

Calibration of Glass Electrode in Terms of H⁺ Concentration by Titration of Weak Acid in Cells with and without Liquid Junction

Vladislav Tomišić,* Tamara Gopurenko, Kazimir Majorinc, and Vladimir Simeon

Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia

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Calibration of glass-electrode cells with and without transference in terms of hydrogen ion concentration was performed by potentiometric titrations of aqueous solutions of two weak acids, 2-amino-2-hydroxymethyl-1,3-propanediol hydrochloride, TrisHCl, and potassium hydrogenphthalate, with a strong base (KOH). Cell calibration parameters were computed from the titration data, along with the values of stoichiometric protonation equilibrium constants, by using an iterative optimisation procedure. No significant difference between the E vs. $[H^+]$ responses of the glass-electrode cells with and without liquid junction was observed. For both kinds of cell, the imposed model of linear E vs. $p[H]$ relation proved to be a satisfactory approximation only in the buffer regions of the titration curves. The values of protonation equilibrium constants, expressed as $\lg(K_1^H/\text{dm}^3 \text{ mol}^{-1})$, determined at 25 °C, $I_c = 0.1 \text{ mol dm}^{-3}$ (KNO₃ or KNO₃ + KCl) in the cell with transference (Tris: 8.058, phthal²⁻: 4.933) are in very good agreement with those determined in the cell without transference (Tris: 8.091, phthal²⁻: 4.928), as well as with comparable literature values.

INTRODUCTION

Glass-electrode potentiometry at constant ionic strength is one of the most frequently used experimental techniques for the study of (de)protonation and coordination equilibria in solution, its main advantage being the fact that the 'stoichiometric' $p[H]$,

$$p[H] = -\lg \frac{[H^+]}{\text{mol dm}^{-3}} \quad (1)$$

(unlike the conventional,¹ 'activity' pH) is a well-defined, transparent quantity.

In most $p[H]$ calibration procedures, the electromotivity** of a glass-electrode cell is measured in one or more

solutions containing known concentration(s) of a strong acid (or base), using either titration or batch technique.^{3–8} A Nernst-like linear formula usually serves as calibration model. A popular empirical procedure, proposed by Irving *et al.*,⁹ is based on the assumption that the $pH - p[H]$ difference is constant. An extensive discussion about this procedure can be found in Ref. 10.

The calibration range of the above mentioned methods is rather narrow ($2 < p[H] < 3$ and $10.8 < p[H] < 11.5$, approximately) and, in many instances, there is no overlapping with the $p[H]$ range of interest. In order to shift the calibration range to a more favourable position, several methods based on potentiometric titration of a

* Author to whom correspondence should be addressed. (E-mail: vtomisic@chem.pmf.hr)

** The term electromotivity has recently been proposed to replace the traditional inaccurate phrase "electromotive force" (Ref. 2)

weak acid have been proposed.^{11–13} These procedures require accurate knowledge of protonation equilibrium constants of the weak acid involved. In the so-called internal calibration methods some or all calibration parameters are optimised along with the acid protonation constant(s).^{14–25} Although computationally more complex, such procedures have certain advantages (no separate calibration experiment is needed, the adverse effects of the drift of the glass-electrode potential are largely reduced). In the present paper we use this approach and describe examination of glass-electrode calibration performed by titration of two weak acids of different strengths, *viz.* 2-amino-2-hydroxymethyl-1,3-propanediol (Tris) hydrochloride and potassium hydrogenphthalate, KHPhtal. We have particularly focussed our interest on comparing the results obtained by the commonly used combination glass electrode with those by the glass-electrode cell without transference having an external reference electrode. We have also qualitatively examined the influence of the titrand solution buffer capacity on the calculated calibration parameters and protonation constants.

EXPERIMENTAL

Chemicals

Analytical reagent grade chemicals were dried to constant mass and then used without further purification. "Carbonate-free" water was used as solvent throughout. It was prepared by boiling bidistilled water and then cooling it under a stream of argon. Whenever necessary, the solutions were additionally deaerated by bubbling through previously equilibrated argon gas.

Potentiometric titrations

Electromotivities were measured (to ± 0.1 mV) by means of a Metrohm 731 pH meter; Mettler Toledo (DG 111-SC) and Metrohm (6.0238.000) combination glass/reference electrodes were used.

