can. As an example, the Raman spectrum of cocaine is shown in Fig. 4.66. The spectrum in Fig. 4.66(a) was collected with an FT-Raman spectrometer using an NIR laser, while that in Fig. 4.66(b) was collected with a dispersive Raman system and a visible laser. Figure 4.66(b) shows a large fluorescence band that obscures most of the Raman spectrum below 2000 cm^{-1}. With appropriate mathematical "smoothing" algorithms and multipoint baseline correction, it is possible to extract a useable Raman spectrum from samples that exhibit strong fluorescence, as shown in Fig. 4.67. One consideration in FT-Raman is that the laser line at 1064 nm is very close to a water absorption band. While this does not prevent aqueous solutions from being studied by FT-Raman, aqueous solutions cannot be studied as easily as they can with dispersive Raman.

4.8.2.4. *Samples and Sample Holders for Raman Spectroscopy*

Because the laser light source can be focused to a small spot, very small samples can be analyzed by Raman spectroscopy. Samples of a few microliters in volume or a few milligrams are sufficient in most cases. Liquid samples can be held in beakers, test tubes, glass capillary tubes, or NMR tubes. Aqueous solutions can be analyzed since water is a very weak Raman scatterer. This is a significant advantage for Raman spectroscopy over IR. Other solvents that can be used for Raman studies include chloroform, carbon tetrachloride, acetonitrile, and carbon disulfide. Solid powders can be packed into glass capillary tubes, NMR tubes, or glass vials for analysis. The spectra are obtained through the glass. Solid samples can also be mounted at the focal point of the laser beam and their spectra obtained "as is" or pressed into pellets. Gas samples do not scatter radiation efficiently, but can be analyzed by being placed into a multipath gas

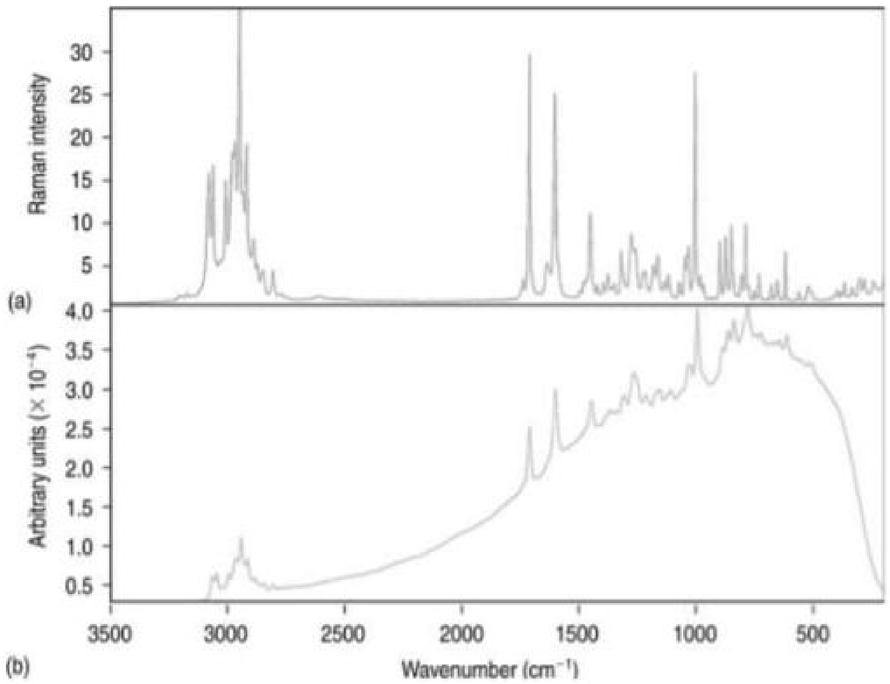

Figure 4.66 Analyses of crack cocaine using (a) FT-Raman and (b) 785 nm dispersive Raman. Note the lack of fluorescence in the FT-Raman spectrum and the rich spectral information between 2500 and 3300 cm^{-1}. This information is obscured by the fluorescence band in the dispersive spectrum. (Reprinted from Weesner and Longmire, with permission from Advanstar Communications, Inc.)

