LOCATION OF END POINT IN POTENTIOMETRIC ARGENTOMETRIC TITRATION USING GRAN PLOT AND TITRATION ERRORS

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ABSTRACT

End point location in potentiometric titrations by usual method may be inaccurate if there is supersaturation, coagulation and adsorption of ions near the end point. Gran plot, which does not need the value of electrode potential near the end point, is a better alternative method to locate the end point. The influence of the number of data points and spacing between the points for the location of end point in the potentiometric titration of KI, KBr and KCl with AgNO₃ using laboratory made silver/silver halide and silver ion selective electrodes has been investigated. Titration errors and end point uncertainties can be minimized by wisely selecting the number of points before and after the end point and fitting in the Gran plot. Accurate end point can be obtained even using last 40% of data points near the equivalence point before the end point. The advantages of Gran plot in locating the end point in the potentiometric titration are discussed.

INTRODUCTION

End point in potentiometric titration is generally located by plotting the successive values of the cell emf on ordinate and corresponding values of volume of titrant added on the abscissa. The steepest portion of this curve corresponds to the end point. The potential change near the end point in the titration of weak acid with weak base or dilute solution is very small and location of end point in such method by conventional plot is difficult. These difficulties can be removed and end point can be more accurately determined by derivative curves. The first derivative curve involves the plot of slope of the titration curve ($\Delta E/\Delta V$) against the volume of the titrant added. Peak of the curve which represents maximum slope of the titration curve is the end point. In second derivative curve, slope of first derivative curve ($\Delta^2E/\Delta V^2$) is plotted against volume of titrant added. The point on volume axis where the curve cuts through zero on the ordinate gives the end point.$^7,^{10}$
In these methods greater weightage is given to the data points near the end point and for better and accurate result large number of data points corresponding to very small change ion volume of titrant added near the end point must be used. But near the end point influence due to chemistry of reaction is maximum. Near the end point, there may occur super-saturation of ions, equilibrium may be attained slowly and the ions may be adsorbed on the precipitate. Recording large number of values of emf near end point is difficult and tedious due to instability of the readings. These facts introduce titration error. Furthermore results obtained by above methods may be in error if the reaction is not symmetrical e.g. in titration of silver ions with chromate ions.\textsuperscript{10, 2, 11, 12}

In 1952 G. Gran\textsuperscript{6} proposed a graphical end point detection method by a numerical manipulation of titration curve into two linear straight lines intersecting at the equivalence point. This method does not need data points near the end point. This new method can be applied to acid-base, redox, complex formation and precipitation potentiometric titrations.

**Theory of Gran Plot**

Consider a reaction: \( A^+ + B^- \rightarrow AB \)

Let \( V_0 \) mL of \( B^- \) with initial concentration \( C_B^0 \) is titrated by adding \( V_m \) mL of \( A^+ \) having concentration \( C_A \) at each time. The Emf of the cell is given by

\[
E = E^0 - \frac{2.303RT}{nF} \log a_B
\]

or,

\[
E = E^0 - \frac{2.303RT}{nF} \log \gamma C_B
\]

or,

\[
E^0 - E = \frac{2.303RT}{nF} \log \left[ \frac{C_B^0 V_0 - C_A V}{V_0 + V} \right]
\]

or,

\[
\frac{nF}{2.303RT} (E^0 - E) = \log \left[ \frac{C_B^0 V_0 - C_A V}{V_0 + V} \right] + \gamma \left( V_0 + V \right) \cdot 10^{\frac{nF}{2.303RT} E^0 / 2.303RT}
\]

or,

\[
\frac{(V_0 + V)}{V_0} \cdot 10^{\frac{nF}{2.303RT} E^0 / 2.303RT} = \gamma \left( V_0 V_0 - C_A V \right)
\]

or,

\[
\frac{(V_0 + V)}{V_0} \cdot 10^{\frac{nF}{2.303RT} E^0 / 2.303RT} = \frac{C_B^0 V_0 - C_A V}{V_0}
\]

Where \( E \) = Emf of the cell at temperature \( T \) Kelvin, \( E^0 \) = Standard emf of the cell, \( n \) = no. of electrons involved. Remaining symbols have their usual meanings.
At equivalence point: \( C_B^0 V_0 = C_A V_e \), where \( V_e \) is the volume of \( A^+ \) added at equivalence point.

