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Multiple-Point Calibration with Linear Regression as a Proposed Standardization Procedure for High-Precision pH Measurements

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Multiple-point calibration with linear regression is proposed as a standardization procedure for measuring pH values with high precision. Contrary to the bracketing procedure recommended by IUPAC, which uses two standard buffer solutions for the standardization of cells with glass electrodes and thus introduces uncertainties with the possibility of choosing different pairs of buffer solutions, the proposed method is based on a calibration function obtained by linear regression of several $E(S)/pH(S)$ couples and yields only one $pH(X)$ value for each solution if the standard buffers and their number are fixed. Besides, the method yields residual liquid junction potentials, i.e., deviations, $\Delta pH(S)$, of measured $pH(S)$ from the calibration line, and the internal consistency of the calibration by the average of the $\Delta pH(S)$ and allows one to choose the best suited liquid junction device. The experiments resulted in slightly different $pH(X)$ but an equally high precision of the $pH(X)$ values, independent of whether they were based on the NIST or BSI standard scale. It is recommended that the method is used together with the NIST scale, which adds a thermodynamic meaning to the calibration function. The multiple-point calibration procedure with linear regression thus eliminates the problem of overdefinition caused by both the bracketing procedure and the NIST scale and yields high-precision $pH(X)$ values with maximum thermodynamic meaning if applied with the multiprimary standard scale according to NIST.

1. INTRODUCTION

The standardization of pH measurements has not been solved sufficiently in the past. Thus, the operational definition of pH allows the application of various standard pH scales, and in fact, two different scales are recommended simultaneously by IUPAC:[1] the multiprimary standard scale according to NIST[2,3] emphasizing thermodynamic meaning rather than highest precision of the standard pH(S) values and the single-primary standard scale by BSI[4,5] stressing

precision rather than thermodynamic meaning. Two pH values can be obtained for an unknown solution, depending on which scale is chosen as the basis. For most practical pH measurements, the differences can be neglected; they are, however, significant when high-precision pH values with $\Delta pH \leq \pm 0.01$ are required.

A further uncertainty arises from the standardization of pH measurements with practical cells containing glass electrodes according to IUPAC,[1] which employs two standard buffer solutions because of the imperfect slope of these cells.[1,6] With this so-called bracketing procedure the unknown pH(X) is bracketed by a higher and a lower standard pH(S) value. Since different standard buffer solutions can be chosen for this purpose, the procedure also results in more than one pH(X) value for an unknown solution, independent of whether the NIST or the BSI scale is chosen, if a practical, undefined, liquid junction device is used.

It is proposed in this paper to replace the bracketing procedure by a multiple-point calibration with linear regression if high-precision pH measurements are to be conducted. This standardization method was first reported in 1975,[7] is recommended by DIN for measuring pH with highest precision,[8] was studied in detail,[9] and has been applied for quality assurance at Merck since 1975.[10] Linear regression of several, instead of two, $E(S)/pH(S)$ couples results in only one pH(X) for each unknown solution if the number and kind of buffers are fixed, yields residual liquid junction potentials, i.e., deviations $\Delta pH(S)$ of the pH(S) values from the regression line, for each standard buffer applied, informs about the internal consistency of each calibration function by the average, $\Delta pH(S)_{av}$, of all $\Delta pH(S)$, and allows the selection of the best suited liquid junction device. Besides, it was found experimentally that pH(X) values of unknown solutions based on NIST and BSI standard buffers are equally precise. The use of the NIST standard scale with the multiple-point calibration procedure is thus recommended since it offers a thermodynamic meaning of the calibration function.[2,3] Multiple-point calibration with linear regression thus eliminates the problem of overdefinition caused by the NIST scale as well as the bracketing procedure and yields high-precision pH values with maximum possible thermodynamic meaning if applied on the basis of the multiprimary standard scale according to NIST.

† Chairman, DIN Committee Technical pH Measurements.
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(10) Naumann, R. Unpublished results, Merck, Darmstadt, Germany.

2. THE CONCEPT OF PH: CURRENT STATUS

Definition of pH. Difficulties encountered in the determination of pH are closely related to the concept of pH, which is not based on straightforward thermodynamics but, according to its notional definition,[1,11] eq 1, involves a single ion

$$pH = -\log(a_H/m^\circ) = -\log(m_H\gamma_H/m^\circ) \tag{1}$$

activity, which, in principle, is immeasurable. Since the hydrogen ion activity, on the other hand, is indicated by the Pt, H_2 electrode in a thermodynamically correct way, pH can be measured by means of electrochemical cells, and the operational definition was introduced on the basis of cell I,

ref el/KCl ($m \geq 3.5$ mol kg^{-1})//soln, pH(S or X)/Pt, H_2 (I)

by

$$pH(X) = pH(S) - (E(X) - E(S))/(RT/F) \ln 10 \tag{2}$$

referring the unknown pH(X) to the pH(S) of an accepted standard by the difference of $E(X)$ and $E(S)$ measured when cell I contains the unknown and the standard solutions, respectively. This notion of the relative hydrogen ion activity involves the assumption that, except for the potential ϵ_H of the a_H-indicating Pt, H_2 electrode, any contributions to the overall emf of cell I do not change with pH. This, however, is not exactly true since the emfs, E, of cells with transference such as cell I contain liquid junction potentials ϵ_j, eq 3, where

$$E = \epsilon_H - \epsilon_R + \epsilon_j \tag{3}$$

ϵ_R is the potential of the reference electrode. This means that the difference pH(X) – pH(S) in cell I is a measure of the relative hydrogen ion activity only if the liquid junction potential ϵ_j at the boundary KCl//X exactly matches that at the boundary KCl//S, which, in the majority of practical pH measurements, is not the case.

pH Scales. In order to complete the operational definition, standard pH values, pH(S), must be assigned, at each temperature, to one or more buffer solutions designated as standard reference solutions. According to the approach of the National Institute of Standards and Technology (NIST),[2,3] suitable buffer solutions are measured in cells without transference,

