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Dr. Raman's Legacy Shines With Renewed Interest

Raman spectroscopy may be worth another look because of dedicated instrumentation and a host of exciting new applications.

By Howard J. Goldner, Associate Editor, R&D Magazine

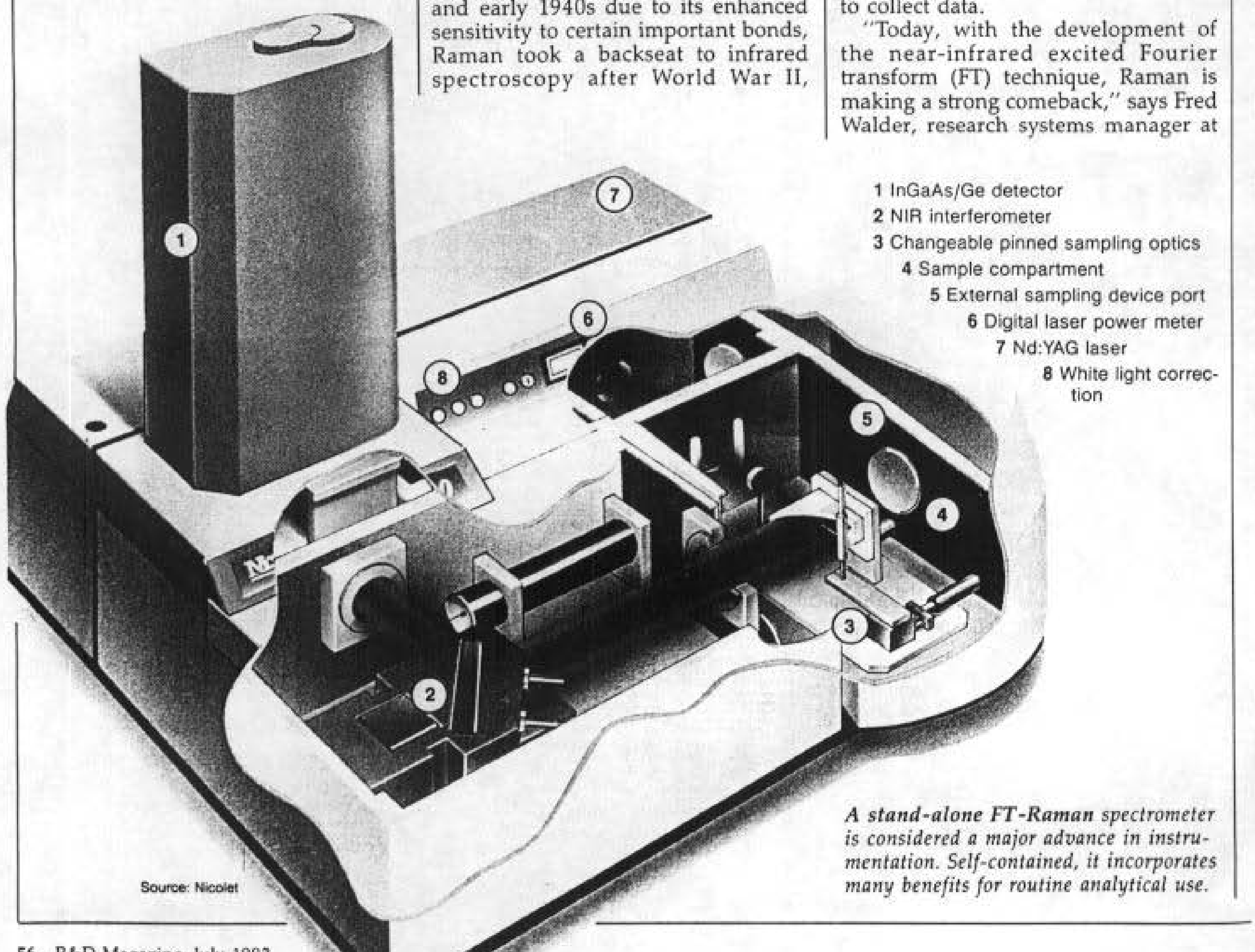
R&D

Ever see spectra of chocolate chip cookies, plastic foam cups, or felt-tip pens generated within seconds of placing the items, without special preparation, into a sample chamber? It's now a reality, not a pipe dream, with Raman spectroscopy.

The favorite spectroscopic technique of chemists in the late 1930s and early 1940s due to its enhanced sensitivity to certain important bonds, Raman took a backseat to infrared spectroscopy after World War II, when IR became ubiquitous in analytical laboratories around the world.

IR spectroscopy's popularity was prompted by the development of sensitive infrared detectors and advances in electronics. IR then became more convenient than Raman, which still required a skilled operator, darkroom facilities, and hours—or even days—to collect data.

