Instrumental Precision Limits for Analytical Reagents and Chemical Analysis

Dr. Grady D Carney
Life Sciences Department
New York Institute of Technology
1855 Broadway, New York City, NY 10023
Email: Gcarney@nyit.edu

Abstract
This paper presents instrumental limit precision constants calculated for molarity of standardized AgNO₃ solutions and for %Cl content determined with Fajans, Mohr, and gravimetric methods. Calculated instrumental limit precision constants provide baseline reference for evaluating precision quality in determinations of chloride content, and for discovery of other significant sources of variability like sampling and identification of titrimetric end-point. Combining instrumental limit precision constant with Chi-squares statistics provides 95% level confidence intervals which serve to define acceptable levels of variability in quantitative chemical analysis

Keywords: Instrumental precision limit, analysis precision, confidence intervals

1.0 Introduction
This paper presents instrumental limit precision constants calculated for standardized AgNO₃ solutions and for %Cl content results determined by Erin Lyon(2013) with Fajans analysis method, by Deniz Korkmaz(2014) with Mohr method, and by Diane Krehbiel(2014) with both Fajans volumetric and gravimetric methods. Chi-square confidence intervals at the 95% level are derived for the precision in molarity of the AgNO₃ titrating reagent and also for the %Cl results of chemical analysis. The topic of instrumental limit precision is first introduced in quantitative analysis where students work mostly with precision measuring instruments, analytical balance, volumetric pipets, 50 mL burets and volumetric flasks for which specific precision or tolerances are given in numerous sources Fritz and Schenk(1974), Hughes(1959), and Skoog, West and Holler(1990). Students are taught to perform chemical analysis with both accuracy and precision. However, the manner in which these instruments are used determines whether precisions in prepared reagents and chemical analysis will occur within acceptable tolerances. Precisions might not meet desired expectations because of analyst error, lack of focus or simply not understanding the correct way to prepare analytical reagents and to use measuring instruments. Exercises in instrument calibration introduce students to proper technique and help to develop necessary skill in using the instruments. Sampling variability contributes to total variability in a chemical analysis. Non-uniform
composition in samples occur when solutions are not well mixed and particularly when samples are heterogeneous mixtures. So it is helpful to define acceptable expectation by beginning with instrumental precision limit of both sample standard deviation (S\textsubscript{M} for molarity) and coefficient of variation (CV\textsubscript{M} for molarity) for the analytical reagent. This removes any human introduced uncertainty sources and derives variability in reagent molarity solely from the known precision limits of the measuring instruments. Similarly calculating the instrumental precision limit for a chemical analysis result is helpful. Such precision limit provides analysts with a base line of expectation against which actual precision outcomes may be compared. Availability of such precision expectations will inform an analyst as to whether there exists need for improvement in their understanding and skill in performing the steps of quantitative chemical analysis. Confidence intervals at 95\% level are calculated assuming true precision values are the instrumental limit precision constants of reagents and chemical analysis.

Since the studies, Lyon(2013), Korkmaz(2014) and Krehbiel(2014) do not provide comparisons of actual \%Cl precision to instrumental limits in \%Cl precision, instrumental precision limits for the percent chloride are presented here to enable these comparisons. Lyons, Korkmaz and Krehbiel gave excellent discussions of analysis principles and procedures for Fajans, Mohr and gravimetric chloride determinations, so only the calculation and use of instrumental limits in precision for reagent concentration and in percent chloride of the soluble chloride materials need to be outlined here. Of course these techniques can be applied to other types of chemical analysis. Benchmarking actual precisions reported in the previous studies is assisted by calculating 95\% level Chi-square confidence intervals in \%Cl. These confidence intervals are

\[ S_{{\%Cl}(\text{instr})} \left( \chi^2_{\text{min}} / \text{DF} \right)^{1/2} \leq S_{{\%Cl}(\text{actual})} \leq S_{{\%Cl}(\text{instr})} \left( \chi^2_{\text{max}} / \text{DF} \right)^{1/2} , \]

and

\[ CV_{{\%Cl}(\text{instr})} \left( \chi^2_{\text{min}} / \text{DF} \right)^{1/2} \leq CV_{{\%Cl}(\text{actual})} \leq CV_{{\%Cl}(\text{instr})} \left( \chi^2_{\text{max}} / \text{DF} \right)^{1/2} . \]