Ag/AgCl(s), std buffer, pH(S), Cl$^-$(m_{Cl})/Pt, H_2 (II)

whose emf is given by the potentials of the Pt, H_2 electrode, ϵ_H, and the reference electrode, ϵ_R, respectively, eq 4, and in

$$E = \epsilon_H - \epsilon_R \tag{4}$$

which uncertainties due to liquid junction potentials are excluded. The cell emfs yield the acidity function, eq 5, where

$$p(a_H\gamma_{Cl}) = (E^\circ - E)/(RT/F) \ln 10 + \log(m_{Cl}/m^\circ) \tag{5}$$

m_{Cl} is the molality of added chloride and E° is the standard emf of cells II and III,

Pt, H_2/HCl (0.01 mol kg^{-1}), AgCl(s)/Ag   (III)

After an extrapolation of p($a_H\gamma_{Cl}$) to $m_{Cl} \rightarrow 0$, which yields the limiting value p($a_H\gamma_{Cl}$)$^\circ$, pa_H is obtained from eq 6, by

$$pa_H = p(a_H\gamma_{Cl})^\circ + \log \gamma_{Cl} \tag{6}$$

assigning a numerical value to the single activity coefficient γ_{Cl} on the basis of the so-called Bates–Guggenheim conven-

tion, which is a quasi-thermodynamic approach, and pH(S) is defined as pH(S) $\equiv$ pa_H.[11,12] Although pH(S) values thus obtained are not defined in a purely thermodynamic way, they are as close to true thermodynamic values as possible at the present state of solution theory. A detailed discussion is given elsewhere.[3]

pH(S) values were assigned independently to seven primary and two secondary standard reference solutions, which constitute the multiple-standard pH scale of NIST.[2,3,11,12] When these solutions are measured in the operational cell (I) with transference, small inconsistencies in the E vs pH function due to ϵ_j are found. They are the so-called residual liquid junction potential errors,[2,3] which limit the accuracy of pH measurements based on these standard buffers.

Strictly sticking to the operational definition of pH (eq 2) the British Standards Institution (BSI) chose a different approach to establish standard pH values.[4,5] Only one reference solution, i.e., 0.05 mol kg^{-1} potassium hydrogen phthalate, also applied by NIST, is measured independently in cell II without transference. Its pH is also assigned according to the Bates–Guggenheim convention, and it is designated pH(RVS) where RVS stands for reference value standard.[1] This buffer is the basis of the single-standard scale by BSI. Further standard solutions are derived by measuring emfs of cell I with transference employing a free diffusion liquid junction within a 1-mm-diameter capillary. They are called operational standards (OS),[1] whose pH values, pH(OS), are assigned by comparing with pH(RVS) on the basis of eq 2. Their number is unlimited. Since pH(OS) are determined in the operational cell (I), the E vs pH(OS) function has a perfect internal consistency. The assigned pH(OS) values, however, contain a contribution from ϵ_j, which is, in principle, unknown. pH values determined on the basis of these standard buffer solutions should thus exhibit a better reproducibility, although at the expense of their thermodynamic interpretation.

The different approaches are mutually exclusive. The primary notion of the NIST scale is to endow pH values with as much thermodynamic meaning as possible and to obtain information on the accuracy of the measurements rather than highest precision. The British scale follows the opposite philosophy by treating pH values as mere numbers without a thermodynamic meaning but with a high precision. The debate about the two scales has been going on for more than 15 years without reaching an agreement, as the simultaneous recommendation of both scales by IUPAC[1] is neither an agreement nor a harmonization but a rather unfortunate decision, which supplies two pH values, for the same standard buffer solution, which differ by up to as much as $\Delta pH = 0.02$.

Practical pH Measurements. Practical pH measurements are usually carried out in cells with glass electrodes,[1,8] e.g., in cell IV,

ref el/KCl ($m \geq 3.5$ mol kg^{-1})//soln, pH(S or X)/glass el   (IV)

Since these cells exhibit imperfect slopes, the pH cannot be calculated according to the operational definition (eq 2). For the determination of an unknown pH, the so-called bracketing procedure is recommended by IUPAC.[1] Two standard buffer solutions with pH(S) or pH(OS) values, respectively, bracketing the unknown pH(X) but not specified otherwise are used for the cell calibration, and pH(X) is calculated by

$$pH(X) = pH(S_1) - (E(X) - E(S_1))/k' \tag{7}$$

(11) Bates, R. G. *Determination of pH. Theory and Practice*, 2nd ed.; Wiley: New York, 1973.

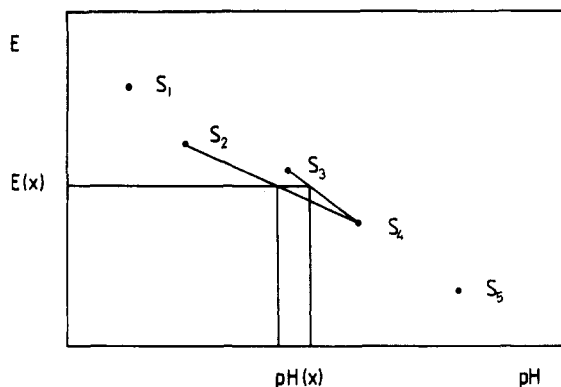(12) Bates, R. G. *J. Res. Natl. Bur. Stand.* **1962**, *66A*, 2, 179–183.

