

# Carbon Black Analysis

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## Key Words

- OMNIC Spectra Multi-component Searching
- Advanced ATR Correction
- Ge ATR
- High Carbon Black Rubbers
- Polymers and Additives

## Attenuated Total Reflection: Diamond and Germanium

Attenuated Total Reflection (ATR) is increasingly the method of choice for sampling materials using Fourier transform infrared spectroscopy (FT-IR). The simplicity of the sampling device and ease of cleaning are major benefits. However, ATR devices alter the appearance of the spectrum relative to what would be seen in transmission. A systematic understanding of the differences and the tools for addressing them available from Thermo Scientific will greatly enhance the utility of ATR in the laboratory.

Light passing between two different materials changes direction—this is how a magnifying glass works to focus the sun's rays. The change in direction is determined by the index of refraction of the two materials. In eyeglasses, high index of refraction materials like polycarbonate can be used to make thinner lenses than lower index materials like glass, because the polycarbonate redirects the light more effectively.

To understand ATR, consider a rectangular fish aquarium. Looking straight through, the far window is transparent. However, the side windows look like mirrors, an effect caused by internal reflection. When a finger is placed on the side glass, the ridges of the fingerprint are visible, but not the valleys between. Simply stated, at this angle, the light exits the side window very slightly, and this “evanescent wave” interacts with the finger ridges. The depth of penetration—how far the light travels out of the glass—is very shallow, so the valleys of the fingerprint are not seen.

In infrared, the same basic ideas hold true. With proper alignment, IR light can be made to emerge slightly from an infrared transmissive crystal. This will interact with any sample in intimate contact with the crystal—like the fingerprint. This is why most ATR accessories come with pressure towers, to press the sample against the crystal. The sample attenuates the beam through absorption, which gives the spectrum.

The spectrum depends upon the depth of penetration  $d_p$  which, in turn, depends upon several factors. Mathematically, this is given by

$$d_p = \lambda / \{2 \pi n_c [\sin^2 \theta - (n_s/n_c)]^{1/2}\}$$

where  $\lambda$  is the wavelength of the light,  $\theta$  is the angle at which the light strikes the surface of the crystal, and  $n_s$  and  $n_c$  are the index of refractions of the sample and crystal, respectively. Thermo Scientific has developed a proprietary Advanced ATR Correction<sup>1</sup> which accounts for all the variables, permitting the use of transmission databases for comparison to ATR spectra for the first time. The critical difference between the advanced correction and older ATR corrections is recognition that the sample's index of refraction changes (increases) near an absorption. The effect of this is seen in figures 2 and 3.

Two common ATR crystals are diamond and germanium (Ge). Diamond is highly robust, being both hard and chemically inert. For diamond,  $d_p$  is over 2 microns at  $1000 \text{ cm}^{-1}$ . Ge is also hard and inert, though less so than diamond. The key difference is the  $d_p$ , which is around 0.7 microns at  $1000 \text{ cm}^{-1}$ , due to the much higher index of refraction for Ge. It is this quality—the lower depth of penetration for Ge—that makes it ideal for carbon black rubbers.

## Carbon Black Rubbers

Carbon black rubbers (CBRs) are heavily used in tires. The material adds reliability and conducts heat effectively away from the tread, extending tire life. CBRs have traditionally been difficult to analyze by IR, as they are opaque even when cut extremely thinly. More critically for ATR, CBRs have a high index of refraction—close to that of diamond. In the equation above, if the sample index is too close to that of the crystal, the ratio of indices is almost 1, the square root term is negative and there is no ATR effect.

The effect of this is clearly seen in the spectra shown in Figures 2 and 3. These were obtained on a Thermo Scientific Nicolet™ iS™10 FT-IR spectrometer using the Smart iTR™ diamond or germanium ATR crystals. Near the strong absorption bands, the sample index is approaching or exceeding the index for the crystal, and there is a sudden change in  $d_p$ . This badly distorts the spectra, and cannot easily be corrected. In contrast, the Ge spectra in the two figures show clean and well-defined peaks. This is the result of the much higher index of refraction for Ge, and the shallow depth of penetration.



Figure 1: Carbon black rubbers, such as this tire, represent a challenging sample for infrared analysis

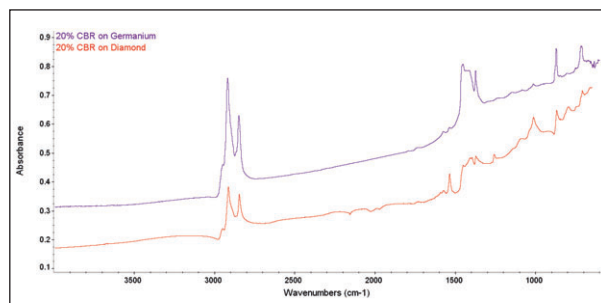


Figure 2: Comparative raw spectra from 20% CBR. The diamond ATR spectrum shows several problems, while the Ge ATR spectrum is clean.

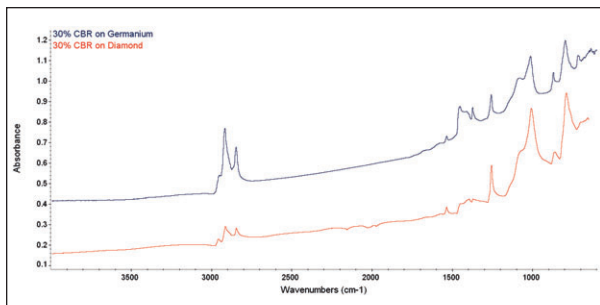


Figure 3: Comparative raw spectra from 30% CBR. Again, there are artifacts in the diamond ATR spectrum, but not in the Ge ATR.

