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Gravimetric and Potentiometric
Determination of the Percent Weight of
Chloride in an Unknown Sample

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Theory and Practice of Quantitative Chemistry
Chemistry 134

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Gravimetric and Potentiometric Determination of the Percent Weight of Chloride in an Unknown Sample

ABSTRACT

The percent weight of chloride (Cl\(^-\)) in an unknown sample (#22) was determined both gravimetrically by precipitation with Ag\(^+\) ions, and potentiometrically by the use of an ion selective electrode (ISE). The percent chloride, at the 95% confidence level, was calculated to be 24.08 (± 0.32) %Cl by the gravimetric analysis (standard deviation= 0.25) and 25.0 (± 0.5) %Cl by the potentiometric analysis (standard deviation= 0.2). In addition, after statistically comparing the calculated percent chloride data with that of other unknowns, the gravimetric analysis suggested that unknown #22 could be from the same bulk sample as unknowns # 23 and #30 to a 99% confidence level (Spooled =0.385). Overall, the gravimetric and potentiometric analyses yielded very similar precisions as indicated by the close standard deviations, but the ISE analysis turned out to be the more efficient method in terms of labor, cost, and time.

THEORY

Gravimetric analysis is a quantitative method involving the determination of the mass of a compound that is chemically related to the analyte in question. One major form of gravimetric analysis is the precipitation method where the analyte is converted from a soluble to an insoluble form which can be mechanically separated from solution and can be accurately weighed.

One useful application of gravimetric analysis is the determination of the weight percent of chloride ions in an unknown mixture of white, crystalline solids. The amount of chloride ions can be calculated by adding Ag\(^+\) ions to an aqueous solution of the unknown to form an insoluble AgCl precipitate.

\[
\text{Cl}^- \text{(aq)} + \text{Ag}^+ \text{(aq)} \rightarrow \text{AgCl} \text{(s)} \quad (K_{sp}=1.8*10^{-10})
\]

By determining the mass of this precipitate, and knowing the amount of unknown used in the reaction, the weight percent of chloride ions can be calculated by simple stoichiometry, as shown in Appendix A. Although simple in theory, a gravimetric analysis such as the one described above is subject to a wide range of sources of error including incomplete reaction, formation of undesired precipitates, and incomplete precipitate transfer. Therefore, a number of precautions must be taken in order to minimize such errors.
For instance, in order to avoid the formation of undesired Ag₂CO₃ and Ag₂O salts from free CO₃²⁻ and OH⁻ ions in solution, a small amount of aqueous acid, HNO₃, is used to shift the equilibria away from these species:

\[
2 \text{H}^+ (\text{aq}) + \text{CO}_3^{2-} (\text{aq}) \rightleftharpoons \text{H}_2\text{O} (\text{l}) + \text{CO}_2 (\text{g}) \\
\text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightleftharpoons \text{H}_2\text{O} (\text{l})
\]

In addition, in order to avoid the formation of the soluble AgCl₂⁻ species from the insoluble AgCl, a small excess of Ag⁺ ions is used in the reaction. Furthermore, digestion, the process of heating a precipitate to induce coagulation, (see p.82-97, Skoog, West, and Holler) is utilized to increase the particle size of the AgCl thus minimizing its loss during filtration. Finally, the exposure of AgCl to strong sources of light is limited (especially when wet) in an attempt to minimize the photodecomposition of AgCl to elemental silver and chlorine gas:

\[
\text{AgCl(s)} + \text{hv} \rightarrow \text{Ag(s)} + \text{Cl}_2(\text{g})
\]

Besides for the wide range of possible errors, gravimetric analysis can also be quite expensive, time-consuming, and labor-intensive. However, the advantages are that the theory is quite simple resulting in straightforward calculations, and this method does not require sophisticated instrumentation.

The potentiometric determination of the percent chloride, on the other hand, involves the use of an ion selective electrode specific for free Cl ions. The electrode develops a potential across its membrane that depends on the activity of free Cl ions in solution. The generated potential across the membrane is then compared to an internal reference of constant potential. From the Nerst equation, the measured potential E (mV) can be related to the activity of free Cl ions in solution, A:

\[
E = E_0 + S \log(A)
\]

where E₀ is the reference potential (constant) and S is the electrode slope (constant for each particular electrode).

The activity of free Cl ions can be thought of as the "effective concentration". It is proportional to the free Cl concentration by the activity coefficient γₐₐ as shown in the following equation:

\[
A = \gamma_{\text{Cl}} \times [\text{Cl}]
\]

The activity coefficient, γₐₐ, itself depends on the total ionic strength of the solution. It is important to use a strong electrolyte solution in this analysis such that the background ionic strength of the standard and unknown solutions is relatively large and constant. Therefore, the differences in Cl concentrations will not affect their activities, and the
concentration of Cl ions will then be directly proportional to the activity. As a result, the chloride ion concentrations of an aqueous solution of an unknown can be calculated from a standard curve generated from a number of known concentrations. Once again, simple stoichiometry and regression statistics can be used to calculate the percent weight of Cl ions, as shown in Appendix C.

The use of a new calibration curve (standard curve) for every time a set of unknowns are measured cancels much of the determinate error that is inherent in measurements made with electronic instruments. Hence, the determination of the percent Cl using the ISE analysis is fairly accurate, as well as quick and economical. However, this method is subject to contamination errors due to ions that resemble Cl\(^-\) (such as Br\(^-\), I\(^-\), CN\(^-\)), and ions that precipitate free Cl\(^-\) (such as Mn\(^{2+}\), Pb\(^{2+}\), and Ag\(^+\)).

**PROCEDURE**

**Gravimetric Analysis:**
Approximately one gram of the dried unknown sample (#22) was dissolved in 490mL of deionized water and 10mL of 18M nitric acid. This solution was then portioned into five 50mL aliquots. About 5mL of aqueous 0.2M AgNO\(_3\) were added to each aliquot by the procedure given in Skoog, West, and Holler\(^{1}\) (p.815, paragraphs 3–5). The weights of the AgCl precipitate were recorded, and the percent weight of chloride ions in the unknown was calculated from these values, as shown in Appendix A.

**Potentiometric Analysis by Ion Selective Electrode (ISE):**
The procedure under “ISE Analysis” in the Chemistry 134 Student Lab Manual\(^{2}\) (p.19–20) was followed with no significant deviations. The potential measurements of the standard solutions and the unknowns are shown in Appendix B.

**RESULTS**

**Gravimetric Analysis:**
The weights of the AgCl precipitate from the gravimetric analysis were measured and the percent chloride values were calculated. Appendix A shows all the performed calculations and values. In Table 1 below, the gravimetric data is summarized:

<table>
<thead>
<tr>
<th>Trial #</th>
<th>% Cl</th>
<th>error %Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.20</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td>24.40</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>23.81</td>
<td>0.06</td>
</tr>
<tr>
<td>4</td>
<td>24.15</td>
<td>0.06</td>
</tr>
<tr>
<td>5</td>
<td>23.83</td>
<td>0.06</td>
</tr>
</tbody>
</table>
The mean percent chloride value was found to be 24.08 %Cl, and the standard deviation was 0.25 %Cl.

A Q-test was performed on the high and low outliers, but no data could be rejected to 99% confidence. Furthermore, a t-test was performed, and the 95% confidence interval for the calculated percent chloride was 24.08 (±0.32) %Cl.

ISE Analysis:

A regression analysis was performed on the measured potentials vs. the logarithm of the concentrations of chloride standards. The chloride concentrations of the unknown samples were interpolated from this regression. The %Cl of the unknowns were then calculated from these values. Appendix B shows all the calculations while Appendix C shows the regression analysis. The standard curve is shown below in Plot 1, and the ISE data is summarized in Table 2.
Table 2: Calculation of %Cl and Error %Cl for ISE Analysis.

<table>
<thead>
<tr>
<th>Trial</th>
<th>%Cl</th>
<th>error %Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.1</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>25.2</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>25.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The mean percent chloride concentration was found to be 25.2 %Cl, and the standard deviation was 0.2 %Cl.

