INFRARED SPECTROSCOPY AS A CHEMICAL FINGERPRINTING TOOL

Timothy L. Huff
NASA Marshall Space Flight Center
Mail Stop ED36
Huntsville, AL 35812

Telephone: 256-544-4259
Email:tim.huff@msfc.nasa.gov

**Introduction**

Infrared (IR) spectroscopy is a powerful analytical tool in the chemical fingerprinting of materials. Any sample material that will interact with infrared light produces a spectrum and, although normally associated with organic materials, inorganic compounds may also be infrared active. The technique is rapid, reproducible and usually non-invasive to the sample. That it is non-invasive allows for additional characterization of the original material using other analytical techniques including thermal analysis and RAMAN spectroscopic techniques. With the appropriate accessories, the technique can be used to examine samples in liquid, solid or gas phase. Both aqueous and non-aqueous free-flowing solutions can be analyzed, as can viscous liquids such as heavy oils and greases. Solid samples of varying sizes and shapes may also be examined and with the addition of microscopic IR (microspectroscopy) capabilities, minute materials such as single fibers and threads may be analyzed. With the addition of appropriate software, microspectroscopy can be used for automated discrete point or compositional surface area mapping, with the latter providing a means to record changes in the chemical composition of a material surface over a defined area. Due to the ability to characterize gaseous samples, IR spectroscopy can also be coupled with thermal processes such as thermogravimetric (TG) analyses to provide both thermal and chemical data in a single run. In this configuration, solids (or liquids) heated in a TG analyzer undergo decomposition, with the evolving gases directed into the IR spectrometer. Thus, information is provided on the thermal properties of a material and the order in which its chemical constituents are broken down during incremental heating. Specific examples of these varied applications will be cited, with data interpretation and method limitations further discussed.

**Liquid Phase Analysis**

Samples in this physical state can be further categorized as free-flowing aqueous or non-aqueous solutions and viscous liquids. This distinction is important in the selection of a proper technique as certain techniques may be incompatible with the sample or not produce optimal spectra. In Figure 1 below, transmission by liquid cell was chosen because the samples were free flowing, relatively transparent in nature and produced strong infrared spectra. This example was part of a study to determine the feasibility of separating a solvating agent from a solvating agent/fuel mixture with the intention of recovering the solvent for reuse. The first two spectra are the infrared fingerprints of the virgin solvent and hydrocarbon fuel, respectively. The third spectrum was produced following processed separation of the solvent/fuel mixture. Spectral subtraction of the processed mixture from the virgin fuel produced the spectrum shown

at the bottom, which contained peaks consistent with that of the solvent. This was an indication of incomplete separation of the two components under the processing conditions employed.
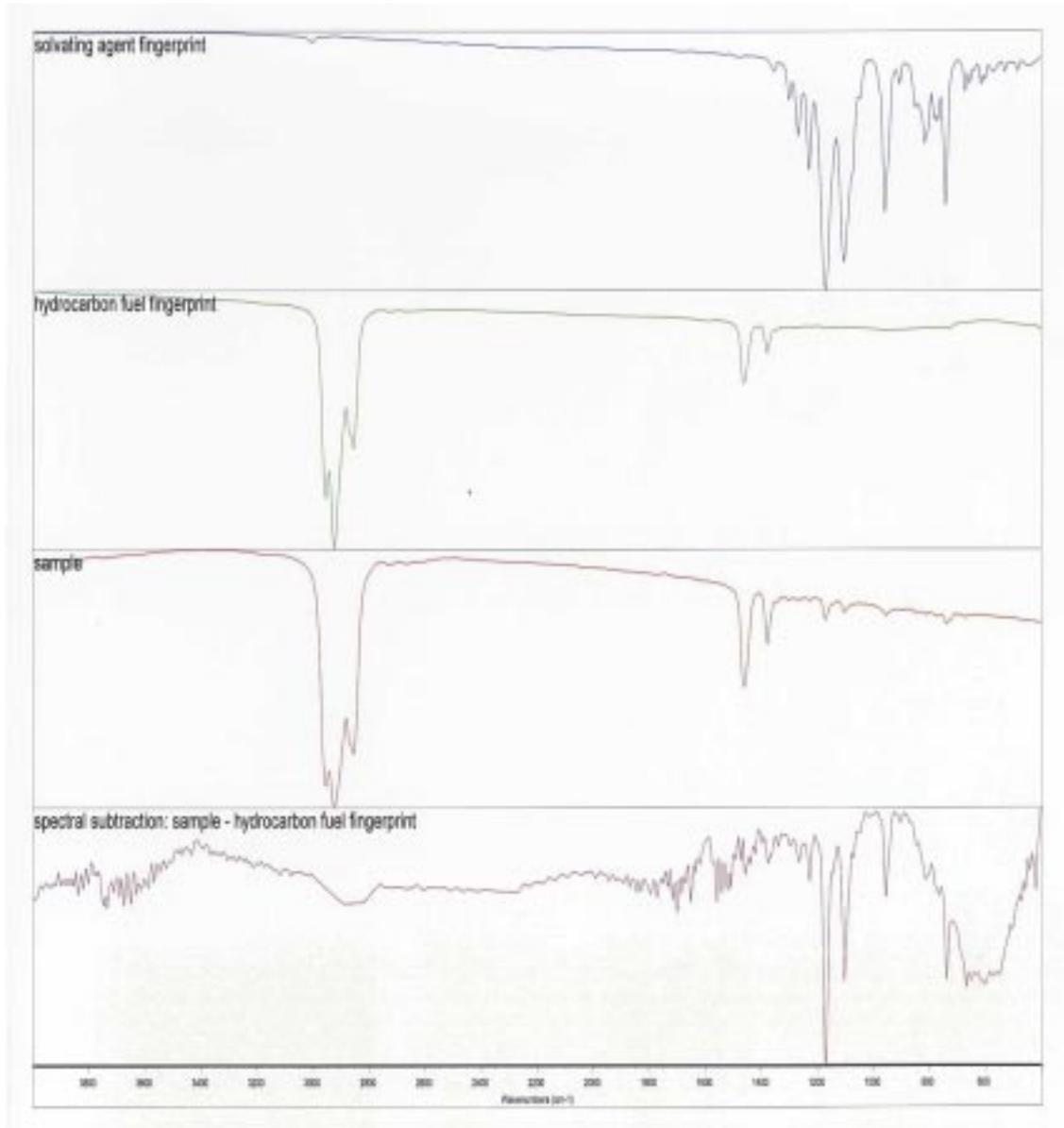


