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RECOMMENDED PROCEDURES FOR CALIBRATION OF ION-SELECTIVE ELECTRODES

(Technical Report)

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Abstract

This report presents the general methods used for calibration of ion-selective electrodes. Calibrations by metal ion buffers, serial dilution and flow procedures are discussed and compared. Comments on activity standards, concentration standards as well as on ionic strength are also presented.

An ion-selective electrode can be calibrated either with solutions of known determinand activity or with solutions of known determinand concentrations, according to which parameter is to be measured in the samples.

ACTIVITY STANDARDS

To prepare a standard solution containing a known activity of any ion is strictly impossible, as it requires knowledge of the activity coefficient of that ion. On theoretical and practical grounds, single ion activity coefficients cannot be assigned without recourse to a non-thermodynamic assumption (1). The assumption, while arbitrary, is judged by its "reasonableness". In the case of the solutions of "known" hydrogen ion activities and to establish the pH scale, two nearly consistent assumptions were made for the U.S. National Bureau of Standards (now, National Institute of Standards and Technology) scale and the British Standards Institution Scale (2). The NIST chose to ascribe a conventional value to the chloride ion activity coefficient in series of dilute buffer solutions (the Bates-Guggenheim convention), whereas the BSI took the approach of ascribing a conventional value only to the hydrogen ion activity in a 0.05 mol dm^{-3} potassium hydrogen phthalate solution. In the formulation of series of solutions of standard activities of other ions, a similar assumption or convention is explicitly or implicitly used.

The choice of conventions available for the assignment of single-ion activities to solutions for the calibration of ion-selective electrodes has been discussed by Bates (3,4). When the ionic strengths of solutions are below 0.1 mol kg^{-1}, the straightforward MacInnes convention ($\gamma_{Cl^-} = \gamma_{K^+}$ in KCl solutions) may be used, or the Debye-Huckel convention, based on the equation:

$$\log \bar{\gamma}_{XY} = \frac{A\,|z_x z_y|\,I^{\frac{1}{2}}}{1 + BdI^{\frac{1}{2}}} \qquad (1)$$

(A and B are conditional constants depending upon such variables as temperature and the density and electric permittivity of the solvents; z_x and z_y are the charges on ions X and Y; d is termed the average effective diameter of the ions; I = ionic strength), which gives $\gamma_X = \gamma_Y$ for any equivalent electrolyte XY or the pH convention (by fixing a value for γ_{Cl^-} from the above equation, with conventional values for A and Bd). If the convention only gives the activity coefficient of one of the ions in the simple electrolyte, the activity coefficient of the other may be calculated from a general form of the equation:

$$\bar{\gamma}_{XY}^2 = \gamma_X \gamma_Y \qquad (2)$$

where γ_{XY} is the measureable mean activity coefficient, again for a univalent electrolyte XY. Additionally, the activity coefficient may be assumed to have the same value in other electrolytes of the same charge type at the same ionic strength; hence, by further use of Eq. (2), more activity coefficients may be obtained.

For example, if the activity coefficients γ_{K+} and γ_{Cl-} are "known" from measurements of γ_{KCl} in a given solution of potassium chloride and adoption of the MacInnes convention, the activity coefficient of sodium ions, γ_{Na+}, in solutions of sodium chloride of the same ionic strength can be calculated from measured values of γ_{NaCl} by means of the equation:

$$\gamma_{Na+} = \overline{\gamma}_{NaCl}^2 / \gamma_{Cl-} \tag{3}$$

This procedure may be then extended using this value of γ_{Na+} to calculate, for example γ_{Br-} in solutions of sodium bromide from measured values of γ_{NaBr}. Alternatively, if the convention and values are consistent, the same value of γ_{Br-} should be obtainable by use of the original value of γ_{K+} and measurements of the mean activity coefficient, γ_{KBr}.

However, when the ionic strengths of solutions are greater than 0.1 mol kg^{-1}, a more complex theory is required to account for properties of different ions and also for the dependence of the ionic activities upon the composition of the solution, instead of solely upon the ionic strength. The concept of ionic strength becomes progressively less useful as the concentrations increase. Bates, Staples and Robinson (4) have proposed a convention for these concentrated solutions which is based on the hydration theory of Stokes and Robinson (5). This theory seeks to explain ionic activities in terms of the number of water molecules associated with each ion (a measure of which is referred to as the hydration number) and the activity of the residual unassociated water. The convention adopted within the terms of this theory is the assignment of a hydration number of the chloride ion; values of 0 and 0.9 have been proposed. The uncertainty in these hydration numbers has been assessed by Bates (3,4) as 0.5 - 1.0. After one value is assumed, all the rest may be calculated from the experimental results. A full discussion of this theory is given in the book by Robinson and Stokes (6).

