“What’s better and more than Mohr? Fajans!”

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Abstract

This paper updates the findings on the comparison of two classical titration techniques used to determine the chloride concentration in a NaCl solution or the chlorinity, and in turn the salinity of seawater samples. The comparisons show that the Fajans and Mohr techniques yield comparable results. However, the Fajans technique should be preferred for many reasons including the safety of the indicator, its increased precision, its improved end point detection, the reversibility of the reaction and its use over a broader range of pH and concentration. Important teaching opportunities include absorption chemistry, the use of dextrin, the importance of blanks and making blank corrections, the use of the two-balance technique, the switch from volume to weight titrations, and the adaptability of the technique to classroom settings.
In the attached SOP, procedures are designed to show how one can make and use inexpensive modified plastic pipettes as weight burettes, minimize reagent requirements, and introduce a simplified scheme for doing the computations.

Introduction

The Mohr titration technique (1) (hereafter simply Mohr) to determine the chloride concentration in a solution using a chromate indicator was published in 1856. In 1923, 68 years later, the Fajans titration technique (2) (hereafter simply Fajans) was published. It provided an alternate approach to the determination of chloride in solution using an organic indicator, dichlorofluorescein (hereafter simply DCF). There has been an understandable reluctance to adopt the Fajans, most likely because there are few papers addressing how the Fajans compared to the Mohr.

The difference in the uses of the two techniques is clearly seen in Figures 1 and 2 from recent Google Scholar papers searches.

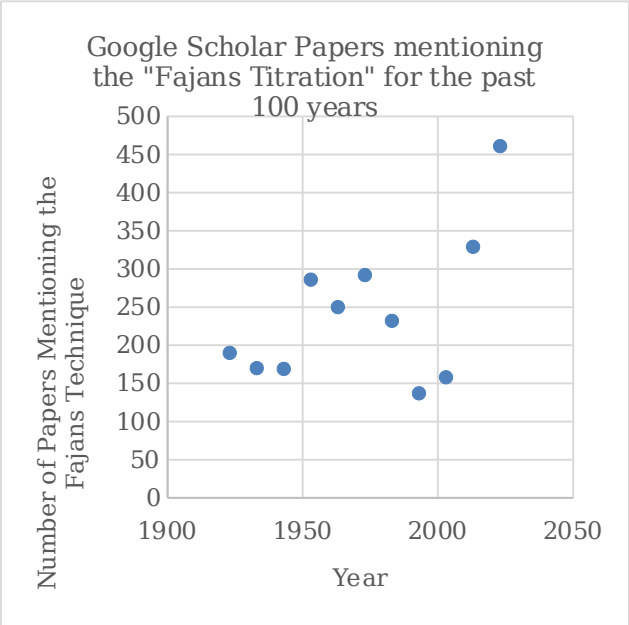

Figure 1. The Number of New Google Scholar Papers Mentioning the “Fajans Titration” Published Since 1923. (The data are plotted in 10-year increments.)

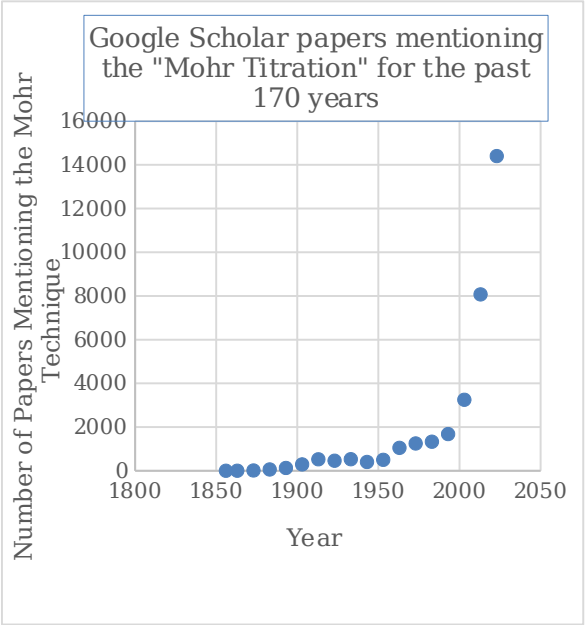

Figure 2. The Number of New Google Scholar Papers Mentioning the “Mohr Titration” Published since 1856. (The data are published in 10-year increments.)

From Figure 1, a slight uptick in the use of Fajans is apparent in recent years, but the Mohr (Fig 2.) dominates by a wide margin, since 1993, by a factor of 37.7. The following paper draws on the results of 4 articles comparing the two techniques, but the one by Campbell (3) is the clearest and most recent demonstration that both techniques give comparable results. Along with a discussion of the comparisons, the wide-ranging favorable qualities of the Fajans will be detailed.

