

The Basics Of IRD Data Analysis

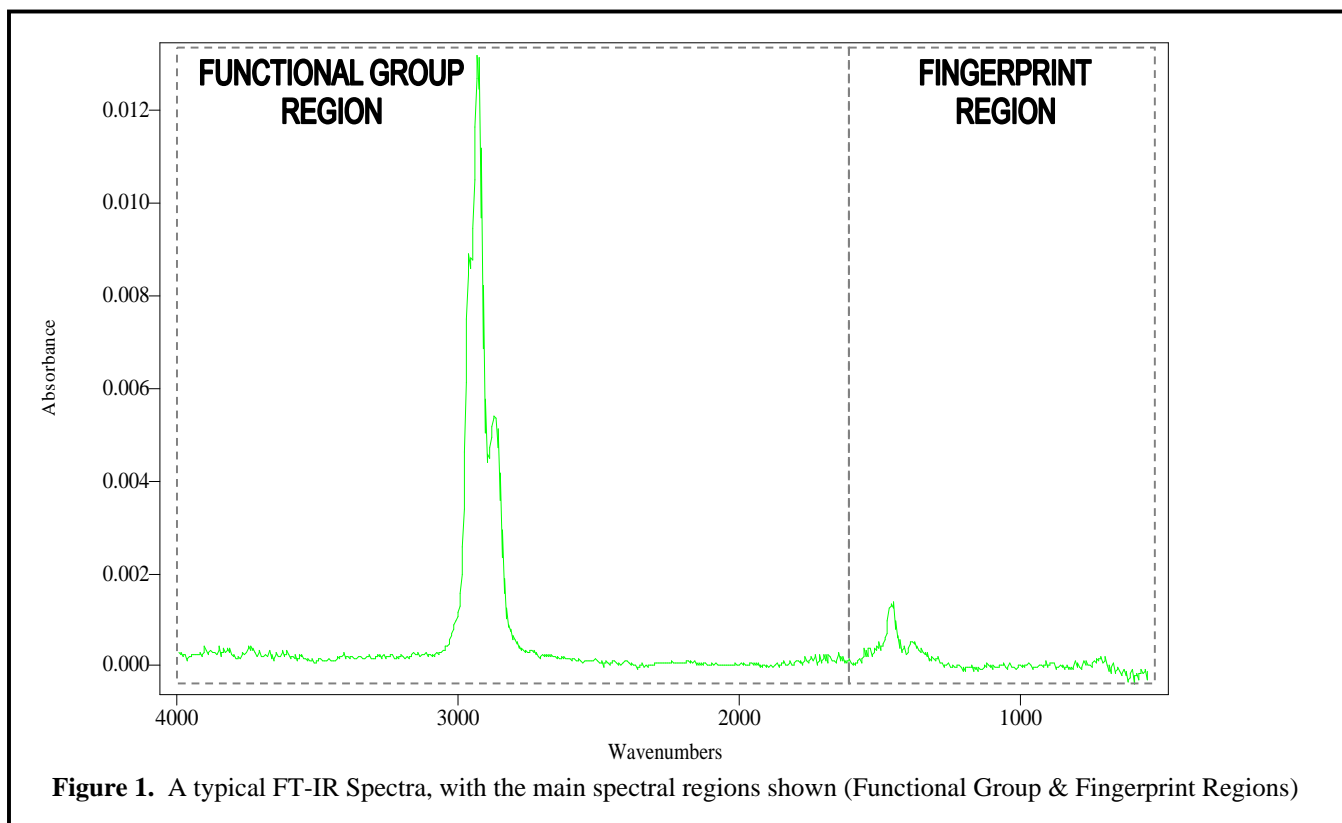
For most people, when they are doing data analysis of a sample run on a bench FT-IR, the data is simpler in that there is no retention time domain due to a GC separation. They run a scan of a sample (typically a solid or liquid), and they end up with a spectrum that can be analyzed. This analysis can be performed with a library search on the spectra, or just by looking at the spectra and interpreting the data based upon knowledge of the absorption of mid-infrared light in molecules.

Library searching is useful, but there are times when a good library match cannot be found, or a single, clear search match is not in the result. In those cases, it is helpful to actually look at the spectra, and do some basic interpretation.

