62

From the predicted data in table-3, it is clearly found that samples 1 and 2 have the higher purity gypsum. While the lower purity gypsum was shown in sample 3, figure-12 confirm this result by appearance of new absorption bands at 873 and 987 cm^{-1} due to impurities content.

Conclusions

A new quantitative chemical analysis method was developed to accurately determine the compositions of powder mixtures of calcite ($CaCO_3$), and gypsum ($CaSO_4.2H_2O$) from FTIR absorbance peak intensity measurements. Data collected from the study were used to create a calibration curve for prediction the weight percentages. The testing results show that this curve was successfully created and could be used to predict unknown compositions.

Any impurity that does not influence the measured peak intensities is not expected to affect the calibration. Provided that the concentrations of impurities are determined by other analytical techniques, the calibration results obtained in this study can always be normalized through multiplication by (100-% impurities)/100.

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