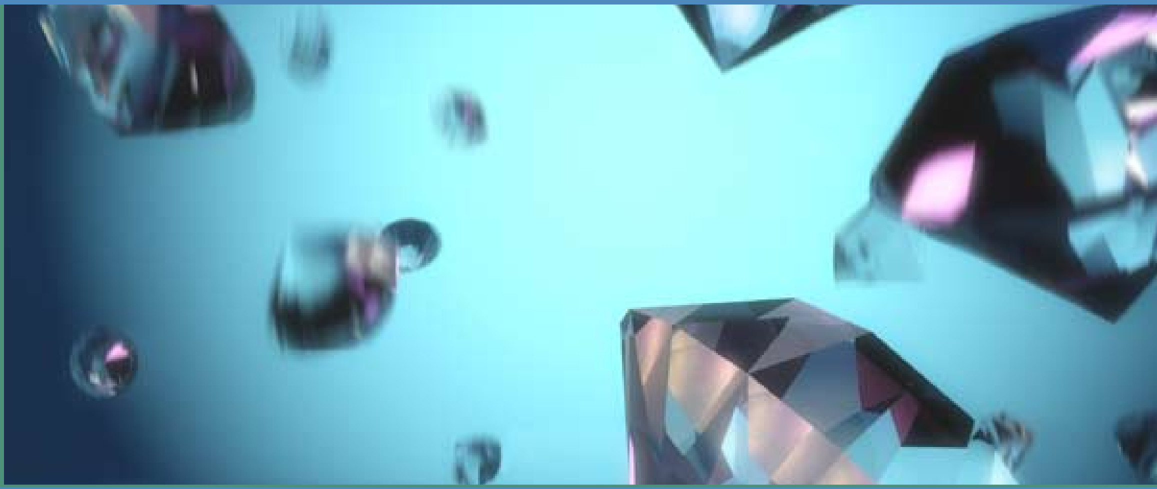
Analysis of Gemstones by FTIR Spectroscopy

Dr. Steve Lowry

Additional contributions by:
Dr. Jerry Workman, Gagan Choudhary, and Dr. Michael Bradley



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Preface

It has become apparent over the last few years that infrared spectroscopy plays a very important role as a general analysis technique in the modern gemological laboratory. FTIR has proven to be an excellent tool for detecting treatments and gem simulants as well as providing key information in differentiating natural gems from their synthetic forms. While no analytical technique can solve all of the problems, FTIR spectroscopy is often the first choice of advanced instrumentation techniques and an infrared spectrum can be a critical part of the certification process. The purpose of this booklet is to describe some of the applications of FTIR in the analysis of gemstones and to discuss various sampling techniques for acquiring high quality infrared spectra from gemstones. This can be a significant challenge for cut or polished stones where the faceting process is designed to internally reflect the light as much as possible. Sophisticated computerized analysis methods have been applied to FT-IR spectroscopy in many other industrial and QC operations. One goal of this work is to demonstrate how these chemometric techniques can be applied to the analysis of gemstones.

Acknowledgements

I encountered a steep learning curve during the development of this application. I thank Gagan Choudary from the Gem Testing lab in Jubai India for valuable discussions and more importantly the contribution of infrared spectra from various gemstones that are included in the example library. I found the visit and discussion with Matt Hall of the GIA laboratory in New York extremely helpful. It was very valuable to see the instrumentation being used in a “real world” setting. I also learned a great deal from discussions and a visit to the laboratory of Dr. George Rossman with the California Institute of Technology.

From Thermo Electron, I would like to acknowledge Jerry Workman for helpful discussions on gemstones and more importantly letting us actually make measurements on samples from his collection. I would like to thank Ross Boyle for assistance on the explanation of IR spectroscopy and Mike Bradley for contributing the section on jade analysis.

Contents

Chapter 1 Introduction

From the very beginning, people have been attracted to stones that were colored, bright and beautiful. Frequently these shiny strange stones were assigned magical or religious significance and provided the owner with great power and prestige. Throughout history gemstones have been a clear indication of the owner's wealth and success. Because of this great value, from the beginning other people have attempted to create, enhance or simulate the appearance of gemstones. Until recent history, these techniques were rather crude, generally involved heating the stones or treating with available natural oils and waxes. Now, very sophisticated techniques have been developed to improve the appearance of a stone through various chemical and physical processes and commercial synthetics are available for almost all popular gemstones.

The vast majority of gemstones are naturally occurring minerals found in the earth that have been crystallized and produce a brilliant reflection or bright color.[1] Most of these crystals were formed over great lengths of time under conditions of high temperature and pressure. Because the geological processes were rarely controlled, the resulting stones were seldom perfect and almost always had flaws and inclusions. The value of the stone is often related to the quality of the crystal and a lack of major flaws, cracks or inclusions significantly increases the price. As with any product of great value, people with the ability and knowledge to identify, verify and classify gemstones have always been in demand.

Until recently, most gemstones could be classified based on experience and a good visual examination. A few basic physical tests for density and hardness were the limits of sophisticated testing. However, in the last century the knowledge of chemistry has led to a number of challenges to the identification, classification and even definition of a gemstone.

The majority of gems are minerals consisting of a combination of atoms in a precise crystal structure. In some cases the chemical structure is well defined, but many gems consist of a mixture of atoms or trace levels of specific atoms that often create the unique color of the stone.

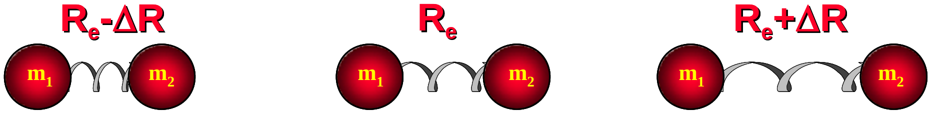
Obviously most gemstones are crystal formations created from the atoms found in the earths crust. They contain a broad range of metal and ions such as chromium, iron, magnesium, calcium, aluminum and beryllium. They generally also contain a negative group or ions such as silicates (SiO_4), oxides (Al_2O_3), hydroxides (-OH) and occasionally borates (BO_3), phosphates (PO_3) and carbonates (CO_3). The majority of gems with the exception of diamond contain oxygen in some form. Many gemstones consist of a major chemical composition that might be colorless such as corundum (Al_2O_3), but the presence of trace amounts of certain metal atoms can create the bright colors. Sapphire and ruby are both corundum. The blue color in sapphires is caused by the presence of iron and titanium, and the red in ruby is due to chromium and iron. Most of the gemstones were formed under high pressure and temperature over great lengths of time.

Infrared Spectroscopy of Minerals

Infrared spectroscopy is a powerful analytical technique that is based on the fundamental vibrations of the atoms in a molecule or crystal. Many of the vibrational modes occur at unique frequencies and can be used to confirm the presence of specific groups in the sample. The frequency of the vibration is often directly related to the atomic weight of the two atoms whose bond is in motion. The simplest model for these vibrations is a harmonic oscillator which can be described by Hook's Law

$$freq.(cm^{-1}) = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} ;$$

where: *k = force constant,* μ = *reduced mass =* $(m_1 \times m_2) / (m_1 + m_2)$ *and c = speed of light.*



The bonds with the highest frequency often contain a hydrogen atom such as O-H or N-H. Heavier atoms such as aluminum or silicon are often bonded to oxygen and these frequencies are significantly lower. When infrared radiation is focused on a mineral, and the light is at the same frequency as a fundamental vibration of the bond, some of the light is absorbed; exciting the molecule into a higher vibrational state. While a vibrational mode is generally based on a specific bond in the molecule, the local environment around it also affects the frequency of the vibration. This greatly increases the usefulness of infrared spectroscopy for analyzing complex systems such as gemstones. The figure below shows the energy level diagram for the vibrational and rotational modes. For a gemstone containing many different atoms the infrared spectrum can become quite complex.

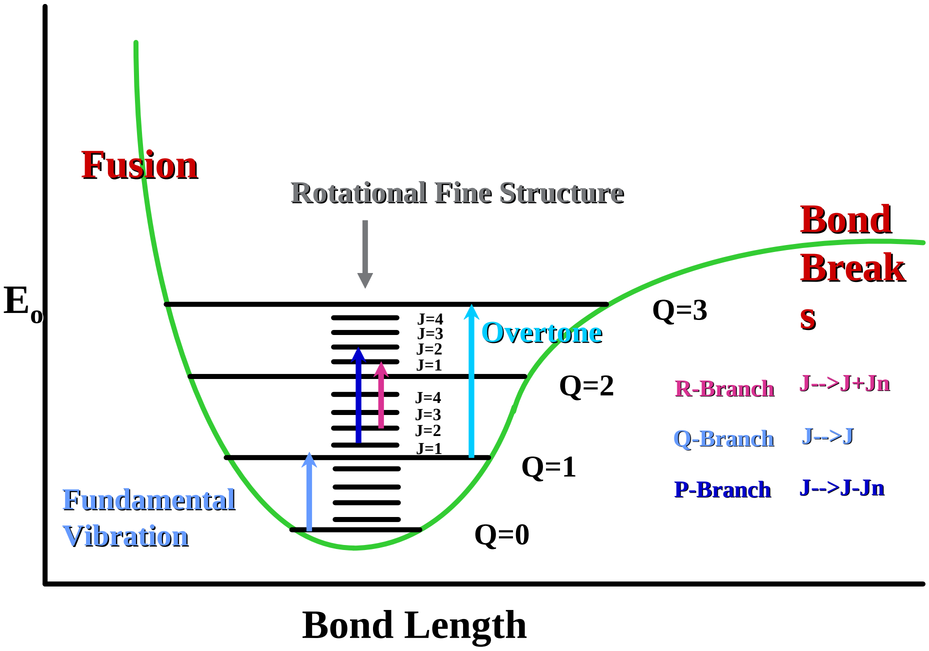


Figure 1-1. Energy level diagram for infrared spectral modes

An FTIR spectrometer measures the amount of light absorbed by the sample at each frequency and reports the difference from the original intensity as an infrared spectrum of the mineral. Besides the fundamental vibrational modes, spectral features can be caused by crystal lattice modes as well as overtone and combination bands that appear in the near infrared spectral region. The following figure shows the crystal structure of Zircon ($ZrSiO_4$), which consists of precisely positioned atoms of zirconium, silicon and oxygen.

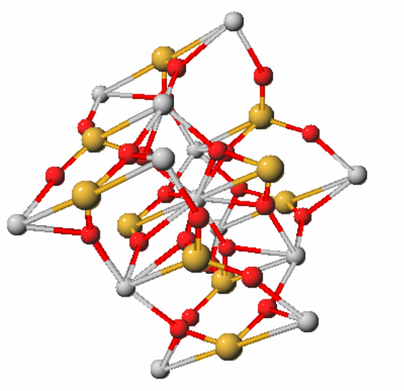


Figure 1-2. Crystal structure of Zircon

Diamond is a very unique example of a gemstone in that it does not contain oxygen as a major component of its chemical structure. Diamond consists of pure crystalline carbon, and the only spectral features in a perfect sample are the phonon bands due to the crystal lattice. However natural diamonds are rarely pure and the presence of nitrogen or other atoms in the stone causes distortions in the crystal structure that create specific peaks in the infrared spectrum. Similar effects are observed in many gems due to the presence of water, CO_2 or hydroxyl groups in the sample. **Figure 1-3** shows the infrared spectrum of a diamond with significant peaks corresponding to the presence of nitrogen.

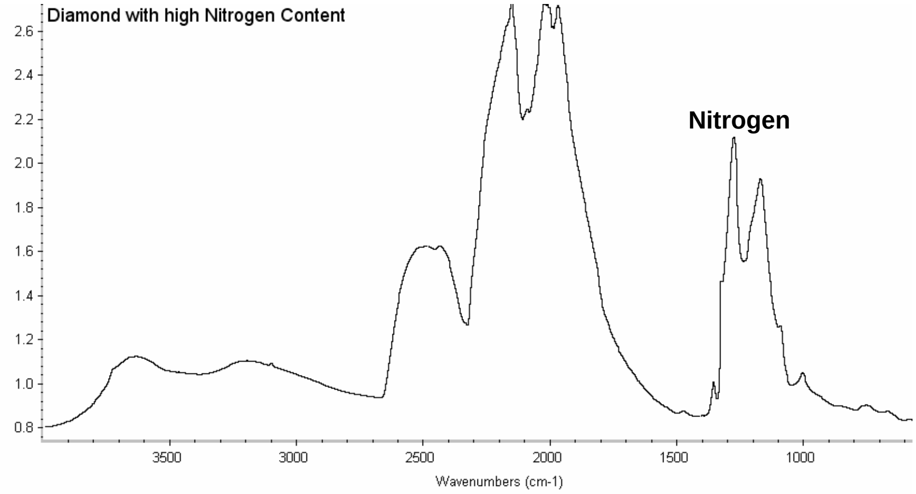


Figure 1-3. Spectrum of a diamond with high nitrogen content

An important feature of infrared spectroscopy is that the height of the peaks corresponds to the amount of the specific material in the path of the infrared light. This is called Beer's Law where A=abc. If one gemstone is twice as big as another the peaks in the spectrum will be twice as large or if the amount of a certain chemical in the stone is much less than another, the corresponding peak will be much smaller. This is not important for the predominant chemicals in the sample but can be quite valuable in differentiating samples based on the amount of nitrogen or hydroxyl in the sample. In fact for diamonds, stones are classified on the basis of the amount and type of nitrogen in the stone.

The downside of Beer's law is that for many large gemstones the peaks are totally absorbing. This is seen in **Figure 1-4**, which shows the spectra from several different gems that were acquired in this laboratory. In this figure the spectra are plotted showing the percent of light that is transmitted through the stone, and in several spectral regions the signal goes to zero.

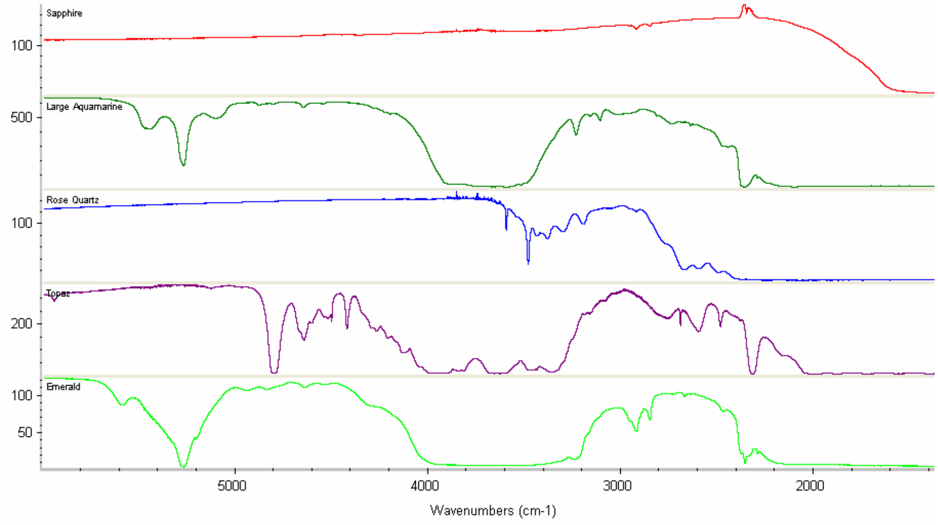


Figure 1-4. Spectra of gemstones, showing the affect of signal saturation, in percent transmission.

The top spectrum is from a sapphire. Sapphire is totally absorbing below 1000 cm^{-1} but has very few features in the remainder of the spectrum, particularly in the OH spectral range between 3000 and 4000 cm^{-1}. The remaining spectra all have strong absorptions in this region as well as strong peaks in the overtone/combination region above 4000 cm^{-1}. The spectrum of quartz shows some interesting peaks in the OH region but no significant features in the NIR region above 5000 cm^{-1}.

