Experiment 3

ANALYSIS OF ALUMINUM(III) IN WATER

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PURPOSE

Determine the aluminum(III) ion concentration in a prepared unknown using a spectrophotometric analysis based on the aluminum(III)-Eriochrome Cyanine R complex.

THE ALUMINUM-ACID RAIN CONNECTION

The concentration of aluminum(III) ion in surface water is related to its acidity since aluminum(III), present in the soil as insoluble mineral compounds, becomes soluble at low pH. Thus, acidic mine drainage and acid rain can affect the aluminum(III) concentration in water.

The term "acid rain" is somewhat misleading because atmospheric carbon dioxide gives even "pure" rain water an acidic pH of 5.6. This natural acidity results from the following reactions:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \quad (1)$$

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \quad (2)$$

Additional acidity, what we call acid rain, results from the reaction of sulfur and nitrogen oxides in the atmosphere to form nitric and sulfuric acids, which ultimately are carried to the ground as acidified rain, snow or fog. The sulfur oxides are formed from the combustion of sulfur compounds in fossil fuels. Nitrogen oxides form by reaction of atmospheric O_2 and N_2 whenever it is heated, as in the combustion chamber of an engine.

Aluminum is the third most abundant element in the Earth's outer crust. The following reaction (unbalanced) shows how the H^+ from acid rain leaches the aluminum in feldspar, $KAlSi_3O_8$, into surface water.

$$KAlSi_3O_8(s) + H^+(aq) \rightleftharpoons Al_2Si_2O_5(OH)_4(s) + H_4SiO_4(aq) + K^+(aq) + Al^{3+(aq)} \quad (3)$$

The Environmental Protection Agency classifies surface water of pH 5 or lower as "critical" or "acidified", and has recommended that aluminum(III) levels in drinking water be maintained below 0.1 ppm. Growth reduction in fish has been observed at this level, and damage to fish gills and tree roots has been reported at even lower concentrations. To avoid human renal failure, aluminum(III) concentration in kidney dialysis water must be below 0.02 ppm.

Another possible source of aluminum is water treatment plants, which often use aluminum sulfate and polyaluminum chlorides in their purification process. These compounds are very insoluble and serve to coagulate and precipitate other contaminants from the water. Of course, a small amount of the aluminum must dissolve.

A NEW CONCENTRATION UNIT

For dilute solutions a common unit of concentration is parts per million (ppm). This unit is similar to weight percent, except the amount of solute is so small that instead of saying there are so many g of solute in 100 g of solution (which is pph – parts per hundred – more commonly referred to as the percentage), the number of g of solute per 1,000,000 g of solution is used.

$$ppm = \frac{mass\ solute}{mass\ solution} x10^6 \qquad (4)$$

For dilute aqueous solutions the density is approximately equal to that of water (1.00 g/mL). Therefore, for aqueous solutions ppm is **defined as the g solute per 10^6 mL of solution**.

$$ppm = \frac{mass\ solute}{mL\ solution} x10^6 \qquad (5)$$

This is more commonly expressed as mg solute per L solution (1 ppm = 1 mg/L).

$$ppm = \frac{mg\ solute}{L\ solution} \qquad (6)$$

Notice that this last form looks a lot like the definition of molarity (quantity per liter). Consequently, **calculations involving ppm can be treated analogously to those involving molarity. This includes the always useful dilution formula.**

THE SPECTROPHOTOMETRIC ASSAY FOR ALUMINUM

Spectrophotometric analysis of aluminum(III) is possible using a compound called Eriochrome Cyanine R (ECR) which forms a red complex with aluminum(III) having an absorbance maximum at 535 nm. The equation for formation of the complex is:

$$Al^{3+}(aq) + 2\ ECR^{3-}(aq, orange\ red) \rightarrow Al(ECR)_2^{3-}(aq, red) \qquad (7)$$

By measuring the absorbance for a solution of known concentration, the molar absorptivity ε can be calculated ($\varepsilon = A/bc$). The concentration of an unknown solution can then be obtained by measuring its absorbance and using Beer's law.

A better way to determine an unknown solution is to construct a **standard curve** by plotting the absorbance of standard (known) solutions versus their concentrations. This works because Beer's law ($A = \varepsilon bc$) is in the form of the equation of a line, y = mx + b, where the y-intercept b is equal to zero. Thus, a plot of absorbance *A* (y-axis) vs. concentration *c* (x-axis) will be linear with a slope equal to εb. Such a graph is also called a **Beer's law plot**.

