Analytical Chemistry Cumulative Exam
Thursday Nov. 1, 2012
Various methods and analytical applications of
Raman Spectroscopic techniques.
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Focus on those problems you can answer. Some correct, well thought out responses are better than poorly framed attempts at every question. Normally, 50 points will pass.

Answer only enough questions to total = 100 -- I will stop grading at ~ 100.

(8) 1. We had a couple analytically oriented seminars so far this year, Fall 2012. [Analytical talks are those hosted by an analytical faculty member or those having to do with the science of measurement.] For one of these, please give the speaker’s name and affiliation and, more importantly, summarize his/her experimental results and conclusions. State how you think this work will affect development of practical analyses in the future.

Raman spectroscopy is an inelastic scattering experiment where the wavelength, and hence energy or frequency of an incoming light beam is shifted and scattered by interaction with a sample. While most often used for study of molecular vibrations, Raman is actually quite general, and also can be done in a wide variety of ways that enhance detection, involve nonlinear processes and probe different aspects of the sample beyond vibrational transitions.

(25) - 2. Conventional Raman spectrometers for measuring vibrational spectra use cw lasers as a light source, since they offer bright single frequency light resulting in sharply shifted scattered radiation to determine the Raman shift. Although first detected in the 1920s, Raman spectroscopy was rare until after the invention of the laser in the 1960s.

a. What kind of a light source did Sir C. V. Raman use (actually his student, K. S. Krishnan!) ? What (or type of) sample did he measure spectra to observe the first Raman spectrum (and earn a Nobel Prize)? How did he determine that the wavelength shifted?

b. What kind of sources were commonly used before the invention of the laser? Why?

c. Ar-ion lasers were common excitation sources for many years (and still are used, even in my lab!). Why are they chosen? What excitation frequency is possible? Briefly discuss why people are now choosing different types of cw lasers.

d. Briefly discuss why the color/frequency of the laser is important for making good analytical measurements with ordinary (spontaneous) Raman?

e. Why would you want to tune the laser frequency in a Raman experiment? Give an example of how you might achieve practical tunable cw excitation for a Raman system.

f. Briefly discuss why one might want to use a pulsed laser to do Raman experiments.

g. These intense sources have a tendency to heat the sample. How is this often avoided?
Raman spectrometers often use a monochromator or spectrograph with a grating to disperse the light and separate the shifted frequencies.

- Many older spectrometers used a double monochromator of relatively long focal length, e.g. ½ to 1 m, that synchronously scanned two gratings. Explain what the advantage of this design is in terms of detection and analytical separation of signals.

- Some spectrometers used a prism based pre-disperser as well. Give an application or problem to solve where this addition might be useful and briefly explain why.

- Modern compact Raman spectrometers often use a single spectrograph of quite short focal length. Explain why this is an advantage and how the problems that previously required a double of triple monochromator are avoided. What are some disadvantages?

- Explain why it is crucial to filter out the excitation frequency in Raman spectra.

- Some commercial Raman spectrometers are sold based on FTIR technology as FT-Raman instruments. Explain the advantages of this design for analytical purposes. What kind of source would be used for FT-Raman? Briefly explain.

Light scattering as a mechanism for spectroscopy has intrinsically small signals, which is one reason to use a powerful excitation source, as discussed above. The corollary is that high sensitivity detectors are also needed.

- Detectors used in Raman instruments from the 1960s to 1990s were photomultiplier tubes (PMT). Explain their advantages and restrictions for Raman detection.

- Many instruments now use CCD detectors. How do these work to detect light? Explain the advantages on these over PMTs. What disadvantages do they have?

- What is the signal to noise advantage of such a detector, briefly explain.

- Why are cosmic rays an issue for CCD detection?

- Early work used photographic plates. How are these similar or different from CCDs?

- PMTs do not work in the IR, so what kind of detector can be used for FT-Raman?

Fluorescence instrumentation is functionally the same as Raman instrumentation, yet different spectrometers are sold for each purpose.

- Briefly explain difference in design goals in fluorescence and Raman instruments.

- Often Raman samples fluoresce with intensity greater than the Raman intensity. Briefly explain why. Propose and explain a way to eliminate the interference.

A hot area in Raman spectroscopy now makes use of uv-laser excitation.

- Briefly discuss advantages of uv excitation in terms of the types of samples that can be studied and the types of vibrations that will dominate the spectra.

- Suggest a laser useful for uv-Raman excitation at 200-220 nm. Describe how it works.

- Many samples absorb in the UV. Briefly explain how one can avoid photochemical damage and excess heating. How is fluorescence controlled with uv excitation?
Another popular, but not at all new, area in analytical uses of Raman is SERS, surface enhanced Raman spectroscopy.

a. Briefly discuss how SERS works and why its Raman signal strength is enhanced.

b. Some single molecule SERS experiments have been proposed. Briefly explain what this means, propose how it could possibly realized and what new information might be obtained.

c. SERS experiments have long been plagued with irreproducible results. Briefly explain what this is often a problem for metal colloid based SERS.

Continuing on with the letters beyond SERS, there are a number of Raman variants such as CARS, RIKES, RRS, HyperRaman, Stimulated Raman spectroscopies.

a. Briefly explain what CARS, coherent anti-Stokes Raman, means and how it works?

b. CARS has a non-resonant part, what is the impact of this on the spectra?

c. Briefly discuss why CARS is so useful for microscopy and imaging.

d. Stimulated Raman is now being suggested as an improvement for CARS, what is its advantage?

e. Propose a source for non-linear (3,4-wave mixing) Raman experiments (like CARS). Briefly describe it and give your reason for using it in this application.

Polarization has some application in IR, for crystals and other oriented samples, but it is used more often in Raman spectroscopy.

a. Briefly explain why there is an intrinsic (linear) polarization component to Raman, even for solution samples. What can it be used for?

b. Normally one only needs a polarizer to analyze the scattered beam in Raman, briefly explain why. What kind of polarizers and used for this? Why?

c. Why might a depolarizer be needed? (Briefly explain)

d. ROA, Raman optical activity, also uses polarization. Briefly explain what ROA measures, how it uses polarization, what kind of molecules are studied and what information it provides.

e. Briefly discuss the main optical components needed to convert an ordinary Raman spectrometer to measure ROA.

Imaging has become one of the newer and faster growing analytical tools. Both IR and Raman are often used for imaging studies.

a. Why are these imaging methods “better” (more information content) than conventional (white light) microscopy or histological staining for bio-medical application? Briefly explain.

b. Why is Raman imaging higher resolution than IR imaging? Explain.

In Raman the signal varies with the source intensity and with any variation in the collection geometry or sample quality. Thus Raman is not often used for concentration measurements, even though scattering is linear in concentration. Suggest a means of normalizing the detector response to correct for source and sample fluctuations.