Since there were only three data points, no Q-test was performed. However, a t-test yielded a 95% confidence interval of 25.2 (±0.5) %Cl.

Using the data sets from the gravimetric analysis of the other unknown samples, statistical comparisons suggested, at 99% confidence, that unknowns #22, #23, and #30 may have come from the same bulk sample. These calculations can be seen in Appendix D.

Finally, a simple check for consistency between the experimental uncertainty and the uncertainty associated with the volumetric glassware was performed. Two theoretically identical concentrations of chloride standard solutions resulted in different potential measurements due to different dilution methods. In Appendix E, the necessary calculations are shown to demonstrate that the experimentally determined uncertainty is consistent with the volumetric uncertainty of the glassware.

DISCUSSION

Both the gravimetric and potentiometric analysis yielded reasonably precise data values. The standard deviation values for both analyses were well under the pooled standard deviation value \(s_{\text{pooled}}\) over all the unknowns, indicating above average precision. In addition, many of the error values from the propagation of uncertainty were below 1% error, and virtually all were at or below 5% error.

The results of the gravimetric analysis had numerous inherent limits on their accuracy. First of all, it was almost impossible to avoid physical losses due to the amount of measurement and mechanical transfers of the chemical substances. There were also unavoidable method errors due to incomplete precipitation and side reactions.

However, the precision of this method was reasonably good. The calculated %Cl values were given to two decimal places due to the propagation of error values to the hundredth place. This allowed the reported values to have four significant figures and less than 0.3% error. Regardless, a number of systematic errors were unavoidable. In the mass measurements, a poorly calibrated scale may have offset all the calculated values. Also, as mentioned before, incomplete mechanical transfer of the precipitate to the filtering crucibles and the subsequent loss of precipitate through the filter may have caused a negative determinate error. Furthermore, the AgCl precipitate developed a moderate
purple tint possibly indicative of photodecomposition into elemental silver and chlorine gas, another likely source of negative determinate error.

The ISE results were much more likely to have yielded accurate values than the gravimetric analysis by virtue of the fact that a fresh set of standards were always run alongside the measurements of the unknowns. This probably canceled out a number of sources of systematic error. Nonetheless, an important determinate error to consider was the preparation of the NaCl stock solution from which the chloride standards were made by subsequent dilutions. A small error in the preparation of the stock solution would have clearly offset all the values in the entire experiment.

The precision of the ISE data, much like the gravimetric data, was reasonably good. The reported values of the percent chloride were given to one decimal place due to the standard deviation starting in the first decimal place. In this case, the standard deviation was used to give a reasonable approximation for the magnitude of the error because the propagation of uncertainty gave an unreasonably large number. This was due, in part, to the accumulation of the standard uncertainties in measuring throughout so many manipulations, and also in part, due to the large error associated with the antilog operation of the \( \log[\text{Cl}] \) values calculated from the standard curve. Due to the large discrepancy between the standard deviation and the propagation of uncertainty, the former was chosen as a more reliable indicator of precision.

As mentioned before, the precision of both analyses were quite close if standard deviation is used as the determining criteria. There was, however, a considerable difference in the size of the 95% confidence intervals between the two sets of data. The range of the interval for the gravimetric analysis was 0.64 whereas the range of the interval for the ISE analysis was 1.0. This can be explained by the fact that the number of degrees of freedom in the ISE analysis were 2 since there were only 3 data points. This made the \( t \)-value very high (\( t = 4.30 \)) for the 95% confidence interval. On the other hand, the number of degrees of freedom for the gravimetric analysis were 4 since there were 5 data points, and this resulted in a lower \( t \)-value (\( t = 2.78 \)) and a tighter confidence interval.

Furthermore, the relatively small number of data points (N=5 and N=3) in both experiments also made it difficult to reject any values using the Q-test. For 99% confidence, the value of \( Q_{\text{critical}} \) was far out of the range of \( Q_{\text{exp}} \). As a result, no data values were rejected.

