Volumetric Determination of Chloride Content in Seawater

Reading assignment: Chang, Chemistry 10^{th} edition, pages 151-155.

Goals

We will measure the chloride content of a sample of local seawater by titration with silver nitrate. We will become familiar with the use of precipitation reactions and the use of titrations in quantitative analysis.

Safety Note: Safety glasses are required when performing this experiment

Discussion

Seawater

The determination of the salt content of seawater is an important area of research since ocean currents and global climate are affected by salt content. The primary ionic components of seawater are shown in the table below. These include large amounts of chloride (Cl^-) and sodium (Na^+) ions. Several methods are used to measure the concentrations of ions in water. One method involves measuring electrical conductivity. Electrical conductivity is dependent on ionic concentration since ions are electrolytes. Measuring the conductivity can, therefore, give information about dissolved salt concentrations. Another method for measuring salt concentration is to simply measure the density, or specific gravity, of a water sample. The density of water increases with increasing amounts of dissolved salts, thereby giving concentration information. But these methods give only the total ionic concentration, not specific information regarding concentrations of individual ions, like sodium or chloride. Today, there are devices called ion-selective electrodes that can measure the concentration of a specific ion. Another method, called ICP-MS (inductively-coupled plasma mass spectrometry), can measure very low concentrations of specific elements. In this experiment we will use a rather simple method for measuring the concentration of chloride ions in seawater. The method is called a titration and is a quick and inexpensive procedure.

Ion	**Grams per 1000 g seawater**	**Mass %**
Cl^-	19	1.9
Na^+	10.7	1.07
SO_4^{2-}	2.7	0.27
Mg^{+2}	1.3	0.13
Ca^{+2}	0.4	0.04
K^+	0.4	0.04

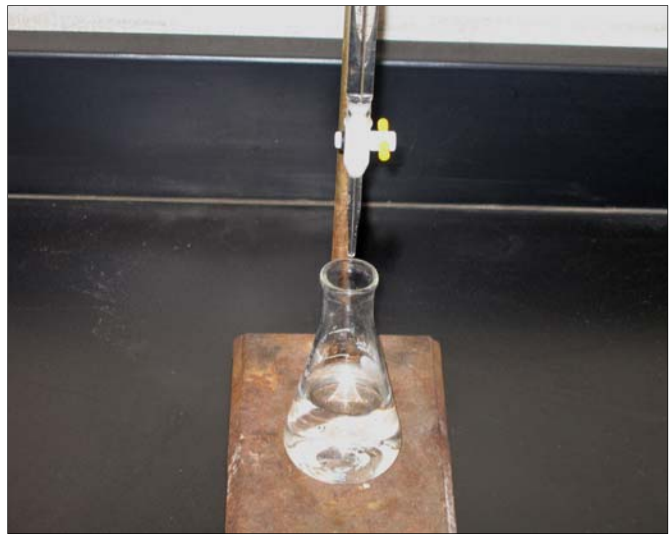
Titrations

A common method used to determine the chloride content of seawater is to use a precipitation reaction between the silver nitrate and sodium chloride:

$$\underset{\text{silver(I) nitrate}}{AgNO_3\,(aq)} + NaCl\,(aq) \longrightarrow \underset{\text{silver(I) chloride}}{AgCl\,(s)} + NaNO_3\,(aq)$$

Silver(I) nitrate, sodium chloride, and sodium nitrate are all very soluble in water. On the other hand, solubility rules predict that silver chloride should be insoluble in water. In fact, silver chloride is quite insoluble in water. Only about 0.0018 grams will dissolve in one liter of water. Since AgCl is insoluble in water, adding $AgNO_3$ to a sample of seawater will result in the formation of AgCl because seawater possesses chloride ions. If we can measure the amount of $AgNO_3$ required to react with all of the Cl^- in the seawater, then we can determine the concentration of the Cl^- in the seawater. This is the basis of a titration. We use a reactant of known concentration (in this case silver nitrate) to determine the concentration of a chemical species in which we are interested (in this case chloride). The reactant for which we know the concentration is called a titrant. The titrant is usually standardized, meaning its concentration is accurately measured before performing the titration. The species for which we don't know the concentration is often called an analyte. The analyte concentration is found by performing the titration.

The experimental apparatus used for performing titrations is shown below. In our experiment, silver nitrate is placed in a buret, an apparatus used to deliver known volumes of the titrant. The analyte (seawater) is placed in an Erlenmeyer flask. The titrant is slowly added from the buret into the flask, drop by drop, where the two react with one another. The volume of the analyte is accurately known, as is the concentration of the titrant. What isn't known is the concentration of the chloride in the seawater or the volume of the silver nitrate required to react completely with the chloride. The volume of the titrant required to react with the analyte is measured from the buret, which contains markings that allow us to determine how much liquid has passed through the opening at the bottom. Once the volume of the titrant required to react with all of the analyte has been determined, we can calculate the analyte concentration.