When looking at an FT-IR spectrum, there are 2 basic regions that exist, as shown in Figure 1 below. They are the Functional Group Region and the Fingerprint Region. Both regions are the result of IR absorption from intra-molecular vibrational energy such as stretching or bending.

In the 4000 to 1500 wavenumber range, spectral peaks are typically a result of a specific functional group absorbing a specific band of the mid FT-IR energy. This region is referred to as the Functional Group Region. In this region, each functional group has a very specific band of absorption, such as Alcohols having a –OH functional group that absorbs in the range of 3680 to 3600 wavenumbers.

In the range of 1500 to 550 wavenumbers, spectral peaks are typically a result of very specific intermolecular phenomena. What this means in practice, is that two different alcohols might have the same spectral peak in the 3680 to 3600 wavenumber functional group region, but will have unique spectral peaks that differentiate the compounds in the fingerprint region. These differences are what allow a library match to be accurate and yet specific to a particular structure.



The Infrared Detector, or IRD, is a specialized FT-IR instrument, dedicated to analyzing vapor phase samples in Gas Chromatographic eluents. That means, much like a bench FT-IR, spectral data will be obtained. However, using a Gas Chromatograph, or GC, as the mechanism to introduce the vapor phase samples into the IRD, it is possible to have the components in a sample separated during the elution, so they can be analyzed individually. What this means with regards to data, is that the complete data set will not be a single spectrum, but rather a series of spectra obtained at a rate of multiple spectra per second. This multidimensional data is viewed in a similar fashion as with GC-MS data. Both are multidimensional data with a time domain, a spectral/fragmentation domain and an intensity domain.

In order to minimize the time necessary to examine all of the spectra obtained during a lengthy GC run, it is necessary to have some sort of chromatogram that will help in indicating which spectra contain interesting information, and which are just baseline information. This is done by applying a Gram-Schmidt Algorithm to the spectral data to create a Total Reconstructed Chromatogram, or TRC. It serves the same function as a Total Ion Chromatogram, or TIC, file in the GC-MS world. Each data point on the TRC has been derived by analyzing the spectral data acquired at a specific time. Figure 2 below shows a TRC that has a couple of chromatographic peaks, and shows the spectral data for each of those peaks.

