Diamond Analysis

- Reliable identification and type determination by FTIR spectroscopy

FTIR

Innovation with Integrity

Since the appearance of synthetic diamonds, nearly perfect imitates and treated diamonds it has become harder and harder to assess the real value of a gemstone. Infrared spectroscopy constitutes an elegant way for the classification of diamonds and the detection of imitates. It provides valuable information whether the stone is natural, synthetic or can be treated by using high pressure high temperature technique (HPHT).

Bruker Optics is offering the right tools for all typical applications; they assist you with the identification and type determination of polished and rough diamonds as well as mounted stones and melee-sized diamonds. From large rough diamonds with dozens of carats to tiny fragments in the sub millimeter range – anything can be tested!

- Reliable type determination
- Detection of imitates
- Polished and rough diamonds
- Diamonds mounted in jewelry
- Automated screening

Type classification: Requirement of a changing market

Since the first reproducible process for diamond synthesis was reported in the 1950s technology has continuously improved. Nowadays diamonds can be synthesized not only with properties suitable for industrial use, but also with gem quality. Furthermore, treatments have been developed that allow quality enhancement of both natural and synthetic stones. As a result analytical techniques are sought after which provide information about the stone's genesis and history. There is no single indicator that always will give the absolute answer if a stone is natural or synthetic or has undergone certain quality enhancement treatments – but knowledge of the diamond type allows extensive conclusions.

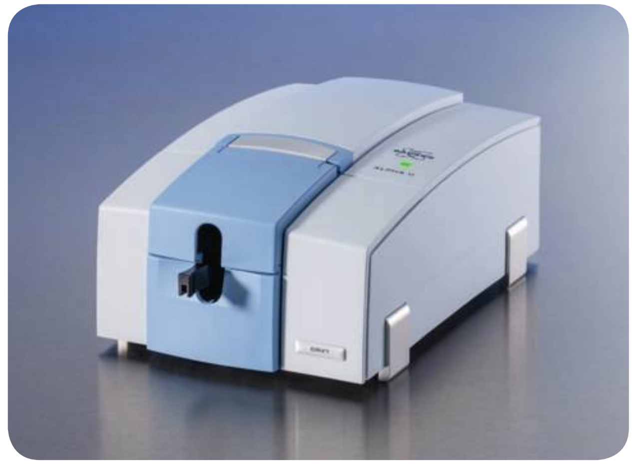


Figure 1: ALPHA II Diamond Analyzer.

How to determine the diamond type

In fact diamond is not just a simple carbon modification; in most cases also foreign atoms such as nitrogen, hydrogen or boron are present inside the crystal lattice. These foreign atoms and their arrangement as isolated atoms, pairs or larger aggregates can affect the color of the diamond. Nitrogen is the most important impurity and its presence or absence is therefore used as the foundation of the type classification system:
Diamonds are defined to be of type I when containing sufficient nitrogen to be detectable by infrared (IR) spectroscopy. Diamonds in which no nitrogen can be found are assigned to type II. These two main types are further divided into different subtypes like for instance Ia (aggregated nitrogen) and Ib (isolated nitrogen).
Knowledge of the diamond type is very important, as it allows the detection of synthetic and HPHT treated stones. Furthermore potential candidates that can be subjected to high pressure high temperature (HPHT) treatment can identified.

As the before mentioned definition of the two main types is already indicating, the method of choice for the assignment of these different diamond types is IR-spectroscopy. Until now the IR-spectroscopic analysis of diamond samples was a complex task performed by educated specialists. On the one hand traditional IR-spectrometers are rather bulky and difficult to operate but on the other hand it is particularly the interpretation of the resulting IR-spectra which is complicated since there are many different types and mixture types.

Now Bruker in collaboration with HRD Antwerp is offering the ALPHA II Diamond Analyzer (see Figure 1) that allows even spectroscopically untrained users to measure and classify a diamond in less than a minute. For very large sample batches like melee-sized stones, the high throughput screening accessory (HTS-XT) is the tool of choice, since it allows automatically measuring and classifying a large number of samples in a very short time. Smallest diamonds and complex arrangements on jewelry can be measured with the FTIR microscope LUMOS that also can be used for visual inspection of the diamond.

