Chapter 10: End-of-Chapter Solutions

1.
The following comparison provides general trends, but both atomic absorption spectroscopy (AAS) and atomic absorption spectroscopy (AES) will have analyte-specific exceptions. Due to the atomization requirement, both methods destroy the sample and measure the total concentration of a given element, i.e., neither provides information on analyte speciation. Obtaining speciation-specific results is possible by separating analytes before measurement.

	AAS	AES
scope	usually single analyte	simultaneous multi-element analysis
sensitivity	ppm range for flame AAS can be more sensitive than AES for easily ionized elements	ppb range for ICP-OES in general AES is more sensitive than AAS
atomization sources	sufficient signal at lower temperature (simpler and cheaper)	excitation efficiency increases with temperature

2.
The key difference between potentiometry and atomic spectroscopy is that an ion-selective electrode can be used in situ and it can be specific for a given speciation of an element. Atomic spectroscopy is generally more sensitive and provides total analyte concentration. The two methods are often used together to provide complementary information.

	potentiometry	atomic absorption spectroscopy
general	can be portable and used in-situ does not destroy sample simpler and less expensive	Lab-based destroys sample more expensive
sensitivity	sensitive (10^{-5} M, 1 ppm)	very sensitive (0.1 ppm typical)
selectivity	usually very selective	narrow line, so intrinsically selective
interferences	interferences for specific ion-selective electrodes are usually known and correctable with selectivity factors and additional measurements	high concentrations of refractory substances can reduce atomization efficiency
calibration	requires calibration standards	requires calibration standards
speciation	oxidation-state specific	total analyte concentration

3.
(a) Ca^{2+} and Mg^{2+} in leafy vegetables: The matrix is expected to contain multiple substances that can complex the analytes. In this case ashing the sample will reduce interferences. AES and AAS are both very sensitive for alkali and alkaline earth metals and will be the faster and preferred method. Ca^{2+} and Mg^{2+} ISEs can be used after digesting the sample and using the standard addition method for calibration.

(b) NO_3^- and NH_4^+ in surface water: nitrate and ammonium ISEs will be the preferred analysis. These two measurements will distinguish the analytes from each other and from other nitrogen species. Surface water will be a reasonably clean matrix.

(c) multiple metals: ICP-AES will provide simultaneous multi-element quantitation at the ppb level.

(d) ClO_4^- in sea water: A perchlorate ISE is suitable with correction for Cl^- in the seawater. ICP-MS is suitable but requires prior separation of perchlorate from Cl^- and any other chlorine-containing species.

(e) Co in steel: Spark source AES is sensitive and rapid (does not require dissolving the steel).

4.

The difference in these two masses is 111.91460 u − 111.90276 u = 0.01184 u. Using this value and the approximate *m* of 112:

$$\frac{m}{\Delta m} = \frac{112\text{ u}}{0.01184\text{ u}} = 9460$$

The required resolution is approximately 10,000.

5.

A simple interpolation between the calibration data is sufficient, but the equation is also easy to determine. The slope is:

$(1.284 – 0.033)/(10.0\text{ ppm}) = 0.1251\text{ ppm}^{-1}$

and the calibration function is:

$y = (0.1251\text{ ppm}^{-1})[Pb^{2+}] + 0.033$.

For the unknown measurement:

$0.471 = (0.1251\text{ ppm}^{-1})[Pb^{2+}] + 0.033$

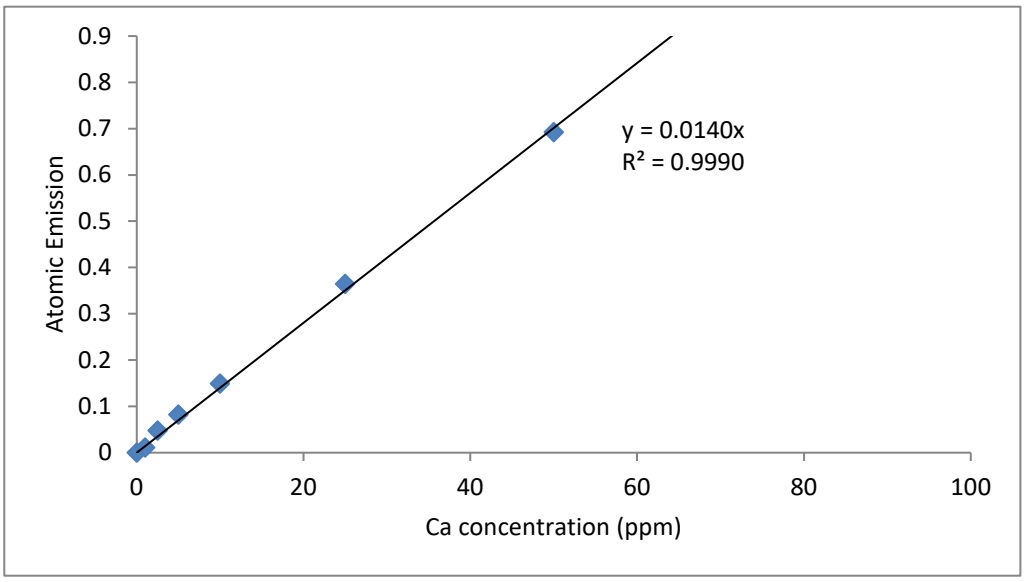
$[Pb^{2+}] = 3.50\text{ ppm}$

6.

The inductively coupled plasma (ICP) generates a much higher temperature than a flame, 6000-8000 K versus 1700-2700 K. The higher temperature results in much more efficient atomization and excitation. Detection limits are generally lower in the plasma, on the order of 1 ppb for ICP-AES vs. 0.1 ppm for flame AES.

7.

(a) A plot shows that the data is linear from 0 to 50 ppm.



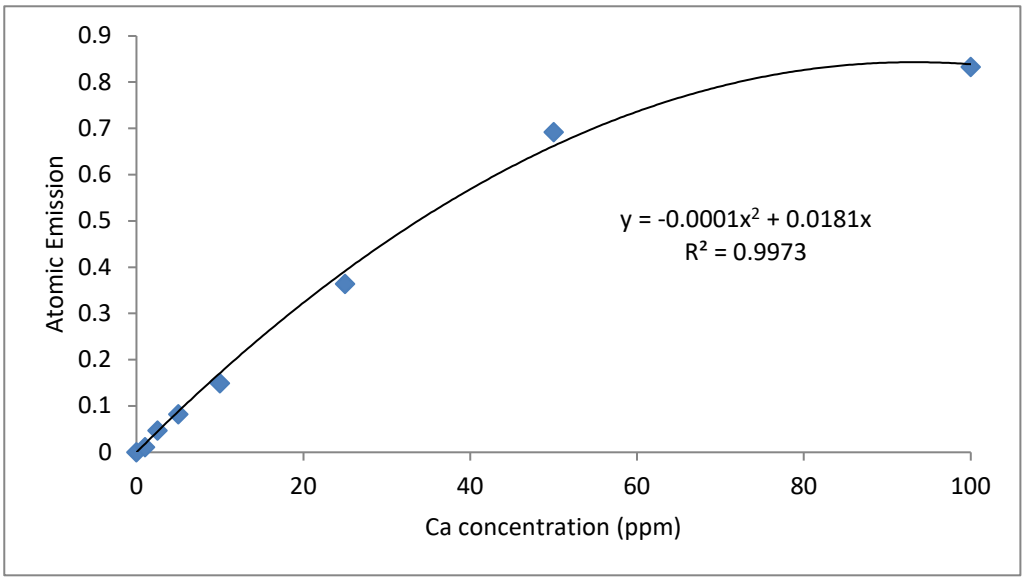
(b) Using the trendline shown in the plot:

$0.455 = (0.0140\ ppm^{-1})[Ca^{2+}]$

$[Ca^{2+}] = 32.5$ ppm

Given that the blank measurement was zero, I chose to force the calibration function through zero. There is only a small difference in the result if the trendline is allowed to vary the intercept.

