# EXPERIMENT 3
FAJANS DETERMINATION OF CHLORIDE

Silver chloride is very insoluble in water. Addition of $AgNO_3$ to a solution containing chloride ions results in formation of a finely divided white precipitate AgCl. This reaction provides a basis for determination of chloride ions.

The Analytical Reaction

The reaction of $AgNO_3$ with Cl^- may be represented as:

$$Ag^+ + Cl^- = AgCl \text{ (s)}$$
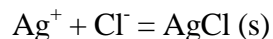
Suppose that we have a sample containing an unknown quantity of chloride ions. The number of moles (or weight) of chloride might be determined by titration with a silver nitrate solution of known concentration, C. (This stuff doesn't grow on trees but its preparation is discussed shortly.) The known silver nitrate solution is added to the unknown chloride solution until we have added exactly the same number of moles of $AgNO_3$ to the mixture as there are moles of chloride present. This is termed the **equivalence point** of the **titration**.

> NOTE: The term "titrate" refers to a process of addition of one substance to another.
> It implies that we seek to add just exactly the right amount. The equivalence point
> in a titration happens when, in fact, we have added just exactly the right amount.

The volume in mL of $AgNO_3$ solution required to reach the equivalence point is symbolized by $\mathbf{v}^*$. Thus, v^*C is the number of millimoles of $AgNO_3$ required to react with all of the chloride present in the titration sample and because 1 mmole of $AgNO_3$ reacts with 1 mmole of chloride, v^*C is also equal to the number of millimoles of chloride present. The weight of chloride present is then mmole Cl^- x 35.453 mg/mmole $=(v^*C$ x 35.453) mg.

How will we establish the equivalence point volume of $AgNO_3$ in the titration of chloride? We will not. The equivalence point is a quantity that exists only in theory and in text books. In the world we must satisfy ourselves with the "**endpoint**" which is an experimental estimate of the equivalence point. Our objective in a titration analysis is to match the experimental endpoint as closely as possible with the theoretical equivalence point. Just how this is to be accomplished depends on the amounts and nature of the substances involved in the analysis as well as the amounts and nature of other substances present in the sample. In any case we will assume that the experimental endpoint is an accurate approximation to v^*.

The Fajans analysis for chloride employs a color-change indicator, dichlorofluorescein, to signal the endpoint of a titration of chloride ions with a "standard" $AgNO_3$ solution. We will assume that the visual endpoint of this titration is also the equivalence point and use this assumption to calculate the quantity of chloride present in an unknown sample. In other words, the analysis depends on two quantities: the concentration of "standard" $AgNO_3$ solution and the endpoint

volume v*, as follows.

The AgNO₃ Standard

In the experiment that follows we will use a AgNO$_3$ solution of known concentration - a standard AgNO$_3$ solution. This has been prepared in one of two ways. The first involves weighing out an appropriate amount of very pure solid AgNO$_3$ then dissolving and diluting to an accurately known volume. The resulting solution is said to employ AgNO$_3$ as a "**primary standard**". A second and preferable procedure involves analyzing a AgNO$_3$ solution by titrating carefully weighed samples of pure NaCl whose chloride content is known. From the measured endpoint volume and known amount of chloride, C is calculated. In this case the AgNO$_3$ solution is said to have been "standardized against a primary standard of NaCl" or, more simply, "standardized against NaCl".

The first of these methods is certainly simpler but it is not widely applicable because it depends on the availability of the titration reagent in very pure form. Additionally, this approach relies heavily on the assumption that the experimental endpoint volume really does accurately approximate the equivalence point volume.

The second approach of standardizing against a standard sample is more commonly used and has the advantage of allowing for some "cancellation" of errors. This method is essential with complex analyses.

We continue with a brief description of the dichlorofluorescein indicator to be used to signal the titration endpoint.