Potentiometric titrations were first performed in a glass-electrode cell without transference, *i.e.* by using an external reference electrode:

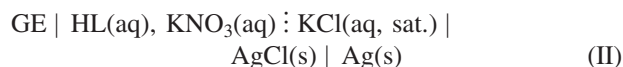


GE standing for the glass electrode, *i.e.* $\text{Ag}(\text{s}) \mid \text{AgCl}(\text{s}) \mid \text{H}^+(\text{aq}), \text{Cl}^-(\text{aq}), \dots \mid \text{glass membrane} \mid$, and HL for weak acid (HTris^+ or Hphthal^-).

The cell solution (initial volume: 30 cm^3) contained HL (*ca.* $0.005 \text{ mol dm}^{-3}$) and the "supporting electrolyte", *viz.* KNO_3 ($0.095 \text{ mol dm}^{-3}$) + KCl ($0.005 \text{ mol dm}^{-3}$). In this way the constancy of the reference electrode potential was ensured and the ionic strength was kept approximately constant at 0.1 mol dm^{-3} . The titrant, carbonate-free aq. KOH (*ca.* 0.1 mol dm^{-3}) + KCl ($0.005 \text{ mol dm}^{-3}$) – standardised against KHPhtal primary titrimetric standard – was delivered from a Metrohm Dosimat unit (precision *ca.* $\pm 1 \text{ mm}^3$).

The titrand solution was held under an argon atmosphere and thermostatted at $(25.0 \pm 0.1) ^\circ\text{C}$.

In order to match more closely the conditions in routine determinations of ligand protonation and complex stability constants, analogous experiments were performed in a cell *with* transference (by using the in-built reference half-cell):



As the solution in cell (II) did not contain KCl , concentration of KNO_3 was 0.1 mol dm^{-3} . A slight difference in the compositions of supporting electrolytes in cells (I) and (II) could be neglected.

THEORETICAL

Response of glass-electrode half-cell

The electromotivity (E) of cell (I) depends on several factors, some of which (potentials of internal and external reference electrodes, potential difference on the inner solution/glass interface) are virtually constant and the slowly drifting asymmetry potential can be taken to be approximately constant within the duration of a titration experiment. Therefore, the electromotivity response of cell (I) to changes in $[\text{H}^+]$ can be approximated by a two-parameter formula:

$$E = E'_0 + s \cdot \lg([\text{H}^+] / c^\ominus) + s \cdot \lg \bar{\gamma} \quad (2)$$

where $c^\ominus = 1 \text{ mol dm}^{-3}$, $\bar{\gamma}$ is the effective activity coefficient, being dependent on the kinds and concentrations of all ionic species in the solution, E'_0 is a constant, and the slope s is defined as

$$s = \partial E / \partial \text{p}[\text{H}] = \alpha RT \cdot \ln 10 / F \quad (3)$$

α is an empirical factor, sometimes called electromotive efficiency.

Since the titrand contained a constant concentration (0.1 mol dm^{-3}) of inert strong electrolyte and total HL concentration did not exceed $0.005 \text{ mol dm}^{-3}$, the change in total ionic strength during titration could not exceed $0.005 \text{ mol dm}^{-3}$. Thus, the corresponding change in the activity coefficients, (over)estimated by using the Debye-Hückel limiting law, was less than 1 per cent, corresponding to the actual change of electromotivity less than 0.24 mV . Therefore, Eq. (2) reduces to:

$$E = E_0 - s \cdot \text{p}[\text{H}] \quad (4)$$

The electromotivity of cell (II) contains an additional term, the liquid-junction potential, E_j . The change in E_j on the titrand $\mid \text{KCl}(\text{aq, satd.})$ junction can be roughly estimated from the approximate figures computed by Bates:²⁶ In the solution containing HCl (0.01 mol dm^{-3})

+ KCl (0.09 mol dm⁻³), $E_j = 2.1$ mV; by neutralising this solution with KOH ($p[H] \approx 7$), a KCl solution (≈ 0.01 mol dm⁻³) is obtained and E_j will change to 1.8 mV, *i.e.* by 0.3 mV, corresponding to $\Delta p[H] \approx 0.005$. Since the $p[H]$ range of interest here is approximately $3 < p[H] < 11$, E_j is expected to be safely included into the calibration parameter E_0 (*i.e.* it is not necessary to include the additional terms concerning the liquid-junction potential into the calibration formula).

