Chapter 15

1. Answers will vary depending on the labs you have done and the guidelines provided by your instructor. Of the examples cited in the text, those that likely are most relevant to your experience are properly recording data and maintaining records, specifying and purifying chemical reagents, cleaning and calibrating glassware and other equipment, and maintaining the laboratory facilities and general laboratory equipment.

2. Although your answers may include additional details, here are some specific issues you should include.

    (a) If necessary, clean and rinse the buret with water. When clean, rinse the buret with several portions of your reagent and then fill the buret with reagent so that it is below the buret's 0.00 mL mark. Be sure that the buret's tip is filled and that an air bubble is not present. Read the buret's initial volume. Dispense the reagent, being sure that each drop falls into your sample's flask. If splashing occurs, rinse the walls of the sample's flask to ensure that the reagent makes it into the flask. If a drop of reagent remains suspended on the buret's tip when you are done adding reagent, rinse it into the sample's flask. Record the final volume of reagent in the buret.

    (b) Calibrate the pH meter using two buffers, one near a pH of 7 and one that is more acidic or more basic, depending on the samples you will analyze. When transferring the pH electrode to a new solution, rinse it with distilled water and carefully dry it with a tissue to remove the rinse water. Place the pH electrode in the solution you are analyzing and allow the electrode to equilibrate before recording the pH.

    (c) Turn on the instrument and allow sufficient time for the light source to warm up. Adjust the wavelength to the appropriate value. Adjust the instrument's 0%T (infinite absorbance) without a sample in the cell and with the light source blocked from reaching the detector. Fill a suitable cuvette with an appropriate blank solution, clean the cuvette's exterior surface with a tissue, place the cuvette in the sample holder, and adjust the instrument's 100%T (zero absorbance). Rinse the cuvette with several small portions of your sample and then fill the cuvette with sample. Place the cuvette in the sample holder and record the sample's %T or absorbance.

3. Substituting each sample's signal into the equation for the calibration curve gives the concentration of lead in the samples as 1.59 ppm and 1.48 ppm. The absolute difference, d, and the relative difference, $(d)_r$, are

$$d = 1.59 \text{ ppm} - 1.48 \text{ ppm} = 0.11 \text{ ppm}$$

$$(d)_r = \frac{0.11 \text{ ppm}}{0.5 (1.59 \text{ ppm} + 1.48 \text{ ppm})} \times 100 = 7.2\%$$

For a trace metal whose concentration is more than $20\times$ the method's detection limit of 10.0 ppb, the relative difference should not exceed 10%; with a $(d)_r$ of 7.2%, the duplicate analysis is acceptable.

4. In order, the differences are 0.12, -0.08, 0.12, -0.05, -0.10, and 0.07 ppm. The standard deviation for the duplicates is

$$s = \sqrt{\frac{\sum_{i=1}^{n}(d_i)^2}{2n}} = \sqrt{\frac{\left[\begin{array}{c}(0.12)^2 + (-0.08)^2 + \\ (0.12)^2 + (-0.05)^2 + \\ (-0.10)^2 + (0.07)^2\end{array}\right]}{2 \times 6}} = 0.066 \text{ ppm}$$

The mean concentration of NO_3^- for all 12 samples is 5.005 ppm, which makes the relative standard deviation

$$s_r = \frac{0.066 \text{ ppm}}{5.005 \text{ ppm}} \times 100 = 1.3\%$$

a value that is less than the maximum limit of 1.5%.

5. For the first spike recovery, the result is

$$R = \frac{0.342 \text{ mg/g} - 0.20 \text{ mg/g}}{0.135 \text{ mg/g}} \times 100 = 105.2\%$$

The recoveries for the remaining four trials are 103.7%, 103.7%, 91.9%, and 90.4%. The mean recovery for all five trials is 99.0%.

6. (a) Using the equation for the calibration curve, the concentration of analyte in the spiked field blank is 2.10 ppm. The recovery on the spike, therefore, is

$$R = \frac{2.10 \text{ ppm} - 0 \text{ ppm}}{2.00 \text{ ppm}} \times 100 = 105\%$$

Because this recovery is within the limit of $\pm 10\%$, the field blank's recovery is acceptable.

(b) Using the equation for the calibration curve, the concentration of analyte in the spiked method blank is 1.70 ppm. The recovery on the spike, therefore, is

$$R = \frac{1.70 \text{ ppm} - 0 \text{ ppm}}{2.00 \text{ ppm}} \times 100 = 85\%$$

Because this recovery exceeds the limit of $\pm 10\%$, the method blank's recovery is not acceptable and there is a systematic error in the laboratory.

