

# Building a Better Search by Combining Raman and IR Spectroscopy

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## INTRODUCTION

For many laboratories, infrared and Raman spectroscopies can be used as complimentary techniques because each looks at different aspects of a given sample. While IR is sensitive to functional groups and to highly polar bonds (such as O-H stretches), Raman is more sensitive to backbone structures and symmetric bonds (such as C=C). Using both measurements on a sample gives the scientist twice as much information on the vibrational structure of the sample than could be attained using either technique alone.

FT-IR has been a key technique in many analytical and research labs for a number of years and library searching is a well established method of identifying an unknown compound from the measured spectrum. A wide variety of infrared databases exist for infrared library searching varying from very large general collections, such as the Nicolet/Aldrich Condensed Phase Library with over 16,200 compounds, to more specialized databases, such as the Automobile Paint Chip Library. In addition, many people create custom libraries for compounds that are proprietary or are of a very specialized nature.

By contrast, FT-Raman is a new technique for most laboratories. In addition to providing unique information about a sample, FT-Raman offers several benefits which are allowing it to gain rapid acceptance in the analytical community. These include:

- No sample preparation
- Non-destructive analysis  
(*the same sample can therefore be used in other analyses*)
- Non-intrusive analysis  
(*subtle aspects of the sample such as crystal structure can be studied*)
- Sample directly from glass containers
- Minimal water interference.
- No atmospheric CO<sub>2</sub> or H<sub>2</sub>O in spectra.

Because the FT-Raman technique is relatively new, there are very few Raman library collections available in digital form

(Nicolet introduced the first commercially available FT-Raman library in 1993). From a scientific view point, Raman spectra are ideal for library searching since they are generally comprised of relatively sharp, distinct bands with very little interference from broad features associated in IR with water, highly polar bonds or additives such as Nujol.

## LINKED SEARCH SOFTWARE

All of Nicolet's Raman instruments are designed to make collection of spectra and comparison of the data with FT-IR measurements as easy as possible. Nicolet, in partnership with Aldrich Chemical Corp., has also developed a comprehensive database of the most common and useful FT-Raman spectra. This library searches spectra in the same manner as an IR library, matching one measured spectrum against a chosen database. When both an IR and Raman spectrum are available for a particular unknown compound, the quality of the library search results and the confidence that can be placed in them dramatically improve.

Nicolet's innovative Linked Search software does just that, taking the measured spectra from an unknown sample in **both** the IR and Raman instruments. These two spectra together give a much more complete 'picture' of the sample than either measurement alone. Linked Search then searches both spectra against their respective databases and produces a hit table which corresponds to the best library matches when **all** of the information is considered. The reported results from the Linked Search algorithm show hit tables from individual Raman and infrared searches as well as the combined table. This provides a cross check

on the result and two separate analyses to support any published data.

As you might expect the results of a linked search can be quite dramatic since the addition of the Raman data often clearly differentiates between compounds which look similar when only the IR data is available.

Several search methods exist for maximizing the performance of an individual search by optimizing the comparison of data points in the unknown to that of a spectrum in the database. These methods include absolute value, squared value, first derivative, squared derivative and correlation. Selection of these methods and other optimizations of the individual IR or Raman searches can be made within OMNIC software and a more detailed discussion of each is available.<sup>1</sup> However, the correlation method yields the best results for most unknowns and is the method used in the examples given below.

## RESULTS

An example of how Linked Search works is given in figures 1a and 1b. Figure 1a shows spectra of liquid acetophenone, the top run by ATR in the infrared and the bottom run by standing the sample bottle in the sample compartment of the Raman. While both spectra give information on the structure of the compound, the range of the Raman spectrum – in a single

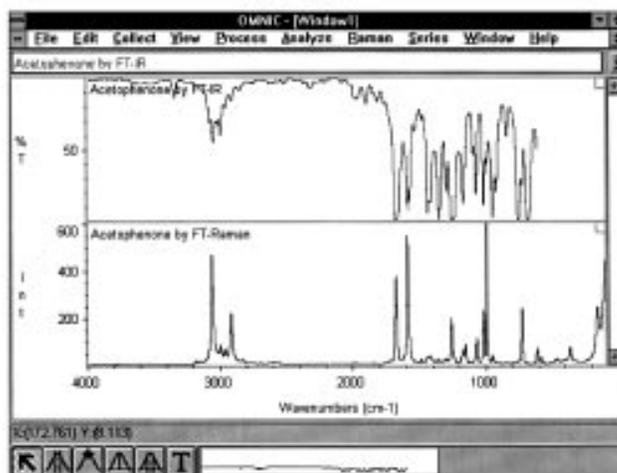


Figure 1a: Spectra of liquid Acetophenone using FT-IR with an ATR accessory (top) and FT-Raman (bottom).

