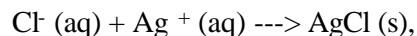


GRAVIMETRIC DETERMINATION OF CHLORIDE AS SILVER CHLORIDE

1. Summary of Method

The chloride in a soluble sample can be measured by precipitating the chloride with silver,



and weighing the recovered silver chloride.

The entire analysis is accomplished by:

- digesting the sample in a high ionic strength solution;
- precipitating the silver chloride in a previously weighed filter crucible;
- washing the precipitate with dilute nitric acid and
- drying the silver chloride to constant weight.

The chloride in the original sample is calculated from the mass of the recovered silver chloride.

2. Comments

During digestion, the silver chloride first forms a colloidal suspension that is coagulated with heat and a high electrolyte concentration. Nitric acid in the wash solution minimizes peptization and decomposes into volatile products that are eliminated during drying.

The recovered silver chloride should be saved for future use or resale.

Hazards.

The concentrated acid solutions used in sample digestion are corrosive and require caution in handling, particularly when hot. The fume hood should be used for the sample washing process, which gives off poisonous nitrogen oxides, as well as acidic vapors.

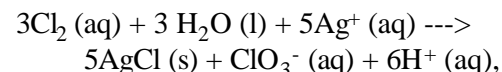
Interferences.

The sample solution is kept mildly acidic during precipitation to eliminate interference from the anions of weak acids (e.g., CO_3^{2-}) that could react with the silver in a neutral solution. A moderate excess of silver is added to reduce the solubility of silver chloride, but a large excess of added silver is avoided to prevent coprecipitation of silver nitrate.

Silver chloride can also undergo photodecomposition,



Which produces elemental silver that can be detected by a violet color in the precipitate. In theory, this produces a low result for the chloride determination, but in practice the effect is minimal if care is taken to avoid prolonged exposure direct sunlight. If photodecomposition occurs before filtration, the additional reaction,



can lead to high results.

3. Sample Handling and Preparation

Solution

Pipet three 25.00 mL aliquots of your sample into three 500 mL beakers. Dilute each sample to 100-150 mL of distilled water. Add about 0.5 mL of concentrated nitric acid to each beaker and cover with clean watch glasses.

Solid

Place about 1 gram of the sample in the drying oven for at least an hour. Allow the samples to cool in a dessicator for 30-40 minutes, then accurately weigh three 0.2-0.3 g samples into numbered 400 mL beakers. Dissolve the sample in distilled water and dilute to 150 mL. Slowly add 0.5 mL chloride free concentrated nitric acid to each beaker.

4. Apparatus

- a. *Filtering crucible [3] - either glass or porcelain*
- b. *Vacuum filtration apparatus consisting of 500 mL filter flask and crucible holder with funnel*

5. Reagents

- a. *Concentrated HNO₃ [10 mL/sample]*
- b. *0.2 M AgNO₃ [5-15 ml/sample]*

6. Procedure

- a. *Clean and weigh three filter crucibles.*
Thoroughly clean three filtering crucibles on a suction apparatus by pouring about 5 mL of concentrated HNO₃ (caution! corrosive!!) into the crucibles and allowing them to stand for about 5 minutes. Use the vacuum to draw the acid through the

crucibles and then rinse the crucibles with three 10 mL portions of tap water.

Mark the crucibles with a file or permanent marker and heat them in the oven for one hour at 110°C -130°C. Cool them for 20 minutes and weigh on the analytical balance. Reheat the crucibles for 20 to 30 minutes, cool them and weigh as before. This heating, cooling and weighing cycle should be repeated until consecutive crucible weights are within ± 0.0004 g of each other. Be consistent with heating and cooling times. The crucibles must be protected from pick-up of foreign matter by careful handling and storage.

- b. *Calculate the amount of precipitating reagent.*

- c. *Digest and precipitate the samples.*

Slowly and with good stirring, add the required amount of 0.2 M AgNO₃ to each of the cold sample solutions until AgCl is seen to coagulate; then add an 3 or 5 mL more. Use a separate stirring rod for each beaker. Heat to almost boiling and digest the sample for 10 minutes. Add a few drops of AgNO₃ to confirm that the precipitation is complete. If additional precipitate forms, add about 3 mL of the AgNO₃ solution, digest and again check for completeness of precipitation. Pour any unused AgNO₃ solution into the silver waste container. Cover each beaker and store in a dark place for at least 2 hours and preferable until next lab period.

- d. *Filter the precipitate.*

Decant the supernatant liquid through weighed filtering crucibles. Wash the precipitate several times while still in the beaker with a wash solution composed of 2-5 mL of 6 M HNO₃ per liter of water. Decant these washing through the filters. Quantitatively transfer the AgCl from the beakers to the individual crucibles with fine streams of wash solution. Use the rubber policeman to dislodge any particles that adhere to the walls of the beaker. Continue washing until the filtrates are essentially free of Ag⁺ ion. Check for Ag⁺ by collecting small amount of the filtrate in a

test tube and adding a few drops of HCl. Washing is complete if there is little or no *turbidity*.

e. Dry the precipitate.

Dry the precipitate at 110°C for at least 1 hour. Store the crucibles in a desiccator while they cool. Determine the weight of the crucibles and their contents. Repeat the cycle of heating, cooling and weighing until consecutive weighings are within 0.2 mg.

f. Clean the crucibles

Remove the silver chloride from the crucibles and transfer to a silver waste container. Clean the crucibles as you did in part *a*, transferring all of the filtrate to the silver waste container.

7. Calculations and Conclusions

Calculate the percent chloride (w/w) in each sample from the sample amount and the mass of AgCl obtained. Calculate the mean percent chloride, the standard deviation and relative standard deviation [in %]. Also determine the 90% confidence interval. A sample may be omitted from the set if there was a documented error in its analysis or if it can be rejected by the Q-test. Whenever possible, rejected samples should be repeated to provide at least three reliable analyses.

8. Bibliography

1. Daniel C. Harris, *Quantitative Chemical Analysis*, 2nd edition, W.H. Freeman, New York, 1987, pages 25, 127, 129-30.
2. Douglas A. Skoog, Donald M. West, and F. James Holler, *Fundamentals of Analytical Chemistry*, 6th edition, Saunders, New York, 1988, pages 835-837.

3. W.F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis*, Wiley, New York, 1953.

4. Gary D. Christian, *Analytical Chemistry*, John Wiley and Sons, Inc. 1994, pp 683-686.

QUESTIONS

1. Write a *complete*, balanced net ionic equation for the precipitation of iodide with silver.
 - a) there is excess carbonate (CO_3^{2-}) in solution:
 - b) the silver chloride decomposes during digestion:
2. What undesirable precipitates might contaminate the product if:
 - a) there is excess carbonate (CO_3^{2-}) in solution:
 - b) the silver chloride decomposes during digestion: