

Fiber-Optic Sampling Combined with an Imaging Spectrograph for Routine Raman Spectroscopy

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A 250-mm imaging spectrograph was combined with a CCD detector, fiber-optic sampler, and diode laser (783 nm) to yield an efficient Raman spectrometer. A variety of sampling modes for liquids and solids were demonstrated, none of which required careful optical alignment. Of practical interest are spectra obtained from liquids inside glass containers, rapid (30 seconds each) spectral acquisition from successive solid and liquid samples, and spectra of normally fluorescent materials such as rhodamine 6G and common plastics.

Index Headings: Instrumentation, Raman; Raman spectroscopy; Fiber-optic sampling; CCD Raman detection; Diode laser Raman spectroscopy.

INTRODUCTION

In several reports from a variety of laboratories, the advantages of Raman spectrometers based on charge-coupled-device (CCD) detectors, single-stage spectrographs, and in some cases diode lasers have been discussed.¹⁻⁸ The high quantum efficiency and low noise of Si-based CCDs combined with high-throughput spectrographs greatly decrease detection limits and partially compensate for typically small Raman scattering cross sections. Furthermore, the extended red response of CCDs permits operation with NIR lasers, which results in reduced interference from fluorescence. Finally, the development of fiber-optic sampling for Raman spectroscopy greatly simplifies spectral acquisition, and raises the prospect of routine application of Raman spectroscopy in addition to improved performance in the research lab.⁹⁻¹⁷ Although integrated spectrometers based on these technological innovations are not yet available commercially, the combination of CCD detectors, compact spectrographs, and NIR lasers is beginning to emerge as a viable alternative to conventional spectrometers or FT-Raman systems.¹⁹⁻²²

The purpose of this communication is to report two developments which enhance the utility of diode laser/CCD Raman spectroscopy. The first is a flat field imaging spectrograph specifically designed for CCD Raman spectroscopy. The second is a demonstration of a fiber-optic interface for the spectrograph, which permits rapid spectral acquisition from a variety of liquid and solid samples without any optical alignment between samples.

EXPERIMENTAL

The spectrograph was a bench-top prototype constructed at Chromex from a modified 250IS imaging spectrograph. In addition to the toroidal mirrors, the

system differs from a conventional Czerny-Turner configuration by the addition of integral laser rejection filter(s) preceding an internal entrance slit. Figure 1 shows a schematic drawing of the Raman spectrometer system. The toroidal mirrors correct for astigmatism, providing stigmatic imaging in a useful focal field of approximately 25 mm × 8 mm. The definition of "useful field" used here is that image deterioration either horizontally (affecting resolution) or vertically (affecting usable slit height) is smaller than 50% of the central spot size. The Raman spectrograph is an *f*/4 system with a 250-mm focal length, and the 600 grooves/mm grating results in a reciprocal linear dispersion of 50 Å/mm. Stated as Raman shift relative to a 783-nm laser, the dispersion is 69 cm⁻¹/mm at 850 nm or 1000 cm⁻¹ Raman shift. Thus a CCD with 1152 pixels of 22.5 μm width yields a dispersion of about 1.6 cm⁻¹/pixel and a spectral coverage of about 1800 cm⁻¹ for a spectrum centered on 1000 cm⁻¹. Obviously the resolution and spectral coverage will depend on grating choice and/or slit width.

The light source used for the experiments was a Li-conix Diolite diode laser with a wavelength of 783 nm operated at 15°C with an output of 30 mW. The diode laser was a turnkey system with an integral temperature controller, and was described previously.^{2,14} An interference bandpass filter, BP, was placed after the laser focusing lens with a peak transmission of 65% at 783 nm and FWHM of 9 nm. The laser was coupled to a fiber-optic probe (C-Technologies) based on a previous design¹¹ of a 200-μm-diameter excitation fiber surrounded by two concentric circles of collection fibers; the inner most ring contained 6 fibers and the second ring contained 13 fibers. The collection fibers were all 200 μm in diameter as well.

The central fiber of the fiber optic probe was on a mount allowing fine adjustments for X, Y and Z to optimize coupling of the laser. The 19 collection fibers were arranged in a linear array at the entrance slit image of the collection optics. The light from the sample passed through the collection optics, where it was collimated, and the Rayleigh light was rejected with the use of a band-rejection filter, BR (either a dielectric filter from Pomfret Research, Orange, VA, or a holographic filter from Kaiser Optical Systems, Ann Arbor, MI). The band-rejection filter has an optical density of at least 3.0 at the laser line, with ~75% transmission greater than 20 nm away from the rejection wavelength.

