

Gravimetric Determination of Chloride
in Unknown Chloride Mixture by
Precipitation with Silver Nitrate

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CONTENTS

<u>Page</u>	<u>Section</u>
3	Abstract
4	Experimental Methods
6	Results
7	Discussion
9	Conclusions
10	Acknowledgements
11	References
Appendices	
12	Appendix I — Sample (Representative) Calculation
13	Appendix II — Computation of Statistical Measures of Precision

ABSTRACT

Gravimetric analysis is an analytical procedure commonly used to determine the mass of substances in mixtures, such as lactose in milk products and nicotine in pesticides (2).

Gravimetric analysis was used to determine the mass percent composition of chloride ions in an unknown mixture (#1801) of chloride salts, by precipitation with silver nitrate, AgNO_3 (aq), to form silver chloride, AgCl (s), to be filtered and weighed. Various methods were used to mitigate possible sources of systematic error, such as photodecomposition of the silver chloride, reaction with atmospheric anions, and peptization. The average calculated experimental mass percent of chloride ions in the unknown mixture was 52.06%, and the true mass percent of chloride in the unknown is calculated to be in the interval between 48% and 56% with a 90% confidence level.

EXPERIMENTAL METHODS

[Exp. 1] A precipitation gravimetric determination is performed on an unknown mixture of a soluble chloride mixture. A solution of the unknown is reacted with a solution of silver nitrate to form silver chloride precipitate, and the mass of the precipitate can be measured to determine the amount of chloride in the unknown sample. The specific procedure followed was based on the procedure stated in “The Gravimetric Determination of Chloride in a Soluble Unknown,” from *The Official Cooper Union General Chemistry Laboratory Guide* (1). The discussion behind the methods used, such as keeping the solution slightly acidic and rinsing with a dilute acidic solution, are explained in more detail in the discussion section. The following is a summary of the tasks completed.

[Exp. 2] Three clean Gooch crucibles with filter mats were dried in an oven for a week, and their final masses were recorded. The masses of three samples of the dry unknown compound #1801 were measured by difference and dissolved into a mildly-acidic solution of nitric acid (see Dis. 5). A small excess of silver nitrate was added to a solution of the unknown chloride mixture (see Eq. 1 for the calculated minimum silver nitrate required) to ensure complete precipitation of the chloride, and the solution was digested until no additional precipitation was observed when a few drops of silver nitrate were added; this process was repeated for each sample. After sitting in a dark cabinet for a week, the solutions were filtered, through the filtration apparatus, into their respective crucibles. After the second and following filtrations, the filtrate was tested for the presence of silver ions by adding drops of concentrated hydrochloric acid (HCl) and re-filtered if any turbidity was observed. The crucibles were then dried in the oven and their masses taken after one interval of one hour and two intervals of 30 minutes, and the final mass was recorded as the dry mass.

[Exp. 3] The laboratory guide stated to continue the drying-weighing cycle for the crucible and filter paper, and the crucible with filter paper and precipitate, until the mass is constant. Due to time restrictions, the mass of the dried crucible and filter paper left in the oven for a week was assumed to be dry weight, and the mass of the crucibles with precipitate after three weighings was assumed to be the dry weight, but this is a possible source of gross error. Care was taken to only digest one solution at a time and perform one filtration at a time to minimize light exposure of the silver chloride precipitate (see Dis. 6). During the digestion, a sheet of paper was held up to shade the solution as a further attempt to mitigate photodecomposition. During the filtration, the rubber policeman to move the precipitate in sample 3 was not cleaned properly, and there is the chance for possible contamination. Also during the filtration, the first filtrate for sample 2 was extremely cloudy. After the first weighing of the mass of sample 1, the crucible was tipped onto its side briefly while in the dessicator, and the mass from the second weighing of sample 1 was approximately 20mg lower than the first, which is a possible source of gross error.

RESULTS

The mass of the dry crucible and filter mat, and the mass of the dry precipitate, crucible, and filter mat are the final weighings after multiple dryings to completion (see Exp. 3 for specifics on the drying).