The parameters of Eq. (4) can be computed from the experimental data ($p[H]$, E) by the weighted linear least-squares method. Statistical weights are defined as follows (see *e.g.* Ref. 27):

$$\frac{1}{w_i} = (\delta E)^2 + \left(\frac{\Delta E}{\Delta V} \right)_i^2 \cdot (\delta V)^2 \quad (5)$$

δE and δV are estimated potentiometric and volumetric uncertainties (here ± 0.1 mV and ± 1 mm³, respectively), while $(\Delta E / \Delta V)_i$ is an estimate of the slope of titration curve at i -th data point.

Computation of $[H^+]$

Stoichiometric protonation constant of L(aq) is defined as*

$$K_1^H = \frac{[HL]}{[H][L]} \quad (6)$$

and the degree of protonation as

$$\bar{N}_H = \frac{[HL]}{[L]+[HL]} = \frac{K_1^H \cdot [H]}{1+K_1^H \cdot [H]} \quad (7)$$

it is easy to show that

$$\frac{K_1^H \cdot [H]}{1+K_1^H \cdot [H]} = \frac{(n_{HX} + n_{HL} - n_{MOH}) / V - [H] + K_w / [H]}{[L] + [HL]} \quad (8)$$

n_{HX} , n_{HL} and n_{MOH} denote the added amounts of strong acid (if any), weak acid and strong base, respectively, V is the total volume of cell solution. The value of $K_w = [H][OH] = 10^{-13.778}$ mol² dm⁻⁶, determined by Jameson and Wilson²⁸ for KNO₃(aq, 0.1 mol dm⁻³) at 25 °C, was used in computations. Provided K_1^H is known, Eq. (8) can be solved numerically for $[H]$.

The three calibration parameters, E_0 , s and K_1^H , were computed from titration data by using the following iterative algorithm:

Given: n_{HX} , n_{HL} (scalars),
 δE , δV (scalars),
 $n_{MOH} = \{n_{MOH}(1), n_{MOH}(2), n_{MOH}(3), \dots, n_{MOH}(N)\}$ (vector),

$E = \{E(1), E(2), E(3), \dots, E(N)\}$ (vector),
 δ (tolerance for comparing K_1^H estimates);

Step 1. Define search interval,

$$I = [x_0 = (K_1^H)_{\min}, x_m = (K_1^H)_{\max}];$$

Step 2. Divide I into m equal subintervals:

$$x = \{x_0, \dots, x_i, \dots, x_m\};$$

Step 3. For $i = 0, m$:

Solve (numerically) **Eq. (8)** for: $\{[H](1,i), [H](2,i), [H](3,i), \dots, [H](N,i)\}$,

Compute **Eq. (1)** $p_{[H]}(i) = \{p[H](1,i),$

$$p[H](2,i), p[H](3,i), \dots, p[H](N,i)\},$$

Compute $w(i)$ (**Eq. (5)**),

WLR of E vs. $p_{[H]}(i)$ (**Eq. (4)**) yielding $E_0(i), s(i), R^2(i)$;

Step 4. Find maximum R^2 ;

Step 5. If $I < \delta$ Then

Compute final values of $E_0, s, K_1^H, R^2, \varepsilon, \varepsilon_{\text{rms}}$,
 Else

Define a narrower search interval,

GoTo **Step 2**;

End.

Legend:

i subinterval counter: $i = 0, 1, 2, \dots, m$

N number of data points

$p_{[H]}$ vector of $p[H]$ values: $p_{[H]} = \{p[H](1), p[H](2), p[H](3), \dots, p[H](N)\}$

R^2 coefficient of determination

w vector of statistical weights

WLR weighted linear regression

ε vector of residuals: $\varepsilon = E - (E_0 - s \cdot p_{[H]})$

RESULTS AND DISCUSSION

The calibration parameters (E_0 and s) of the glass-electrode cells (with transference and without it) determined by processing the data of several potentiometric titrations with the simple iterative algorithm described above, as well as the calculated stoichiometric protonation constants of Tris and phthal²⁻, are given in Tables I and II. It must be pointed out that these results were obtained by taking into account only the data in the buffer regions of the titration curves, *i.e.* in the ranges of, approximately, $p[H] = \lg(K_1^H / \text{dm}^3 \text{mol}^{-1}) \pm 1$ and $10.8 < p[H] < 11.3$ (Figures 1 and 2). When the rest of the titration points were included (particularly the data near the inflection point), the assumed linear $p[H]$ response of electromotivity was not obtained (Figures 1 and 2) and, moreover, the calculated electrode parameters and protonation constants were considerably different from the reasonably expected values. Obvious systematic deviations from the linear model can

* Charge numbers are omitted for simplicity.