The first significant paper comparing the two techniques was published in 1936 (4). In this paper there is much discussion about the problems associated with the determination of the chlorinity of a sea water sample using the Mohr. Miyataka states, “It is proposed to use an improved version of the Fajans method instead of the Mohr method, and excellent results have been obtained in practical experiments.” (4) [translation of the original Japanese text using Google translate.] One comparison using the Mohr and Fajans technique to determine the chlorinity of a sample of IAPSO seawater (5) showed an agreement of 0.14% accompanied by the author’s comment that the Fajans gave better agreement with the accepted value. A second comparison of the two techniques, using a KCl solution with a chloride concentration identical to that in the IAPSO seawater tested, showed a very similar agreement between the two techniques (4).

The 1958 paper by Park (6) compared 3 techniques for the determination of chloride in solution. Although the paper lacks essential details on the equipment used, the concentration of reagents and the chloride solution(s) analyzed, the volumes of all solutions used in the titrations, and the possible inclusion of a blank correction in the computations, the conclusions indicate that the Mohr and Fajans techniques give comparable results and precisions.

In a very recent effort by Campbell (3) comparing the two techniques using sodium chloride solutions and IAPSO standard seawater (5), the two methods showed excellent agreement. It should be noted that between the work of Park (6) and that of Campbell (3), the titrations described by Campbell (3) are based on the use of modern equipment and technology and updated techniques.

In a very recent paper (7) detailing the results of experiments conducted on a syrup spiked with KI or NaCl solutions, rather different conclusions were reached. The chloride concentrations using the Mohr or Fajans were statistically different with the Fajans giving a percentage of chloride in the NaCl solution of ~1.07 %, while for the Mohr, the percentage was ~0.92% (The two percentage values were read from a graph in the paper) (7). In reviewing this article and the supporting information, the use of syrup spiked solutions instead of chloride containing solutions makes a direct comparison with the work of Miyataka (4), Park (6), and Campbell (3) difficult. It is likely that the nature of the syrup solution was a confounding variable that led to the conflicting results of this experiment.

Discussion

Safety

Safety is of special concern in school environments with teenage and young adult students. The chromate or chromate-dichromate indicator used in the Mohr is a toxic substance. The indicator is carcinogenic, mutagenic, and it can cause lung and organ damage, genetic defects, and skin and eye irritation. These problems occur via passage through the skin and inhalation of the indicator (8,9). Based on the limited tests conducted on the DCF indicator, it is considered low hazard (10). As such, the Fajans indicator is much safer than the Mohr indicator. Like many reagents, the DCF indicator is associated with possible skin and eye irritation and its safety data is not conclusive, so best laboratory practices should still be used when handling the DCF reagent (10).

In addition to the health hazards associated with the Mohr indicator, chromium (VI) compounds are listed as carcinogens and disposal of these compounds must follow the requirements for the disposal of extremely hazardous waste through one's EH&S facility (8,9). Especially in classrooms, it is difficult to monitor proper disposal and ensure that students do not dispose of their titration solutions down the sink. Therefore, the safer Fajans method, which is less toxic and has minimal disposal requirements, is particularly preferred in educational settings.

Precision

Fajans had better precision, with a %RSD of 0.17% compared to 0.28% for Mohr (3). Blanks were determined for each procedure and were included in the

computations. For the Fajans, the blank was determined to be 0.0006 grams while the Mohr blank was 0.006 grams, approximately 10 times that of the Fajans. Since the $AgNO_3$ titers were similar in weight for both the Fajans and Mohr, namely ~1.7 g, not correcting the Fajans results for the blank would lead to an error of ~0.04% in the calculated concentrations, while for the Mohr, the error would be ~0.4%, a significant difference.

"In the preparation of a TRIS buffer solution (11) the $AgNO_3$ solution used for all titrations is standardized using recrystallized and oven dried NaCl and an indicator. As standardized, this $AgNO_3$ solution is used to determine the concentration of the greater than two molar magnesium and calcium chloride solutions used in the preparation. A blank correction for the $AgNO_3$ solution is determined and applied. Density measurements (12) on 5 TRIS solutions in which the Fajans DCF indicator was used averaged 1.02618 ± 0.00005 g/cm^3. For 5 TRIS solutions using the Mohr chromate/dichromate indicator, the results were 1.02614 ± 0.00003 g/cm^3. The precisions of 0.005% RSD or less are excellent, while the difference between the two values of 0.0034% RSD also shows excellent agreement between the two methods." (Author 2, paraphrased personal communication, July 16, 2024).