The CCD detector was a Photometrics (Tucson, AZ) EEVP88131 CCD array with an active area of 6 mm ×

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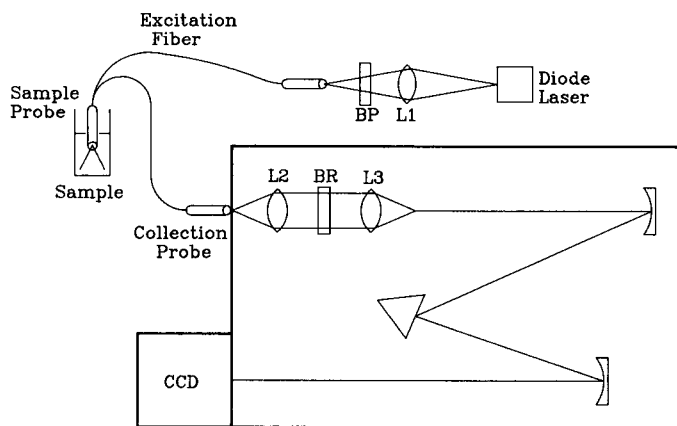


FIG. 1. Imaging Raman Spectrometer diagram. L1 is a focusing lens built into the diode laser, L2 and L3 are 25.4 mm $f/4.0$ plano convex lenses. BP is an interference bandpass filter; BR is a band rejection filter. The fiber-optic probe design is described in the text.

25 mm. The quantum efficiency for this device is 27% to 5% for the 0–3000 cm^{-1} Raman shift range relative to a 783-nm laser. The 298×1152 array was electronically “binned” so that the 298 vertical pixels were summed before readout. The CCD was thermoelectrically cooled to -40°C , and dark counts were routinely subtracted from experimental spectra. Unless noted otherwise, no further smoothing or data analysis was performed.

RESULTS AND DISCUSSION

An inherent consideration for CCD Raman spectrometer design is the trade-off of wavelength resolution and spectral coverage. Since the number of CCD pixels along the wavelength axis is fixed, any decrease in spectral resolution from a wider entrance slit or optical aberrations in the spectrograph will also decrease the effective number of resolution elements. Thus it is essential to minimize optical aberrations in the spectrograph while still providing adequate useful focal field and variable spectral coverage. As the aperture ratio and focal length of the spectrograph are decreased to improve sensitivity and decrease physical size, the task of minimizing aberrations becomes more difficult. The prototype Chromex spectrograph employs toroidal collimating and focusing mirrors with a flat grating to minimize aberrations. This approach retains access to the wide range of gratings available commercially and therefore retains flexibility in dispersion and spectral region. For the case of the 600 grooves/mm grating, the spectral resolution is linear with slit width above a width of $50 \mu\text{m}$, with the expected slope of $69 \text{ cm}^{-1}/\text{mm}$ at 850 nm. For slits of less than $50 \mu\text{m}$, the resolution is determined by optical aberrations, so that the slit image is a minimum of $40\text{-}\mu\text{m}$ wide over its entire 4.5-mm height. This corresponds to 2 pixels or 3.2 cm^{-1} for the 600 grooves/mm grating, but can be varied at will by using different grating groove densities. Of course, a larger slit width also implies higher sensitivity, so one must be cognizant of the resolution/sensitivity trade-off. As a semiquantitative resolution test, the 992-cm^{-1} band of benzene was observed with a 600 grooves/mm grating and very narrow ($<20 \mu\text{m}$) entrance slit, with the CCD acting as a two-dimensional detector.