**Figure 1**

**Solid Phase Analysis**

The categories within this material state vary greatly, as do the techniques for their analysis. The material may be present as a powder, a thin or thick film and vary in shape from a pellet to a fiber. Other factors to consider include if only surface characteristics is required or depth profiling is necessary. The example in Figure 2 is a surface scan of a reflective material using an automated microscopic technique. In operation, infrared radiation travels through the microscope objective, striking the surface and reentering the lens where the signal is directed to the infrared detector. A spectral fingerprint of the virgin material was previously collected and served as the background for the run. At each pre-programmed point, the collected spectrum is subtracted from the background and the difference presented. This particular scan

encompassed a linear range of approximately 5000 micrometers with a surface contaminant detected from approximately 2000 to 3500 micrometers.
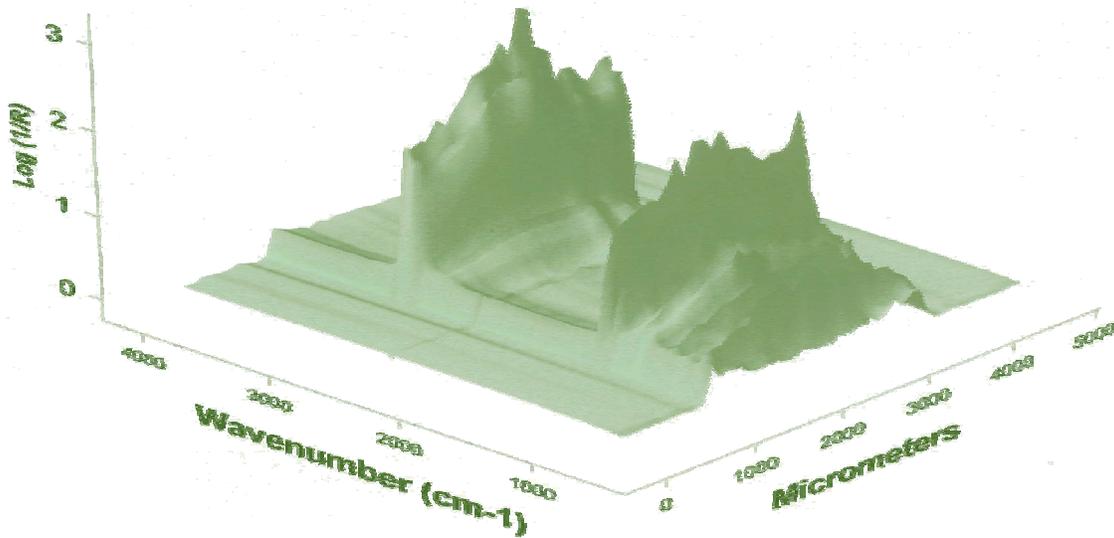


