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Tips for Successful Spectrum Searches—Part 3
—Differences Between Library Spectra—

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—Differences Between Library Spectra—

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When searching for spectra, they can be identified and evaluated more efficiently by using difference spectra functionality in combination with searches.

This article describes the difference spectra functionality available in the search window of LabSolutions IR software.

1. Introduction

Customers using Shimadzu FTIR systems contact Shimadzu relatively frequently with questions about searching libraries for contaminant spectra. In *FTIR Talk Letter* vol. 22, *Using Difference Spectra*, we provided advice on how to analyze spectra data using difference spectra. Subtracting one spectrum from another can highlight the differences between the spectra and make it easier to identify components. Consequently, determining difference spectra is one of the most important tools in spectral analysis. Functionality for determining difference spectra is generally included as a data processing tool but, when searching for spectra, LabSolutions IR software now also includes functionality for determining difference spectra with respect to library spectra. Consequently, components can be identified more efficiently by using the difference spectra functionality in combination with spectrum searches.

2. Calculating Difference Spectra in the Spectral Search Window

The following describes calculating a difference spectrum in the spectral search window using a spectrum obtained from measuring a contaminant on polyethylene plastic by the ATR method. Fig. 1 shows a screen shot of the [Search] window immediately after performing a spectrum search.

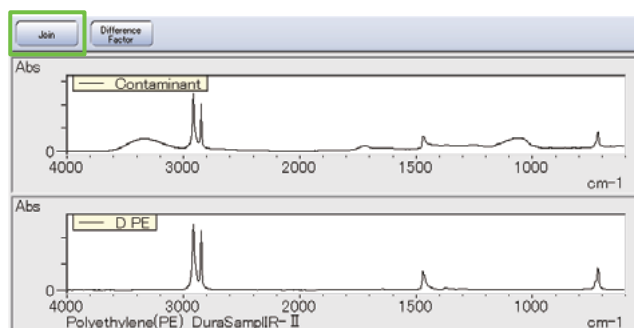


Fig. 1 Screen Shot Immediately After Spectrum Search

Clicking the [Join] button displays the measured spectrum overlaid with the library spectrum, as shown in Fig. 2, so that the two spectra can be visually compared.

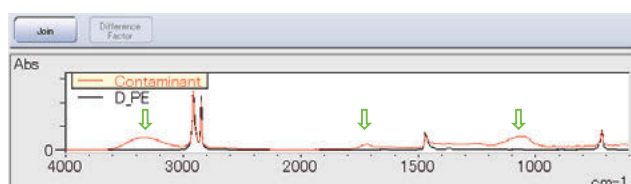


Fig. 2 Overlay of Contaminant and Library Spectra

The overlay shows that part of the contaminant spectrum is almost a perfect match with the spectrum for polyethylene. Since the contaminant is attached to polyethylene, presumably the contaminant spectrum has overlapped with the polyethylene substrate material. In other words, the peaks marked with green arrows in Fig. 2 are probably from the contaminant. Therefore, the library search results are ranked for these peaks in particular. However, in many cases, appropriate spectra cannot be found listed near the top of such search results. Therefore, to search for spectra focusing on the indicated contaminant peaks, the difference between the contaminant and polyethylene spectra is determined. Given the state shown in Fig. 2, click the [Join] button again to return to the window shown in Fig. 3, which is the same as immediately after the spectrum search.

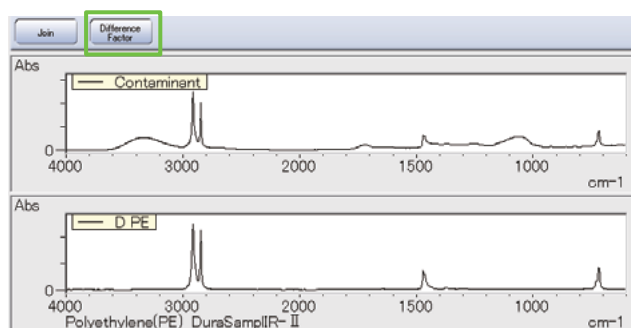


Fig. 3 Screen Shot Immediately After Spectrum Search

Next, click the [Difference Factor] button, located next to [Join].

Fig. 4 shows the window immediately after clicking [Difference Factor].

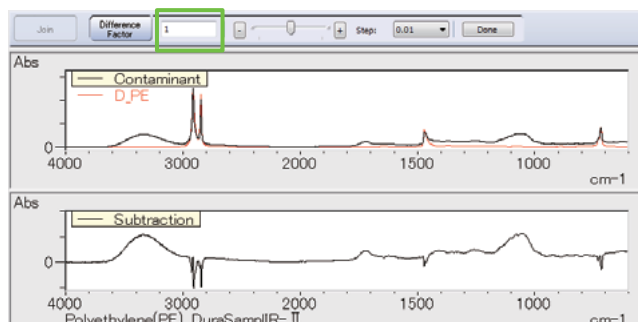


Fig. 4 Screen Shot Immediately After Clicking [Difference Factor]

Immediately after clicking [Difference Factor], "1" is displayed next to the [Difference Factor] button. This [Difference Factor] setting of 1 specifies simply displaying the difference between the spectra, subtracted in the form $A - B$, where the library spectrum (B) is subtracted from the measured spectrum (A).

3. Difference Factor

Normally, spectra A and B are subtracted by subtracting B from A in their entirety. However, with actual measurement results, spectra A and B typically have different overall intensity levels and the peak intensity levels for component peaks included in both A and B do not match. In such cases, simply subtracting spectrum B from spectrum A will leave some peaks remaining that ideally should be eliminated or will cause inverted peaks due to subtracting too much. Therefore, calculation results are adjusted by multiplying one spectrum by a coefficient that results in eliminating certain target peaks, in the form $A - kB$, where k is the coefficient. This coefficient k is displayed in the window as the difference coefficient. The process of adjusting this coefficient is also required for determining difference spectra using the [Data processing] - [Data calculation] (spectral calculation) function.

4. Adjusting the Difference Factor

The following describes varying the difference coefficient. Try moving the [Difference Factor] slider in Fig. 5 left or right or clicking the [-] or [+] buttons. If the buttons change the value too much or too little, click the [Step] pull-down menu to choose from four step sizes for changing the value, from 0.001 to 1.

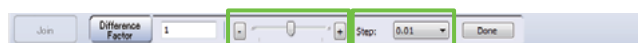


Fig. 5 Adjusting the Difference Factor

Given the difference spectrum shown in Fig. 6, the difference factor setting of 1 is too large, resulting in some prominent peaks facing downward from the baseline at zero absorbance.

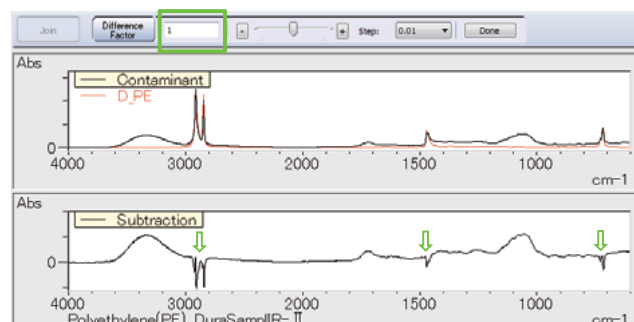


Fig. 6 Calculation Results Using a Difference Factor That Is Too Large

In contrast, given the difference spectrum in Fig. 7, the difference coefficient setting of 0.57 is too small, resulting in less benefit from the calculation and a difference spectrum that resembles the original contaminant spectrum.

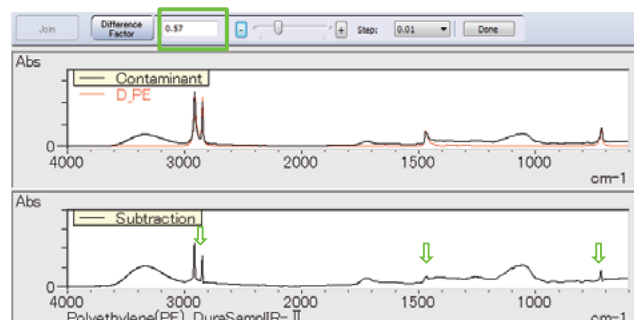


Fig. 7 Calculation Results Using a Difference Factor That Is Too Small

Ideally, the peaks from polyethylene, marked with green arrows, should be canceled out. In reality, residual upward or downward facing peaks typically remain no matter what coefficient is selected. This is caused by differences in the measurement conditions specified for measured and library spectra and by dissimilarities between the shapes of respective spectra. Therefore, rather than obsess about picking the optimal coefficient, in this case the adjustment process was finished by selecting a difference factor of 0.82, which results in as little residual spectra as possible, as shown in Fig. 8. To confirm the difference coefficient setting, click [Done].

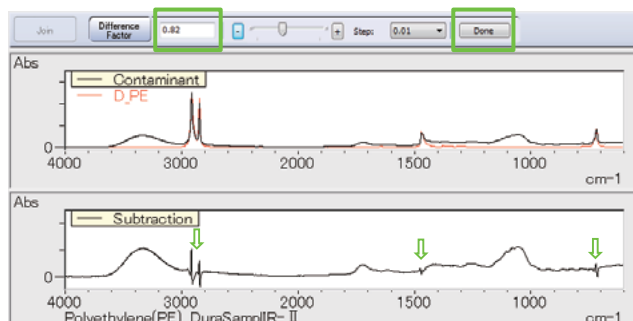


Fig. 8 Calculation Results with the Difference Factor Adjusted to Minimize Residual Spectra

After clicking [Done] in Fig. 8, the same window as displayed immediately after the spectrum search is displayed again, as shown in Fig. 9. In addition, "Subtraction1" is displayed in the tree view on the left side of the window, as shown in Fig. 10, for the difference spectrum that was created and saved. To quit searching for the contaminant spectrum, click [Fix search results] - [Close].

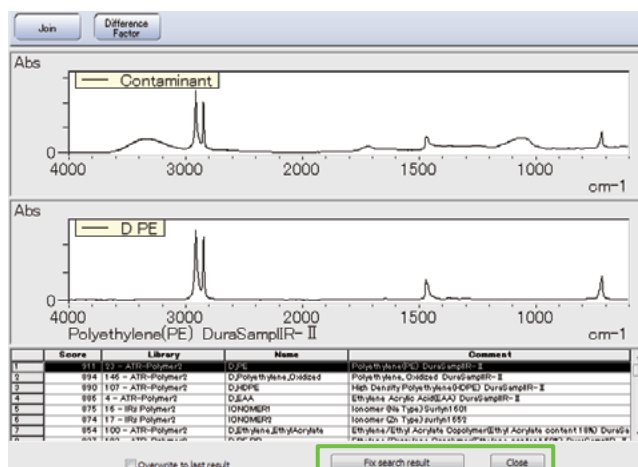


Fig. 9 Screen Shot Immediately After Clicking [Done] When Finished Adjusting the Difference Factor

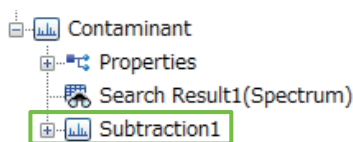


Fig. 10 Tree View

Double-click "Subtraction1" in the tree view to activate the corresponding difference spectrum. When a spectra search is performed for this difference spectrum, cellulose is listed among the top results, as shown in Fig. 11. Consequently, the contaminant is presumably a fiber such as cellulose.

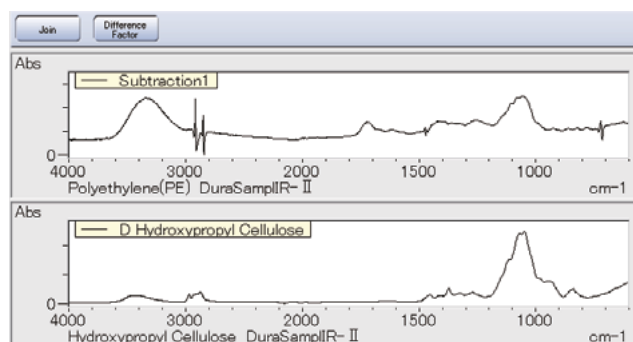


Fig. 11 Search Results for Difference Spectrum

However, when compared to the library spectrum, the difference spectrum includes broad peaks near 3400 cm^{-1} and 1640 cm^{-1} . Therefore, the contaminant probably contains an even greater amount of a substance with a hydroxyl group ($-\text{OH}$).