Furthermore, the strong diamond absorption bands in the center of the spectrum no longer ratio correctly. These diamond bands ratio out effectively when the light path through the crystal is the same in the background and the sample spectra. However, the close match of the index of refraction between the crystal and the CBR is causing the path the light takes to change, and the diamond bands no longer ratio; indeed, they are sizeable. Again, the Ge spectrum is totally clean. These two phenomena show clearly the need for Ge in the analysis of CBRs.

The complete analysis of the CBR can now continue, using the powerful OMNIC<sup>™</sup> Specta<sup>™</sup> software. First, the spectrum is baseline corrected and processed. Figure 4 shows the (baseline corrected) spectrum before ATR correction, with the ATR correction supplied by most vendors, and with Thermo Scientific Advanced ATR Correction. The change in the latter is more profound than just application of an intensity correction – the algorithm corrects the bands where strong absorbance alters the index of refraction. The corrected spectrum can now be searched against normal transmission libraries.

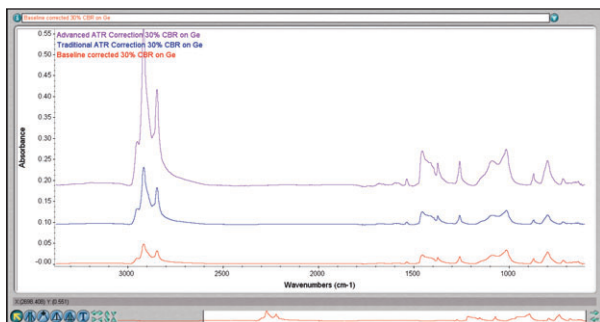


Figure 4: 30% CBR on Ge. Bottom spectrum is baseline corrected only, the middle has the traditional ATR correction applied, and the top has the Advanced ATR Correction applied. Common scaled, offset for clarity.

A simple search gives the results in Figure 5. The match is good, as the base polymer has been identified and a high match index is recorded. However, visual examination shows that several peaks around 1000  $\text{cm}^{-1}$  are not present in the search result – a second component is present.

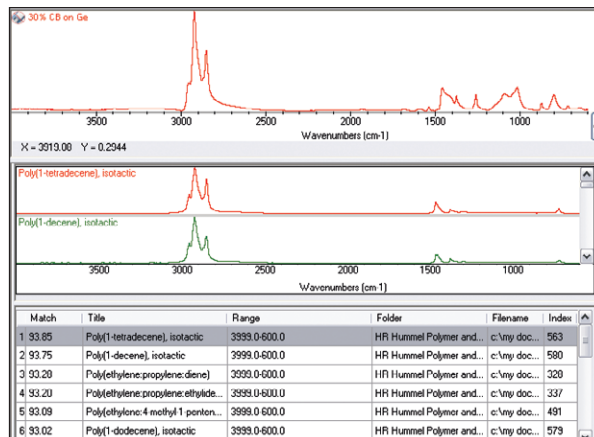


Figure 5: Simple search result for the top spectrum in Figure 4. The result is good, but there are extra peaks visible not in the result.

OMNIC Specta's unique multi-component search algorithm completes the analysis as shown in Figure 6. The powerful algorithm, described elsewhere<sup>2</sup>, extracts two components from this CBR – the base polymer (notably, the same as the simple search) and the silane slip aid. The sample, a car door insulation strip, uses a silane coating to prevent adhesion of the window to the insulation. The composite spectrum is visually remarkable – it represents an almost perfect agreement with the original spectrum.

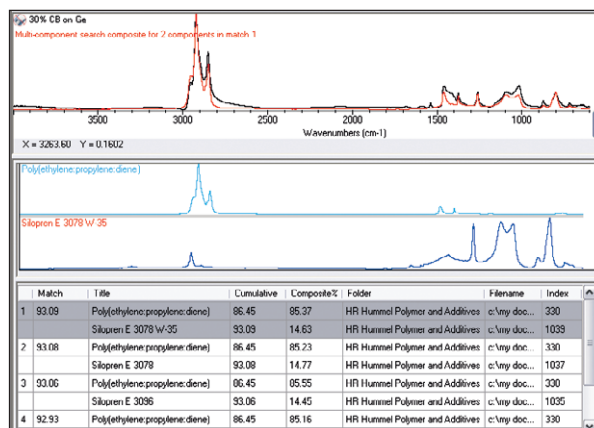


Figure 6: Multi-component search result from OMNIC Specta. The search result is now complete and agrees remarkably well with the spectrum.

## Conclusion

Carbon black rubbers represent a challenging IR sample. Diamond proves to not be a universal solution for CBRs, as the bands observed are distorted. Ge provides clean peaks. Thermo Scientific then provides all the tools required to complete the analysis, including Advanced ATR Correction and OMNIC Specta's multi-component search. The hardware and software combine into a powerful analysis tool.

## References

1. Thermo Scientific Application Note AN01153 by Dr. S. Nunn and Dr. K. Nishikida.
2. Thermo Scientific Technical Note TN51506 by Dr. G. Ritter and Dr. M. Bradley.

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