"Today, with the development of the near-infrared excited Fourier transform (FT) technique, Raman is making a strong comeback," says Fred Walder, research systems manager at



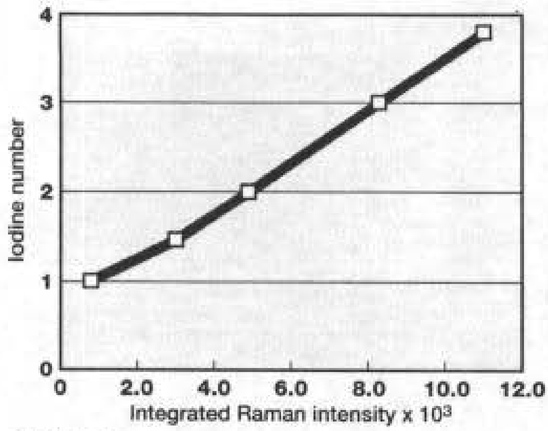
A ***stand-alone FT-Raman*** *spectrometer is considered a major advance in instrumentation. Self-contained, it incorporates many benefits for routine analytical use.*

Nicolet Instruments, Madison, WI.

"Because it is now applicable to a variety of samples, Raman is no longer limited to the research domain, but is advancing to the routine analytical lab, and may well be on its way to the process area," Walder adds.

Sensitive to nonpolar bonds, Raman spectroscopy detects changes in polarization as a molecule vibrates. It is especially useful for work involving unsaturated hydrocarbons, aromatics, pharmaceutical products, polymer backbone structures, and biological materials.

Iodine Number Correlates To Raman Bands



Source: Nicolet

Low iodine values, indicating the degree of unsaturation in catalytically hydrogenated oils for foods and cosmetics, can be measured by Raman.

FT-Raman was first commercialized by manufacturers of Fourier transform infrared (FTIR) spectrometers as an accessory or add-on device for FTIR systems, available primarily with top-of-the-line research instruments.

Recently, stand-alone FT-Raman spectrometers incorporating the latest technology have become commercially available—with more affordable price tags. These improvements could significantly extend the use of the Raman technique.

In addition to near-infrared laser energy sources, the new stand-alone systems contain holographic filters to reject the scattered Rayleigh radiation, and improved detectors to increase signal-to-noise ratios.

Another important advance is freedom from fluorescence interference. Many samples of industrial and biochemical interest contain small amounts of materials that are highly fluorescent when excited with a visible source. This causes a tremendous background to be superimposed on the Raman spectrum, often obscuring useful vibrational information.

However, when the appropriate laser frequency is used, background fluorescence is virtually eliminated. FT-Raman uses a near-infrared excitation source operating at 1064 nm.

Perhaps the best feature of FT-Raman, however, is that the entire spectrum is sampled with each scan, which can take less than one second to perform. Unlike monochromator systems, the entrance aperture of the interferometer system is large, making the sampling geometry less sensitive to absolute positioning of the sample.

One benefit of all Raman techniques is that, because of the spectral region involved, Raman offers the convenience of using glass containers. This simplifies sample preparation and speeds the collection of data. With Raman, NMR tubes, capillary tubes, test tubes, and GC vials all are ideal sample holders.

Some specific applications of Raman are worth noting. It is an excellent technique for studying the composition of blended gasolines, because it can provide information about the relative ratio of methyl groups to methylene groups in the gasoline mixture, and hence the degree of alkane branching. Raman spectroscopy is also highly sensitive to the unsaturated hydrocarbons in the fuel.

Feasibility also has been demonstrated in the analysis of edible oils and fats. Because certain properties of these materials are currently a hotly debated health issue, rapid and accurate analysis is essential. Two important parameters used to characterize these materials are the ratio of unsaturation to saturation in the acid chains and the ratio of trans/cis isomers in unsaturated materials.

Of further significance is the enhanced sensitivity of Raman spectros-

Sir Raman's Technique Enjoys a Renaissance

Using the bright Calcutta sun as his energy source and bits of colored glass for filtering, C.V. Raman in 1928 demonstrated the phenomenon of inelastic light scattering.

Raman originally called the effect weak fluorescence. However, it was later named after him, with the shifting of frequency referred to as the Raman effect and the frequency-

shifted light as Raman radiation. He was knighted in 1929 for these achievements.

Soon thereafter, research groups worldwide began generating Raman spectra. Most laboratories had the necessary equipment to make Raman measurements: a vapor discharge lamp for excitation, a conventional spectrograph for dispersion of the light, and photographic plates for detection.

By 1939, Raman spectroscopy had become the principle method of nondestructive chemical analysis, but its popularity was surpassed after World War II, when technological advances made IR more convenient.

