Waldemar Gottardi · Jörg Pfeleiderer

Redox-iodometry: a new potentiometric method

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We apologize to the reader that this paper contains a number of printing errors. The corrections are listed below according to the pages on which they occurred.

Page 1329, Algorithm 1

$$\begin{aligned} \Phi &= 2 \quad \Psi = 1 \\ \Phi &= 5 \quad \Psi = 3 \\ \Phi &= 4 \quad \Psi = 2 \\ \Phi &= 1 \quad \Psi = 1/2 \\ \Phi &= 0 \quad \Psi = 1 \end{aligned}$$

Equation (9)

$$c(\text{I}_2)_2 = \Psi c(\text{Ox}) \quad (9)$$

Equation (10)

$$c(\text{I}^-)_2 = c(\text{I}^-)_1 - \Phi c(\text{Ox}) \quad (10)$$

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Equation (15)

$$c(\text{I}_2)_2 = \Omega c(\text{I}_2)_1 \quad (15)$$

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W. Gottardi (✉)
Institute of Hygiene and Social Medicine,
Innsbruck Medical University,
6010 Innsbruck, Austria
e-mail: waldemar.gottardi@uibk.ac.at

J. Pfeleiderer
Institute for Astrophysics, University of Innsbruck,
6010 Innsbruck, Austria

Equation (16)

$$c(\text{I}^-)_2 = \Omega c(\text{I}^-)_1 + \Delta \quad (16)$$

Calibration (*Algorithm 3*)

The potential actually measured comprises the potential E_{red} of the redox reaction $\text{I}_2 + 2\text{e}^- \leftrightarrow 2\text{I}^-$, the potential of the reference electrode (E_{ref}), and its liquid junction potential (E_{j}):

$$E_{\text{meas}} = E_{\text{red}} - E_{\text{ref}} - E_{\text{j}}$$

E_{red} is clearly defined, for a chosen temperature, by the Nernst equation

$$E_{\text{red}} = E_{0, \text{I}_2/\text{I}^-} - S \log \left([\text{I}^-]^2 f^2 / [\text{I}_2] \right) \quad (17)$$

where $E_{0, \text{I}_2/\text{I}^-} = 622.4 \text{ mV}$, $S = 29.58 \text{ mV/decade}$ at 25°C , and f is the activity coefficient. E_{ref} and E_{j} , however, are also influenced by the concentration of the salt bridge, and they are generally not known exactly.

From the expressions for the measured and calculated redox-potentials of the standardizing solution

$$\begin{aligned} E_{\text{meas}} &= E_{0, \text{I}_2/\text{I}^-} - S \log \left([\text{I}^-]^2 f^2 / [\text{I}_2] \right) - E_{\text{ref}} - E_{\text{j}} \\ E_{\text{calc}} &= E_{0, \text{I}_2/\text{I}^-} - S \log \left([\text{I}^-]^2 f^2 / [\text{I}_2] \right) \end{aligned}$$

it follows easily that the sum of the unknown potentials comes to

$$E_{\text{ref}} + E_{\text{j}} = E_{\text{calc}} - E_{\text{meas}}$$

which yields the standard value

$$E_0^* = E_{\text{meas}} + S \log (y^2/x) \quad (18)$$

where $[I^-]$ and $[I_2]$ are the equilibrium concentrations calculated with *Algorithm 3* (see “Supporting Information”). Since the measurements are performed at a high, nearly constant ionic strength (see below), the activity coefficient can be waived.

Page 1332, Statistics

Calculations and graphs were done with GraphPad PRISM Version 4.00. The SD of the crucial difference $\Delta E = E_0^* - E$ (see constant A in “Supporting Information”, Algorithm 2) was calculated with $SD_{\Delta E} = (SD_{E_0^*}^2 + SD_E^2)^{0.5}$. The levels of significance (*t*-test) were calculated with a TI-58-59 calculator fitted with Applied Statistics Modul-2.

Page 1335, second to last line under a) should read

Calculations [5] show that at the conditions of Procedure B at pH 6.6, the relative equilibrium concentration of HOI comes to 0.014% of the total oxidation capacity ($c(\text{Ox}) \leq 10^{-4}$ M), while it is <0.05% with Procedure A at pH 8.3 ($c(\text{Ox}) \leq 0.01$ M).

Page 1336, last line under a) should read

... expected at pH < 8.4

Legend to Fig. 3 should read

Fig. 3 Calculated redox-potentials [5] of decimal dilutions of 0.01 M I_2 with addition of zero (○) 0.001 (□), 0.01 (△), and 0.1 M KI (◇) at pH 4; dotted line indicates theoretical slope (29.58 mV/decade)

Page 1337, Supporting information

Equation (19)

$$\begin{aligned} & y^2 [\Phi + (\Phi + \Psi)K_3y] \\ & + y^5 K_3 [(2\Phi + \Psi)K_5 + 2(\Phi + \Psi)K_3K_6y] / A \\ & - \Psi A (C - y) \\ & = 0 \end{aligned} \quad (19)$$

Page 1338. *Algorithm 3* should correctly read

Algorithm 3: The mass balances Eqs. 7 and 8 and the mass-law expressions Eq. 4–6 were transformed by the substitution to the polynomial Eq. 20

$$C - xR - x^2(M - xQ - x^2N + x^3T) = 0 \quad (20)$$

where

$$\begin{aligned} C &= \Psi * c(\text{Ox}), \quad D = c(I^-) - \Phi * c(\text{Ox}), \\ B &= C - D, \quad R = 1 - BK_3, \quad T = -(K_5K_3)^2, \end{aligned}$$

$$\begin{aligned} M &= K_3 \{ 2[DK_5 + B^2K_6K_3] + 1 \}, \\ N &= K_3^2 [K_5^2(2D - C) + K_5 - 2K_6], \end{aligned}$$

and $Q = BK_3^2(4K_6 - K_5)$

The root of Eq. 20 i.e. $x = [I_2]$ was found by iteration. The second equation

$$y = [I^-] = (x - B) / (1 - K_5K_3x^2)$$

is then easily solved.