Figure 1. Determination of an unknown pH(X) by the bracketing procedure recommended by IUPAC[1] using standard buffer solutions (S) of the multistandard scale according to NIST.
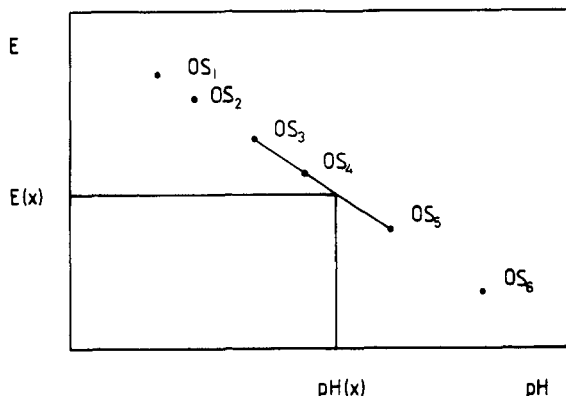

Figure 2. Determination of an unknown pH(X) by the bracketing procedure recommended by IUPAC[1] using operational standard buffer solutions (OS) of the single-standard scale according to BSI provided the free liquid junction device according to Covington[4] is applied.

where k' is the practical slope of the E vs pH function,

$$k' = |(E(S_2) - E(S_1))/(pH(S_2) - pH(S_1))| \qquad (8)$$

The effect of using the bracketing procedure is shown in Figures 1 and 2 for the NIST and the BSI scales, respectively. Because of the residual liquid junction potential error, pH-(X) based on the NIST scale depends somewhat on the choice of the pH(S) values used (Figure 1), whereas pH(X) based on the BSI scale is independent of the pH(OS) chosen (Figure 2) if a free diffusion liquid junction device is used. Practical cells such as cell IV, however, contain commercial liquid junction devices, e.g., ceramic porous plugs, fiber junctions, or Pt diaphragms, which are known[3,4,13] to cause liquid junction potentials different from those of the free diffusion liquid junction by up to 2 mV. Nevertheless, practical cells with commercial junction devices are usually calibrated by the bracketing procedure,[1] using two standard buffer solutions according to NIST or BSI, and the internal consistency is never redetermined under these conditions.

3. PROPOSAL OF A STANDARDIZATION PROCEDURE FOR HIGH-PRECISION pH MEASUREMENTS

Uncertainties caused by the bracketing procedure are in the order of ΔpH = ±0.05 and are thus negligible for many practical applications. They do become significant, however, when a precision of ΔpH = ±0.01 or better is required since the pH obtained depends not only on the choice of the standard scale and standard buffers but also on the cell used,
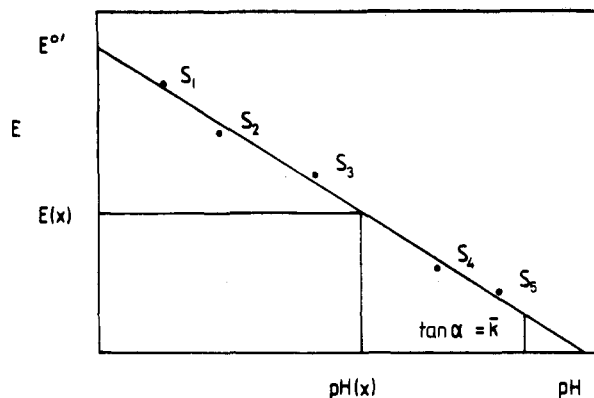
(13) Covington, A. K.; Whalley, P. D. *Anal. Chim. Acta* **1985**, *169*, 221–229.

Figure 3. Determination of an unknown pH(X) by multiple-point calibration with linear regression as proposed in this paper; k, average practical slope; $E^{\circ\prime}$, standard potential of the cell used.

i.e., on the liquid junction device. In these cases, multiple-point calibration with linear regression[7,8] is recommended for the standardization of pH measurements. As shown schematically in Figure 3, this method uses several, instead of only two, standard buffer solutions, and the calibration line, eq 9, is calculated by linear regression, where $E^{\circ\prime}$ is the

$$E(S) = E^{\circ\prime} - k pH(S) \qquad (9)$$

standard potential and k is the average practical slope. The pH values of unknown solutions are then obtained by eq 10,

$$pH(X) = (E^{\circ\prime} - E(X))/k \qquad (10)$$

Multiple-point calibration with linear regression has probably not been recommended in the past because of the laborious and time-consuming manual measurements of the necessary number of emfs. Modern pH meters, however, can be designed to conduct the calibration automatically within a short time, and one such instrument is already available commercially (Metrohm, pH meter Model 713). The recommendation of the new calibration method for pH measurements with highest precision and accuracy thus seems to be in line with the present state of good laboratory practice (GLP).

The proposed calibration procedure was verified by the application to two cells with liquid junction, cell V,

(Pt)Hg, Tl/TlCl(s),

KCl (m = 3.5 mol kg^{-1})//buffer soln/Pt, H$_2$ (V)

and cell VI,

(Pt)Hg, Tl/TlCl(s),

KCl (m = 3.5 mol kg^{-1})//soln(S or X)/glass el (VI)

The fundamental cell (V) was chosen to study the effect of liquid junction potentials, and the practical cell (VI) was to determine the highest precision and accuracy achievable with glass electrode-containing cells.

4. EXPERIMENTAL SECTION

The jacketed glass vessel used for cell V[9] with a Pt, H$_2$ electrode had a tilted bottom and a drain and was equipped with a platinized (or palladinized) platinum double-wire electrode (Schott Geräte Hofheim), a hydrogen inlet tube with G4 frit, a thermometer, and a Thalamid reference electrode [Tl, Hg(40 wt %)/TlCl(satd), KCl (3.5 mol kg^{-1})] (Schott Geräte Hofheim). The equipment was a special construction (Schott Geräte Hofheim), which also employed standard parts. Three types of liquid junction devices, i.e., a ground-glass sleeve, a Pt diaphragm, and a ceramic porous plug, were used. The ground-glass sleeve was preselected for a leak rate below 5 μL h^{-1}. Temperatures were 25 and 40 °C (±0.1

