A Volumetric Analysis (Precipitation Titration) of Chloride in Butter

In this laboratory exercise, we will analyze a sample of Butter for its Chloride Ion (Cl\(^-\)) content. We will use Precipitation Titrimetry, a form of Volumetric Analysis, to carry-out this determination. Standard Silver Nitrate (AgNO\(_3\)) titrant will be added to a solution of the Chloride analyte until colloidal particles of Silver Chloride (AgCl) cease forming; at which point an Adsorption Indicator will change color, signaling the Endpoint of the titration has been reached. As usual, the stoichiometry of the Titration Reaction can then be used to determine the Chloride Ion content of the sample.

Precipitation titrimetry is one of the oldest methods of volumetric titration, dating back to the mid-1800's.

... precipitation titrimetry was a tedious form of analysis, for it was customary to estimate the endpoint by noting when the addition of more standard solution caused no further precipitate to form. This meant that the analyst had to undertitrate, let the precipitate settle, and then add the solution drop by drop at widely separated intervals so he could see whether more precipitate formed when another drop was added. Titration of a set of samples was frequently a daylong operation.

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The slow rate of formation of most precipitates limits the number of Precipitating Agents that can be used in these titrations. Most practical precipitation titrations today employ Silver Nitrate (Argentometric Titration) as a precipitating agent for the Halides, halide-like anions (SCN\(^-\), CN\(^-\), CNO\(^-\)), mercaptans and fatty acids. The general Titration Reaction for an Argentometric Titration is as follows:
(Eq. 1)

Several Indicators can be used for the Endpoint determination in Argentometric Titrations. One such class of indicators is Adsorption Indicators. Adsorption indicators are organic dyes, typically weak organic acids, which absorb onto the positively charged Counter-Ion layer of the solid particles formed during the titration. In the ideal precipitation titration, the adsorption of the dye occurs near the Equivalence Point and results in a color change for the dye.

Fajans’ Method for the Argentometric Titration of Chloride Ion with Silver Nitrate involved, originally, the use of Fluorescein ($Ind$) as an Adsorption Indicator.

(Eq. 2)

In an aqueous solution at pH 7, fluorescein will partially dissociate to form negatively-charged yellow-green Fluoresceinate Ions ($Ind^-$).

(Eq. 3)

Because this indicator is weakly basic, the indicator works best above pH 5. However, the pH must be below about 9 to prevent precipitation of AgOH.

(Eq. 4)

In more current Argentometric Titrometric analyses, the preferred indicator is Dichlorofluorescein, which requires a more acidic solution (pH ~ 4), but behaves in a manner similar to Fluorescein.

In the early stages of a titration of Chloride Ion with Silver Nitrate, the Colloidal Silver Chloride particles formed are negatively charged because of the adsorption of excess Chloride Ions onto the particles. The Fluoresceinate Ions, which are negatively charged, are repelled by the negatively charged particles and impart a Yellow-Green color to the solution. Beyond the Equivalence Point, where the Chloride Ion concentration is very low, the Colloidal Silver Chloride particles strongly adsorb positively charged Silver Ions, Ag$^+$. Fluoresceinate Ions are now attracted into the counter-ion layer that surrounds the particles and their color changes to Red.
Note that the use of this indicator introduces a systematic error into our methodology; the Titration Error. We desire to know how much titrant must be added to reach the Equivalence Point. Instead, we measure how much titrant is added to reach the Endpoint. And, the Endpoint is not reached until we are slightly beyond the Equivalence Point; a point at which the AgCl particle’s counter-ion layer is sufficiently positive to attract the adsorption indicator. However, since we standardize the titrant using the same procedure that we use for the samples, this error is negligible.

Additionally, because the Colloidal Particles are uncharged at the Equivalence Point, they can coagulate. Unlike a Gravimetric Analysis where large particles are desired, here this is undesirable; colloidal particles have a very high surface area onto which the Indicator can absorb. The stabilizer Dextrin is added to the analyte solution in order to prevent the coagulation of these colloidal particles.

Another source of error in titrations employing Silver is photodecomposition of the Silver Halide, catalyzed by light as well as the adsorption indicator. With proper storage and standardization, however, highly accurate analyses can be obtained. Titrations using Adsorption Indicators are rapid, accurate, and reliable, with their application limited only by the relatively few precipitation reactions in which a colloidal precipitate is formed quickly.