With the exception of very thin samples, the best way to obtain the spectral features from the fundamental vibrations between 2500 cm^{-1} and 400 cm^{-1} is to reduce the particle size of the sample to several microns and disperse it in a transparent medium such as potassium bromide (KBr). This normally requires grinding, which obviously destroys the sample. Example spectra of representative materials from the Thermo Electron HR Inorganic spectral library are shown below.[2] The spectra displayed above show the spectra with the intensity plotted as the percent of the incoming light that is absorbed by the sample at each wavelength. If all of the light is absorbed by the sample, the value is zero as seen in the 3500 cm^{-1} region for several samples. In the figure below the spectra are displayed in absorbance mode where the intensity is proportional to the number of absorbing species in the light. This scale is better for determining the concentration of a species in the sample and the areas of stronger absorption appear as peaks instead of valleys. In the spectrum of emerald shown below, the peaks for the O-H vibrational modes at 3500 cm^{-1} are barely visible while they are often totally absorbing in a spectrum acquired by passing light through an intact gemstone as shown above.

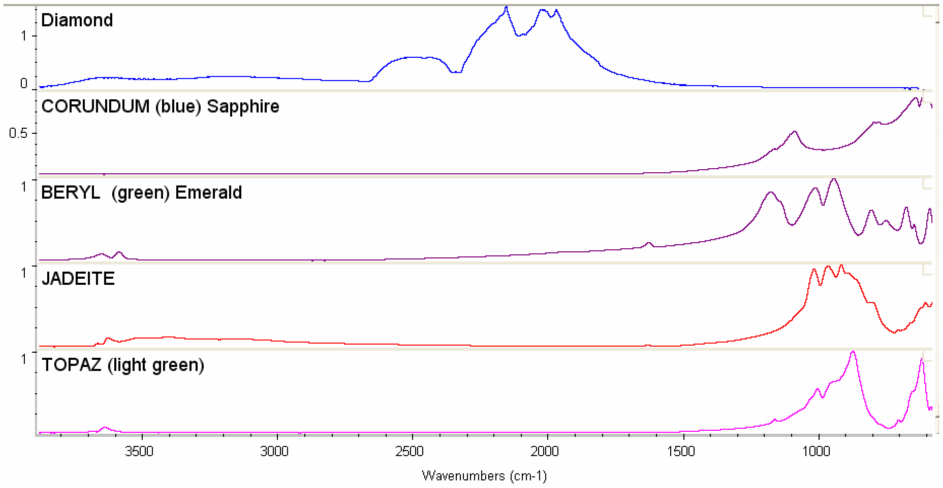


Figure 1-5. Spectra acquired from powder samples mixed with KBr and pressed into a pellet.

The Website developed by Professor George Rossman of the geoscience department at the California Institute of Technology contains a great deal of useful information as well as an extensive reference list.[3] The website contains reference spectra collected by different techniques including attenuated total reflectance (ATR) and specular reflectance.

Acquiring Infrared Spectra from Gemstones

A very unique feature of faceted stones is their ability to internally reflect the light within the gem. While this is designed to optimize their beauty for visible light, it is equally effective for infrared light. This means that it is not a simple task to shine infrared light through a faceted stone to obtain an infrared spectrum. Because of these reflections, the amount of infrared signal reaching the detector after passing through the stone can be quite low. With FT-IR spectroscopy, the sensitivity can be improved by taking a longer measurement from the sample. When the measurement time is increased by a factor of four, the noise is reduced by a factor of two. A second way to improve sensitivity is to use a detector that is cooled with liquid nitrogen. These high sensitivity detectors can greatly reduce the time required to obtain a high quality spectrum. A second important consideration is spectral resolution. For many measurements a resolution of 4 cm^{-1} or even 8 cm^{-1} is adequate to extract the desired information from the infrared spectrum. However, there are other measurements that require higher resolution. The most important requirement for higher resolution is measuring the peaks in a diamond spectrum related to the low level atoms such as hydrogen and nitrogen. A resolution of 1 cm^{-1} reveals several of these peaks to be very sharp, and the improved resolution is very important in these analyses. A resolution of 4 cm^{-1} is adequate for many analyses including determining diamond types. For a more detailed analysis of a diamond sample, 1 cm^{-1} resolution and longer measurement times can greatly improve the results.

4X Beam Condenser

Laboratories with extensive experience in the analysis of diamonds and other gemstones use a 4X beam Condenser for much of their work. They mount the gem in the accessory and then manually adjust the X, Y, Z position of the diamond until they get the best signal possible. This is very important because of the large difference in the size of the stones and the different cuts. They generally try to focus the light on the flat area at the girdle. Focusing on most other areas results in very little light getting out of the sample and to the detector. Remember the whole purpose of the expensive diamond cutting process is to increase the internal reflections in the stone. A gemstone is a complex optical component with many characteristics of a lens and it takes some experience to acquire a high quality spectrum. It is almost impossible to acquire quality spectra without the correct accessory. The stone is placed face down on the X, Y, Z stage of the beam condenser. In some cases Blu-Tack™ may be used to hold stone but cut stones with a stable flat surface may be laid directly on the mounting block. The height and focus are adjusted so that the light enters through the girdle of the stone. Usually the final adjustments are made while observing the spectrum in preview mode on the monitor to maximize the signal.

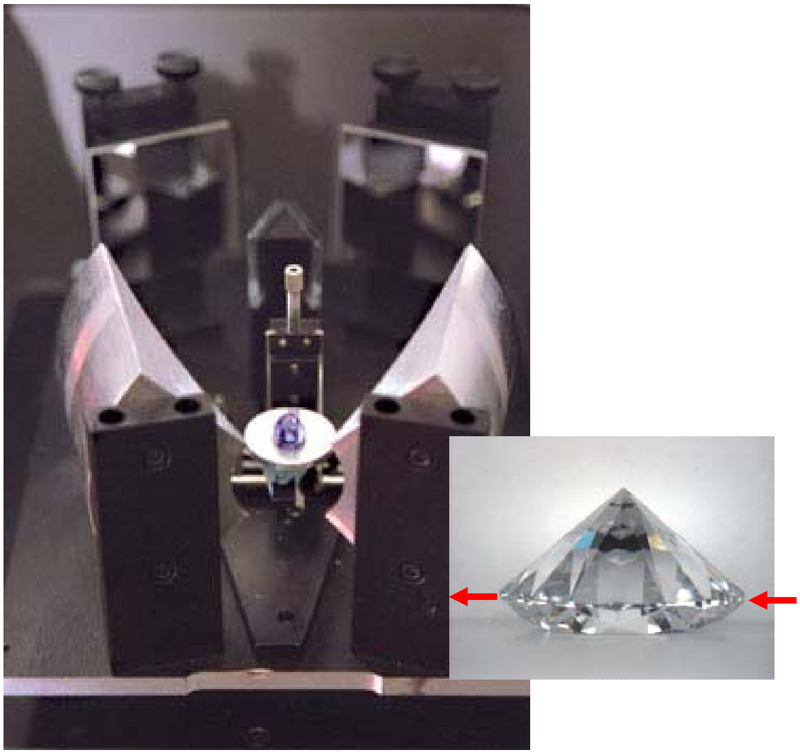


Figure 1-6. Beam condenser and a schematic of the light entering the stone

Some of the peaks attributed to the presence of different atoms in the crystal can be quite sharp and higher resolutions such as 1 cm^{-1} may be required. The spectra shown below were obtained from different types of diamonds.

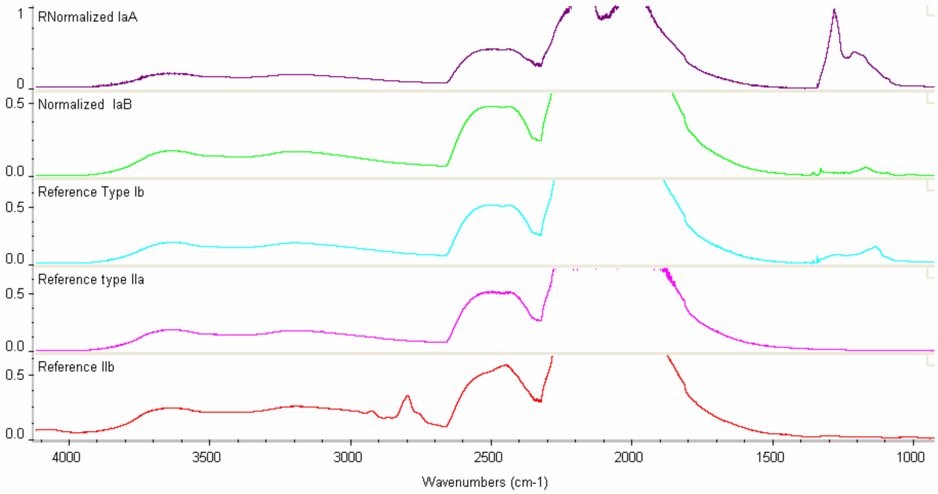


Figure 1-7. Infrared spectra from different diamond types.

The Collector II™ reflectance accessory

The second accessory that is used extensively for gem analysis is the Collector II diffuse reflectance accessory. Two large mirrors are positioned over the sample to focus the light down and to collect the light reflected back from the sample. These large mirrors provide a good way to obtain spectra from cut stones with different angles and shapes. The stone is simply placed on top of the mirrored surface and the height is adjusted to get the best signal. The signal from a transparent gemstone is not actually diffuse reflectance, but predominantly light that has been internally reflected off of the faces of the stone. In some cases, particularly with smaller stones, light may be back reflected off of the mirror creating a transflectance signal. The spectral quality is generally not as pure as those acquired with the beam condenser, but spectra can be acquired from pieces that cannot fit in the beam condenser, and it is usually easier to acquire the spectrum even though the height of the sample needs to be adjusted for best results. The path length through the stone is also slightly longer, so there may be more peaks that totally absorb.

Figure 1-8. Collector II reflectance accessory and a schematic of the light entering the stone

An important advantage of the Collector II accessory is in obtaining spectra from samples that are not transparent. In these samples, infrared light is actually diffusely reflected from particles in the material and collected by the large mirror above the sample. Good spectra can often be obtained from materials such as jade, opal or turquoise using this accessory.

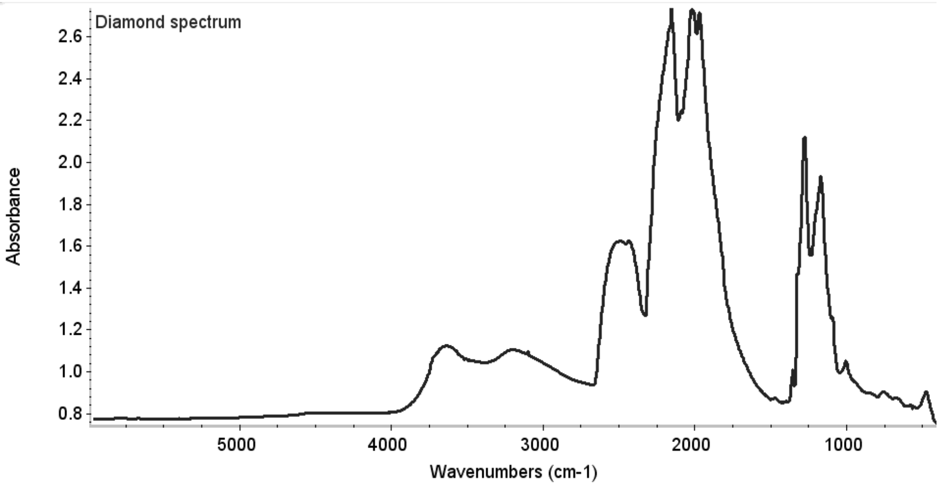


Figure 1-9. A diffuse reflectance spectrum acquired from a diamond with the Collector II accessory.

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Transflectance spectra acquired by infrared microscopy

Dr. Sanong Ekgasit recently published the results of his research using an infrared microscope to obtain spectra from faceted diamonds[4,5]. In this application Dr. Ekgasit utilizes the internal reflecting properties of the cut stone to obtain a spectrum in reflectance mode. The figure below describes the light path through the stone and shows the Continuum™ infrared microscope.

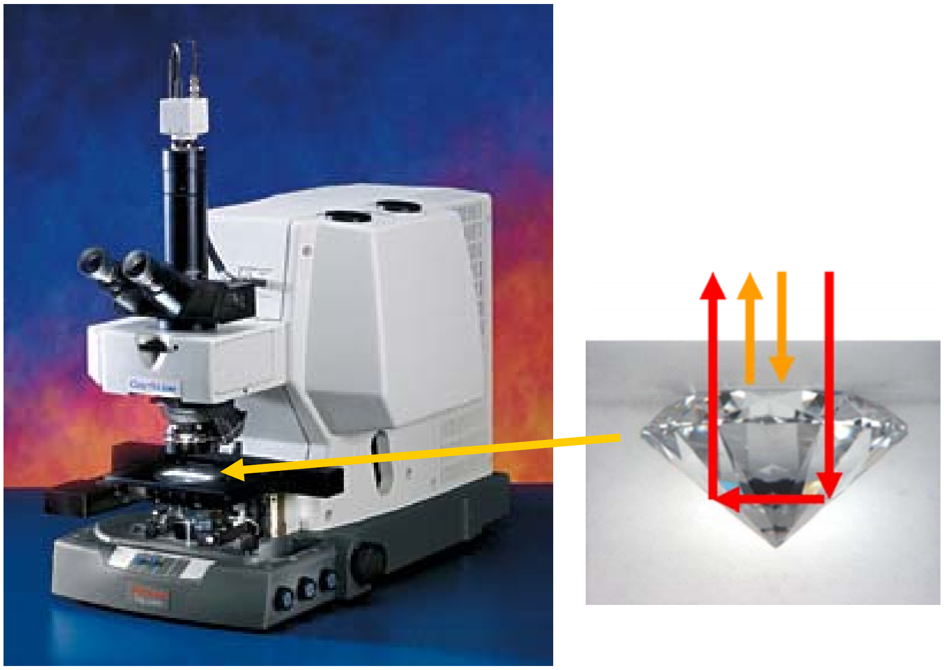


Figure 1-10. Continuum infrared microscope and the light path through the stone by internal reflection (red)

The diamond is positioned on the microscope stage with the table up. The infrared light is focused on the stone, and the reflected light is returned to the detector. Dr. Ekgasit compares the results of this measurement to the spectra acquired with the diffuse reflectance accessory. Dr. Ekgasit chose to convert the "diffuse reflectance" spectrum to Kubelka-Munk units, which is common for true diffuse reflectance. However, the signal is not diffusely reflected but internally reflected with no actual scatter. A better scale for comparative purposes might be absorbance or log(1/R).

An interesting possibility with the microscope configuration is the ability to measure a complete tray of stones automatically with a motorized microscope stage and the Array Automation™ software. This software is designed to work with 96 well or 384 well biological microwell plates, but would work with a special plate designed to hold each stone with the table up in a precise array of X, Y positions such as 10 x 10.

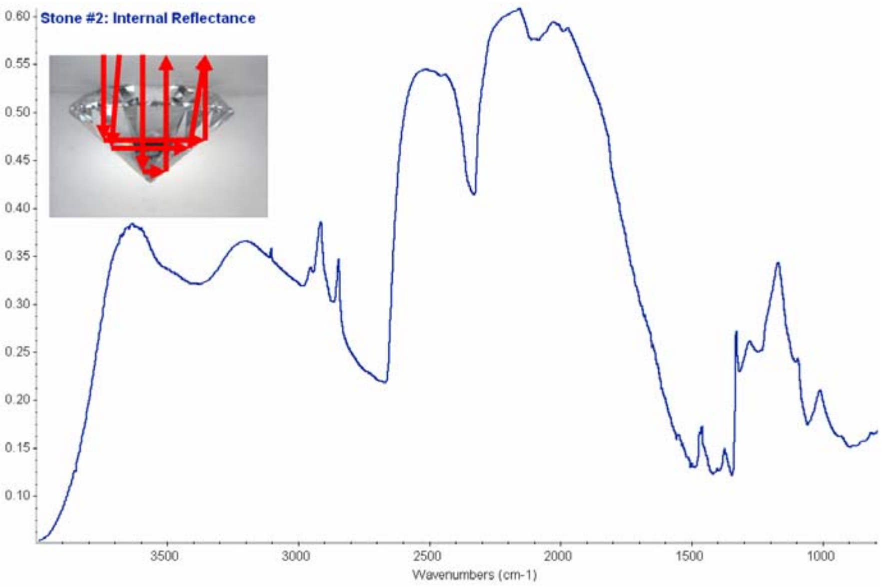


Figure 1-11. Spectrum of a diamond acquired in transflectance mode

Extended range spectral acquisition for NIR information

While many of the FTIR applications only look at the mid-IR spectral region (5000 – 400 cm-1), the near IR (NIR) region can also provide some valuable information. For colored stones the region above 3000 cm^{-1} contains valuable information for identifying and classifying stones. Many of the peaks are water and OH that is present in the stone. The Nicolet™ 6700 with extended range KBr beamsplitter, NIR source and MCT detector can provide good spectra out to almost 10,000 cm^{-1} (1000nm).