Table I. Standard Buffer Solutions, Their Compositions, and Recommendations, As Applied in This Work[a]

buffer soln	composition	standard NIST	standard BSI
tetroxalate	potassium tetroxalate dihydrate, 0.05 mol kg^{-1}	SS	OS
tartrate	potassium hydrogen tartrate, 0.01 mol kg^{-1}	PS	OS
citrate	potassium hydrogen citrate, 0.05 mol kg^{-1}	(PS)	OS
phthalate	potassium hydrogen phthalate, 0.05 mol kg^{-1}	PS	RVS
acetate	CH_3COOH + CH_3COONa, 0.1 mol kg^{-1} each		OS
phosphate 1:1	KH_2PO_4 + Na_2HPO_4, 0.025 mol kg^{-1} each	PS	OS
phosphate 1:3.5	KH_2PO_4, 0.008 695 mol kg^{-1}, + Na_2HPO_4, 0.030 43 mol kg^{-1}	PS	OS
Tris 1:3	Tris-HCl, 0.05 mol kg^{-1}, + Tris, 0.016 67 mol kg^{-1}		OS
borate	$Na_2B_4O_7\cdot10H_2O$, 0.01 mol kg^{-1}	PS	OS
carbonate	$NaHCO_3$ + Na_2CO_3, 0.025 mol kg^{-1} each	PS	OS
Ca(OH)$_2$	satd at 25 °C	SS	OS

[a] PS, primary standard; SS, secondary standard; RVS, reference value standard; OS, operational standard.

Table II. Application of Standard Buffer Solutions According to NIST in Cell V with Three Different Liquid Junction Devices (25 °C)[a]

buffer	pH(S)	sleeve E/mV	sleeve ΔpH$_1$	sleeve ΔpH$_2$	ceramic E/mV	ceramic ΔpH$_1$	ceramic ΔpH$_2$	Pt E/mV	Pt ΔpH$_1$	Pt ΔpH$_2$
tetroxalate	1.679	474.3 ± 0.78		−0.007	474.6 ± 0.35		−0.015	476.7 ● 0.45		+0.014
tartrate	3.639	358.0 ● 0.26	−0.006	0.000	357.7 ± 0.32	−0.008	+0.004	358.8 ● 0.35	+0.004	+0.012
citrate	3.776	349.6 ● 0.38	−0.001	+0.005	349.1 ● 0.76	+0.002	+0.013	351.1 ● 0.29	−0.002	+0.005
phthalate	4.006	335.4 ● 0.55	+0.010	+0.015	335.0 ± 0.15	+0.012	+0.022	337.6 ± 0.06	−0.003	+0.004
phosphate 1:1	6.863	167.6 ± 0.51	−0.003	−0.004	168.0 ± 0.56	−0.005	−0.008	168.9 ● 0.06	+0.004	+0.004
phosphate 1:3.5	7.415	135.1 ● 0.38	−0.004	−0.007	135.6 ± 0.49	−0.006	−0.011	136.7 ± 0.50	−0.002	−0.003
borate	9.180	30.6 ± 0.40	+0.002	−0.004	31.5 ± 0.57	0.000	−0.014	32.9 ± 0.81	−0.005	−0.010
carbonate	10.011	−18.4 ± 0.49	+0.002	−0.007	−17.7 ± 0.53	+0.006	−0.012	−16.6 ± 0.12	+0.004	−0.003
Ca(OH)$_2$	12.454	−163.8 ± 0.46		+0.009	−163.9 ± 0.56		+0.020	−161.3 ± 0.46		−0.005
ΔpH$_{av}$			±0.004	±0.006		±0.005	±0.013		±0.004	±0.007

[a] E, average values of measured emfs with standard deviations (n = 3); ΔpH, deviations of measured pH from the regression line, eq 9, for seven primary (ΔpH$_1$) and for seven primary and two secondary standard buffer solutions (ΔpH$_2$); ΔpH$_{av}$, average values of ΔpH.

K). Hydrogen was better than 99.99%; traces of CO_2 were removed by passing the gas through Ca(OH)$_2$. All measurements were referred to a hydrogen pressure of 1013.25 hPa according to ref 11.

Before platinizing, the Pt double-wire electrodes (5 mm long, 0.5 mm diameter) were treated in hot aqua regia and rinsed with deionized water. Platination/palladination was carried out in an H-shaped cell using a Pt gauze anode and constant current (10 mA) for 5 min. The solution for platinizing contained 1 g of PtCl$_2$ and 2 mg of Pb(CH$_3$COO)$_2$ in 30 mL of HCl (2 mol L^{-1}), and that for palladinizing 2 g of PdCl$_2$ in 100 mL of HCl (1 mol L^{-1}). Plating was carried out every day. The plated electrodes were kept in aqueous solution, avoiding but not excluding contact with air.

Cell VI was made up of a 20-mL commercial, jacketed, titration vessel with a lid (Metrohm, Herisau) equipped with a glass electrode (H 1120, Schott Geräte Hofheim) and a Thalamid reference electrode system (see above) in a glass tube with ground-glass sleeve junction device (Metrohm) preselected for a leak rate below 5 μL h^{-1}. A magnetic stirring bar was agitated by a synchronous stirrer (Metrohm). The temperature was 20 ± 0.1 °C.

NIST/DIN 19 266 standard buffer solutions were prepared from pH reference materials (Merck, Darmstadt) traced back to the respective NIST standard reference materials (SRMs) within ΔpH = 0.001.[1,14,15] BSI operational standard buffers, Tris 1:3 and acetate, and KCl solution were prepared from analytical-grade reagents. "Unknown" solutions were "ready-to-use" buffer solutions (Merck) with pH of 4.00 ± 0.02 (20 °C) (No. 9435) and 7.00 ± 0.02 (20 °C) (No. 9439). All buffer solutions are listed in Table I.

emfs were measured with a high impedance digital volt/pH meter with an accuracy 0.1 mV (Model 645, Knick, Berlin). The potential drift was followed by a recorder with 2-mV full scale, the main part of the emf being compensated by a constant-voltage

generator (Model 913, Knick). Readings were taken after the emfs had been constant within 0.1 mV for 5 min.