The quantity DF is degrees freedom in the actual precision constant \( S_{{\%Cl}(\text{actual})} \). For DF = 2 the \( \chi^2_{\text{min}} = 0.0506 \) and \( \chi^2_{\text{max}} = 7.38 \). Note that CV depends upon variability in measure of chloride content through \( S_{{\%Cl}} \) and upon level of chloride content through \(<\%Cl>\): \( CV_{{\%Cl}} = 100 \cdot S_{{\%Cl}} / <\%Cl> \).

### 3.0 Precision for standardized silver nitrate molarity

Instrumental precision limit for molarity of the AgNO\textsubscript{3} as well as for the \%Cl obtained using Fajans analysis method are calculated. Standard silver nitrate solution can be obtained using primary standard AgNO\textsubscript{3} and measuring instruments, analytical balance and volumetric flask or by using primary standard NaCl and measuring instruments, analytical balance and 50 mL buret for titration. Both Mohr and Fajans methods were used to determine AgNO\textsubscript{3} molarity by titration.

#### 3.1 Gravimetric standardization

The standard silver nitrate reagent prepared by Lyon(2013) involved weighing 4.3036 g dried primary standard AgNO\textsubscript{3} using an analytical balance (tolerance \( S_\text{A} = 0.0001 \text{g} \)) followed by dissolving the sample in enough distilled water to give 250.00 mL solution using a volumetric flask (tolerance \( S_\text{F} = 0.12 \text{ mL} \)). This is a gravimetric standardization. Reported molarity is 0.1013 mole L\textsuperscript{-1} for the AgNO\textsubscript{3}(aq). The instrumental standard deviation for molarity, \( S_\text{instr} \) is calculated using the Law of Variance for quotients and products applied to \( M = (W/FW)/V \), namely
\[(S_M/0.1013 \text{ mole L}^{-1})^2 = (0.0001 \text{ g/4.3036 g})^2 + (0.12 \text{ mL/250 mL})^2 \]. Solving gives \(S_M(\text{instr}) = 4.9 \times 10^{-5} \text{ moleL}^{-1}\) and \(CV_M(\text{instr}) = 0.048\%\). The 95\% level Chi-square confidence interval for \(S_M(\text{actual})\) is calculated,

\[7.8 \times 10^{-6} \leq S_M(\text{actual, AgNO}_3 \text{ gravimetric}) \leq 9.4 \times 10^{-5} \text{ M},\]

and

\[0.0076 \leq CV_M(\text{actual, AgNO}_3 \text{ gravimetric}) \leq 0.092\%\].

### 3.2 Standardization by Fajans titration

An alternative way to obtain the standard silver nitrate solution is by titration using NaCl as the primary standard. This is a titration standardization. Krehbiel (2014) used three Fajans titrations resulting in \(<M>_{\text{AgNO}_3} = 0.1031 \text{ M}\), actual standard deviation \(S_M(\text{actual}) = 1.00 \times 10^{-4} \text{ M}\), and \(CV_M(\text{actual}) = 0.097\%\). The corresponding instrumental limit precisions reported here are \(S_M(\text{instr}) = 1.4 \times 10^{-4} \text{ M}\) and \(CV_M(\text{instr}) = 0.14\%\). The 95\% level Chi-square confidence interval for precisions recommended here for standardization by means of titration are

\[2.3 \times 10^{-5} \text{ M} \leq S_M(\text{actual, NaCl primary standard}) \leq 2.8 \times 10^{-4} \text{ M},\]

and

\[0.022\% \leq CV_M(\text{actual, NaCl primary standard}) \leq 0.27\%\].