**Figure 2**

Figure 3 is a second example of a spectroscopic scan of a material using the automated microscope system. In this case, the base material was non-reflective in nature and required analysis by an infrared technique known as Attenuated Total Reflectance (ATR). Unlike reflectance, this method requires surface contact using a suitable crystal for transferring the infrared radiation to and from the material. As with reflectance, the method is non-destructive. The data is presented in what is sometimes referred to as a waterfall representation, again showing surface contamination as the sample moves across the microscope stage.
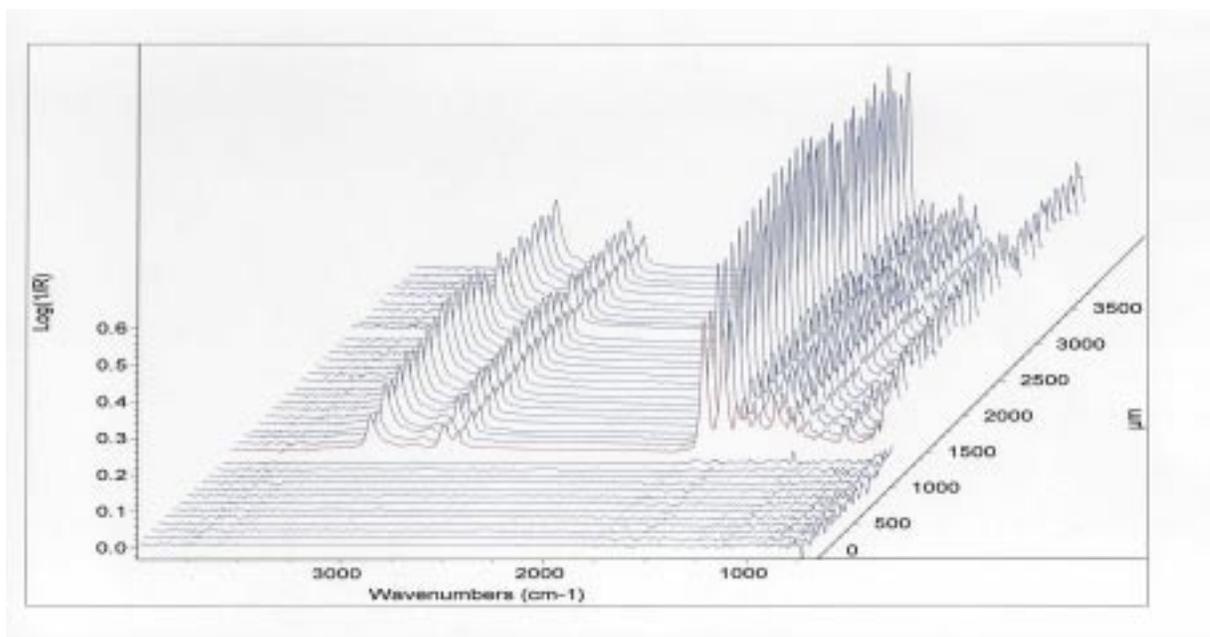


**Figure 3**

As mentioned previously, minute materials may also be examined by infrared techniques. The photographs in Figure 4 were taken of a fiber measuring approximately 15 micrometers in diameter. The rectangular light is the infrared beam area, which can be varied along the X and Y axes such that discrete sample areas can be analyzed. This is shown in the second of the two photographs, with the beam positioned only over the single-stranded fiber.
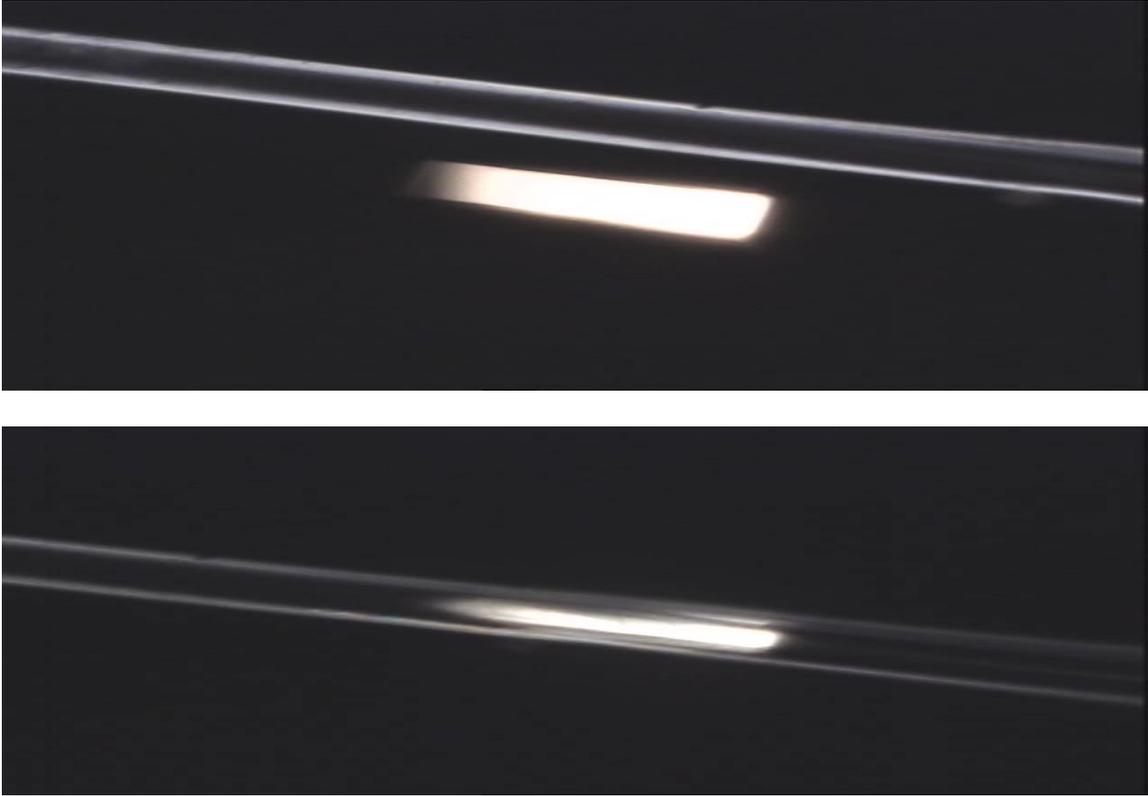


