Analysis of Diamonds by FT-IR Spectroscopy

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Introduction

Diamonds are by far the most popular gemstone in America and many other parts of the world. Because of this popularity and the high prices of quality gemstones, there is a large market for cheaper stones that resemble diamonds as well as diamonds that have been treated to improve their appearance. Detecting these stones can be a significant problem for diamond buyers if these stones are represented as natural diamonds by unscrupulous sellers. FT-IR spectroscopy can be a useful tool for buyers and sellers to determine whether diamonds are natural.

Diamonds are unique among gemstones because they are composed of a single element (carbon), while virtually all other gems contain multiple elements including significant amounts of oxides. The infrared spectrum of diamond is equally unique and can be used to easily confirm that a stone is actually a diamond. A diamond consists of crystalline carbon and the extreme conditions required to create them also provide a way for trace amounts of other elements to be trapped in the crystal matrix. The most important trace element is nitrogen, which can be found in different forms in the diamond crystal. These nitrogen aggregates create unique features in the infrared spectrum and are key in classifying diamonds. Hydrogen, boron and carbonates are other important trace elements, all of which have identifiable features in the infrared spectral region. While it is easy to confirm that a stone is a diamond, it is much more difficult to determine if it is synthetic or treated. Laboratory grown high pressure-high temperature (HPHT) diamonds are now commercially available and their identification is one of the major challenges for the gem industry today. The infrared peaks corresponding to the nitrogen aggregates or presence of other elements can be used to provide valuable evidence that a stone is not natural. In this application note, we will describe several techniques based on FT-IR spectroscopy that are extremely valuable to gemological laboratories.

The Thermo Scientific Nicolet™ 6700 FT-IR spectrometer equipped with an optimized beam condenser or reflection accessory has the sensitivity to rapidly acquire high quality spectra from faceted diamonds. When the system is configured with the Thermo Scientific TQ Analyst™ multi-variate analysis software, automated workflows can be created to automatically analyze the spectral data and quickly report the results. Once the stone has been properly positioned in the instrument, a complete analysis can be completed in less than a minute with no effect on the stone itself.

Experimental

Rapid Confirmation that a Stone is a Diamond

Automatic material confirmation is a technique that has been extensively used in the pharmaceutical industry to ensure that incoming material is correctly labeled. Reference spectra are acquired from all of the materials that are used in the products and then a computer algorithm is employed to calculate the similarity of the spectrum from the incoming material with the reference spectrum from the specified material. In this case, a reference spectrum from a type IIa diamond was used to develop a Similarity Match method using the TQ Analyst software. A match value is then computed. The value will be 100 if the spectrum from the sample is identical to the reference and zero if there is no similarity between the two spectra. Since the spectra for all diamonds are slightly different, the match value will always be less than 100. In our experience, setting a threshold for a pass of 80 gave no false positives and yet accepted a certain amount of variance in the sample spectra. The major exception that was found was Type IIb diamonds with high boron levels which severely distorted the phonon region. The only features observed in a spectrum of pure diamond are the phonon bands from the crystal lattice structure that are observed in the 1500 cm^{-1} to 4000 cm^{-1} spectral region. There are three phonon bands but the one phonon band is not infrared active. An example of analyzing a typical diamond is shown in Figure 2.
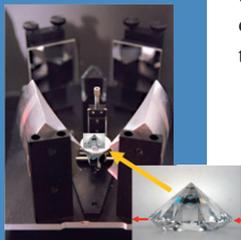

Figure 1: The Thermo Scientific Nicolet 6700 FT-IR spectrometer and 4X beam condenser

The 4X beam condenser photo is courtesy of the Gemological Institute of America, ©2002. All rights reserved. Reprinted by permission.
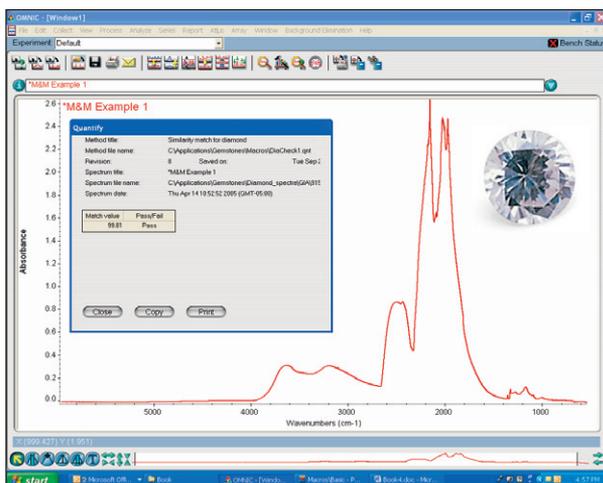
Figure 2: Diamond confirmation based on TQ Analyst Similarity Match