The development of commercial lasers in the 1960s spurred renewed interest in the Raman technique, but growth was slow due to the instrumentation's complexity.

However, in 1986 near infrared excitation and FTIR were successfully combined to produce a dramatic breakthrough in Raman spectroscopy. Sir Raman would have been proud.

Raman spectroscopy could become an essential tool to help biochemists study blood at the cellular level.

Conventional Dispersive Raman Also Is Advancing

In a direct challenge to FT-Raman, conventional dispersive Raman is being dramatically updated to provide greater sensitivity and faster output.

In separate programs, Chromex Inc., Albuquerque, NM, and Instruments SA, J-Y/Spex Div., Edison, NJ, have developed Raman instrumentation that could offer significant competition to FT-Raman.

By using laser diodes as the monochromatic light source in the red region, these systems can produce nearly fluorescence-free spectra.

To substantially increase sensitivity, charge-coupled devices (CCD) are used as detectors. These CCDs, when cooled sufficiently, can have quantum efficiencies of up to 90% and are virtually noiseless.

So, even though Raman has a relatively weak signal, it's now being detected on top of a nearly zero background.

These improvements, coupled with the latest in holographic notch filters to remove the stray light, have effectively overcome many inherent problems with ordinary dispersive Raman spectroscopy.

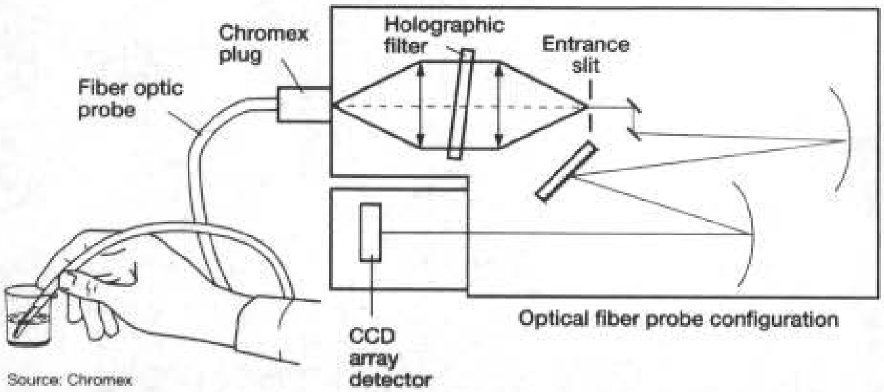
At the same time, these advances have contributed to reducing the complexity, size, and cost of the resulting systems.

In addition, these systems can be fitted with fiber-optic probes to permit in situ analysis of many processes.

Fiber-optic probes can be placed in production pipes, blood arteries, and other normally hostile environments to obtain Raman spectra on materials that were previously difficult to analyze on-line.

"The shoot-out between FT-Raman and CCD dispersive Raman has just begun," says Eugene Watson, a Chromex founder. He might be right on target.

Raman Moves Into the Process Stream



Traditional dispersive Raman *spectroscopy is being significantly improved. Laser diodes reduce fluorescence, holographic filters eliminate stray light, and CCD array detectors greatly increase sensitivity. Fiber optic probes capture Raman spectra on-line.*

copy to the C=C structure found in unsaturated fatty acids. C=C stretching yields a strong band in the Raman spectrum, located around 1660 cm^{-1}.

This advantage is particularly useful for unsaturation analysis because it is not normally cluttered by the presence of neighboring bands. Raman is the chosen technique for these unsaturation measurements because this band is inactive in IR spectroscopy.

"From a production standpoint, the ability to rapidly and easily monitor the hydrogenation of seed oils could prevent a major catastrophe in the form of an undesirable final product," says Michael Garry, Nicolet's industrial product manager.

"This benefit has application not only in the food industry, but also in the manufacture of surfactants, which provides base materials for cosmetics and personal care products, as well as detergents and home products," Garry says. "An undesirable starting material could lead to physical or odor instability of the final product after it's on the consumer's shelf."

Another Raman application is polymer processing, where manufacturers typically start out with various unsaturated monomers and react them to form the polymer chains. Monitoring the amount of unsaturation can provide essential information on the extent of the reaction's progress. These carbon-carbon linkages are easily identified by Raman spectra.

The pharmaceutical industry could benefit from Raman's ability to differentiate isomers. This feature should be helpful in quality assurance applications to verify that chemical contents are correct, especially where one isomeric form may be toxic to the system.

Finally, Raman spectroscopy could become a valuable analytical technique in biotechnology. It could be an essential tool to assist biochemists in elucidating the structure and reactivity of amino acids, studying antibody/antigen complexes, or investigating blood at the cellular level.

With such renewed interest and exciting applications, a new dawning for Raman spectroscopy appears to be on the horizon. **R&D**

Raman Instrumentation

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