Endpoint Detection

The Fajans technique results in a clear shift from greenish yellow to pink at the endpoint (2,13) while the Mohr endpoint has a much more gradual color change that is only a difference in the shade of a reddish-brown color (1,13). The challenge in determining the endpoint of the Mohr could be a major factor leading to its lower precision (3). The lack of definition in the endpoint also causes the Mohr to require more examination of the color's shade in between dispensing drops of titer, and thus a titration requires more time. With its better-defined endpoint, more trials could be conducted using the Fajans in a class period, and the results would likely be more precise (3).

Reaction Reversibility

The reversibility of the Fajans reaction allows students to quickly get comfortable with the color change at the endpoint (SI, Video Three). If the students discover that their titrated solution's pink color is too dark**,** they can add more chloride-containing solution to the titrated solution to reverse the reaction and return the solution to the yellow color. The students can then add $AgNO_3$ to the solution until they reach the desired light-pink color (SI, Video Three). This reversibility, which is not available in a Mohr, enables the students to get used to the endpoint so they can decrease the time needed for future trials while likely increasing their precision. (2, 3).

Boarder Range of pH and Concentration

The Fajans also allows students to analyze a broader range of samples based on concentration and pH (13). The DCF indicator is effective with very low

halogen concentrations and a greater range of pH, namely ~4.4 to 10. The ideal pH range for a Mohr titration is 6.5 to 9 (13).

Teaching Opportunities

Adsorption Chemistry

The Fajans involves more opportunities for teaching moments. As mentioned in the introduction, the Fajans involves unique adsorption chemistry (2,13) that is not present in the Mohr's more common precipitation titration. Therefore, the Fajans would offer an opportunity to teach a type of chemistry that students are not commonly exposed to through other laboratory experiments.

Use of Dextrin

Teachers can provide insight into advanced methodical proceedings in the Fajans. Dextrin makes the endpoint much easier to see by preventing coagulation of the AgCl precipitate (SI, Titration Protocol). This provides an additional teaching moment when students experience problems because of the coagulation of the precipitate. Students will be exposed to problem solving in the laboratory since the coagulation can be effectively addressed by experimenting with Dextrin, particularly in chloride containing solutions with concentrations greater than one mole/kg-soln (3,4,13).

Blank Corrections

A teacher could choose to have students determine a blank correction by titrating varying weights of seawater or a NaCl solution (SI, Appendix Five). Though the Fajans blank is more time consuming than determining the Mohr blank, it provides an opportunity for the students to learn an important calibration curve technique applicable to other experiments. Since the Fajans blank is typically 0.0006 grams, the error in a titration of ~1.7 g would be approximately 0.04%, so in many cases it could be ignored (data set in the Supplementary Materials). Without the need to spend the extra time and effort required to determine a blank correction, students can focus on the chloride analyses with fewer extra details to consider. At approximately 10 times greater than the Fajans titration blank, the blank correction of the Mohr titration cannot be ignored (1,3).

Two-Balance Technique

Students can learn the efficient two-balance technique while performing the Fajans (SI, Appendix Two & Video Two). If analytical and top loader balances are available, students can quickly determine sample weights to 0.0001 g. This technique will also be useful to students in other experiments that require quick but accurate weight measurements. An additional benefit of using the two-balance technique to determine the approximate and then accurate weight of one's sample is that all the weighing, except the final weight, are made on the top-loader balance. Because of this, the wear and tear on the analytical balance is greatly

reduced, and the balance is likely to be usable over a much longer period of time thus reducing the classroom costs of buying new analytical balances.

Using Weight Rather Than Volume Procedures

In the technical report, (3) analyses were primarily performed by weight. Titration volumes were converted to weight using appropriate densities. In reviewing the literature, it is obvious that more and more journal articles and textbooks are advocating for the substitution of weight based for volume titrations (14,15,16,17,18,19,20). The authors of this paper highly support this direction.

Adaptability

The Fajans method can be adapted for settings ranging from regular classrooms to advanced labs based on what materials may be available in the classrooms.

With inexpensive plastic pipettes and alcohol burners, students can prepare modified pipettes (SI, Appendix One & Video One) capable of dispensing drops as small as 0.01 grams (SI, Appendix Three). Using these modified pipettes and the attached procedure resulted in %RSD values of approximately 0.2 (SI, Appendix Four, Titration Protocol)

Using the small amounts of reagents recommended in the Titration Protocol for seawater of ~35.000, a unitless number (21), or a NaCl solution of ~3.5% and a $AgNO_3$ solution of ~ 0.35 moles/kg-soln, only ~1 gram (~1 mL) of the seawater or NaCl solution is required along with ~1.7 g $AgNO_3$, and ~0.2 g (5 drops) of DCF per titration (SI, Titration Protocol). Therefore, a class of 30 students working in pairs could perform 6 trials per group (3 knowns, 3 unknowns) with ~100 g of either seawater or NaCl solution, ~150 g of $AgNO_3$, and ~20 g of DCF. With these minimal amounts of reagents, the overall expenses of the lab would be low.

