**Experiment 5:** Analysis of Ethanol in Vodka Samples Using FTIR and Raman Spectroscopy

**NOTES:**
- You have TWO weeks to complete this laboratory. Focus on measurements using ONE of the methods each week.
- Perform all calculations for standard addition sample preparations BEFORE coming to the laboratory. The same solutions will be used for both the IR and Raman measurements. Therefore, in your calculations including total sample volume, be prepared so as to perform each measurement on each instrument AT LEAST 3 times.
- Carefully prepare all standard addition samples being sure to use the most appropriate measurement devices for volume and/or mass accuracy. If you are prepared, sample preparation should take ~1 hr.

**REFERENCES:**
- *Journal of Chemical Education* 80(2003)672.
- For information on the standard additions method and how to prepare samples, see Skoog pp. 15-18 and Harris section 5-3.
- For information on the attenuated total reflectance (ATR) cell used in the FTIR measurements, see Skoog pp. 420-421.
- For general information on the theory of vibrational spectroscopy, see Skoog pp 381-389.
- For comparison of IR and Raman methods, see Skoog pp 432-433.

**GOALS:**
1) To prepare standard addition samples for quantitative measurements of an analyte in a complex matrix.
2) To perform quantitative measurements of these samples using the attenuated total reflectance (ATR) cell on the FTIR.
3) To perform quantitative measurements of the same samples using the Raman instrument.
4) To compare (quantitatively whenever possible!) these two methods in their ability to quantitate ethanol in vodka samples.
5) To calculate the theoretical vibrational energies of ethanol (using normal mode analysis in Cerius²) and compare them to the observed IR and Raman frequencies.
LABORATORY INSTRUCTIONS:

Samples:
Vodka samples are provided. Assuming that the concentration of ethanol in vodka is approximately 40%, prepare a series of AT LEAST four standard addition samples suitable for analysis of ethanol in your sample. Be sure to work through all of the calculations needed to prepare these samples BEFORE YOU COME TO LAB. Pure ethanol (100%, 200-proof, dehydrated) should be used for your additions. A 10-fold dilution of your unknown in each standard addition sample is recommended. A HINT: To make your calculations easier in the end, consider adding the same total volume to each standard addition sample – this means you will need to add varying amount of pure ethanol and water to each sample, with the sum of the two added volumes being the same for all samples (please see the instructor if you have questions).

Materials Available
Unknown solution: Vodka samples of various brands and ages (~40% ethanol by volume)
Pure ethanol (200-proof)
18 MΩ water
Volumetric glass pipettes and bulbs (in 1, 2, 3, 4, 5, 10, and 15 mL sizes)
Volumetric flasks with caps (in 10, 25, 50, and 100 mL sizes)
Plastic 50-ml tubes for sample storage (Please do not store samples in volumetric flasks!)
ATR Cell for FTIR: ~3 mL of sample needed per measurement
1-cm Quartz cuvette for Raman: ~3 mL of sample needed per measurement

FTIR Measurements:
Ethanol signals throughout the spectrum will be observed but quantitative measurements will be made at 1044 cm$^{-1}$. Solutions containing water absorb too strongly in the IR to use conventional sample cells. Instead we will use an ATR cell which is shown in figure 1.

The cell is a 3-cm long zinc selenide crystal surrounded by your sample. The IR light beam is focused so that it bounces off of the crystal-sample interface approximately 20 times as it propagates through the cell. If the light at a given wavelength is absorbed by the sample, the amount of reflected light will be reduced or attenuated, and thus the name of the technique: Attenuated Total Reflectance.

Assembly, loading and operation of the cell will be demonstrated by your instructor during your training session. Operation of the FTIR will also be demonstrated. Collect the spectrum of each sample and a water reference on the Galaxy 4010 FTIR spectrometer. Use the following FTIR settings for these measurements:
Print out all raw data and make quantitative measurements of the signal at ~1044 cm\(^{-1}\) for each spectrum (signal intensity and area are recommended). You may also want to save your spectra on the computer hard drive or on the ChemServer for further processing. For your sample with the highest ethanol concentration, be sure to note the wavenumber and intensity of EVERY signal originating from the ethanol (to compare to theoretical data for ethanol).

**Raman Measurements:**

The layout and operation of the Raman instrument will be demonstrated by your instructor during the training session. Be sure to take notes on the layout and the instrument specifications. On this instrument, measure the Raman signal of each sample, using water as the blank. The samples should be contained in a conventional 1-cm quartz cell. Record the pixel number and intensity of the maximum of each signal due to ethanol. Either calibrate the instrument with CCl\(_4\) or use a previous calibration of the instrument to convert pixel number of each signal to a wavenumber. Be sure to tabulate all data in your notebook, as there may not be a printer connected to this instrument!

**Cerius\(^2\) Calculations:**

In problem set #5, you should already have predicted the number of normal modes for ethanol and used Cerius\(^2\) to determine the frequencies, degeneracies, relative intensities, and origins of the IR and Raman active normal modes for this molecule. Please use this information to help you identify analyte signals and to make comparisons described in the next section.
TO HAND IN:

- Clearly tabulate and/or explain each standard addition sample prep. Be sure that all raw data for these dilutions is in your notebook or in a spreadsheet.
- For each sample measurement on each instrument, tabulate the amount (or concentration) of added acetic acid and the signal intensity or signal area measured. Generate a standard addition plot of your data (Signal vs. concentration) and calculate the concentration of acetic acid in the vinegar sample. Report the value in percent volume and in molarity with appropriate uncertainties.
- Compare the measurements from the two spectroscopic methods. Which is more precise? What is more sensitive? How do the methods compare in terms of time per sample and technical expertise of the user? Use your answers to the previous questions to justify which method you believe to be better for this application.
- From the results of the Cerius² calculations of acetic acid normal modes, describe the vibrations most likely responsible for the IR and Raman signals in your samples. Plot these theoretical frequencies against the experimentally observed frequencies for both IR and Raman. Briefly discuss this plot. Are all Raman peaks IR active and visa versa? Are the observed intensities of peaks as expected from theory? Please explain your observations.