The concentration of an unknown is then found by measuring its absorbance, and finding the corresponding value of *c* on the standard curve (graphically or algebraically from the equation of the line). This procedure is better than relying on a single value of ε because, as discussed later, it allows you to see if there was a "blank error", or if the standard curve is not linear (in fact, *curved*).

This analysis of this $Al(ECR)_2^{3-}(aq)$ colored complex involves several complications that you may not have encountered before, but which frequently arise in spectrophotometric analyses:

(1) The composition of the colored complex is pH dependent. For this experiment, the optimum pH is around 6.2. This will be handled by addition of a buffer solution to all of the samples.

(2) The colored complex is not stable. This requires that the absorbance of each solution be measured a fixed time after preparation, rather than preparing all solutions first and then reading their absorbances.

(3) The uncomplexed detection reagent (ECR) is colored. This requires that a blank solution other than distilled water be used in the spectrophotometer.

(4) Other interfering substances may be present in the sample being analyzed. In this analysis, certain metal ions other than aluminum(III) are known to also react with ECR, and fluoride competes with ECR for the aluminum. So, some provision must be made to eliminate the effects of these possible interferences.

(5) Finally, the standard curve may not be a perfectly straight line.

WHAT IS A GOOD BLANK?

Life is simple when the chemical being analyzed is the only thing in the solution that absorbs light. However, often there are additional species in the solution that absorb light. If a distilled water blank is used for such a solution, at zero concentration of the chemical being analyzed, there will still be absorbance due to the other absorbing species.

This problem is solved by using a proper blank. A blank should contain everything in the standard solutions and unknowns *except* the species of interest. In this experiment, the ECR reagent is colored, even in the absence of Al(III). Therefore, the blank must include the same amount of ECR as the other solutions will contain. Furthermore, we should include all of the other colorless reagents in the blank, just in case they affect the ECR's absorbance.

When the standard curve doesn't go through the origin, the fault is most often due to an improperly prepared blank. If the blank is too light, the other measured absorbances will be too high, and the *y*-intercept of the standard curve will be greater than zero. Conversely, if the blank is too dark, the other measured absorbances will be too low, and the *y*-intercept will be negative. However, the standard curve will still be useful since the absorbances of the standards and unknowns will all be *off by the same amount*, and the displaced standard curve will make the appropriate corrections.

HOW INTERFERENCES ARE ELIMINATED

In this experiment, the same ECR reagent that produces a colored complex with Al(III) also produces a colored complex with any iron or manganese that might be present in the sample. This can't be fixed with the blank because the amount of iron or manganese present is unknown. Rather, the possible interference is eliminated by pretreating the sample to remove any iron or manganese that might be present. The sulfuric acid and ascorbic acid (vitamin C) reagents are added to reduce any Fe(III) to Fe(II), and then complex the Fe(II) and Mn(II) so tightly that the ECR can't react with them.

NONLINEAR STANDARD CURVES

There's no law that says a standard curve *must* be straight to be useable. However, we strongly prefer a linear standard curve because it is easier to locate the best position for a straight line than for a curve

There are two main reasons why a spectophotometric standard curve might not be straight. First, at high absorbances (low *%T*) very little light is transmitted so "stray light" from leaks or reflectance can make the measured absorbance lower. This is often a problem for absorbances greater than 1.

The second reason is that something is going on in the solution. For example, at high concentrations, dissolved species may combine to form aggregates with different molar absorptivities than the separate molecules.

If it is obvious that your standard curve is not straight, the "best smooth curve" should be drawn through the points. This is not a license to follow-the-dots through scattered absorbance readings. If it is not linear, the standard curve will gently curve either up or down, but it will not have wiggles or kinks. Most often, the low-concentration end of the plot will be linear, with curvature setting in at higher concentrations.

For this reason, *the plot of absorbance versus concentration must always be made and visually inspected*, rather than trusting solely in a numerical analysis of the data.

IN THIS EXPERIMENT

In this experiment you will prepare five standard solutions of Al(III). The wavelength of maximum absorbance will be determined from the Al-ECR complex's spectrum. The absorbances of the standard solutions will be measured at the wavelength of maximum absorbance and a standard curve will be constructed. The concentration of Al(III) in an unknown sample will be determined by measuring its absorbance and using the standard curve.

If you wish, you may bring a water sample from home, work, a pond, or wherever and measure the aluminum concentration.

PRE-LABORATORY PREPARATION

1. Read the procedure and data analysis sections of the experiment.
2. Complete the PRELAB assignment in Canvas. Refer to the procedure and data analysis sections of the experiment as needed. The prelab questions for this experiment exactly replicate the questions in the data analysis section.
3. You may, if desired, bring a water sample of your choice to analyze for aluminum content.

EXPERIMENTAL SECTION

REAGENTS PROVIDED

Acetate buffer solution.
Aluminum(III) stock solution, 5.00 mg/L or 5.00 ppm.
Ascorbic acid solution. Vitamin C.
ECR solution. Eriochrome Cyanine R in dilute aqueous acetic acid.
Sulfuric acid, 0.010*M*.
Unknown Al(III) solution.

Hazardous Chemicals

Handle the sulfuric acid solution with care.

WASTE DISPOSAL

All of the chemicals used in this experiment may be safely disposed of by washing down the sink.

PROCEDURE

You will work with a partner to prepare the standard solutions and determine the standard curve. However, each student must analyze his/her own unknown.

PREPARATION OF THE BLANK SOLUTION

1. Prepare a blank solution in a clean 100.00 mL volumetric flask by adding the following solutions, in the order given:
(a) **10.00 mL ECR solution**
(b) **20.0 mL buffer solution**
(c) **2.0 mL ascorbic acid solution**
(d) **2.0 mL 0.010*M* sulfuric acid**

Mix well after each addition, fill with distilled water to the calibration mark, and mix the final solution thoroughly by inverting the capped flask.

An auto-fill buret, providing both accuracy and convenience, should be used to dispense the ECR solution. If you are careful not to add too much, it is simplest (and most accurate) to add the ECR directly into the volumetric flask from the buret. Graduated cylinder accuracy is sufficient for the last three solutions.

2. Clean a 50-mL buret and pour about 40 mL of the stock Al(III) solution into it.

This amount will be sufficient to prepare all of the standard solutions.

Be sure to rinse the buret before filling it. Always place a buret in a buret stand and use a funnel when pouring into a buret.

Record the concentration of the stock Al(III) solution.

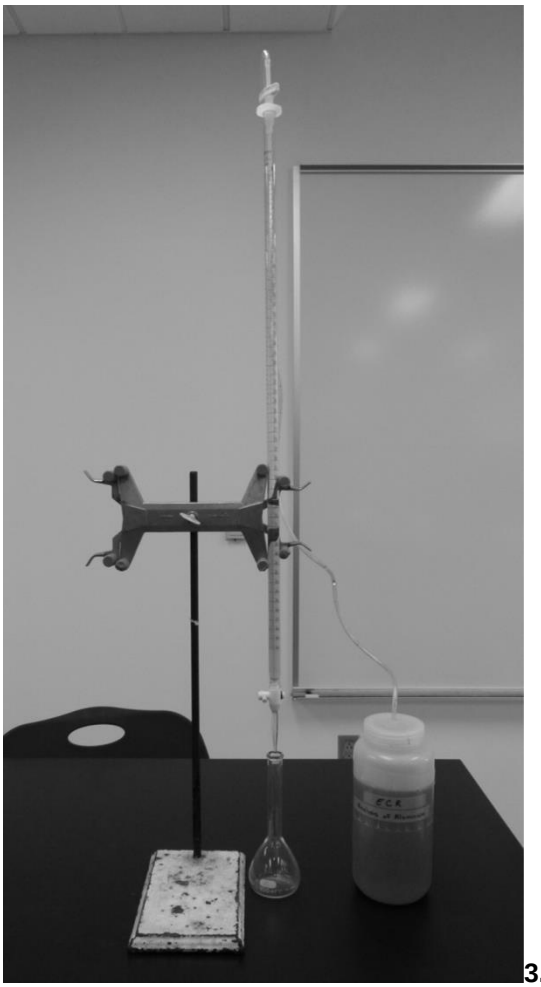

Figure 1. An Auto-fill buret.

3. Prepare standard solution 1.

Into a clean 100.00 mL volumetric flask, add the same four solutions used to prepare the blank, see 1(a)-(d). Then add the amount of aluminum stock solution, from the buret, indicated in the table below. Next fill to the mark with distilled water. Finally, mix thoroughly.

Note the time. *You need to wait exactly 8 minutes after adding the Al(III) until you measure* the spectrum of this solution (step 6).

The aluminum—ECR complex takes time to form and is not stable for more than about 20 minutes. Thus, the absorbance of each standard changes with time and all absorbances must be measured a fixed time interval after preparation. The same will apply for the unknown (but not for the blank since it contains no aluminum).

Solution #:	1	2	3	4	5
mL Al(III) soln:	8.00	6.00	4.00	2.00	1.00

Record the actual volume of Al(III) used (to the nearest 0.01 mL) on your data sheet.