5. RESULTS AND DISCUSSION

Fundamental Cell (V) with Pt, H$_2$ Electrode. Measurements were conducted on 11 standard buffer solutions (Table I) of the NIST and BSI scales in cell V containing three different liquid junction devices, i.e., ground-glass sleeve, ceramic, and Pt junctions, at 25 and 40 °C. As examples, Tables II and III present mean values, E, of three experimental emfs and their standard deviations, s, for the standard buffers according to NIST,[2,12] Table II, and BSI,[5,16] Table III, at 25 °C. The data were evaluated according to eq 9,[17] and Table IV shows the resulting practical average slopes, $\bar{k}$, and the standard potentials, $E^{o\prime}$, for seven primary (PS) and for seven primary and two secondary (SS) standard buffer solutions of the NIST scale and also for the reference value standard (RVS) and eight operational standard buffer solutions (OS) of the BSI scale for the three liquid junction devices at 25 and 40 °C. Also calculated were deviations, ΔE, of the mean emfs, E, from the regression line, which are given as pH differences, ΔpH, together with their average values, ΔpH$_{av}$,[18] for each set of data, in Tables II and III.

The most remarkable and unexpected result is that the practical average slope, $\bar{k}$, is smaller than the theoretical slope, k (Table IV); i.e., the electromotive efficiency, $\beta = \bar{k}/k$,[11] of cell V is smaller than unity, independent of the liquid junction devices. Besides, $\bar{k}$, or β, is not a function of pH within the pH range studied, as indicated by the independence of ΔpH

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(17) Doerfeld, K. Beurteilung von Analysenverfahren und Ergebnissen; Springer; Berlin, 1962.

Table III. Application of Standard Buffer Solutions According to BSI in Cell V with Three Different Liquid Junction Devices (25 °C)[a]

buffer	pH(OS)	sleeve		ceramic		Pt	
		E/mV	ΔpH_3	E/mV	ΔpH_3	E/mV	ΔpH_3
tetroxalate	1.646	474.3 ± 0.78	+0.008	474.6 ± 0.35	+0.018	476.1 ± 0.45	+0.018
phthalate	4.005	335.4 ± 0.55	−0.001	335.0 ± 0.15	+0.020	337.6 ± 0.06	+0.002
acetate	4.644	296.8 ± 0.12	+0.014	299.7 ± 0.44	−0.022	301.1 ± 0.36	−0.020
phosphate 1:1	6.857	167.6 ± 0.51	−0.013	168.0 ± 0.49	−0.008	168.9 ± 0.06	+0.004
phosphate 1:3.5	7.406	135.1 ± 0.38	−0.012	135.6 ± 0.49	−0.009	136.7 ± 0.50	−0.001
Tris	7.648	119.9 ± 0.40	+0.003	120.8 ± 0.50	−0.001	122.6 ± 0.15	−0.004
borate	9.179	30.6 ± 0.49	−0.017	31.5 ± 0.57	−0.022	32.9 ± 0.81	−0.018
carbonate	9.995	−18.4 ± 0.46	−0.003	−17.7 ± 0.53	−0.006	−16.6 ± 0.12	+0.004
Ca(OH)$_2$	12.431	−163.8 ± 0.53	+0.021	−163.9 ± 0.56	+0.031	−161.3 ± 0.46	+0.016
ΔpH_{av}			±0.010		±0.015		±0.009

[a] $\bar{E}$, average values of measured emfs with standard deviations ($n = 3$), ΔpH_3, deviations of measured pH from the regression line, eq 9, for one reference value standard and eight operational standard solutions; ΔpH_{av}, average values of ΔpH_3.

Table IV. Practical Average Slopes, $\bar{k}$, and Standard Potentials, $E^{\circ\prime}$, of the Calibration Function, eq 9, Determined by Linear Regression of the emfs (Given in Tables II and III) of Cell V with Three Different Liquid Junction Devices (25 and 40 °C)[a]

T/°C	scale	buffers	sleeve			ceramic			Pt		
			$\bar{k}$/mV	$1 - \beta$	$E^{\circ\prime}$/mV	$\bar{k}$/mV	$1 - \beta$	$E^{\circ\prime}$/mV	$\bar{k}$/mV	$1 - \beta$	$E^{\circ\prime}$/mV
25	NIST	7 PS	59.00 ±0.05	0.0027	572.4 ±0.36	58.79 ±0.07	0.0063	571.2 ±0.47	58.92 ±0.09	0.0041	573.5 ±0.67
		7 PS + 2 SS	59.13 ±0.05	0.0005	573.2 ±0.37	59.06 ±0.09	0.0017	572.9 ±0.70	59.05 ±0.05	0.0019	574.4 ±0.38
	BSI	1 RVS + 8 OS	59.07 ±0.09	0.0015	572.0 ±0.67	59.13 ±0.13	0.0005	573.0 ±0.98	59.11 ±0.09	0.0008	574.4 ±0.67
40	NIST	7 PS	62.08 ±0.08	0.0008	581.1 ±0.58	61.99 ±0.11	0.0023	581.0 ±0.76	62.02 ±0.15	0.0018	582.9 ±0.99
		7 PS + 2 SS	62.14 ±0.07	0.0002	581.5 ±0.46	62.02 ±0.09	0.0013	581.4 ±0.58	62.07 ±0.11	0.0010	583.3 ±0.73
	BSI	1 RVS + 8 OS	62.01 ±0.12	0.019	579.9 ±0.81	61.95 ±0.12	0.0029	579.9 ±0.81	61.91 ±0.09	0.0034	580.9 ±0.63

[a] Three groups of the standard buffer solutions were treated separately: NIST, seven primary standards (PS); NIST, seven primary and two secondary (SS) standards; BSI, one reference value standard (RVS) and eight operational standards (OS). Also listed are the electromotive loss factors $(1 - \beta)$, where β is the electromotive efficiency.