At the other extreme of concentration for solutions of ionic strength less than 10^{-4} mol kg^{-1}, the activity coefficient may be assumed to be unity, making the activities of ions equal to their concentrations.

Several ranges of activity standards have been proposed, employing one or the other of these conventions; they are mostly standards of alkali metal and halide ions. A summary of solutions proposed as standards and others which may be used for calibration purposes is given in Table 1.

TABLE 1. Calculated standard values of pX

		Salt		
	KF(7,8)	CaCl$_2$(4)	NH$_4$Cl(4)	KCl(7,8)
molality,m	pF = pK	pCa	pNH$_4$	pCl
0.01	2.044			2.041
0.0333		1.900		
0.05	1.387			
0.1	1.111	1.570	1.112	1.113
0.2	0.837	1.349	0.840	0.840
0.5	0.475	0.991	0.483	0.486
1.0	0.190	0.580	0.208	0.216
2.0	-0.119	-0.198	-0.080	-0.059

Data adapted from Refs. 4, 7, 8.

CONCENTRATION STANDARDS

The analyst usually wishes, rightly or wrongly, to measure the concentrations of ions rather than their activities. Thus, concentration standards are far more widely used than activity standards. Moreover, concentration standards, may readily be prepared for any ion without the relatively difficult problems associated with single ion activities discussed in the previous section. No conventional scales need to be established; it is simply sufficient to prepare a range of solutions of the required concentrations and take steps to ensure the constancy of the activity coefficient. The ion-selective electrode may then be calibrated in these concentration standards and used to determine the concentration of the determinand in other solutions in which the activity coefficient of the determinand is the same as in the standards. The ionic activity, which an electrode senses, is then proportional to the ionic concentration.

The purpose of the calibration is to enable the responses of the electrodes in standard solutions to be compared with the responses in samples. In order for the comparison to be valid, both standards and samples must be treated identically. Thus, any reagents added to samples before measurement should also be added to standards in the same proportions, so that the background compositions of samples and standards are identical. If sample pretreatment is not necessary, because the conditions for satisfactory measurement are already met by the sample in its untreated state, then it is necessary to prepare the standards with the same background composition as the sample. Concentration standards, as presented to the electrode, should be as similar as possible in all respects to the samples, and the determinand concentration in the standards should closely bracket the expected range in the samples (1).

Preparation of concentration standards from single salts

The range of concentration standards for calibrating an electrode may usually be prepared by serial dilution of a standard stock solution of a salt containing the determinand. Normal criteria of analytical chemistry should be used in the selection of this salt so that, where possible, the salt is of a high and defined purity and the stock solution is stable for long periods to avoid the necessity for frequent standardization. The more dilute standards, because of their instability, particularly those containing less than 10^{-3} mol dm^{-3} determinand, should be prepared by dilution of the stock solution immediately before use. In some cases, for example solutions of sulfide ion-soluble salts are not available in sufficiently pure form and moreover, the solutions are unstable; thus, the stock standard solution must always be standardized before use. Similar to the problem with sulfide standards is that with sulfur dioxide standards; no salts are available with sufficiently precise purity for calibrating a sulphur dioxide probe. Additionally, the solutions are subject to aerobic oxidation and must therefore be standardized by an iodine-thiosulfate titration method. Coulometric generation (9) of ion concentration standards has been used to increase accuracy and reduce solution handling: unfortunately only a few ions, notably the halide ions and silver ions, may be generated in this way.

Establishment of ionic strength

In conjunction with the concentration standards, a reagent must be used to stabilize the activity coefficient of the determinand and perform other important functions such as buffering the pH of the sample and decomplexing the determinand. The formulation of this reagent will depend on the chemical properties and concentration of the determinand, the form in which it is to be measured and the optimum working conditions for the electrode. Commonly, samples have low ionic strength and the determinand concentrations is also low ($< 10^{-2}$ mol dm^{-3}); in all cases it is best to limit the concentrations of the background electrolyte, in the treated samples and standards, to about 10^{-1} mol dm^{-3} to minimize the difficulties with the liquid junction potential and minimize sample dilution.