MEASURE THE ABSORBANCE Vs. WAVELENGTH SPECTRUM

4. Turn on the LabQuest2 by pressing the red power button on the top and connect the cable from the SpectroVis spectrometer to the USB port on the LabQuest2.

The USB port is on the left side of the Lab Quest2 near the top.

5. Calibrate the spectrometer.

a. Tap on ***Sensors*****.** Next choose ***Calibrate*** and then ***USB: Spectrometer***.
b. Allow the spectrometer to go through the 90 second warm up.
c. Insert the blank cuvet, filled with the solution prepared in step 1. The clear sides of the cuvet should be facing in the direction of the ► on the spectrometer.
d. Tap **Finish Calibration**. The calibration will finish in a couple of seconds. Then tap **OK**.

While waiting to perform step 6, you can begin preparing solutions 2-5 using the same procedure described in step 3. Again, note the time of preparation for each solution. You will want to analyze each solution 10 minutes after it is prepared. (We only wait 8 minutes for solution 1 because it will take a couple minutes to choose the wavelength of maximum absorbance and configure the software before taking the reading.)

Once a solution has been prepared you can pour it into another container so that you can re-use the volumetric flask. Rinse the flask thoroughly with distilled water, but it does not need to be dried before reuse, because more water is going to be added.

6. Exactly 8 minutes after preparing solution 1, fill a clean cuvet with this solution, insert it into the spectrometer, and tap the Start button.

7. Wait a few seconds for the spectrum to roughly stabilize, then tap *Stop*.

In the boxes to the right of the spectrum you will be able to see the selected wavelength and the absorbance at that wavelength.

If you have an older Labquest2, it will automatically select the wavelength of maximum absorbance (λ_{max}) for you, while newer ones will not. *The wavelength listed in the box should be 535 (±15) nm.* If the selected wavelength is NOT equal to λ_{max}, tap on your A vs. λ curve at its highest point to change the boxed reading to λ_{max}. This is very important since the subsequent readings you take will be at this wavelength

Record λ_{max} on your data sheet.

Note that it is NOT necessary to remeasure the spectrum for solutions 2-5.

PREPARATION OF THE STANDARD CURVE

8. Change mode to collect absorbance vs. concentration data as follows:

a. Tap on the **Meter icon** (in the screen's upper left corner) to return to the initial screen).
b. Tap on the **Mode box** (on the screen's right side)
c. Select ***Events with Entry*** from the top scroll box.
d. Enter *conc* as the name and *ppm* for the units. Tap ***OK***.
e. Choose to ***Discard*** your spectral data.

9. Tap the *Start* button.

10. With solution 1 still in the spectrometer, tap *KEEP* (this button should appear to the right of the Stop button). Enter the calculated concentration of solution 1 into the dialog box and then tap *OK*. Also, record the concentration and the measured absorbance.

If you added exactly the prescribed volume of Al(III), the concentration should be the same as that calculated for the prelab.

By default, the LabQuest2 will display entered data to 2 places after the decimal in the Data Table. You can change this by tapping on the data column name and choosing the desired precision.

11. Finish preparing standard solutions 2-5, as described above. Wait 10 minutes after each solution is mixed and then follow the steps below to read and record the absorbance of the standard solution at the wavelength of maximum absorbance.

a. Rinse a cuvet (three times) with the standard solution you have prepared. Discard the rinsings each time.
b. Fill the cuvet (3/4 of the way to the top) with the standard solution and insert it into the spectometer.
c. Wait for the absorbance reading to roughly stabilize.
d. Tap on the **KEEP** button.
e. Enter the concentration of the standard solution into the dialog box that appears and tap ***OK***. If you added exactly the prescribed volume of Al(III), the concentration should be the same as that calculated for the prelab.
f. Record the absorbance and concentration on your data sheet.

If you enter the wrong concentration, you can edit it after you have stopped data collection. Just tap on the data table icon (in the upper right) and then double-tap on the cell and enter the new concentration.

At any time, you can rescale the graph axes by tapping on the ***Graph*** menu and then ***Autoscale once***.

12. Decide whether your data looks good, or whether any points need to be redone. Consult your instructor if you unsure.

If you have data points that do not fit with the other points on the standard curve:

a. Remake the solution(s) and measure the absorbance(s) as in step 11, above.
b. Carefully examine the new results. The graph will be a bit cluttered since it also contains the old, erroneous points. After you tap on the **Stop** button, p*oints can be removed by tapping on the row in the data table and then selecting **Table** from the top menu, followed by **Strike Through Data**. (A data point can be restored by following the*

*same procedure, but tapping on **Restore Data**, instead.)*

c. You can collect additional data by tapping the **Start button** and choosing to ***Append***.

