Titration Errors Associated with the Use of Gran Plots in Selected Potentiometric Titrations

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Abstract

Uncertainties introduced into endpoint determinations when Gran plots are used to analyze data from selected types of potentiometric titrations were investigated. Two approaches were employed to evaluate these errors. First, errors arising from the precision of pH measurements and the number and spacing of the data points were evaluated for a strong acid-strong base titration. Second, contributions to the titration error due to variation in activity coefficients during the course of the titration, constancy of the parameter 2.303RT/nF, and scatter in volume and potential measurements were evaluated for a 1:1 potentiometric precipitation titration. Inconstancy of the parameter 2.303RT/nF, or inaccuracy in its determination, was shown to be the most significant error investigated when the effect of dilution was minimized.

A procedure for transforming conventional titration data into a form which when plotted gives rise to straight lines intersecting at the equivalence point was introduced in 1952 by Gran (2). Fundamentally, this technique consists of plotting a quantity related to the antilogarithm of the pH or potential as ordinate *versus* volume of titrant added as abscissa. In many instances only points preceding the endpoint need to be plotted; in other instances, only points following the endpoint are plotted. In either of these cases, a single straight line is obtained which intersects the abscissa at the endpoint volume. Little use of this method is found in the literature, but, because it has potential utility in conjunction with ion-selective electrodes, interest in the method has been revived (5, 6).

Plots resulting from the application of Gran's technique are called "Gran plots" or "Gran's plots" (5). Volume-corrected semi-antilogarithmic paper has recently been made commercially available to facilitate making Gran plots directly from potential-volume data (5).

Advantages favoring the use of this technique have been suggested (5) as including the following: 1) fewer titration points need to be taken than with conventional methods; and 2) measurements need not be made close to the equivalence point since this point may be obtained by extrapolation.

Even though one recent study reported an evaluation of errors encountered when ion-selective electrodes are used in conventional titrations (7), no evaluation of errors peculiar to the Gran procedure is available.

Theory

Two approaches were used in this study to evaluate the titration errors incurred with the use of Gran plots. First, titration errors arising from scatter in pH measurements and the number and spacing of data points used in the analysis were evaluated for a strong acid-strong base

titration. Second, the individual and combined contributions to the titration error arising from uncertainties in several specific experimental variables were examined. Random scatter was introduced into the potential and/or volume measurements in 10 sets of theoretical titration data for a 1:1 precipitation titration and the precision and accuracy of the resulting endpoints were evaluated.

To avoid limitations in accuracy involved in plotting on and reading from commercially available, volume-corrected, semi-antilogarithmic paper, the Gran plots in this study were made by performing a least-squares fit on points generated from pH-volume or potential-volume data and appropriate mathematical expressions (2). This procedure, when used as part of a linear regression analysis, lends itself readily to computing the confidence limits of the end-point. All calculations were performed on a PDP-8/L minicomputer. Since the expression used to compute the quantity plotted versus volume is different for different types of titrations, this study considered only the two types of titrations mentioned previously.

For a strong acid-strong base titration the pertinent Gran expression for points prior to the equivalence point is (2, 5):

$$\frac{V_S + V}{V_S} \; 10^{(pH-K)} = K_1 V + [S]_O \quad [1]$$

where V_S is the initial volume of sample, (liters), V is the volume of titrant added, (liters), pH is the negative logarithm of hydrogen ion activity, (moles/liter), $[S]_O$ is the initial concentration of sample, (moles/liter), K is an arbitrary scaling constant (taken to be zero in this study), and K_1 is a constant which includes the activity coefficients. Plotting the left-hand side of equation [1] as ordinate *versus* V as abscissa results in a straight line. The value of V when the left-hand member of equation [1] is zero is the endpoint volume. Since this value is normally obtained by extrapolation, the uncertainty associated with it is dependent upon the uncertainties associated with the slope and intercept of the line. The statistical uncertainty of the endpoint may be estimated at any desired level of confidence by means of parameters computed from a linear regression analysis of the data and appropriate statistical equations (5).