TABLE I. Concentration calibration of a glass-electrode cell without liquid junction: protonation equilibrium constants of Tris and phthalate(2-) ($t = 25\text{ }^\circ\text{C}$, $I = 0.1\text{ mol dm}^{-3}$, $\text{KNO}_3 + \text{KCl}$) and cell calibration parameters

Base	$\lg(K_1^{\text{H}} / \text{dm}^3 \text{ mol}^{-1})$	$-s$ (SE) ^(a) / mV	E_0 (SE) ^(a) / mV	ε_{rms} / mV
Tris	8.086	57.57(4)	228.7(4)	0.48
	8.093	57.67(4)	233.5(3)	0.40
	8.092	58.85(2)	236.9(2)	0.23
	8.093	58.81(1)	236.1(1)	0.15
	8.091	± 0.005 ^(b)		
phthal ²⁻	4.926	58.79(2)	235.9(2)	0.33
	4.947	58.45(3)	237.2(2)	0.51
	4.912	58.46(3)	235.4(2)	0.52
	4.928	± 0.044 ^(b)		

^(a) standard error in units of last decimal place

^(b) $\pm 95\%$ confidence limits

TABLE II. Concentration calibration of a glass-electrode cell with liquid junction: protonation equilibrium constants of Tris and phthalate(2-) ($t = 25\text{ }^\circ\text{C}$, $I = 0.1\text{ mol dm}^{-3}$, KNO_3) and cell calibration parameters

Base	$\lg(K_1^{\text{H}} / \text{dm}^3 \text{ mol}^{-1})$	$-s$ (SE) ^(a) / mV	E_0 (SE) ^(a) / mV	ε_{rms} / mV
Tris	8.074	58.46(4)	397.5(4)	0.41
	8.055	58.39(3)	394.3(3)	0.37
	8.052	58.31(3)	394.5(3)	0.36
	8.049	58.20(4)	392.7(4)	0.43
	8.058	± 0.018 ^(b)		
phthal ²⁻	4.941	58.95(3)	393.9(2)	0.46
	4.958	59.01(3)	393.9(2)	0.48
	4.917	58.79(2)	390.2(2)	0.37
	4.914	58.68(3)	389.0(2)	0.48
	4.933	± 0.033 ^(b)		

^(a) standard error in units of last decimal place

^(b) $\pm 95\%$ confidence limits

be clearly seen from the residual plots in Figures 3b and 4b (only one example for each weak acid is shown, the patterns obtained in all other titrations being similar). It should be mentioned that the model was even less appropriate when a lower concentration (0.001 mol dm^{-3}), and consequently a lower buffer capacity ($dc/dp[\text{H}]$, c denotes the added titrant concentration), of the weak acid solution was used in titration (data not shown). A non-random, systematic trend of residuals was observed

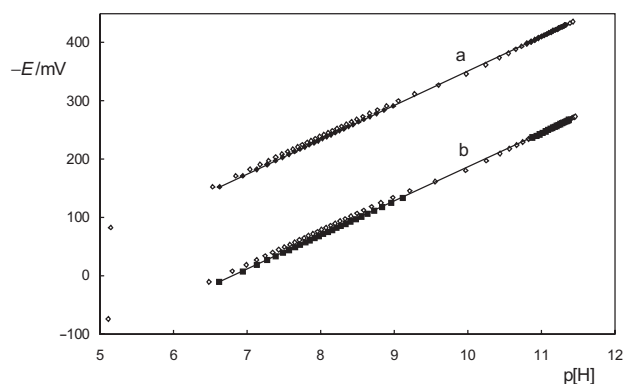


Figure 1. Calibration of glass-electrode cells with (a) and without (b) transference by titration of $\text{TrisHCl}(\text{aq})$ with $\text{KOH}(\text{aq})$. $p[\text{H}]$ values calculated by taking into account the whole data body (\diamond); $p[\text{H}]$ values calculated by considering only the buffer regions of the titration curve (\blacksquare).