FTIR Diamond Analysis

Polished and rough diamonds

Depending on the sample type and number Bruker is offering the right solution to your specific measurement demands. Single loose diamonds can be best measured by using the ALPHA II Diamond Analyzer that is based on the very robust and compact Fourier-Transform-IR (FTIR) spectrometer ALPHA II. The ALPHA II has a weight of only 7 kg and the footprint of a laboratory book. The measurement process itself is very comfortable. The diamond just needs to be placed on the gold coated sample plate and moved inside the DRIFT-unit (DRIFT = Diffuse Reflectance Infrared Fourier Transform). The measurement is then initiated by means of a specially designed user interface. Even untrained users are able to measure and evaluate a sample in less than a minute.

During the measurement and evaluation process, the user interface changes its appearance dynamically presenting the functionality to perform the next step. The ALPHA II Diamond Analyzer offers an automated, easy to use and dedicated solution for diamond detection and type analysis based on the FTIR method. It distinguishes diamonds from imitations or other precious gemstones using the FTIR diffuse reflectance method.

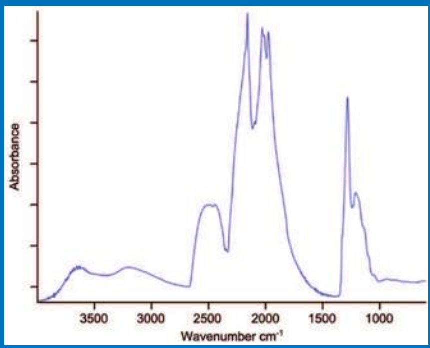
Rough Diamonds

Due to their irregular shape rough diamonds require a different measurement approach than polished diamonds. With the ALPHA II transmission module (see figure 2) it is possible to measure rough diamonds – from small ones up to a weight of a few tens of carats. Since the ALPHA II measurement modules are easily interchangeable within seconds, it is possible to combine the different measurement approaches for polished, rough and mounted diamonds in one ALPHA II system.

Principle of IR-spectroscopy

IR-spectroscopy uses thermal radiation which is invisible to the human eye and interacts with matter by triggering molecular or lattice based vibrations. Each diamond type has its characteristic wavelength-regions where these vibrations occur. Since the energy of the IR-light is converted into vibrational motion at these specific wavelength regions the light is being absorbed and the diamond is more or less nontransparent in these regions. These absorptions can be measured by an IR-spectrometer system with appropriate measurement setup.

The plot of the intensity of these absorptions in the IR spectral range against the wavelength is called an IR-spectrum and it contains enough information to classify a diamond.



IR-spectrum of diamond

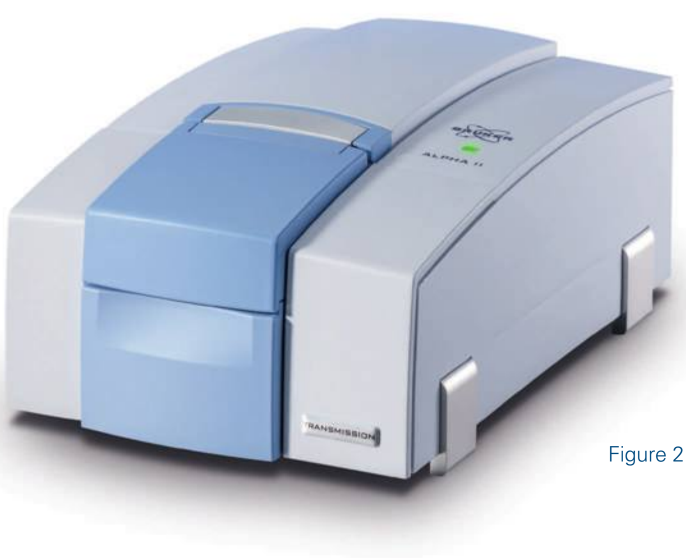


Figure 2: ALPHA II with transmission module.

