

TITRIMETRIC ANALYSIS OF CHLORIDE

Introduction

The purpose of this experiment is to compare two titrimetric methods for the analysis of chloride in a water-soluble solid. The two methods are:

- a weight titration method using a chemical indicator;
- a volumetric titration method using potentiometric detection.

The most important difference between the methods is how the endpoint is determined. In the first case, the color change of the indicator signifies that the titration is complete, while the second method generates a titration curve from which the endpoint is determined. For the potentiometric method, an automatic titrator will be used to perform the titration, and to obtain the titration curve.

Background

Argentometric Titrations

In order for a titrimetric method to be viable, the titration reaction (1) must be complete (i.e., $K_{\text{titration}}$ is large) and (2) should be rapid. There are many precipitation reactions that can satisfy the first requirement, but far fewer that satisfy the second. Precipitation reactions of silver salts are usually quite rapid, and so **argentometric titrations**, which use AgNO_3 as the titrant, are the most common precipitation titrations. Argentometric titrations can be used to analyze samples for the presence of a number of anions that form precipitates with Ag^+ ; table 7-1 in Harris lists some of these.

Weight Titrations

The goal of any titrimetric method is to determine the number of moles of titrant needed to reach the equivalence point of the titration reaction:



where a and t are the stoichiometric coefficients in the reaction between titrant and analyte. In a titrimetric analysis, solution of titrant is added until the *equivalence point* of the titration reaction is reached. At the equivalence point, neither analyte nor titrant is present in excess. By definition, the equivalence point is the point during the titration at which the following relationship is true:

equivalence point
$$\frac{n_A}{a} = \frac{n_T}{t}$$

where n_A is the number of moles of analyte originally present in the sample solution, and n_T is the number of moles of titrant that must be added to the sample to reach the equivalence point.

From this last expression, we see that, in order to determine the number of moles of analyte originally present in the sample solution, we must (a) know the stoichiometry of the reaction, and (b) determine how many moles of titrant are needed to reach the endpoint. In order to meet this last requirement, we must somehow keep track of the quantity of titrant solution that is added to the sample solution.

In *volumetric titrations*, the *volume* of the titrant solution is used to calculate n_T . By simple dimensional analysis,

$$n_T = \frac{\text{mol } T}{\text{vol soln}} \times \text{vol added soln} = C_T \times V_T$$

where C_T is the concentration of the titrant solution in M, and V_T is the volume of titrant solution needed to reach the equivalence point.

By contrast, in *weight titrations*, the *mass* of the titrant solution is used to determine the value of n_T :

$$n_T = \frac{\text{mol } T}{\text{mass soln}} \times \text{mass added soln} = C_T \times m_T$$

where m_T is the mass of titrant solution delivered to reach the equivalence point, and C_T is the concentration of the titrant solution **in units of mol/kg**. A concentration that is expressed in these units is sometimes called the *weight molarity* of the solution¹, and is abbreviated M_w . Note that, since for most solutions $1 \text{ L} \approx 1 \text{ kg}$, the numeric values for molarity and weight molarity are similar.

In order to calculate the number of moles of analyte, n_A , in the dissolved sample, the titration procedure must consist of the following two steps:

1. *Standardization*, in which concentration of the titrant solution is determined. In weight titrimetry, the concentration of titrant is determined in units of mol/kg.
2. *Titration of sample(s)*, where the quantity of titrant solution that must be delivered to the sample solution to reach the equivalence point is measured. In weight titrimetry, the mass of delivered titrant solution is measured.

Endpoint Detection for Argentometric Titration

Another requirement of titrimetric analysis is that there must be some method of determining when the titration reaction has reached its equivalence point. In this experiment, you will compare two methods of endpoint detection, one using a chemical indicator and another using potentiometric detection. We will now describe the common methods of endpoint detection for argentometric titrations.

Chemical Indicators

There are three common chemical indicators that are associated with argentometric titrations:

1. The chromate ion, CrO_4^{2-} (the Mohr method);
2. The ferric ion, Fe^{3+} (the Volhard method);
3. Adsorption indicators such as fluorescein (the Fajans method).

In this experiment, we will be using dichlorofluorescein, a Fajans (adsorption) indicator, to detect the endpoint chemically; however, it is useful to briefly describe all three methods of endpoint detection.