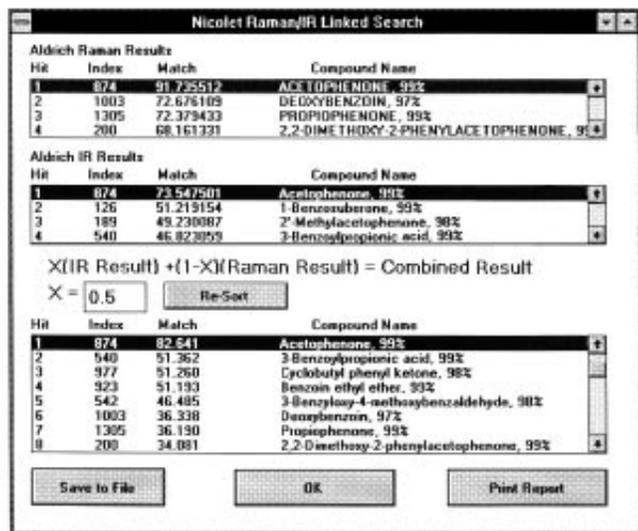


Figure 1b: Linked search of Acetophenone.

measurement – extends down to about 50 cm<sup>-1</sup> while at the other end of the range the IR extends as far as 4000 cm<sup>-1</sup>. The complimentary nature of the two techniques is illustrated by the fact that the strongest bands in the Raman spectrum tend to correspond to weaker bands in the infrared and visa versa.

Figure 1b shows the output table produced from the linked search run. Processing the search takes no more than a couple of seconds and is launched from the Analyze menu within standard OMNIC software. The first two boxes on the table contain results from the IR and Raman searches independently – these boxes scroll to show as many hit results as required. Combined results are displayed in the larger box. Results are ranked in

order of the match number – a correlation factor indicating the closeness of the unknown spectrum to each spectrum in the database. In analyzing the results of a library search the match number is used in two ways. First, a large match number indicates a close match to the library spectrum. Second, for a positive (unique) identification, the match number of the first hit should be noticeably larger than the bulk of the subsequent matches. The uniqueness of a library search is commonly analyzed using a relative match number which calculates how much separation exists between first and second hits relative to the difference between the second and third hits. In this way a high value indicates a selection which stands clear of subsequent suggestions. In the example from figure 1 the relative match number would be

$$\frac{(82.64 - 51.36)}{(51.36 - 51.26)} = 312.8$$

This is a significant improvement over either the FT-IR or the Raman search alone, which have relative match numbers of 11.2 and 56.1 respectively.

As every spectroscopist knows, there are times when perfect spectra are not available. This may be for a number of reasons – data may be needed in a short time period, accessories may be necessary which involve some signal loss (such as fiber optic probes or microscopes), the sample may not be pure or, for FT-IR measurements, sample preparation may affect the final appearance of the spectrum.

The power of the linked search algorithm for identifying poor quality spectra is illustrated in figures 2a and 2b. Using the same acetophenone sample as the first example, spectra were recorded to **deliberately** reduce the quality of the data. All measurements were made in one second, inactive regions of the IR spectrum were not blanked before searching and the Raman measurement was made at very low excitation power, using a remote fiber probe and through the wall of a brown glass chemical bottle.

Figure 2b demonstrates that the individual Raman and IR searches do not adequately identify this compound. In this particular case, because the spectra are so poor, the infrared search identifies the compound, but has a low match number (the relative match is only 1.14) and acetophenone is the second pick from the Raman library. However, the combined results show a great improvement. Not only is acetophenone the first pick, but the relative match has been increased to 2.34 indicating greater uniqueness.