Table 1. Experimental mass measurement data

Unknown chloride sample number: 1801

	Sample 1	Sample 2	Sample 3
Mass of dry crucible and filter mat (g)	18.8399	18.9965	18.0009
Mass of dry unknown sample (g)	0.1325	0.1011	0.1161
Mass of dry precipitate, crucible, and filter mat (g)	19.1068	19.2104	18.2544

The mass of the chloride ions (Cl^-) in a sample is calculated by a stoichiometry calculation from the mass of the precipitate (see Eq. 2), and the percent mass composition of the chloride ions is the quotient of the mass of the chloride ion and the mass of the unknown sample (see Eq. 3).

Table 2. Calculated mass percent composition of chloride in unknown

	Sample 1	Sample 2	Sample 3
Percent chloride (%)	49.83	52.34	54.01

A descriptive statistical analysis was performed on these data points (see St. 1), and a summary is displayed below:

Table 3. Statistical summary of percent composition

Sample mean	Sample standard deviation	90% confidence interval for the mean
52.06% $\pm$ 1.22%	2.11%	52% $\pm$ 4%

The sample mean of the percent chloride was 52.06% with a standard error of 1.22% and a standard deviation of 2.11%. The distribution of the three points was roughly uniform, and a

Q-test (see St. 2) did not predict any statistically unreliable data points. The confidence interval indicates that there is a 90% chance that the actual percent composition of chloride in the unknown is in between 48% and 56%.

DISCUSSION

Much of the insight on the discussion of the experimental method and systematic error was based off content from *Fundamentals of Analytical Chemistry* (2).

[Dis. 1] The double-replacement reaction between silver nitrate and the unknown chloride mixture forms a colloidal suspension of silver chloride in water. A colloidal suspension is a form of heterogeneous mixture, in which one particle forms microscopic, insoluble particles inside another. In order to be able to separate the colloid from the water, the particles must be coagulated first to maximize the size of the silver chloride particles, which maximizes the amount of particles being caught by the filter mat. If the colloidal suspension is not coagulated or a significant portion is not coagulated, the calculated percent chloride will be systematically too low because some of the precipitate will have been lost through the filter mat and not weighed. Secondly, larger particles of precipitate are more pure than fine particles of precipitate, which allows for a more accurate weighing of the precipitate.

[Dis. 2] A colloidal suspension is kept stable because of the formation of an electric double layer. In an excess of silver, a primary adsorption layer of positively-charged silver ions, and a secondary adsorption layer of oppositely-charged nitrate ions, create an overall-negative shell. The negative charge of all of the colloidal particles prevents the particles from colliding and keeps the suspension stable. Coagulation occurs by keeping an excess of silver nitrate electrolyte and heating the solution, which decreases the width of the double-layer and increasing the kinetic energy of the particles, allowing colloid particles to approach each other more closely and increasing the chance for coagulation. The solution should be heated almost to boiling to maximize kinetic energy but avoid the mechanical disruption caused by boiling bubbles that may separate large colloidal particles— this process of heating is called digestion.

[Dis. 3] The likely sources of systematic and random error, from most to least, are: the peptization of silver chloride, the formation of silver carbonate precipitate, $\text{AgCO}_3(\text{s})$, the photodecomposition of silver chloride, and the tolerance of normal equipment operation. Each of these possible sources of error are discussed in more detail below.

[Dis. 4] A possible source of systematic error is the peptization of the silver chloride precipitate. Peptization is the process of breaking down large, coagulated chunks of precipitate into a stable, dispersed colloidal form, and is unwanted for this experiment. If peptization occurs, the calculated percent chloride will be systematically low, because the particles of silver chloride that have reverted to microscopic particle sizes may not be filtered and their masses not included in the mass of the precipitate. It may happen if the electrolyte concentration is decreased, which increases the width of the electric double-layer and causes colloidal particles to separate again.

This is mitigated by using a wash solution of mildly-concentrated nitric acid to maintain the electrolyte concentration instead of using deionized water, when possible, to move the precipitate from the beaker to the filtering crucible. There appeared to be some peptization in sample 2 (see Exp. 3), in which the filtrate was very cloudy, which is likely due to using too much deionized water to wash out the precipitate. As a result, it is possible that the calculated percent chloride for sample 2 is too low.