Finally, it is interesting to note that the mean %Cl calculation from the ISE analysis was a bit higher than that of the gravimetric analysis. This would be consistent with the hypothesis that the results of the ISE experiment were more accurate due to the mentioned physical and chemical losses associated with the gravimetric analysis. However, there is no evidence to strongly support this speculation.
CONCLUSION

Both the gravimetric and potentiometric analyses yielded % Cl values of similar precision. The gravimetric analysis gave a value of $24.08 \pm 0.32 \% Cl$ (standard deviation $= 0.25$) while the potentiometric analysis gave a value of $25.0 \pm 0.5 \% Cl$ (standard deviation $= 0.2$) (uncertainties are to 95% confidence). In addition, it was statistically determined from the gravimetric data that the unknowns #22, #23, and #30 may have come from the same bulk data (to 99% confidence) ($S_{pooled} = 0.385$).

In general, despite the similarity in the level of precision of these results, the ISE method of analysis proved to be far superior to the gravimetric method in many respects: ease of procedure, time-efficiency, cost, and labor. Furthermore, the speculation over its higher accuracy may very well have had some merit to it. It would have been an interesting addition to this experiment to have been provided with a very highly accurate source of data which would have allowed some examination as to the validity of these hypotheses.
REFERENCES


APPENDIX

Appendix A:
Raw data from gravimetric analysis, percent weight chloride calculations, and statistical calculations.

Appendix B:
Raw data from the potentiometric analysis, percent weight chloride calculations, and statistical calculations.

Appendix C
Regression analysis of potentiometric data.

Appendix D:
Calculation of $s_{\text{pooled}}$ and statistical analysis of the probability of unknowns coming from the same bulk sample.

Appendix E:
Consistency calculation between experimental uncertainty and the uncertainty associated with volumetric glassware.
Appendix A: Gravimetric Analysis

Number of Samples

\[ N := 5 \quad i := 0 \ldots N - 1 \]

Calculation of the Mass of Cl in Each Unknown Sample

<table>
<thead>
<tr>
<th>total measured mass of crucible and AgCl (g)</th>
<th>measured mass of crucible (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.2217</td>
<td>29.1235</td>
</tr>
<tr>
<td>31.8256</td>
<td>31.7266</td>
</tr>
<tr>
<td>29.9467</td>
<td>29.8501</td>
</tr>
<tr>
<td>31.0589</td>
<td>30.9609</td>
</tr>
<tr>
<td>30.1258</td>
<td>30.0291</td>
</tr>
</tbody>
</table>

\[ \text{error}_{-\text{mass total}} := 0.0001 \quad \text{error}_{-\text{mass crucible}} := 0.0001 \]

calculated mass of AgCl (g)

\[ \text{mass}_{\text{AgCl}} := \text{mass}_{\text{total}} - \text{mass}_{\text{crucible}} \]

\[ \begin{bmatrix} 0.0982 \\ 0.99 \\ 0.0966 \\ 0.098 \\ 0.0967 \end{bmatrix} \]

\[ \text{error}_{-\text{mass AgCl}} := \sqrt{\text{error}_{-\text{mass total}}^2 + \text{error}_{-\text{mass crucible}}^2} \]

\[ \text{error}_{-\text{mass AgCl}} = 1.4142136 \times 10^{-4} \]

calculated mass of Cl in each unknown sample (g)

\[ \text{mass}_{\text{Cl}} := \frac{\text{mass}_{\text{AgCl}}}{\text{mass}_{\text{AgCl}} + 107.8682} \quad \text{--- weight fraction of AgCl that is Cl} \]

\[ \begin{bmatrix} 0.0242913 \\ 0.0244892 \\ 0.0238955 \\ 0.0242419 \\ 0.0239203 \end{bmatrix} \]

\[ \text{error}_{-\text{mass Cl}} := \frac{\text{error}_{-\text{mass AgCl}}}{\text{mass}_{\text{AgCl}} + 107.8682} \]

\[ \text{error}_{-\text{mass Cl}} = 3.4982818 \times 10^{-5} \]
Calculation of the Mass of Unknown in Each Sample