Classifying Diamonds

A technique used extensively in quantitative analysis is Classical Least Squares (CLS). The basis of CLS is the assumption that the spectrum from a sample that is a mixture of known materials can be modeled by a linear combination of the spectra from the pure reference materials. In this case we are using spectra from diamonds with well defined nitrogen aggregates: Type IaA, Type IaB and Type Ib. Because we do not know the actual concentrations of nitrogen in the spectra, we have arbitrarily assigned the value to be 100 ppm so the actual values reported here are relative to the arbitrary value for illustrative purposes.
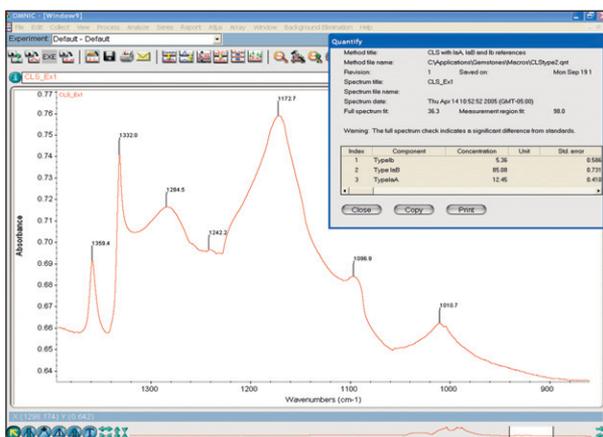
Figure 3: Quantitative analysis of nitrogen aggregates by CLS

The results of this example CLS method are shown above. Although the calculated standard error terms indicate that all three nitrogen types are present, adding more standards to the method might resolve any questions about the presence of the Type Ib aggregates.

Many diamond spectra have a peak in the 1360 cm-1 region which has been attributed to the formation of platelets in the crystal. This peak is interesting in that it both shifts and broadens depending on the overall makeup of the sample. Curve resolution, or peak fitting, is a technique that can be very effective in this type of situation. This technique synthesizes peaks based on a pre-defined line shape and minimizes the difference between the actual spectrum and a linear combination of the synthetic peaks. The following figure shows two platelet peaks that are shifted by several wavenumbers.
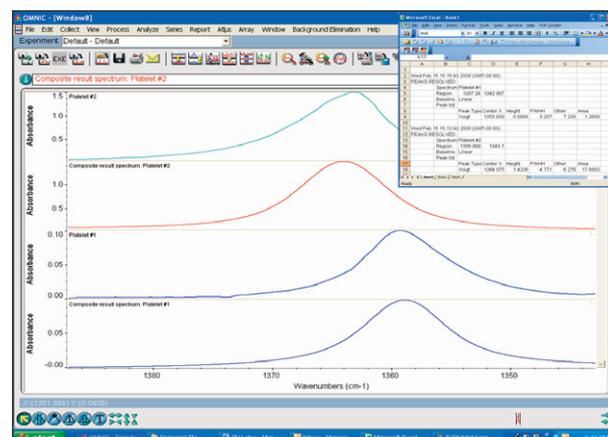

Figure 4: Characterizing the Platelet Peak in two diamond spectra by Curve Fitting

The results of the Peak Resolve™ curve fit reveal that the Full Width at Half Maximum (FWHM) has gone from 3.2 cm-1 to 4.8 cm-1 as the peak has shifted from 1359 cm-1 to 1364 cm-1. A closer examination of the curve fit results also shows that the peaks are asymmetric and can be fitted better with two synthetic peaks.

Assisting in the Detection of Synthetic Diamonds

Besides the platelet peak, several other peaks in the spectrum can be helpful in trying to identify treated stones. In many of these cases the amount of nitrogen in the diamond is very low, so it can be difficult to confirm the presence of particular peaks. In this example, a simple CLS method was developed to confirm the presence and measure the intensity of peaks at 3107 cm^{-1}, 1344 cm^{-1} and 1332 cm^{-1}. A key advantage to the CLS approach is that a standard error term is reported with the analysis. While it is not a rigorous statistical confidence level, if the peak intensity is three to five times the reported error term, the presence of a peak has been confirmed. An example for a sample containing very low levels of nitrogen is shown below in Figure 5. In this example all three peaks are present at detectable levels.
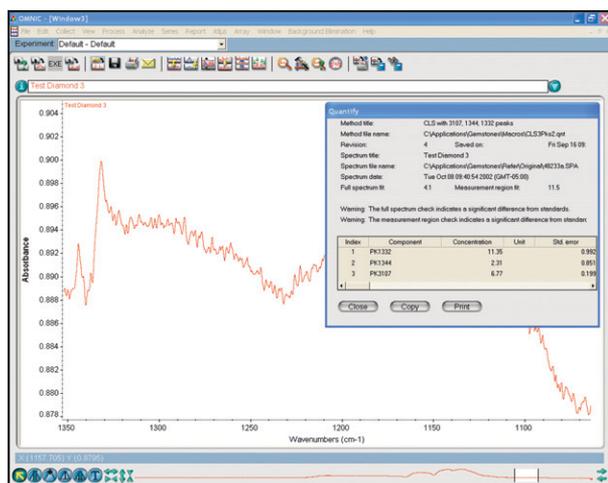
Figure 5: Measuring low level peaks in the diamond spectrum by CLS

Conclusions

Numerous gemological laboratories employ FT-IR on a daily basis to characterize diamonds and other gemstones. In this application note, we have provided several examples where the combination of a Thermo Scientific Nicolet series FT-IR spectrometer and an optimized accessory has been used with multivariate statistical analysis techniques to provide a rapid, reliable information source of great importance to classifying gemstones. By automating these methods, the results are consistent and supported by a quality, or confidence, metric. In many cases, FT-IR is used by an operator to rapidly screen out the samples that clearly pass or fail the test, allowing the outliers to be examined by an expert.

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