[Dis. 5] Another possible source of systematic error is the formation of silver carbonate precipitate, by the reaction of silver with carbonate ions formed when environmental carbon dioxide, CO_2 (g), dissolves in the solution. This would cause a systematic increase in the calculated percent chloride ions, because the unwanted mass of silver carbonate would be added to the mass of the desired silver chloride precipitate. This effect is reduced by keeping a low concentration of nitric acid in the solution to react with the carbonate ions to produce soluble carbonic acid.

[Dis. 6] Silver chloride undergoes photodecomposition. The effect of photodecomposition should be negligible without prolonged, direct exposure to sunlight. Silver chloride photodecomposes into elemental silver and chlorine gas. If dry, the calculated percent chloride will be systematically low, because the mass of the chlorine gas from the photodecomposed silver chloride will not be included in the weighing of the precipitate. When in solution, there may be an additional reaction involving that produces soluble chlorate ions that will be lost during the filtration process, also causing less silver chloride to be formed and also a loss of mass of the precipitate, resulting in a systematically low calculated percent chloride.

[Dis. 7] The only precise measurements were taken with an analytical balance, which has a tolerance of approximately 0.0002g (0.2mg). The other measurements were approximate and would not be a source of error. Because the tolerance of the analytical balance is so small, the random error associated with the equipment is negligible.

[Dis. 8] Possible sources of gross error are discussed in Exp. 3. If the mass of the crucibles and filter paper assumed to be dry were not actually dry, the difference between the mass of crucibles with precipitate and the mass of the crucibles without precipitate would be smaller, which would cause the calculated mass of percent chloride to be too low. If the mass of the crucibles, filter paper, and precipitate assumed to be dry were not actually dry, the reverse would be true and the calculated mass of percent chloride would be too high. If some precipitate was lost when the crucible for sample 1 was tipped over, the calculated percent chloride was too low.

[Dis. 9] Because the true percent composition of the chloride is not known, nothing is certain about the accuracy of the gravimetric analysis method.

CONCLUSIONS

The mean experimental percent composition of chloride from the gravimetric analysis of the silver chloride precipitate was 52.06%. A confidence interval of the true percent composition of chloride in the sample was $52\% \pm 4\%$. A small standard deviation of the data points indicates that this method of determining percent composition is precise. However, due to the many possible sources of systematic error (see Dis. 4-6) and gross error (see Dis. 8), the calculated percent chloride determined by this method is likely not very accurate.

This experiment will be immediately followed with another determination of the percent composition of the same unknown solution by means of titration with ion exchange and back-titration, and the two experiments will be compared in terms of precision, accuracy, and the amount of resources necessary.

Improvements to the lab procedure for future investigations to mitigate the sources of error would include the creation of a precipitate that does not photodecompose as silver chloride does (see Dis. 6) and drying at a hotter temperature than 110°C or for longer periods than those stated in the laboratory manual to ensure complete drying of the crucible with and without the precipitate (see Dis. 8).

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The scientific journal article “Infrared Spectroscopy of Water Cluster Anions, $(\text{H}_2\text{O})_{n=3-24-}$ in the HOH Bending Region: Persistence of the Double H-Bond Acceptor (AA) Water Molecule in the Excess Electron Binding Site of the Class I Isomers” was consulted for the style of this laboratory report (citation below).

Roscioli, Joseph R., Hammer, Nathan I., and Johnson, M. A. Infrared Spectroscopy of Water Cluster Anions, $(\text{H}_2\text{O})_{n=3-24-}$ in the HOH Bending Region: Persistence of the Double H-Bond Acceptor (AA) Water Molecule in the Excess Electron Binding Site of the Class I Isomers. *The Journal of Physical Chemistry Letters*. **2006**, 110, 7517-7520.

