Determining Aluminum(III) Concentration in Natural Water

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PURPOSE OF THE EXPERIMENT

Determine the aluminum(III) ion concentration in samples of natural and treated water using a prepared standard absorption curve at 535 nm for the aluminum(III)–Eriochrome Cyanine R complex.

BACKGROUND INFORMATION

During recent years, increasing concern has been expressed as to the effect of aluminum(III) ion concentration in natural and treated waters. Aluminum(III) has been identified as one of the products of acid rain that is harmful to fish and trees. Acid rain includes all types of precipitation that are significantly more acidic than natural rain.

Brook trout show a specific toxic response to aluminum(III) levels greater than or equal to 0.2 mg L^{-1} in the pH range 4.4–5.9. Growth reduction of the fish occurs at aluminum(III) levels of 0.1–0.3 mg L^{-1}. Lakes of about neutral pH show aluminum(III) levels 10–50 times lower, that is, about 4×10^{-3} mg L^{-1}. Even such relatively low aluminum(III) levels cause young salmon to die from gill malformations, and damage to tree root systems is observed.

The Environmental Protection Agency has not set a maximum contaminant level for dissolved aluminum. However, dissolved aluminum has been associated with renal failure in humans, and the aluminum(III) concentration in kidney dialysis water must be below 1×10^{-2} mg L^{-1}. Thus, a recommendation has been made that aluminum(III) levels in drinking water be maintained below 1×10^{-1} mg L^{-1} (0.1 ppm).

Precipitation with pH below 5.6 is considered to be acid rain. Atmospheric carbon dioxide is responsible for the slight natural acidity in precipitation of pH 5.6. This acidity is the result of the following reactions.

Dissolution:	$CO_2(g) \rightleftharpoons CO_2(aq)$	(Eq. 1)
Hydrolysis:	$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$	(Eq. 2)
Dissociation:	$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^{-1}(aq) + H_3O^+(aq)$	(Eq. 3)

Acid rain is considered to result from atmospheric pollutants, largely derived from fossil fuels. Some of these fuels contain sulfur and sometimes nitrogen compounds as impurities. Combustion of such fuels produces oxides of sulfur and nitrogen. These oxides react with water in the atmosphere to form sulfuric acid and nitric acid. These substances are carried by the prevailing winds and later fall as acid rain. As the acid rain enters surface water, the pH of the water is lowered. The resulting acidic water can leach aluminum(III) from the minerals in the soil.

Aluminum is the third most abundant element in the Earth's outer crust, rocks, and soils. In soils, aluminum is found in some clay minerals such as kaolin, muscovite, and white mica silicates. The typical formula for the kaolin group of silicates is $Al_2Si_2O_5(OH)_4$, whereas that of white mica is $KAl_2(AlSi_3O_{10})(OH)_2(F)_2$.

Aluminum(III) is rarely found in concentrations greater than 0.5 mg L^{-1} in fresh water. However, leaching caused by acid rain introduces additional aluminum(III) to the surface water. The following *unbalanced* reaction shows the effect of acid rain, H_3O^+, on feldspar, $KAlSi_3O_8$. As a result of this reaction, aluminum(III) is leached into surface water and becomes part of our water system.

$$KAlSi_3O_8(s) + H_3O^+(aq) \rightarrow Al_2Si_2O_5(OH)_4(s) + H_4SiO_4(aq) + K^+(aq) + Al^{3+}(aq) \quad \text{(Eq. 4)}$$

There is a direct relationship between the concentration of aluminum(III) and the alkalinity of natural waters. Increased aluminum(III) concentrations are found in areas of the United States where the pH of the natural water is about 5. The EPA classifies these natural waters as "critical" or "acidified." In some parts of the country, the natural waters are alkaline or well buffered. We would not expect to find significant concentrations of aluminum(III) in such waters.

When natural water enters a water-purification plant, aluminum(III) is often added to the waters. Part of the treatment of natural water involves the addition of coagulates to remove undesirable color from the water. Aluminum sulfate and polyaluminum chlorides are often used as coagulates. Thus, any aluminum(III) in treated water could have been introduced in several different ways.

