Glass Electrode Calibration for Use in the Voltammetric Determination of Stability Constants under Extreme Acidic Conditions

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ABSTRACT

A glass electrode (GE) can be successfully employed to measure pH in the study of metal-ligand equilibria by voltammetry at extremely low pH (between 0 and 2); two consecutive strong acid–strong base titrations involving different base concentrations (recommended to avoid corrosion of the GE in very basic solutions) are best suited to establish the response parameters of a GE. A novel approach of using a combined linear and binomial GE calibration was developed; this procedure allows measurements between pH 0 and 2 with uncertainty better than ±0.01 pH unit. From an extensive error analysis, it has been established that the uncertainties of about ±0.5 mV in the response slope and ±1.3 mV in $E^{o'}$ might result in an absolute error in pH of about 0.02 which should not generate errors larger than 0.3 % in optimized stability constants (as log K values) determined by voltammetry at extremely low pH. A test of GE suitability for the study of metal complexes by voltammetry is also proposed; it should be implemented only for suspect electrodes that show response parameters outside the limits recommended in this work.

1. Introduction

The glass electrode (GE) is the most commonly used measuring device employed in analytical (clinical, biological, environmental, industrial, etc.) and research laboratories for numerous applications where information on the hydrogen ion concentration is required. Specifications of commercial high-quality electrodes often suggest a full-range linear response of GE, between pH 0–14. However, it is well established that (i) most accurate measurements of the free proton concentration can only be achieved in the pH range between 2 and 12, and (ii) the departure of GE response from linearity below pH of about 2 makes the glass electrode an unreliable and not recommended sensor in studying metal-ligand equilibria. This is unfortunate because there is a need for more work in this area in order extensively to study highly acidic metal ions, such as Bi(III), Sb(III), or metal-ligand systems where complexation occurs already in 1 mol L^{-1} acidic solutions. Although the hydrogen electrode is considered as the 'ultimate' standard for the determination of pH values, there are many experimental difficulties associated with its use and hence the GE is conveniently used instead in most cases.[1]

Regardless of the analytical technique employed (be it potentiometry, voltammetry, spectrophotometry, NMR, etc.) in studies involving ligands of the form H_nL, the change in the proton concentration or activity must be monitored. Conveniently, concentration rather than activity is measured.[2–5] This is because, even though various methods have been used to estimate activity coefficients, simplifying assumptions always need to be made[6–15] and regardless of the value used, it carries some uncertainty.

The accurate calibration of a GE, particularly in formation constant determinations, is critical in producing reliable results and there has been much debate on how best to do this.[16–18] The recommended GE calibration procedure involves strong acid–strong base titration performed in the pH range between 2 and 12 at constant ionic strength. Two other approaches for calibrating the GE could be considered, namely the titration of (i) a background electrolyte, or (ii) a weak electrolyte solution (acid or base) by a strong base or acid,[19] with the need for protonation constants of the weak electrolyte employed to be very accurately known.[20] Each of the mentioned calibration approaches has been discussed in detail by Brandariz *et al.*,[19] but neither of these is suitable for low pH studies.

Because stability and protonation constants determined below pH 2 might carry significant errors, regardless of the analytical technique used,[4,5] usually they are not included in critically selected databases.[21] These errors are not only due to uncertainty related to diffusion junction potentials. In the case of glass electrode potentiometry (GEP) the main source of error would most likely be due to the fact that the mass-balance equation (MBE) for the total hydrogen ion concentration H_T must be solved to obtain the free proton concentration. The change in the free proton concentration must predominantly be due to the deprotonation of the ligand involved in complex formation reactions. In GEP, a typical ligand concentration is 10^{-3}–10^{-2} mol L^{-1} as the ligand must not significantly contribute to the ionic strength of a sample solution. It is obvious that the higher the ligand concentration the more accurate the results should be, but unfortunately experimentally achievable concentrations are often lower due to the limited solubility of a ligand or its complexes as well as the limited availability of a ligand.

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It is clear that GEP cannot be used for the determination of stability constants at very low pH values due to MBE and experimental limitations. In the case of voltammetric studies of metal-ligand systems, we are not solely reliant on pH measurements. Voltammetric data (shift in the signal, ΔE, and the normalized change in the signal intensity) are combined with pH readings. Since in voltammetric studies MBEs for only the total metal (M_T) and total ligand (L_T) concentrations are solved,[22–24] the metal-ligand equilibria studies can, in principle, be undertaken in solutions below pH 2. This is because the concentration of hydrogen ions, being several orders of magnitude larger than that of a metal ion, does not cause analytical or theoretical limitations when voltammetry (or polarography) is employed.

In this work we focus on the most appropriate and rigorous use of the GE and interpretation of its response in metal-ligand equilibria studies by voltammetry under extreme acidic conditions. The aim of this work is to (i) develop a procedure optimally to calibrate the GE used in polarographic metal-ligand equilibria studies, (ii) design a GE performance test and criteria needed to assess the suitability of a GE for such studies, and (iii) evaluate expected uncertainties introduced by pH measurements in determined stability constants by polarography.

2. Basic Equations and Procedures for Calibration of GE

The overall potential measured, when using a GE and a reference electrode (RE) with a liquid junction, consists of a combination of potentials

$$E_{cell} = E_r + E_j + E_g , \tag{1}$$

where E_r is the combined potential due to the internal and external REs used. These REs should have a potential that is similar in magnitude but opposite in sign (provided the two REs are of the same type) and remains constant throughout a titration. E_j is the diffusion junction potential that is formed between the external RE solution and the test solution. E_g is the potential across the glass membrane and includes the asymmetry potential, E_{as}. The cell potential expression (Eq. 1) can be extended to reflect the pH dependence,[2,17,19,25] as shown in Eq. 2 and 3.

$$E_{cell} = E_r + E_j + E_g^o + k(RT/F)\ln(\gamma_{H^+}[H^+]) \tag{2}$$

$$E_g^o = E_r + E_{as} - k(RT/F)\ln a_{H^+,int} \tag{3}$$

where $[H^+]$ and γ_{H^+} are the concentration and activity coefficient, respectively, of the hydrogen ion in a sample, $a_{H^+,int}$ is the activity of the hydrogen ion in the inner reference system, k denotes the electromotive efficiency of the glass membrane showing how closely the electrode exhibits behaviour predicted by the Nernst equation. Usually, $k < 1$[26,27] and in commercial pH meters is expressed as a percentage of a theoretical slope (59.16 mV/pH at 25 °C) of a true potentiometric sensor. The value of k is dependent on the ionic strength of the solution but is approximately equal for all types of glass simply because the inner and outer surfaces of the glass membrane have the same composition and any influence by the glass composition cancels out.[27] Although the asymmetry potential can drift with time, it does not fluctuate suddenly, thus can often be assumed to be stable throughout an experiment.[1] For solutions of constant ionic strength, the constant terms can be collected into a single term, E_{const}, as shown in Eq. 4.

$$E_{const} = E_r + E_g^o + k(RT/F)\ln(\gamma_{H^+}) \tag{4}$$

and hence

$$E_{cell} = E_{const} + E_j + k(RT/F)\ln[H^+] \tag{5}$$

From Eq. 5 it follows that the measured potential varies predominantly with (i) the hydrogen ion concentration and (ii) the diffusion junction potential. The value of the junction potential is practically constant between pH 2 and 12, but unfortunately its magnitude varies significantly outside this range. It means that, strictly speaking, Eq. 5 does not hold under the experimental conditions employed and one cannot theoretically predict the exact variation in measured potential of the GE. The only way forward is to develop an analytical procedure that would compensate the unavoidable errors and estimate the free proton concentration with an acceptable accuracy for this application.