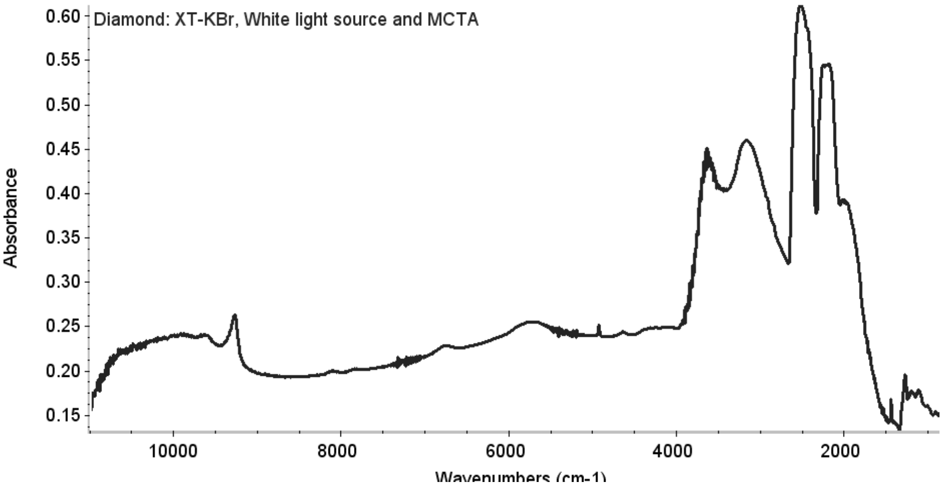


Figure 1-12. Extended range spectrum out to 1000 nm

This chapter has shown two ways to acquire spectra from cut stones. In most cases the beam condenser provides a more flexible approach. Because of the limited amount of light that gets through a gemstone, an analysis may require extensive signal averaging to reduce noise.

For opaque materials the diffuse reflectance capability of the Collector II accessory will generally provide better spectra than the beam condenser.

Chapter 2 Analysis of Diamonds by FTIR

The huge popularity of diamonds and their great value has led to extensive research into finding ways to identify and classify the different types of diamonds. FTIR has proven to be an easy, reliable technique for much of this work. Much of the early FT-IR development work was done by researchers in the geological community and focused on understanding the processes that created diamonds.DD[1,2,3,4,5,6,7] Most of this work was performed on the original stones or thin slices with precisely known pathlengths. FTIR spectrometers have become one of the more important instruments for analyzing diamonds in the modern gemological laboratory. While it is considered an expensive "hi-tech" instrument in the diamond trade, FTIR has proven to be a reliable straightforward technique to characterize diamonds as well as a very useful research tool in developing a better understanding of the geological process that created this unique material. Because of it's unique chemical structure and the extensive research into the spectral effects of the trace components, confirmation that a sample is not a simulant as well as classifying by type are very straightforward analyses. Recenlty, FT-IR spectroscopy has been shown to be a valuable aid in identifying HPHT treated and lab grown diamonds.[6,7,8] The FT-IR spectrum is considered a valuable piece of evidence in the effort to confirm that a stone is natural and untreated.

Detection of Diamond Simulants

The high price of diamonds has created a large demand for jewelry that has a similar appearance but not the cost of natural stones. The preferred marketing term for these materials has become “simulants” as opposed to fakes. Because of the unique features in the infrared spectrum of a diamond, it is very easy to differentiate a diamond from any of the simulants by FTIR. It can be more difficult to identify the exact stimulant because of the similar structures for several of the materials sold as diamond simulants. All of these materials contain metal oxide bonds that absorb strongly where diamond is transparent. Spectra of several materials frequently sold as colorless gemstones are shown below. Gagan Choudhary of the Gem Testing Laboratory in Jaipur, India, kindly provided the spectra.

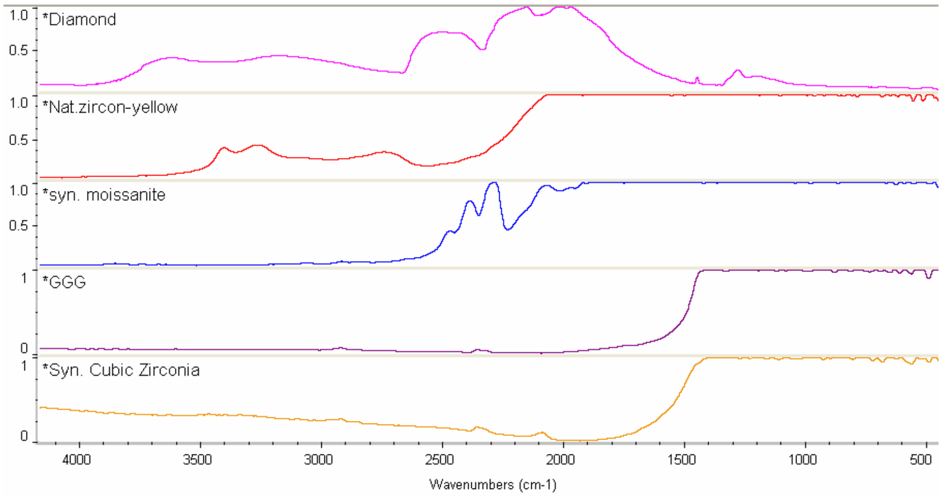


Figure 2-1. Infrared spectra of materials commonly mistaken for diamonds

Once a high quality spectrum has been acquired from a diamond, the next step is to extract the desired information from the spectrum. In the remainder of this chapter, examples utilizing the chemometric tools provided with the Nicolet FTIR spectrometer to learn more about the stone will be given.

Extracting Features from the Spectrum of a Diamond

The unique properties of the diamond crystal structure not only produce its desired optical characteristics but also result in some very interesting infrared spectral features. While the symmetric structure of the pure diamond crystal prohibits any infrared spectral features from appearing in the one-phonon absorption in the mid-infrared spectral region, any defects in this structure may lead to a spectral feature in this region. The presence of small amounts of nitrogen in the crystal structure produces such peaks. The exact location of the peaks depends on the position of the nitrogen atoms in the crystal lattice. The amounts of each of these aggregation defects reveal a great deal about the creation and history of the stone. The amounts of the IaA and IaB aggregates are particularly important. This analysis has been described in detail in the work of Mendelssohn and Milledge.[1]

A macro program is described in this section that automatically extracts the features reported by Mendelssohn, et al. Once the spectrum has been acquired, the software does a quick check of the spectral intensity in the one-phonon region to insure that the peaks are not totally absorbing. If the maximum intensity exceeds 3.5 absorbance units a warning is issued, and the user is asked if they wish to continue. The spectrum is baseline corrected so that the minimum intensity is set to 0.0 Abs. The spectrum is then normalized by setting the intensity of the 2-phonon band at 1992 cm^{-1} to 1.23/mm. If this peak is off-scale, the peak at 2500 cm^{-1} is scaled to 0.48/mm. The peak locations and intensities are then determined as shown in **Figure 2-2**.

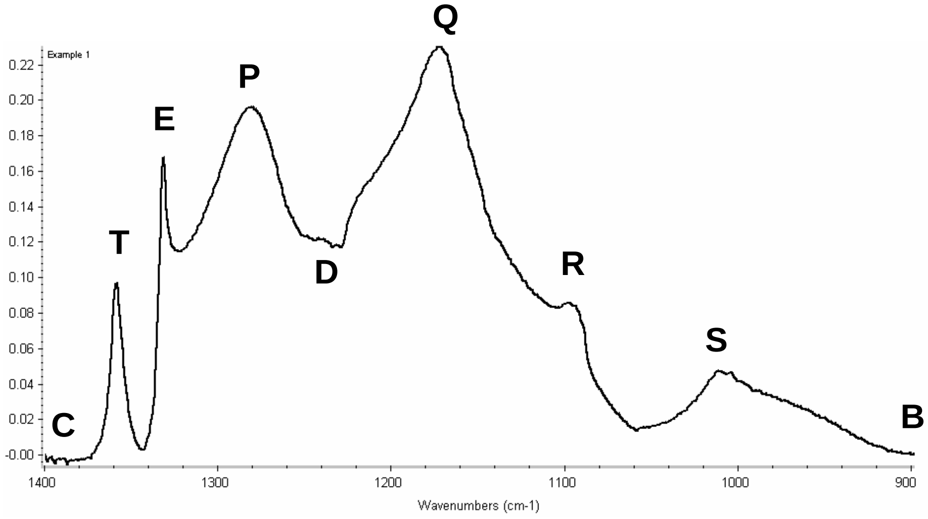


Figure 2-2. The locations of important features as reported in Mendelssohn, et al.

The second region used in analyzing diamonds is on top of the two-phonon band and contains a peak due to the presence of hydrogen in the crystal.

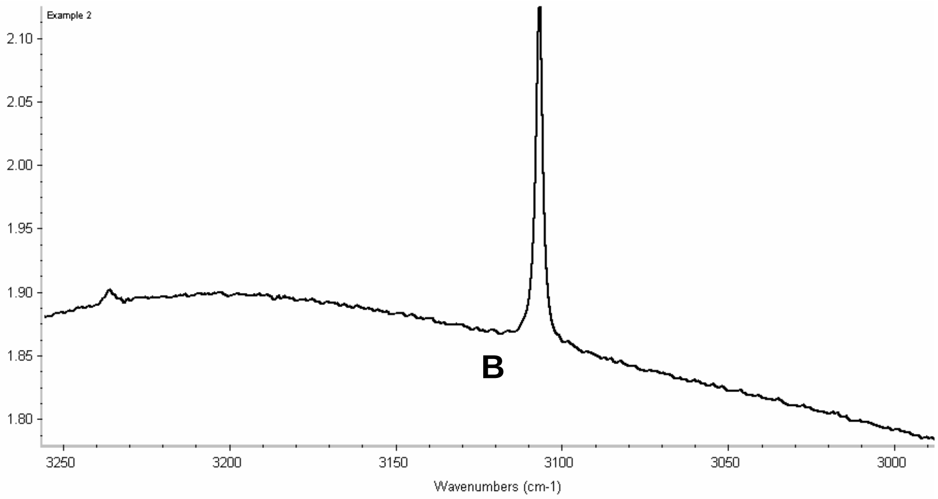
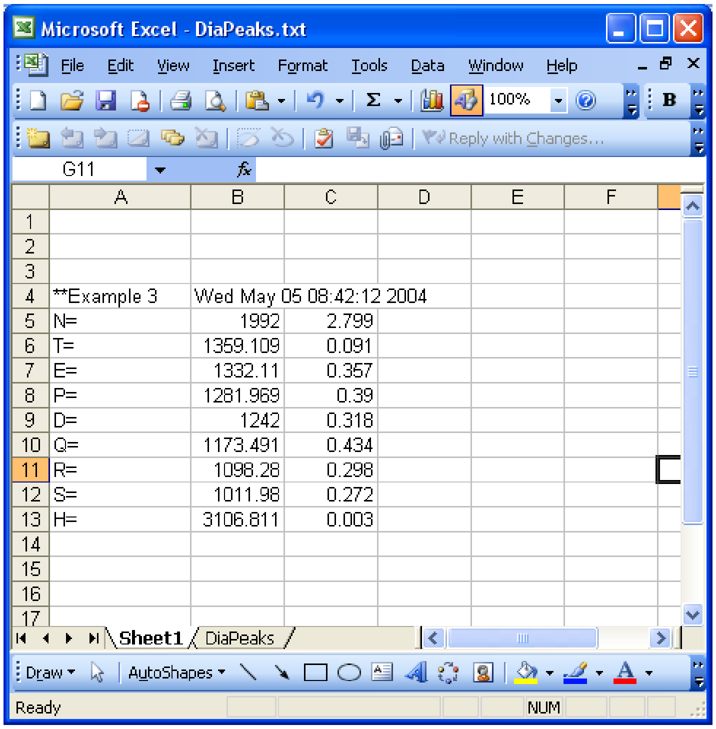


Figure 2-3. Hydrogen peak at 3107 cm^{-1}

The calculated values are stored in the comment section of the spectrum as well as in a comma separated text file. The text file can be opened in Excel™ for further processing as described by Mendelssohn and Milledge.



	A	B	C
4	**Example 3	Wed May 05 08:42:12 2004	
5	N=	1992	2.799
6	T=	1359.109	0.091
7	E=	1332.11	0.357
8	P=	1281.969	0.39
9	D=	1242	0.318
10	Q=	1173.491	0.434
11	R=	1098.28	0.298
12	S=	1011.98	0.272
13	H=	3106.811	0.003

Figure 2-4. Location and intensity of important features in the diamond spectrum

All of these values are accessible in an extended macro that would calculate the parameters used for actually classifying diamonds. This includes such measurements as D/P that can be used to estimate the amount of type IaA in the sample.

Analysis by the Classical Least Squares Technique

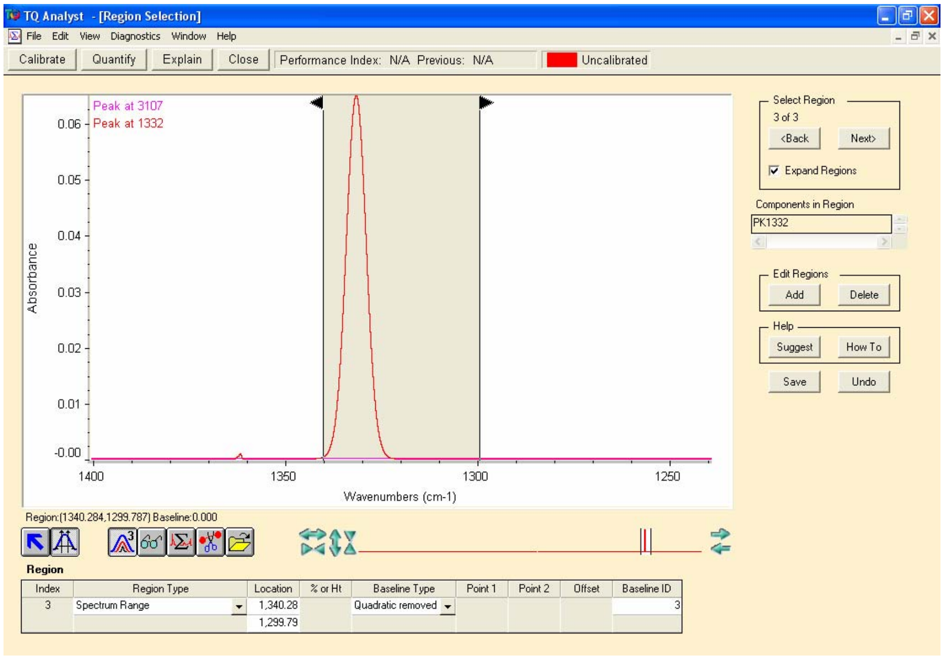
The presence or absence of certain peaks in the infrared spectrum obtained from a diamond can provide very important information about the type and history of the stone.

In many infrared spectroscopic applications the intensity of specific peaks in the absorbance spectrum corresponds to the concentration of the material in the sample. This very simple “law” forms the basis of the Classical Least Squares (CLS) approach to spectral analysis. This approach assumes that the sample spectrum is a linear combination of spectra from the independent components found in the sample. This implies that the peaks do not change their locations but only their intensity as the concentration increases. Since the technique minimizes the difference of the sample spectrum from a set of standard spectra, if the concentrations of the components in the standard spectra are known, the CLS results provide a very good estimation of the concentrations in the sample spectrum. In many cases this is true to at least to a first approximation. An important feature of the CLS technique is that a standard error is determined as part of the calculation. This can be very important in confirming the presence of small peaks because it provides a confidence value that the defined peak is actually present.