Measurement procedure for polished diamonds

The ALPHA II Diamond Analyzer allows you to classify any diamond within a minute. The first step is to measure a background spectrum of the empty gold-coated sample holder. Then the diamond is placed in the center of this holder (figure 3) and after moving it into the instrument the measurement is ready to start. The software gives detailed instructions to the user (see figure 4).

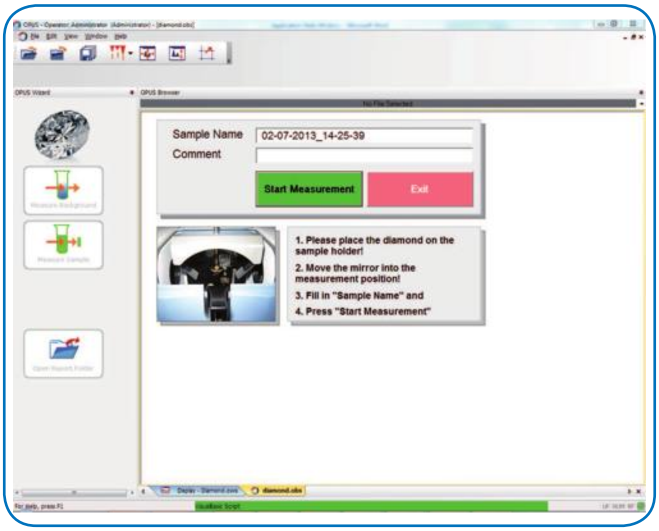


Figure 4: Entering sample information.

Measurement and evaluation take less than 30 seconds. The result is displayed in combination with the spectrum of the diamond (see figure 5).

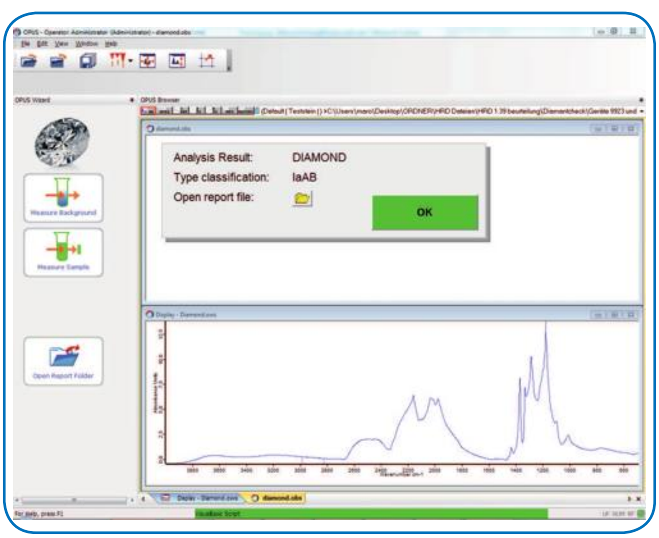


Figure 5: Display of the analysis result.

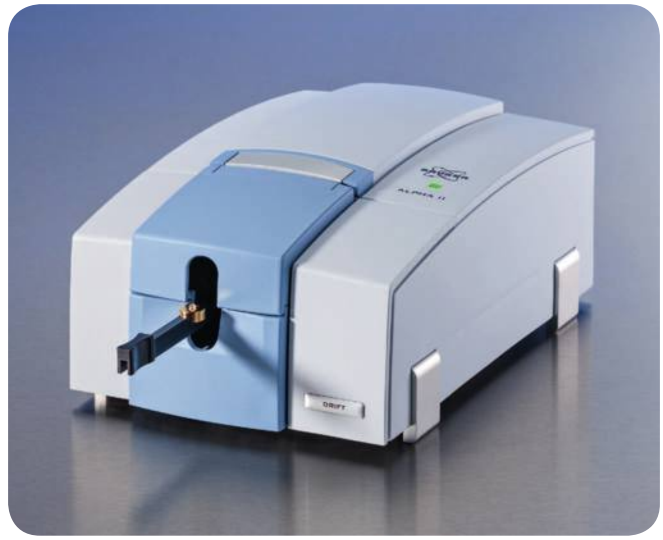


Figure 3: Diamond placed on gold-coated sample holder of the ALPHA II Diamond Analyzer.

