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Rapid Secondary Analysis Offers Great Potential for Improving Product Quality

Abstract

The rapid secondary analysis of wood products, such us measuring the lignin content in pulp, the resin level in a wood composite or the amount of preservative in treated poles, is a much more rapid process than if each sample were analyzed by the traditional (primary) method. Consequently, a more uniform product is manufactured.

The process (or processes, because there are several somewhat similar ones) is hard for the lay person to understand, so an analogy may be drawn: If you saw evidence of several gun shots in one area, you would be justified in assuming that the target was somewhere in that area Scientists using some type of secondary analysis can chemically test a number of samples and find the range of for example, the adhesive level of a composite board, and calibrate the machine doing the testing accordingly They can then test samples on a production line to ensure that they fall within the set range. That is, they can employ rapid secondary analysis using the electromagnetic spectrum to find within seconds whether each sample shows the same pattern that has been established. Any sample showing a different pattern is suspect and can be analyzed by the slower, more traditional methods to find out why it is far from the norm. Thus a more uniform product is manufactured, and processing costs are sometimes lowered.

The process is often called secondary analysis because samples are first analyzed by the primary (traditional chemical; method. Various methods such us near infrared reflectance analysis (NIRA), Fourier transform infrared spectroscopy (FTIR), and near infrared Raman spectroscopy (NIR-Raman)

are being used. Non-scientists may not readily understand these terms, but they are simply ways of using the electromagnetic spectrum to swiftly check samples to ensure that they fall within the set limits calibrated for that specific sample.

A little "black box" and a great deal of "know-how" is helping make rapid secondary analysis of many wood products feasible. It has rnade the use of near-infrared reflectance analysis, referred to as NIRA, a complement to the more traditional and definitive, but slower, analysis. The black box takes readings from the near-infrared portion of the electromagnetic spectrum and helps researchers rapidly analyze samples of pulp or wood in other forms. Some sophisticated mathematics are necessary to program the black box so that numbers emerging from it are significant. If numbers are off, it's an indication that something is wrong with either the sample or the method.

The operative word in these analyses is "rapid." In fact, says Dr. Tor Schultz, of the Mississippi Forest Products Laboratory (MFPL), the system can be used for at-line or on-line analysis. At-line analysis represents taking a sample from the processing line to be checked. On-line analysis is done continuously while the product is being made.

Rapid secondary analyses are already widely used in agriculture. For example, every overseas grain shipment is now analyzed -- in seconds -- by NIRA for protein and moisture content. Rapid secondary methods are sometimes used in wood industries, but not as often. One reason, Dr. Schultz explains, is that agricultural products usually have a low level of moisture. In forest products, however, the moisture content can vary widely in, for example, pulp samples, and this causes errors in measuring other components.

This makes the analysis more complicated.