And there are other considerable cost benefits using the modified pipettes compared to standard glass burets. Should a modified pipette, with its cap, fall to the floor, it won't break. This would not be the case for a glass burette. Dealing with the broken glass and AgNO3 solution on the floor would require considerable time and care.

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Protocol for Determining the Chlorinity of an Unknown Seawater Sample: the Fajans Method

Background

Either the Mohr or Fajans titration methods can be used to determine the concentration of halides in a solution, most commonly chloride, using silver nitrate

($AgNO_{3)}$ as the titrant. The Mohr titration was introduced in 1856 by Karl Friedrich Mohr, a German analytical chemist. An indicator composed of potassium chromate and/or the chromate and dichromate was used. In the titration, Ag^+ and Cl^- react to form silver chloride (AgCl). Then excess silver ions react with the indicator to form an insoluble red salt. Some years later, with some modifications, the technique was used to determine the chlorinity (all titratable halides) of a seawater sample using the Knudsen adaptations. From the chlorinity and the relationship between the chlorinity of a seawater sample and its salinity, the salinity could be calculated. This technique remained the bench mark for determining the salinity of a seawater sample until the early 1960s when conductivity measuring salinometers were introduced.

In 1923, an organic dye, dichlorofluorescein, was introduced by Kasimir Fajans, a Polish-American physical chemist as an alternate indicator that could be used in determining the endpoint in these titrations. In this titration, precipitated AgCl adsorbs chloride ions to form a primary adsorption layer. After the equivalence point, excess silver ions are primarily adsorbed. Next, the negatively charged fluorescein component of the indicator forms a secondary adsorption layer on the surface of the precipitate, creating a pink-colored complex with the silver. The pink complex produces a distinct color change from greenish yellow to pink at the endpoint.

The Fajans protocol, which closely follows procedures used in the 100A lab at UCSD, is designed to determine the chlorinity of a seawater sample with an unknown salinity using the DCF indicator and a seawater with known salinity. This laboratory procedure will introduce you to this titration, a modified plastic pipette with a drop size of ~0.01 gram, the 2-balance technique for determining sample weights, and a simplified processing scheme where the concentration of the $AgNO_3$ titrant does not need to be determined.

Safety and PPE (Personal Protective Equipment)

Safety in the lab is always a primary concern. To that end, the following safety requirements should be observed:

Wear the appropriate PPE including a lab coat and safety glasses or googles.

$AgNO_3$ is a strong oxidant. Contact with the skin will lead to staining and possible irritation, so gloves should be worn when working with this reagent. Should this reagent be spilled, it needs to be cleaned up immediately. If you have any questions about doing this, ask your instructor or teaching assistant (TA).

The DCF is considered to be a minimally hazardous reagent, but care should be exercised while using this reagent.

Equipment and Reagents

Equipment

Alcohol lamp
Aluminum foil
Balances

Top loader balance, readable to 0.1 or 0.01 gram
Analytical balance, readable to 0.0001 g (0.1 mg)
Funnel
Glass dropper bottle, 30 mLs
Gloves
Labeling tape and marker
Lighter for alcohol lamp
Magnetic stir plate –and stir bars (1 “ by 5/8” with pivot ring)
Plastic pipettes – Fisherbrand disposable polyethylene transfer pipets, Catalog No. 13-711-6M
Pyrex beakers, 10, 30 or 50, 100 or 150 mLs
Razor blade, single edge
Reagent storage bottle, brown, for ~ 100 mLs of the prepared AgNO3 solution
Scrub brush
Serum bottle, 5 or 10 mL, with a rubber stopper
Spatula
Tissues or wipes such as Kimwipes
Tongs
Tygon tubing 1/16”ID, 1/8” O.D., formulation E-3603
White paper or cardboard for color contrast in the background behind the titration beaker
Wash bottle for Deionized Water (500 mL or similar)
Waste container

Reagents, their preparation and storage

2′,7′-Dichloro-3′,6′-dihydroxy-3*H*-spiro[[2]benzofuran-1,9′-xanthen]-3-one
or more commonly, 2’,7’-Dichlorofluorescein [hereafter DCF]
Dissolve 0.1 gram DCF in 100 mLs of a 60 to 70% ethanol solution
Store the solution in a 30 mL glass dropper bottle
Deionized water [hereafter DIW]
Dextrine, Acros Organics
Ethanol 95%, Koptec, 190 proof, USP Specs
OSIL, IAPSO standard seawater
Silver nitrate, $AgNO_3$, a solution of 0.35 moles/kg-soln in DIW
Dissolve 59.46 grams of AgNO3 in DIW and bring to a final weight of 1000 grams with DIW.
Store the solution in a 1-liter brown bottle or a clear reagent bottle wrapped in aluminum foil
Soap solution