\[
\text{So, } \left( \frac{0 + V}{V_0} \right) 10^{-nFE/2.303RT} = 10^{-nFE/2.303RT} \gamma \frac{C_A (V_e - V)}{V_0} \quad \ldots \ldots . \quad 1
\]

If a plot of \( \left( \frac{0 + V}{V_0} \right) 10^{-nFE/2.303RT} \) versus is made a straight line will be obtained. At the intercept of the straight line on x-axis:

\[
\left( \frac{0 + V}{V_0} \right) 10^{-nFE/2.303RT} = 0 \quad \text{i.e.} \quad 10^{-nFE/2.303RT} \gamma C_A \left( \frac{V_e - V}{V_0} \right) = 0
\]

\[\therefore \quad (V_e - V) = 0 \quad \text{So,} \quad V_e = V\]

This shows that the volume corresponding to the intercept on x-axis is the equivalence point.

Equation 1 best fits for the data points taken only before the equivalence point. The end point can also be obtained from the data points after the end point by plotting \( \left( \frac{0 + V}{V_0} \right) 10^{-nFE/2.303RT} \) against the volume of titrant added.

At the time when Gran developed this method, semi-log papers should be used for calculations but those papers were not readily available. This difficulty decreased the use of Gran Plot. By the development of calculator, later on computer and using ion selective electrode, use of Gran Plot is now increasing.

The advantages of using Gran’s method of locating end point are \(^3, 4\) Simplicity of measurement, Simplicity of calculation, Versatility and Precision.

Burden and Euler\(^1\) suggested that the advantages favoring Gran plots are significantly influenced by the number of data points chosen, the spacing between the data in the titration of strong acid with strong base. Detailed study of argentometric titration and titration errors associated with Gran plot by varying the number of data points and spacing between the points is presented in this paper.
EXPERIMENTAL

Potentiometric titrations were performed with AR and LR grade reagents like KCl, KI, KBr, AgNO₃ etc. using silver and silver ISE fabricated in the laboratory of Central Department of Chemistry, T.U, as working electrodes and SCE as reference electrode. These electrodes are found to behave Neptian manner. OSWA digital potentiometer, India, was used for potential measurement and all calculations were performed on computer using Excel program.

RESULTS AND DISCUSSION

Figure 1 represents the plot of Gran function against ‘V’ for the potentiometric titration of 100mL of 0.01M KI with 0.1M AgNO₃ solution. Two straight lines with R² value 0.9998 are obtained. The first one is obtained by plotting the values of data points before the end point and the second line is obtained by plotting the values of data points after the end point. On extrapolations of both these lines meet the volume axis, which is the end point of the titration. Thus data points either before the end point or after the end point separately can be used to locate the end point by Gran Plot. Gran’s method of locating the end point has one distinct advantage over classical methods that it does not need the data points near the end point and thus overcomes the difficulties associated with the errors due to incomplete precipitation, adsorption, slow attainment of equilibrium etc. Moreover the end point is located by extrapolation of straight lines which eliminates error due to personal bias.

![Gran Plot](image-url)

**Figure 1:** Location of end point by Gran plot for the titration of 100mL of 0.01M KI with 0.1M AgNO₃, using data points before and after the end point.
The number of data points that should be used by Gran’s method is not definite for the location of end point. One would expect that number of data points used should not affect the end point, since the end point is obtained by the extrapolation of linear plot either before or after the end point. But the value of end point obtained from Gran's method is found to be deviated from its stoichiometric end point. To evaluate titration error data points representing initial 30% of the data points before the end point in the titration of 100mL of 0.01M KI with 0.1M AgNO₃ are used. The points taken one at 0, 1 and 2mL addition of titrant, represent 20% completion of reaction. Percentage titration errors are calculated from deviations of each Gran plot end point from its respective stoichiometric end point. At the beginning of the titration the change in emf per each milliliter addition of titrant is small. Small errors in the values of emf at the beginning of the titration has a much more profound effect on Gran Plot to give titration error than does the values of emf at a higher completion of titration even with a constant instrumental error. Therefore one should not choose points which all lie near the beginning of the titration. If we increase the number of data points from beginning toward near the end point (e.g. when data points at 0, 1, 2, 3mL and 0, 1, 2, 3, 4mL are taken), the corresponding values of end point obtained are progressing to reach to minimum percentage titration. When the points at the beginning of titration are neglected and points corresponding to 40 to 80% completion of reaction (when data points at 4, 5, 6, 7, 8mL are taken), the values of end point are very close to the stoichiometric end point. In the same manner, when data points corresponding to last 40% of titration (when data points at 7, 8, 9, 10mL are taken), minimum percentage titration are found in all six trails. The results obtained when we use data points covering 80 to 100% of completion of reaction with or without spacing (points at 0, 2, 4, 6, 8mL or 1, 3, 5, 7, 9mL or 0 to 10mL are taken), are in good agreement with stoichiometric end point. Similar results are obtained when data points after the end point are used (Table 1). The percentage titration error is high for the end point which is more deviated from its stoichiometric end point. Similar percentage titration errors are also found to occur in case of the titration of KBr and KCl by AgNO₃. In all these three cases the maximum percentage errors are found when the data points at 0, 1 and 2 ml of titrant added are taken.
Table 1: Titration errors (%) related to the number and spacing of data points for the titration of 100.0mL of 0.01M KI with 0.1M AgNO₃ solution using silver electrode.