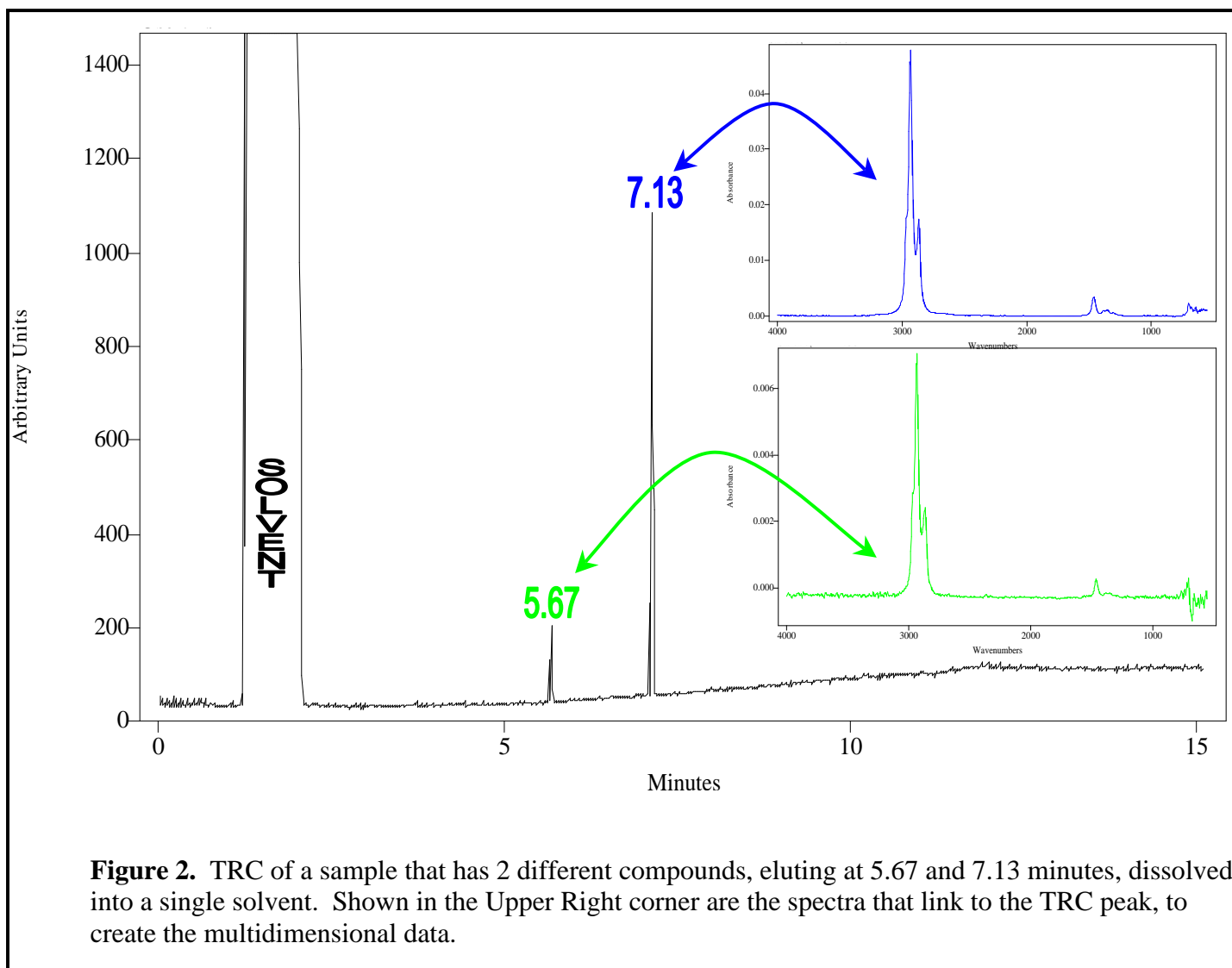
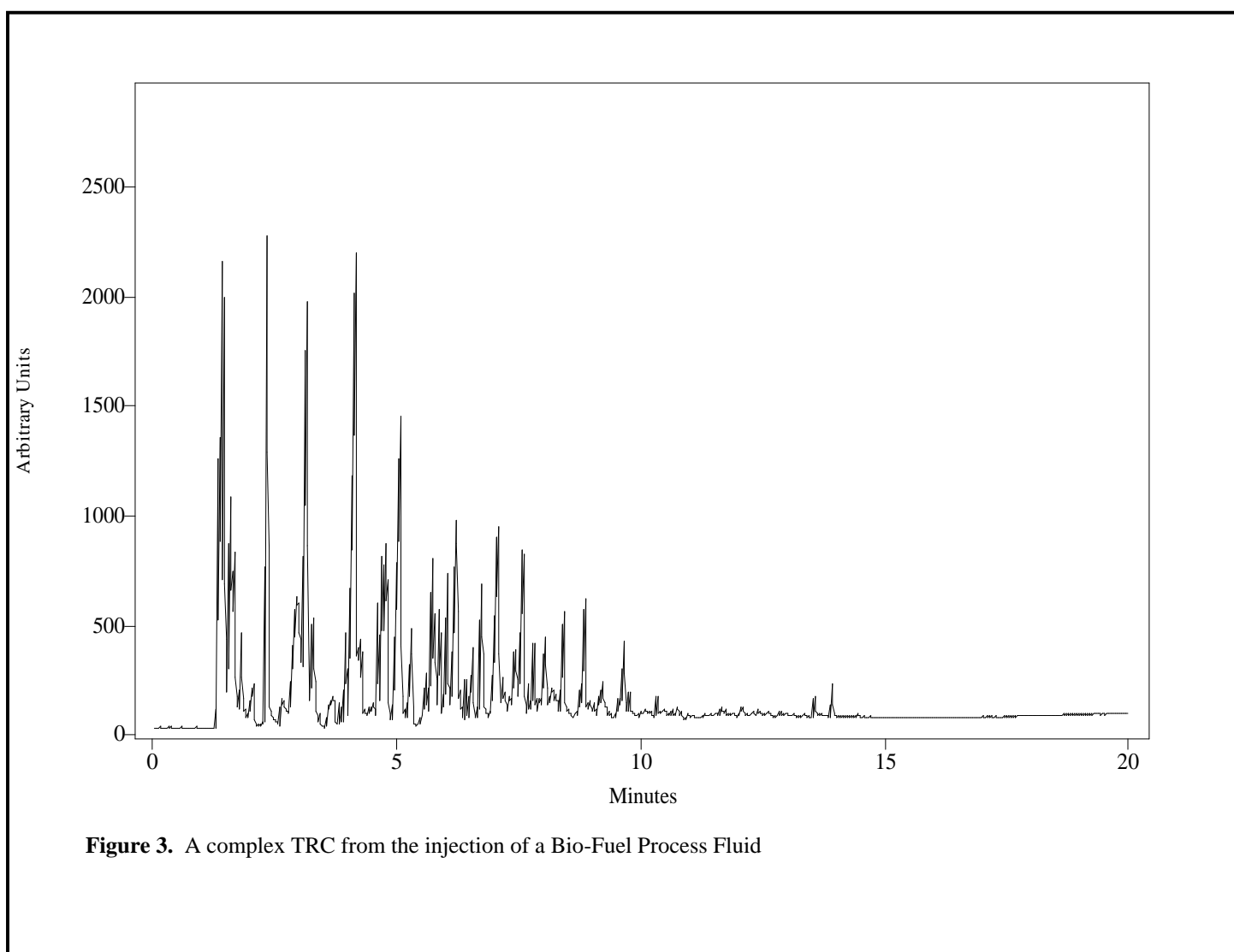