of pH (Tables II and III) and by the small standard deviations of $\bar{k}$ (Table IV). The meaning of β is found by differentiating the emf (eq 3) of cell V with respect to pH (eq 11),

$$dE/dpH = -\bar{k} = d\epsilon_H/dpH - d\epsilon_R/dpH + d\epsilon_j/dpH \quad (11)$$

and taking into account that the Pt, H$_2$ electrode exhibits the theoretical slope,

$$d\epsilon_H/dpH = -k \quad (12)$$

and that the pH dependence of the reference electrode potential is zero,

$$d\epsilon_R/dpH = 0 \quad (13)$$

Thus,

$$-\beta k = -k + d\epsilon_j/dpH \quad (14)$$

is obtained, and, after rearranging,

$$d\epsilon_j/dpH = k(1 - \beta) \quad (15)$$

$1 - \beta$, which may be called the electromotive loss factor according to

$$E = E^{\circ\prime} - (k - (d\epsilon_j/dpH))pH \quad (16)$$

(resulting from a combination of eqs 9 and 15, thus represents the average pH dependence of the liquid junction potential in cell V. Table IV lists this quantity for cell V, and Table V presents corresponding values of $d\epsilon_j/dpH$. With one exception (which is zero), $d\epsilon_j/dpH$ is positive, and its relative magnitude is characteristic of the sets of standard buffer solutions for each liquid junction device and of the liquid junction devices for each set of buffers. The relative sequence

is similar at 25 and 40 °C, as demonstrated by the average values for the liquid junction devices (Table V). They are smaller for the sleeve than for the ceramic and Pt junction devices and comparable for the two latter ones.

Bates has discussed the significance of the liquid junction potential for the accuracy of pH determinations[3] and has reported calculated liquid junction potentials for the continuous-mixture junction KCl(satd)//buffer solution.[3,11] They are plotted as a function of pH in Figure 4, and it is interesting to note that they also [and particularly those with equal total buffer concentrations, 0.05 mol kg^{-1} (closed points)] can be represented, as a first approximation, by a straight line with a positive slope, $d\epsilon_j/dpH = 0.19 \pm 0.03$ mV, which is in the order of the values for cell V. A similar result is found when the residual liquid junction potentials reported by Bates[11] for two variants of the free diffusion liquid junction are plotted vs pH (Figure 5). They show the same trend and, as a first approximation, can also be represented by a straight line with a positive slope if the data for borax buffer, which has a different concentration (0.01 mol kg^{-1}), above 25 °C are omitted. Also in this case, the average slope, $d(\Delta\epsilon_j)/dpH = 0.16$, is in the order of the values for cell V.

According to eq 15, the average quantity $d\epsilon_j/dpH$ is constant as long as the electromotive efficiency, β, is not a function of pH, and it seems to be an observation of general validity that, for buffer solutions with equal concentrations, ϵ_j in cell I containing a particular liquid junction device increases in proportion to pH, the proportionality constant being characteristic of the buffers and the liquid junction device applied. This result is understood qualitatively in terms of the products (concentration × mobility) of the ions, which determine the

Table V. Average pH Dependence of the Liquid Junction Potential at the Boundary KCl (m = 3.5 mol kg^{-1})//Buffer Solution As Determined Experimentally by Cell V with Different Liquid Junction Devices for Three Groups of Buffer Solutions (25 and 40 °C)[a]

T/°C	scale	buffers	($d\epsilon_j$/dpH)/mV exptl[b]			calcd cont mixt	($d(\Delta\epsilon_j)$/dpH)/mV[c]
			sleeve	ceramic	Pt		
25	NIST	7 PS	0.160	0.373	0.243		
	NIST	7 PS + 2 SS	0.030	0.101	0.112		
	BSI	1 RVS + 8 OS	0.090	0.030	0.047		
	NIST + BSI + others	14 buffers + 0.1 m NaOH				0.19	
	av		0.093	0.168	0.134		
40	NIST	7 PS	0.050	0.143	0.112		
	NIST	7 PS + 2 SS	−0.001	0.081	0.062		
	BSI	1 RVS + 8 OS	0.118	0.180	0.211		
	av		0.056	0.135	0.128		
10–40	NIST	5 PS					0.16

[a] Also given are one value obtained from liquid junction potentials calculated for the continuous-mixture boundary KCl (satd)//buffer solution at 25 °C[3,11] (see Figure 4) and one average value (10–40 °C) obtained from experimental residual liquid junction potentials at the free diffusion liquid junction KCl (satd)//buffer solution[11] (see Figure 5). [b] This work. [c] For the residual liquid junction potentials at the free diffusion liquid junction.

liquid junction potential. Buffers with different pH values differ mainly in their hydrogen and hydroxyl concentrations, respectively, in a systematic way, whereas the concentrations of all other ionic species are comparable in certain limits. Besides, the mobilities of hydrogen and hydroxyl ions are much larger than those of all other ions present. It is thus conceivable that the liquid junction potential at the boundary KCl (m ≥ 3.5 mol kg^{-1})//buffer solution, although greatly suppressed by the large concentration of K$^+$ and Cl$^-$ ions with nearly equal mobilities,[11] shows a continuous change with pH, which reflects the changing concentration of hydrogen (or hydroxyl) ions since the effect of the systematic change of the products $m_H u_{H^+}$ and $m_{OH} u_{OH^-}$, respectively, is greater than the effect of the change of $m_i u_i$ of all other ions. It is thus expected that an increase of the hydrogen ion concentration causes a more positive potential of the KCl solution relative to that of the buffer solution and thus a more negative liquid junction potential, $\epsilon_j = \epsilon_{buffer} - \epsilon_{KCl}$, i.e., $d\epsilon_j$/dpH > 0, as found experimentally and by calculation. A quantitative treatment which is more general than that represented by Figure 4, however, does not seem feasible because of the individual compositions of the buffer solutions involved.

