4.8.5. Surface-Enhanced Raman Spectroscopy (SERS)

Surface-enhanced Raman spectroscopy (SERS) is another technique for obtaining strong Raman signals from surfaces and interfaces, including species adsorbed onto surfaces. Fleischmann and coworkers developed SERS in 1974. The SERS technique requires adsorption of the species to be studied onto a "rough" metal or metal colloid surface, where the roughness is at the atomic level. Inorganic and organic species adsorbed onto such surfaces show enhancement of Raman signals by up to 10^6 over normal Raman signals. The reasons for the enhancement are not yet well understood. Metals used as surfaces include gold, silver, and copper. Metal electrodes, metal films, and metal colloids have been used. The adsorbed or deposited analyte molecule must be less than 50 Å from the surface for the enhancement to be observed. Samples have been deposited electrolytically onto electrode surfaces, or mixed with colloidal metal suspensions. Samples separated on thin layer chromatography (TLC) plates have been sprayed with metal colloid solution.

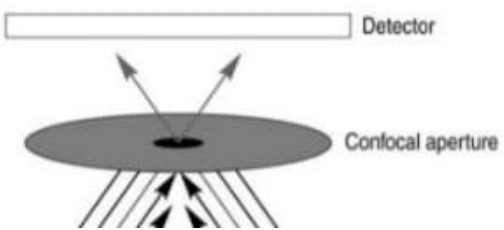
The enhancement leads to the ability to detect extremely small amounts of material, making SERS an effective tool for a variety of problems, from corrosion studies to detection of chemical warfare agents. Detection limits for SERS are in the nanogram range.

4.8.6. Raman Microscopy

Raman spectroscopy coupled to a microscope permits the analysis of very small samples nondestructively. The use of Raman microscopy allows the characterization of specific

domains or inclusions in heterogeneous samples with very high spatial resolution. With dispersive Raman microscopy, the spatial resolution is often better than 1 μm. FT-Raman microscopy is limited to spot sizes of about 2–10 μm, but with no interference from fluorescence. The use of a confocal microscope (Fig. 4.71) allows only the light at the sample focus to pass into the detector; all other light is blocked. This permits nondestructive depth profiling of samples without the need for cross-sectioning of the sample. For example, confocal Raman microscopy can identify the polymers in complex layered structures, such as multilayer films used for food packaging. Characterization of heterogeneous materials includes inclusions in minerals, the pigments, and other components in cosmetics, and the study of pigments, resins, and dyes in art and archeological objects. Using Raman microscopy, it is possible to identify if a red pigment in a painting is expensive cinnabar (HgS), cheaper hematite (Fe_2O_3), a mixture of the two, or an organic dye. The article by Edwards provides a detailed table of Raman bands from common minerals used in art and an overview of the use of Raman microscopy for the study of art objects. Raman microscopy is particularly useful for art and archeological objects, because there is no sample preparation required and the natural water present in paintings, manuscripts, and ancient textiles does not interfere, as it does in IR spectroscopy.

FTIR microscopy was discussed earlier in the chapter, and given the complementary nature of IR and Raman, it is reasonable that laboratories performing IR microscopy might well need Raman microscopy and vice versa. Two microscope systems were required and the sample had to be moved from one system to the other. The difficulty of relocating the exact spot to be sampled can be imagined. A new combination dispersive Raman and FTIR microscopy system was introduced in 2002. The system, called the LabRam-IR (JY Horiba, Edison, NJ), allows both Raman and IR spectra to be collected at exactly the same location on the sample. The resolution depends on the