A well-known example of a reagent formulated to meet all these conditions is that called TISAB (Total Ionic Strength Adjustment Buffer), which is added to various sample containing fluoride before analysis of fluoride ions with a fluoride electrode. Three TISAB solutions of different compositions have been proposed (11-13)(Table 2). All three solutions consist of ionic strength adjusting salt (NaCl, NaNO$_3$), complexing ligand and pH buffer. From the three TISAB solutions, the most suitable should be chosen by considering the interferring components present in the sample (10). In fluoride measurements, when aluminium ions are present in great quantity, it is expedient to use TISAB III, while at high iron (III) and

TABLE 2. TISAB Solutions

TISAB I (11)	TISAB II (12)	TISAB III (13)
500 mL water	500 mL water	17.65 g cyclohexane-1,2 diamine-N,N,N',N'-tetraacetic acid (DCTA)
57 mL glacial acetic acid	170 g sodium nitrate	500 mL water
58 g sodium chloride	68 g sodium acetate trihydrate	40% NaOH, drop by drop until the salt is dissolved
0.3 g sodium citrate dihydrate (Dilute to 1L)	92.4 g sodium citrate dihydrate (Dilute to 1L)	300 g sodium citrate dihydrate
		60 g Sodium chloride (Dilute to 1L)

silicate concentration, TISAB II solution is recommended. TISAB I, developed by Frant and Ross (11) is recommended for use in fluoride measurements when magnesium, calcium, chloride, nitrate, sulphate, and phosphate are present at high concentration. TISAB I contains sufficient sodium chloride to give a background concentration of 0.1 mol dm^{-3} in the treated sample and, hence, fix γ_{F^-}.

Use of equilibrium reactions, pH and metal ion buffers

Baumann (14) used fluoride ion buffers consisting of fluoride complexes of H^+, Zr^{4+}, Th^{4+} and La^{3+} to study the behavior of the fluoride electrode in very low fluoride concentrations. She showed that solutions prepared by serial dilution are useful to an effective lower limit of detection of about 10^{-6} mol dm^{-3}. When fluoride ion buffers are used, Nernstian response is obtained right down to $10^{-9.5}$ mol dm^{-3}. The response of the electrode below 10^{-6} mol dm^{-3} fluoride was systematically determined by comparing free fluoride concentrations measured with a calibrated electrode with those calculated from published stability quotients of Zr-, Th-, La-, and Hf-fluoride systems.

By analogy with the definition of a pH buffer, which is a solution for which the pH value is only slightly affected by dilution or by the addition of a relatively small amount of a strong acid or strong base, a metal buffer solution can be defined as a solution for which the pM-value is only slightly affected by the addition of the metal ion (15). Normally, the pM-value would be also almost independent of dilution. Such solutions can be prepared by adding an excess of a chelating agent to a solution of the metal ion. As the chelating agents very often are anions or polyprotic acids, the solution also has to be buffered for pH.

As it was pointed out recently by Hulanicki et al. (16), when metal buffers are used for the calibration of ion-selective electrodes, the following points should be remembered:
    --the linearity of the electrode working curve may, especially in the low concentration range, be affected, e.g., by the membrane solubility;
    --some membrane materials may, in certain ligand systems, exert a specific interaction, which may lead to erroneous results.
    The main requirements for ion-buffers are (17):
    --accurately known activity or concentration of free (hydrated) ions of interest, evaluated from known equilibrium constants;
    --well established correlation between concentration and activity of free (hydrated) ions;
    --sufficient ion buffer capacity to eliminate the effect of dilution or changes of the concentration of the ion of interest;
    --sufficient pH buffer capacity, because buffers based on ligands with weakly basic properties are significantly pH sensitive.

The principle of buffering action is the formation of a slightly dissociated compound of the ion of interest and this may be achieved through a relatively stable soluble complex or through a slightly soluble precipitate in equilbrium with a common ion.

For the ion-selective measurement of copper(II) a complexing antioxidant buffer (CAB) is advised by Smith and Manahan (18), the composition of which is as follows: 0.05 mol dm^{-3} sodium acetate, 0.05 mol dm^{-3} acetic acid, 0.02 mol dm^{-3} sodium fluoride and 0.002 mol dm^{-3} formaldehyde. The buffer is added to the sample in the ratio of 1:1 prior to the potentiometric measurement. This buffer ensures an optimum pH value (pH 4.8) for copper(II) measurements. The acetate ions in excess have a double role, in part, they keep the ratio of the fixed and the free copper ions at a constant value; in part, they impede adsorption on the wall of the vessel. Also, there is no loss of copper(II) ions if Fe^{3+} ions are present, which could lead to the formation of hydrated iron(III) oxide precipitate occurring with copper(II) coprecipitation. Formaldehyde is the antioxidant component of the CAB solution, but ascorbic acid is also used for this purpose (19).