In this section are two examples of the use of CLS in the analysis of diamond spectra. In the first example, a method to report on the presence and intensity of three peaks in the diamond spectrum has been created. These are 3107cm^{-1}, 1344 cm^{-1} and 1332 cm^{-1}. In the spectra from many samples these peaks are very small, and it may be difficult to distinguish them from the background spectral noise but they can provide important information on possible treatments[8]. In the second example, a method that uses “pure” spectra from Type IaA, IaB Ib, and IIb diamonds has been created to estimate the amount of each type in the spectra from test gemstones.

Detecting the presence of small peaks

In this example TQ Analyst™ was used to create a method to determine the intensity of three peaks that are commonly found in a diamond spectrum. These peaks are the hydrogen peak at 3107cm^{-1}, the IaB peak at 1332cm^{-1} and the single nitrogen peak at 1344cm^{-1}. A standard spectrum for each component was used to develop the method. The following figure shows the **Region Select** function in TQ Analyst that is used to select the region to be utilized in measuring a specific component in the spectrum.



Performance Index: N/A Previous: N/A

Select Region: 3 of 3

☑ Expand Regions

Components in Region: PK1332

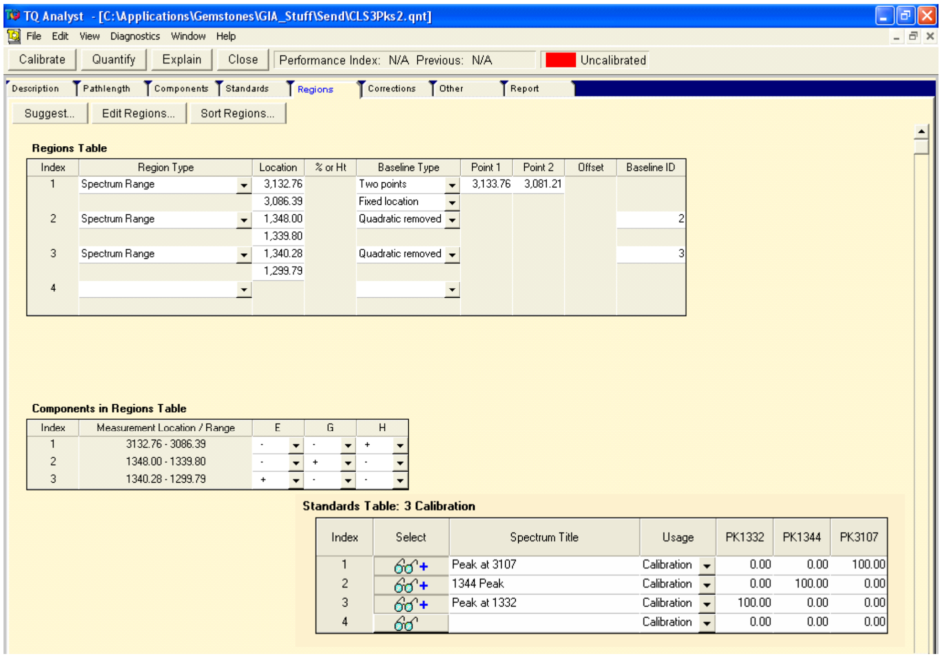
Region:(1340.284,1299.787) Baseline:0.000

Region

Index	Region Type	Location	% or Ht	Baseline Type	Point 1	Point 2	Offset	Baseline ID
3	Spectrum Range	1,340.28		Quadratic removed				3
		1,299.79						

Figure 2-5. Region selection tools in TQ Analyst.

In this example a spectral region is defined, and a baseline correction technique is chosen for each component. The region used for measuring the 1344cm^{-1} peak is shown in the figure above. All of the parameters required for this analysis are shown below. In this case the “concentration” for each of the three standard spectra was set to 100. If the actual concentrations were known, those values would be entered, and the analysis would report out the calculated amounts in the sample spectrum. In this example the report simply gives the percent of intensity relative to the standard spectrum. In many cases a particular component may have spectral features in several of the selected regions. This will be discussed in the next section.



Performance Index: N/A Previous: N/A

Regions Table

Index	Region Type	Location	% or Ht	Baseline Type	Point 1	Point 2	Offset	Baseline ID
1	Spectrum Range	3,132.76		Two points	3,133.76	3,081.21		
		3,086.39		Fixed location				
2	Spectrum Range	1,348.00		Quadratic removed				2
		1,339.80						
3	Spectrum Range	1,340.28		Quadratic removed				3
		1,299.79						
4								

Components in Regions Table

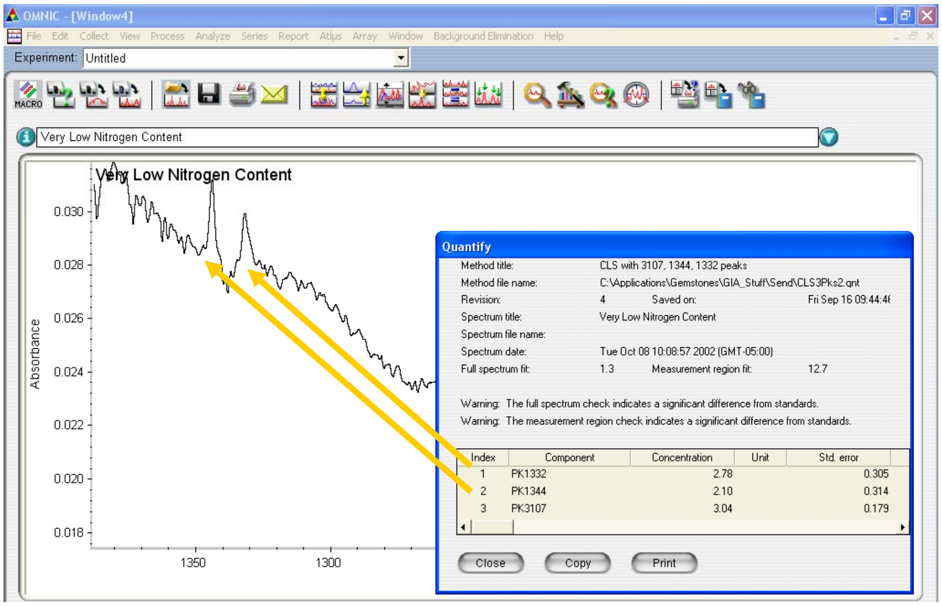
Index	Measurement Location / Range	E	G	H
1	3132.76 - 3086.39	-	-	+
2	1348.00 - 1339.80	-	+	-
3	1340.28 - 1299.79	+	-	-

Standards Table: 3 Calibration

Index	Select	Spectrum Title	Usage	PK1332	PK1344	PK3107
1	+	Peak at 3107	Calibration	0.00	0.00	100.00
2	+	1344 Peak	Calibration	0.00	100.00	0.00
3	+	Peak at 1332	Calibration	100.00	0.00	0.00
4			Calibration	0.00	0.00	0.00

Figure 2-6. Setup screens for the TQ Analyst method.

Once a method has been developed and calibrated, it can be used directly from an OMNIC™ window or in a macro for automated processing. The figure below shows the results from using this method on a spectrum with very low nitrogen concentrations. In this example the actual concentrations were not known so the results are a best estimate.



Experiment: Untitled

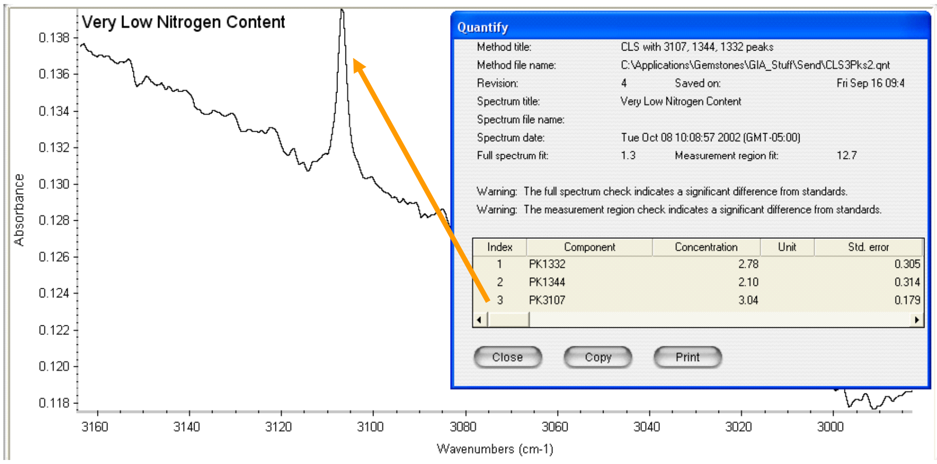
Method title: CLS with 3107, 1344, 1332 peaks
Method file name: C:\Applications\Gemstones\GIA_Stuff\Send\CLS3Pks2.qnt
Revision: 4 Saved on: Fri Sep 16 09:44:4
Spectrum title: Very Low Nitrogen Content
Spectrum file name:
Spectrum date: Tue Oct 08 10:08:57 2002 (GMT-05:00)
Full spectrum fit: 1.3 Measurement region fit: 12.7

Warning: The full spectrum check indicates a significant difference from standards.
Warning: The measurement region check indicates a significant difference from standards.

Index	Component	Concentration	Unit	Std. error
1	PK1332	2.78		0.305
2	PK1344	2.10		0.314
3	PK3107	3.04		0.179

Figure 2-7. Automatic detection of very weak peaks in the spectrum.

For most applications we believe a result that is several times larger than the reported standard error clearly defines the presence of a peak. In this example both peaks are 7-8 times the calculated standard error. The peak corresponding to the presence of hydrogen is shown below with the **Analysis Report**. The peak is at least 15 times larger than the standard error.



Method title: CLS with 3107, 1344, 1332 peaks
Method file name: C:\Applications\Gemstones\GIA_Stuff\Send\CLS3Pks2.qnt
Revision: 4 Saved on: Fri Sep 16 09:4
Spectrum title: Very Low Nitrogen Content
Spectrum file name:
Spectrum date: Tue Oct 08 10:08:57 2002 (GMT-05:00)
Full spectrum fit: 1.3 Measurement region fit: 12.7

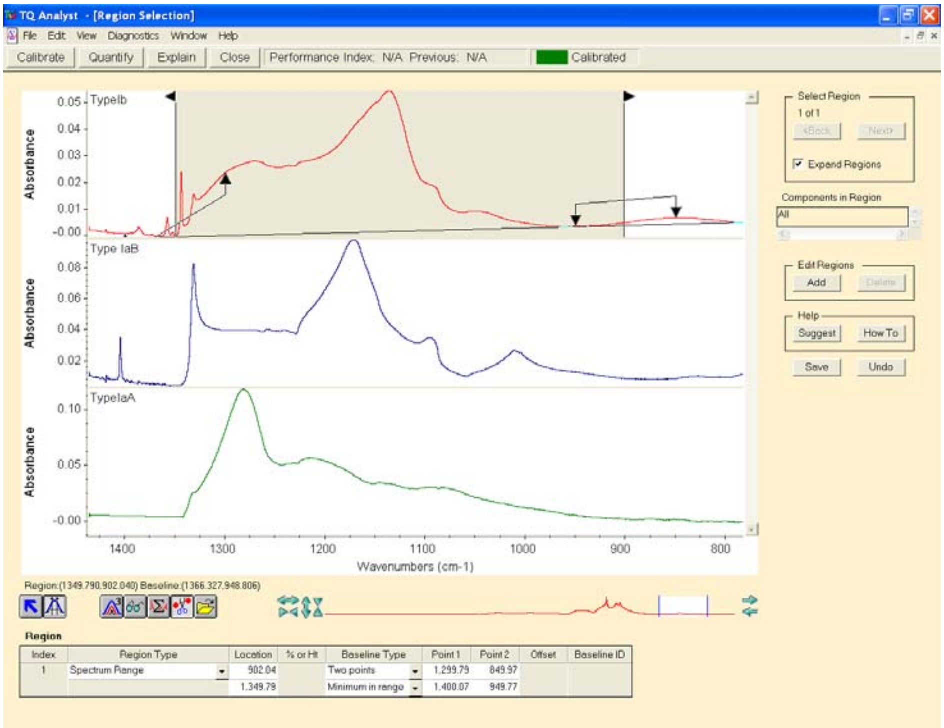
Warning: The full spectrum check indicates a significant difference from standards.
Warning: The measurement region check indicates a significant difference from standards.

Index	Component	Concentration	Unit	Std. error
1	PK1332	2.78		0.305
2	PK1344	2.10		0.314
3	PK3107	3.04		0.179

Figure 2-8. Measurement of hydrogen from the 3107cm^{-1} peak.

In this section it was demonstrated how to confidently determine the presence and intensity of small peaks that might be near the noise level or in the presence of water vapor interference. By normalizing the spectrum to a specific path length and using standards with known amounts of the species of interest, this can also provide reliable quantitative information on trace levels of hydrogen and nitrogen in the sample.

In the next section, a CLS method will be shown that fits reference spectra for Type IaA, Type IaB and Type Ib to the spectra from various diamonds. Because the actual concentrations in the reference spectra are unknown, the values have been arbitrarily set to 100 for this example. The spectra have also been scaled based on the intensity of the phonon band around 2500 cm^{-1}. **Figure 2-9** shows one of the method setup screens for TQ Analyst with the three reference spectra and the spectral region used for the analysis.

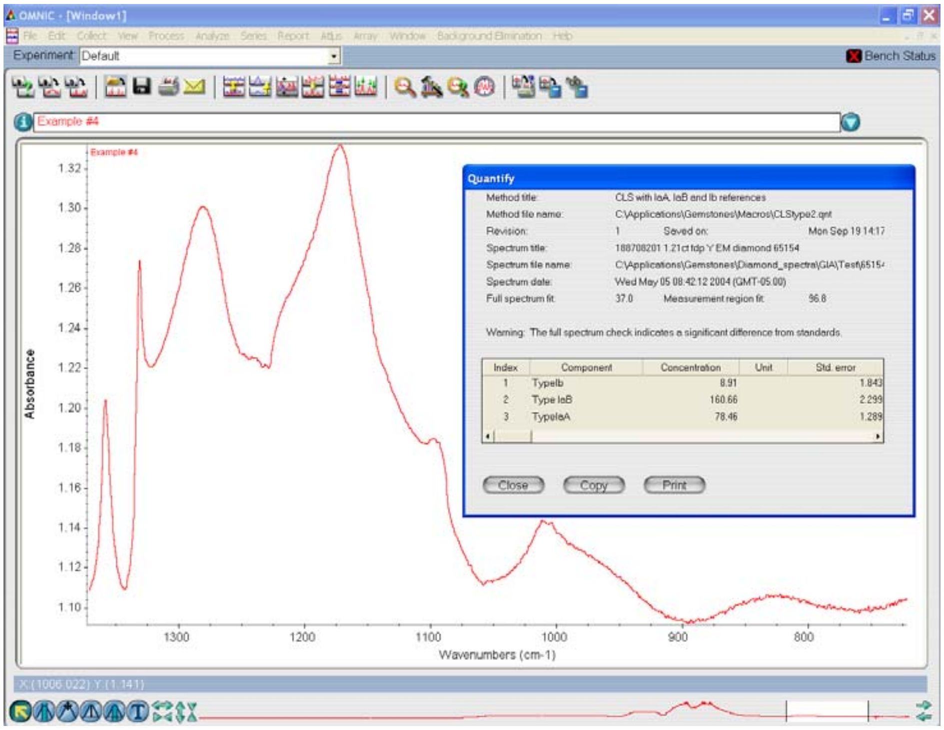


Region:(1349.790,902.040) Baseline:(1366.327,948.806)

Index	Region Type	Location	% or Ht	Baseline Type	Point 1	Point 2	Offset	Baseline ID
1	Spectrum Range	902.04		Two points	1,299.79	849.97		
		1,349.79		Minimum in range	1,400.07	949.77		

Figure 2-9. Reference spectra and analysis region for CLS example method to determine the amount of each diamond type in a sample

Once the method has been calibrated, it can be applied to sample spectra as shown in the figure below. This sample appears to contain significant amounts of both Type IaA and Type IaB aggregates with perhaps a trace of Type Ib. Even though the fact that the value for Ib is over 8 with a standard error of less than 2 suggests that this component is present, this could still be due to a small shoulder in the spectrum from the sample.



Method title: CLS with IaA, IaB and Ib references
Method file name: C:\Applications\Gemstones\Macros\CLStype2.qnt
Revision: 1 Saved on: Mon Sep 19 14:17
Spectrum title: 188708201 1.21ct fdp Y EM diamond 65154
Spectrum file name: C:\Applications\Gemstones\Diamond_spectra\GIA\Test\6515
Spectrum date: Wed May 05 08:42:12 2004 (GMT-05:00)
Full spectrum fit: 37.0 Measurement region fit: 96.8

Warning: The full spectrum check indicates a significant difference from standards.

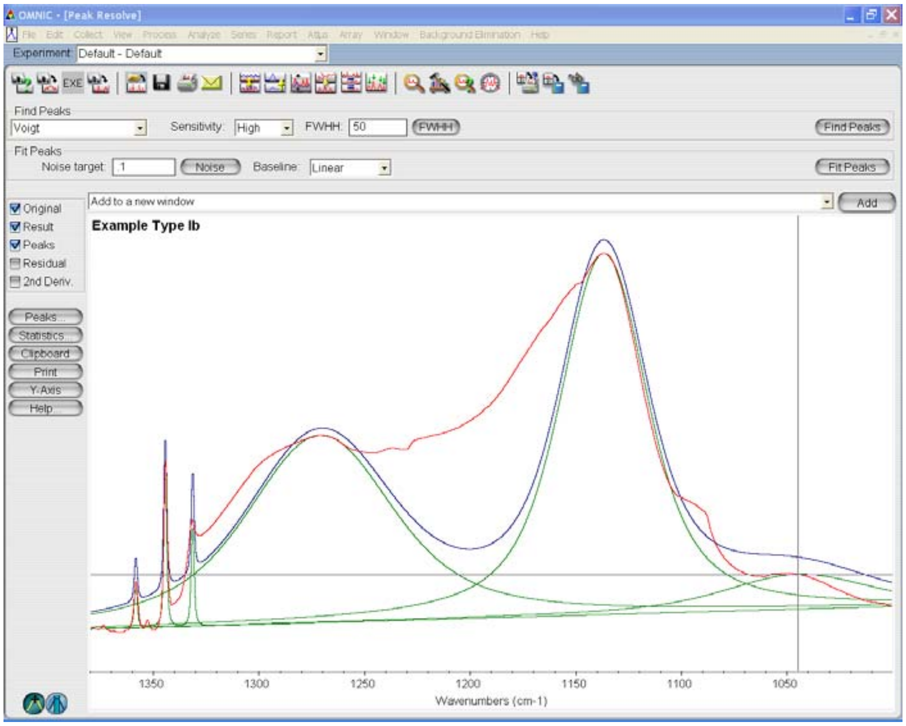
Index	Component	Concentration	Unit	Std. error
1	TypeIb	8.91		1.843
2	Type IaB	160.66		2.299
3	TypeIaA	78.46		1.289

Figure 2-10. Results of TQ Analyst method

Both of these examples have employed Classical Least Squares fitting techniques to provide valuable information about the constituents of a diamond from the infrared spectrum. More sophisticated chemometric techniques such as partial least squares and multivariate curve resolution can be used, but in cases where the observed spectral features are well defined a simple CLS method may be best. For accurate quantitative analysis results the spectra should be scaled for differences in pathlength and standards are required with known concentrations for the components of interest. In any CLS analysis the quality of the results is totally dependent on the spectral quality and the accuracy of the concentrations assigned to the standards. A very valuable feature of CLS is the reporting of a standard error value with the results. This gives a helpful indication of the goodness of fit and reliability of the answers.

Curve Fitting the Infrared Spectrum of Diamond

The location and intensity of the spectral features in the one-phonon region of the infrared spectrum from a diamond provides valuable information related to the sample. This section describes the use of the **Peak Resolve** feature of OMNIC to characterize the peaks. **Peak Resolve** models, or fits, a number of individual synthetic peaks to a complex set of overlapping peaks in a spectrum. The operation is performed on the specified region of the selected spectrum and can be used on spectra with Y-axis values in units of absorbance, log (1/R), Kubelka-Munk or Raman intensity. You can print the resulting table of resolved peaks or copy it to the Windows® Clipboard. The any of the resultant spectra can be displayed in a standard OMNIC spectral window and save them. When **Peak Resolve** is chosen from the **Analyze** menu, the **Peak Resolve** window appears. The first parameter in the Find Peaks box defines the peak type. The choices are **Gaussian** (good start for solids), **Lorentzian** (good start for gases) and mixed Gaussian/Lorentzian or **Voigt** (both good starts for liquids). The **Log-Normal** peak shape works well for fluorescence or broad, sloping backgrounds. Once the peak shape is set, the peak characteristics are described by the location, height and full width at half height (FWHH). Also, the **Voigt** peak has a Lorentzian width, mixed peak has as a parameter the percent Lorentzian character (0 to 100%), and the **Log-Normal** peak includes a symmetry factor. (To see these features after finding peaks with the **Find Peaks** button, click the **Peaks** button and then click the **Edit Peak** button.) In a case like this where the peak widths vary and there are broad features that are a combination of multiple peaks, it may be better to manually select the starting peaks as shown below.



Experiment: Default - Default

Find Peaks
Voigt Sensitivity: High FWHH: 50

Fit Peaks
Noise target: .1 Baseline: Linear

☑ Original
☑ Result
☑ Peaks
☐ Residual
☐ 2nd Deriv.

Add to a new window

Figure 2-11. Setting up the Peak Resolve function.

The figure below shows the results of fitting a series of peaks to the sample spectrum. The red spectrum is the sample spectrum and the blue trace on top is the summation of the peaks used in the curve fit. The area of interest includes the sharp peaks above 1300 cm^{-1}.

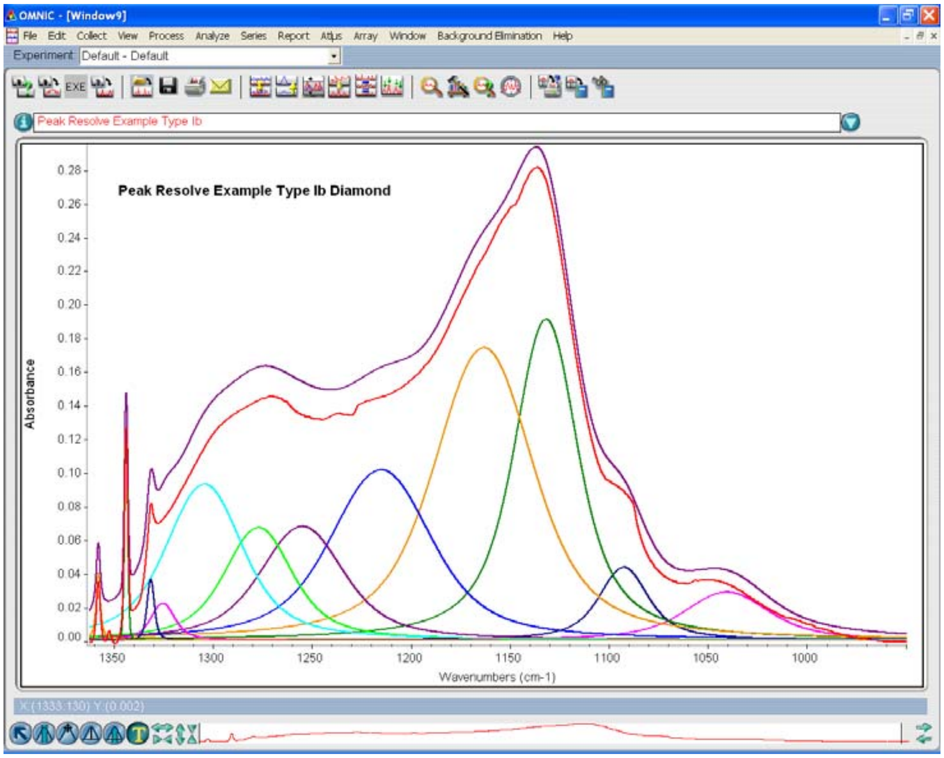


Figure 2-12. Curve fitting result for Type Ib spectrum.

Figure 2-12 shows the curve fit of this region. The upper trace is the original spectrum, and the one below shows the overall fitted result. The remaining traces show the individual peaks used to minimize the difference. **Figure 2-13** shows these peaks moved into separate panes for clarity. The gold trace shows the peak at 1358 cm^{-1} corresponding to the platelet peak. The peak in the green trace provides an excellent fit to the 1344 cm^{-1} peak. If the concentrations are known, any of these peaks can be used as "noise free" standards in a classical least squares fit quantitative application.

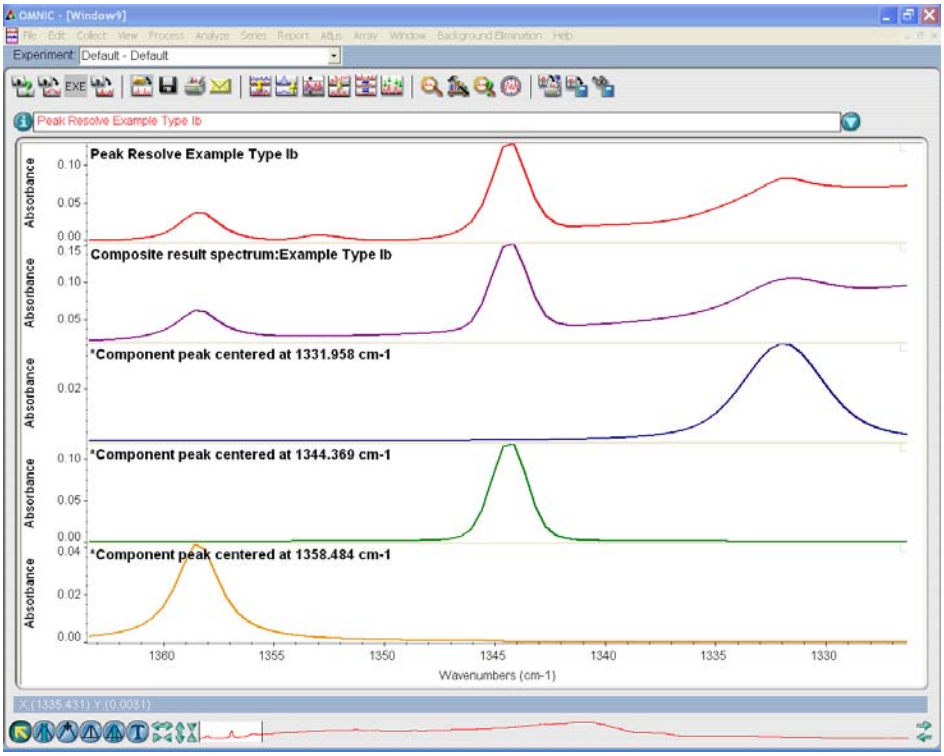


Figure 2-13. Expansion of sharp peaks in the 1350cm^{-1} region.

The details of the generated curves can also be saved in an Excel spread sheet for further processing. These results are shown below. In this example the peak located at 1132 cm^{-1} is the strongest.

Table 2-1. Resolved peaks for Ib diamond

Peak type	Center X	Height	FWHH	Other	Area
Voigt	1040.9	0.0285	31	31.3	1.8465
Voigt	1092.9	0.0435	15.5	21	1.7485
Voigt	1132.1	0.191	20.8	26.6	9.882
Voigt	1163.6	0.1742	37.9	34.1	13.1324
Voigt	1215.6	0.1014	39.4	33.8	7.7094
Voigt	1255.4	0.0678	31.9	28.9	4.2901
Voigt	1277.5	0.067	24.6	25.4	3.5177
Voigt	1304.9	0.0928	29.6	26.2	5.228
Voigt	1325.9	0.0219	9.2	8.3	0.4077
Voigt	1332	0.0364	3.1	2.1	0.2014
Voigt	1344.4	0.1215	1.7	0.3	0.2618
Voigt	1358.5	0.0417	0.5	2.2	0.1391

The following figure shows the original spectrum and curve fit composite for a quite different diamond. The curve fit for this spectrum used the values reported above for the starting point. Note that it even fit the small 1344 cm^{-1} peak in the minimization.

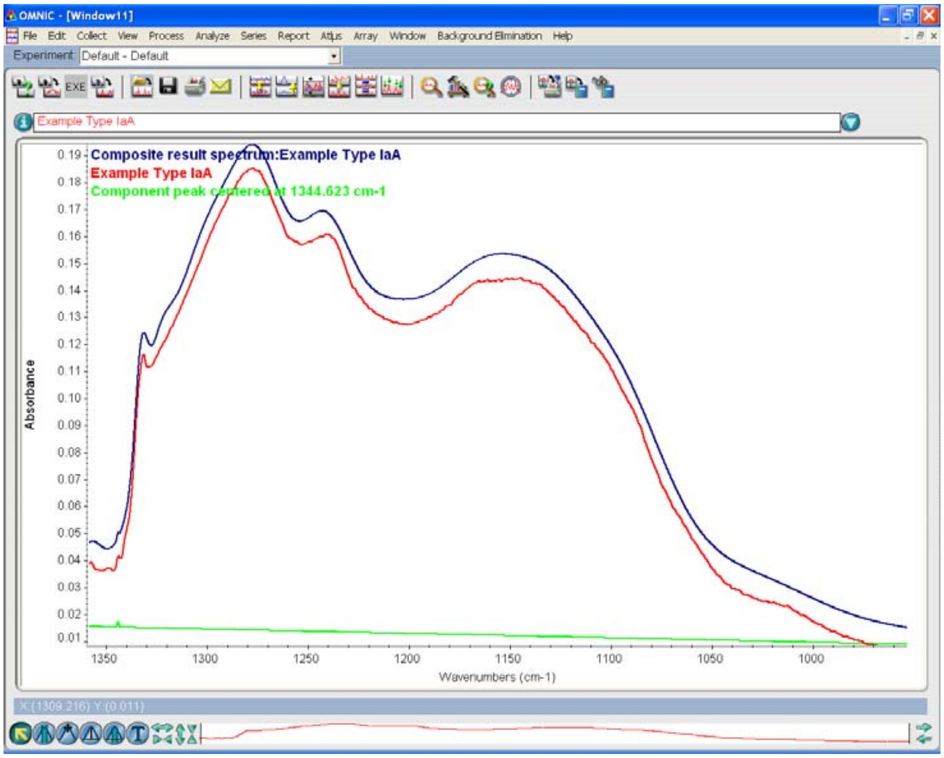


Figure 2-14. Peak Resolve results for a different diamond.

In this case none of the peak parameters were locked so location, width and intensity are all adjusted to minimize the difference. **Table 2-2** shows the actual peak values for the fit.

Table 2-2. Fit for component peak

Peak type	Center X	Height	FWHH	Other	Area
Voigt	1024.4	0.0106	46.9	42	0.917
Voigt	1094.6	0.0608	36.9	38	4.7457
Voigt	1128.2	0.0562	32.9	35.2	4.0359
Voigt	1164	0.0912	43.7	39	7.8177
Voigt	1212.8	0.0665	41.8	35.4	5.3034
Voigt	1242.7	0.0762	21.3	24.1	3.7184
Voigt	1275.6	0.1183	25.1	23.5	6.0148
Voigt	1304.4	0.0954	29.3	21.2	4.8685
Voigt	1325.8	0.0408	14.4	8.5	0.9652
Voigt	1333.2	0.0346	6.4	0.6	0.2562
Voigt	1344.6	0.0025	0.8	0	0.0021
Voigt	1358.6	0.0144	9.6	7.6	0.1545

Curve fitting is an excellent choice if the peak locations and widths can vary by small amounts between spectra. If the peaks only change in intensity, a classical least squares approach may provide better results.