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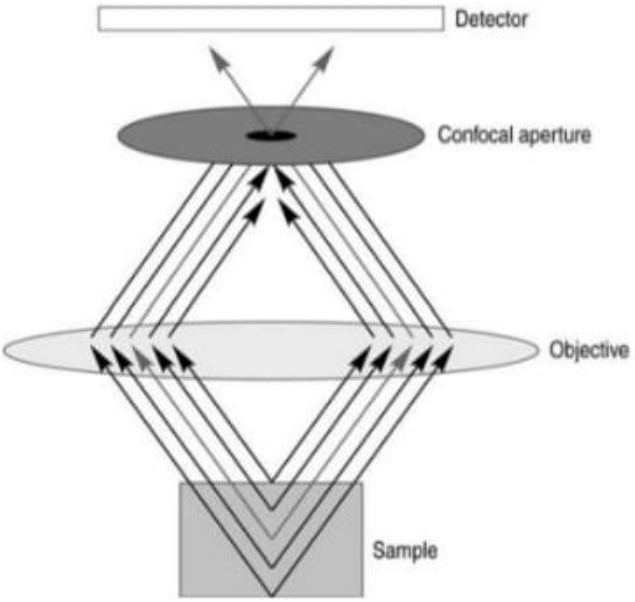

Figure 4.71 A simplified illustration of confocal microscopy. A spectrum is collected only from the area of the sample denoted by the middle arrow; only that light exits the confocal aperture. Information from all other sample areas is blocked. (Reprinted from Weesner and Longmire, with permission from Advanstar Communications, Inc.)

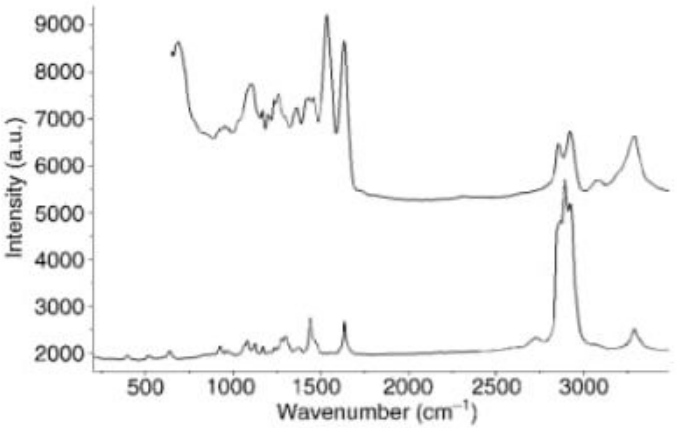

Figure 4.72 The Raman and FTIR spectra of a 10 μm fiber of a nylon 6-polyethylene glycol block copolymer. Spectra were collected at exactly the same spot on the fiber with the JYHoriba LabRam-IR microscope with Same Spot™ technology. [Courtesy of Jobin Yvon, Horiba Group, Edison, NJ (www.jyhoriba.com).]

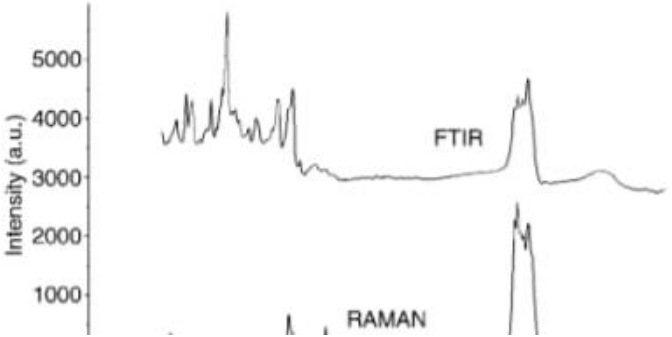

Figure 4.74 A schematic representation of a 3D spectral data cube. Sample spatial positions are represented by the x and y coordinates; the spectral wavelength is represented by the λ axis. (Reprinted from McLain et al., with permission from Advanstar Communications, Inc.)

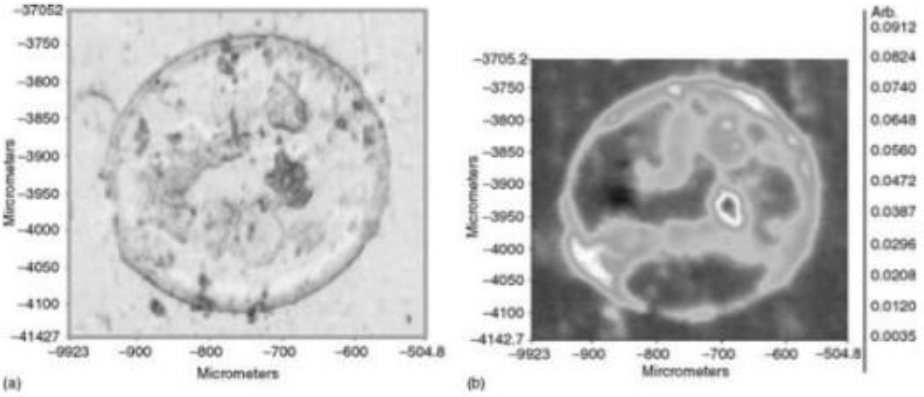

Figure 4.75 Use of FTIR imaging. (a) The visible light image of an inclusion in polypropylene film. Sample size is approximately 450 × 450 μm. (b) The IR image of the same inclusion showing the distribution of a carbonyl contaminant through the inclusion. The image contains more than 5000 spectra at 6.25 μm pixel size. The total data collection time was 90 s. Collected on a Spectrum Spotlight 300 FT-IR Imaging System. [Courtesy of PerkinElmer Instruments, Shelton, CT (www.perkinelemer.com).]

wavelength observed, because resolution is limited by diffraction, but is <1 μm for the Raman spectrum and 10–20 μm for the IR spectrum. Examples of the type of data that can be obtained with this combination microscopy system are shown in Figs. 4.72 and 4.73.

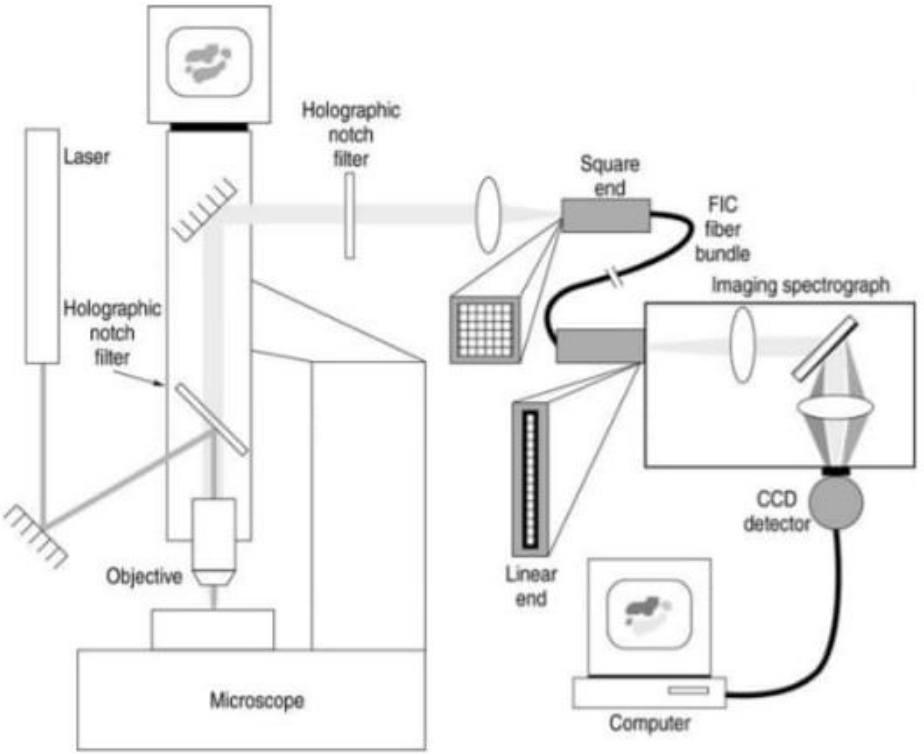

Figure 4.76 Schematic of the NIRIM. (Reprinted from McLain et al., with permission from Advanstar Communications, Inc.)