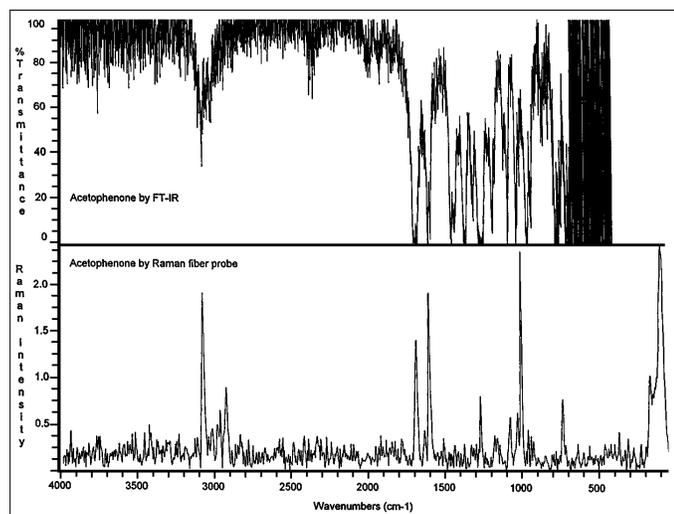


Figure 2a: Poor quality Acetophenone spectra.

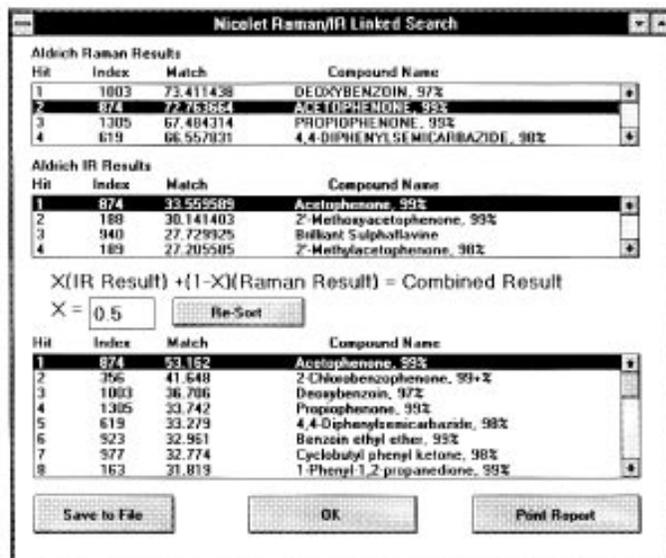


Figure 2b: Linked search of poor quality spectra.

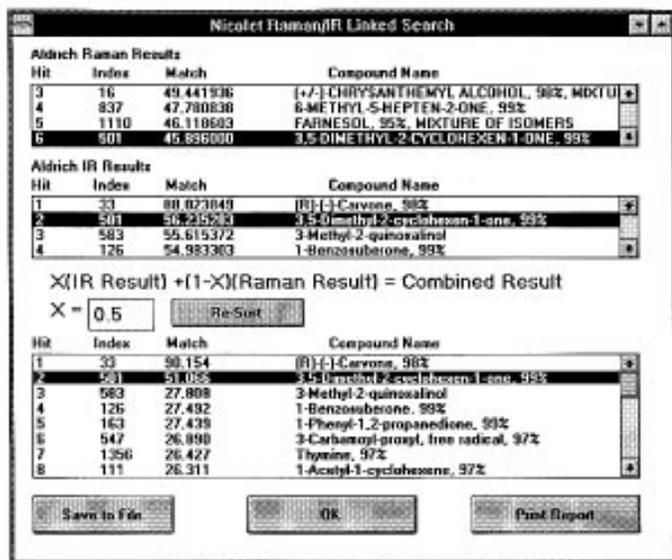


Figure 3a: Linked search of Carvone spectra showing origins of subsequent library hits.

## FEATURES

### Factor and Re-sort

The Linked Search algorithm allows different weights to be assigned to the Raman and IR search results when they are combined. This is helpful in situations where the user has greater faith in one of the measurements. For example, if the IR data has totally absorbing bands, a strongly sloping base line and the data is good to around  $650\text{ cm}^{-1}$  due to absorptions in an ATR crystal, while the Raman contains a wealth of clean bands throughout the full spectral range, the user might choose to weight the combination more in favor of the Raman spectrum. This can be done quickly and easily by entering a factor in the box. For example a factor of 0.4 would combine the searches with 40% IR result and 60% Raman. The re-sort button allows experimentation with different factors without the need to repeat the individual searches.

### Check List

The source of each value in the combined hit table can be checked by highlighting it. This shows the position of that compound in both the Raman and IR individual search lists. This feature is useful in interpreting data which is close to the top of the combined list since if the search rates the suggested compound low on either of the individual lists, it is probably a poor pick. Since the Raman and IR techniques look at very different aspects of the vibrational spectrum, it is unlikely that a wrong answer would be near the top of both individual

searches, and therefore unlikely that it would rise to the top of the combined search.