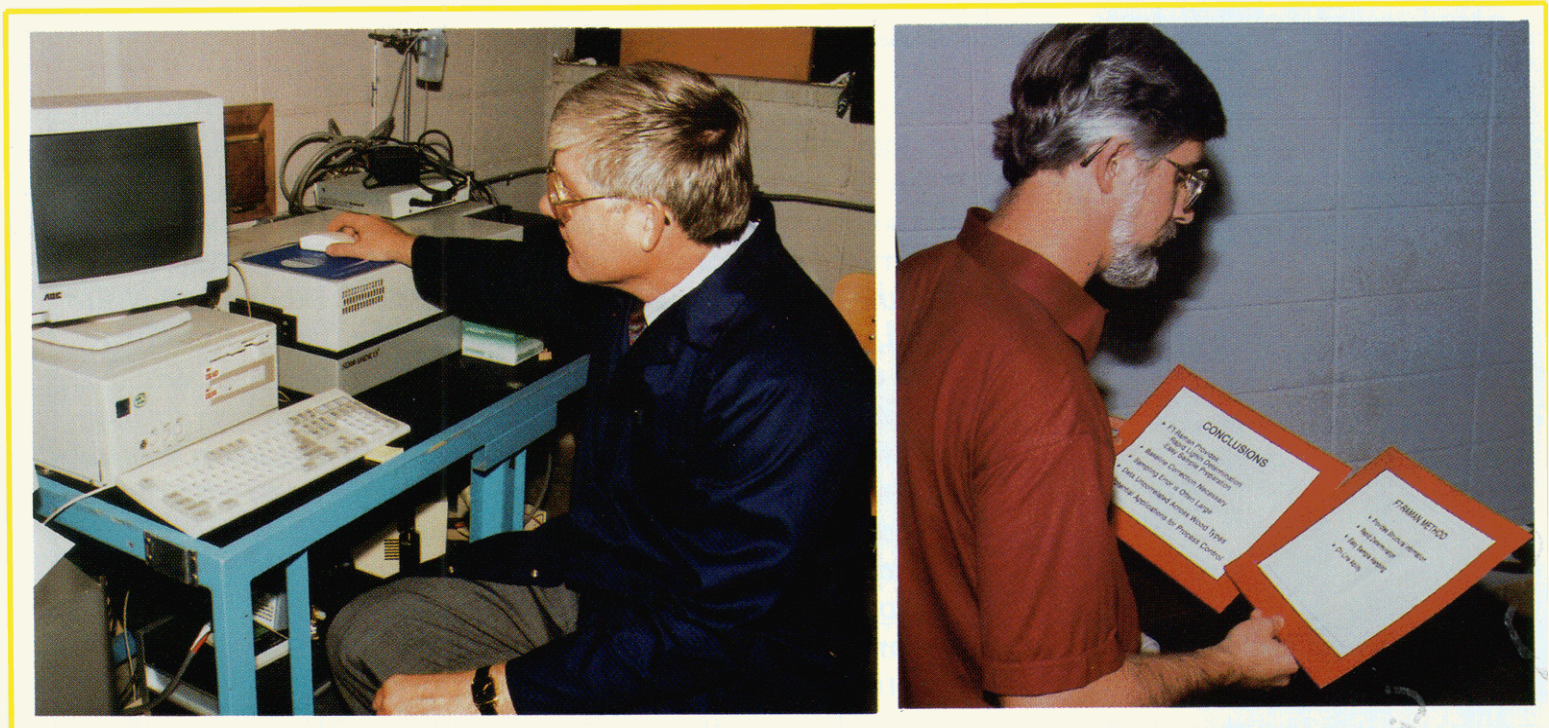
Dr. Philip Oldham, a chemistry professor at Mississippi State University, works closely with Dr. Schultz. He says, "NIRA does not give as much chemical information as infrared on the molecular level but can still provide acceptable quantitative results in most cases.

"The computer will give only the information asked for: it does not inform you about other components in the sample. Different components of the sample interact with different light frequencies in the electromagnetic spectrum. By setting the parameters by which the sample is to be tested wide enough, you can often get reproducible analyses of the material being manufactured."

Some possibilities

Dr. Schultz sees several possible areas for indirect analysis:

(1) Analysis of pulp, both before and after bleaching, for lignin content (researchers call it the kappa number) and possibly other factors such as physical



'Professor Tor Schultz of the Forest Products Laboratory (FPL) prepares to examine spectral data (left photo). Associate 'Professor Terrance E. Conners, FPL, prepares a presentation on his work (right photo).

strength properties. (Lignin is the natural "glue" that holds wood products together.)

(2) Determination of level of additives, such as resin and sizing, during the manufacture of various wood composites like oriented strand board (OSB), and flakeboard

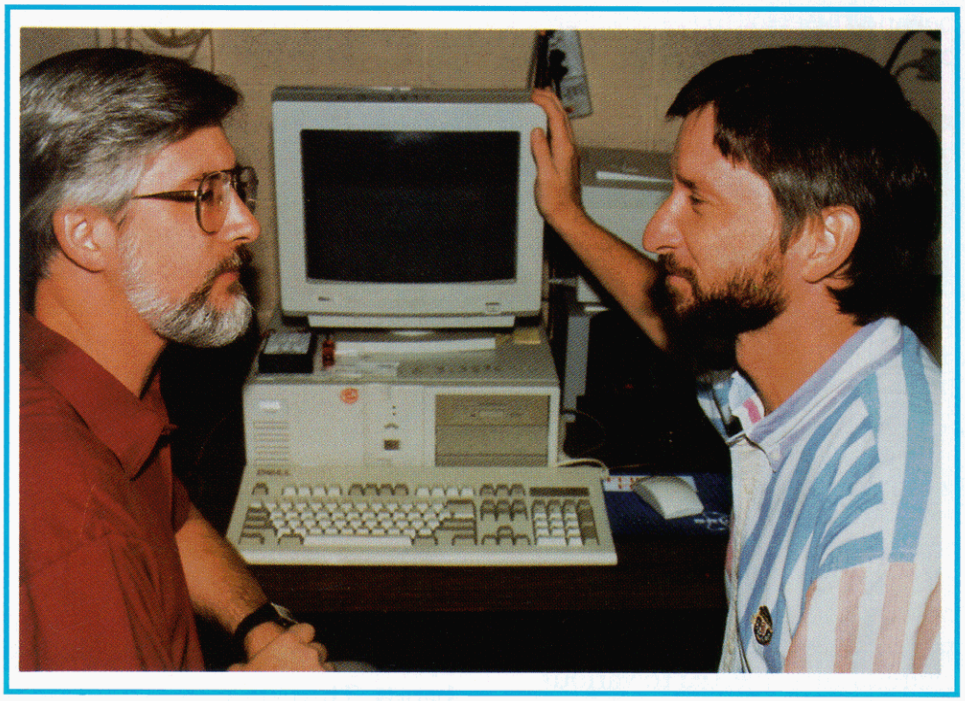
(3) Continuous quality control of wood adhesive resins during manufacture for such things as molecular weight, viscosity, moisture content and free formaldehyde.

(4) Quality control of wood preservatives for such things as contaminants, active ingredients and moisture content.

(5) Monitoring chips before pulping for such factors as storage life and extractive content,

(6) Analysis of wood treated with wood preservatives or fire retardants for the retention level.

Indirect or rapid secondary analysis has the advantage of being much faster than traditional methods but it does have some limitations. Dr. Schultz reports, "The technician needs to recalibrate the instrument each time different samples are analyzed, and this takes time. Thus, indirect analysis is useful only if a large number of very similar samples are run every week. Also, it is hard to transfer the procedure to another laboratory." Some forest products companies are already using rapid secondary analysis in a production setting.



Dr. Conners and Dr. Phillip Oldham, associate professor of Chemistry, discuss pulp analysis (top photo). Drs. Oldham and Schultz (bottom) prepare pulp samples for rapid analysis.

The operative word in these analyses is "rapid."

A manufacturer's practice

One manufacturer of a wood composite product is using NIR to measure at-line the level of an additive. NIR is well-suited in this case since the manufactured product is hot-pressed and thus has a uniform and very low moisture content, and the additive can easily be measured to determine the level used.

In another example, a commercial NIR system has been developed for the pulp and paper industry, but no results are available. In cases where the pulp moisture can vary it may be better to use a moisture-insensitive instrument such as Raman. Prior to purchasing any system a manufacturing facility will need to carefully consider its particular product, needs and limitations to pick which instrument(s) may be best, and then to run some studies using that same instrument with some actual samples to ensure that the system will work.

Schultz and Oldham say the initial procedure is to obtain a representative set of samples from a diverse group. The samples should be analyzed using a traditional chemical method, then divided into two subsets. The first subset is used to calibrate the secondary analysis instrument. The second subset verifies or confirms results from the first,

"This is very important because of the ease of making a slight error in calibration," says Oldham. "A calibration error often dominates the overall secondary analysis error and thus accuracy is ultimately dependent on the standard analysis technique. Careful analysis of the standards by the primary method is essential."

Consider other factors

He goes on to say, "No manipulation of the independent variables such as wavelength, sensitivity or sample preparation can improve the secondary analysis

beyond the error in the original calibration.

"Another point is that the samples analyzed by the secondary technique must belong to the same 'universe' as the calibration set -- that is, must be similar in form and composition. It often occurs that the operator does not identify or recognize samples whose composition or processing history lies outside the training set 'universe'."

Samples are critical!

The reason calibration samples are critical for indirect analysis is that spectral differences in secondary analysis are often very minor, These minor spectral changes are subjected to various data-analysis methods to detect subtle differences which, in turn, predict the component levels. If real samples are different from the calibration samples in any appreciable way, such as in moisture content, the relatively small differences reflected in the spectrum are overwhelmed by large and extraneous changes. In other words, the analytical difference is "covered" by the difference between calibration samples and "real" samples. "Never trust," say Schultz and Oldham, "always verify."