Figure 2. TRC of a sample that has 2 different compounds, eluting at 5.67 and 7.13 minutes, dissolved into a single solvent. Shown in the Upper Right corner are the spectra that link to the TRC peak, to create the multidimensional data.

While some data analysis can be done on the TRC just by Retention Time index analysis, what is more useful is to analyze the spectral data. For the sample shown in Figure 2, there are 2 TRC peaks, and thus 2 spectra that are of interest to analyze. As mentioned previously, it is possible to perform a library search on these spectra, and determine exactly what each component is, or just to examine the Functional Group and Fingerprint regions of these spectra to determine their identities.

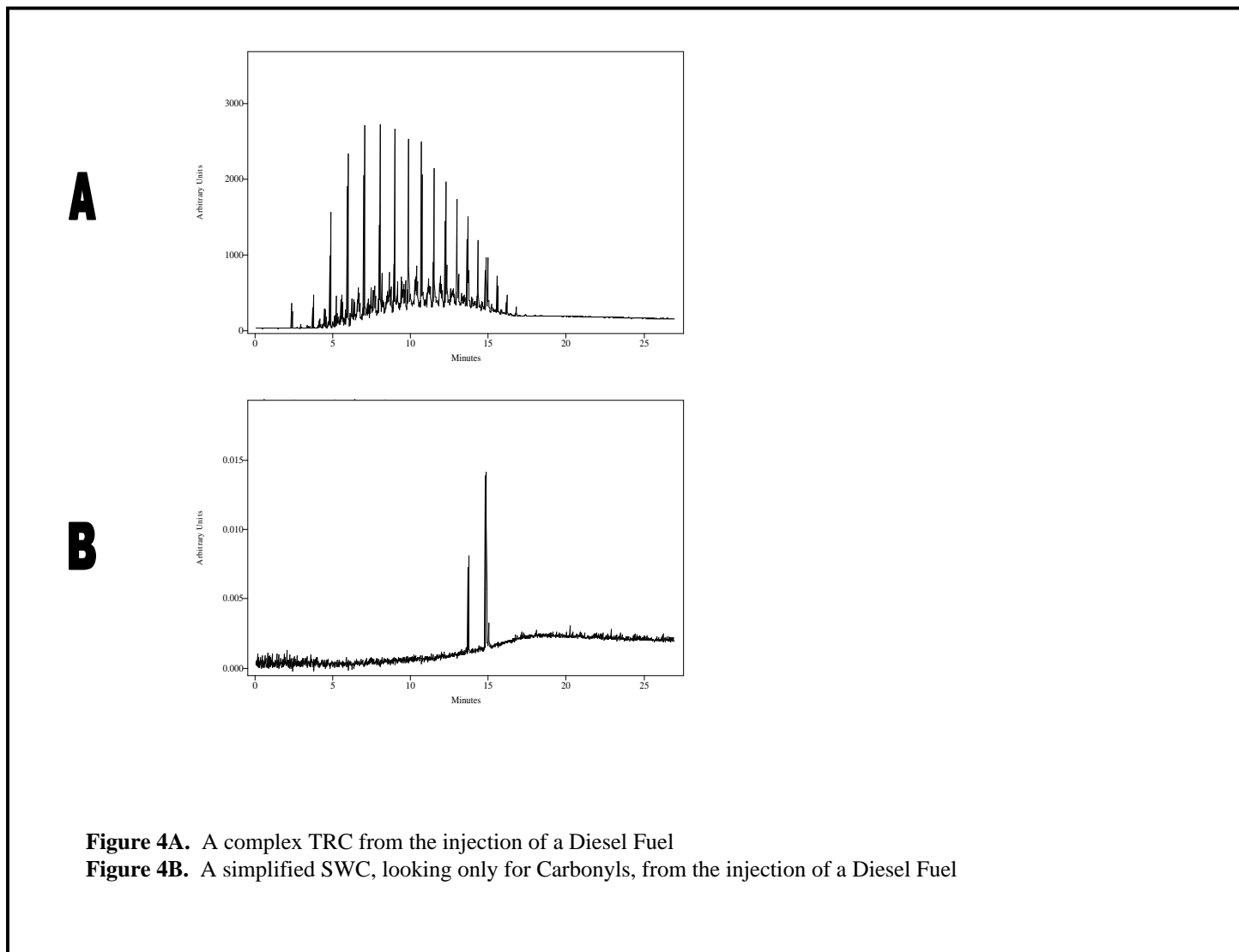
Simple samples, as shown in Figure 2 with only a couple of chromatographic peaks, do not require much time to analyze the entire data set. However, in many real world samples, there are so many chromatographic peaks, that analyzing the entire data set in its entirety is more time intensive. For these samples, an alternative is to simplify the TRC, to show only the chromatographic peaks of interest in a particular analysis.