Mass of Unknown Used (g)  Volume of Solution (mL)  Volume of Solution used in each Sample (mL)
\( M_{\text{total}} := 1.0037 \)  \( V_{\text{total}} := 500 \)  \( V_{\text{sample}} := 50 \)
error_{M_{\text{total}}} := .0001  error_{V_{\text{total}}} := 0.50  error_{V_{\text{sample}}} := 0.1

Mass of Unknown used in Each Sample (g)
\( M_{\text{sample}} := \frac{M_{\text{total}} \cdot V_{\text{sample}}}{V_{\text{total}}} \)
\( M_{\text{sample}} = 0.10037 \)

error_{M_{\text{sample}}} := \sqrt{\left(\frac{\text{error}_{M_{\text{total}}}}{M_{\text{total}}} \right)^2 + \left(\frac{\text{error}_{V_{\text{total}}}}{V_{\text{total}}} \right)^2 + \left(\frac{\text{error}_{V_{\text{sample}}}}{V_{\text{sample}}} \right)^2}
\[
\text{error}_{M_{\text{sample}}} = 2.2465681 \times 10^{-4}
\]

Calculation of %Cl in Each Sample
\( \text{percent}_{\text{Cl}} := \frac{\text{mass}_{\text{Cl}}}{M_{\text{sample}}} \times 100 \)

\[
\begin{bmatrix}
24.2017824 \\
24.3989456 \\
23.807456 \\
24.1524916 \\
23.8321014
\end{bmatrix}
\]

\( \text{percent}_{\text{Cl}} = [24.2017824, 24.3989456, 23.807456, 24.1524916, 23.8321014] \)

error_{\text{percent}_{\text{Cl}}} := \sqrt{\left(\frac{\text{error}_{\text{mass}_{\text{Cl}}}}{\text{mass}_{\text{Cl}}} \right)^2 + \left(\frac{\text{error}_{M_{\text{sample}}}}{M_{\text{sample}}} \right)^2}
\[
\text{error}_{\text{percent}_{\text{Cl}}} = [0.0644146, 0.0647861, 0.0636741, 0.0643218, 0.0637203]
\]
Statistical Calculations

\[
\text{percent\_Cl} = \begin{bmatrix}
24.2017824 \\
24.3989456 \\
23.807456 \\
24.1524916 \\
23.8321014 \\
\end{bmatrix}
\]

Calculation of Average Percent Cl (%)

\[
\text{percent\_Cl\_mean} = \frac{\sum_{i} \text{percent\_Cl}_i}{N}
\]

\[
\text{percent\_Cl\_mean} = 24.0785554
\]

Calculation of Standard Deviation

\[
s := \sqrt{\frac{\sum_{i} \left( \text{percent\_Cl}_i - \text{percent\_Cl\_mean} \right)^2}{N - 1}}
\]

\[
s = 0.2537399
\]

95% Confidence Limits (Using t-test)

degrees\_freedom := N - 1

degrees\_freedom = 4

t := 2.78 \quad (\text{From Table 4-2, Skoog, West, Holler})

Confidence Limit

\[
\text{CL} := \frac{t \cdot s}{\sqrt{N}} \quad \text{CL} = 0.3154631
\]

95% Confidence Limit = 24.08 +/- 0.32 %Cl

Rejection of Outliers (Using Q-test)

For 99% Confidence and N=5 (From Table 4-4, Skoog, West, Holler)

\[
Q\_\text{critical} := 0.821
\]

\[
\text{percent\_Cl\_sorted} := \text{sort}(\text{percent\_Cl})
\]

\[
\text{percent\_Cl\_sorted} = \begin{bmatrix}
23.807456 \\
23.8321014 \\
24.1524916 \\
24.2017824 \\
24.3989456 \\
\end{bmatrix}
\]

\[
\text{range} := \text{percent\_Cl\_sorted}_{N-1} - \text{percent\_Cl\_sorted}_0
\]

\[
\text{range} = 0.5914896
\]
\[ Q_{\text{high}} := \frac{\text{percent}_{\text{CI}}_{\text{sorted}}_{N-1} - \text{percent}_{\text{CI}}_{\text{sorted}}_{N-2}}{\text{range}} \]

\[ Q_{\text{high}} = 0.333333 \]