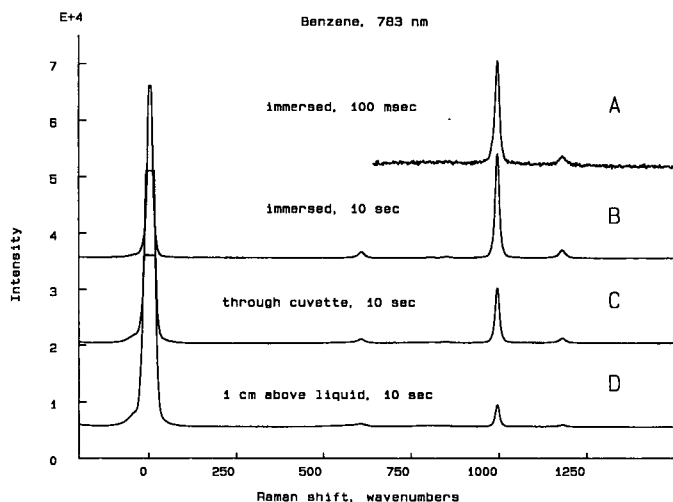


FIG. 2. Spectra of neat benzene obtained with the device of Fig. 1 and about 10 mW of laser light at the sample. Spectrum A: probe immersed in benzene, 100 ms exposure time; B, same as A, but 10-s exposure; C, same as B, but the fiber probe was positioned against the outside of the cuvette containing benzene, and normal to its surface; D, same as B, but the fiber probe end was positioned 1 cm above benzene liquid level. B, C, and D are on same Y-axis scale; A was multiplied by 100.

The Raman line covered 2–3 CCD pixels at FWHM along the wavelength axis over the entire slit height of 4.5 mm. Since the 992-cm^{-1} band has an inherent linewidth of 3 cm^{-1} , the spectrograph is exhibiting very close to the expected optical performance, with predictable trade-offs of resolution, sensitivity, and spectral coverage.

As pointed out previously, the versatility and ease of use of the fiber-optic sampler result from the fact that no optical alignment is required once the interface is aligned with the spectrometer. The user needs only to bring the distal end of the fiber optic probe near to or into the sample, with no further alignment. Thus rapid sample changes and a variety of sampling geometries are possible. The preliminary results shown in Figs. 2 to 5

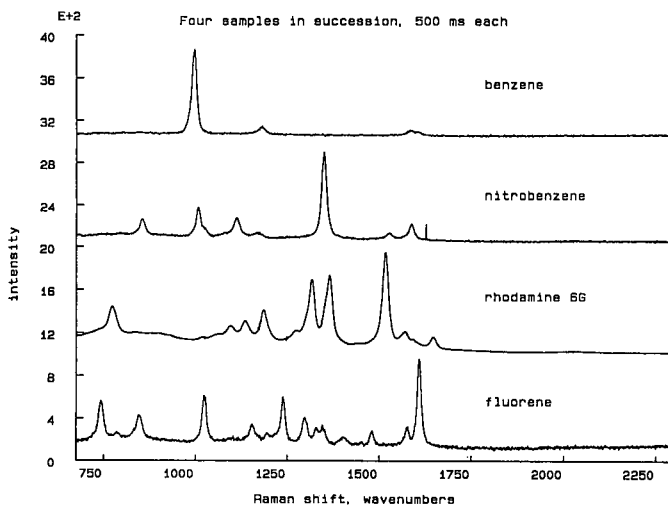


FIG. 3. Successive spectra of four samples obtained over a total period of two minutes. The exposure was 500 ms in all cases, and amplitudes were mathematically adjusted to be comparable. The probe was immersed in benzene and nitrobenzene, and positioned 2–3 mm above rhodamine and fluorene solids.

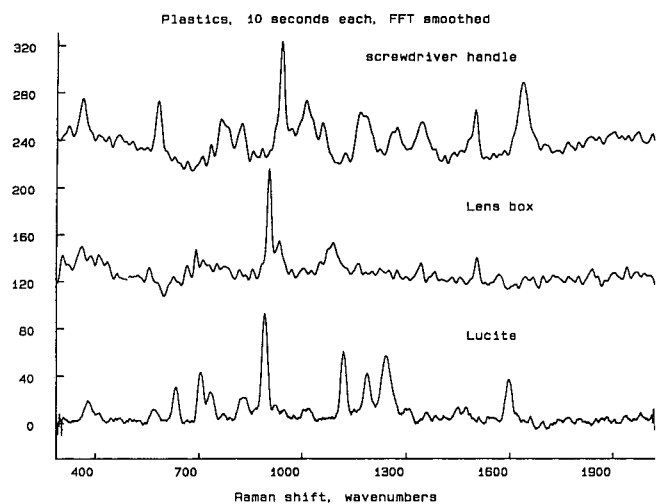


FIG. 4. Spectra of four common laboratory plastics, obtained with the fiber probe at 45° to the solid surface, 10-s exposures, ~10-mW laser power at sample. The spectra were Fourier smoothed, and a sloping baseline was subtracted.