¹ the weight molarity is easy to confuse with another measure of concentration, the *molality* of the solution. Molality is mass solute per mass *solvent*, while weight molarity is mass solute per mass *solution*. Both, however, have units of mol/kg.

The Mohr Method

The Mohr method is based on the following reaction between the titrant and the indicator:



The concentration of titrant rises sharply near the equivalence point, and the solubility of Ag_2CrO_4 is exceeded. The appearance of red precipitate marks the endpoint. The applicability of the Mohr method is limited compared to either of the other chemical indicator methods: it can be used to analyze for Cl^- or Br^- anions.

The Volhard Method

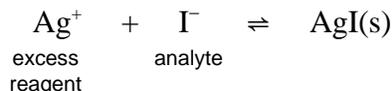
The Volhard method of Ag^+ determination is associated with argentometric titrations even though the titrating agent is actually SCN^- :



The indicator in Volhard titrations is Fe^{3+} , which reacts with titrant to form a red colored complex:



This is a good method for the analysis of Ag^+ in solution. We can extend the applicability of this method to anions such as I^- through the procedure known as *back-titration*. A measured excess of Ag^+ is added to the dissolved sample:



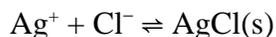
After the precipitation of AgI is complete, the concentration of excess Ag^+ titrant is determined by a Volhard titration. The number of moles of I^- analyte originally present in the solution is easily calculated:

$$\# \text{ mol } \text{I}^- = \# \text{ mol } \text{Ag}^+ \text{ originally added to solution} - \# \text{ mol } \text{Ag}^+ \text{ as determined by Volhard titration}$$

In a similar manner, the Volhard titration method can be used to analyze for a number of anions.

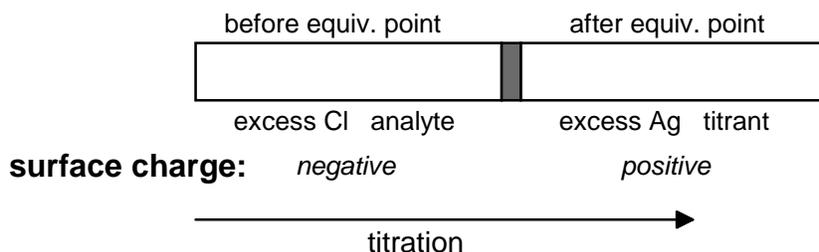
The Fajans Method

Adsorption indicators function in an entirely different manner than the chemical indicators described thus far, and they can be used in many precipitation titrations, not just argentometric methods. Let's imagine that we wish to analyze Cl^- in a sample solution by titrating with Ag^+ ; the titration reaction would be

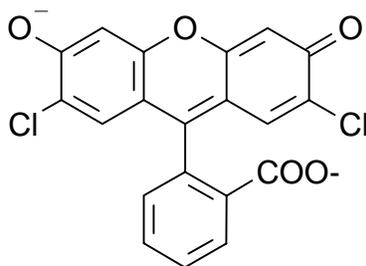


Silver chloride forms colloidal particles. Before the equivalence point, the surface of the precipitant particles will be negatively charged due to the adsorption of excess Cl^- to the surface of the particles. A

diffuse positive counter-ion layer will surround the particles. When the equivalence point is reached, there is no longer an excess of analyte Cl^- , and the surface of the colloidal particles are largely neutral. After the equivalence point, there will be an excess of titrant Ag^+ , some of these will adsorb to the solid AgCl particles, which will now be surrounded by a diffuse *negative* counterion layer. The next figure illustrates this concept.



Adsorption indicators are dyes, such as dichlorofluorescein (shown below), that usually exist as *anions* in the titration solution.