The High Outlier is: \[ \text{if } Q_{\text{high}} > Q_{\text{critical}}, \text{percent}_{\text{CI}}_{\text{sorted}}_{N-1} = 0 \]

\[ Q_{\text{low}} := \frac{\text{percent}_{\text{CI}}_{\text{sorted}}_{1} - \text{percent}_{\text{CI}}_{\text{sorted}}_{0}}{\text{range}} \]

\[ Q_{\text{low}} = 0.0416667 \]

The Low Outlier is: \[ \text{if } Q_{\text{low}} > Q_{\text{critical}}, \text{percent}_{\text{CI}}_{\text{sorted}}_{0} = 0 \]

Therefore, none of the data can be rejected to 99% confidence.
Appendix B:
ISE Analysis

Calculation of Concentrations of Chloride Standards

<table>
<thead>
<tr>
<th>Mass of sodium chloride used to make stock solution (mg)</th>
<th>Volume of sodium chloride stock solution (mL)</th>
<th>Molecular Weight of sodium chloride (mg:mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass_{NaCl} := 292.2</td>
<td>volume_{stock} := 50</td>
<td>MW_{NaCl} := 22.9898 + 35.452</td>
</tr>
<tr>
<td>error_{mass NaCl} := 0.1</td>
<td>error_{volume stock} := 0.1</td>
<td>MW_{NaCl} = 58.4425</td>
</tr>
</tbody>
</table>

Number of Standards

N := 7
i := 0..N − 1

<table>
<thead>
<tr>
<th>Volume of stock solution used in each standard (mL)</th>
<th>Total Volume of each standard (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>volume_i :=</td>
<td>volume_{standard} :=</td>
</tr>
<tr>
<td>error_{volume_i} :=</td>
<td>error_{volume standard} :=</td>
</tr>
<tr>
<td>1.00</td>
<td>25.00</td>
</tr>
<tr>
<td>1.00</td>
<td>50.00</td>
</tr>
<tr>
<td>1.00</td>
<td>100.00</td>
</tr>
<tr>
<td>2.00</td>
<td>25.00</td>
</tr>
<tr>
<td>2.00</td>
<td>100.00</td>
</tr>
<tr>
<td>2.00</td>
<td>250.00</td>
</tr>
<tr>
<td>5.00</td>
<td>50.00</td>
</tr>
</tbody>
</table>

Chloride Concentration of each standard (M)

\[
Cl_i := \frac{\text{mass}_{NaCl}}{\text{MW}_{NaCl}} \frac{1}{\text{volume}_{stock}} \frac{\text{volume}_i}{\text{volume}_{standard_i}}
\]

\[
\begin{bmatrix}
3.9998289 \times 10^{-3} \\
1.9999144 \times 10^{-3} \\
9.9995722 \times 10^{-4} \\
7.9996578 \times 10^{-3} \\
1.9999144 \times 10^{-3} \\
7.9996578 \times 10^{-4} \\
9.9995722 \times 10^{-3}
\end{bmatrix}
\]
The values of $P$ and $\log([Cl])$ were subjected to a regression analysis using Kaleidagraph (see Appendix C).

The slope $m$, intercept $b$, error of $m$, error of $b$, and $\chi^2$ were calculated:

$m := -56.934 \quad b := -91.57$

$error_m := 0.3632 \quad error_b := 0.94419 \quad \chi^2 := 0.70846 \quad error_P_{unknown} := \frac{\chi^2}{N - 2}$
Potential Measurements for Unknown Solutions (mV)

\[ M := 3 \quad j := 0 \ldots M - 1 \]

\[ P_{\text{unknown}} := \begin{bmatrix} 30.9 \\ 30.8 \\ 30.5 \end{bmatrix} \]

