Water Quality 2 - Determination of Ca, Mg, Fe, and Na by Flame Atomic Spectrophotometry

Introduction

Atomic spectroscopy is one of the most widely used methods for quantitative elemental analysis. There are a number of situations where elemental composition is important – *e.g.*, how much iron in an ore sample, how much lead in your drinking water, calcium in intracellular fluids. In a sense, it's the simplest type of analysis, since there are only about 120 possible analytes. But to do the analysis, the sample has to be completely destroyed (chemically and physically) and reduced to individual gas phase atoms (or related species, like ions) in well defined states that you can do spectroscopy on. Obviously this requires a very highly energetic environment and a lot of modification of the sample, both of which lead to a number of complications. These problems can be addressed if their presence is anticipated and the physical mechanism is understood. In addition to giving you a little experience with AAS (Atomic Absorption Spectrophotometry) and AES (Atomic Emission Spectrophotometry) for quantitative determination of a few elements, we'll also investigate some of these practical concerns during the experiment.

An obvious (if somewhat simplistic) application of the determination of calcium and magnesium in water is testing for hard water. Water hardness is defined as the total concentration of alkaline earth metal ions in water. Because the concentrations of Ca^{2+} and Mg^{2+} are usually much higher than those of other alkaline earth ions, hardness can be equated to $[Ca^{2+}] + [Mg^{2+}]$, although this is usually expressed as mg/L of $CaCO_3$. Individual hardness refers to the individual concentration of each alkaline earth ion. Thus, if $[Ca^{2+}] + [Mg^{2+}] = 1$ mM, we would say that the hardness is 100 mg $CaCO_3$ per liter (because 1 mmol $CaCO_3$ = 100 mg $CaCO_3$). Water that is more than 60 mg $CaCO_3$ per liter is considered to be "hard". Hard water causes the formation of scale (insoluble compounds formed from alkaline earth metals and organic acids in soap) in pipes, water boilers, and water heaters, and consumes soap that would otherwise be useful for cleaning. It is not currently believed that "hard" water is unhealthy – in fact drinking deionized water is bad because it does not contain the normal electrolyte balance.

Hardness can be determined by a number of methods including EDTA titration (as is done in CH 321) and atomic absorption and emission spectrophotometry. In this experiment, you will use flame atomic absorption spectrophotometry (AAS) to determine the concentrations of Ca^{2+} and Mg^{2+} in both cold and hot tap water, and in “unknown” challenge samples. You can bring your tap water from home or use some from the school. We also recommend that you bring a bottle of mineral water and test it as an unknown, since these samples typically contain high levels of both cations.

We will then use AAS to determine iron, allowing you to compare this method to the colorimetric complexation reaction / spectrophotometric determination used in the other experiment of this set. You will thus use the same calibration set and unknowns as you did in the previous experiment (without the colorimetric reagent, buffer, and hydroxylamine) to facilitate a head-to-head comparison of the two methods. Calcium and magnesium are both determined with a combination hollow cathode lamp (HCL) but iron requires a separate lamp (as do most elements) as well as a different operating wavelength. Iron is an interesting non-toxic surrogate for heavy metals, whose presence in drinking water supplies is an important public health issue.

Atomic emission spectroscopy (AES) is a convenient method for the determination of alkali metals in water samples. These metals are easily excited in flames and consequently can be determined at low concentrations by flame emission. The characteristic emission lines of these metals (*e.g.*, 589.0 nm and 589.6 nm for the $3p \rightarrow 3s$ transition of sodium atoms) can be used in both qualitative and quantitative analyses of unknown samples. In this experiment, you will use AES to determine concentrations of sodium in the tap water and unknown samples. Sodium is nearly omnipresent in water – it is difficult to find a solution in the laboratory that isn’t extensively contaminated with sodium. You will also study the effect of flame pathlength on the linearity of the calibration curve and the sensitivity of the measurement. Previously we also studied the effect of an ionization suppressant, but that was found to have little effect on the linearity of the sodium working curve, so we discontinued this procedure (but you might find it interesting to read about it in the text from the lecture or online).

Apparatus

500 μL automatic pipettor (1)
5.0 mL pipet (1)
100 mL volumetric flask (1)
1000 mL volumetric flask (1)
400 or 500 mL beakers (6)
200 mL beakers (4)

Instrumentation (See Appendices for Operating Instructions)

Shimadzu 6300 AAS AA/AE Spectrophotometer

Solutions to be prepared (or obtained)

(1) Calcium stock solution: Accurately weigh out about 0.252 g (to 0.001 g) of dry primary standard calcium carbonate ($CaCO_3$, FW=100.087). Rinse into a 100 mL volumetric flask with a few milliliters of deionized water. Dissolve in a minimum amount of 6 M HCI (a few mL) then dilute to the mark with deionized water and mix thoroughly.

(2) Magnesium stock solution: Accurately weigh out about 0.101 g (to 0.001 g) of dry magnesium oxide (MgO, FW = 40.304). Rinse it into a 1000-mL volumetric flask with a few milliliters of deionized water. Dissolve in a minimum amount of 6 M HCI (a few mL) then dilute to the mark with deionized water and mix thoroughly.

(3) NaCl stock solution: Accurately weigh out about 0.510 g (to 0.001 g) of NaCl (FW = 58.442), quantitatively transfer into a 200 mL volumetric flask, dissolve in deionized water, dilute to the mark, and mix thoroughly.

