Solution to titration endpoint challenge

Diego A. Ahumada Forigua¹ · Juris Meija²

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This challenge invites us to think about the endpoint estimates in acid-base titration [1]. The purpose of titration is to establish the amount of a substance present in solution by chemically reacting that substance with a standard solution of known concentration. The amount of the substance can then be calculated from the smallest volume of standard solution required to completely deplete the analyte (i.e., to complete the reaction). The measurement model thus incorporates the stoichiometry of the chemical reaction(s) that occur during the titration. One of the trickiest issues with titrimetry is accurately measuring the point when titration is complete; the distinction between the titration endpoint and the equivalence point is crucial and deserves full attention in any titrimetry setup.

In the data obtained from a titration experiment, the independent variable (stimulus) is often the mass or volume of the titrant, and the dependent variable (response) is the measured response quantity. The latter can be, for example, the pH of the system, the electrical current consumed, or the absorbance of

the system. In the case of acid-base titration, neither the endpoint nor the equivalence point is measured. The endpoint is estimated from the data using a variety of methods; opinions vary as to which method is the most accurate. The gap between the endpoint and the stoichiometric point, however small, must also be modeled and evaluated. An example of such an analysis has been published for Mohr's method, which utilizes a physicochemical model of the entire titration process [2]. At a much more practical level, Table 1 summarizes several reasonable options for estimating the titration endpoint and its uncertainty for the titration curve presented in this Challenge [1].

It is clear that there is a 2% spread in the various inflection point estimates, which requires further contemplation by the analyst. In addition, this spread in the endpoint estimates reflects only the influence of the measurement model; it does not incorporate the measurement uncertainty for either the volume or the pH. The uncertainty estimates for the endpoints were evaluated using parametric bootstrap resampling of the data, whereby the uncertainties in the volume and pH measurements were considered to be $u(V) = 0.02$ mL and $u(\text{pH}) = 0.002$, respectively. It is apparent from Table 1 that the uncertainty in the endpoint estimate is significantly influenced by the measurement model applied.

Much like in potentiometric titration, the uncertainty in the endpoint for the visual titration method can be estimated using several approaches. The excess volume due to the pH difference between the equivalence point ($V = 5.00$ mL) and the indicator color change ($V = 5.05$ mL [1]) is $V_{\text{ex}} = 5.05$ mL –

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✉ Diego A. Ahumada Forigua
dahumada@inm.gov.co

¹ Chemical Metrology Division, National Metrology Institute
Colombia, Bogotá, Colombia

² Metrology, National Research Council, Ottawa, Canada

Table 1 A summary of endpoint estimates from a potentiometric titration of potassium hydrogen phthalate (KHP) with NaOH [1]

Measurement model for titration endpoint	Estimation method	Result
Inflection point	First-order derivative (forward method)	5.00 mL ($u = 0.05$ mL)
	First-order derivative (central method)	4.95 mL ($u = 0.06$ mL)
	5P logistic curve fitting [3]	4.92 mL ($u = 0.04$ mL)
	4P logistic curve fitting [3]	4.90 mL ($u = 0.02$ mL)
	Extremum distance estimator [4]	4.88 mL ($u = 0.03$ mL)
Point at pH 7	5P logistic curve fitting [3]	4.94 mL ($u = 0.02$ mL)

The titration curve is a small dataset containing seven data points: $\{V \text{ in mL, pH} \} = \{4.30, 4.104\}, \{4.70, 4.624\}, \{4.85, 5.781\}, \{5.00, 7.681\}, \{5.05, 8.147\}, \{5.20, 8.731\}, \{5.30, 8.844\}$

5.00 mL = 0.05 mL, which leads to an uncertainty of 0.05 mL/ $(2\sqrt{3}) = 0.02$ mL. Similarly, if only the burette resolution (0.05 mL) is considered, one obtains $u(V_{\text{endpoint}}) = 0.05$ mL/ $(2\sqrt{3}) = 0.02$ mL. Both of these uncertainty estimates are comparable with the Eurachem Guide suggestion that $u(V_{\text{endpoint}}) = 0.03$ mL for phenolphthalein titrations [5]. Still, it remains important to distinguish between the endpoint estimate and the equivalence point.

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