Chapter 3 Analysis of Colored Gems by FTIR

While diamonds may be the most important gemstone in the United States, colored stones are also popular and may be even more popular in other parts of the world. In this chapter we will describe examples of applying infrared spectroscopy to the analysis of emerald, ruby, sapphire and jade. Although the examples deal with these very popular gemstones, the techniques can be applied to many other materials. The sampling techniques employed with transparent colored stones are the same as discussed above for diamonds. The figure below compares the spectra from an emerald that were acquired with the Beam Condenser and the Collector II reflectance accessory. For samples that are not transparent, the Collector II may prove better. The large mirrors in this accessory are very good at collecting the diffuse reflectance that is frequently encountered with these samples.

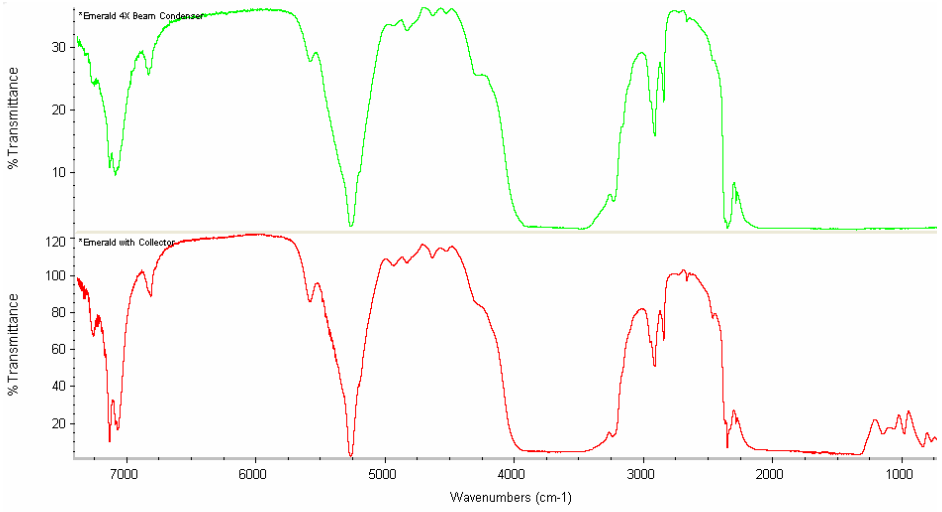


Figure 3-1. Comparison of spectra acquired with the Beam Condenser and the Collector accessories

Although small differences can be observed between the two spectra the overall features are very similar. While the spectral region between 1500 and 900 cm^{-1} is very valuable for diamonds, this region is generally totally absorbing due to metal-oxygen peaks that dominate in the spectra from other minerals. However the spectral regions above 2000 cm^{-1} can provide valuable information in identifying stones and maybe more importantly detecting enhancements and treatments of the stone. The region between 3200cm^{-1} and 4000 cm^{-1} contains peaks corresponding to the presence of water and hydroxyl groups in the sample.DD[1] The region around 3000 cm^{-1} is particularly valuable in detecting the presence of organic chemicals or polymers such as polystyrene or epoxy resins. While many gems have traditionally been "oiled" with natural oils and waxes to improve their appearance, the use of index matching polymers or synthetic materials is considered an unacceptable enhancement to the natural stone. The peaks between 2900 and 3000 cm^{-1} in the emerald spectra shown above indicate the presence of an organic material. However the peaks are most similar to mineral oil and may even be due to oil from the skin. The spectra from a number of gems are shown below.

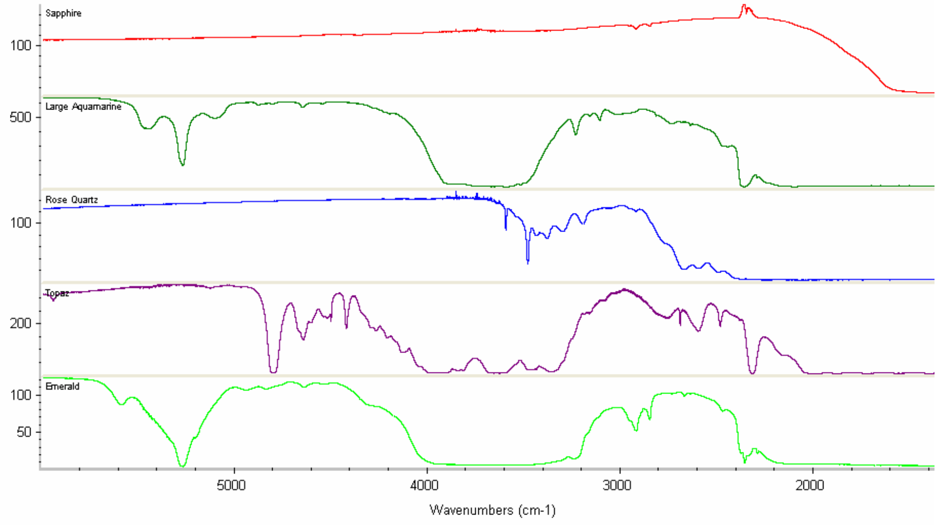


Figure 3-2. Spectra of various gemstones showing the region above the totally absorbing range.

The top spectrum was acquired from a sapphire and has almost no peaks above the total absorption at 1000 cm^{-1}. The spectrum from rose quartz shows some sharp features in the OH stretch region. The other three gems are totally absorbing in the OH region but have some interesting features in the combination/overtone region above 4000 cm^{-1}. While these peaks are usually very weak, the fact that the fundamental vibrations are totally absorbing means that they are easily observable in most gemstones.

Emeralds

Three of the greatest concerns today related to emeralds are 1) identifying treated stones, 2) identifying synthetic stones and 3) identifying simulants. Infrared spectroscopy can provide valuable information to assist in all three. As with most colored stones the vibrational modes corresponding to the fundamental inorganic vibrations are due to the silicate, silicon dioxide (quartz) or metal oxide groups in the stone and are completely absorbing in a gemstone with a diameter greater than a millimeter. While this can make analysis more difficult, there are several spectral regions that contain peaks that are useful in analyzing stones. In this section, examples using FTIR to differentiate between natural emeralds, synthetics, treated stones and simulants will be given. Some of this work is based on an excellent research paper[2] available from Gemlab in the Research section of their website; http://www.gemlab.net/. A number of other papers describe the use of infrared spectroscopy for analyzing emeralds.[3,4,5,6]

Detection of treated emeralds

Because of the formation process, emeralds often contain inclusions and fractures. Frequently these reach the surface of the stone. These cracks are visible and significantly reduce the appearance of the stone. Throughout history people have improved the appearance by rubbing the stone with natural oils such as paraffin or other available materials. The presence of these higher refractive materials in the cracks made them much less obvious and greatly improved the appearance of the stone. In recent times people have found that certain polymers and epoxy resins can closely match the refractive index of the emerald and a stone treated with these materials will appear much better than before the clarity enhancement. While the use of natural oils that can be removed or cleaned away is not generally considered a problem, the use of polymers and synthetic resins to enhance the appearance of a stone should always be documented. Obviously the fact that this relatively straightforward treatment can greatly improve the appearance (and value) of the stone has tempted many people to not declare the treatment.

Many of the materials used to enhance the appearance of an emerald are organic chemicals that have strong peaks in the infrared spectral region. This makes the detection of a hydrocarbon material in the stone easy with a FTIR instrument. However, differentiating between an “acceptable natural oil” and the polymers used in treatments is not as simple. **Figure 3-3** shows a spectrum acquired from an emerald, a reference spectrum from a paraffin, and the result of subtraction of the paraffin spectral features from the original spectrum.

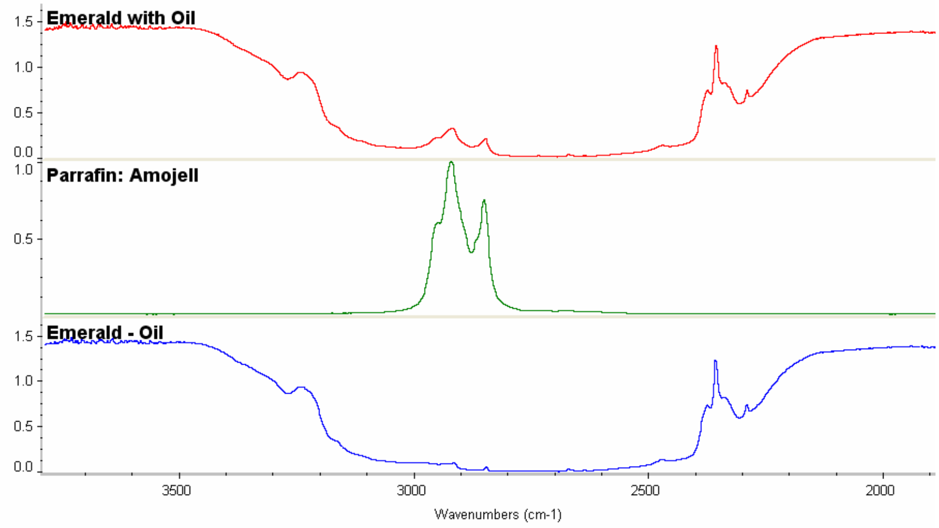


Figure 3-3. Emerald spectra

This example of a spectral subtraction of a reference spectrum from the spectrum of the emerald demonstrates that an oil has probably been applied to this stone. However, the sensitivity of the instrument also allows the detection of the presence of oils from the skin that may present from simply rubbing or playing with the stone. In many cases the presence of small amounts of hydrocarbon does not affect the value of the stone. The next figure shows some spectra from epoxy resins. These are generally the type of materials used to artificially enhance the appearance of the stone. While these materials have peaks in the same spectral region that were used in the previous example to detect the presence of an oil, there are some peaks in the epoxy spectra that can be used to detect a difference. Most of these polymers contain aromatic hydrocarbons that have peaks above 3000 cm^{-1}. **Figure** 3-4 compares the spectrum of the paraffin and those of several epoxy resins. The **Peak Find** software can be used to precisely identify the locations of the peaks. Several of the peaks in the epoxy spectrum correspond to functional groups also found in the paraffin spectrum, but other peaks can be clearly observed that are not present in the paraffin spectrum. These features are highlighted by the blue box below.

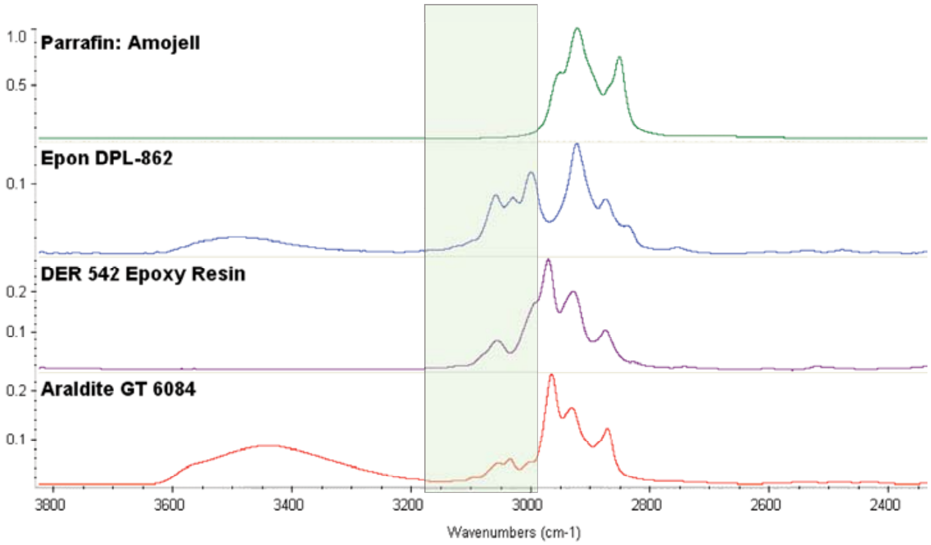


Figure 3-4. Spectra of possible additives

While this example suggests that FTIR can clearly differentiate between an "oiled" and treated stone, the use of other natural oils such as clove oil or cinnamon oils which contain aromatic groups similar to certain polymers seriously confuses the issue. **Figure 3-5** compares three oil spectra with the spectrum from an epoxy material. While there are clear spectral differences, it would be extremely difficult to definitively identify the epoxy from the natural oils by FTIR. In this section it was demonstrated that FTIR can clearly detect the presence of oils or polymer treatments of the stone. The polymer treatment from aliphatic oils or oils from the skin can also be differentiated. However, it would require an extensive reference library of all possible "natural oils" and materials that are known to be used in treating emeralds, before the difference between a natural "aromatic oil" and some of the materials used in polymer treatments could be stated with confidence.

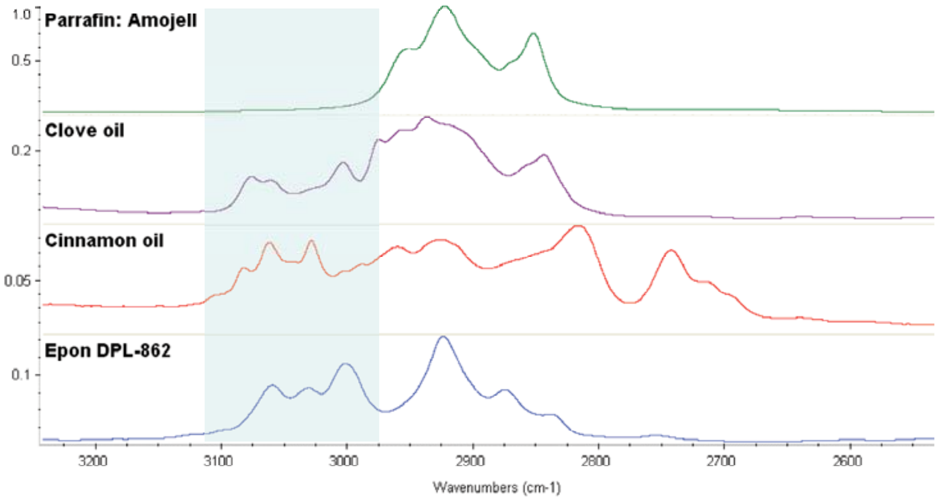


Figure 3-5. Comparison of oil spectra with an epoxy spectrum

Full spectral chemometric techniques could be used to model the differences and possibly provide a robust method for telling the difference.

Detection of synthetic emeralds

As with many other gemstones, recent advances in chemistry have led to several processes for producing synthetics. Gemstones are commercially available that have been produced by either the Flux process or the Hydrothermal process. Natural emeralds contain a significant amount of water and hydroxide. These components have strong infrared peaks in the region around 3500 cm^{-1}. Natural emeralds also appear to contain more trapped CO_2 in the beryl matrix. A spectrum from a green stone was acquired and compared to a group of reference spectra kindly provided by Mr. Gagan Choudhary from the Gem Testing Laboratory in Jaipur, India. The comparison is shown in the figure below.