The data of Table 1 were used to evaluate the effect on the titration error of scatter in pH measurements, of the number of data points used in the analysis, and of the location of and spacing between the points on the titration curve. The activity coefficients were assumed to remain constant during the titration since dilution was minimized by utilizing a titrant 10 times more concentrated than the titrate. The antilogarithm term shown in the right-hand column corresponds to the left side of equation [1]. These data were chosen since they correspond to the same titration used by Gran to illustrate the use of his equations in a discussion subsequent to the presentation of his original work (2). The antilogarithm values used in all subsequent computer calculations were six-digit, floating-point values rather than the rounded values shown in Table 2.

TABLE 1. *Theoretical titration data for the titration of 100.00 ml of 0.0100 N strong acid with 0.1000 N strong base.*

V, ml	pH	$10^{(4.00-pH)}$	$\times \frac{100.00+V}{100.00}$
0.00	2.00	100	
1.00	2.05	90	
2.00	2.105	80	
3.00	2.17	70	
4.00	2.24	60	
5.00	2.32	50	
6.00	2.425	40	
7.00	2.55	30	
8.00	2.73	20	
9.00	3.04	10	
10.00	7.00	0	

To evaluate the effect on the titration error created by scatter in pH measurements, computer-generated random scatter was introduced into the first 10 pH values listed in Table 1. Random errors between zero and an arbitrarily chosen maximum value were generated using a pseudo-random number generator; these errors were added to or subtracted from the pH values in Table 1. A separate random number was used to determine whether the scatter was to be added to or subtracted from the tabulated pH value. The maximum values of scatter are listed in Table 2 in the ΔpH column. For each maximum value, 10 sets of titration data containing scatter were generated. The left-hand member of equation [1] was computed for each pH value in a set of points using the associated volume, V, from Table 1. A least-squares fit was made to each of these sets of data.

The constants K_1 and $[S]_0$ were assigned values corresponding to the slope and intercept, respectively, and the resulting equation was solved for the endpoint volume. The statistical uncertainty at the 95% confidence level was estimated for the endpoint volume using the method and formulae given by Bauer (1). This procedure was repeated for all 10 sets of data and for each of the 3 ΔpH values listed. The average titration error, average per cent deviation from the mean error, and average uncertainty in the endpoint volume at the 95% confidence level were computed for each series of 10 sets of data. The results are shown in the last three columns of Table 2.

To demonstrate the effect on the titration error caused by decreasing the number of data points, the above procedures were repeated using three sets of five data points and three sets of three data points. The results of these computations are also shown in Table 2.

When fewer than 10 data points were used in the analysis, the points were chosen to cover various regions of the titration curve prior to the endpoint. This was done to demonstrate how the location of the points on the titration curve and the spacing between these points affected the titration error. For example, one of the sets of three points represented 90% of the titration curve prior to the endpoint, the second

set represented 60% of the curve, and the third set only the first 20% of the titration prior to the endpoint. It is evident that the titration error is less when a larger portion of the titration curve is represented.

TABLE 2. *Titration errors arising from the precision of pH measurements as a function of the number and spacing of data points.*

Titration of 100.00 ml of 0.0100 N strong acid with 0.1000 N strong base.

No. of Points	ΔpH	Average Titration Error[7] Random Scatter (%)	Average Deviation[7] (%)	Average Uncertainty at 95% C.L.[7] (%)
10	0.005	+0.02	0.08	1.40
10	0.01	—0.07	0.28	2.66
10	0.1	+0.68	1.71	25.98
5	0.005	—0.04[1] (+0.16)[2]	0.02[1] (0.10)[2]	1.42[1] (1.35)[2]
5	0.01	—0.21[1] (+0.13)[2]	0.40[1] (0.23)[2]	2.91[1] (2.22)[2]
5	0.1	1.09[1] (—0.34)[2]	4.89[1] (3.01)[2]	30.91[1] (21.75)[2]
5[3]	0.005	—1.05	0.73	1.95
5[3]	0.01	—0.05	1.39	3.73
5[3]	0.1	+11.34	21.74	34.39
3	0.005	—0.06[4] (—0.23)[5]	0.14[4] (0.23)[5]	1.42[4] (2.75)[5]
3	0.01	+0.06[4] (—0.27)[5]	0.34[4] (1.09)[5]	3.56[4] (4.04)[5]
3	0.1	+0.05[4] (+2.24)[5]	3.44[4] (7.31)[5]	24.43[4] (50.19)[5]
3[6]	0.005	—0.30	2.23	2.39
3[6]	0.01	+1.12	3.29	5.78
3[6]	0.1	—11.49	15.90	44.03

[1] Point at 0,2,4,6,8 ml
[2] Points at 1,3,5,7,9 ml
[3] Points at 0,1,2,3,4 ml
[4] Points at 2,5,9 ml
[5] Points at 0,2,6 ml
[6] Points at 0,1,2 ml
[7] Average of ten trials

To evaluate the individual and combined contributions to the titration error incurred in a Gran analysis due to variation in activity coefficients, inaccuracy in the value of 2.303RT/nF, and scatter in the potential and volume measurements, a 1:1 potentiometric precipitation titration was considered. The reaction considered was of the form:

$$X_1S + TX_2 \rightarrow TS_{(S)} + X_1X_2$$

where X_1S, TX_2 and X_1X_2 are soluble. If X_1S is titrated with TX_2, the expression necessary for a Gran analysis using points prior to the equivalence point is identical to equation [1] except that the term $10^{(pH-K)}$ is replaced by $10^{17n(K-E)}$ (2). In this modified equation, 17 is a constant (2.303RT/nF, rounded to two significant figures), n is the number of electrons transferred per mole, E is the potential of the indicating electrode (millivolts) versus a suitable reference electrode, and K is an arbitrary scaling constant (taken to be zero in this study). To reduce the error introduced by the inaccuracy of the volume measurements, the titrant and titrate were taken to be equal in concentration. This choice, however, increases the error resulting from the effect of dilution upon the activity coefficients.

TABLE 3. *Titration errors encountered with Gran plots due to variation in activity coefficients and scatter in potential and volume measurements.*

Titration of 25.00 ml of 0.1000 F X_1S with 25.00 ml of 0.1000 F TX_2

Type of Error	Electrode Slope Used for Least Squares Fit (mv)	Average Normality of Sample (10 Trials) (eq/l)	Relative Average Deviation of Individual Trials (%)	Average Titration Error (%)	Average Uncertainty at 95% C.L. (%)
Variation in Activity Coefficients[1]					
No. ISA	59.16	0.1017[2]		+1.7	6.60
0.1 F ISA	59.16	0.1009[2]		+0.9	3.61
1 F ISA	59.16	0.1002[2]		+0.2	0.71
Potential Measurements	58.16	0.0990	0.23	—1.0	
E ± (0—0.5 mv)	59.16	0.1000	0.20	0.0	1.93
	60.16	0.1010	0.14	+1.0	
Volume Measurements	58.16	0.0990	0.03	—1.0	
V ± (0—0.05 ml)	59.16	0.1000	0.04	0.0	0.51
	60.16	0.1009	0.04	+0.9	
Combined Effects:	58.16	0.0992	0.17	—0.8	
E ± (0—0.5 mv)	59.16	0.1002	0.17	+0.2	4.50
V ± (0—0.5 ml)	60.16	0.1012	0.19	+1.2	
Activity Coefficient Variation in Presence of 1 F ISA					

[1] Activity coefficients were calculated from the E.D.H.E. using the appropriate constant for fluoride, (see text).
[2] Only one set of data was analyzed since the error introduced was systematic.