In the example in figures 1a and 1b the first combined result (the correct compound) is at the top of both the Raman and IR list. The second combined result however is hit 5 on the Raman and hit 14 on the IR, the third combined result is hit 14 on the Raman and hit 4 on the IR. This feature is illustrated in figure 3a: a linked search is selected for the Raman and IR spectra of carvone. The first selection of the combined search is the correct result. However, by clicking on the second pick (3,5-Dimethyl-2-cyclohexen-1-one) the highlight bars on the Raman and IR hit tables indicate that this compound was second on the IR search and hit 6 on the Raman search.

### Display library spectra

Double clicking on any compound in the combined list pulls both the Raman and IR library spectra of this compound for comparison with the unknowns. This is shown for Carvone in figure 3b, the two recorded spectra (top) are compared with the spectra of carvone selected from the library as most likely match (bottom).

### Save to File and Print Report

Results can be saved to a standard disk file and exported to a variety of spreadsheet

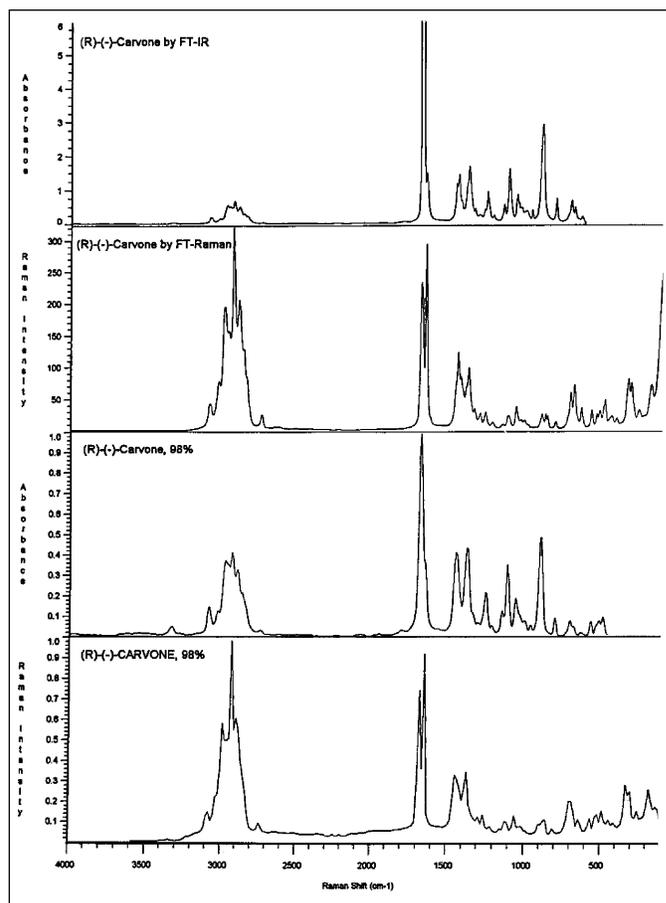


Figure 3b: "Unknown" spectra (top) and top linked search hits.

and word processing programs, like Word and Excel. The print report file generates a standard report format consisting of a single page plot of the unknown spectra and tabulated hit results for both the IR and Raman individual searches and the combined search hit table.

### Get Raman/IR

This utility allows the combined library to be used as a teaching aid in situations where both techniques are not available. In this case, a student can search the infrared spectrum of an unknown compound against the IR library and then display, for comparison purposes, the corresponding FT-Raman spectrum from the combined library.

## CONCLUSIONS

Both the Raman and infrared spectra of an unknown sample gives a much more complete picture of the molecules vibrations and both techniques can be used in independent searches to attempt to identify the compound. Nicolet's Linked Search routine aids in this identification

process by combining both the Raman and IR data sets, greatly increasing the quality of search results and thereby increasing the users confidence in making a positive identification.

Having two independent measurements on an unknown which can be made quickly and easily can be very valuable both where certainty is essential (*e.g.* pharmaceutical research) or where a back up measurement can provide additional evidence (*e.g.* forensic work). For these and many other occasions, the linked search package is ideal.

## REFERENCES

1. Nicolet Applications note AN9367, *Spectral Library Searching and FT-IR/FT-Raman Spectroscopies: Effects of Resolution and Search Algorithms*, Michael Fuller and Bob Rosenthal (1993).