Procedure

1.. Record the salinity of the Known Standard Seawater Sample (KSW).
2.. Using the Tygon tubing, prepare caps for two disposable pipettes. Use tape and a marker to
label the disposable pipettes as follows:

a. Known Standard Seawater (KSW)
b. Unknown seawater (UKSW)

3.. Modify a disposable pipette (see Appendix One and Video One) and prepare a cap for this pipette using the Tygon tubing. Using tape and a marker, label this pipette $AgNO_3$.
4. In the hood there is a small brown bottle of the $AgNO_3$ solution. Remove its lid. Remove the cap from the modified pipette and carefully fill it (see Video One). Using a tissue, wipe the tip of the pipette and replace the cap. Put the lid back on the bottle of the $AgNO_3$ solution.
5… Before doing the first sample titration, it is very helpful to do what is called a "Quick & Dirty" titration. The "Quick & Dirty" titration can be accomplished by following the procedure detailed in steps 7 – 10 but with only 5 to 6 drops of seawater instead of ~1.0000 grams of seawater. Add the $AgNO_3$ solution from the modified pipette slowly. When you believe the endpoint has been reached, add another drop of the $AgNO_3$ solution to confirm. The reaction is reversible so after the endpoint, adding a drop or two of seawater should restore the yellow color to the solution. Add $AgNO_3$ dropwise to the new endpoint to get used to the titration and develop a good sense of the color change at the endpoint.
6.. For sample titrations, using the two-balance technique, weigh ~ 1.0000 gram of seawater into a titration beaker. (see Appendix Two and Video Two).
7.. Add ~80 mLs of DIW to the titration beaker. Use the markings on the side of the beaker to gauge the volume of DIW added. The exact amount of water isn't critical, but use about the same amount for each titration. Then slide a stir bar down the side to avoid splashing.
8.. From the dropper bottle, add 10 drops, approximately 0.2 grams, of the DCF indicator to the solution and stir moderately on the stir plate. It is helpful to use white paper or cardboard behind the stir plate to facilitate detecting the color change at the end point.
9.. Use the spatula to add 0.05 grams of Dextrin. This is a very small amount.
10.. Zero the analytical balance. Using a small beaker to hold the $AgNO_3$ pipette and tongs, weigh the capped pipette containing the $AgNO_3$ solution on the analytical balance. Record the weight to 0.1 milligrams
11.. Titrate the sample in the beaker by adding $AgNO_3$ dropwise. At the first signs of the transient pink color in the solution, increase the stirring rate but not to the point of splashing.
12.. The endpoint has been achieved at the first appearance of pink color that persists with stirring
13.. Using the small beaker to hold the $AgNO_3$ pipette and tongs, reweigh the pipette on the analytical balance, recording the weight to 0.0001 g (0.1 mg).
14.. After completing a titration, dispose of the solution and $AgNO_3$ precipitate in the provided waste container. Rinse the beaker with three 20 mL volumes of DI water, pouring these rinses into the waste container.
15.. After thoroughly rinsing the beaker, it can be used for a subsequent titration. Be sure to dry the outside bottom of the beaker before future weighings and titrations
16. Titrate at least 3 samples of your known seawater (KSW) and 3 samples of your unknown seawater (UKSW).
17.. Clean-up

After completing all titrations, use a soap solution and brush to clean the white film from the inside of the beakers. After scrubbing, rinse the beaker with tap water, then DIW, and set it aside to dry. Scrub and rinse the stir bars as well.

Any $AgNO_3$ left in the pipette should be dispensed into the waste container. Rinse the pipette twice with a small amount of DIW which also should go into the waste container.

Any remaining seawater in either of your seawater pipettes can go into the sink. After that, dispose of the pipettes and gloves in the appropriate waste container for these items.

Calculate the chlorinity of your unknown seawater using the equations shown in Appendix three of this SOP (see also Video 4). Report the average chlorinity of your unknown seawater, the standard deviation, and the %RSD, that is the relative standard deviation.

Sample computations: Calculating the Chlorinity of a Seawater Sample of Unknown Salinity

The data for titration 1, from the attached Excel worksheet, have been used.
The salinity of our known seawater sample is 34.994.
To calculate the chlorinity from the salinity, where Salinity / 1.80655 = Chlorinity

Eq. 1.