If your standard curve looks straight (or, at least, smooth):

a. Tap on the **Stop** button. (If necessary, you can go back and add points by tapping the Start button and choosing to Append.)

b. Unless it clearly is a curve, perform linear regression on your data. By default, all of the points will be used. A smaller range of points can be selected by dragging your finger/stylus across the graph. Choose ***Analyze*** (from the top menu on the Graph screen) then ***Curve Fit***. Tap on the name of your data set that appears. Then select ***Linear*** for the Fit Equation. *Record the slope and y-intercept on your data analysis page (question 2)*. Be sure they have correct units (remembering that absorbance is unitless). Tap ***OK*** to return to the Graph screen.

c. Print out a copy of the graph. To do so:
   i. Tap on the **Graph icon** (if you are not on the Graph screen).
   ii. Tap ***File*** from the top menu.
   iii. Tap ***Print*** and then ***Graph***.
   iv. Tap on ***Print Graph Title***.
   v. Enter an appropriate graph title. Usually, the title tells what is graphed in the format "Y" vs "X" (e.g., Absorbance vs Concentration).
   vi. Tap ***Print***.

ANALYSIS OF THE UNKNOWN SOLUTION

Each student should do his/her own unknown.

13. Bring your instructor a clean, dry 50-mL beaker.

You will receive about 20-30 mL of unknown.

14. Pipet 10.0 mL of your unknown solution into a 100.0 mL volumetric flask.

15. Add the first three solutions used to prepare the blank (1a, b, and c), mixing after each addition. Do NOT add the sulfuric acid (this has already been added to the solution you receive). Fill to the mark with distilled water, cap and mix.

16. Wait 10 minutes and then read the absorbance of the unknown at the wavelength of maximum absorbance.

You do NOT need to use the Start button to collect data for the unknown. Simply tap on the Meter icon (in the upper left corner of the screen and read the absorbance off of the screen.

Record the absorbance and unknown number.

ANALYSIS OF YOUR OWN WATER SAMPLE (Optional)

17. Using a graduated cylinder, measure 50.0 mL of your water sample into a 100.0 mL volumetric flask.

18. Add the same four solutions used to prepare the blank, mixing after each addition.

Fill to the mark with distilled water, cap and mix.

19. Wait 10 minutes and then read the absorbance of your water sample.

CLEANUP

20. Shutdown the LabQuest2.

This can be done by first tapping ***File**, then **Quit***. Choose to ***Discard*** the data. Next, tap on the ***System*** folder and then ***Shut Down*** and, finally, ***OK***.

It is always a good idea to wash your hands before leaving lab.

Name _____ Station Used _____ Instructor/Day/Time _____

Partner _____ Station Checked & Approved _____

DATA SHEET

You may wish to record other data and observations below, for which there are no lines (e.g., the absorbance of an optional water sample or the time when each solution was mixed -- to be sure you read the absorbance after exactly 10 minutes).

Concentration of the stock aluminum(III) solution _____

Wavelength of maximum absorbance _____

Volume of Aluminum Stock Solution (mL)	Absorbance	Concentration (ppm)

Unknown Number	Absorbance	Name

Water Samples:

DATA ANALYSIS

Each individual should attach this page to the Data Sheet and standard curve generated by the group. Calculations must be clearly organized, with proper significant figures and units.

1**.** The concentration of aluminum(III) in ppm was calculated in the Prelab for each of the standard solutions (assuming the assigned volume was used). **Enter these results alongside your absorbance data on the Data Sheet**.

2. **If your standard curve is linear**, enter the slope and y-intercept below (with proper units):

slope _____ y-intercept _____

If your standard curve is nonlinear, either draw the best smooth curve through the points on the computer printout or figure out how to get the computer to do it.

In either case: extrapolate your standard curve back to the y-axis. Does the standard curve go exactly through the origin? If not, is your blank too dark or too light? How do you know?

3. **What is the Al(III) concentration (in the cuvet) of your unknown, based on its absorbance and the standard curve?** If you calculate it from the linear regression data, show your calculation below. Otherwise, draw tie lines on the graph to show how the value was obtained.

unknown [Al(III)] _____

4. **Allowing for the dilution required to prepare the unknown sample for spectrophotometric analysis, calculate the Al(III) concentration in your original unknown solution**. Show your calculation below.

unknown [Al(III)] _____

unknown # _____

Name _____