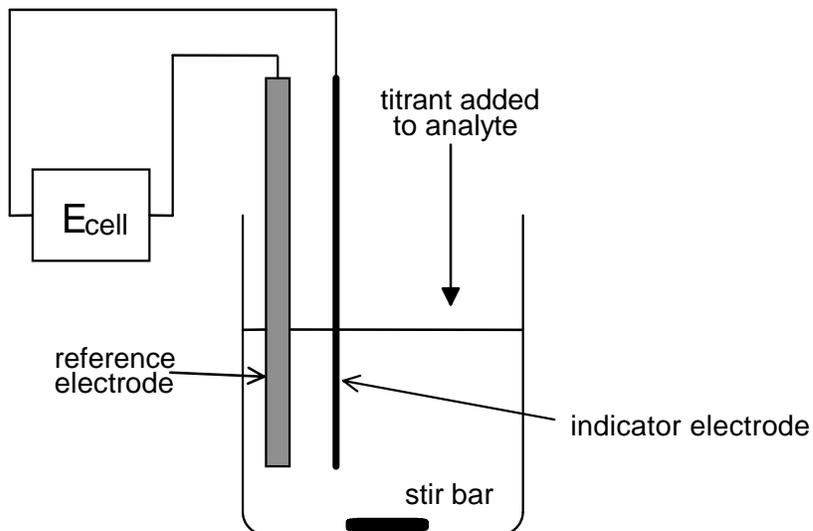


dichlorofluoroscein

The doubly charged dichlorofluoroscein anion is attracted into the counterion layer immediately following the equivalence point, when the surface charge of the particles changes from negative to positive. For reasons that are not fully understood, the closer proximity of the dye to the particles changes the color of the molecule, providing a visual indication of the titration endpoint. In the case of dichlorofluorescein, the indicator changes to a pinkish color (*see Harris color plate #2*).

Potentiometric Endpoint Detection

The progress of the reaction as the titrant is added to the analyte solution can be followed potentiometrically using an *indicator electrode*. A schematic for the general setup is shown in the next figure.



The analyte solution is part of an electrochemical cell that can be represented by

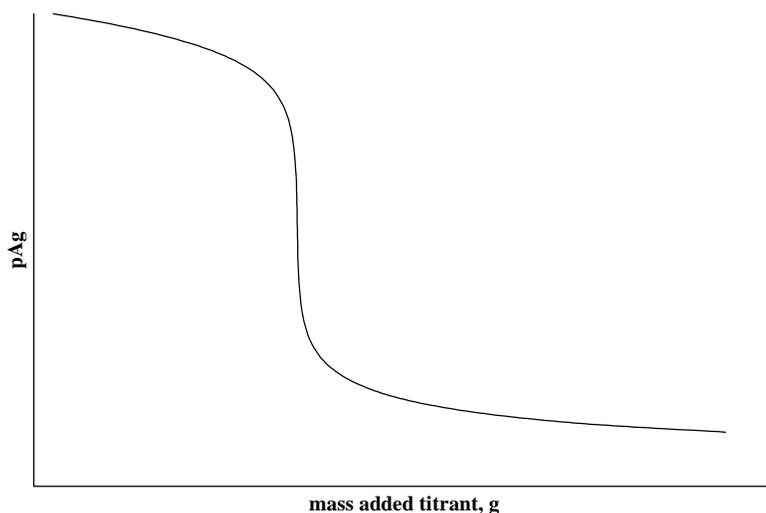


The reference electrode usually contains a liquid junction that completes the electrical circuit. The potential of this cell can be written as

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}}$$

where E_{ind} is the half-cell potential at the indicator electrode due to species in the analyte solution and E_{ref} is the half-cell potential of the reference electrode. The reference electrode is chosen to be stable: E_{ref} is assumed to be constant during the titration. *Any changes in measured cell potential are due to changing species concentrations in the analyte solution.*

Let's imagine that we wish to monitor the course of the argentometric determination of Cl^- . The titration curve in argentometric titrations is sometimes represented by a plot of p[Ag] vs added titrant, and the curve should be sigmoidal in shape.



We will now show that we observe the same sigmoidal shape if we plot E_{cell} instead of $p[\text{Ag}]$ as the x -axis, so long as we use the proper indicator electrode to measure E_{cell} . If we use a bare silver wire as our indicator electrode, our electrochemical cell can be represented as



At the indicator electrode, the dissolved Ag^+ will have a certain tendency towards reduction to the silver metal:



The potential of this half-reaction will depend on the concentration $[\text{Ag}^+]$ in the analyte solution, according to the Nernst equation:

$$E_{\text{ind}} = E_{\text{ind}}^0 - \frac{0.0592}{n} \log Q$$

Since $n = 1$ and $Q = [\text{Ag}^+]^{-1}$, we may write for this cell

$$E_{\text{cell}} = K + 0.0592 \cdot \log[\text{Ag}^+] = K - 0.0592 \cdot p[\text{Ag}^+]$$

where K is a constant that accounts for various constant contributions to the cell potential, such as the reference half-cell potential. Thus, as we see, the measured cell potential is directly related to $p[\text{Ag}^+]$, and can be used to follow the course of the titration reaction. A plot of E_{cell} vs added titrant will yield a sigmoidal titration curve similar in appearance to the one in the previous figure. The endpoint, which is usually taken as the inflection point of this curve, can be estimated from a plot of the first or second derivative of the titration curve.

References

Titrimetry (general): Harris 7

Precipitation titrations: Harris 7.4-7.7

TITRIMETRIC ANALYSIS: *Procedure*

General

There is one titrator that is to be shared by everyone. You will use the titrator in order of your unknown numbers (i.e., alphabetical order). While waiting for the titrator, you should proceed with the Fajans titration described below.

By the time it is your turn to use the titrator, you should have your three titrator samples prepared and ready to go (steps 1-3 on the next page). Each person will take 10-15 minutes to analyze their samples with the titrator. If your samples are not ready when it is your turn, you will lose your place in “line!” The first few people should prepare their titrator samples immediately, before beginning the Fajans titration.

Handling of Titrant (AgNO_3) Solution

Aqueous silver nitrate is photosensitive and should not be exposed to light any more than is necessary during this procedure. It should be stored in darkened storage bottles, and be kept in your drawer except when being used.

Fajans Method of Endpoint Detection

Chemicals and materials:

Silver Nitrate, 0.07 - 0.10 M_w

Dextrin, 2%

Dichlorofluorescein, 0.1%

1. Dry the sample and NaCl primary standard for at least one hour at 110 °C. Cool in a desiccator.
2. Weigh by difference three 0.1 g samples of the pure NaCl (to the nearest 0.1 mg) into three separate 250 mL Erlenmeyer flasks. Weigh by difference three 0.1 g samples of the unknown sample into another three 250 mL Erlenmeyer flasks. Add approximately 100 mL of deionized water to each of the six beakers to dissolve the solid.
3. Add 5 mL of 2% dextrin solution and 10 drops of 0.1% dichlorofluorescein solution to the first flask. The purpose of the dextrin solution is to stabilize the colloidal suspension of AgCl(s) formed once the titration begins, and the dichlorofluorescein is the adsorption indicator.
4. Titrate with AgNO_3 solution at a fairly rapid rate, using continuous swirling. When the rate of fading of the pink color becomes slow, reduce the rate of addition to a drop-wise rate, swirl constantly, and continuously observe the color of the suspension to detect the endpoint, which is a change from a light peach color to a darker “Pepto Bismol” pink. Color plate 2 in Harris shows the expected endpoint.
5. Repeat steps 3 and 4 for the other five flasks.

After completing your titrations, dispose of the AgCl(s) and titrating solutions by pouring them into the waste bottles in the hood that are marked “AgCl(s)Waste.” *Also return any unused titrant solution to the instructor.* Anything that contained AgNO_3 should be rinsed **thoroughly** before being put away.

Potentiometric Method of Endpoint Detection

Chemicals and materials:

Silver Nitrate, approximately 0.3 M

Nitric acid, 6 M

solid KNO_3

1. Dry the sample for at least one hour at 110 °C. Cool in a desiccator.
2. Weigh three approximately 0.1 g samples of the “unknown” into your plastic titrator sample beakers. The sample masses should be recorded to the nearest 0.0001g using the analytical balances. Add 0.5 g potassium nitrate; this can be massed using the top-loader balances on the lab benches.
3. Add about 40 mL of deionized water to each beaker and stir until dissolved. Rinse your stir rod into the sample solution (i.e., you do not want any analyte chloride to leave the solution). Also add a few drops of 6M nitric acid into each beaker.
4. You will titrate your sample solutions with the Mettler-Toledo DL58 titrator using a silver ring indicator electrode to follow the progress of the titration. For your first sample, your instructor or a TA will show you how to use the titrator.
5. Repeat the titration for your other samples. **Be sure to wash the titrator thoroughly after each titration.** Dispose of the silver chloride waste in the appropriate container (found in the HOOD). When you are finished, wash your titrator sample beakers thoroughly and rinse with deionized water.
6. You will be provided with data from three titrations that were used to standardize the titrant solution just prior to the experiment.