The automatically generated PDF-report is displayed in figure 6. It can be opened by just one single mouse click and contains all necessary information, including the spectrum, the identification result (diamond or not a diamond) and the type classification.

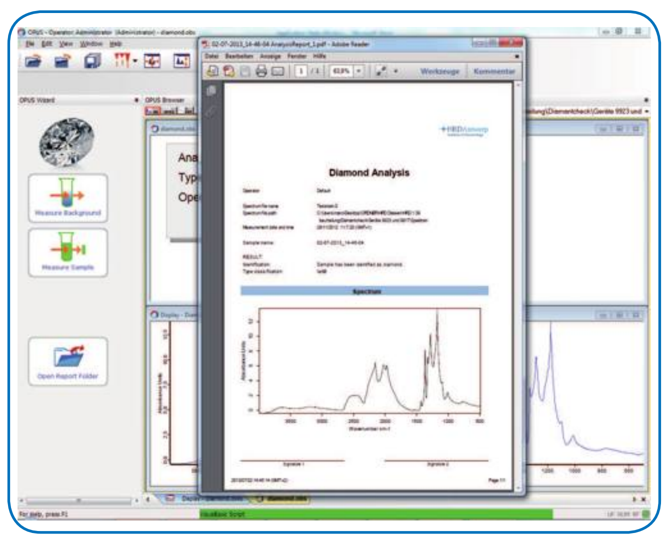


Figure 6: PDF-report.

Mounted diamonds

Mounted stones from jewelry can be measured by using the ALPHA II with the forward looking reflection module shown in figure 7. For the analysis, the stone just has to be placed in front of the aperture hole. A build in camera helps to position the stone correctly and thereby enables the user to selectively measure even smaller stones that are in a narrow arrangement. The inset of figure 7 shows a picture of a 0.25 carat diamond that was taken with the internal camera of the ALPHA II reflection module.

Very small mounted stones

Very small mounted stones in jewelry that are in close contact with each other can be measured selectively with the FTIR microscope LUMOS (figure 8). The LUMOS stands out due its full automation and ease-of-use combined with sample visualization and infrared spectroscopic performance of highest quality. It has an excellent accessibility of the sample stage and a large working distance of 30 mm. Samples with a height of up to 40 mm can be investigated without any changes of the hardware. Mounted stones can be inspected with the aid of a special sample holder vice that allows fixing all kinds of jewelry. Figure 9 shows the sample holder vice with a diamond ring, the whole ring is shown in the picture inset. As an example the measurement of one of the stones is shown in figure 10 together with the according visual image. The spectrum clearly indicates a diamond of type IaA. Typically for diamonds in jewelry, the spectrum shows additional signatures from organic contaminations like for instance from skin fat. The double peak below 3000 cm^{-1} results from the C-H stretching vibrations that are typical for organic substances.

Figure 7: ALPHA II with front reflection module. Inset: Picture of a diamond taken with the integrated camera.

Figure 8: LUMOS FTIR microscope.

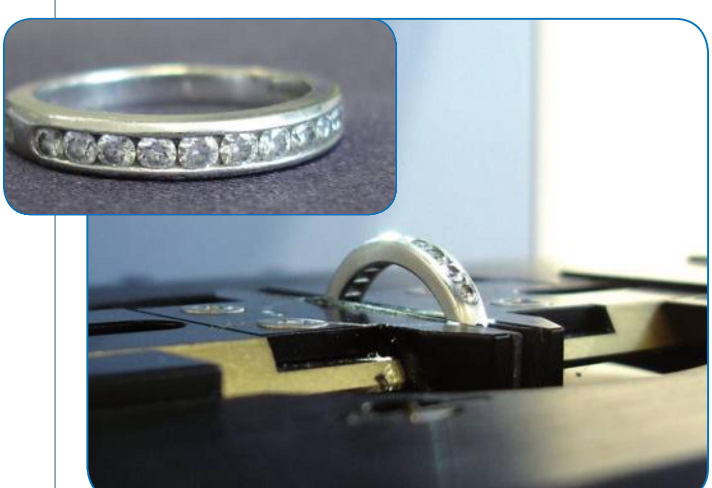


Figure 9: Diamond ring fixed in the sample holder vice on the LUMOS stage.