In this experiment, a spectrophotometric method is used to determine the concentration of aluminum(III) in several different water samples. For this procedure, the aluminum(III) must be quantitatively converted to a colored complex. A suitable agent for complexing aluminum(III) is Eriochrome Cyanine R (ECR). A solution containing the aluminum(III)–ECR complex ion is red and has a maximum absorbance at 535 nm. The composition of the complex is affected by pH, with the greatest stability at a pH of approximately 6.2. The equation for formation of the complex is:

$$\underset{\text{(orange-red)}}{Al^{3+}(aq) + 2\,ECR^{3-}(aq)} \rightleftharpoons \underset{\text{(red)}}{Al(ECR)_2{}^{3-}(aq)} \quad \text{(Eq. 5)}$$

In addition to ECR, several other reagents are added to the sample being analyzed for aluminum(III). Very dilute sulfuric acid and an acetate buffer are added to maintain optimum pH. Ascorbic acid is added to complex dissolved iron and manganese, which would otherwise interfere with the aluminum(III) determination. The ascorbic acid solution must be freshly prepared, as it oxidizes if left standing.

A blank solution containing all reagents, but no aluminum(III), is prepared first for zeroing the spectrophotometer. Then, a series of standard solutions is prepared with known concentrations of aluminum(III). The percent transmittance of these solutions is measured and converted to absorbance, from which a Beer's Law curve is prepared, which is then used as a standard aluminum(III) curve. From this standard curve, the concentration of aluminum(III) in several water samples is determined.

A measured quantity of a water sample is prepared by adding the reagents to form quantitatively the aluminum(III)–ECR complex. The measured absorbance of the sample is used to calculate the concentrations of aluminum(III) in the sample.

A different blank must be used for natural and treated water samples. The compositions of the blank solutions are different in order to prevent the trace components that might be present in the water sample from interfering with the analysis. The water sample itself is used to prepare the blank. The preparation is identical to that for the previous solutions, except that a small amount of EDTA is added. EDTA is a complexing agent for metal ions. EDTA complexes have very high formation constants, which assures the removal of any possible interfering metal ions. For the synthetic water samples, the same blank can be used as the one used with the aluminum(III) standards.

This investigation will involve determining the concentration of aluminum(III) in several different types of water samples. One sample will be from natural water, such as a lake, pond, stream, or river. A second sample will be from treated water that has been processed at a purification plant for human consumption. The third sample will be a synthetic one prepared by your laboratory instructor, containing a fixed concentration of aluminum(III) that is unknown to you.

You will complex the aluminum(III) in each sample, measure the percent transmittance of the solution, and calculate its absorbance. From your standard aluminum(III) curve, you will determine the concentration of aluminum(III) in each of the samples.

PROCEDURE

I. Sampling a Water Source

NOTE: Samples of natural water should be collected no sooner than 24 hours prior to doing the analysis. For better and more consistent results, refrigerate the sample or place it on ice until the determination is done.

A. Selecting the Stream Site

For stream sampling, choose a location that will provide representative samples. Collect samples as near to the center of the stream as practical. Sample only flowing water; avoid stagnant or still water. If you plan to monitor the stream again, mark the original sampling site with a stake and sign.

Lake or pond sampling is more complex. A mid-lake sample is preferable to a shoreline sample. For mid-lake monitoring, select three permanent objects on shore and use them to triangulate the sampling site.

B. Collecting the Sample

Use a container specified by your laboratory instructor. Collect the sample below the surface, but avoid disturbing the bottom sediment. Sample at a depth of an arm's length in a lake or pond.

Collect a sample by lowering the bottle upside down into the water to the desired depth. Turn the bottle right side up and allow it to fill completely. Cap the filled bottle while it is underwater. Be sure no air is trapped above the sample in the bottle.

Label the bottle with your name, the date, and the sample location.

II. Obtaining Data to Prepare the Standard Aluminum Curve

CAUTION

Wear departmentally approved eye protection during the experiment.

A. Preparing the Spectrophotometer for Use

Turn on the instrument and let it warm up for 10–15 min. Set the wavelength at 535 nm. With no cuvette in the instrument, use the on-off-zero knob to obtain a steady reading of 0% transmittance.

