

Measurement uncertainty over the concentration range for potentiometric titration of glycine



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Introduction

The measurement uncertainty provides complete information about an analytical result. Without such information, measurement results cannot be compared, either among themselves or with reference values given in a specification or standard.

The value of measurement uncertainty can vary over the measurement range, if the relationship between the value of the uncertainty and the quantity concerned is not known, the dependence can be determined experimentally.

The measurement uncertainty can be expressed as an absolute value (same unit as the measured value) or a relative value (in %) (Eurachem/Citac Guide, 2012). In general, absolute measurement uncertainty can be expected to increase steadily with concentration and relative measurement uncertainty will be high at low analyte concentrations but might be expected to stabilize at high analyte concentrations (JCGM GUM-6, 2020). When the uncertainty varies over the measurement range, it is essential to take into account the changes in the combined standard uncertainty with the level of analyte. The purpose of this study was to estimate the measurement uncertainty over the measurement range as a function of the mass for the potentiometric titration of glycine.

Materials and methods

Reagents, materials and equipment

Glycine (99.0-101.0 %) was obtained from Merck KGaA. Perchloric acid 0.1 M in glacial acetic acid (PCA) volumetric solution (Fisher Chemical) was used for titration (certified concentration: 1.0002 mol/L). Potassium hydrogen phthalate, RV (KHP) purchased from Merck KGaA (100.00 % ± 0.05 %, k = 2, approximately 95 % level of confidence) was used as a primary volumetric standard. The solvents used for the analysis were analytical grade formic acid (FA), and glacial acetic acid (GAA) purchased from Fisher Chemical.

The titration was performed on DL 50 METTLER TOLEDO titrator, equipped with automatic burette with capacity of 10 mL and analytical balance (Sartorius BP221S, d = 0.1 mg).

Standardization of 0.1 M Perchloric acid in glacial acetic acid

The volumetric solution, 0.1 M perchloric acid in glacial acetic acid, was standardized before use according to *European Pharmacopoeia*, 4.2.2, by titration of 0.170 g of potassium hydrogen phthalate, dissolved in 50 mL of anhydrous acetic acid, determining the end point potentiometrically.

The titer of PCA was calculated according to the formula:

$$\text{Titer} = \frac{m_{(\text{KHP})} \cdot P_{(\text{KHP})}}{M_{(\text{KHP})} \cdot V_{(\text{PCA})} \cdot C_{(\text{PCA})}}$$

Potentiometric titration of glycine

The quantitative determination of glycine consists of a non-aqueous titration with potentiometric end-point detection. Ten samples of glycine in the range of 20 % to 90 % of the burette volume (10 mL) were dissolved in 3 ml of anhydrous FA and 30 ml of GAA and titrated with 0.1 M PCA.

Linear regression determined the relationship between the end-point volume (y_0) and the weight of glycine. The fitness for purpose of the regression model was evaluated using numerical parameters such as the coefficient of determination (R^2), the slope (b) and the extrapolated intercept (a). The quantity of glycine (x_i) was obtained with interpolation of the measurement (y_0) through the regression equation.

$$x_i = \frac{y_0 - a}{b}$$

Estimation of uncertainty over the measurement range

Microsoft Excel Spreadsheet Software was applied to estimate the uncertainty (standard error) of the regression ($S_{y/x}$) and uncertainties (random errors) in the values for the slope (S_b) and intercept (S_a). The confidence limits for the slope of the line are given by $b \pm t(n-2)S_b$, where the t-statistic is taken at 95 % confidence interval and (n-2) degrees of freedom. Similarly the confidence limits for the intercept are given by $a \pm t(n-2)S_a$ at 95 % confidence interval.

The standard uncertainty (u_{x_i}) associated with the purity estimate (x_i) was estimated using following equation:

$$u_{x_i} = S_{x_0} = \frac{S_{y/x}}{b} \cdot \sqrt{1 + \frac{1}{n} + \frac{(y_0 - \bar{y})^2}{b^2 \cdot \sum(x_i - \bar{x})^2}}$$

where, is volume from which the value is determined, is the estimated standard deviation, is the slope of the regression line, is the standard error of the regression analysis and is the number of points used in the regression calculations (Miller & Miller 2010). The standard uncertainty was expressed in % as a relative value.

Results and discussion

Standardization of 0.1 M Perchloric acid in glacial acetic acid

The mean value of 1.008 for the titer was obtained from three independent determinations, with relative standard deviation, RSD = 0.05 %.

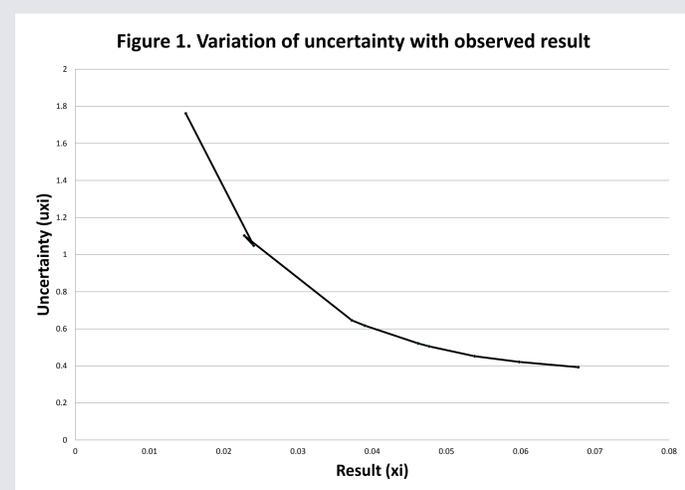
Potentiometric titration of glycine

The relationship between the end-point volume and mass of glycine was expressed by the equation, ($y_0 = 131.4 x_i + 0.0543$), R^2 was 0.9998.

Estimation of uncertainty over the measurement range

The standard error of the regression ($S_{y/x}$) was 0.03 ml, the uncertainty for the slope (S_b) was 131.4 ± 1.4 , the uncertainty for the intercept (S_a) was 0.054 ± 0.059 .

The relative standard uncertainty of the estimate (x_i) was in the range of 1.8 % - 0.4 %. The relative uncertainty was high at low quantities for glycine and decreases as the amount of the substance increases (Figure 1).



The obtained results are in line with the recommendations in the EURACHEM/CITAC guide to use the absolute measurement uncertainty in the low range, while it is appropriate to use a relative measurement uncertainty in the high range (Eurachem/Citac Guide, 2012). Nevertheless, the relative uncertainty is not stabilized, which may lead to overestimating the uncertainty. The Nordtest report TR 537 states that a relative uncertainty is most appropriate for methods applied only in the high measurement range, for titrations and physical methods, it may be appropriate to use an absolute measurement uncertainty in the whole range (Magnusson et al., 2017).

Conclusion

This study showed that the relative standard uncertainty depends on the quantity of the analyte and is higher at low amounts and decreases as the quantity of the substance increases. The relative standard uncertainty was in the range of 1.8 % - 0.4 %.

Even though the relative uncertainty decreases over the measurement range, it is not stabilized, leading to overestimating the uncertainty.

References

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