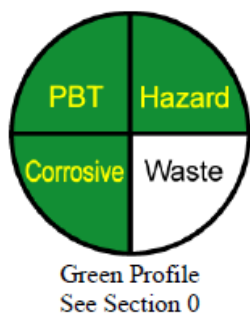
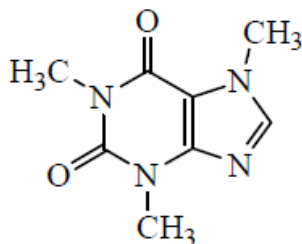


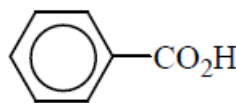
23. Spectrophotometric Analysis of a Mixture: Caffeine and Benzoic Acid in a Soft Drink³⁹



In this experiment we use ultraviolet absorbance (Figure 1) to measure two major species in soft drinks. Caffeine is added as a stimulant and sodium benzoate is a preservative.



Caffeine
FM 182.18



Benzoic acid ($pK_a = 4.20$)
FM 122.12

All solutions will contain 0.010 M HCl, so the sodium benzoate is protonated to make benzoic acid. Caffeine has no appreciable basicity, so it is neutral at pH 2.

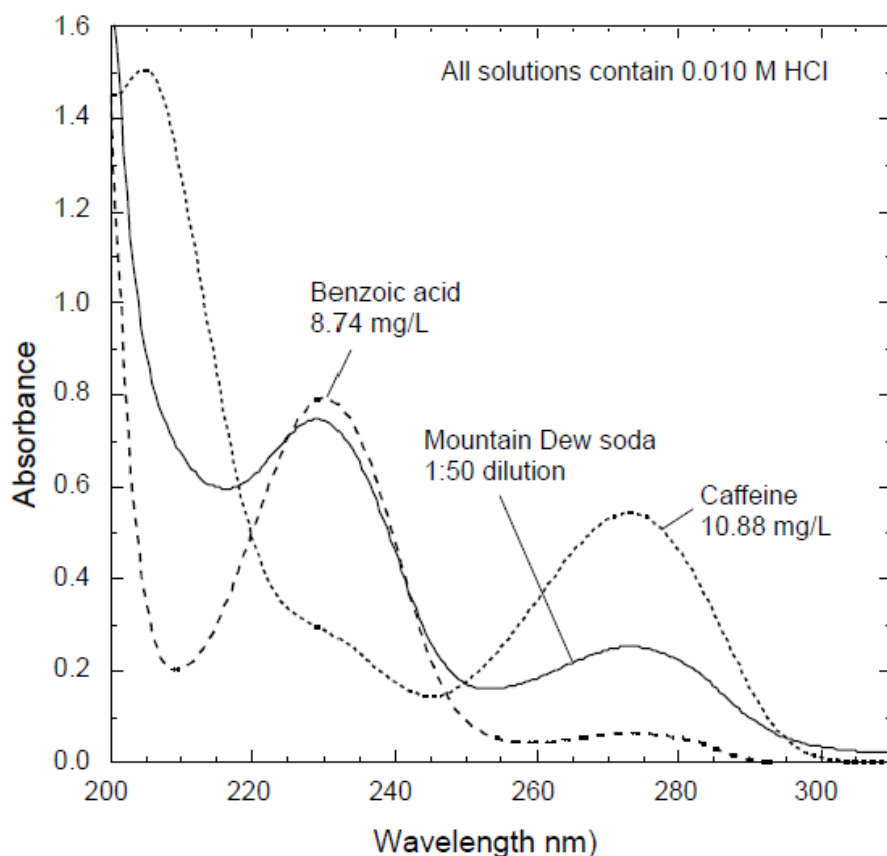


Figure 1. Ultraviolet absorption of benzoic acid, caffeine, and a 1:50 dilution of Mountain Dew soft drink. All solutions contain 0.010 M HCl.

We restrict ourselves to non-diet soft drinks because the sugar substitute aspartame in diet soda has some ultraviolet absorbance that slightly interferes in the present experiment. We also avoid darkly colored drinks because the colorants have ultraviolet absorbance. Mountain Dew, Mello Yello, and, probably, other lightly colored drinks are suitable for this experiment. There is undoubtedly some ultraviolet absorbance from colorants in these beverages that contributes systematic error to this experiment.

The procedure we describe includes the construction of calibration curves. The experiment could be shortened by recording just one spectrum of caffeine (20 mg/L) and one of benzoic acid (10 mg/L) and assuming that Beer's law is obeyed. The experiment could be expanded to use high-performance liquid chromatography (HPLC) and/or capillary electrophoresis to obtain independent measurements of caffeine and benzoic acid (and aspartame in diet drinks).³⁹

Reagents

Stock solutions: An accurately known solution containing ~100 mg benzoic acid/L in water and another containing ~200 mg caffeine/L should be available.

0.10 M HCl: Dilute 8.2 mL of 37 wt% HCl to 1 L.

Procedure

1. *Calibration standards:* Prepare benzoic acid solutions containing 2, 4, 6, 8 and 10 mg/L in 0.010 M HCl. To prepare a 2 mg/L solution, mix 2.00 mL of benzoic acid standard plus 10.0 mL of 0.10 M HCl in a 100-mL volumetric flask and dilute to the mark with water. Use 4, 6, 8 and 10 mL of benzoic acid to prepare the other standards. In a similar manner, prepare caffeine standards containing 4, 8, 12, 16 and 20 mg/L in 0.010 M HCl.
2. *Soft drink:* Warm ~20 mL of soft drink in a beaker on a hot plate to expel CO₂ and filter the warm liquid through filter paper to remove any particles. After cooling to room temperature, pipet 4.00 mL into a 100-mL volumetric flask. Add 10.0 mL of 0.10 M HCl and dilute to the mark. Prepare a second sample containing 2.00 mL of soft drink instead of 4.00 mL.
3. *Verifying Beer's law:* Record an ultraviolet baseline from 350 to 210 nm with water in the sample and reference cuvetts (1.000 cm pathlength). Record the ultraviolet spectrum of each of the 10 standards with water in the reference cuvet. Note the wavelength of peak

absorbance for benzoic acid (λ') and the wavelength for the peak absorbance of caffeine (λ''). Measure the absorbance of each standard at both wavelengths and subtract the baseline absorbance (if your instrument does not do this automatically). Prepare a calibration graph of absorbance versus concentration (M) for each compound at each of the two wavelengths. Each graph should go through 0. The least-squares slope of the graph is the molar absorptivity at that wavelength.

4. *Unknowns:* Measure the ultraviolet absorption spectrum of the 2:100 and 4:100 dilutions of the soft drink. With the absorbance at the wavelengths λ' and λ'' , use Equation 19-6 in the textbook to find the concentrations of benzoic acid and caffeine in the original soft drink. Report results from both dilute solutions.
5. *Synthetic unknown:* If your instructor chooses, measure the spectrum of a synthetic, unknown mixture of benzoic acid and caffeine prepared by the instructor. Use Equation 19-6 in the textbook to find the concentration of each component in the synthetic unknown.