Calculation of Unknown Solution Concentrations (M)

\[ C_{\text{unknown}} := \frac{P_{\text{unknown}} - b}{m} \]

\[ C_{\text{unknown}} = \begin{bmatrix} 7.0740505 \times 10^{-3} \\ 7.1027079 \times 10^{-3} \\ 7.1893788 \times 10^{-3} \end{bmatrix} \]

\[ \text{error}_{C_{\text{unknown}}} := C_{\text{unknown}} \cdot \ln(10) \cdot \frac{P_{\text{unknown}} - b}{m} \cdot \left[ \sqrt{\frac{\text{error}_{P_{\text{unknown}}}^2 + \text{error}_{b}^2}{P_{\text{unknown}} - b}} + \frac{\text{error}_{m}}{m} \right] \]

\[ \text{error}_{C_{\text{unknown}}} = \begin{bmatrix} -3.666047 \times 10^{-4} \\ -3.679783 \times 10^{-4} \\ -3.721302 \times 10^{-4} \end{bmatrix} \]

Mass of Unknown used (mg)

\[ M_{\text{total}} := 250 \]

\[ \text{error}_{M_{\text{total}}} := 0.1 \]

Volume of Unknown Solution (mL)

\[ V_{\text{total}} := 250 \]

\[ \text{error}_{V_{\text{total}}} := 0.20 \]

Molecular Weight of Cl (g/mol)

\[ \text{MW}_{\text{Cl}} := 35.4527 \]
Calculation of Percent Chloride:

\[
\text{percent}_{\text{Cl}} = \frac{V_{\text{total}}}{M_{\text{total}}} \cdot C_{\text{unknown}} \cdot MW_{\text{Cl}} \cdot 100
\]

\[
\text{percent}_{\text{Cl}} = \begin{bmatrix} 25.0794189 \\ 25.1810173 \\ 25.4882889 \end{bmatrix}
\]

\[
\text{error}_{\text{percent}_{\text{Cl}}} := \text{percent}_{\text{Cl}} \cdot \sqrt{\frac{\text{error}_{V_{\text{total}}}^2}{V_{\text{total}}} + \frac{\text{error}_{M_{\text{total}}}^2}{M_{\text{total}}} + \frac{\text{error}_{C_{\text{unknown}}}^2}{C_{\text{unknown}}}}
\]

\[
\text{error}_{\text{percent}_{\text{Cl}}} = \begin{bmatrix} 1.2999062 \\ 1.3047768 \\ 1.319499 \end{bmatrix}
\]

\[
\sum \text{percent}_{\text{Cl}}
\]

\[
\text{percent}_{\text{Cl mean}} := \frac{\sum \text{percent}_{\text{Cl}}}{M}
\]

\[
\text{percent}_{\text{Cl mean}} = 25.249575
\]

\[
\sum \frac{\text{percent}_{\text{Cl}} - \text{percent}_{\text{Cl mean}}^2}{M - 1}
\]

\[
s := \sqrt{\frac{\sum \text{percent}_{\text{Cl}} - \text{percent}_{\text{Cl mean}}^2}{M - 1}}
\]

\[
s = 0.2128821
\]

95% Confidence Limits (Using t-test)

degrees_freedom := M - 1

degrees_freedom = 2

t := 4.30 \quad \text{(From Table 4-4, Skoog, West, Holler)}

Confidence Limit

\[
\text{CL} := \frac{t \cdot s}{\sqrt{M}}
\]

\[
\text{CL} = 0.5285024 \quad 95\% \text{ Confidence Limit} = 25.25 \pm 0.53 \% \text{Cl}
\]
Appendix C:
Regression Calculations

potential vs. log[Cl]

<table>
<thead>
<tr>
<th>log[Cl]</th>
<th>potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.3979</td>
<td>44.500</td>
</tr>
<tr>
<td>-2.6990</td>
<td>61.800</td>
</tr>
<tr>
<td>-3.0000</td>
<td>79.400</td>
</tr>
<tr>
<td>-2.0969</td>
<td>28.200</td>
</tr>
<tr>
<td>-2.6990</td>
<td>62.600</td>
</tr>
<tr>
<td>-3.0969</td>
<td>84.800</td>
</tr>
<tr>
<td>-2.0000</td>
<td>22.300</td>
</tr>
</tbody>
</table>

\[ y = m_1 + m_2 \cdot M_0 \]