B. Preparing the Standard Aluminum(III) Solutions

NOTE: You will prepare six solutions, each containing a different concentration of aluminum(III) ion. You will prepare these solutions from a stock standard solution.

1. Preparing Blank Solution #1: Label a clean 100.00-mL volumetric flask "Blank Solution #1."

CAUTION

Handle dilute sulfuric acid with care.

Use a graduated cylinder to measure each of the following and then add them to the flask.

20.0 mL of buffer solution

2.0 mL of ascorbic acid solution

2.0 mL of $2.0 \times 10^{-2} N (1.0 \times 10^{-2} M)$ H_2SO_4

Pipet 10.00 mL of ECR solution into the flask. Mix thoroughly. Add distilled water to the calibration mark. Mix the solution thoroughly again.

2. Determining the percent transmittance of Blank Solution #1: Fill a clean, dry cuvette with Blank Solution #1. Use this blank to set the instrument to

100% transmittance at 535 nm. Record on Data Sheet 1 the percent transmittance of Blank Solution #1.

3. *Preparing standard aluminum(III) solutions:*

NOTE: The aluminum(III) complex is not stable after 20 min. Determine the percent transmittance of the following solutions within 10–20 min after preparation.

Record on Data Sheet 1 the aluminum(III) concentration in mg L^{-1} of the aluminum(III) stock solution.

Prepare Standard Solutions #1, 2, 3, 4, and 5, each in a clean 100.00-mL volumetric flask. Follow the procedure used in preparing Blank Solution #1, but add aluminum(III) stock solution as follows: 1.00 mL for Standard Solution #1, 2.00 mL for #2, 4.00 mL for #3, 6.00 mL for #4, and 8.00 mL for #5.

4. *Determining the percent transmittance of the standard aluminum(III) solutions:* Measure the percent transmittance of each solution within 10–20 min after preparation. Record on Data Sheet 1 the percent transmittance of each solution.

NOTE: Your laboratory instructor will inform you whether your investigation is to involve samples prepared from a stock solution, treated water, natural water, or some combination of all three.

III. Determining the Concentration of Aluminum(III) in a Synthetic Water Sample

Record on Data Sheet 2 the code number of the synthetic water sample assigned to you.

A. Preparing the Solution of the Synthetic Water Sample

Label a clean 50.00-mL volumetric flask "Synthetic Water Solution". Pipet 25.00 mL of the synthetic water sample into the flask.

Use a graduated cylinder to measure each of the following and add them to the sample in the flask:

10.00 mL of buffer solution

1.0 mL of ascorbic acid solution

1.0 mL of $2.0 \times 10^{-2}N(1.0 \times 10^{-2}M)$ H_2SO_4

Pipet 5.00 mL of ECR solution into the flask. Mix the solution thoroughly. Add distilled water to the calibration mark. Mix thoroughly again.

Be sure to make your determination within 10–20 min after preparing the synthetic water solution.

B. Determining the Percent Transmittance of the Synthetic Water Solution

At 535 nm, set the instrument at 100% transmittance with Blank Solution #1. Fill a clean, dry cuvette with your synthetic water solution and place the cuvette in the instrument. Determine the percent transmittance at 535 nm. Record the transmittance on Data Sheet 2.

Do a second and third determination if time permits.

IV. Determining the Concentration of Aluminum(III) in a Natural Water Sample

Record on Data Sheet 3 the code number of the natural water sample assigned to you.

A. Preparing the Natural Water Sample for Analysis

1. *Estimating the volume of H_2SO_4 to be used:* Measure 25.0 mL of the natural water sample in a graduated cylinder. Transfer this portion of your sample to a porcelain evaporating dish or 250-mL Erlenmeyer flask. Add 2 drops of methyl orange indicator. Titrate with $2.0 \times 10^{-2} N (1.0 \times 10^{-2} M)$ H_2SO_4 to a faint pink color. Record the volume of titrant used on Data Sheet 3.