34.994 / 1.80655 = 19.371 Cl $^0/00$

For two titrations involving the weights of $AgNO_3$ solution needed to titrate weights of our seawater samples with known and unknown chlorinities, the following equivalent ratio can be set up [the seawater sample with known salinity is indicated as KSW and UKSW will be used for the unknown]

$$\frac{\frac{AgNO_3\ (g)\ (KSW)}{Seawater\ (g)\ (KSW)}}{Chlorinity\ (KSW)} = \frac{\frac{AgNO_3\ (g)\ (UKSW)}{Seawater\ (g)\ (UKSW)}}{Chlorinity\ (UKSW)} \qquad \text{Eq. 2.}$$

Solving for the Chlorinity of the unknown seawater sample:

$$Chlorinity_{(UKSW)} = \frac{\frac{AgNO_3\ (g)\ (UKSW)}{Seawater\ (g)\ (UKSW)} * Chlorinity_{(KSW)}}{\frac{AgNO_3\ (g)\ (KSW)}{Seawater\ (g)\ (KSW)}} \qquad \text{Eq. 3.}$$

Simplifying:

$$\text{Chlorinity}_{(UKSW)} = \frac{AgNO_3\ (g)\ (UKSW)}{AgNO_3\ (g)\ (KSW)} * \frac{\text{Seawater (g)}\ (KSW)}{\text{Seawater (g)}\ (UKSW)} * \text{Chlorinity}_{(KSW)} \quad \text{Eq. 4.}$$

Data for Titration One

	Known (KSW)	Unknown (UKSW)
Weight of Seawater sample (g)	1.0104	1.0385
Weight of $AgNO_3$ solution (g)	1.7112	1.6651
Chlorinity of our known seawater Cl $^0/00$	19.371	

Substituting all values in the expression above, the chlorinity of the unknown seawater sample is calculated to be 18.350 Cl $^0/00$. The units of grams of $AgNO_3$ in the numerator and denominator cancel, likewise for the units of grams of seawater leaving us with the Cl $^0/00$ units for the unknown seawater sample.

((1.6651 g / 1.0385 g) / (1.7112 g / 1.0104 g)) * 19.371 Cl $^0/00$ = 18.350 Cl $^0/00$ Eq. 5.

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Appendix One: Preparation of a Modified Pipette and its Cap; Filling a Pipette Completely

Creating a modified pipette leaves a smaller hole at the end of a disposable pipette to dramatically reduce its drop size.

1.. Using an appropriate lighter, light the alcohol lamp.
The flame is approximately 70 degrees Celsius so be careful.
2.. With one hand, hold the thin end of the pipette. With the other, hold the pipet about an inch or so from the thin end. Rotate the pipette above the flame. Start several inches above the flame and slowly lower the pipette to about one inch

above the flame. As the pipette is rotated, the plastic will heat, become clear, and sag.
3.. Remove the pipette from the flame and slowly pull the two ends apart.
If this is done too quickly, the plastic will break. As you pull, when you feal a bit of resistance, stop pulling and while still holding the stretched tubing, allow the plastic to cool completely. As it cools, the opaque coloration will reappear.
Depending on the heating and the speed at which the short end is pulled, the plastic can stretch anywhere from 6 inches to about 2 feet.
4.. After cooling, cut the stretched part of the plastic about 2 1/2 centimeters (about 1 inch) from the unstretched part.

Preparing a cap for the pipette

1.. To prepare a cap for the modified pipet, tie an overhand knot in the Tygon tubing. Holding the knot, pull on one end of the tubing to cinch the knot tight.
2.. Cut one end of the tubing about 1/2 centimeter (about 1/4") from the knot. At the other end, allow enough tubing to fully enclose the tip without it touching the knot. This end of the tubing may be as much as 1 ½" long.
3.. Caps for the unmodified pipettes can be short on both sides of the knot, perhaps ½ centimeter
(about 1/4"). Because the diameter of the tubing is about the same diameter as the thin end of the
pipette, you may have some difficulty getting the cap onto the end. If so, place the cap on the counter
and roll it back and forth under a finger to soften the tubing.
4.. All pipettes with their caps need to be labeled. Using a marker, write what is to be
contained in the pipette on the bulb. If colored tape is available, color code the pipette to the container
from which the pipette is to be filled. Write what the pipette contains on the tape.

Filling a pipette completely

Working with a less than full pipette is not good. Running out of solution part way through a titration means the pipette would have to be weighed, refilled, and weighed again before proceeding.
This will add uncertainty to the weight of titer. What follows is an easy way to fill the pipette fully.