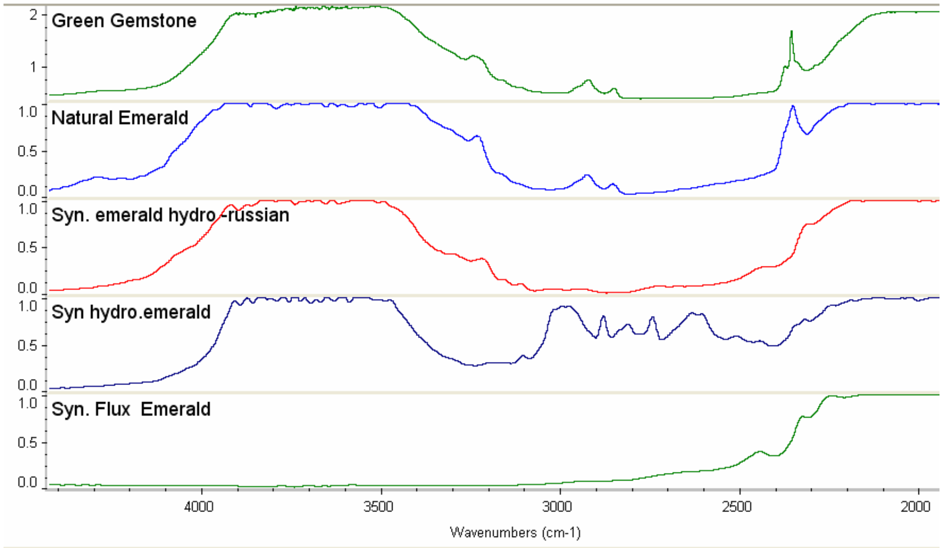


Figure 3-6. Comparison of emerald spectra

The top spectrum is from the sample, and the four spectra below are from a natural emerald and three examples of synthetic emeralds. The bottom two spectra from a flux process stone and a hydrothermal process stone are easily differentiated from the natural samples. The flux has very low water content as indicated by the lack of significant peaks between 3500 and 4000 cm^{-1}. The Russian hydrothermal sample shows strong peaks in the 2500 to 3000 cm^{-1} region. These peaks have been observed in numerous synthetic emeralds. The Russian hydrothermal process seems to produce a stone that has a spectrum very similar to the natural emerald. However the natural emerald appears to have a stronger peak at 2358 cm^{-1} that is not obvious in the spectrum from the stone prepared by the Russian process. Other peaks in the 2300 cm^{-1} region can also be helpful in identifying these stones. Two articles in Gems & Gemology[4],[5] provide an excellent discussion of the use of FTIR for verifying emeralds.

Evidence of Beryllium Treatment in Rubies and Sapphires

Both ruby and sapphire are members of the corundum group in which the major chemical component is aluminum oxide. A recent paper in Gems & Gemology describes how FTIR can provide valuable information related to detecting the treatment of corundum with beryllium.[7] Pure corundum is colorless, but both rubies and sapphires are types of corundum that contain trace amounts of specific metal ions. These trace metals give these stones their characteristic color. Treatment with beryllium has been shown to improve the color of some gemstones. While FTIR cannot detect the very low levels of metal ions even after a treatment, many natural stones contain detectable amounts of water and hydroxyl groups. The harsh conditions encountered during the treatment process can cause a loss of these natural components of the stone. The figure below shows some example spectra of stones in the OH spectral region (4000 – 3200 cm^{-1}). The peak at 3310 cm^{-1} is frequently found in natural rubies and sapphires. The lack of a peak in the small pink sapphire provides a warning that this stone might have been treated. This is an excellent example of a way that FT-IR might aid in the identification of a process when it cannot actually detect the material used in the treatment i.e. beryllium.

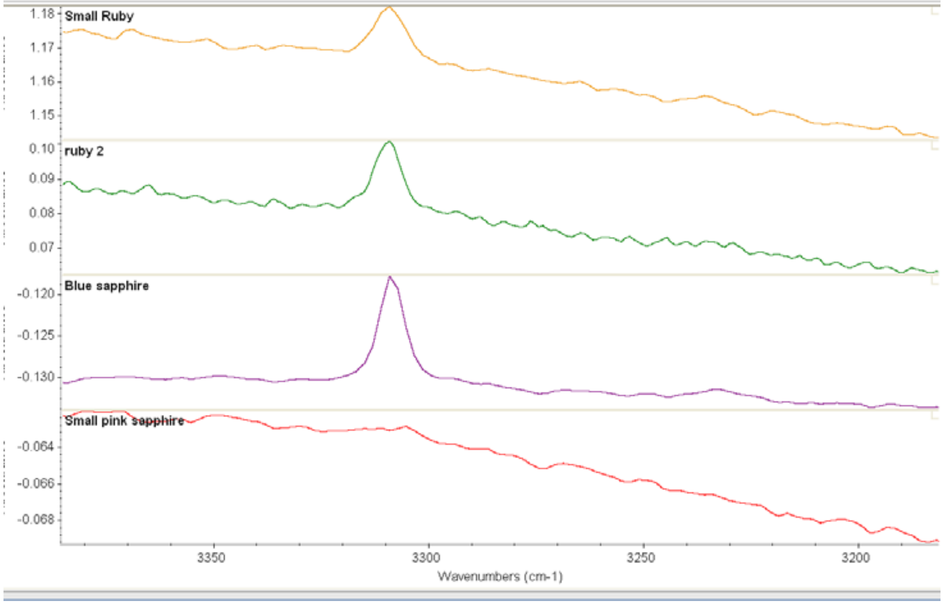
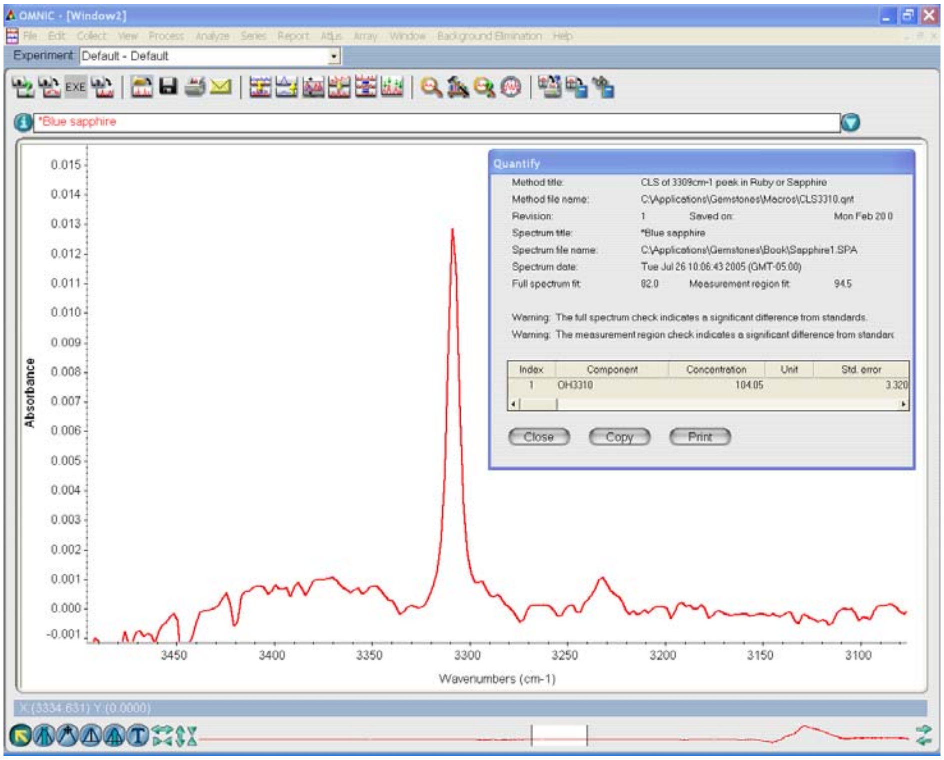


Figure 3-7. Examples of 3310cm^{-1} peak in spectra from rubies and sapphires.

The presence or absence of this peak can be determined automatically with a simple CLS method developed to measure the magnitude of this peak. In this example a reference peak was created using the **Peak Resolve** function. The noise free peak was used as the standard in the CLS method with an intensity value set to 100. The result of this measurement is shown below:



Method title: CLS of 3309cm-1 peak in Ruby or Sapphire
Method file name: C:\Applications\Gemstones\Macros\CLS3310.qnt
Revision: 1 Saved on: Mon Feb 20 0
Spectrum title: *Blue sapphire
Spectrum file name: C:\Applications\Gemstones\Book\Sapphire1.SPA
Spectrum date: Tue Jul 26 10:06:43 2005 (GMT-05:00)
Full spectrum fit: 82.0 Measurement region fit: 94.5

Warning: The full spectrum check indicates a significant difference from standards.
Warning: The measurement region check indicates a significant difference from standarc

Index	Component	Concentration	Unit	Std. error
1	OH3310	104.05		3.320

Figure 3-8. Example of CLS method to confirm the presence of the 3310cm^{-1} peak in a ruby or sapphire.

Jade

While not as popular in the US and Europe, Jade has long been one of most valued gemstones in Asia. Jade was originally used extensively in creating tools and weapons because of its toughness and the ability to create precise shapes. These same characteristics as well as its beauty have made jade carving a cornerstone of art in many parts of the world. There are actually two different minerals that are considered "true jade". The original mineral used in China for thousands of years is now called nepherite. The second mineral is called jadeite and is considered the more valuable of the two forms. Deposits are found in Burma including the very valuable "imperial jade". As with many other gemstones, various treatments have been developed to enhance the appearance of jade.

There are three classes of jadeite jade now commonly available.[8] "A" grade jade is totally natural (jadeite), and has the highest true market value. The "B" material has been treated as discussed below, and "C" grade material has been artificially color-enhanced. Typically, "C" jade is fairly easy to spot, but the treatments applied to "B" materials are more subtle.

"B" jade starts as raw jadeite with brown or black stains. The jade is soaked in strong mineral acids to remove the stains, which also weakens the stone by leaching out some structural materials (mostly metallics like sodium). The pores generated are filled with a melted wax or polymer resin whose index of refraction closely matches that of jade. A hardener may be applied to the outside of the jade to seal the stone. Besides the issue of potential fraud, the "B" treatment has several long-term issues – some skin burns from residual acid have been reported, and discoloration of the epoxy resin can occur. All of this underscores the need for a rapid and sensitive analysis method.

"B" grade samples are often uniform in color and translucent. Green jade is the main example, but pink and yellow "B" jade has recently appeared. Normal gemstone analyses showed "B" jade was jadeite jade and not color-enhanced "C" jade. Critically, the refractive index was in the correct range for jadeite, and normal (UV) spectroscopic analysis did not indicate the presence of dyes. Microscope examination may not show enough detail to identify the treatment, and even in cases where it can, this requires considerable skill. Essentially, the "B" material passes most of the normal testing done by a jeweler.

Fourier Transform infrared (FT-IR) provides an excellent tool for analyzing "A" and "B" jade. Signals due to the wax or epoxy resin are quite definitive.

The analysis takes only a few seconds, and the procedure yields unambiguous results.

A Nicolet 380 FT-IR spectrometer, shown in Figure 3-9, was used in the following analysis. Samples of “A” and “B” jadeite jade were mounted easily using “Blu-tack”, although care had to be taken to prevent contamination of the gem stone. A 4X beam condenser was used here, although other work has shown this is not generally necessary to obtain definitive spectra.

Figure 3-9. The Nicolet 380 FT-IR spectrometer is ideal for gemstone analysis.

The data were collected using the OMNIC software. A small number of scans was needed (4-16) to see the presence of resin; the spectra shown here were collected over a longer time (64 scans) to improve the s/n ratio. A resolution of 4 cm^{-1} was easily sufficient. The full spectrum was obtained, but the glassy nature of the material obscured all signals below 2300 cm^{-1}; the critical range is between 2600 and 3800 cm^{-1}, so this is no impediment to the analysis.

Spectra from “A” and “B” jade are shown in **Figure 3-10**. The “B” jade has a large peak located in the aliphatic hydrocarbon region. The differences between the spectra are immediately obvious.

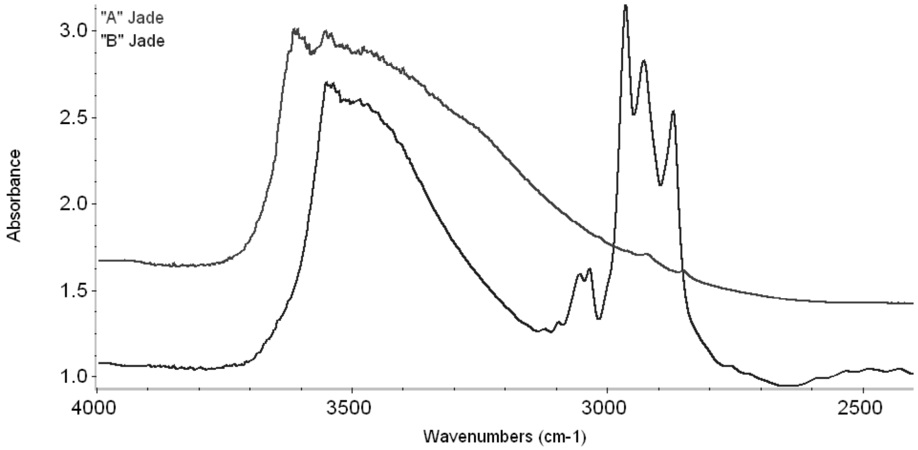


Figure 3-10. Spectra peaks of "A" and "B" jade differentiate the two stones

Amazingly, the spectral region between 4000 and 2500 cm-1 is sufficiently diagnostic to identify the class of material used in the treatment. Searching this region against the whole of Thermo's FT-IR libraries yields the results shown in **Figure 3-11**. The top hits are all epoxy resins, in excellent agreement with the expected results.

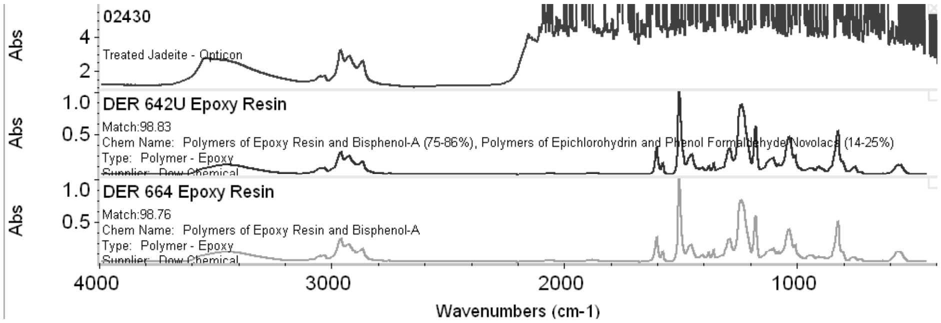


Figure 3-11. Class of materials identification used in the treatment of gemstones.

The FT-IR analysis of gemstones is simple and non-destructive. The ability of the OMNIC software to be customized will allow a standardized procedure to be built, and then operated by workers unfamiliar with FT-IR – the spectrometer becomes a black-box. The speed of the analysis would allow incorporation of this method into bulk testing facilities; the inexpensive nature of the unit would allow even small retailers to use the method.

This analysis could easily be extended using TQ Analyst. A quality check coupled with a simple report would result in a simple "A-B-C" discrimination, and could be used to identify known treatments of the "B" and "C" jades, or other gemstones.

As has been stated,[9] "B jade is here to stay." This is not inherently an illegal activity, unless the treatment is hidden from documentation accompanying the gem. FT-IR is an effective tool for uncovering treated jades, which should assist in enforcing proper disclosure.