2. *Preparing Blank Solution #2:* Label a clean 50.00-mL volumetric flask "Blank Solution #2". Pipet 25.00 mL of the natural water sample into this flask.

NOTE: Prepare the following solutions by using the same volume of acid as was used in the titration in Step 1 of Part IV*A*, plus 1.0 mL.

Use a graduated cylinder to measure each of the following, and add each to the sample in the flask:

the volume of $2.0 \times 10^{-2} N (1.0 \times 10^{-2} M)$ H_2SO_4 to be used

1.0 mL of ascorbic acid solution

10.0 mL of buffer solution

Pipet 5.00 mL of ECR solution into the flask. Measure 1.0 mL of $1 \times 10^{-1} M$ EDTA solution in a graduated cylinder, and add this solution to the flask. Mix thoroughly. Add distilled water to the calibration point. Mix thoroughly again.

Be sure to make your determination within 10–20 min after preparing your natural water solution.

3. *Preparing the solution of the natural water sample:* Follow the procedure used to prepare Blank Solution #2, but *do not* add the EDTA solution. Label this flask "Natural Water Solution."

B. Determining the Percent Transmittance of the Natural Water Solution

At 535 nm, set the instrument at 100% transmittance with Blank Solution #2. Place a cuvette containing the natural water sample in the instrument. Measure the percent transmittance. Record the transmission on Data Sheet 3.

Do a second and third determination if time permits.

V. Determining the Concentration of Aluminum(III) in a Treated Water Sample

Record on Data Sheet 4 the code number of the treated water sample assigned to you.

A. Preparing the Treated Water Sample for Analysis

1. *Estimating the volume of H_2SO_4 to be used:*

NOTE: Some water from water treatment plants will have a pH of 8.0 or above. In such cases, the following procedure must be adjusted to avoid exceeding a total solution volume of 50.00 mL. Your laboratory instructor will describe the changes that should be made.

Measure 25.0 mL of the treated water sample in a graduated cylinder. Transfer this portion of the sample to a porcelain evaporating dish or 250-mL Erlenmeyer flask. Add 2 drops of methyl orange indicator. Titrate with $2.0 \times 10^{-2}N(1.0 \times 10^{-2}M)$ H_2SO_4 to a faint pink color. Record on Data Sheet 4 the volume of titrant used.

2. *Preparing Blank Solution #3:* Label a clean 50.00-mL volumetric flask "Blank Solution #3." Pipet 25.00 mL of the treated water sample into this flask.

NOTE: Prepare the following solutions by using the same volume of acid as was used in the titration in Step 1, Part V*A*, plus 1.0 mL.

Use a graduated cylinder to measure each of the following, and add each to the sample in the flask:

the volume of $2.0 \times 10^{-2}N(1.0 \times 10^{-2}M)$ H_2SO_4 to be used

1.0 mL of ascorbic acid solution

10.0 mL of buffer solution

Pipet 5.00 mL of ECR solution into the flask. Measure 1.0 mL of 1×10^{-1} *M* EDTA solution in a graduated cylinder, and add this solution to the flask. Mix thoroughly. Add distilled water to the calibration mark. Mix thoroughly again.

3. *Preparing the solution of the treated water sample:* Follow the procedure used to prepare Blank Solution #3, but *do not* add the EDTA solution. Label this flask "Treated Water Solution."

Be sure to make your determination within 10–20 min after preparing your treated water solution.

B. Determining the Percent Transmittance of the Treated Water Solution

At 535 nm, set the instrument at 100% transmittance with Blank Solution #3. Place a cuvette containing the treated water solution in the instrument. Measure the percent transmittance. Record the transmission on Data Sheet 4.

Do a second and third determination if time permits.

CALCULATIONS

II. Preparing the Standard Aluminum(III) Curve

NOTE: (Record all data calculated in this section on Data Sheet 1.)