Surprisingly, no special interpretation is necessary with indirect analysis. When the calibration has been set, the computer interprets the data using specialized software such as multiple linear regression (MLR) or principal component analysis (PCA). In stepwise MLR, the regression procedure selects peaks difficult to justify based on conventional interpretations but which give the best statistical fit.

Researchers point out that the total error of rapid secondary analysis or NIRA is the total error of the primary error plus the additional error of the secondary instrument and the laboratory procedures. "Thus," they say, "the total error of indirect analysis will always be greater than that of the primary or traditional procedure used to calibrate the secondary instrument."

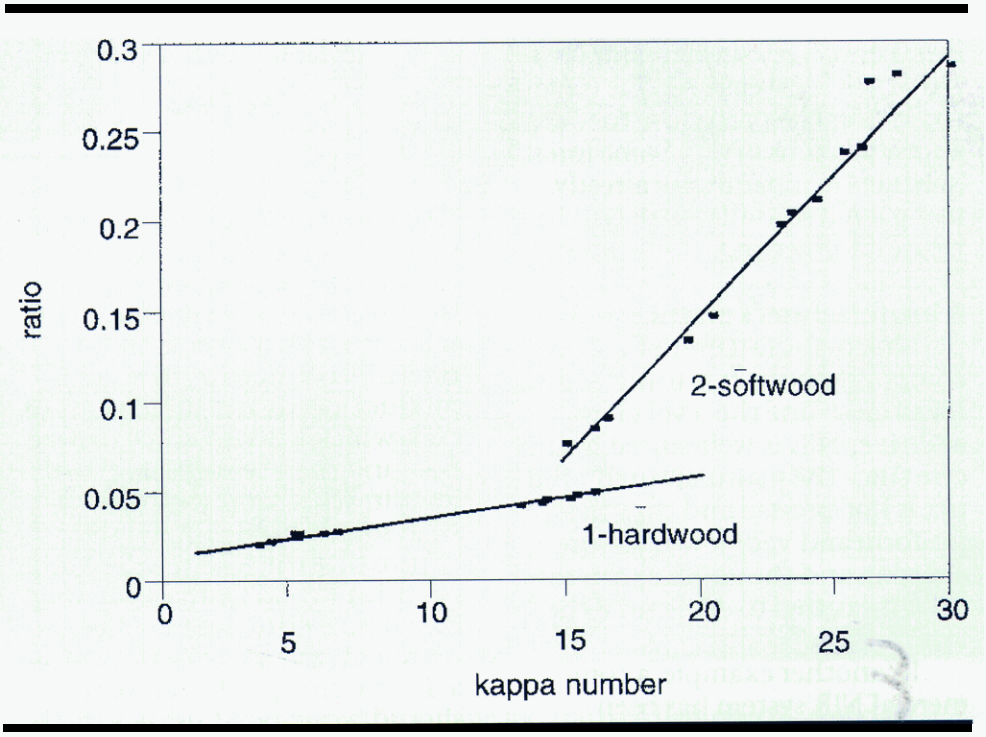
Despite limitations, secondary analysis has potential for certain uses.

One advantage of NIRA over FTIR is that the near-infrared spectrum has combination and overtone bands of much lower intensity than the fundamental infrared bands. Thus, no sample dilution is necessary (one of the reasons samples can be analyzed on-line).

Another problem is that the near-infrared, like the infrared, spectrum of natural products is essentially a composite of the individual components. So, the lower level for which a constituent part of the sample can be accurately analyzed is limited for natural and other complex products, unless the constituent being analyzed has a unique spectral band -- one easily recognizable.

NIRA is the most-oftenused method of secondary analysis. But other methods are available, such as the FTIR mentioned, ultraviolet reflectance (UV) spectroscopy, multidimensional fluorescence (MDF). and Raman spectroscopy. These last three are relatively insensitive to moisture content, and thus helpful in certain applications.

Dr. Terry Conners of the MFPL has been using the NIR-Raman method for determining lignin content of pulp samples. He finds it very advantageous for its rapidity, but prepares samples and calibrates the instrument very carefully. That, more than anything, makes it possible for secondary analysis to work.



Plot of Kappa number vs. average area for softwood and hardwood samples using NIR-Raman spectroscopy.