**Figure 4**

Figure 5 is the collected spectrum, which allowed identification of the fiber as a polypropylene material.
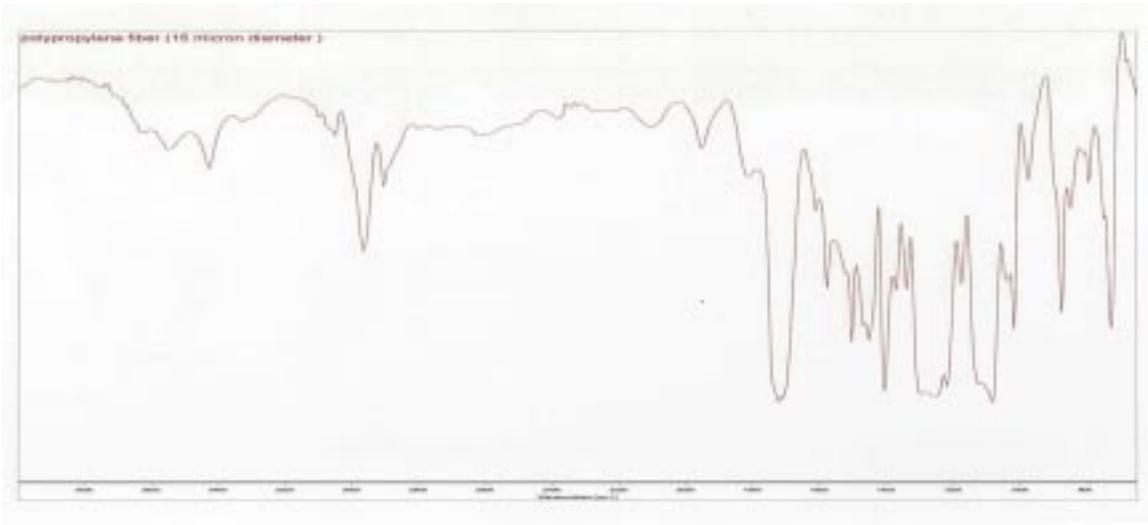