(4) Standard iron solution (5.0×10^{-4} M). Accurately weigh out about 0.100 g $Fe(NH_4)_2(SO_4)_2$-$6H_20$ (FW = 392.14). Transfer quantitatively into a 500-mL volumetric flask. Add about 10 mL of 2 M H_2SO_4 and 50-mL deionized water to the flask to dissolve the $Fe(NH_4)_2(SO_4)_2$-$6H_20$ completely. Fill the flask to the mark with deionized water and mix thoroughly.

Calculate and record the actual concentration of the four standard solutions.

(5) Prepare mid-range challenge “unknown” samples of all four analytes to test for method recovery and accuracy. Also bring (or obtain) unknown samples (optimally including your water from home and some mineral water that you like) for the Ca, Mg, and Na experiments. Finally, obtain hot and cold tap water samples from home or the SRTC taps.

Procedure

(1) AAS Measurement of calcium:

To five dry beakers add 250 mL of deionized water (use a graduated cylinder but measure the volume as carefully as you can.) Use the 500 µL automatic pipettor to add 0.0, 0.5, 1.0, 1.5, and 2.0 mL of the calcium stock solution to the beakers and mix thoroughly. The concentrations of calcium in these standards should be calculated.

Set up the flame atomic spectrophotometer as described in the operating instructions. Measure the full set of standards and unknown samples before switching to another element. Dilute any unknown sample(s) if the measured absorbance is too large – i.e., outside of the range of the standards.

(2) AAS Measurement of magnesium:

Repeat procedure (1) using the magnesium stock solution and the unknown samples. Remember that the element selection on the AA (the drop down box) has to be changed to measure magnesium.

(3) AAS Measurement of iron:

Use a 5.0mL pipet (or a graduated cylinder, if you prefer) to add 0, 5.0, 10.0, 15.0, 20.0, and 25.0 mL of the standard iron solution into a series of six 50 mL volumetric flasks. Fill each flask to the mark with deionized water and mix thoroughly. Mix the solutions again before measuring the absorbance. Be quick in your measurements, since the AAS will consume the 50 mL of solution very rapidly. Also remember that the element selection on the AA (the drop down box) has to be changed to measure iron.

(4) AES Measurements of sodium:

(A) Preparing the standard solutions:

To the six dry 400 mL beakers add 250 mL of deionized water (use a graduated cylinder but measure the volume carefully), and then accurately pipet 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of the NaCl stock solution, and mix each thoroughly. Again, the concentrations of sodium in these standards should be calculated and recorded.

(B) Setting up the instrument:

Set up the spectrophotometer according to the operating instructions. In this experiment, the measurements will be made with the long axis of the flame *both* parallel and perpendicular to the light path. (You'll probably go ahead and do the parallel measurements first, since that's the orientation used for the AAS measurements above.) After you finish the measurements with one flame position, turn the bumer head 90 degrees. Then continue on to make the rest of the measurements in the other flame position (on the separate MRT).

(C) Measuring the emission intensity:

Auto zero the instrument with deionized water, and measure the emission intensity of all the standards and water samples. Dilute the unknown samples if the emission intensity is too high (*i.e.*, beyond the range of the calibration curve). Don't forget to make the measurements with the flame in both the parallel and perpendicular positions.

Report: In preparing your Final Report, you should consider/complete/discuss the following (not necessarily in this order) in addition to the issues you discussed in connection with the first part of the experiment in the Partial Report:

(1) Tabulate and plot the absorbance *vs.* concentration for the calcium, magnesium, and iron measurements. You can display the magnesium and calcium calibrations on a single figure because their concentrations are similar. Derive the calibration equations and calculate the concentrations of calcium and magnesium in the tap

water and the unknown samples. Comment on the concentrations of iron determined in the challenge and tap samples. Include estimates of the uncertainties for all calculated concentrations. Calculate the hardness of the water samples and comment on whether they are "soft" or "hard". Discuss the difference in hardness between the cold and hot tap water if any is observed.

(2) Compare the atomic absorption method and the spectrophotometric measurement in this set for determining iron. (Compare the accuracy, recovery, and limit of detection for the two methods and comment on the relative difficulty and cost of performing the two methods.) If you wish, you can also compare the AAS method to the EDTA titration method for the determination of total hardness, based on your past experience with the ETDA method (*e.g.*, in CH 321.)

(3) Tabulate and plot the emission intensity vs. sodium concentration for the NaCl standards and derive the calibration equation for the two sets of measurements (both burner orientations). You should probably use a polynomial equation (*e.g.*, a cubic equation) to fit the data if either of the calibration curves are nonlinear. Be sure to comment on what you end up using in the Discussion section of your report. Calculate the concentration of sodium in the tap water samples and the other unknown samples. If you use a linear calibration curve, you should also report the standard error in the calibrated results for the unknowns. (We don’t have the formulas to do this for the non-linear forms.)

(4) It is likely that the calibration curve obtained with the flame in the parallel position will have a larger degree of nonlinearity but a higher sensitivity (*i.e.*, a larger slope of the calibration curve) than the one obtained with the flame in the perpendicular position. Explain why the sensitivity of the measurement is higher when the flame is in the parallel position, but this still might not be the preferable orientation. {Logically, you would only report the “best” value for the sodium concentration of the unknowns in the abstract of this report.}

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