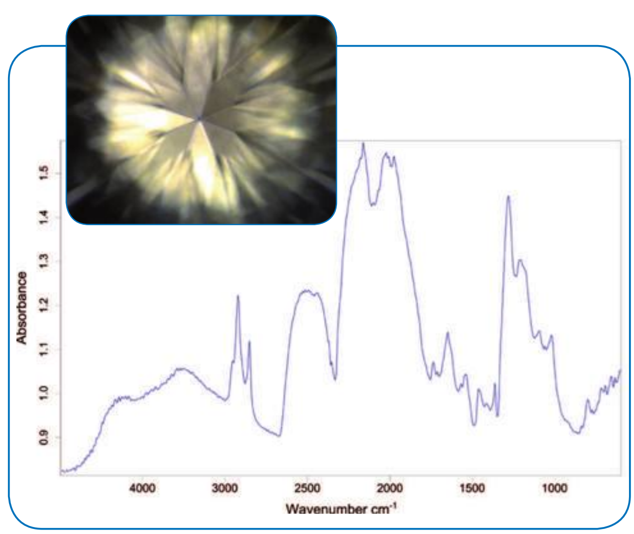


Figure 10: Diamond spectrum of one of the stones from the ring.

Automated Screening

The high-throughput-screening accessory (HTS-XT, see figure 11) is capable to measure and classify large numbers of diamonds automatically. The diamonds are placed in specially designed sample plates that are available with 96, 384 and 1536 measurement positions. This measurement setup allows to measure even very small melee-size diamonds from the sub millimeter range up to diameters of several millimeters. The measurement time for one position is about five seconds. After the measurement the spectrum is automatically evaluated and classified. Like the ALPHA II Diamond Analyzer the HTS-XT based analyzer can distinguish between more than a dozen different diamond types and can also detect diamond imitates.

Figure 11: HTS-XT high throughput accessory with INVENIO S spectrometer.

FTIR Spectra and diamond types – the basics

Generally, diamonds are divided into type I and II where type II contains no measurable traces of nitrogen (N). The subtypes are:

- Type Ia: Diamond with aggregated N
- Type Ib: Diamond with isolated N (often synthetic)
- Type IaA: Diamond with groups of 2 N's
- Type IaB: Diamond with groups of 4 N's
- Type IIa: Diamond without N or Boron (potentially CVD synthesized)
- Type IIb: Diamond with Boron (blue or grey)

Additionally there are many mixture types. The analysis software used in the ALPHA II Diamond Analyzer and the HTS-XT Diamond Analyzer can discriminate between more than a dozen different types. Figure 12 shows example spectra of the most important types. The y-axis shows the absorption and the x-axis the reciprocal value of the wavelength in cm^{-1} (i.e. how many waves exist over one cm) which is a unit commonly used in IR-spectroscopy. Nitrogen impurities typically show absorptions between ca. 500 and 1500 cm^{-1} and boron impurities show typical peaks around 2800 and 2460 cm^{-1}. The strong and broad bands between ca. 1600 and 2700 cm^{-1} are so called two phonon bands and characteristic for all diamonds. They are an excellent marker than can be used to differentiate between diamonds and imitates.