(c) The unknown measurement is outside of the linear range of the experiment. You have two options. If you discover the situation as you are making measurements, you can dilute the unknown by a factor of 2 and measure the AES signal again. If you discover the situation after the instrument is turned off, you can try fitting the calibration data to a different function. The detector response in atomic spectroscopy is known to be non-linear at higher concentrations. A 2^{nd}-order polynomial is shown in the plot below. For a measurement of 0.952, the 2^{nd}-order polynomial trendline does not provide a good calibration curve. The analyst can be conservative and quote a result of > 50 ppm Ca. Depending on past data sets, it might acceptable to provide an estimate of 70 – 80 ppm Ca and note that calibration data was not measured at this concentration.

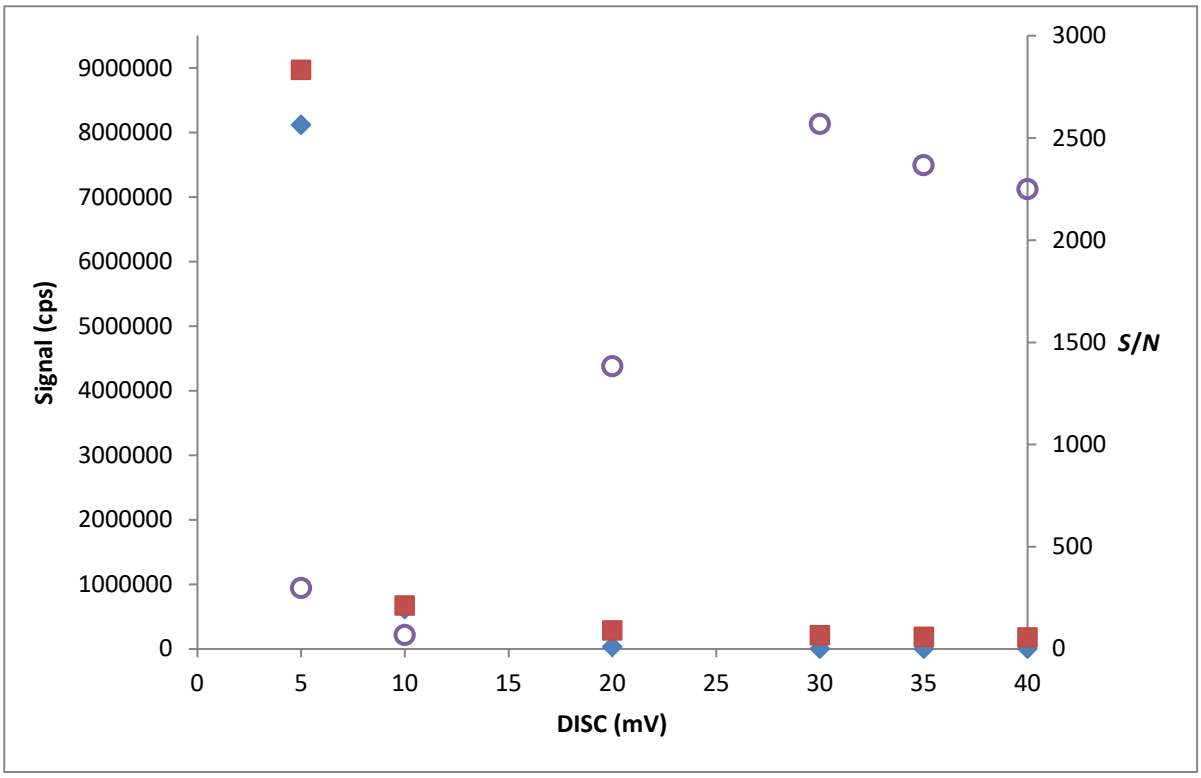


8.