Blum and Fog (20) proposed the use of metal ion buffers of the type previously used by Chaberek and Martell (21) for the calibration of electrodes and in particular demonstrated the efficacy of buffer solutions containing various proportions of cupric ions to EDTA or nitrilotriacetic acid (NTA) for calibrating copper electrodes. An ionic strength of about 0.1 mol dm^{-3} was maintained, which helped to keep constant the activity coefficient of the free copper(II) ions in equilibrium with the Cu^{II}/EDTA or Cu^{II}/NTA complex. The values of pCu for the different buffers were calculated from the published stability constants by Ringbom's method (22).

For calcium determination, Hulanicki and Trojanowicz (23) suggest a constant complexation buffer (CCB) of the following composition: one liter solution containing 40.4 g potassium nitrate, 3.6 g disodium iminodiacetate, 160 mL 0.5 mol dm^{-3} aqueous acetylacetone solution, 2 mL 10 mol dm^{-3} ammonia, and 1.07 g ammonium chloride. The acetylacetone masks magnesium, the KNO_3 (0.4 mol dm^{-3}) adjusts the ionic strength, and the iminodiacetate (0.02 mol dm^{-3} serves to complex the calcium. In biological samples, TEA (1 mol dm^{-3} triethanolamine) background solution can advantageously be applied to calcium measurement.

For the selective measurement of sulfide ions, it is essential to prevent the oxidation of the sample. Therefore, the main component of sulfide antioxidant buffer (SAOB) solution used (24) for the sulfide measurement is the antioxidant, ascorbic acid. SAOB solution is prepared with a glycine-sodium hydroxide buffer for adjusting the ionic strength; its pH is 13.5. Other metal-ligand systems used as metal buffers for calibration of ion-selective electrodes are presented in Table 3.

In the case of metal buffers the equilibrium concentration of a metal ion is readily calculated on the basis of the relevant equilibrium. It has been shown (17) that a relation of type (4) is valid for pM calculation:

$$pM = \log \beta'_n + \log \alpha_M + n\log(C_L - nC_M) - \log C_M \qquad (4)$$

where:

$$\beta'_n = [ML'_n]/[M'][L']^n = \beta_n \cdot \frac{\alpha_{MLn}}{\alpha_M \alpha^n_L}$$

$$C_M = [ML'_n]; \quad M' = \alpha_M[M]; \quad L' = C_L - nC_M$$

$$\alpha_M = ([M] + [MOH] + [M(OH)_2] + ...)/[M]$$

$$\alpha_L = ([L] + [HL] + [H_2L] + ...)/[L]$$

$$\alpha_{MLn} = ([ML_n] + [MHL_n] + [M(OH)L_n] + ...)/[ML_n]$$

(The α-coefficients are taken from tables published elsewhere; ligand L is assumed to be in a large excess).

TABLE 3: Some metal-ligand systems used as metal buffers (16)

Metal ion	Ligand	pM range	Ref.
Cu(II)	EDTA	10.72-18.31	25
	NTA	6.91-13.05	25
	[12]one N*₄	23-26	26
	[16]one N*₄	20-22	26
	NH_3	9.55-11.92	27
	Ethylenediamine	3-19	28
Cd(II)	EDTA	8.46-16.12	29
	NTA	4.10-10.05	29
	IDA	4-11	30
Pb(II)	EDTA	9.84-18.56	31
	NTA	5.78-11.91	31
Ca(II)	NTA	3.6-7.3	32
	EDTA	5.0-7.7	33
	EDTA	4.4-10.28	34
	NTA	3.6-6.63	34
	EGTA+HEDTA+NTA	3.3-8.4	35

*Macrocylic polyamines

EDTA, Ethylenediaminetetraacetic acid
EGTA, Oxybis(ethylenenitrilo)tetraacetic acid
HEDTA, *N*'-(2-Hydroxyethyl)ethylenediamine-*N*,*N*,*N*'-triacetic acid
IDA, Iminodiacetic acid
NTA, Nitrilotriacetic acid

In practical application of metal buffers it is advantageous to use systems when n=1, because of avoiding often incomplete stepwise complexation and because the effect of dilution which disappears when n equals unity. The maximal buffer capacity is attained when $C_n = (C_L - n\ C_M)$ (15,17).

Details on theoretical as well as practical considerations on metal buffers in ion-selective electrodes calibration may be found in Refs. 15, 16 and 36.