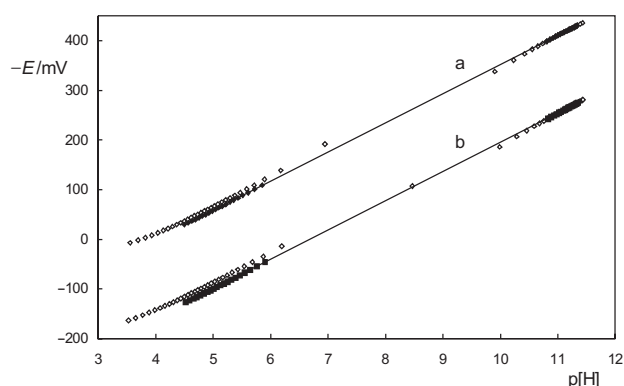


Figure 2. Calibration of glass-electrode cells with (a) and without (b) transference by titration of $\text{KHphthal}(\text{aq})$ with $\text{KOH}(\text{aq})$. $p[\text{H}]$ values calculated by taking into account the whole data body (\diamond); $p[\text{H}]$ values calculated by considering only the buffer regions of the titration curve (\blacksquare).

even when computations were done without taking into account the data corresponding to the steeper parts of the titration curves (low buffer capacity of the solutions and greater experimental error), as shown in Figures 3a and 4a. The exact reasons for deviation from linearity remain unclear, but from the practical point of view this is of no great importance as in that case the values of residuals (expressed as $\Delta p[\text{H}]$ in Figures 3 and 4) are mainly comparable with the expected uncertainties of potentiometric pH measurements.

No significant difference between the $p[\text{H}]$ responses of the glass-electrode cells with and without transference was observed. The differences in the E_0 values in Tables I and II were mainly due to the different potentials of the reference electrodes in cells (I) and (II). Both cells showed rather satisfactory E vs. $p[\text{H}]$ linearity in almost identical regions where the buffer capacity of the titrand solutions was sufficiently high (Figures 1 and 2). Therefore, a possible influence of the change in the liquid-junction potential during titration in cell (II) can be ruled out. A

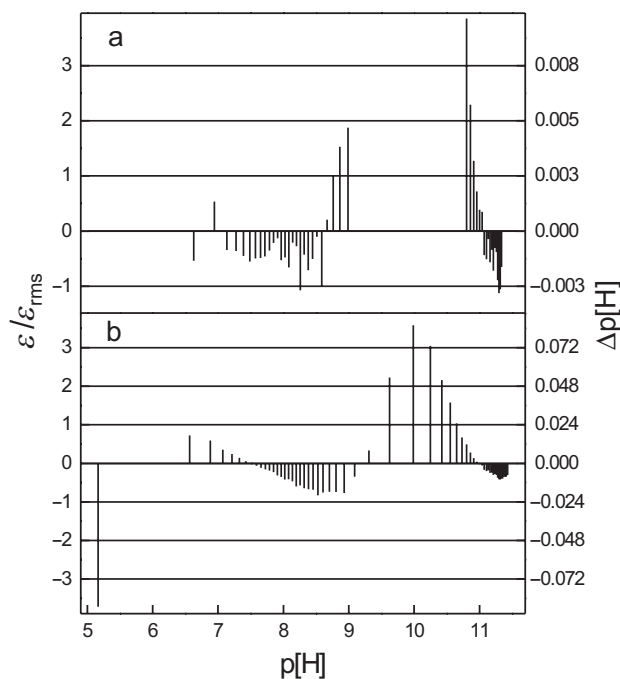


Figure 3. Pattern of residuals in potentiometric titrations of TrisHCl with aq. KOH, expressed relative to root-mean-square error (left ordinate axis) and corresponding p[H] deviations (right ordinate axis): results based upon data in buffer regions (a) and on whole data body (b).

similar conclusion has been made recently by Brandariz *et al.*⁸ who compared glass-electrode calibrations performed by strong acid/strong base titration or by adding strong acid to an inert electrolyte solution in cells with and without liquid junction.

The average values $\lg(K_1^H/\text{dm}^3 \text{ mol}^{-1}) = 8.091$ (cell I) and 8.058 (cell II) determined in this work for Tris (Tables I and II) are in rather good agreement with those determined previously under the same conditions ($t = 25$ °C; $I_c = 0.1 \text{ mol dm}^{-3}$, KNO_3), e.g. 8.09 (Ref. 29) and 8.13 (Ref. 30). The same holds for the case of phthal²⁻ where the values $\lg(K_1^H/\text{dm}^3 \text{ mol}^{-1}) = 4.928$ (cell I) and 4.933 (cell II) are quite close to the literature values of 4.92 (Ref. 31) and 4.88 (Ref. 32). As can be noticed, there is also a good agreement between the protonation constants of Tris and phthal²⁻ determined by means of glass-electrode cells with and without liquid junction.