In the TRC shown below in Figure 3, a Bio-Fuel Process Fluid has been injected into the GC, and has provided a multitude of chromatographic peaks. In this TRC, there are literally hundreds of peaks, making it very difficult to find all of the important characteristics of this sample.



The data analysis software for the IRD is called EssentialFTIR, or eFTIR. In this software, a feature exists that allows for selectively looking at chromatograms within a narrow IR absorption region. This is called the Selective Wavenumber Chromatogram, or SWC. This allows for the TRC to be redrawn such that it only shows peaks that have specific functional group on that molecule. This behaves similarly to the Selective Ion Chromatogram in GC-MS.

Figure 4, shown below, is a TRC of a diesel fuel sample along with a SWC that is specifically able to show carbonyl type functional groups. As can be easily seen in this example, it is possible to reduce the data analysis from hundreds of peaks shown in Figure 4A, to just a few peaks of interest as shown in Figure 4B. This approach requires knowledge or anticipation that carbonyl functional groups might be in the sample.



There is a software tool inside eFTIR that allows for the observation of all of the spectra at once to help determine which SWCs should be applied to a particular sample for quick data analysis. This software tool displays a Contour Plot of the entire spectral data set as shown below in Figure 5. In this Contour Plot, it is still possible to examine the Functional Group and Fingerprint Regions separately.