Comparison of calibrations by metal ion buffers with serial dilutions

The conventional calibration of an ISE by serial dilutions, typically at constant ionic strength of an inert salt, will provide, at best, a lower response limit set by the sensor solubility. For example, serial dilution of KCl or $AgNO_3$ leads to a common low level response given by the solubility of the AgCl membrane. Tests of this result are best done using serial dilutions with addition of powdered AgCl to maintain saturation. Similarly, the lower level of Ca^{2+} response of a liquid ion exchanger is set by the

solubility of the calcium dialkyl phosphate ion exchanger salt that will escape from the electrode into Ca^{2+} free solutions. When the low limit response is set by solubility of the membrane components, approach by serial dilutions of either soluble cation standards or soluble anion standards can only occur when the electrode is reversible to both species. In the LaF_3 electrode case, the response to soluble La^{3+} salts is irreversible so the lower limit is tested only by F^- dilutions.

Serial dilution lower limits of responses are not the same as the detection limits determined by metal ion buffers. This difference occurs mainly when ion exchange kinetics and dissolution kinetics are slow. But also the detection limit may be found only from buffers because reliable very dilute solutions cannot be made by simple dilution. In the F^- case, the detection limit from fluoride buffers is about two orders of magnitude smaller than the serial dilution lower limit (14).

Use of dilution and flow methods

The so-called "liter-beaker method" (37) is based on the application of a measuring cell of great volume (about one liter). In the calibration, the measuring and the reference electrodes are placed into the measuring cell containing an appropriate electrolyte. The concentrated standard solution in increasing volume increments is added to the solution, then, after each mixing, the value of e. m. f. is measured. The calibration curve is plotted on the basis of the concentration calculated by considering the dilution.

A new continuous calibration process was proposed by Pungor and co-workers (38). In this method, the measuring cell is a vessel of constant volume supplied with a stirrer and inflow and overflow channels (Fig. 1). Prior to the calibration, the whole vessel is filled with the standard solution of the highest concentration intended to be measured. Then, with continuous measuring of the e. m. f. of the cell, an inert background electrolyte (TISAB, CAB, SOAB, etc.) is brought into the cell at a constant volummetric rate. As a consequence, solutions leave the cell at the same rate. In this way, the concentration of the determinand is gradually changing with time. The relationship between the concentration (C) and the time (t) is given by:

$$C = C_o e^{-(vt/w)} \qquad (5)$$

where C_o is the initial concentration, v is the rate of volume flow, and w is the volume of the container (constant). From this:

$$\log C = \log C_o - \frac{vt}{2.303w} \qquad (6)$$

As can be seen, if a constant volummetric rate is maintained, then a linearity exists between the log of the concentration of the solution in the cell and the time elapsed since starting the dilution.
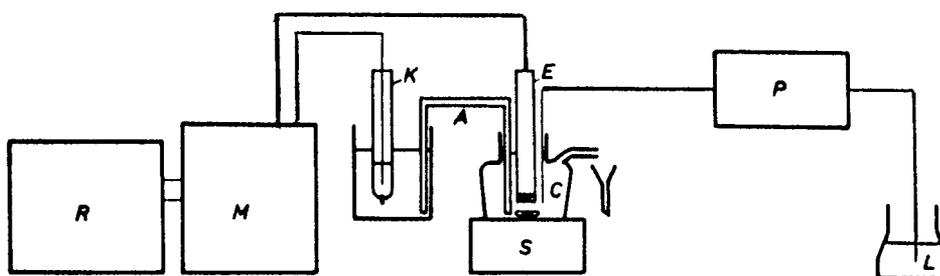

Fig. 1. Schematic diagram of the apparatus used for continuous calibration: R - recording apparatus; M - pH/mV - meter; K - reference electrode; A - electrolyte bridge; E - indicator electrode; C - cell with overflow; S - magnetic stirrer; P - peristaltic pump; L - flask containing the "washing" solution (From Ref. 38, with permission).

So the E vs. t values recorded during the continuous calibration, without changing the ionic strength of the solution in the measuring cell, can be simply converted into a calibration curve of E vs. log C by the appropriate transformation of the scale of the t axis.

The precision of the method depends on how accurately the flow rate is constant. It is obvious that the continuous calibration method can be used only if the response of the electrode is sufficiently fast to follow reliably he concentration change occurring in the cell.

Preparation of calibration plots

When preparing the calibration curve, the standards are chosen so that the concentration of the sample would be in the range covered by the standards. It is expedient to repeat the calibration three times at least, first measuring more and more diluted standards, then taking them in the opposite order toward the more highly concentrated standard solutions; finally, the first step is repeated (19). The calibration curve is prepared by averaging and plotting the measured values against the concentration or calculating the parameters of the curve by regression analysis to reduce inaccuracy deriving from the drift or hysteresis.

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