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>m_1</td>
<td>-91.57</td>
<td>0.94419</td>
</tr>
<tr>
<td>m_2</td>
<td>-56.954</td>
<td>0.3632</td>
</tr>
<tr>
<td>Chisq</td>
<td>0.70846</td>
<td>NA</td>
</tr>
<tr>
<td>R</td>
<td>0.9999</td>
<td>NA</td>
</tr>
</tbody>
</table>
Appendix D:
S_{pooled} Data Calculations

Number of samples in each data set
N := 5 \quad i := 0..N - 1

Number of data sets to be considered in S_{pooled}
M := 10 \quad j := 0..M - 1

One Data Set in Each Row, 10 Rows

\[
\begin{bmatrix}
24.20 & 24.40 & 23.81 & 24.15 & 23.83 \\
23.25 & 22.98 & 22.76 & 22.81 & 23.28 \\
27.38 & 27.75 & 27.42 & 28.04 & 27.80 \\
25.70 & 25.85 & 25.70 & 25.58 & 25.73 \\
23.83 & 24.30 & 24.69 & 23.83 & 24.91 \\
27.21 & 28.44 & 27.18 & 28.09 & 27.84 \\
21.80 & 22.69 & 21.80 & 21.51 & 22.22 \\
25.08 & 24.74 & 26.00 & 24.64 & 24.64 \\
23.52 & 23.13 & 23.60 & 23.85 & 23.67
\end{bmatrix}
\]

\[
S_{pooled} := \sqrt{\frac{\sum_{i=0}^{N-1} \sum_{j=0}^{M-1} (C_{j,i} - C_{j,mean})^2}{N \cdot M \cdot (M - 1)}}
\]

C_{j,mean} := \frac{\sum_{i=0}^{N-1} C_{j,i}}{N}

S_{pooled} = 0.385
Statistical Analysis to determine whether individual samples come from the same bulk sample (at the 99% confidence level):

\[ t := 2.423 \quad s_{\text{pooled}} = 0.385 \]

Test Array (if element = 1, then data set comes from same bulk as Unknown #22)

\[ \text{Test}_j := \text{if} \quad |C_j \text{mean}_j - C_0 \text{mean}_0| < t \cdot s_{\text{pooled}} \sqrt{\frac{N + N}{N \cdot N}}, 1, 0 \]

<table>
<thead>
<tr>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>1</td>
</tr>
</tbody>
</table>

It can be determined to a 99% confidence level that unknown #30 and unknown #23 also come from the same bulk sample as unknown #22.
Appendix E:
Comparison of Experimental Uncertainty
With Volumetric Uncertainty of Glassware

The values of P and log[Cl] were subjected to a regression analysis using Kalsidigraph
(see Appendix C)

The slope m, intercept b, error of m, error of b, and \( \chi^2 \) were calculated:

\[
m := -56.954 \quad b := -91.57 \\
error_m := 0.3632 \quad error_b := 0.94419 \quad \chi^2 := 0.70846 \quad error_P \text{ unknown} := \frac{\chi^2}{\sqrt{5 - 2}}
\]

\[i := 0..1\]

\[P_{\text{standard}} := \begin{array}{c}
61.8 \\
62.6
\end{array} \quad \text{<----- Standards 1mL in 50mL and 2mL in 100mL} \]

\[C_{\text{standard}} := \frac{P_{\text{standard}} - b}{m} \]

Calculated Concentrations From Regression

\[
C_{\text{standard}} = \begin{bmatrix}
2.028 \times 10^{-3} \\
1.964 \times 10^{-3}
\end{bmatrix}
\]

From Appendix B we know that the theoretical concentration of both the 1mL in 50mL and the 2mL in 100mL samples are \( 2.00 \times 10^{-3} \) with uncertainties \( 0.0208 \times 10^{-3} \) and \( 0.0207 \times 10^{-3} \), respectively, calculated from the glassware.

It can be seen from the data that the Concentration Values calculated from the regression are slightly outside the uncertainty limits of the theoretical concentrations, but not by too much.