5. Reducing Residual Spectra

So far, I have described the procedure for calculating difference spectra in the spectral search window. Though this function is very useful, in reality large residual spectra often remain after calculation, due to differences in the measured and library spectra, as mentioned above. From that perspective, it should be possible to reduce residual spectra by subtracting a spectrum B that was actually measured. In that case, the difference spectrum is determined using the [Data processing] - [Data calculation] (spectral calculation) calculation process.

A new contaminant spectrum is displayed in the upper level of Fig. 12. The spectrum in the lower level was measured from contaminant-free polyethylene resin. When identifying contaminants or analyzing defects, it is important to also measure a presumably normal area near where the contaminant or defect was discovered, as a reference for comparison purposes.

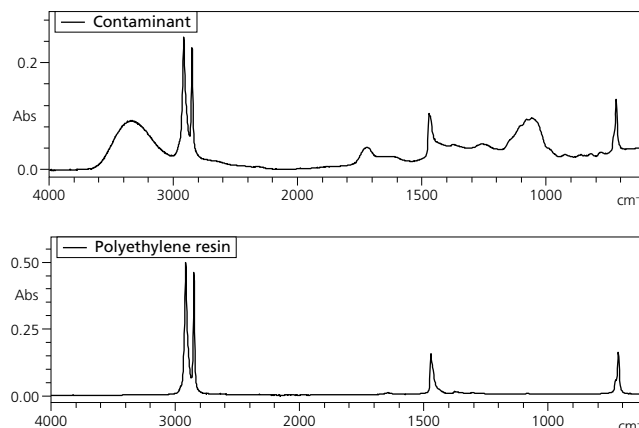


Fig. 12 Contaminant and Polyethylene Resin Spectra

The results in Fig. 13 were obtained by subtracting the polyethylene resin spectrum from the contaminant spectrum using the [Data processing] - [Data calculation] (spectral calculation) calculation process. The difference spectrum obtained in the spectral search window, as described above, is also shown for comparison. The "Subtraction1" spectrum, calculated using the library spectrum, includes relatively large upward and downward peaks derived from residual polyethylene peaks, but the difference spectrum calculated by subtracting actually measured spectra (polyethylene resin from the contaminant) resulted in lower residual spectrum levels.

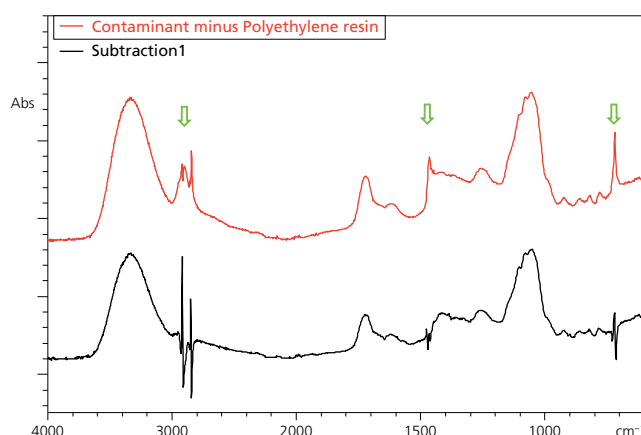


Fig. 13 Comparison of Difference Spectra

6. Conclusion

Calculating difference spectra in the spectral search window is a very convenient function. It offers the ability to compare the spectrum being searched for with library spectra listed in search results to clearly show the areas where they do not match. When analyzing the spectra from mixtures, this function also serves to successively identify the components, even if spectra are not available for individual components included in the mixture. On the other hand, the function can produce large residual spectra, due to differences in measurement conditions and other factors, which requires particular care. Therefore, when identifying contaminants or analyzing defects, it is generally important to also measure a presumably normal area, as a reference for comparison purposes. For more information, also refer to *FTIR Talk Letter* vol. 22, *Using Difference Spectra*, which presents the concept and examples of using difference spectra.

Due to publication circumstances,
the Q&A section has been omitted in this issue.



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