Chapter 4 Spectral Libraries and Automated Comparisons

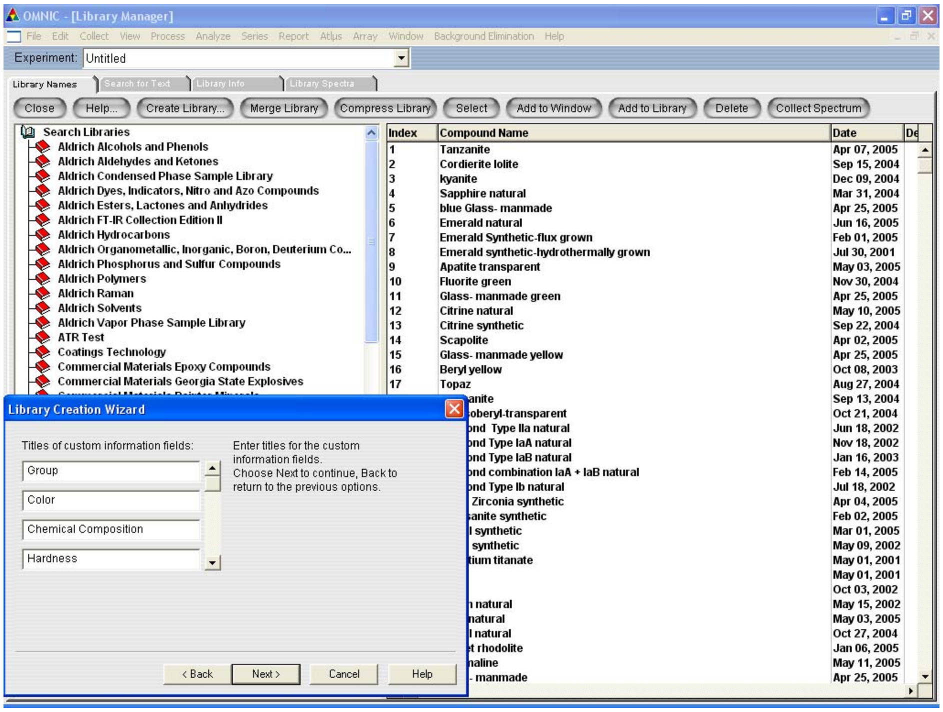
Infrared spectroscopy has traditionally been a technique of choice for chemical QA/QC and identifying unknown materials. FTIR spectra are frequently used as evidence in forensics cases and as part of the new drug submission to the FDA. Almost all FTIR instruments provide the capability of automatically comparing the spectrum from an unknown sample with a library of reference spectra. Sophisticated search algorithms and preprocessing techniques have been developed to make this process automatic and reliable. Infrared spectral reference libraries containing several thousand spectra from known compounds are available for the identification of organic and polymer materials[1]. In the last few years FTIR has become a very important tool in the advanced analysis of gemstones. A recent paper by Fernandes, Khan and Choudhary[2] published in the Australian Gemologist discussed the use of FTIR spectra as an aid to the identification of Gemstones. The authors reported that a number of peaks in the 2700-6000 cm^{-1} spectra region are unique to different gemstones and in many cases can be used to identify treated or synthetic gems. This information was compiled into several tables that provided an easy way to help identify gemstones from the presence or absence of specific peaks in the spectrum. While these look-up tables provide a valuable tool, the process is time consuming and requires many steps. We believe that the same automated spectral searching techniques used for polymer and pharmaceutical analysis should be applicable to gemstone identification. Infrared spectral searching is fundamentally a vector matching technique that calculates a correlation value between a vector representation of the unknown spectrum and each member of the spectral library. Those library members with the highest match value are retrieved and displayed. In this chapter the process of creating a small reference library from spectra of gemstones will be described as well as a discussion of the results of some evaluations of searching spectra from unknown gemstones using the reference library.

Experimental

Gagan Choudhary of the Gem Testing Laboratory Jaipur, India, provided the spectra used to create the library. Spectra were acquired on a Nicolet 360 FTIR spectrometer using 4 cm^{-1} resolution and co-adding 50 to a 100 scans. The spectra used for testing were acquired from different gemstones in our laboratory using a Nicolet 6700 FTIR spectrometer and a 4X Beam Condenser. 32 scans were signal averaged with a high sensitivity MCT detector. This results in a measurement time of less than 20 seconds for each sample. All of the results reported here are based on a 4 cm^{-1} spectral resolution. While this resolution is sufficient for this application, a number of laboratories use 1 cm^{-1} resolution, particularly for analysis of diamonds, where some very sharp peaks may be present. In both cases the spectral intensity was normalized by setting the lowest absorbance value to zero and the highest to one absorbance unit. Spectral normalization is required so that the relative intensities of the peaks are consistent between the sample spectrum and the reference library. While this is straightforward if none of the peaks in the spectrum are totally absorbing, the process is somewhat arbitrary when peaks are off-scale. However, we feel that this is the best compromise for creating a reference library.

The spectral searching software packages that used for this research is provided with the OMNIC FTIR software on the Nicolet FTIR spectrometers. One powerful feature of this software is the ability to perform an extended search using other information about the unknown sample. In this example the following was entered; the color, gem group, chemical composition, Mohs' hardness, specific gravity, refractive index for each spectrum when the spectral library was created.

Figure 4-1 shows the screen during the **Create Library** process. This is a wizard in the **Library Manager** software. The right side of the figure lists the spectra in the resulting library.



Experiment: Untitled

Search Libraries
Aldrich Alcohols and Phenols
Aldrich Aldehydes and Ketones
Aldrich Condensed Phase Sample Library
Aldrich Dyes, Indicators, Nitro and Azo Compounds
Aldrich Esters, Lactones and Anhydrides
Aldrich FT-IR Collection Edition II
Aldrich Hydrocarbons
Aldrich Organometallic, Inorganic, Boron, Deuterium Co...
Aldrich Phosphorus and Sulfur Compounds
Aldrich Polymers
Aldrich Raman
Aldrich Solvents
Aldrich Vapor Phase Sample Library
ATR Test
Coatings Technology
Commercial Materials Epoxy Compounds
Commercial Materials Georgia State Explosives

Index	Compound Name	Date	De
1	Tanzanite	Apr 07, 2005	
2	Cordierite Iolite	Sep 15, 2004	
3	kyanite	Dec 09, 2004	
4	Sapphire natural	Mar 31, 2004	
5	blue Glass- manmade	Apr 25, 2005	
6	Emerald natural	Jun 16, 2005	
7	Emerald Synthetic-flux grown	Feb 01, 2005	
8	Emerald synthetic-hydrothermally grown	Jul 30, 2001	
9	Apatite transparent	May 03, 2005	
10	Fluorite green	Nov 30, 2004	
11	Glass- manmade green	Apr 25, 2005	
12	Citrine natural	May 10, 2005	
13	Citrine synthetic	Sep 22, 2004	
14	Scapolite	Apr 02, 2005	
15	Glass- manmade yellow	Apr 25, 2005	
16	Beryl yellow	Oct 08, 2003	
17	Topaz	Aug 27, 2004	
	anite	Sep 13, 2004	
	oberyl-transparent	Oct 21, 2004	
	ond Type IIa natural	Jun 18, 2002	
	ond Type IaA natural	Nov 18, 2002	
	ond Type IaB natural	Jan 16, 2003	
	ond combination IaA + IaB natural	Feb 14, 2005	
	ond Type Ib natural	Jul 18, 2002	
	Zirconia synthetic	Apr 04, 2005	
	anite synthetic	Feb 02, 2005	
	l synthetic	Mar 01, 2005	
	synthetic	May 09, 2002	
	tium titanate	May 01, 2001	
		May 01, 2001	
		Oct 03, 2002	
	n natural	May 15, 2002	
	natural	May 03, 2005	
	l natural	Oct 27, 2004	
	t rhodolite	Jan 06, 2005	
	naline	May 11, 2005	
	- manmade	Apr 25, 2005	

Titles of custom information fields:
Group
Color
Chemical Composition
Hardness

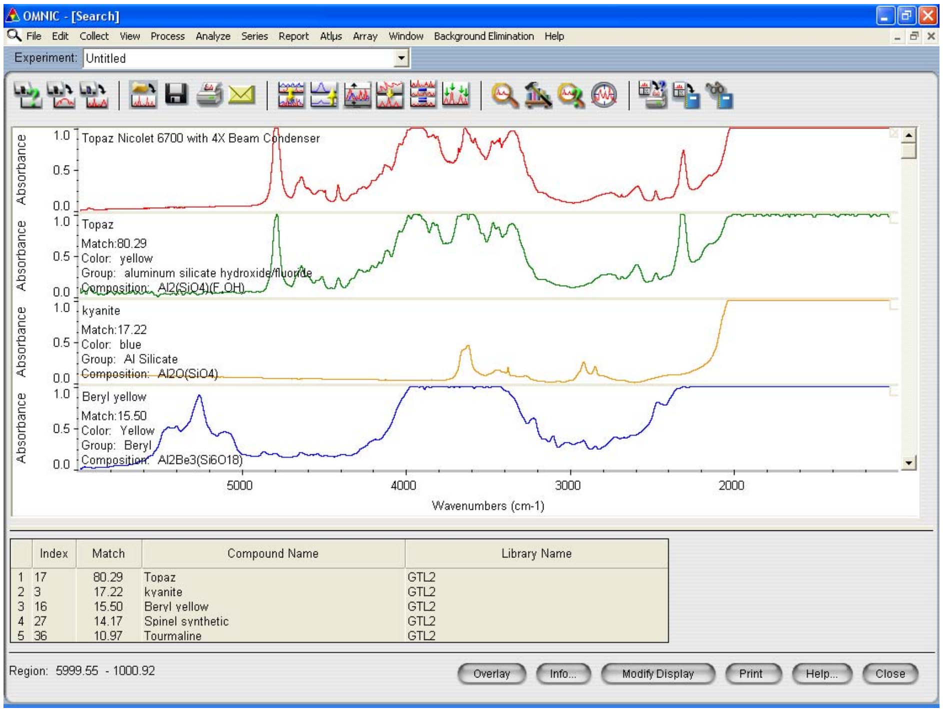
Enter titles for the custom information fields.
Choose Next to continue, Back to return to the previous options.

Figure 4-1. Creating a library for automated spectral searching

Once the library had been created a number of experiments were performed to determine the performance of the search system. Because of the thickness of the samples, the main peaks from the inorganic vibrational modes are completely absorbing. Most of the valuable information for these samples is in the spectral region between 2000 and 6000 cm^{-1}. These peaks are mainly caused by the –OH and water in the crystal structure of the stone. In many cases the fundamental O-H vibrations around 3500 cm^{-1} are completely absorbing, but the small peaks related to unique O-H binding in the lattice and combination bands are specific to a particular gem or synthetic process. The spectral region around 2900 cm^{-1} may contain peaks corresponding to the presence of organic materials such as polymers or epoxies.

The diamond spectra are the exception. The one-phonon region between 900 and 1500 cm^{-1} contains very important information concerning the nitrogen content of the stone and can be used to differentiate among the different types of diamonds.

Figure 4-2 shows the results of searching the library for spectra most similar to the sample spectrum that was acquired from an unknown gemstone. The report screen shows the spectrum from the sample at the top and the spectra from the most similar spectra in the library below. The actual spectral region used to create the vector is shown in the lower left of the screen. The selection of the spectral region can have a large effect on the search results particularly if there is a totally absorbing peak in the region. The extended search information is shown with each spectrum. How to use this feature will be covered later in the discussion. In this example the best match was topaz with a match value of 80 and the second best was kyanite with a match value of 17. The high value for the best match and the low value for the second match indicate that this sample is very likely topaz. A perfect match would be 100, so there is some spectral variance, but this may be due to a difference in thickness of the two stones or small differences on chemical structure. For real world analysis a match value greater that 75 provides strong evidence that the gems are the same or similar.



Experiment: Untitled

Topaz Nicolet 6700 with 4X Beam Condenser

Topaz
Match:80.29
Color: yellow
Group: aluminum silicate hydroxide/fluoride
Composition: Al2(SiO4)(F,OH)

kyanite
Match:17.22
Color: blue
Group: Al Silicate
Composition: Al2O(SiO4)

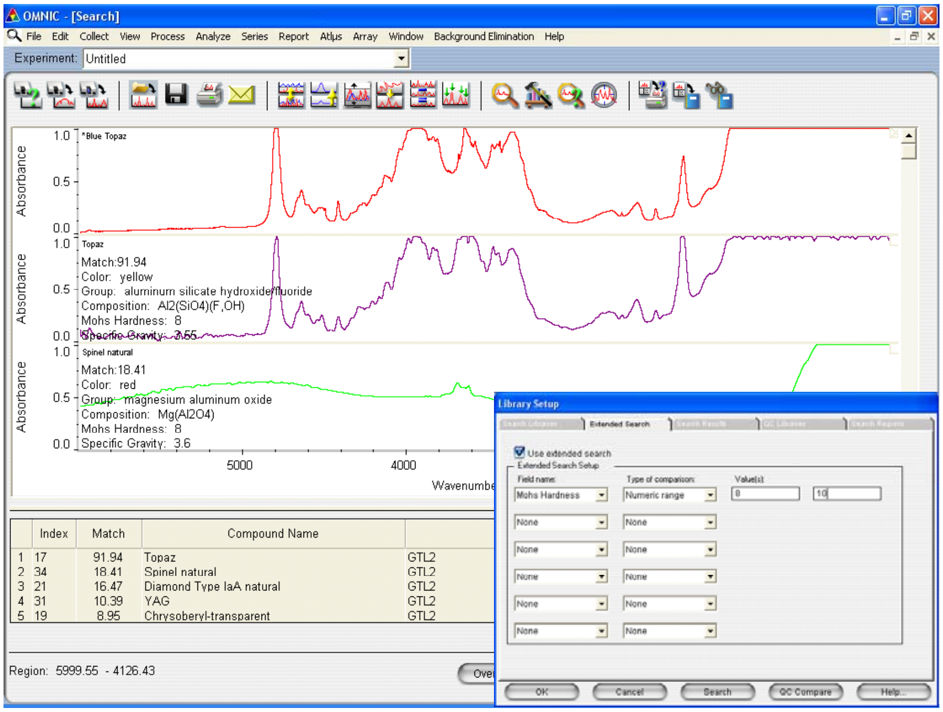
Beryl yellow
Match:15.50
Color: Yellow
Group: Beryl
Composition: Al2Be3(Si6O18)

	Index	Match	Compound Name	Library Name
1	17	80.29	Topaz	GTL2
2	3	17.22	kyanite	GTL2
3	16	15.50	Beryl yellow	GTL2
4	27	14.17	Spinel synthetic	GTL2
5	36	10.97	Tourmaline	GTL2

Region: 5999.55 - 1000.92

Figure 4-2. Search results for a sample acquired on a Nicolet 6700 FTIR

An important feature that has not yet been discussed is the use of the additional information that was entered with each spectrum. In this example a range of hardness values that are acceptable for this sample (8-10) was entered. The spectral search only retrieves members of the library that pass this test and ranks them according to their spectral match value. The results are shown in **Figure 4-3** for a spectral search using the 4125 – 6000 cm^{-1} spectral range.



Experiment: Untitled

*Blue Topaz

Topaz
Match:91.94
Color: yellow
Group: aluminum silicate hydroxide/fluoride
Composition: Al2(SiO4)(F,OH)
Mohs Hardness: 8
Specific Gravity: 3.55

Spinel natural
Match:18.41
Color: red
Group: magnesium aluminum oxide
Composition: Mg(Al2O4)
Mohs Hardness: 8
Specific Gravity: 3.6

	Index	Match	Compound Name	
1	17	91.94	Topaz	GTL2
2	34	18.41	Spinel natural	GTL2
3	21	16.47	Diamond Type IaA natural	GTL2
4	31	10.39	YAG	GTL2
5	19	8.95	Chrysoberyl-transparent	GTL2

Region: 5999.55 - 4126.43

☑ Use extended search

Extended Search Setup

Field name:	Type of comparison:	Value(s):	
Mohs Hardness	Numeric range	8	10
None	None		
None	None		
None	None		
None	None		
None	None		

Figure 4-3. Filtering search results based on value for Mohs’ Hardness test

In this chapter the use of the OMNIC Library Manager to create a search library of spectra acquired from various gemstones was described. For this example information on the color of the stone as well as chemical composition, Mohs’ hardness, specific gravity and refractive index was included. Several examples of using the spectral library to identify unknown spectra acquired on a different instrument were also provided. These examples demonstrate that a quick search of a reference library can provide a great deal of information about a gemstone. While FTIR spectroscopy cannot always provide a definitive answer particularly in the case of a treated or synthetic stone, it frequently contributes important evidence that can assist in the final decision. In this example a small library was created to show the potential of the technique and the capability of the OMNIC software. As the number of spectra and quality of the library increases, the probability of identifying an unknown sample also increases.

Chapter 5 Conclusions

While this booklet provides a broad overview of the potential of FTIR in gem analysis, it does not cover every application or some of the subtle details. Because natural gems were produced under extreme conditions and frequently contain a complex mixture of numerous metals, anions and trace components, no technique is foolproof or provides the solution to all problems. However the information that can be obtained from a high quality infrared spectrum can reveal a great deal about the structure of the sample and frequently can provide definitive evidence about the makeup of a stone.

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We thank the GIA Gem Laboratory for providing the spectra and details for the example of jade analysis by FTIR.

Chapter 4

We gratefully acknowledge Gagan Choudhary of the Gem Testing Laboratory in Jaipur India for contributing the spectra used to create the example library.

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