**Figure 5**

**Gas Phase Analysis**

In general, any sample that is a gas at room temperature may produce an infrared spectrum using appropriate techniques. These techniques may also be expanded to include both solid and liquid samples through coupling of infrared techniques with other analytical methodologies such as thermogravimetric (TG) analysis. In TG analysis, the solid or liquid sample is heated at a controlled rate and the sample weight monitored. As sample heating proceeds, a weight change occurs due to sample decomposition, with the gaseous decomposition products being released. Normally, these constituents are exhausted from the system without further characterization. However, by redirecting these evolving gases into an infrared analyzer, chemical speciation of these products is possible. Thus a more complete material characterization may be achieved by providing both a chemical and thermal fingerprint of the sample. In practice, the evolving gas is purged through a transfer line into a gas cell within the FTIR. Temperatures in both the transfer line and gas cell are held at approximately 250 degrees Celsius ($^{o}$C) to prevent condensation of the gases during the sample run. The purge gas may be either high purity air or an inert gas such as nitrogen to allow oxidative and pyrolytic processes to be examined, respectively. Spectra collected during an oxidative run are usually characterized by a predominant carbon dioxide peak due to oxidation of some evolving carbon constituents with the air or sample charring. An inert atmosphere generally provides more functional group information, as the evolving species are less reactive with the atmosphere. During the decomposition process, the evolving gases directed to the FTIR are analyzed real-time for chemical groups. At the end of a run, the data can be presented as a "stacked plot" that presents the spectral data plotted against time (or temperature) throughout the heating cycle for the sample. This allows for the observation of increases and decreases in individual chemical groups (based on peak height and location) as the run progresses. An example of such a plot is presented in the upper region of Figure 6 below.
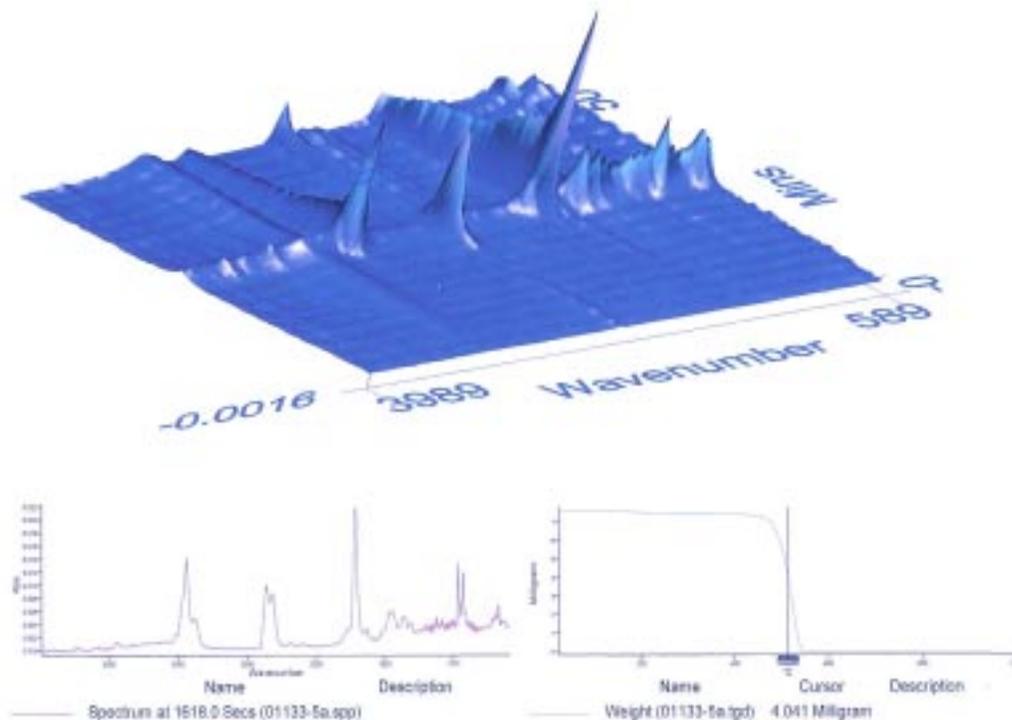


**Figure 6**

Additionally, weight loss data can be incorporated into the spectral data, with specific "slices" in the plot generated that correlate individual point-in-time spectra with observed weight changes. In the example above, a spectrum collected during a weight loss event occurring at approximately 500$^{o}$C in seen in the lower left of the figure with the corresponding weight loss profile to the right. By observing the peak

locations on the X-axis, information on the types of chemical groups evolving at that time are obtained. In this example, the observed peaks indicate the presence of carbon dioxide, carbon monoxide, carbonyl (C=O) and non-aromatic hydrocarbon functional groups.

**Practical Considerations**

Although useful in the chemical fingerprinting of materials, considerations must be made in the use of these infrared techniques. Notable is the importance of reproduction of the infrared data, a function of both the technique and specific instrument parameters. Different techniques may produce differing spectra for the same material, both in terms of observable spectral peaks and, for quantitative applications, varying peak areas. In Figure 7 below, a halogenated film was run using both transmission and ATR techniques. As can be seen, the spectral profiles of the same material differ depending on the technique chosen.
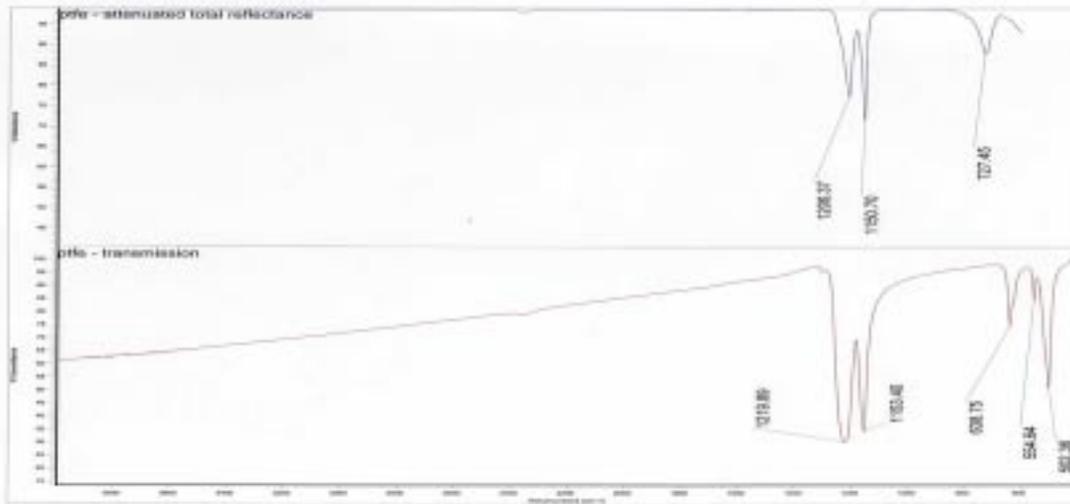