### 3.3 Standardization by Mohr titration

Korkmaz (2014) determined the %Cl in soluble chloride unknowns using the Mohr method, but neither actual nor instrumental precision constants were reported. Used as primary standard material was dried NaCl rather than AgNO\(_3\). For standardization of the silver nitrate reagent, three dried NaCl samples were titrated. Approximately nine g AgNO\(_3\) was weighed and transferred to a 500 mL volumetric flask and made up to volume with distilled water. Silver nitrate molarity was calculated from titration results using

\[M = (W_{\text{NaCl}}/FW_{\text{NaCl}})/V_{\text{AgNO}_3} \].

Korkmaz(2014) reported mean molarity \(<M_{\text{AgNO}_3}> = 0.1002 \text{ mmole/mL}\). The actual sample standard deviation for AgNO\(_3\) molarity calculated here is \(S_M(\text{actual}) = 1.528 \times 10^{-4} \text{ M}\) with two degrees of freedom. Calculated \(CV_M(\text{actual})\) is 0.0152\%. Calculation of the instrumental limit precision for molarity requires as input the mean NaCl mass \(<W_{\text{NaCl}}> = 0.2583g\), mean AgNO\(_3\) titre volume \(V_{\text{AgNO}_3} = 44.10 \text{ mL}\), analytical balance tolerance \(S_A = 0.0001g\) and buret tolerance \(S_B = 0.05 \text{ mL}\). With these the Law of Variance for products and quotients is expressed as

\[(S_M/0.1002 \text{ moleL}^{-1})^2 = (0.0001g/0.2583g)^2 + (0.05 \text{ mL/44.10 mL})^2 \].

Calculation gives instrumental limit sample standard deviation for silver nitrate molarity \(S_M(\text{instr}) = 1.200 \times 10^{-4} \text{ moleL}^{-1}\) and also \(CV_M(\text{instr}) = 0.12\%\). These silver nitrate molarity standard deviations, actual \(1.528 \times 10^{-4} \text{ M}\) and instrumental limit \(1.200 \times 10^{-4} \text{ M}\), compare favorably with titrimetric values presented above for the Fajans analysis.

### 4.0 Precision for the %Cl analysis

The analysis for %Cl in soluble chloride samples is based upon, Fajans, Mohr and gravimetric determinations of chloride. Care must be taken to eliminate possible sampling variability before performing the analysis for %Cl.

#### 4.1 Fajans titration

Lyon(2013) analyzed four chloride replicates for %Cl. Application of a 95\% level outliers Qtest to the determined %Cl values, 54.82, 54.62, 54.79 and 54.73 reveals no outliers. Lyon(2013) reported mean
percent chloride $<\%\text{Cl}>$, 54.74%, and sample standard deviation $S\%\text{Cl}(\text{actual})$, 0.088% with 3 degrees of freedom, and 95% level Student's confidence interval in $\%\text{Cl}$, 54.5995 $\leq <\%\text{Cl}> \leq 54.8805$. The chloride content was known to be 54.45 percent, so Lyon(2013) was able to report analysis accuracy as a 0.53% error in the mean $\%\text{Cl}$, and for analysis precision coefficient of variation, $CV\%\text{Cl}(\text{actual}) = 0.16\%$ was reported. Instrumental limits in precision were not reported. Calculating the $\%\text{Cl}$ analysis instrumental precision constant $S\%\text{Cl}(\text{instr})$ requires as input the precision constant $S_M$, 4.9x$10^{-5}$ moleL$^{-1}$ for AgNO$_3$ molarity, analytical balance precision constant $S_A$, 0.0001 g and 50 mL buret precision constant $S_B$, 0.05 mL. Also needed are the mean dried soluble chloride sample mass 0.2644 g, AgNO$_3$ molarity, 0.1013 moleL$^{-1}$ and the mean AgNO$_3$ titre volume, 40.30 mL. With these the Law of Variance for products and quotients is applied to, $\%\text{Cl} = 100 \frac{M_{\text{AgNO}_3}V_{\text{AgNO}_3}FW_{\text{AgNO}_3}/W_{\text{samp}}}{W_{\text{samp}}}$, and the resulting equation is $(S\%\text{Cl}/54.74\%)^2 = (4.9x10^{-5} \text{ mole L}^{-1}/0.1013 \text{ mole L}^{-1})^2 + (0.0001\text{g}/0.2644\text{g})^2 + (0.05\text{mL}/40.30\text{mL})^2$ Solving gives $S\%\text{Cl}(\text{instr})$, 0.078% and instrumental $CV\%\text{Cl}(\text{instr})$, 0.14%. The 95% level confidence interval for $S\%\text{Cl}(\text{actual})$ and $CV\%\text{Cl}(\text{actual})$ are