In the experimental procedure employed in this work, the ionic strength varies between 0.5 and 0.25 mol L^{-1} and the ionic medium composition also changes somewhat at lowest pH values. We have not used a concentrated neutral electrolyte to minimize the change in ionic strength because our main interest is in results that could be relevant to the solution chemistry of metal ions of possible medicinal significance. Fortunately, computed stability constants should not differ significantly as deduced from published data[21] at ionic strength between 0.5 and 0.1 mol L^{-1}. Also uncertainties in computed stability constants from voltammetric experiments when performed under extreme acidic conditions should be of a similar magnitude compared with errors due to variation in ionic strength. It is impossible to maintain constancy in solution composition when one starts recording data at pH close to zero and continues to pH values much above 2 (the proton concentration must vary by orders of magnitude from about 1 mol L^{-1} down to 10^{-pH} mol L^{-1}).

It is generally recommended that the GE be calibrated over narrow pH ranges, such as from 2.3–2.9 to 10.8–11.3, to obtain a theoretically expected linear response.[2,4,19,25] These ranges correspond to low acid and base concentrations of 1.5×10^{-3} to 5×10^{-3} mol L^{-1}, thus avoiding significant junction potential and alkaline errors. Unfortunately, the linear correlations for the acidic and the basic regions do not coincide[20] and due to experimental errors should not be extrapolated to extreme pH regions. Frequently, the correlation coefficient, R^2, is found to be 1.0000 for the linear fit across the entire pH region and it is only on closer inspection of the collected data that the deviations at extreme pH values are noticed. It will be demonstrated that the correlation coefficient is not rigorous enough in assessing either the GE calibration or its performance.

3. Experimental

3.1. Materials

All reagents used were of analytical grade (Merck, Darmstadt, Germany). Water was deionized using a Milli-Q water purification unit. Alkaline solutions of NaOH or KOH were standardized against potassium hydrogen phthalate; HNO$_3$ or HCl solutions were standardized against these alkaline solutions, using phenolphthalein to indicate the end point. Hydroxide solutions were protected from atmospheric CO$_2$ by using Ascarite® in a drying tube. All stock solutions, if required, were adjusted to ionic strength of 0.5 mol L^{-1}.

3.2. Instrumentation

Experiments were carried out using an automated setup[28] run under Labview software interfaced to Metrohm (Herisau, Switzerland) 663 VA stand with a 728 stirrer, a 713 pH meter, and a 765 Dosimat. A water-jacketed titration vessel was used and the temperature was maintained at 25.0 ± 0.1 °C by a water bath with a Labcon (Johannesburg, South Africa) CPE100 thermostat. A Metrohm GE (6.0234.100) was used, which consisted of a lithia

glass membrane to reduce alkaline errors, and Ag/AgCl reference electrode with 3 mol L⁻¹ KCl filling solution. Solutions were deoxygenated by purging with UHP (99.999 %) nitrogen.

3.3. Procedure

In general, 25.00 mL of acid solution was purged for 20 min before the titration. Stirring and purging continued throughout the GE calibration operation to simulate the polarographic experiment. The acidic solution was then titrated with base solution, of the same concentration, added in 0.50 mL steps. To ensure that the test solution and the electrode had equilibrated, the potential was measured at 2 s intervals. Only when nine out of ten potential readings were the same, was the final reading of the GE potential recorded. Hydrogen ion concentration was calculated after each titrant addition. The pK_w used was 13.74 as is reported for 0.5 mol L⁻¹ ionic strength at 25 °C.[21] The calibration curve was obtained by plotting the GE potential against the calculated pH. It has been reported[20,25] that deviations from linearity in the low buffer region occur. Regardless of the cause, we observed the same effect and hence data points close to the equivalence point were omitted from all calibration graphs in this work.