**Figure 7**

When these same techniques were used to analyze a polyethylene film, significant differences were observed in the measurable peak areas of the sample (Figure 8).
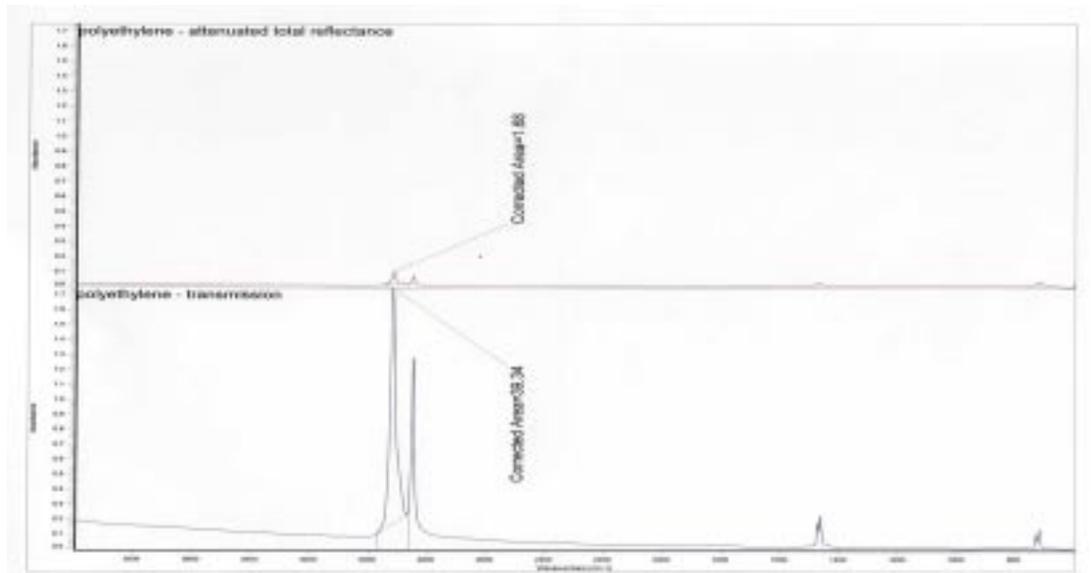