1.. Remove the cap from the pipette, squeeze the bulb, put the tip into the solution, release the bulb, and allow the pipette to fill. It should fill about half way.
2.. Now bend the thin end of the pipette with the tip just inside the bottle but not in the solution.
3.. Squeeze the bulb gently to remove all the air.
4.. When solution starts coming out of the pipette, continue squeezing gently, unbend the pipette, put the tip of the pipette into the solution, continue squeezing just a bit, then relax the bulb so it can fill.
5.. Remove the tip from the solution and check that the pipette is full. A small air space at the end of the pipette is expected, maybe 1/4 inch or less. Because the hole in a modified pipet is small, these pipettes take longer to fill. Be patient.

6.. Wipe the tip of the pipette with a tissue, then replace the cap on the pipette. The pipette is ready for weighing and use for a titration.
7.. Unmodified pipettes are filled the same way, but they fill much faster.

Appendix Two: Two-Balance Technique, A Quick and Accurate Determination of Sample Size Using Two Balances, a Top Loader and an Analytical Balance

The two-balance technique provides a quick and accurate determination of sample size and also eliminates unnecessary wear and tear on the analytical balances. The described operations only take about two minutes. During this time do not let someone else use either of the balances.

1. To the balances, take a titration beaker, a small beaker, the pipette with its cap and sample, a pair of tongs, your computer or laboratory notebook, and if your notebook, a black pen to record your sample weight(s).
2. Put the titration beaker (100 or 150 mL) onto the top loader. After the reading stabilizes, tare the balance.
3. Place the pipette holding the sample into the small beaker. Place the small beaker onto the analytical balance with tongs. Make sure that the pipette does not touch the sides of the analytical balance. After the reading stabilizes, tare the balance.
4. Remove the small beaker with the pipette from the analytical balance, remove the pipette's cap, and while holding the pipet vertically, add drops to the titration beaker until there is at least 1 gram of sample in the beaker. This should be about 25 drops.
5. Replace the cap on the pipette, return it to the small beaker, and put the beaker on to the pan of the analytical balance.
6. Record the reading to 0.0001 g (0.1 mg) on your computer or in your notebook. The reading on the analytical balance should be negative because the volume in the sample pipette has decreased. However, know that the value is actually positive since sample was added to the beaker on the top loader. There is now ~ 1 gram of sample in the titration beaker, and the weight of the sample is known to 0.0001 g (0.1 mg).
7. Take everything back to your workbench and proceed with the titration.

Appendix Three: Notes to Instructors, Determining the Chlorinity of an Unknown Seawater Sample, the Fajans Method

Introduction

The protocol for these titrations has been simplified to make the work for the students straight forward. However, there are many things, which will

be detailed below, that depending on the students can add to the understanding of the technique, the results and the major source of error.

Safety and Waste Disposal

Although $AgNO_3$ titrations of halogens have been done for years, typically by technicians without wearing gloves, the wearing of gloves is recommended as in keeping with the best laboratory safety practices. In a pre-lab it could be pointed out to the students that $AgNO_3$ solutions have been used, also for years, for nasal cauterization, i.e., treating recurring nose-bleeds with excellent success.

Most labs have general containers for used pipettes, gloves, etc. For the AgCl and $AgNO_3$ waste, a plastic carboy is suggested. The size will depend on the number of class(es) and the number of students. If one uses a large funnel in the top of the container into which a piece of plastic mesh has been molded, stir bars cannot accidentally be dumped into the container. There are other ways of addressing this problem such as using a second magnet on the outside of the titration beaker to keep the stir bar in the beaker from falling out.

Equipment

Regarding the top loader balance, since these titrations involve minimal weights, a high-capacity balance isn't required. It is worthwhile warning students that adding weights to any balance that exceed its capacity can damage the balance and lead to inaccurate results.

If one has an option for colored labeling tape, students could color code their solutions and pipettes. This visual reminder of contents can be very helpful.

Titration

Bring to the attention of the students that the $AgNO_3$ solution as well as the precipitated silver halides are photo-sensitive, so it is advised to perform these titrations in minimal light.

Regarding the "Quick and Dirty" titrations, students doing this have much better success and precision than colleagues that do not do this. They also can save time when it comes to doing the actual seawater samples. For this reason, a special effort has been made to include this as a first step in using this titration procedure.

When weighing a sample, one plus gram, e.g., 1.0025 g, is better than a weight of 0.9990 gram, because the former weight gives one additional significant figure.

The videos showing the preparation and filling of a modified pipette and cap and the two-balance technique can be really helpful if the students

take the time to view them. The written descriptions should be sufficient, but they aren't as helpful as the videos.