demonstrate these points. Figure 2 shows four spectra of neat benzene obtained under various conditions. Spectra *A* and *B* were obtained with the probe immersed in the benzene contained in a conventional spectrophotometer cuvette. The signal-to-rms-background ratio increased from 107 for a 100-ms exposure time to 1300 for 10 s. Obviously the high efficiency of the spectrometer/CCD combination yielded high S/N spectra for short exposures and low laser power. Spectrum *C* was obtained by placing the fiber-optic probe directly against the outside of the cuvette containing benzene, and *D* with the probe 1 cm above the liquid surface. Although the signal intensity is diminished somewhat, high-quality spectra were obtained without contact between the probe and the sample.

Figure 3 illustrates rapid spectrum acquisition from four different samples. The probe was simply moved from one sample to the next, either immersed in liquids or placed ~3 mm above solids. The exposure time for each sample was 500 ms, and the total time for acquisition of four spectra was 2 min. Most of this time involved operator interaction with the computer and software overhead, so there is no significant reason why the total measurement time could not be reduced to less than 10 s per sample. An obvious application of this capability is routine quality control or repetitive, on-line sampling of a production line.

Figure 4 shows spectra of several transparent solids in use in the laboratory. In all cases the fiber probe was positioned on the solid surface at 45°, which minimized backscattered laser light into the collection fibers (see below). An exposure time of 10 s yielded useful S/N. Figure 5 illustrates a simple example of spectral subtraction which enabled acquisition of a spectrum of scotch whisky from outside its bottle. The upper spectrum was obtained by positioning the probe against and normal to the bottle surface where liquid was present, while the next spectrum was taken in the same way, except above the liquid level. The difference is the spectrum of the liquid only, with the spectrum for an immersed probe

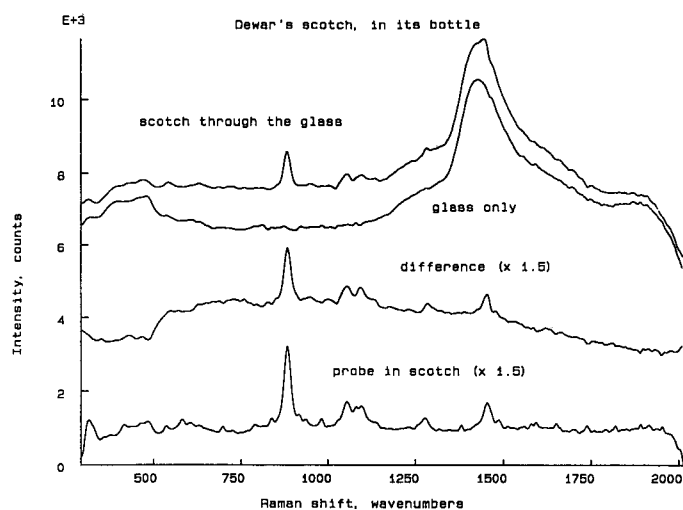


FIG. 5. Spectra of Dewar's Scotch whiskey, obtained through its glass bottle. The spectra were Fourier smoothed and a sloping baseline was subtracted. See text for sampling details.

included for comparison. The five largest bands in the 800–1500 cm^{-1} range are due to ethanol.

The problem of background Raman scattering from the silica in the optical fibers has been noted,^{9,13,17} and was occasionally encountered here. If significant elastic scatter occurs at the sample (e.g., for a powder or turbid liquid), Raman scattering generated in the fibers can interfere with sample scattering. For most liquids the problem is negligible and can be avoided with most solids by orienting the probe at a non-normal angle. In cases where the silica scattering is severe, filters at the distal end of the fiber have been used to reduce the effect.¹⁷ In our experience with the current system, silica interference is usually avoidable, and was never a problem with clear liquid samples.

Since the combination of diode lasers, CCD detectors, compact spectrographs, and fiber-optic sampling is quite new, there will undoubtedly be significant improvement in the future. Further development of the approach will be driven by the attractions of high-sensitivity, reduced-fluorescence interference, and ease of operation.

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