**Figure 8**

Spectral differences can occur even within a common technique if the parameters employed in the collection of the data are not consistent. In Figure 9, a polyethylene film was analyzed at different resolutions, a parameter used to determine how close two peaks can be and still be identified as separate peaks. At a resolution of eight (8) the peaks are indistinct whereas a resolution of four (4) produces well-defined spectral peaks. This can be an important distinction in chemical fingerprinting when comparing "standard" spectrum peaks with subsequent samples. In this instance, the doublet observed at 730 and 719 cm-1 is actually an important indicator of whether the sample is a low density or high density polyethylene materials.
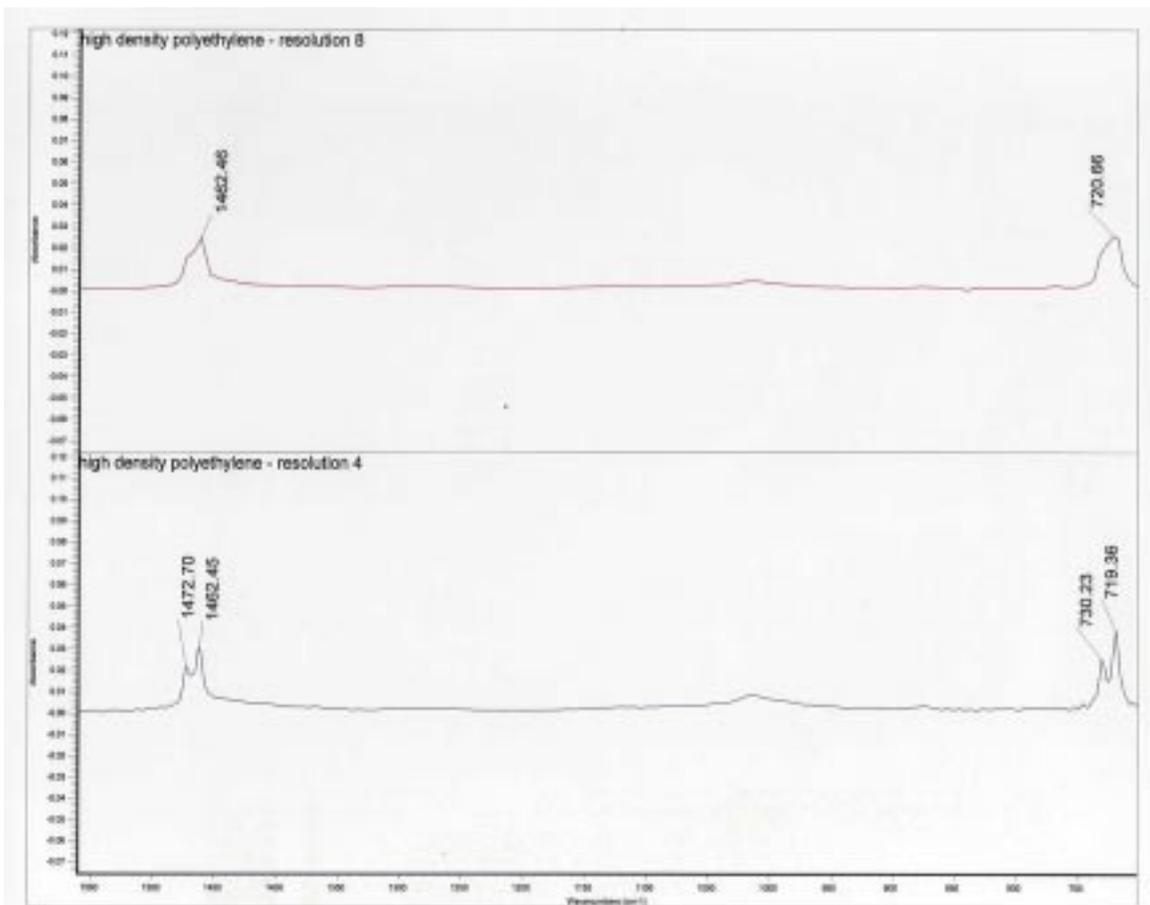


**Figure 9**

**Limitations**

Infrared spectroscopy depends upon interaction of infrared light with specific chemical functional groups. However, not all chemical groups are readily detectable due to the nature of the infrared-chemical bond interaction. Diatomic groups such as disulfides (S-S) and symmetrically substituted carbon-carbon double bonds are only weakly infrared active, if at all. Instrument limitations also must be considered when these techniques are employed. For example, infrared interactions with metal atoms are below the wavenumber range of most detectors employed in infrared spectrometers. In some instances these differences may be overcome by converting infrared inactive groups to a more active form. In Figure 10 below, a metal disulfide constituent in a mixture was being investigated for thermal breakdown characteristics. Since the mixture was complex in nature, it was difficult to determine by thermal analysis alone when this particular constituent was decomposing. Also, the nature of the metal disulfide complex prohibited TG-IR analysis due to the limitations mentioned above. However, by performing the thermal portion of the TG-IR run in an oxidative atmosphere, the complex was oxidized upon decomposition to form infrared active