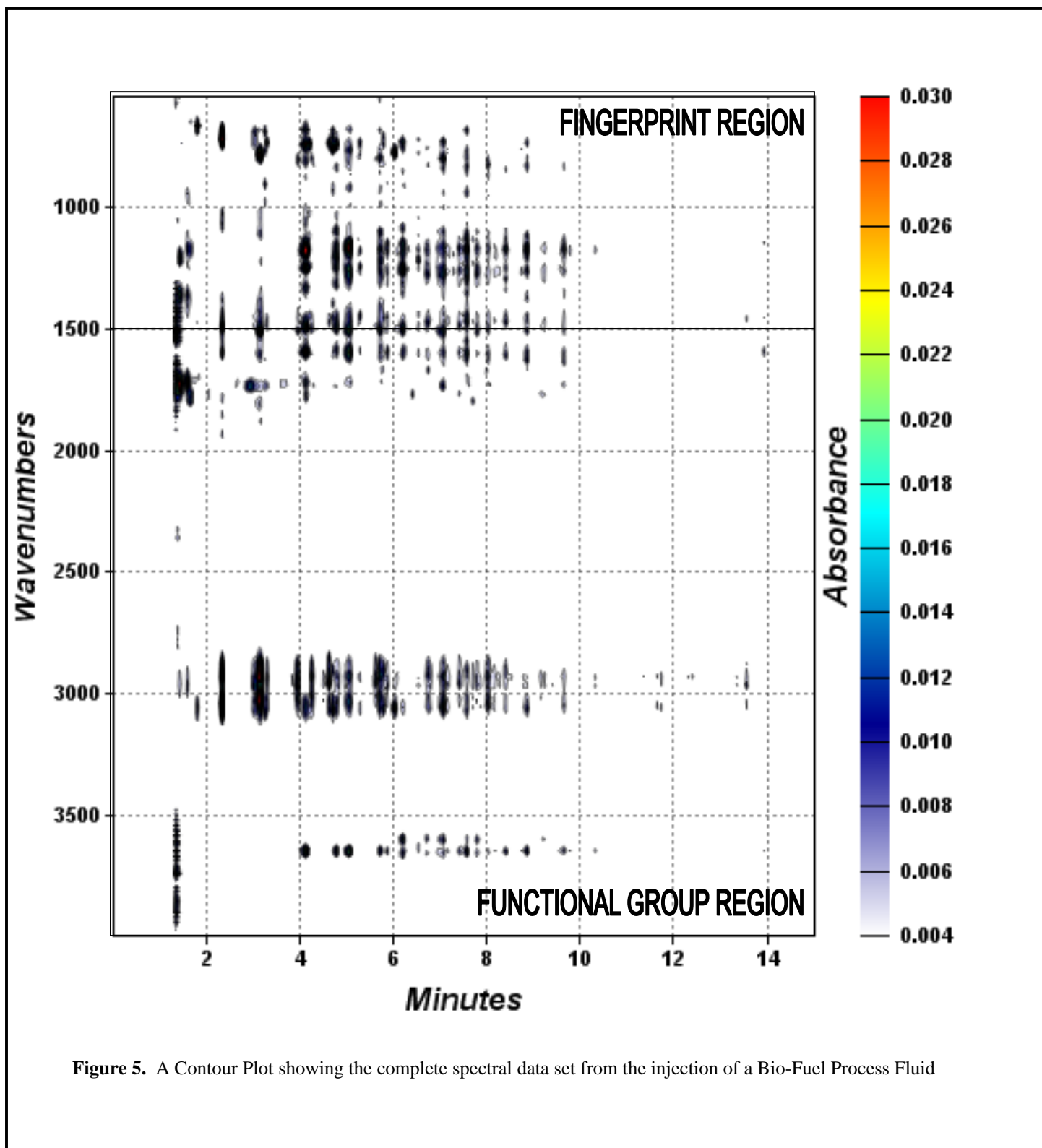


Figure 5. A Contour Plot showing the complete spectral data set from the injection of a Bio-Fuel Process Fluid

In looking at the Functional Group Region of the Contour Plot shown in Figure 6, there are 4 distinct functional group bands that have characteristic IR absorption.