The effect of an ionic strength adjustor (ISA), used to minimize the error due to changing activity coefficients during the course of the titration, is shown in Table 3. For each of the three ISA concentrations shown, activity coefficients were computed at 2.50 ml increments of titrant added using the extended Debye-Hückel equation (EDHE)

$$-\log f = \frac{Az^2\sqrt{\mu}}{1 + Ba\sqrt{\mu}} \qquad [2]$$

where f is the activity coefficient, μ is the ionic strength, A and B are 0.509 and 0.328, respectively, at 25° C in water, and a is an adjustable parameter characteristic of a particular ion. For illustrative purposes, the ion being sensed by the electrode was taken to be fluoride for which a = 3Å(3). For each 2.50-ml increment of titrant added, the activity of the species being monitored, F^-, was calculated. A corresponding potential was computed by substituting this activity into the Nernst equation. These potential values, along with the corresponding titrant volumes, were submitted to a linear regression analysis as described previously and the average normality of the sample, the titration error and endpoint uncertainty at the 95% confidence level were calculated. The results are shown in Table 3. Only one such series of calculations was made for each ISA concentration shown, since the error introduced by the changing activity coefficients was systematic.

The effect on the titration error of scatter in the potential measurements was evaluated by introducing random scatter ranging from zero to ±0.5 mv into 10 sets of theoretical titration data. The theoretical potential values were calculated from the Nernst equation taking 2.303RT/nF = 59.16 mv (n was taken to be unity); activity effects were neglected. Potential values were computed at 2.50-ml increments of titrant added. A linear regression analysis was carried out on each of the 10 sets of scattered data as described previously and the average normality of the sample, the relative average deviation, the titration error, and the endpoint uncertainty at the 95% confidence level were calculated. The results are shown in Table 3. To demonstrate the effect of an inaccurate value of 2.303RT/nF, this same procedure was repeated using values of 58.16 mv and 60.16 mv in the Nernst equation to generate the theoretical potential values.

The effects on the titration error due to scatter in the volume readings were evaluated by introducing scatter from zero to ± 0.05 ml into 10 sets of theoretical titration data. At each 2.50-ml increment of titrant added, a random number between zero and ± 0.05 was added to the titrant volume expressed in milliliters. This modified titrant volume was used to compute a concentration of titrate remaining which was subsequently substituted into the Nernst equation to compute a modified potential. These modified potential values, along with the original volume increments, provided titration data influenced by scatter in the volume measurements. Each of the 10 sets of data was analyzed as described previously and the results are shown in Table 3. This procedure was repeated for three different values of 2.303RT/nF.

The last three rows of Table 3 display the titration errors incurred when scatter in potential, scatter in volume and variation in activity coefficients all occur simultaneously. The results shown are the averages of the values obtained for 10 sets of titration data at each of the indicated values of 2.303RT/nF.

Discussion

For the strong acid-strong base titration upon which the results of Table 2 were based, a typical experimental titration error would not be expected to exceed 0.1-0.3% if conventional endpoint detecting techniques were employed (4). The magnitudes of the average titration errors and average deviations shown in Table 3 indicate that a maximum scatter of 0.01 pH unit or less would be necessary to keep the titration errors less than this if a Gran-type analysis were employed.

The results in Table 2 show that if the number of data points used in the analysis is decreased, the points must be chosen to represent as large a range of added titrant as possible For example, nearly identical average titration errors and average deviations were obtained when 3 points, taken at 2.00, 5.00, and 9.00 ml and containing a scatter of zero to ± 0.01 pH unit, were utilized as when 10 points containing the same amount of scatter were utilized. The average uncertainty of the endpoint at the 95% confidence level was slightly higher in the case of the three data points due to the statistical uncertainty associated with the use of fewer points. When the three data points represented only the first 20% of the titration curve prior to the endpoint, *i.e.*, at 0.00, 1.00, and 2.00 ml, the error and uncertainty were significantly larger. In general, the average titration errors and average deviations in Table 2 indicate that for a scatter of zero to ± 0.01 pH unit, the points used in the analysis should represent a range of titrant delivered which is greater than 60% of the endpoint volume if the titration error is to be kept in the range ±0.1-0.3% or lower.