(c) Using the equation for the calibration curve, the concentration of analyte in the sample before the spike is 1.67 ppm and its concentration after the spike is 3.77 ppm. The recovery on the spike is

$$R = \frac{3.77 \text{ ppm} - 1.67 \text{ ppm}}{2.00 \text{ ppm}} \times 100 = 105\%$$

Because this recovery is within the limit of $\pm 10\%$, the laboratory spike's recovery is acceptable, suggesting a time-dependent change in the analyte's concentration.

7. The mean and the standard deviation for the 25 samples are 34.01 ppm and 1.828 ppm, respectively, which gives us the following warning limits and control limits

$$UCL = 34.01 + (3)(1.828) = 39.5$$

$$UWL = 34.01 + (2)(1.828) = 37.7$$

$$LWL = 34.01 - (2)(1.828) = 30.4$$

$$LCL = 34.01 - (3)(1.828) = 28.5$$

Figure SM15.1 shows the property control chart. Note that the highlighted region contains 14 consecutive cycles (15 samples) in which the results oscillate up and down, indicating that the system is not in a state of statistical control.

8. The mean and the standard deviation for the 25 samples are 99.84% and 14.08%, respectively, which gives us the following warning limits and control limits

$$UCL = 99.84 + (3)(14.08) = 142.1$$

$$UWL = 99.84 + (2)(14.08) = 128.0$$

$$LWL = 99.84 - (2)(14.08) = 71.7$$

$$LCL = 99.84 - (3)(14.08) = 57.6$$

Figure SM15.2 shows the property control chart, which has no features to suggest that the system is not in a state of statistical control.

9. The 25 range values are 4, 1, 3, 3, 2, 0, 2, 4, 3, 1, 4, 1, 2, 0, 2, 4, 3, 4, 1, 1, 2, 1, 2, 3, 3, with a mean of 2.24. The control and warning limits, therefore, are

$$UCL = (3.267)(2.24) = 7.3$$

$$UWL = (2.512)(2.24) = 5.6$$

Figure SM15.2 shows the precision control chart, which has no features to suggest that the system is not in a state of statistical control.
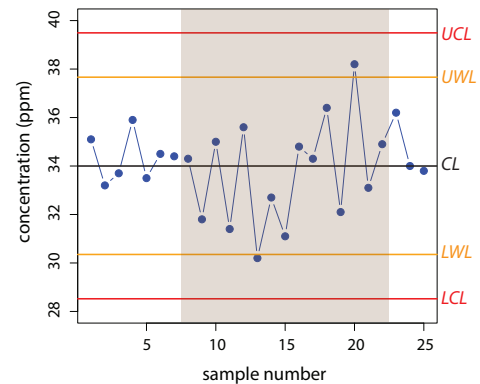

Figure SM15.1 Property control chart for the data in Problem 7. The highlighted region shows 14 consecutive cycles in which the results oscillate up and down, a sign that system is not in a state of statistical control.
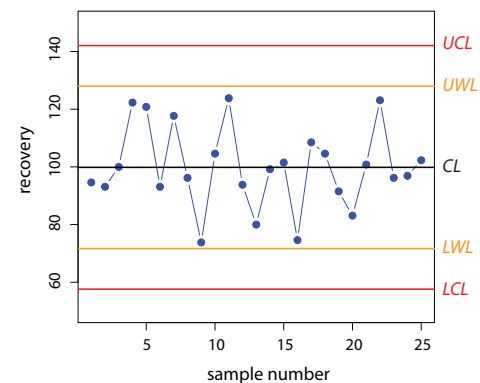

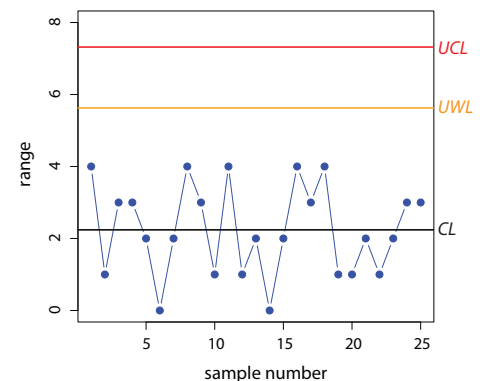**Figure SM15.2** Property control chart for the data in Problem 8.

Figure SM15.3 Precision control chart for the data in Problem 9.