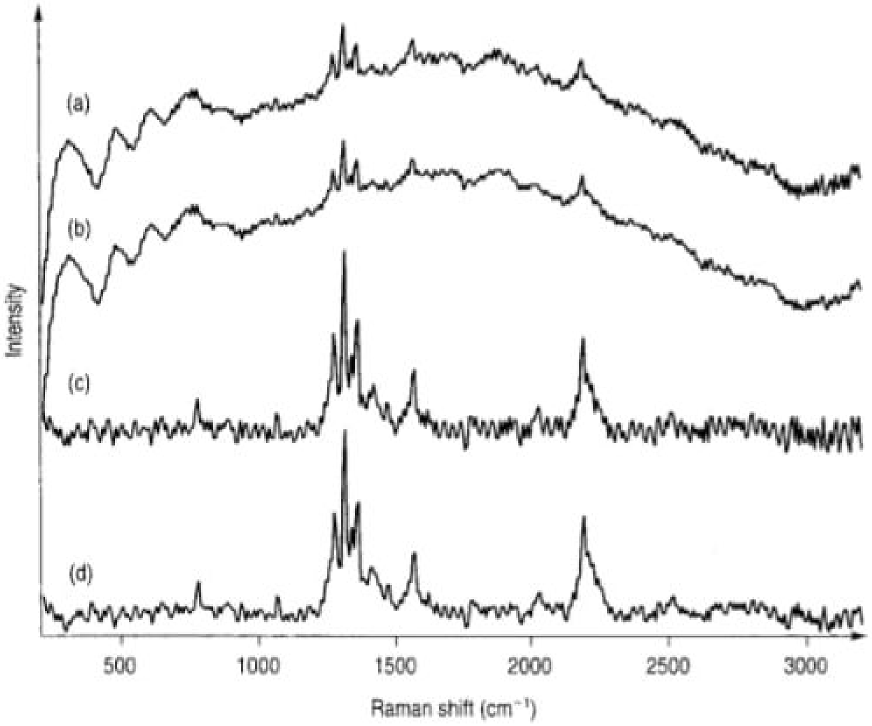

Figure 4.67 It is possible to extract data from a Raman spectrum that exhibits fluorescence interference by the application of mathematical data treatments as shown here. The data treatments were applied sequentially to give the final spectrum shown in (d). (a) is the raw spectrum of a weak scatterer with a fluorescence background, (b) is the spectrum after Savitzky–Golay smoothing, (c) after a multipoint baseline correction performed by the analyst, and (d) after a Fourier smoothing. (Reprinted from Kawai and Janni, with permission from Advanstar Communications, Inc.)

cell, with reflecting mirrors at each end. The body of the gas cell must be of glass to allow collection of the scattered light at 90°.

The sample must be placed at the focal point of an intense laser beam, and some samples may be subject to thermal decomposition or photodecomposition. Accessories that spin the sample tube or cup are available, to distribute the laser beam over the sample and reduce heating of the sample. Spinning or rotating the sample minimizes thermal decomposition, but does not stop photodecomposition. Sample spinning is required for *resonance Raman spectroscopy*, discussed later.

Raman spectroscopy does not suffer interference from atmospheric water vapor or carbon dioxide, as does IR. Gases do not scatter well, so even though Raman-active bands occur for these gases, the contribution to the Raman signal from air in the optical path is insignificant. Materials in the optical path outside of the laser focus also have negligible scattering.

4.8.3. Applications of Raman Spectroscopy

Quantitative and qualitative analyses of inorganic and organic compounds can be performed by Raman spectroscopy. Raman spectroscopy is used for bulk material characterization, online process analysis, remote sensing, microscopic analysis, and chemical