

# Raman Spectroscopy with a Fiber-Optic Probe and Multichannel Detection

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The increased use of fiber optics and detector arrays has substantially changed spectroscopic measurements for applications such as online monitoring of chemical processes and in situ environmental analysis. The evolution of these technologies and other improvements in optical filters and gratings has particularly altered the practice of Raman spectroscopy. Compact Raman systems are now widely used for chemical analysis, especially in applications requiring rapid, nondestructive measurements with little or no sample preparation. These developments have not been reflected in published laboratory exercises for undergraduate laboratories. This report describes an exercise for the undergraduate analytical chemistry course emphasizing instrumental methods of analysis. It illustrates the principles of multichannel spectroscopy with a charge-coupled device (CCD) array detector. It also demonstrates the use of Raman spectroscopy for the analysis of liquids and solids employing an inexpensive, compact spectrometer with a solid-state laser and fiber-optic probe.

Raman spectroscopy has been the subject of several reports in this *Journal*. In an exercise intended for the undergraduate physical chemistry laboratory, a modular spectrometer and its application to the study of symmetric oxyanions was described (1). Raman spectroscopy has been used for the qualitative examination of gemstones (2). A third article emphasizes the connection between theory and solid-state vibrational spectra (3). A number of earlier reports addressed various aspects of Raman spectroscopy but none from the point of view of chemical analysis or employing multichannel detection (4–8).

## Experimental Procedure

### Equipment

In our work we use the inexpensive, low-resolution R-2000 Raman system manufactured by Boston Advanced Technologies, Inc. (Marlborough, MA). It consists of a diode laser, a fiber-optic probe, a miniature spectrograph, a CCD array detector, and an interface card. A detailed description of the properties of this system is available (9). The laser emits at 785 nm. The fiber-optic probe has single-fused silica excitation and collection fibers and incorporates filtering that removes most of the silica Raman signal. The spectrograph is configured to record a spectral range of approximately 780 to 1000 nm on a 25-mm-wide detector array. The detector is a 2048-element linear CCD array with  $0.0125 \times 0.200$ -mm pixels. The host software supplied with the system provides computer control of the relevant operating conditions, displays the spectra, and provides ASCII data files that can be read into a spreadsheet or most other data treatment software packages.

We constructed a neon atomic line source and a white-light source from inexpensive components that were readily available from local sources.

### Software

We use a commercial spreadsheet program (Microsoft Excel) for some data display. We use locally written software for interactive subtraction of spectra and quantitative analysis by least squares fitting of spectra. The software, written in C++, will be supplied with the laboratory documentation.<sup>W</sup>

### Chemicals

We used the following chemicals: salicylic acid, aspirin, acetaminophen, salicylamide, caffeine, toluene, and cyclohexane. A small quantity of each of the five solids was ground to a fine powder with a mortar and pestle. The powders were stored in small brown bottles. Known mixtures of toluene and cyclohexane were prepared by weighing into brown bottles.

### Hazards

The laser emits 500 mW of 785-nm radiation and is a potential eye hazard. In normal operation the beam is available only at the end of the fiber optic probe. This reduces the danger because the beam is divergent as it emerges from the fiber. Nevertheless, we took the precaution of mounting the probe in a holder that limited its range of motion. It allowed the probe to be raised and lowered for insertion in samples but always directed the beam towards the bench top.

The chemicals should pose no special hazard for students in an advanced laboratory. The solids are found in a variety of over-the-counter medicines. However, note should be taken that some of the powders are pure materials, not diluted with excipients as they might be in tablets.

## Results and Discussion

### Ne Atomic Line Spectrum

A neon pilot lamp is a convenient source of atomic lines in this wavelength region. We use acquisition of this spectrum as a way to acquaint the student with the basics of multichannel detection. We want the students to recognize that a spectrum is being recorded simultaneously at 2048 discrete detectors (pixels). The signal recorded at each detector is proportional to the amount of light falling on that detector. Each pixel corresponds to a different point in the focal plane of the spectrograph and hence to a slightly different wavelength. This part of the exercise also provides a graphic illustration of the effect of ensemble averaging on signal-to-noise ratio.

On the video monitor a spectrum appears continuous, much like the spectrum recorded on a strip chart recorder with a scanning spectrometer. Reading the data file into a spreadsheet encourages students to recognize that the spectrum has been digitized at a finite number of discrete positions in space. The student handout provides a sample neon spectrum

with 13 lines identified by wavelength.<sup>W</sup> We ask the students to find the nearest whole pixel number corresponding to the peak of each of the lines and to make a graph of wavelength versus pixel number. Using the spreadsheet regression tools, we find linear and quadratic equations to calculate wavelength for any pixel position. The dispersion of a grating is not linear, and the quadratic equation provides a much better fit to the data.

The atomic line spectrum also provides an opportunity to revisit the notions of spectral band-pass and reciprocal linear dispersion for a spectrometer. For a designated line the students are asked to count the number of pixels between half-intensity points. The half-intensity width in millimeters can be calculated by multiplying the number of pixels by the width of a pixel (given in the handout).<sup>W</sup> This width expressed in terms of wavelength can be calculated by multiplying the number of pixels by the slope of the wavelength-versus-pixel line at the wavelength of the atomic line specified.

### White Light Spectrum

We acquire this spectrum to introduce the idea of an instrument response function. The true spectrum of a hot filament is approximately described by the blackbody equation. The predicted spectrum is calculated in a spreadsheet. The observed spectrum is quite different from this prediction, reflecting the effect of optical filters, grating efficiency and detector quantum efficiency.

### Powder Spectra

The student has a labeled sample of each of the pure materials and an unknown. Spectra are acquired by simply bringing the probe in contact with the powder in its bottle and recording. Structural formulas are provided so that the student can note that even for similar materials, like aspirin and salicylic acid, the spectra are obviously different. We used as unknowns pure powders of salicylamide or salicylic acid or crushed tablets of aspirin, Tylenol, or Anacin. The tablets contain excipients, such as starch, that do not contribute features to the Raman spectra. Students are asked to identify the unknown by comparing its spectrum to those of the known compounds and to confirm the identification by interactively subtracting the known from the unknown using the tools provided in our locally produced software. When the identification is correct for an unknown with a single active component, the subtraction leaves only a noisy baseline. The Anacin unknown contains aspirin and caffeine, but its spectrum will usually be identified as due to aspirin. When the pure aspirin spectrum is subtracted from the unknown spectrum there is an obvious residual spectrum that is easily recognized as due to caffeine. Subtraction of the pure caffeine spectrum leaves the expected noisy baseline. Some sample results are included in the online documentation.<sup>W</sup>

### Toluene/Cyclohexane Determinations

This part of the exercise is designed to illustrate quantitative analysis as it is often done for real samples when there are components with overlapping spectra. Students are given bottles containing neat cyclohexane, neat toluene, and an unknown solution of the two. Spectra for the three samples

**Table 1. Student Results for Determination of Toluene and Cyclohexane in Unknowns**

Student	Prepared (%) Toluene/ Cyclohexane	Found (%)	
		Toluene $\pm$ SD	Cyclohexane $\pm$ SD
1	35/65	34 $\pm$ 2	67 $\pm$ 5
2	35/65	32 $\pm$ 1	68 $\pm$ 2
3	25/75	16 $\pm$ 3	82 $\pm$ 4
4	25/75	19 $\pm$ 3	80 $\pm$ 4
5	10/90	8 $\pm$ 1	87 $\pm$ 3

are acquired under (ideally) identical conditions. The spectra of the two pure materials (the reference spectra) are fitted to the spectrum of the unknown using the tools provided in our software. The least-squares fit values for the two reference spectra are found. These values are the scaling factors by which each reference spectrum must be multiplied so that the sum of the scaled reference spectra gives the best fit to the sample spectrum. Under the conditions of this measurement, these fit values are the fractions of toluene and cyclohexane in the unknown. Some student results are shown in Table 1. Standard deviations are calculated for five measurements of the spectrum of the unknown sample with the same reference spectra fitted to each.

### Conclusions

This exercise illustrates several important concepts of optical instrumentation usually covered in the spectroscopy portion of undergraduate analytical courses: multichannel detection, dispersion, spectral band-pass, and instrument response function. It also demonstrates fiber-optic-based Raman spectroscopy, a technique finding increasing use for online monitoring applications for which few undergraduate laboratory exercises have been published.

### <sup>W</sup>Supplemental Material

Additional background information, the student handout, and notes for the instructor are available in this issue of *JCE Online*.

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