4. Results and Discussion

The chemistry of highly acidic metal ions, such as Bi(III) or Sb(III), is not well known due to difficulties in studying their complexes; experiments must be performed at extremely low pH where GEP, the most commonly used analytical technique in the field, cannot be used at all. Since we employ a GE together with voltammetric measurements in the study of metal-ligand equilibria, it is of paramount importance that the calibration of the GE reflects its true behaviour under the same experimental conditions under which it is used in the polarographic experiments. This would include variations due to changes in ionic strength, medium composition, junction potentials and other errors associated with the glass membrane. There are two major challenges, namely (i) how to calibrate the GE between pH 0 and 2 as there is no recommended procedure available for this purpose, and (ii) how to evaluate the GE performance and reproducibility in order to decide on the suitability of the GE in the study of metal complexes at extremely low pH values. Moreover, since somewhat increased uncertainty in measured parameters is expected, it is of utmost importance to realize the significance of experimental errors and their influence on computed stability constants.

4.1. Strong Acid-Strong Base Titration; Sodium Medium (H,Na)NO₃

GE calibration, employing the titration of 0.5 mol L⁻¹ HNO₃ by a 0.5 mol L⁻¹ NaOH solution added in 0.5 mL steps, produced data points in the pH ranges from 0.3–1.5 to 12.2–13.0. This is far from the recommended pH ranges[2,4,19,25,29] and strongly overlaps with regions where E_j and alkaline errors become significant – see crosses in Fig. S1, Supplementary Material. These errors result in curvature of the calibration graph in both the acidic and basic regions; they are not clearly seen in Fig. S1 because the graph covers the entire pH range investigated. Since polarographic studies start at pH of about 0.3 (0.5 mol L⁻¹ acid solution) we questioned whether fitting a linear function using the two pH ranges would adequately describe the GE response over the entire pH range (i.e. between pH 0.3 and 13.0). This was tested by comparing three sets of data generated from titrating HNO₃ with NaOH of the same analytical concentrations of 0.5, 0.01 or 0.005 mol L⁻¹; where required, the initial acid sample solution or

the titrant solution was adjusted to ionic strength of 0.5 mol L⁻¹. The response slope and $E^{\circ\prime}$ obtained from linear calibrations in these three media are given in Table S1, Supplementary Material. The departure from linearity of the GE response was tested by removing some experimental points in 0.1 pH steps from the data set obtained in the 0.3 to 13.0 pH range. From each reduced data set a pH was calculated at 250 mV and –250 mV, where E_j should be negligible. We found that removing experimental data between pH 0.6 and 12.8 changed the calculated pH values at 250 mV and –250 mV by less than 0.01 pH unit. Thus the experimental data between pH 0.6 and 12.8 were retained – the reduced data set obtained for 0.5 mol L⁻¹ acid and base concentrations is indicated by asterisks in Table S1. The overall electrode performance (Fig. S1) in the entire investigated pH range can be evaluated from the average response slope of –58.58 ± 0.08 mV per log unit, or average $E^{\circ\prime} = 408.0 ± 1.3$ mV obtained in sodium medium. Similar stability in the response slope is also observed in potassium medium (H,K)NO₃ (see Table S1). As will be discussed in more detail below, this kind of GE performance can be regarded as excellent when used in the study of metal-ligand equilibria by voltammetry. It is important to realize that this pH range (here it was from 0.6 to 12.8) must be established experimentally for each glass electrode on regular bases as the GE response depends not only on the quality of the electrode used but also varies with time due to the exposure of a glass membrane to harsh experimental conditions.

To compare the response of the electrode for each molarity of acid and base investigated, linear calibration plots were extrapolated to the widest pH range (0.3–13.0). Using the response slopes and $E^{\circ\prime}$ values from Table S1, pH values at selected potentials were calculated and are given in Table 1. Note that the procedure applied here is the same as that used in studying metal-ligand equilibria; the concentration of free protons is calculated from the electrode calibration plot. Differences in the calculated pH values of about 0.04–0.05 and 0.03 pH unit are observed at the lowest and neutral pH values, respectively. This could be regarded as totally negligible in most biological studies. For illustration purposes, the calibration data sets obtained for 0.5 mol L⁻¹ (crosses, dashed line) and 0.01 mol L⁻¹ (circles, solid line extended over entire pH range) (H,Na)NO₃ solutions are shown in Figs. 1 and S2. It is seen that the dashed and solid trace lines coincide well only at high pH values (Fig. S2). The difference in pH between dashed and solid trace lines is about 0.05 pH unit at low pH values (Fig. 1). For both calibration plots (dashed and solid lines) as well as when both data sets were combined, $R^2 = 1.0000$ was obtained which is misleading when accuracy in measurement of pH is concerned.