From Table 2 the average uncertainty at the 95% confidence level is a considerably more conservative estimate than the average deviation encountered with the 10 trials made for any set of conditions shown. This is due to the statistical uncertainty associated with the relatively few number of data points used in the analyses and the relatively few (10) trials employed to obtain the average titration errors.

Table 3 shows the effects of several experimental parameters upon the titration error when a Gran analysis is used to determine the endpoint of a potentiometric precipitation titration. If the titrate and titrant are taken to be of equal concentration, the error caused by variation in activity coefficients due to dilution is enhanced. Assuming that a maximum titration error of approximately ±0.3% is acceptable for this titration, Table 3 shows that a 1 F ISA is required to reduce the titration error caused by variation in activity coefficients to less than this value.

A comparison of the three average titration errors listed for either the potential measurements, volume measurements or combined effects

shows the effect of a ±1 mv error in the value of 2.303RT/nF. If a 1 F ISA is used to minimize the activity effects, the titration errors shown indicate that the most significant error studied is inaccuracy in the value used for 2.303FT/nF.

The magnitude of scatter introduced into the volume measurements is probably somewhat pessimistic whereas that introduced into the potential measurements is somewhat optimistic in terms of typical experimental uncertainties. Nevertheless, the scatter in volume introduces the least amount of titration error under the conditions evaluated. This is evident even though the average titration errors are identical since the relative average deviation and endpoint uncertainty at the 95% confidence level are both considerably greater for the 10 trials into which scatter in potential was introduced.

In summary, the results of this study support the following conclusions regarding the use of Gran plots for the titrations considered: 1) Although the number of data points used in the Gran plot may be reduced, in comparison to conventional techniques, the points must represent a large (>60%) region of the titration curve prior to the endpoint; 2) Proper attention must be given to the use of a suitably concentrated ISA or the use of a sufficiently concentrated titrant to minimize the error due to variation in activity coefficients caused by dilution; 3) The value of 2.303RT/nF must be known and/or kept constant to considerably better than ±1 to prevent it from being the most important source of titration error; and 4) Since the titrations considered represent optimal titration conditions and since the values of scatter introduced represent rather optimistic estimates of typical experimental errors, considerable caution is warranted when Gran plots are used, rather than conventional techniques, to determine the endpoints of potentiometric titrations.

The conclusions in this work are rigorously applicable only to the specific titration conditions studied. However, the procedures for evaluating titration errors in Gran plots and the computer programs for implementing these procedures may conveniently be used for any other titration conditions. Minor modifications in the program will permit the simulation and error analysis of other types of titrations which require different mathematical expressions for the antilogarithm term in the Gran analysis. Work in this area is currently in progress. In addition, efforts are underway to develop explicit analytical expressions from which titration errors may be computed for Gran plots of various types of titrations.

Literature Cited

1. BAUER, E. L. 1960. A statistical manual for chemists. Academic Press, Inc., New York, N.Y. 156 p.

2. GRAN, G. 1952. Determination of the equivalence point in potentiometric titrations. Part II. The Analyst 11:661-671.

3. BUTLER, J. N. 1964 Ionic equilibrium Addison-Wesley Publ. Co., Inc., Reading, Mass. 547 p.

4. LINGANE, J. J. 1958. Electroanalytical chemistry. (2nd ed.) Interscience Publ. New York, N.Y. 669 p.

5. 1970. Gran's plots and other schemes Newsletter of Orion Res. Inc. 2:11, 12.

6. 1970. More schemes (plot two). Newsletter of Orion Res. Inc. 3:1, 2.

7. SHULTZ, F. A. 1971. Titration errors and curve shapes in potentiometric titrations. Anal. Chem. 43:502-508.