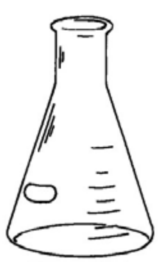
Silver chloride is a white solid that forms soon after any silver nitrate has been added to seawater. This makes a quantitative analysis difficult since we want to know when all of the chloride has reacted.

Indicators
To know when the titration has reached the equivalence point (the point at which the moles of titrant added is equal to the moles of analyte in the sample), we add a material called an indicator to the mixture. Just like the titrant, the indicator also reacts with Ag^+ ions. The indicator we will use is called potassium chromate (K_2CrO_4). Potassium chromate reacts with silver(I) ions:

$$\underset{\substack{\text{potassium chromate} \\ \text{(light yellow)}}}{K_2CrO_4\,(aq)} + 2AgNO_3\,(aq) \longrightarrow \underset{\substack{\text{silver(I) chromate} \\ \text{(light orange-red)}}}{Ag_2CrO_4\,(aq)} + 2KNO_3\,(aq)$$

Once the chloride in the solution has completely reacted with Ag^+ ions any additional silver nitrate reacts with the potassium chromate. Potassium chromate in water is a transparent yellow solution in water. When reacted with silver ions the silver chromate solution is an orange-red color. So once the solution starts to become orange-red, we stop adding the titrant and calculate how much titrant was added.

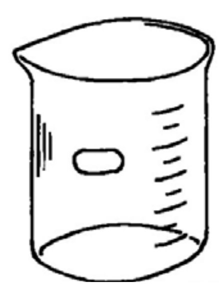
Equipment and Materials



Erlenmeyer flask

Buret

Volumetric Pipet



Beakers

Volumetric flask

Silver nitrate solution ($AgNO_3$), seawater solution with potassium chromate indicator (K_2CrO_4), 50-mL buret, 125-mL Erlenmeyer flask, 10.00-mL volumetric pipet and pipet pump, 100-mL beaker, 250-mL beaker, 250-mL volumetric flask.

Procedure

SAFETY PRECAUTIONS
Silver nitrate will stain skin. Safety glasses or goggles must be worn while this experiment is being performed.

Students perform titrations individually.

1. Start by preparing the buret. The 50-mL buret should be rinsed with tap water two to three times and then one time with distilled or deionized water.

2. Obtain about 70 mL of silver nitrate in a dry 100-mL beaker. Pour a few milliliters of this solution into the buret.

3. Let the silver nitrate solution flow through the bottom tip of the buret into a second clean beaker. Don't pour any silver nitrate into the sink.

4. Fill the buret with the remaining silver nitrate to near (above) the 0 mL mark of the buret.

5. Allow a few milliliters of silver nitrate solution to pass through the buret by opening the stopcock. This will push any trapped air out of the stopcock. Record the new volume of the buret in the data sheet in the row that says initial volume.

6. Record the concentration of the silver nitrate standard solution on the data sheet.

Steps 7-10 involve diluting the seawater and may need to be performed. Check with your instructor. If the dilution has already taken place then skip steps 7-10 and obtain 80 mL of seawater in a clean dry 100-mL beaker and go to step 11.

7. The concentration of chloride in the seawater is high and needs to be diluted so we can perform the titration. Obtain 20-30 mL of seawater in a clean 100 mL beaker.

8. Using the 10-mL volumetric pipette transfer 10.00 mL of the seawater to a clean 100 mL <u>volumetric flask</u>.

9. Add deionized or distilled water until the flask is about 1/2 full. Shake the flask to mix the seawater with the deionized or distilled water.

10. Continue adding the water to the flask until the bottom of the meniscus is right at the 100 mL mark of the flask. This diluted seawater (by a factor of ten) is the solution we will use for the titrations.

11. Using the 25-mL volumetric pipette transfer 25.00 mL of the diluted seawater solution to a 125 mL Erlenmeyer flask.

12. Using a 10-mL graduated cylinder transfer about 5 mL of 1% potassium chromate (K_2CrO_4) solution to the Erlenmeyer flask. It is possible that the potassium chromate has already been added to the seawater. If so, the seawater will appear yellow and you can go directly to the next step.