Single deviations (ΔpH) of standard pH values from the regression line (Tables II and III) can be compared with residual liquid junction potentials reported by Bates[11] although these numbers are not exactly equal, as Bates determined deviations of pH(S) values, measured in cell I containing two kinds of free diffusion liquid junction, from a straight line with theoretical slope and phosphate 1:1 standard buffer solution as the reference. As shown in Table II, deviations (ΔpH$_1$) for the seven primary standard buffer solutions according to NIST are only slightly larger (ΔpH$_1$ = −0.006 to +0.010) for the sleeve junction and the Pt diaphragm than the residual liquid junction potentials reported by Bates (ΔpH = ±0.006), whereas for the ceramic junction they have somewhat larger values (ΔpH$_1$ = −0.008 to +0.012). As expected, deviations (ΔpH$_2$) for NIST buffer solutions including two secondary buffers are larger. The sequence with respect to the liquid junction devices, however, is the same. This result is reflected by the average deviations, ΔpH$_{av}$ (Table II), which characterize the internal consistency of the calibration lines, and it is also found at 40 °C (not given here), the only difference being that ΔpH and ΔpH$_{av}$ are slightly larger at the higher temperature. This is in agreement with the residual liquid junction potentials as reported by Bates.[11]

The evaluation of the data according to the BSI scale yields significantly larger single deviations (ΔpH$_3$) than for the NIST scale (Table III). They are ΔpH$_3$ = −0.017 to +0.020 for the sleeve, ΔpH$_3$ = −0.022 to +0.031 for the ceramic, and ΔpH$_3$ = −0.010 to +0.018 for the Pt junction device and thus show the same relative sequence for the different liquid junction devices as ΔpH$_1$ and ΔpH$_2$. Also for ΔpH$_3$, the same sequence is observed at 40 °C (not given here), and the general trend of the single deviations is reflected by the average deviations (ΔpH$_{av}$) which are, for instance, larger than those for the NIST scale with seven primary standards by a factor 2–3. Obviously, the larger deviations (ΔpH$_3$) are caused by the liquid junction potentials built into the pH(OS) of the operational buffer solutions. The results thus show that the high internal consistency built into the single-standard scale by means of cell I with a free diffusion liquid junction is not reproduced in cells with practical liquid junction devices.

Surprisingly, phthalate buffer solution exhibits the largest single deviations (ΔpH$_1$ and ΔpH$_2$) for the sleeve and ceramic junction devices at 25 °C (and for all three junction devices at 40 °C, not shown here) if the measurements are evaluated according to the NIST scale (Table II), whereas this phenomenon is not observed for the BSI scale (Table III). It must be concluded that phthalate buffer generates a relatively large liquid junction potential in practical junction devices, which either is not the case in the free diffusion liquid junction or is obscured by the assignment of the pH(OS) values to operational buffer solutions according to BSI.

Single deviations (ΔpH), which are distributed at random at 25 (Tables II and III) and 40 °C (not presented), show no dependence on pH. The application of linear regression is thus justified as a numerical treatment of data for the multiple-point calibration, at least in the pH range 1.5–12.5 investigated.

Practical Cell (VI) with Glass Electrode. Cell VI containing a ground-glass sleeve liquid junction device was calibrated with four primary standard buffer solutions according to NIST and one reference value standard and three operational standard solutions according to BSI at 20 °C. This temperature is often required for pH measurements on technical buffer solutions. Since the glass electrode potential does not completely represent the thermodynamic equilibrium at the membrane/solution interface,[19] cell VI was calibrated before each measurement in order to exclude

Table VI. Application of Multiple-Point Calibration with Linear Regression to the Standardization of Cell VI Employing a Glass Electrode and a Ground-Glass Sleeve Liquid Junction Device (20 °C)[a]

std buffers	scale according to	
	NIST	BSI
	tetroxalate	tetroxalate
	tartrate	phthalate
	phosphate 1:1	phosphate 1:1
	borate	borate
k'/mV (20 °C)	57.87 $\bullet$ 0.05	57.66 $\pm$ 0.05
E°/mV	+386.46 $\pm$ 0.36	+384.60 $\pm$ 0.37
pH$^{\circ}$	6.678 $\pm$ 0.012	6.670 $\pm$ 0.012
ΔpH$_{av}$ (n = 5)	$\pm$0.005	$\pm$0.005
$\alpha + \beta - 1$	0.9949	0.9915
pH(X$_1$)	3.998 $\pm$ 0.003	3.981 $\pm$ 0.003
pH(X$_2$)	6.998 $\bullet$ 0.002	6.992 $\pm$ 0.002

[a] k', average practical slope; E°, standard potential; pH$^{\circ}$, zero-potential pH; ΔpH$_{av}$, average deviation of measured pH values from the regression line; $\alpha + \beta - 1$ = electromotive efficiency of cell VI; pH(X$_1$) and pH(X$_2$), pH values of unknown solutions.
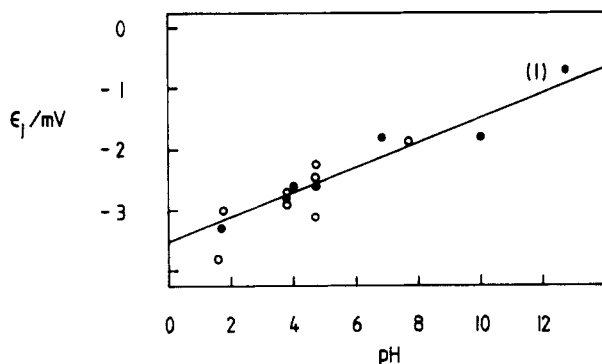

Figure 4. Calculated liquid junction potentials, ϵ_j, at the continuous-mixture junction KCl(satd)//buffer solution[3,11] plotted as a function of pH: ($\bullet$) total buffer concentration, 0.05 mol kg^{-1}; (O) other concentrations, (1) 0.05 mol kg^{-1} NaOH.
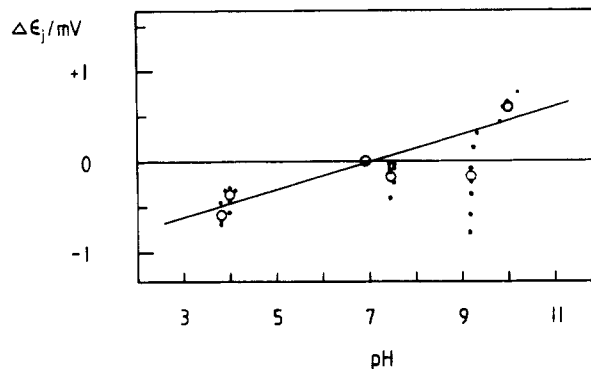

Figure 5. Experimental residual liquid junction potentials, $\Delta\epsilon_j$, referred to NIST phosphate 1:1 buffer, at the free diffusion liquid junction KCl (3.0, 3.5 mol kg^{-1}, satd)//buffer solution at several temperatures between 10 and 40 °C[11] plotted as a function of pH: ($\bullet$) values as given; (O) average values of each buffer. For borax buffer, whose concentration, 0.01 mol kg^{-1}, differs from those of the other buffer solutions, only data below 25 °C were used for the construction of the average straight line.

unnoticed potential changes with time. The measured data were evaluated by linear regression (eq 9),[17] yielding practical average slopes, k', standard potentials, E°, and zero-potential pH values, pH$^{\circ}$. Table VI lists these data in addition to the average deviations (ΔpH$_{av}$) of the measured pH values from the regression lines,[18] the standard buffer solutions applied, and the resulting pH(X). Also presented in Table VI is the electromotive efficiency ($\alpha + \beta - 1$) of cell VI, which is obtained by differentiating its emf, E_{gl}, (potential of the glass electrode)

$$E_{gl} = \epsilon_{gl} - \epsilon_R + \epsilon_j \quad (17)$$

with respect to pH,

$$dE_{gl}/dpH = d\epsilon_{gl}/dpH - d\epsilon_R/dpH + d\epsilon_j/dpH \quad (18)$$

and observing eqs 13 and 15, which, however, applies only for the same liquid junction device and the same buffer solutions in cell VI, yielding

$$dE_{gl}/dpH = -(\alpha + \beta - 1)k \quad (19)$$

where $\alpha = k_{gl}/k$ is the electromotive efficiency, and k_{gl} is the practical average slope, of the glass electrode.

As expected, the electromotive efficiency ($\alpha + \beta - 1$) of cell VI employing a glass electrode is smaller than that, β, of the fundamental cell V involving a Pt, H$_2$ electrode because of

the imperfect slope, k_{gl}, of the glass electrode potential. Equation 19 allows separation of the electromotive efficiency (α) of the glass electrode potential from the electromotive efficiency (β) of cell V if measurements are conducted on both cells V and VI with the same liquid junction device and the same buffer solutions. Due to the different buffer solutions and temperatures applied, however, single values of α and β are not presented here. But it is safe to say that the electromotive efficiency of cell VI is mainly caused by the glass electrode, i.e., by α, and much less by the liquid junction potential, i.e., by β.

The internal consistencies of the calibration line for the two sets of buffer solutions according to NIST and BSI, which are represented by ΔpH$_{av}$ (Table VI), are comparable with the respective ΔpH$_{av}$ obtained for cell V, also employing a ground-glass sleeve junction device (Tables II and III). Thus, equally accurate pH values can be measured by cells employing a glass and a Pt, H$_2$ electrode, respectively, if the multiple-point calibration procedure with linear regression is applied as the standardization procedure. The expected perfect internal consistency on the basis of BSI standard buffer solutions is obtained by neither cell V nor cell VI. The precision of the pH values [pH(X$_1$) and pH(X$_2$)] of the unknown solutions in terms of the standard deviation of the final results is equal for the two scales, ΔpH(X) = $\pm$0.002 to $\pm$0.003; the absolute pH(X), however, differ significantly (in the sense of high precision measurements; Table VI).

6. CONCLUSION

The application of the multiple-point calibration procedure with linear regression to the standardization of pH measurements by cell V with a Pt, H$_2$ electrode and cell VI with a glass electrode shows the advantages of this method compared to the bracketing procedure recommended by IUPAC:

(1) At a given number and identity of standard buffers, only one pH value is obtained for each solution, and an overdefinition of pH is excluded.

(2) The accuracy and precision of pH values measured are better than those found by the bracketing procedure, and the precision of pH(X) values measured by cell VI with a glass electrode is comparable to that of pH(X) values obtained by cell V with a Pt, H$_2$ electrode.

(3) Residual liquid junction potentials characterized by the deviations ΔpH of measured pH(S) values from the regression line can be checked for each calibration.

(18) Deutsches Institut für Normung *Kalibrierung und Auswertung von Analysenverfahren und die Bestimmung von Verfahrenskenngrößen*; DIN 38 402-A5; Beuth-Verlag: Berlin, 1984.

(19) Baucke, F. G. K. *J. Non-Cryst. Solids* **1985**, *73*, 215–231.

(4) The average (ΔpH_{av}) of the residual liquid junction potentials characterizes quantitatively the internal consistency of the calibration line and thus the accuracy referred to independent measurements by cell II.

(5) The most appropriate liquid junction device can be selected for each purpose.

Because of these advantages, multiple-point calibration with linear regression is proposed as a standardization procedure for high-precision pH measurements with glass electrode-containing cells such as cell VI, which means that eqs 7 and 8 are replaced by eqs 9 and 10 as operational equations. As comparable precision is found for NIST and BSI buffer solutions, the application of NIST buffers is recommended since in this case the calibration function (eq 9) has a thermodynamic meaning. This proposal is supported by the finding that the liquid junction potentials included in the assignment of pH(OS) values to BSI operational standard buffers are unveiled when these buffers are used in cells with practical liquid junction devices.

According to the results reported, the average practical slope, $\bar{k}$, of the calibration function of cell V with Pt, H_2 electrode, which is a type of cell I, is not the mean value of, but differs systematically from, the theoretical slope, k. It thus ought also to be discussed whether the operational definition of pH (eq 2) must be replaced by an operational definition by eqs 9 and 10 in order to preserve maximum consistency of highly precise pH values measured in cells I and VI.

Since modern pH meters can be designed to determine the multiple-point calibration function automatically in a short time, the larger number of measurements, compared to the bracketing procedure, is not an obstacle to the recommendation of the multiple-point calibration procedure.