Signals using count rates are common in mass spectrometers and fluorometers, that use electron multipliers and photomultipliers, respectively. The details of setting a discriminator level for a detector is more advanced than we need to consider. The purpose of this question is to think about data and the resulting signal-to-noise ratio. Looking at the tabulated data, the signal of the blank, due to background, decreases rapidly as a function of DISC. The signal of the test solution is the summation due to the analyte and the blank. It also falls off rapidly versus DISC, but levels off at a higher level than the blank. For example, the analyte signal at DISC = 40 mV is 179000 cps – 5920 cps = 173000 cps. Subtracting the high background at lower DISC introduces greater uncertainty in the result. The following plot shows signal counts on the left vertical axis for the data in the table. On the right vertical axis is *S*/*N* for the open circles. The open circles are found from:

$$S/N = \frac{(\text{test solution} - \text{blank})}{\sqrt{\text{blank}}}$$

where the square root of the blank serves as an estimate of the noise. Based on the plot, a discriminator level of DISC = 30 mV provides the best *S*/*N*.



9.

The atomization source, a flame, furnace, or plasma, creates background light emission that will reach the detector. This background signal is not related to analyte concentration and is subtracted from the detector signal. In atomic absorption spectrometry, the absorption signal might be affected by absorption due to molecular species. A background correction technique will also remove this source of error. These background sources can vary depending on the matrix of the sample.

10.

In graphite-furnace atomic spectroscopy (GFAAS), the test portion is introduced as a small plug of liquid or solid directly into the furnace tube. Since only microliters of the test portion are needed, measurements can be made when the amount of sample is very limited. The main disadvantage of GFAAS is that it measures a transient signal, and it is not possible to signal average during any one measurement. The result is a less precise measurement compared to using a nebulizer to measure a signal for a longer time. Multiple GFAAS measurements can be made if sufficient sample is available, requiring a longer time to complete the measurement. The matrix effects in GFAAS can also require more extensive method validation for a given analyte and sample matrix.

11.

Refractory sample constituents can be digested with aggressive acid and redox reagents. The downside is the potential loss of analyte in this process. Other methods include direct

introduction of the sample in graphite-furnace AAS or spark source AES. These methods are rapid. They are best suited for repetitive analysis of similar samples so that matrix effects can be corrected after thorough method validation. The laser ablation sampling method is a third alternative, which has the advantage of providing spatially resolved elemental analysis on a heterogeneous sample.

12.
Atomic spectra have very narrow linewidths of 0.1 nm and less. Molecular spectra consist of broad bands, often 50 to 100 nm wide. An atomic spectrometer must have a resolution on the order of 0.1 nm or less to resolve closely spaced lines. Spectrometers for molecular absorption and fluorescence will have resolution on the order of 1 nm.

13.
The high vapor pressure of Hg leads to loss of analyte when handled in conventional ways. The cold-vapor technique, which keeps the analyte in solution at room temperature before measurement, minimizes this loss for more accurate Hg determinations.

14.
The nonmetals have atomic transitions at wavelengths shorter than 190 nm. This region is called the vacuum ultraviolet (VUV) region because working in this region requires evacuation of atmospheric gases, mainly oxygen, that absorb this light strongly. Although ICP-OES is capable of measuring nonmetals with a suitable evacuated spectrometer, ICP-MS is usually the method of choice.

15.
Measuring isotopic ratios is usually done by mass spectrometry. Isotopes will differ by one or more mass units. Measurement of the stable isotopes of elements requires a mass spectrometer with moderate resolution, on the order of 500. The atomic emission lines of different isotopes will have slightly different wavelengths, but the differences are very small and requires a very high-resolution spectrometer to resolve.

16.
A magnetic-sector mass spectrometer separates two isotopes spatially. It can therefore measure two isotopes simultaneously with two different detectors. The simultaneous measurement maximizes sample utilization and the precision of the measurement. (The precision in counting a low signal is dependent on the number of data points acquired.) Using two detectors also allows measurement of a high dynamic range by using one detector in counting mode for the low abundance isotope and one detector in analog mode for the high abundance isotope.

17.

A time-of-flight mass spectrometer separates ions based on flight time. Unlike other mass analyzers, there is no physical limitation on how large a mass that can be measured. The only requirement to measure high-mass ions is to wait for them to reach the detector.