CONCLUSION

As mentioned in the Introduction, several computational approaches based on the nonlinear regression analysis were proposed in the literature for the estimation of the glass-electrode calibration parameters from the weak acid/strong base titration (e.g. MAGEC¹⁶ and ESAB¹⁸ programs). In all of these procedures, linear dependence of electromotivity on p[H] was assumed. A specific feature of our

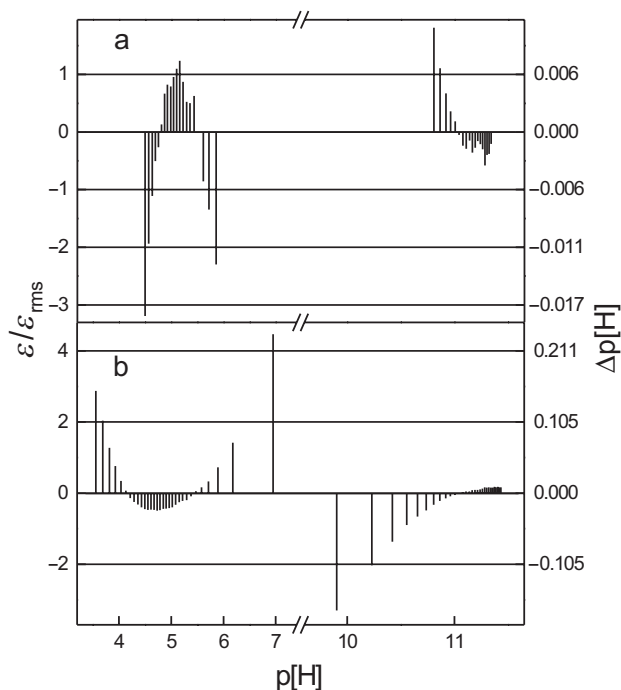


Figure 4. Pattern of residuals in potentiometric titrations of KHphthal with aq. KOH, expressed relative to root-mean-square error (left ordinate axis) and corresponding p[H] deviations (right ordinate axis): results based upon data in buffer regions (a) and on whole data body (b).

program is the explicit maximization of the E vs. p[H] correlation coefficient. This provides a straight-forward criterion for checking of the calibration model validity and, consequently, of the reliability of the corresponding parameters estimates.

Comparison of the results of glass-electrode calibration in cells with and without transference has shown that a simple calibration line (Eq. (4)) is a model equally adequate for both cells. Therefore, there is no need to include the terms concerning the liquid junction potential in the calibration equation for the cell with transference. However, the validity of linear E vs. p[H] calibration model depends rather strongly on the buffer capacity of the titrand (weak acid) solution. The model is appropriate only if the buffer capacity is sufficiently high, *i.e.* in the buffer regions of the titration curve.

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SAŽETAK

Koncentracijska kalibracija staklene elektrode titracijom slabe kiseline u člancima s prijenosom i bez prijenosa

Vladislav Tomišić, Tamara Gopurenko, Kazimir Majorinc i Vladimir Simeon

Koncentracijska kalibracija staklene elektrode u člancima s prijenosom i bez prijenosa izvedena je potencimetrijskim titracijama vodenih otopina dviju slabih kiselina, 2-amino-2-hidroksimetil-1,3-propandiol-hidroklorida, TrisHCl, i kalijeve hidrogenftalata, KHphthal, s jakom bazom (KOH). Kalibracijski parametri članaka, kao i protonacijske konstante uporabljenih kiselina, izračunani su iz titracijskih podataka s pomoću iterativnog optimizacijskog algoritma. Opažena je vrlo slična ovisnost elektromotivnosti o koncentraciji iona H⁺ u oba članka, a modelna pretpostavka o linearnoj relaciji E vs. $p[H]$ pokazala se dobrom aproksimacijom samo u puferskim područjima titracijskih krivulja. Vrijednosti protonacijskih ravnotežnih konstanti (izražene kao $\lg(K_1^H/\text{dm}^3 \text{ mol}^{-1})$) određene pri 25 °C, $I_c = 0,1 \text{ mol dm}^{-3}$ (KNO₃ ili KNO₃ + KC1), s pomoću članka s prijenosom (Tris: 8,058, phthal²⁻: 4,933) vrlo su bliske onima određenima u članku bez prijenosa (Tris: 8,091, phthal²⁻: 4,928), a također se dobro slažu i s usporedivim literaturnim podatcima.