<table>
<thead>
<tr>
<th>Description of Data</th>
<th>No. of points taken</th>
<th>Percentage titration error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trial 1</td>
<td>Trial 2</td>
</tr>
<tr>
<td>Before end point</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>3°</td>
<td>-11.3</td>
<td>-13.6</td>
</tr>
<tr>
<td>4°</td>
<td>-3.1</td>
<td>-5.0</td>
</tr>
<tr>
<td>5°</td>
<td>-2.0</td>
<td>-2.9</td>
</tr>
<tr>
<td>5°</td>
<td>0.3</td>
<td>3.0</td>
</tr>
<tr>
<td>5°</td>
<td>0.5</td>
<td>2.1</td>
</tr>
<tr>
<td>4°</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>4°</td>
<td>1.1</td>
<td>1.5</td>
</tr>
<tr>
<td>3°</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>3°</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>3°</td>
<td>1.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>

| After end point     |         |         |         |         |         |         |
|                     |         |         |         |         |         |         |
| 7                  | 1.0     | 1.3     | 0.8     | 1.8     | 1.9     | 1.8     |
| 7°                  | 1.0     | 0.9     | 0.7     | 1.9     | 1.4     | 1.4     |
| 6°                  | 1.0     | 0.8     | 0.8     | 2.0     | 1.5     | 1.5     |
| 6°                  | 1.2     | 1.6     | 1.2     | 2.3     | 2.2     | 2.2     |

Where a refers points at 0, 1, 2 mL; b 0, 1, 2, 3 mL; c 0, 1, 2, 3, 4 mL; d 0, 2, 4, 6, 8 mL; e 1, 3, 5, 7, 9 mL; f 4, 5, 6, 7, 8, 9 mL; g 7, 8, 9, 10 mL; h 11, 12, 13, 14, 15, 16, 17 mL; i 11, 14, 17 mL; j 11, 12, 13 mL

Percentage titration errors were also analyzed for potentiometric titrations of potassium halides using silver ion selective electrode. The nature of titration errors for the titration of KI, KBr and KCl with AgNO₃ are similar to those obtained using silver electrode. The titration errors and uncertainty in locating the end point is reduced when a large portion (nearly 60%) of the titration curve is represented both before and after the equivalence point. One could use data points near equivalence points, neglecting the points at beginning for best result. The values of end point obtained with successively neglecting the points at the beginning are found similar. In Figure 2 values of end point are plotted with the number of data points taken from near the equivalence point. The end point obtained using only four data points (i.e. using points at 7, 8, 9 and 10mL of titrant added), five data points (6, 7, 8, 9, 10mL), six data points (5, 6, 7, 8, 9, 10mL) and so on have no significant difference. This implies that accurate end point from Gran plot can be obtained by using last 40% of data points near the end point.

Figure 2: Effect of number of points taken from near the equivalence point on end point
CONCLUSION

In Gran's method of locating end point in potentiometric titration, the titration errors can be minimized by not giving weightage to the data at the beginning and near the end point. On the basis of present work following conclusions can be drawn.

- Gran's method of locating end point does not need values of emf at the beginning and near the end point of titration.
- Extrapolation of linear straight lines is used to locate the end point. Data points before the end point are good enough to locate the end point accurately.
- Small numbers of data points are enough to get accurate end point.
- Titration errors inherent with Gran's method can be minimized by wisely selecting the number of data points and carefully fitting the Gran plot.
- End point from Gran plot can be obtained by using last 40% of data points to the stoichiometric equivalent point.

REFERENCES