The Indicator Reaction

Consider the process of adding AgNO$_3$ solution to a sample solution held in a flask and containing chloride ions. At the start, when only a small amount of AgNO$_3$ has been added, the solution contains some AgCl precipitate, a very small concentration of Ag$^+$ ions and an excess of Cl$^-$ ions. (Cl$^-$ ions are just floating around "waiting" for the addition of more AgNO$_3$.) When we have added just enough AgNO$_3$ to reach the equivalence point the solution in the flask contains AgCl and very small and <u>equal</u> concentrations of Ag$^+$ and Cl$^-$ ions. If we continue to add more AgNO$_3$ to the flask very little additional AgCl is produced but the mixture now contains an excess of Ag$^+$ ions. That is, the Ag$^+$ ion concentration is now greater than the Cl$^-$ concentration in the solution. Thus, the solution in the flask, the "analyte solution", is fundamentally different before and after the equivalence point. Before the equivalence point [Cl$^-$]>[Ag$^+$], but after the equivalence point [Ag$^+$]>[Cl$^-$]. We may take advantage of this change in the environment of the analyte solution.

It is a general property of ionic precipitates like AgCl to adsorb their own ions from solution. Thus, a silver chloride precipitate standing in a solution containing excess chloride ions causes a layer of chloride ions to adhere to its surface. Likewise, AgCl in the presence of a solution containing excess Ag$^+$ ions forms an adsorbed layer of Ag$^+$. If the solution contains dichlorofluorescein anion, some of this material will be adsorbed onto the layer of Ag$^+$ ions present

at the precipitate surface and form the red color of silver dichlorofluoresceinate. This silver salt would not ordinarily form in very dilute solutions of Ag^+ and dichlorofluorescein anion. However, adsorption of Ag^+ at the silver chloride precipitate surface results in a <u>locally</u> high concentration of Ag^+ which is capable of precipitating red silver dichlorofluoresceinate onto the precipitate surface. The dichlorofluorescein is termed an **adsorption indicator** and here signals the first presence of excess Ag^+ in the solution. This occurs immediately after the equivalence point as $AgNO_3$ is added to the Cl^- solution. Consequently, the appearance of the first persistent reddish color in the mixture indicates the endpoint in this titration.

Limitations of the Analytical Reaction

We will eventually calculate the quantity of chloride present by knowing the quantity of silver nitrate that reacted with it. The presence of any substance other than chloride ions that reacts with silver nitrate will interfere with the analysis. For example, large amounts of OH^- or SO_4^{2-} present in the sample solution will cause precipitation of insoluble $AgOH$ or Ag_2SO_4 along with $AgCl$. In that case the quantity of $AgNO_3$ added will not correspond to the amount of chloride initially present. Even small amounts of Br^- or I^- which form very insoluble silver salts will interfere as well.

Limitations of the Indicator Reaction

The action of the indicator relies on adsorption at the precipitate surface which, in turn, depends on a large precipitate surface area. The presence of high concentrations of ionic materials will cause the $AgCl$ particles to coagulate, decrease the surface area and make the indicator color change almost invisible. We overcome this difficulty by adding dextrin (starch) to the titration mixture. Dextrin prevents coagulation of the small $AgCl$ particles.

The indicator is a weakly basic substance and reacts with H^+ ions in acid solutions. This reaction has the effect of decreasing the concentration of free dichlorofluorescein anion and preventing its adsorption on the $AgCl$ surface. The indicator works best above pH 5. However, the pH must be below about 9 to prevent precipitation of $AgOH$.

Finally, the visual endpoint provided by the indicator requires a fairly clear and colorless solution. The presence of any highly colored substances would completely obscure the color change reaction.

IN THE LABORATORY

1. The chloride samples have been dried and stored in a desiccator. Take a sample and record its number on your data sheet.

2. Zero (tare) the analytical balance with a clean dry, capped weighing bottle. Add 1.1 to 1.3 g. of your chloride sample to the bottle; replace the cap and weigh as accurately as possible. Record on your data sheet.

3. Rinse a 250 mL volumetric flask with distilled water and quantitatively transfer the chloride sample to the flask. (The instructor will demonstrate.) Dissolve the sample and dilute to the mark. Mix thoroughly.