\[0.012 \leq S\%\text{Cl}(\text{actual, titration}) \leq 0.15\%\]

\[0.022 \leq CV\%\text{Cl}(\text{actual, titration}) \leq 0.27\%\]

With the Fajans method Lyon(2013) produced $\%\text{Cl}$ measures with precision well within the expected 95% level confidence interval. So there is no issue of significant sampling variability in these $\%\text{Cl}$ determinations. Krehbiel(2014) used Fajans method to determine $\%\text{Cl}$ for three replicate samples, and obtained mean $\%\text{Cl}$, 28.34%, sample standard deviation $S\%\text{Cl}$, 0.62% and coefficient of variation $CV\%\text{Cl}$, 2.17%. These precision measures do not have the quality expected for the Fajans method; the corresponding instrumental limits values are $S\%\text{Cl}(\text{instr})$, 0.092% and $CV\%\text{Cl}(\text{instr})$, 0.32%. High levels of sampling variability appear to be embedded in these $\%\text{Cl}$ determinations.

### 4.2 Mohr titration

Three dried samples were examined for chloride content by Korkmaz(2014) using the prepared standard silver nitrate reagent and Mohr analysis. The reported $\%\text{Cl}$, 47.42, 47.60 and 47.56%, have mean $<\%\text{Cl}>$, 47.53% and actual sample standard deviation $S\%\text{Cl}(\text{actual})$, 0.0945% with two degrees of freedom and actual $CV\%\text{Cl}(\text{actual})$, 0.199%. Needed to calculate the instrumental precision constant for the $\%\text{Cl}$ are mean sample mass 0.2100g, mean AgNO$_3$ titre volume 28.10 mL, mean AgNO$_3$ molarity 0.1002 moleL$^{-1}$, buret tolerance 0.05 mL, analytical balance tolerance 0.0001g, and silver nitrate precision constant $S_M(\text{instr})$, 1.200x$10^{-4}$ M. Application of the Law of Variance for products and quotients to the formula for percent chloride, $\%\text{Cl} = 100 \frac{M_{\text{AgNO}_3}V_{\text{AgNO}_3}/W_{\text{samp}}}{W_{\text{samp}}}$, leads to, $(S\%\text{Cl}/47.53)^2 = (1.200x10^{-4}\text{mole L}^{-1}/0.1002\text{ mole L}^{-1})^2 + (0.05\text{mL}/28.10\text{mL})^2 + (0.0001\text{g}/0.2100\text{g})^2$ Solving gives $S\%\text{Cl}(\text{instr})$, 0.104% and $CV\%\text{Cl}(\text{instr})$, 0.220%. Comparison of $S\%\text{Cl}(\text{actual})$, 0.0945% to $S\%\text{Cl}(\text{instr})$, 0.104% reveals favorable agreement, and 95% level Chi-square statistics test confirms that $S\%\text{Cl}(\text{actual})$ is a valid estimate of $S\%\text{Cl}(\text{instr})$. Also these actual and instrumental $\%\text{Cl}$ precision values are consistent with results reported by Lyon(2013) for Fajans method. No significant sampling variability appears in these $\%\text{Cl}$ determinations.
4.3 Gravimetric method
Gravimetric analysis performed by Krehbiel(2014) for %Cl required neither titration or nor use of a standard AgNO₃ solution. Three dried soluble chloride salt samples were examined resulting in %Cl values, 26.52, 26.33 and 27.52% with mean 26.79%, sample standard deviation %Cl (actual) , 0.64% and CV %Cl(actual), 2.39% with two degrees of freedom. These actual precisions are seen to be poor when compared to gravimetric instrumental limits expectations. Our calculated instrumental limits for gravimetric %Cl precision are $S^{\%\text{Cl}(\text{instr, gravimetric})}$, 0.016% and $\text{CV}^{\%\text{Cl}(\text{instr, gravimetric})}$, 0.061%. Our calculated 95% level Chi-square confidence intervals are