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APPENDIX I

SAMPLE (REPRESENTATIVE) CALCULATION

The calculation for the volume of AgNO_3 necessary to dissolve 0.1g NaCl is:

[Eq. 1] $0.1\text{g NaCl} \times \frac{\text{mol NaCl}}{58.443\text{g NaCl}} \times \frac{\text{mol AgNO}_3}{\text{mol NaCl}} \times \frac{L\ 0.2M\ \text{AgNO}_3}{0.2\text{mol AgNO}_3} \times \frac{1000\text{mL AgNO}_3}{L\ \text{AgNO}_3} = 9\text{mL } 0.2M\ \text{AgNO}_3$
(molar masses were calculated from elemental molar masses found in *Fundamentals of Analytical Chemistry* (2))

This value indicates the minimum AgNO_3 that must be added to the unknown solution so that the unknown chlorides completely react. In the experiment, an excess of approximately 5mL (approximately 14mL total of AgNO_3) was added to each solution to ensure the chlorides completely react.

The mass of chloride ion in a sample is calculated from the mass of filtered precipitate in a stoichiometric calculation. The mass of the precipitate is the difference between the final, dry mass of the precipitate in the crucible with the filter paper, and the mass of the crucible and the filter paper.

[Eq. 2] $m_{\text{Cl}^-} = (m_f - m_i) \times \frac{\text{mol AgCl}}{143.321\text{g AgCl}} \times \frac{\text{mol Cl}^-}{\text{mol AgCl}} \times \frac{35.453\text{g Cl}^-}{\text{mol Cl}^-}$

The mass percent composition of chloride in the unknown can be determined by dividing this calculated chloride ion mass by the dry mass of the unknown samples.

$$52\% \pm 4\% \quad \% \text{Cl}^- = \frac{m_{\text{Cl}^-}}{m_{\text{unknown}}}$$

The calculation for the percent composition of chloride in sample 1 is shown below as a representative calculation (see table 1):

$$m_{\text{Cl}^-} = (19.1068\text{g} - 18.8399\text{g}) \times \frac{\text{mol AgCl}}{143.321\text{g AgCl}} \times \frac{\text{mol Cl}^-}{\text{mol AgCl}} \times \frac{35.453\text{g Cl}^-}{\text{mol Cl}^-} = 0.06602\text{g Cl}^-$$
$$\% \text{Cl}^- = \frac{0.06602\text{g Cl}^-}{0.1325\text{g unknown}} = 0.4983 \times 100\% = 49.83\%$$

APPENDIX II

COMPUTATION OF STATISTICAL MEASURES OF PRECISION

[St. 1] The calculations for the mean ($\bar{x}$), standard deviation (s), standard error (s_m), variance (s^2), and relative standard deviation of the percent composition of chloride in the unknown are shown below. Because the data points are roughly spread uniformly over a small range and not heavily skewed, the mean will be used to represent the center and the standard deviation will be used to estimate the range (as opposed to median and IQR). The data shown below were obtained from table 2.

$$n = 3$$

$$\bar{x} = \frac{1}{3}(49.83\% + 52.34\% + 54.01\%) = 52.06\%$$

$$s = \sqrt{\frac{1}{2}((49.83\% - 52.06\%)^2 + (52.34\% - 52.06\%)^2 + (54.01\% - 52.06\%)^2)} = 2.11\%$$

$$s_m = \frac{2.11\%}{\sqrt{3}} = 1.22\%$$

$$s^2 = (4.43\%)^2$$

$$rel. \text{ std. dev. (ppt)} = 1000 \times \frac{2.11\%}{52.06\%} = 40.5$$

The calculation of a 90% confidence interval for the mean percent chloride is shown below.

$$90\% \text{ confidence level } t_3 = 2.920$$

$$uncertainty (u) = 2.920 \times \frac{2.11\%}{\sqrt{3}} = 3.55\%$$

$$90\% \text{ confidence interval} = 52\% \pm 4\%$$

[St. 2] Although the three experimental values are roughly equally spaced out, a Q test is performed below at a 90% confidence level.

$$range = 54.01\% - 49.83\% = 4.18\%$$

$$90\% \text{ confidence } Q_{crit_3} = 0.94$$

$$Q_{54.01\%} = \frac{|54.01\% - 52.34\%|}{4.18\%} = 0.400$$

$$Q_{49.83\%} = \frac{|49.83\% - 52.34\%|}{4.18\%} = 0.600$$

The Q-values for the extreme point do not exceed Q_{crit} , so it is not statistically justified to remove any data points. None of the data points are impossible, so no data points will be discarded.