For each of your samples, the titrator will print out its estimate of the endpoint volume, as well as the raw data (potential as a function of added titrant solution volume). Plot your titration curves and include at least one of them as a figure in your lab report. Please turn in copies of your data and your titration curves with your data sheet - this material is supplemental to your lab report.

DATA SHEET: *Fajans Method*

Directions: fill in this sheet and turn it in with your lab report.

Name: _____

Unknown #: _____

	A	B	C
dry NaCl mass (by difference)	1: _____ g 2: _____ g	1: _____ g 2: _____ g	1: _____ g 2: _____ g
dry sample mass (by difference)	1: _____ g 2: _____ g	1: _____ g 2: _____ g	1: _____ g 2: _____ g
Titration of NaCl (1) initial mass titrant soln (2) endpoint mass titrant soln	1: _____ g 2: _____ g	1: _____ g 2: _____ g	1: _____ g 2: _____ g
Titration of sample (1) initial mass titrant soln (2) endpoint mass titrant soln	1: _____ g 2: _____ g	1: _____ g 2: _____ g	1: _____ g 2: _____ g
estimated analyte conc (as a confidence interval)			

DATA SHEET: *Potentiometric Method*

Directions: fill in this sheet and turn it in with your lab report. You should also turn in your titration curves and your raw data (you can xerox the titrator printout). I do not need the standardization data - I already have a copy. Also turn in plots of your titration curves with your data.

Name: _____ Unknown #: _____

	A	B	C
dry NaCl mass (from handout)			
dry sample mass (by difference)	1: _____ g 2: _____ g	1: _____ g 2: _____ g	1: _____ g 2: _____ g
Endpoint: Titration of NaCl, mL (from handout)			
Endpoint: Titration of sample, mL			
estimated analyte conc (as a confidence interval)			

Results from Hypothesis Testing

Comparison of Accuracy of Methods	
95% CI for d	
Conclusion	
Comparison of Precision of Methods	
Observed value for F	
Conclusion	

TITRIMETRIC ANALYSIS: *Data Treatment*

Effect of Standardization Measurement Error

A requirement for quantitative analysis by titration is that the titrant concentration is known. In many cases, including this experiment, titrant solution concentration is itself determined (*standardized*) in a separate set of titrations. The titrant concentration is thus subject to random measurement error comparable in magnitude to that of the sample titration.

When calculating a confidence interval for the analyte concentration in your “unknown” sample, you will have to use the titrant concentration. A propagation of error approach can be used to account for the effect of standardization error on the final, calculated value for analyte concentration in the sample. Let’s assume that you have one set of standardization titrations and another set of titrations of the sample solution:

- from the standardization titrations, you calculate the mean titrant concentration, C_T , and its standard deviation (i.e., the standard error of the mean)
- from the endpoints of the sample solution titrations, you can calculate the mean analyte concentration, \overline{C}_A , and its *observed* standard deviation, $s_{obs}(\overline{C}_A)$. This standard deviation does *not* include the effect of uncertainty in C_T ; it is calculated directly from the endpoint volumes of the sample titrations.

A propagation of error approach yields a value for RSD_A , the true relative standard deviation of the point estimate (\overline{C}_A) of analyte concentration.

$$RSD_A^2 = RSD_T^2 + RSD_{obs}^2$$

where

$$RSD_T = \frac{s(\overline{C}_T)}{\overline{C}_T} \text{ and } RSD_{obs} = \frac{s_{obs}(\overline{C}_A)}{\overline{C}_A}$$

Note: assume that the value you calculate from this procedure contains 2 degrees of freedom. Although this is not strictly true, it is a conservative estimate of the true degrees of freedom contained in the estimate of standard error.

Comparison of the Accuracy and Precision of Titration Methods

One of the primary goals of this experiment is to compare the ability of two titrimetric methods – weight titration with chemical indicator, and volumetric titration with potentiometric detection – to measure the chloride content of a soluble, solid sample. In particular, it would be meaningful to compare the relative *accuracy* and *precision* of the two methods.

For each method in this experiment, you essentially obtain two results (which you combine into a confidence interval):

- a point estimate of the analyte concentration, which represents your best estimate of the true analyte concentration. In this case, the point estimate will be the mean of three independent measurements. The difference between the point estimate and the true analyte concentration is a measure of the *accuracy* of the method.

- the standard error of your point estimate: the standard deviation of the mean of three independent measurements (corrected for standardization error, as explained above). The magnitude of the standard error indicates the *precision* of the method.

Statistical theory provides a procedure, called *hypothesis testing*, that can be used to objectively compare the accuracy and precision of the two methods in this experiment. You will need to apply this procedure to your results. Hypothesis testing is discussed at length in Chemistry 300, but a very brief summary will be given here of procedures that you may use (since the Full Report for this experiment may be due before the subject is covered!). More detail on hypothesis testing is given in the lecture notes for Chemistry 300.

Comparison of Accuracy

Concerning the accuracy of the two titrimetric methods, there are three general possibilities:

1. Neither method gives biased estimates of analyte concentration;
2. One method is biased but the other is not;
3. Both methods are biased.

In order to determine if bias exists, the true analyte concentration must be known. Since it isn't (to you, anyway!), all you can do is *compare* the bias of the two methods. A relatively simple procedure for doing this is as follows.

Let's define a random variable d , as the difference between the point estimates for the analyte concentration obtained from the indicator and potentiometric methods:

$$d = \widehat{C}_{ind} - \widehat{C}_{pot}$$

This value is the difference between two random variables, and so it too must be a random variable. Use error propagation to calculate the standard deviation of the difference, s_d , and then calculate a 95% confidence interval for μ_d (assume d is normally distributed, and 2 degrees of freedom in s_d). If the confidence interval does *not* contain zero, then there is at least a 95% probability that there is a statistically significant difference in the bias of the two methods. That means that either possibility #1 (only one of the methods has bias) or #3 (both methods have bias, but of different magnitude) must be true.

Comparison of Precision

Let's define a random variable F as follows:

$$F = \frac{se_A^2}{se_B^2}$$

where se_A and se_B are the standard errors of the point estimates obtained using titrimetric method A and method B. Which method is A and which B? You should choose them so that the ratio of the squared standard errors is a value greater than one ($F > 1$). In other words, method A is the one with the larger standard error.

The value F is the ratio of two sample statistics, so it is a random variable. If the measurement precision of the two methods is the same, then the population mean of this variable should be equal to one (i.e., $\mu_F = 1$ if $\sigma_A = \sigma_B$). Values of F that are much larger than one suggest that perhaps method A is less precise than method B.

Hypothesis testing allows us to determine what the “cutoff point” (the *critical value*) should be before we can consider one method to be definitely less precise than the other. For this experiment, the critical value for this hypothesis test is 39.0. If $F > 39.0$, then there is at least a 95% probability that the precision of method A is worse than that of method B.

Why is the critical value so large? The reason is that there are only two degrees of freedom in our standard error values, so that there is a lot of uncertainty in both se_A and se_B (and even more in their ratio). So it will be very hard to “prove” a difference in precision for this experiment. If you wanted to get a smaller value for the critical value, more degrees of freedom (i.e., more measurements) are needed. For example, with six measurements for each method, the critical value would be 7.15.

“Within-Student” and “Between-Student” Variability

When comparing precision, you should be aware of the difference between what we can call “within-student” and “between-student” sources of random error. We can illustrate the difference between these sources by considering a titration using a chemical indicator (like the Fajans method):

- *within-student* variability will be due to the uncertainty a single student experiences in determining the color change from sample to sample. This source of variability is reflected in the spread of each student’s measurements about the mean.
- *between-student* variability is due to the fact that different students will interpret the endpoint color slightly differently. This source of variability is reflected in the spread of the measurement errors of all the students in the class.

The difference between these sources of variability is almost certainly quite significant for the Fajans method – there will be much more between-student variability than within-student variability. There is probably not too great a difference in the case of the potentiometric method, though.

Since you won’t have access to the data of your classmates when you write this laboratory report, there is not much you can do to assess the true variability of the Fajans method. You should be aware the you are actually comparing “between-student” variability when you compare the precision of your point estimates.