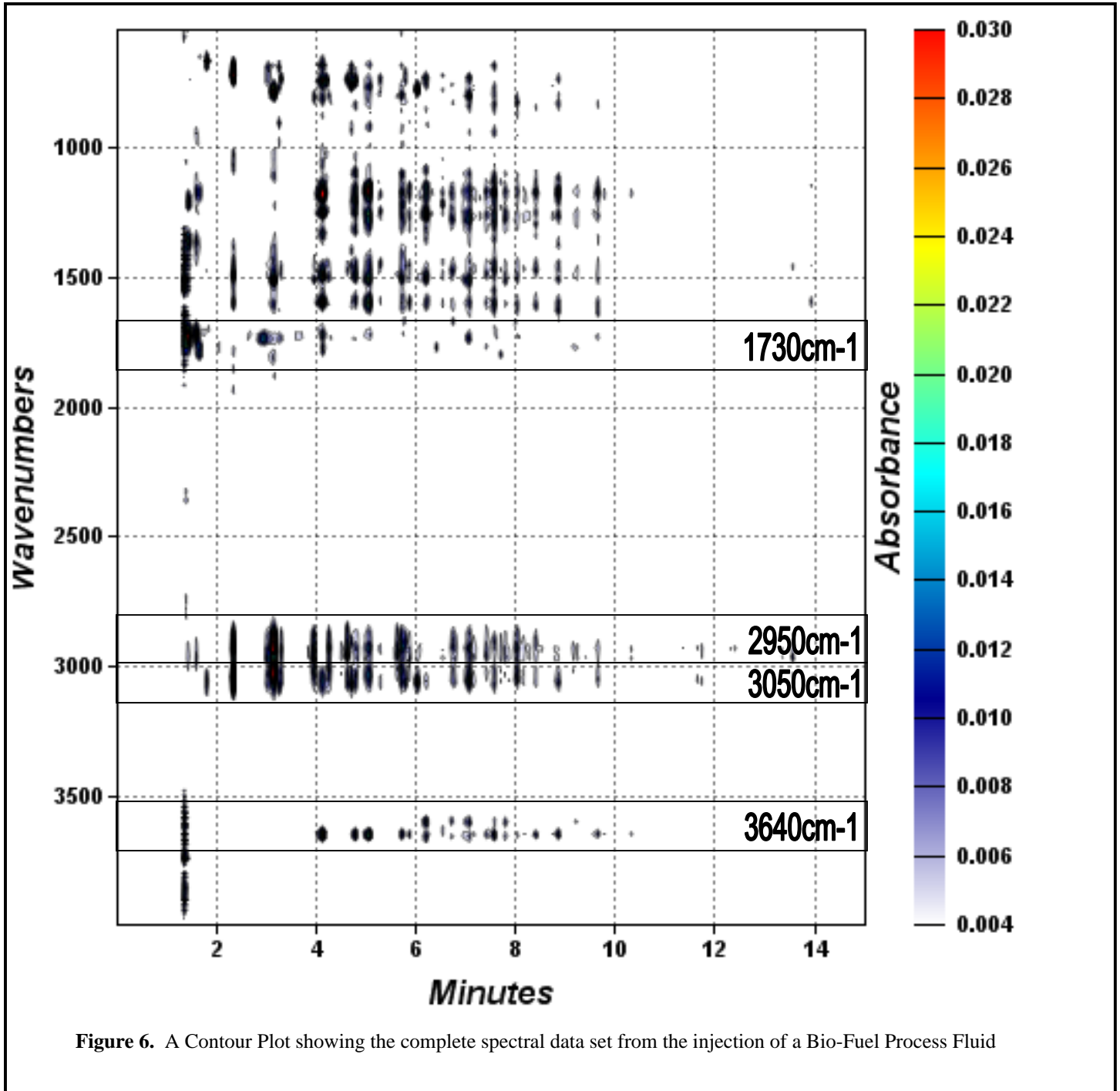


Figure 6. A Contour Plot showing the complete spectral data set from the injection of a Bio-Fuel Process Fluid

In a very simplistic summary of this information with regards to fuels, the goal is to maximize the number of peaks in the 2950 and 3050 wavenumber regions as they are high BTU regions. Peaks in the 1730 and 3640 wavenumber regions are OK, but have less BTUs than the other 2 regions. However, if you have peaks in both the 1730 and 3640 wavenumber regions, this may be particularly undesirable, as it is indicative of compounds with free carboxylic acid groups.

Of course, this approach is far too simplistic, so a little more detail should be given to give the complete analysis of this sample.

Looking at the four distinct functional group bands and applying some logic based upon this being a bio-fuel sample, it can be assumed which functional groups are present

Region	Description	Functional Group
3640 cm-1	Alcohols	Alcohol (-OH)
3050 cm-1	Aromatics	Aromatic (CH)
2950 cm-1	Saturated Hydrocarbons	Alkane (C-H)
1730 cm-1	Carbonyls	Carbonyl (C=O)

A good bio-derived fluid for potential fuel use might contain Aromatics and Saturated Hydrocarbons which are also common in traditional fuels. The presence of the Alcohols and Carbonyls introduce oxygen into the potential bio-fuel. We must consider the loss in potential BTU value as well as other potential impacts such as solubility and corrosivity. For example, when a compound has both an Alcohol and Carbonyl peak, it may indicate that there is a free carboxylic acid present such as acetic acid. Bio-Fuels with these types of acids, which are polar, corrosive, and expensive to remove in the refining process, are less desirable in the potential bio-fuel.