$$0.0026 \leq S^{\%\text{Cl}(\text{actual, gravimetric})} \leq 0.031\%$$

and

$$0.0097 \leq \text{CV}^{\%\text{Cl}(\text{actual, gravimetric})} \leq 0.12\%$$

Clearly the gravimetric method for chloride analysis is capable of better precision than is possible for the titration methods. However, the gravimetric %Cl results, Krehbiel(2014), do not have quality level expected for gravimetric analysis. A possible explanation could be the presence of significant sampling variability.

5.0 Discussion
Variability in measured %Cl arises from non-uniformity in sample composition, uncertainty in titration endpoint location due to difficulty in distinguishing indicator colors, as well as from instrumental variability within the analysis method and other possible human introduced sources. The Law of Variance for combining variability arising from several sources is

$$S^{\%\text{Cl}(\text{actual})} = S^{\%\text{Cl}(\text{sampling})} + S^{\%\text{Cl}(\text{indicator})} + S^{\%\text{Cl}(\text{instr})} + \ldots$$

If variability in measurement arises strictly from the measuring instruments, the sample standard deviation as a measure of variability is characteristic of the property measured and method of chemical analysis as summarized for several reagents and analysis methods in Table 1. Variability in %Cl arising from non-uniformity in sample composition contributes to the actual variability $S^{\%\text{Cl}(\text{actual})}$ observed in the outcome of the chemical analysis in the manner indicated by the above mentioned Law of Variance. With use of dried pure NaCl as primary standard Korkmaz avoided non-uniformity of sample issues in standardization of the AgNO₃ solution: $S^{\%\text{Cl}(\text{sampling})}$ is 0.0%. The issue of non-uniformity in sample composition was also avoided by both Lyon(2013) and Korkmaz(2014) in their Fajans and Mohr determinations of %Cl. However, the gravimetric data for %Cl reported by Krehbiel(2014) appears to be contaminated by significant sampling variability. This shows up in calculating $S^{\%\text{Cl}(\text{sampling})}$, $\left[ (0.6393^2 - 0.01637^2)^{1/2} = 0.6391\% \right]$, as a measure of sampling variability, where $S^{\%\text{Cl}(\text{instr})}$ is 0.01637% and $S^{\%\text{Cl}(\text{total})}$ is 0.6393%. Krehbiel(2014) used the same sample material for the Fajans analysis, so both methods will be contaminated by the same level of sampling variability. Using data of Krehbiel(2014) for the Fajans analysis gives the following:

$S^{\%\text{Cl}(\text{sampling})}$ is $\left[ (0.6158^2 - 0.09200^2)^{1/2} = 0.6089\% \right]$, where $S^{\%\text{Cl}(\text{instr})}$ is 0.09200% and $S^{\%\text{Cl}(\text{total})}$ is 0.6158%. These two estimates of the sampling variability can be compared using a 95% level statistical $F_{\text{test}}$. First the $F_{\text{exp}}$ is 0.6393²/0.6089² = 1.102 with two numerator and two denominator degrees of freedom. Fisher’s Statistical Table gives $F_{\text{crit}} = 19$. Since $F_{\text{exp}} < F_{\text{crit}}$, the 0.6393% and 0.6089% values for $S^{\%\text{Cl}(\text{sampling})}$ should be accepted as two valid estimates of the same sampling variability. This amount of variability is significantly greater than the instrumental variability characteristic of the three chemical analysis methods.
Another source of chemical analysis variability that sometimes arises is when an indicator is used for locating the endpoint of a titration. Difficulty occurs when an endpoint color is orange and the before and after colors are red and yellow. Potentiometric titration provides a way to avoid the indicator problem. As an example, ammonia solution was standardized using methyl red indicator against 0.9207 M HCl for which $S_{\text{M}}(\text{instr})$ is $2.2 \times 10^{-4}$ M. Endpoint color sequence is yellow $\rightarrow$ orange $\rightarrow$ red, with orange being the endpoint color. All the solutions were well mixed to minimize sampling variability. Five replicate titrations for NH$_3$ molarity gave 0.9328, 0.8912, 0.9133, 0.9365 and 0.9174 M. $Q_{\text{test}}$ revealed no outliers. Mean $<M>$ is 0.9128, sample standardization $S_{\text{M}}(\text{actual})$ is 0.018 M and coefficient of variation $CV_{\text{M}}(\text{actual})$ is 2.0%. The instrumental limit $S_{\text{M}}(\text{instr})$ is $2.2 \times 10^{-3}$ M and $CV_{\text{M}}(\text{instr})$ is 0.23. Calculating endpoint related variability arising from difficulty in distinguishing orange from red or yellow gives $S_{\text{M}}(\text{indicator})$ as $\sqrt{0.018^2 - (2.2 \times 10^{-3})^2} = 0.0179$ M and successfully accounts for the observed tenfold increase over the expected instrumental limit variability in molarity.

### Table 1. Calculated instrumental precision limits

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>$S(\text{instr})$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standardizations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgNO$_3$ molarity</td>
<td>Gravimetric</td>
<td>$4.9 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>Mohr</td>
<td>$1.4 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Fajans</td>
<td>$1.2 \times 10^{-4}$</td>
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<tr>
<td>KSCN molarity</td>
<td>Titration</td>
<td>$2.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>NaOH molarity</td>
<td>Titration</td>
<td>$1.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>HCl molarity</td>
<td>Titration</td>
<td>$2.2 \times 10^{-4}$</td>
</tr>
<tr>
<td><strong>Chemical analysis</strong></td>
<td></td>
<td></td>
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<tr>
<td>%Cl in sample</td>
<td>Gravimetric</td>
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</tr>
<tr>
<td></td>
<td>Mohr</td>
<td>0.094%</td>
</tr>
<tr>
<td></td>
<td>Fajans</td>
<td>0.078%</td>
</tr>
</tbody>
</table>

*Assumes tolerances of analytical balance, 50 mL buret, volumetric pipets and volumetric flasks.

#### 6.0 Conclusion

Using chemical analysis data reported for Fajans determination of chloride, Lyon(2013), for Mohr determination of chloride, Korkmaz(2014), and for gravimetric and Fajans determination of chloride, Krehbiel(2014), instrumental limit standard deviations for the %Cl and 95% level confidence intervals for the actual %Cl standard deviations have been calculated. Actual %Cl standard deviations reported for Fajans
analysis, Lyon(2013) are found to meet the quality measure expectations imposed by calculated Chi-square 95% level confidence intervals for precision. Similar comparisons of actual %Cl standard deviations from both gravimetric and Fajans analysis, Krehbiel(2014) do not satisfy the calculated Chi-square 95% level confidence intervals for acceptable precision expectations possibly due to embedded sampling variability. Proposed here is the use of instrumental limit precision as a baseline for evaluating precision quality in reagent standardization and in chemical analysis. To facilitate this suggestion 95% level Chi-square statistics confidence intervals based upon precision limits of the measuring instruments are presented. Now other sources of variability in chemical analysis such as sampling variability and endpoint location due to indicator color variability can be identified.

References


5. Lyon, Erin,(2013), This article focuses on the determination of chloride in an unknown through volumetric measurements specifically Fajan’s method-Digio. [Online] Available: www.digio.me/.../unofficial-transcript-from-drexel-university-Chem-231...