4.2. Significance of Errors in pH

M-L Equilibria by GEP: To understand the significance of these observed differences, as an example, the error of 0.04 pH unit has been analyzed. We assumed (i) typical experimental conditions, namely L_T and $M_T = 1 \times 10^{-3}$ mol L⁻¹, (ii) that ligand is only present as H₂L, and (iii) that the metal ion is fully in a ML form at pH = 2.70 (about 250 mV), meaning that the formation of ML has already started in 0.1 mol L⁻¹ acid solution (for simplicity we ignored dilution). From the reaction H₂L + M = ML + 2H (charges omitted), it follows that the complexation reaction resulted in a change in the proton concentration by 2×10^{-3} mol L⁻¹. On the other hand, the absolute error in the proton concentration caused by uncertainty of ±0.02 pH unit at pH 2.70 is

$$(2.089 \times 10^{-3})_{pH=2.68} - (1.905 \times 10^{-3})_{pH=2.72} =$$
$$1.838 \times 10^{-4} \text{ mol L}^{-1} \text{ H}^+ \tag{6}$$

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Table 1 Evaluation of GE performance in the entire pH range. pH was calculated at indicated potentials from linear calibration plots (response slope and $E^{\circ\prime}$ given in Table S1) obtained from the titration of HNO_3 with either 0.005, 0.1 or 0.5 mol L^{-1} NaOH at 25 °C. For each titration, acid and base solutions had the same concentration. Where necessary, titrant solutions and initial acid sample solutions were adjusted to ionic strength of 0.5 mol L^{-1}.

| | [NaOH]/mol L^{-1} | | | | | | |
| | 0.005 | 0.01 | 0.5 | 0.5 [a] | | | |
E/mV	Calculated pH				Spread	Average	Std. dev.
400	0.149	0.162	0.115	0.122	0.047	0.137	0.022
350	1.001	1.015	0.970	0.976	0.045	0.991	0.021
300	1.854	1.867	1.825	1.830	0.042	1.844	0.020
250	2.706	2.720	2.680	2.684	0.040	2.698	0.019
200	3.559	3.573	3.535	3.538	0.038	3.551	0.018
100	5.264	5.278	5.245	5.246	0.033	5.258	0.016
0	6.969	6.984	6.955	6.954	0.030	6.966	0.014
−100	8.674	8.689	8.665	8.662	0.027	8.673	0.012
−200	10.379	10.394	10.376	10.371	0.023	10.380	0.010
−250	11.232	11.247	11.231	11.225	0.022	11.234	0.009
−300	12.084	12.100	12.086	12.079	0.021	12.087	0.009
−350	12.937	12.952	12.941	12.933	0.019	12.941	0.008

[a] Some experimental points were removed where largest curvature in the electrode response was observed.

This error value constitutes 9.2 % of the protons generated from the complexation reaction and must be regarded as totally unacceptable. With this large uncertainty in the free proton concentration, erroneous M-L models could be generated from the experimental GEP data, or optimization operations could even fail because the MBE for the total hydrogen ion concentration H_T would have to be solved. The situation would become much worse if the degree of formation of ML at that pH was smaller, i.e. the ML complex started to form at higher pH. This simplified example clearly indicates how sensitive GEP-based methodology is towards the smallest errors in the evaluation of pH; experimentally one must keep errors to the third decimal place (preferably within 0.002 pH unit).

M-L Equilibria by Polarography: The polarography-based methodology used to determine stability constants should be far less sensitive to errors in pH values because (i) MBEs only for M_T and L_T are solved and (ii) one works with a large excess of a ligand.