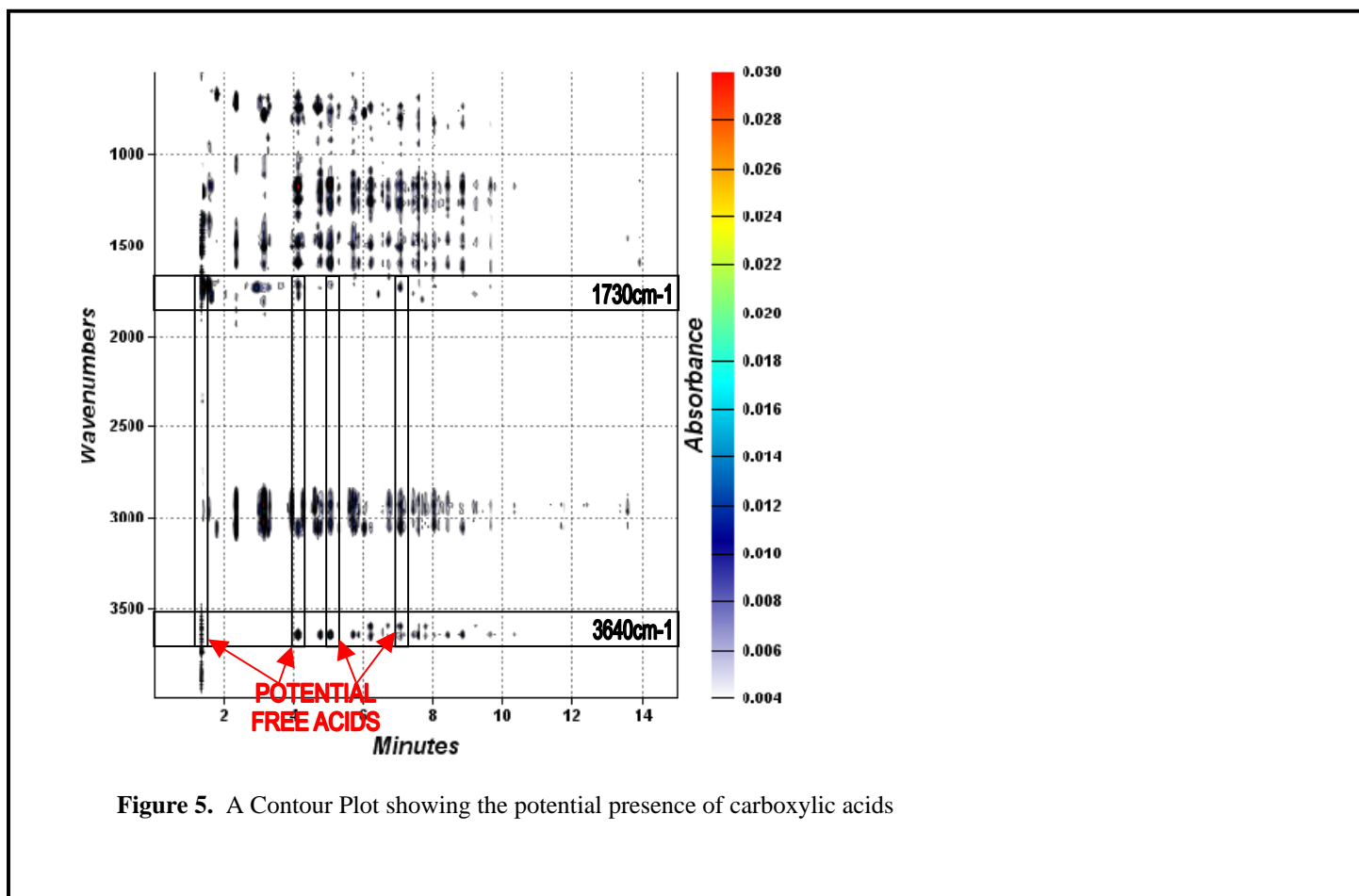


Figure 5. A Contour Plot showing the potential presence of carboxylic acids

So the basic summary of data analysis for the IRD, is that when an injection is made, a series of spectra are acquired. These spectra have 2 distinct regions, the Functional Group region and the Fingerprint Region. A TRC shows which spectra have non-baseline data in them. It is possible to minimize how many peaks are shown by the use of SWC filters. Lastly, it is possible to look at a contour plot of all of the data at once, to quickly determine which functional groups are or are not present anywhere in the sample.