1. Calculate the concentration of the standard solutions.

$$\frac{(\text{mg L}^{-1}\text{ of stock solution})(\text{volume of sample, L})}{(1.00 \times 10^{-1}\text{ L})} = \text{mg L}^{-1} \qquad \text{(Eq. 6)}$$

1.00×10⁻¹L

2. Convert the percent transmittance (%T) of the stock solution to absorbance (A).

$$A = 2 - \log \%T \qquad \text{(Eq. 7)}$$

3. Prepare a standard aluminum(III) curve to be used for determining aluminum(III) concentrations. Plot the absorbance (A) of the standard aluminum(III) solutions against the concentration of aluminum(III) in mg L^{-1}. Use the ordinate (the y-axis) for the absorbance, with scale units of 0.000 to 0.900. Use the abscissa (the x-axis) for the aluminum(III) concentration, with scale units of 0.000 to 0.400.

III. Determining the Concentration of Aluminum(III) in a Synthetic Water Sample

NOTE: (Record all data calculated in this section on Data Sheet 2.)

1. Convert your three determinations of the percent transmittance (%T) of the synthetic water solution to absorbances (A), using Equation 7.
2. Use the standard aluminum(III) curve to obtain the concentration of aluminum(III) in the solution for each of the three determinations.
3. Calculate the concentration of aluminum(III) in the sample for each of the three determinations by using Equation 8, where the dilution factor is 2.

$$(\text{mg L}^{-1} \text{ from standard curve})(2) = \text{mg L}^{-1} \text{ in sample} \qquad \text{(Eq. 8)}$$

4. Calculate the average concentration of aluminum(III) in the sample.

IV. Determining the Concentration of Aluminum(III) in a Natural Water Sample

NOTE: (Record all data calculated in this section on Data Sheet 3.)

1. Convert your three determinations of the percent transmittance of the natural water solution to absorbances, using Equation 7.
2. Use the standard aluminum(III) curve to obtain the concentration of aluminum(III) in the solution for each of the three determinations.
3. Calculate the concentration of aluminum(III) in the sample for each of the three determinations by using Equation 8.
4. Calculate the average concentration of aluminum(III) in the sample.

V. Determining the Concentration of Aluminum(III) in Treated Water

NOTE: (Record all data calculated in this section on Data Sheet 4.)

NOTE: If your treated water sample has been fluoridated, your laboratory instructor will give you a correction factor for these calculations.

1. Convert your three determinations of the percent transmittance of the treated water solution to absorbances, using Equation 7.

2. Use the standard aluminum(III) curve to obtain the concentration of aluminum(III) in the solution for each of the three determinations.
3. Calculate the concentration of aluminum(III) in the sample for each of the three determinations by using Equation 8.
4. Calculate the average concentration of aluminum(III) in the sample.

Name Section Date

Post-Laboratory Questions

(Use the spaces provided for the answers and additional paper if necessary.)

1. EDTA is a complexing reagent for many metalions. In Parts IV*A* and V*A* of the Procedure, why is EDTA added to Blank Solution #2 and Blank Solution #3, but not to the solutions of the natural or treated water samples?

2. The main source of error in this experiment is volumetric measurements, either with a graduated cylinder, pipet, or microburet. Assume, in Part II*B* of the Procedure, that you dispensed 5.00 mL of the stock aluminum(III) solution *instead* of 6.00 mL when preparing Standard Solution #4. Assume the standard aluminum(III) curve you originally drew is still correct, even though the aluminum(III) concentration of Solution #4 has now changed. Use this curve for the following calculations.

   (a) Calculate the absorbance (A) you would expect from this solution.

   answer

   (b) Calculate the relative percent error in the absorbance as a result of adding only 5.00 mL of stock aluminum(III) solution to Solution #4 instead of 6.00 mL.

   answer

3. A student did not add EDTA when preparing Blank Solution #2 in Part IV*A* of the Procedure, part of determining the aluminum(III) concentration of a natural water sample. Assume the student did not make any other mistakes in the determination. Estimate the absorbance of the student's Blank Solution #2. Briefly explain your answer.

answer

4. When the student repeated the determination of the aluminum(III) concentration in a natural water sample, Blank Solution #1 (prepared in Part II*B* for obtaining data to prepare the standard aluminum(III) curve) was used by mistake, instead of Blank Solution #2. Would you expect the student to have a large error in this determination because of using Blank Solution #1? Briefly explain your answer.