Sweet Cream Butter is churned directly from pasteurized fresh cream and is sold in either a salted or an unsalted form. It is at least 80% milkfat and ~18% Water. Salt is added directly as granules or as Brine during processing for flavoring and as a preservative. The National Dairy Council reports butter has an approximate salt content of ~1.6% in salted butter and ~0.028% for unsalted butter. However, it is up to each manufacturer to set the amount of salt in its butter. It is the Chloride content, and by extension the salt content, of salted butter that we will be analyzing for in this laboratory.
So, in this experiment, we will first standardize our AgNO₃ titrant against a Sodium Chloride Primary Standard. This will be followed by a triplicate analysis of a sample of known Chloride composition. This will allow us to independently verify the composition of the mixture and to confirm our ability to conduct an accurate precipitation titration. Finally, we will process a butter sample and determine its Chloride Ion content using this methodology. This will allow us to determine the percentage salt in the butter sample.
Pre-Lab Calculations

1. A 0.0259g sample of Primary Standard grade NaCl was dissolved in 25 mL of Water and titrated to its endpoint using an AgNO₃ titrant. The starting burette volume was 0.33 mL. The ending volume was 21.65 mL. Calculate the concentration of the AgNO₃ titrant.

2. A 0.0531g sample of an unknown powder was dissolved in 25 mL of Water and titrated to its endpoint using the above titrant. The starting and ending burette volumes were 0.15 mL and 32.05 mL respectively. Calculate the percentage Chloride Ion in the sample.

3. 10.0456g of butter are analyzed using our procedure and the titrant above. The burette volumes were 0.57 mL and 28.96 mL. Calculate the % NaCl of the butter. Keep in mind the butter is extracted with 250 mL of Water and only 20 mL is titrated.
Procedure

**Preparation of Silver Nitrate Solution**

Weigh approximately 2.0 g Silver Nitrate, AgNO₃, to nearest 0.1 mg into a small clean beaker. Transfer to a 500-mL volumetric flask, rinse container in which Silver Nitrate was weighed with several small portions of distilled water. Fill the volumetric flask about half-way with distilled water and swirl to ensure complete dissolution of Silver Nitrate. Fill to the mark with distilled water and mix well. Store in the dark when not in use as sunlight will catalyze the decomposition of Silver Nitrate.

**Standardization of Silver Nitrate**

Prepare three 25 mg samples of dried Primary Standard Sodium Chloride (1 hr at 110°C and allowed to cool in a desicator), weighed to the nearest 0.1 mg, and record the mass in your notebook to 4 significant digits. Transfer each Sodium Chloride sample to individual Erlenmeyer flasks and add approximately 25 mL distilled Water to each. Add 1 scoop Dextrin stabilizer and 3 to 5 drops Dichlorofluorescein Indicator to each sample. Titrate with AgNO₃ until the first permanent pink color of the adsorbed Dichlorofluoresceinate Ions remains.

**Notes:**

1) If a gradual indicator change makes Endpoint selection uncertain, record the buret reading. Then add another drop and record any change; repeat this procedure. Select as the Endpoint the reading corresponding to the drop that causes the greatest change. The indicator may be slow to respond at the Endpoint, so be patient while waiting for a color change.

2) Since Silver Chloride is very sensitive to photodecomposition in the presence of the indicator, the titration will probably fail if attempted in direct sunlight. If this is a problem, do a trial titration and use the volume of AgNO₃ added as the approximate volume to reach the endpoint for the subsequent titrations. For these subsequent titrations, wait to add the indicator and Dextrin until just before (a few mL) the Endpoint. Continue the titration without delay.

Calculate the mean molarity of the Silver Nitrate and its standard deviation. Repeat until the precision is better than ±0.005 M. Use the Q-Test to eliminate any potential outliers.

**Determination of Unknown Chloride**

Obtain a pre-dried Unknown Sample vial from your instructor and place it in your dessicator and allow to cool to Room Temperature. Record the unknown number on the assay sheet and in your notebook. Weigh out three replicate 0.04g samples and record their mass to 4 decimal places. Transfer the solid samples to individual Erlenmeyer flasks, add approximately 25 mL distilled Water, dissolve and titrate as above.

Calculate the average wt % Cl⁻ in your unknown sample along with the standard deviation.
**Determination of Chloride in Butter**

Weigh 10 grams of Butter on a piece of glazed weighing paper. Fill a 250 mL Volumetric Flask with warm Distilled Water to the mark. (The Water must be warm enough to melt the butter but should not be too warm.) Add the warm Water to a clean dry pint jar. Drop the paper and Butter into the pint jar. Shake the jar with a rotary motion and let stand 2-3 minutes. Repeat the shaking. Again, let the jar stand. This washes the NaCl out of the Butter and into the Water. The fat will rise to the top of the system.

Attach a Side-Arm Pipet Bulb to a 20 mL Volumetric Pipet. Eject air from the Pipet while at the same time passing the tip of the Pipet through the Butter Fat and into the above wash Water. This keeps the Fat out of the Pipet tip. Transfer 20 mL of the wash Water to an Erlenmeyer flask.

Add 1 scoop Dextrin stabilizer and 3 to 5 drops Dichlorofluorescein Indicator to the sample. Titrate with Silver Nitrate until first permanent pink color remains. Repeat with another 20 mL sample of the wash Water.

Calculate the wt % NaCl in your Butter.

*Modification of a procedure by J.L. Sammis; “The Determination of Salt in Butter at the Creamery”, The Univ. Wisconsin Agricultural Experiment Station, Circular 14, May 1910.*