The standard recommended for these chlorinity titrations is a bottle of IAPSO standard seawater obtainable from OSIL in England (see reference section for details). The cost is not trivial, namely $80 or so per bottle. The bottles contain about 200 grams of solution. Even after removing the aluminum crimp seal, if the rubber stopper is kept in the top, the solution will hold its value very well. If one doesn't want to use the IAPSO seawater for a standard, any seawater would do. If one wanted higher or lower salinities for either the known or unknown seawater sample, evaporation or the addition of some deionized water will solve this problem.

In labs where there is no interest in doing these titrations for chlorinity (the titratable halogens in seawater), one could do the same titrations using a 3.5% NaCl solution for the known and a 3.3% NaCl solution for the unknown to teach the calculation of the concentration of chloride ions in solution. These solutions could easily be prepared in any lab using almost any quality NaCl. However, if you use reagent grade NaCl and oven dry it for an hour or so at 120 degrees C, this NaCl can be used almost the same as a primary standard. The calculation scheme for the NaCl solutions is identical to that for the calculation of the chlorinity, but replacing chlorinity with "concentration of chloride". If the NaCl solutions are used, the students could be provided the preparation data for the unknown NaCl solution to compare with their calculated value. This will give the students a measure of the accuracy as well.

The protocol calls for the use of a small amount of dextrin to prevent the coagulation of the AgCl precipitate near the end point. The dextrin works very well. However, students could be directed to do titrations without the dextrin and then with the dextrin. This could lead to a discussion of the mechanism by which the dextrin prevents the coagulation.

Computations

It is helpful after completing a titration, if the students calculate the ratio between the weight of $AgNO_3$ used for a titration (numerator) and the weight of sample being titrated (denominator). Typically, the ratio calculated this way will be greater than one. A ratio for a sample that is different than the others either for the known or unknown seawater samples, suggests a problem, perhaps the result of a poor endpoint, incorrectly recorded sample or $AgNO_3$ weights, etc., etc.

The video showing how to do the computations is very helpful. A set of titration data and computations have also been included. The plot of calculated chlorinity versus trial number can be helpful in seeing trends in the determination of the endpoint, a possible outlier, etc. If the plot is used and an outlier detected, it takes very little time to do a fourth titration.

It will be useful to quantify the average drop size from the modified pipette by measuring the difference in weight after delivering a known

number of drops. At least 20 drops should be counted. Use the $AgNO_3$ solution for this test. The drop size can be determined using one of the 5- or 10-mL serum vials with its rubber stopper. Put the small serum vial with its cap onto the balance pan of the analytical balance. Tare the balance. Remove the vial from the balance case, remove the cap, and slowly dispense 20 or so drops into the vial. Replace the cap, and put the vial back on the balance pan. Students should record the weight to 0.1 mg and the number of drops. Repeat the drop size determination at least twice. A drop size of 0.01 grams or less is ideal. It is really important when performing this test that the drops of $AgNO_3$ be added similarly as the drops added very near the end of a titration. Therefore, the drops need to be added slowly and deliberately. Failing to do this will give drop sizes that are too small. Assuming that weighings are performed carefully, data are recorded without errors, transfer of solutions including $AgNO_3$ are quantitative (the transfer of a sample from one container to a second so that none is lost), and one's endpoint is reproducible, the principal factor limiting the precision of these titrations is the drop size from the modified pipette. If enough titrations are performed, on average the endpoint should be good to half a drop. If the drop size is 0.008 grams, which was the case for the titration data shown, and 1.7 grams of $AgNO_3$ are needed for a titration, the precision expressed as a percent would be (0.008/2)/1.7*100 = 0.235%. This is about what is calculated for the titrations shown on the spreadsheet, namely, 0.224%. These titrations were performed by an experienced student demonstrating that the size of the drop from the modified pipette is clearly the limiting factor in the precision of one's results.

In the computations, note that a blank was never used to correct the weights of $AgNO_3$ used for the titrations for the reagent blank. Unlike the Mohr titration, in order to see the endpoint, there must be some AgCl precipitate in the solution. Therefore, the procedure to determine the blank correction for these titrations requires the titration of a number of solutions with variable amounts of seawater or NaCl solutions. A plot of the data, which should be linear, is then extrapolated to reach the Y-axis. The Y-intercept, where the weight of AgCl is zero, is the reagent blank. A set of data for this determination is shown in Appendix Five, where the reagent blank was determined to be 0.005 grams. For $AgNO_3$ titers of ~1.65 grams, this blank would represent an error of approximately 0.3%. However, as shown in the spreadsheet with a set of titration data, when the blank is subtracted from all the weights of $AgNO_3$, the difference in the calculated chlorinity is less than 0.01%. To this extent, unless time is available to explain how to carry out the titrations to determine the blank, the Fajans titrations blank can be ignored in the computation of the chlorinity with almost no bearing on the results.