4. Into each of five 200 - 250 mL erlenmeyer flasks carefully pipet 20.00 mL of your chloride sample. (Remember to rinse the pipet with the sample solution before the first transfer.) Use a graduated cylinder to add about 10 mL of 1% dextrin solution and about 20 mL of distilled water to each flask.

5. Rinse and fill a 50 mL buret with 0.04 $\underline{F}$ $AgNO_3$ solution. This solution is not exactly 0.04 $\underline{F}$ in $AgNO_3$. Its concentration is labeled on the bottle. Record the value on the data sheet. Tap to remove bubbles and make certain that the buret tip is filled with solution. Adjust the solution level between 0 and 2 mL; read the buret to the nearest 0.01 mL. (Do not try to set 0.00 mL!) Record the initial reading.

6. Add 3 - 4 drops of dichlorofluorescein indicator solution to the first sample flask and titrate to the **first** appearance of a persistent **faint** pink color. Read the buret to the nearest 0.01 mL and record the value on your data sheet. Repeat the procedure with the other samples. You should have three endpoint volumes within a range of 0.1 - 0.2 mL. If this is not the case, prepare a few more sample solutions and repeat the titrations.

7. Empty the contents of the titration flasks as well as any excess $AgNO_3$ solution into a waste container. (There are large bottles in the fume hoods for this purpose.)

8. Rinse the buret, pipet and volumetric flask with several portions of distilled water and put them away. Use a brush and soapy water to wash the erlenmeyer flasks. **(SCRUB!)**

THE LAB REPORT

1. Calculate:

a.   The percentage by weight of chloride in the original sample;

b.   Its standard deviation (s), standard error (s_e), standard deviation of the mean (s_m), and the 95 % confidence interval.

c.   Repeat a and b for your partner's data.

2.   Statistical Analysis of the data

a.   Does your data have better precision than your partner's data?

b.   Is your data statistically different than your partner's data to the 95 % CI. First use the F-test described on pg 73 of Harris to determine if the standard deviations of the two sets of data our significantly different from the 95 % CI (Table 4-5).

c.   Then, use the Case 2 of the t- test on pg 70 and 71 to determine if the sample means are significantly different. Note: the result from the F test determines the appropriate method for calculating tcalc (eq 4-8 and 4-9 vs eq 4-8a and 4-9a).

Using your data only for 3 and 4

3. Suppose that you made one more titration. Within what range would the titration volume lie with 2/3 probability? (From how many mL to how many mL.)

4. Suppose that you made a very, very large number of titrations with the same sample. Within what range would the mean percentage chloride lie with 90% probability? (That is, what is the 90% C.I. for the mean % Cl? From what % to what %?)

5.   We have expressed the concentration of $AgNO_3$ reagent in terms of "formality" - formula weights per liter of solution. It is sometimes useful to express the concentration of a reagent in terms of "titer" (also called "equivalence"). The titer of a $AgNO_3$ reagent might be defined as "mg Cl per mL of reagent". That is, the titer of a $AgNO_3$ solution is the number of milligrams of chloride titrated by 1.000 mL of that solution. Calculate the titer of the $AgNO_3$ solution you have used.

> NOTE: The titer concentration unit exists to simplify calculation. Suppose that the titer of some $AgNO_3$ solution is 2.00 mgCl/mL. If the titration required 30.0 mL, the sample contained
> (30.0 mL) x (2.00 mg Cl/mL) = 60.0 mg of Cl.

6. A silver nitrate solution is standardized by titrating a known weight of pure NaCl. Exactly 31.20 mL of the solution titrates a 0.1550 g sample of NaCl (FW = 58.44 g/mL). The same silver nitrate solution is used to titrate a sample that contains only NaCl and KCl (FW = 74.56 g/mol). A 0.1400 g sample of the NaCl, KCl mixture is titrated by 24.70 mL of the $AgNO_3$ solution.

a. What is the concentration of the AgNO$_3$ solution?

b. What percentage by weight of NaCl is present in the NaCl, KCl mixture? (Note: The weight of the sample is the sum of weights of NaCl and KCl. The number of moles of chloride present is the sum of the number of moles of NaCl and KCl.).