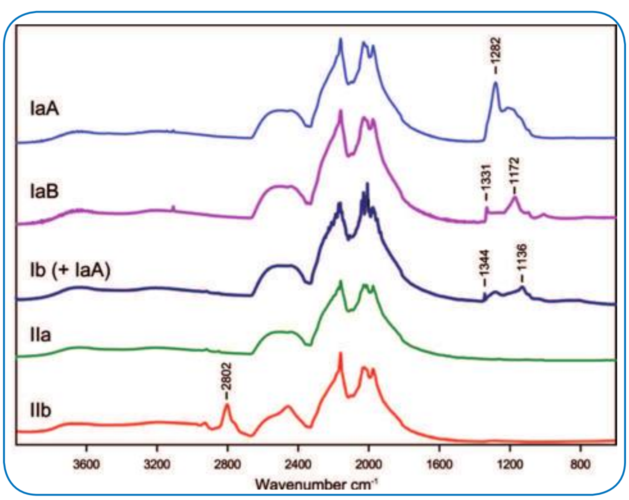


Figure 12: Example spectra of different diamond types with characteristic peak positions.

• Interpreting the Type Information

Knowledge about the type of a diamond is in many cases vital since it can be used to detect synthetic stones and possible candidates for HPHT-treatment. Type IIa and type IaB are of special interest because these diamonds, which are often grey or brown, can be HPHT treated to become colorless or pink. These color changes increase the value of those diamonds significantly. On the other hand Ib type diamonds are almost exclusively HPHT-grown synthetic type stones since they are only very rare in nature. The reason for this rare occurrence is the fact that natural diamonds were subjected to very high temperatures and pressures over very long time periods. Under these conditions the isolated nitrogen atoms of Ib diamonds can move around in the lattice and aggregate into groups. When two N atoms combine, an A-aggregate forms, and when two A-aggregates combine (with a vacancy between them), a B-aggregate forms. Since synthetic CVD-diamonds are also available in gem-quality type IIa diamonds are also potentially synthetic and might be subjected to further evaluation.

Diamond Type	Natural	Synthetic	HPHT enhanced
Type Ia	Yes	No	No
Type IaB	Yes	No	Yes
Type IIa	Rare (~1%)	Yes	Yes
Type Ib	Very rare (<0.1%)	Yes	Yes

Table 1: Occurrence of colorless to near colorless diamonds in relation to the diamond type.

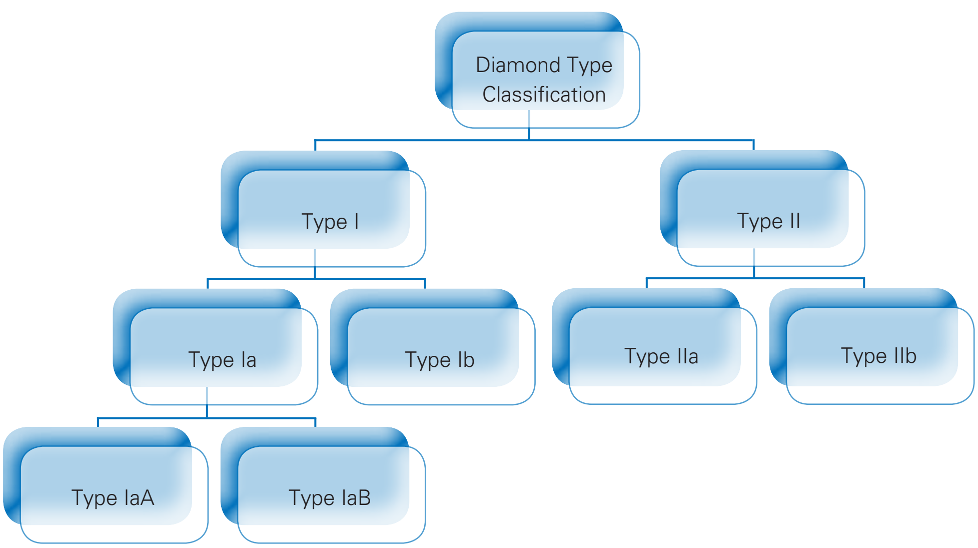


Table 2: Diamond type classification is based on the presence or absence of nitrogen and boron impurities and their specific configurations in the diamond lattice. This diagram shows only "pure" diamond types, most diamond types are "mixed" types.

Covered by one or more of the following patents: DE102004025448; DE19940981.
Additional patents pending.

Bruker Optics is ISO 9001 and ISO 13485 certified.

Laser class 1 product.