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sulfur/oxygen groups at approximately 1375 and 1339 cm-1.  Thus, the temperature of decomposition of the metal disulfide constituent was inferred from appearance of these bonds.  As shown, an inert atmosphere did not produce spectral peaks in this region.
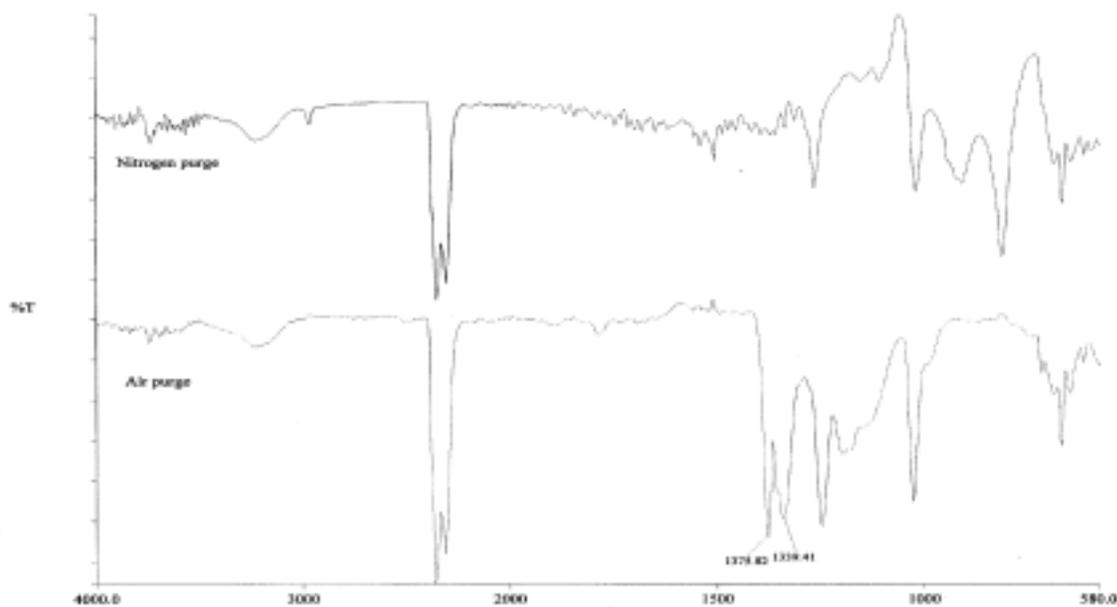


**Figure 10**

In other cases, alternate methodologies such as RAMAN spectroscopy are required.  This technique is actually complementary to infrared techniques in that both are vibrational spectroscopic techniques and operate in the same relative wavenumber range.  However, RAMAN spectra are not dependent on the dissimilarity of molecules i.e. the presence of a strong dipole moment.  Thus, diatomic groups and symmetrical double bonded groups are readily observable.  Also, the instrument operating range extends into lower wavenumber regions where metal complexes are better detectable.  In Figure 11 below, the carbon-carbon double bond present in styrene butadiene is readily apparent in the 1680-1630 cm-1 region using a RAMAN spectrometer but absent in the infrared technique.
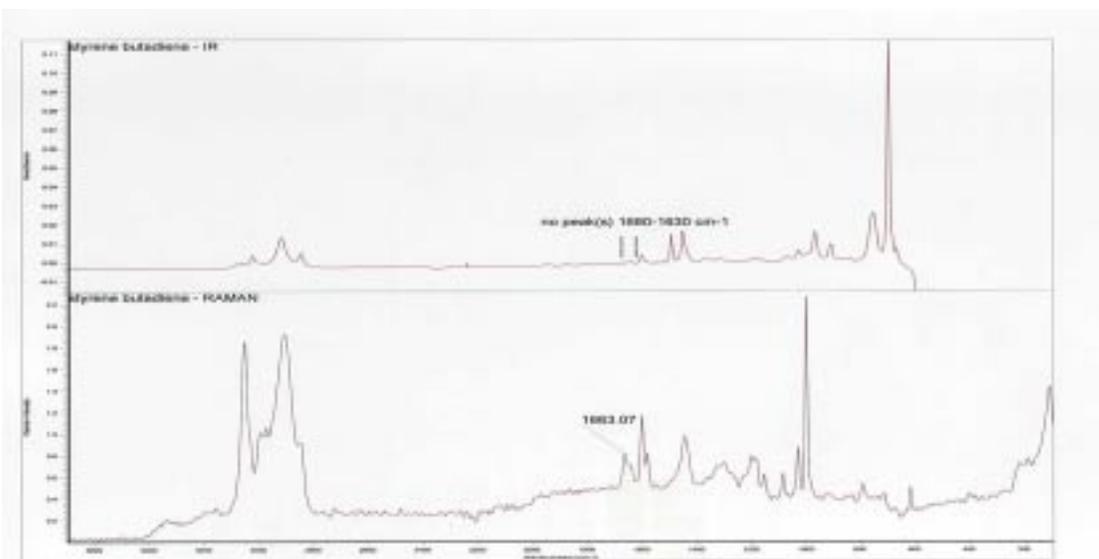


**Figure 11**

Unlike infrared techniques, RAMAN can be destructive to the sample due to heat generated from the intense beam of radiation.  In addition, fluorescing and highly absorbing materials can interfere with spectral analysis.  Another important consideration is cost, which may be considerably greater than that of an infrared spectrometer.


**Conclusion**

Infrared spectroscopy provides a rapid, reproducible means for chemical fingerprinting of materials in any physical state.  That the method is non-destructive allows additional characterization of the material by other analytical techniques such as thermal analysis, coupled thermogravimetric–infrared analysis and RAMAN spectroscopy.  In conjunction, these techniques can provide important information on the properties of a given material.