13. Begin adding the silver nitrate solution to the seawater, slowly drop by drop. As it drops into the flask be sure to swirl the flask to ensure that the titrant (silver nitrate) mixes with the contents of the flask. By adding the titrant slowly you are more likely to obtain good results. You may notice that each drop causes the surface of the solution to turn orange-red. The endpoint is a very light orange-red color. When the entire solution turns this color the endpoint has been reached.

14. Once the endpoint is reached stop the titration by closing the stopcock and recording the volume of the titrant in the buret on the data sheet, in the row that says final volume. The volume delivered is the difference between the initial and the final volume. The volume delivered should be between 7 mL and 15 mL. If your volume is outside this range you may have a problem and should consult with the instructor.

15. Perform two more titrations for a total of three titrations, using the same procedure as you used with the first titration. The initial volume of the second titration will be the same as the final volume of the first titration.

16. Any unused silver nitrate solution should be poured into the collection bottle provided. The buret should then be rinsed out with tap water and deionized water. The products of the titrations should be poured into the appropriate waste container.

9. The density of seawater can be measured by measuring the mass of 25.00 mL of the seawater solution. Use a digital analytical balance to measure the mass of the seawater in a 100 mL-beaker. Use a 25.00-mL volumetric pipette to measure the volume.

Discussion of Calculations

Using the average volume of silver nitrate, calculate the mass percent chloride of the seawater sample. The density of the seawater can be measured or assumed to be 1.02 g/mL.

1. The first step in the calculations is to determine how many moles of titrant ($AgNO_3$) were used. Use the volume of each titration and the known molarity. Recall that $M = \frac{n}{V}$

$\text{moles AgNO}_3 = M_{AgNO3} V_{AgNO3}$ where the molarity is determined prior to performing the experiment.

2. The moles of sodium chloride in the seawater solution can be determined because the moles of $AgNO_3$ are equal to the number of moles of NaCl at the equivalence point:

$AgNO_3(aq) + Cl^-(aq) \rightarrow AgCl(s) + NO_3^-(aq)$

$\text{moles Cl}^- = (\text{moles AgNO}_3)\left(\frac{1\,\text{mol Cl}^-}{1\,\text{mol AgNO}_3}\right)$ at the equivalence point.

3. The mass of chloride can be found using the molar mass of chlorine:

$\text{mass of chloride} = (\text{moles Cl}^-)\left(\frac{35.45\,\text{g Cl}}{1\,\text{mol Cl}}\right)$

4. The mass of the seawater used is found from the density and the volume used. We can assume that the density of the seawater is 1.02 g/mL.

$\text{mass of seawater} = (\text{density of seawater})(\text{volume of seawater})$ Note that there is no need to convert the volume to liters because the density is in g/mL.

5. It is traditional in oceanography to report concentrations in mass percent. Mass percent is defined as:

$$\text{mass } \% = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) \text{ x } 100$$

In our experiment chloride is the solute and seawater is the solution. So to find the mass percent we need to find the mass of chloride in 25 mL of seawater and the mass of seawater in 25 mL.

$$\text{mass} \% = \left(\frac{\text{mass of chloride}}{\text{mass of seawater}} \right) \text{ x } 100$$

6. The seawater sample we used was diluted ten times, so multiply the mass of chloride above by 10 to get the actual moles of chloride in the undiluted seawater sample.

7. Perform a Q test on your mass percent values and calculate an average mass percent concentration.

N	3	4	5
Q*	0.970	0.829	0.710

*95% confidence

$$Q_{calc} = \left| \frac{gap}{range} \right|$$

Date:_________

Data Sheet
Volumetric Determination of Chloride Content in Seawater

Name_________________________________ Section________ Date_________

Concentration of standardized silver(I) nitrate _____________

density of seawater* _____________g/mL
*The density can be assumed as 1.02 g/mL if not measured during the laboratory.

Unknown (circle one) A B C D E

	Titration 1	**Titration 2**	**Titration 3**
Final buret volume	_____________ mL	_____________ mL	_____________ mL
Initial buret volume	_____________ mL	_____________ mL	_____________ mL
Volume delivered	_____________ mL	_____________ mL	_____________ mL
Moles of $AgNO_3$ used in titration	_____________	_____________	_____________
Moles of chloride (Cl^-) in Seawater	_____________	_____________	_____________
mass of chloride (Cl^-) in titration	_____________g	_____________g	_____________g
mass of seawater in titration	_____________g	_____________g	_____________g
mass percent of chloride in seawater (diluted)	_____________	_____________	_____________
mass percent of chloride in seawater (undiluted)	_____________	_____________	_____________

average mass percent of seawater (undiluted) _____________
(include results of Q test)

* Volumes should be recorded to 0.02 mL.