The measured pH is used to calculate the free ligand concentration that is required to calculate stability constants. Suppose that at pH 2.70 the ligand is present only as H_2L and M is fully in a ML form as above, that $L_T = 1 \times 10^{-3}$ mol L^{-1}, but $M_T = 1 \times 10^{-5}$ mol L^{-1}, i.e. $L_T:M_T = 100$. Then the complex formation reaction generates 2×10^{-5} mol L^{-1} of free protons in the solution, which translates to only about 1 % of the total free proton concentration at pH = 2.70 where $[H^+] = 2 \times 10^{-3}$ mol L^{-1}. This means that, in this case, the contribution of the complexation reaction to the total proton concentration under typical polarographic conditions ($L_T:M_T = 100$) might be regarded as negligible. It therefore follows that the main source of error in estimating the free proton concentration comes directly from the GE measurement. The influence of a GE-generated error of ±0.02 pH unit at pH 2.70 on the accuracy of a computed stability constant determined by polarography is of interest now.

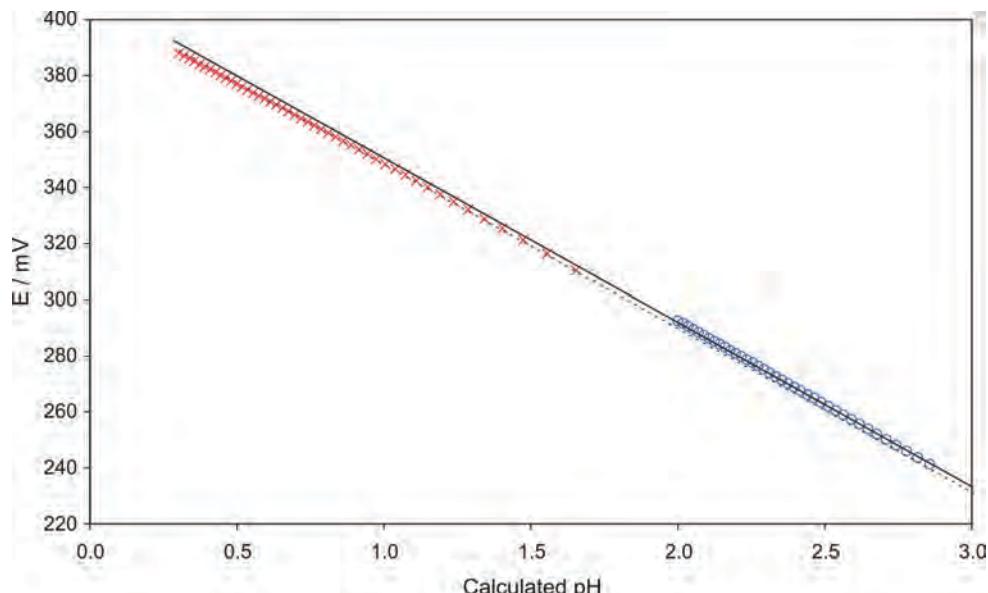*Case 1.* To meet experimental conditions assumed above, the

Figure 1 Acidic region (seen in Fig. S1) of GE calibration data collected from two titrations using the same glass electrode. Titration of 0.5 or 0.01 mol L^{-1} HNO_3 by 0.5 mol L^{-1} (×, dashed line) and 0.01 mol L^{-1} (○, solid line trace) NaOH, respectively. Calibration plot obtained from 0.01 mol L^{-1} HNO_3 and NaOH standardized solutions (circles, solid line trace) was extrapolated to the entire pH range.

Table 2 Evaluation of GE performance in the entire pH range. pH was calculated at indicated potentials from linear calibration plots (response slope and $E^{\circ'}$ given in Table S1) obtained from the titration of HNO_3 with either 0.1 (ionic strength of 0.5 mol L^{-1}) or 0.5 mol L^{-1} KOH at 25 °C. For each titration, acid and base solutions had the same concentration.

| | [KOH]/mol L^{-1} | | | | | |
| | 0.01 | 0.5 | 0.5 [a] | | | |
E/mV	Calculated pH			Spread	Average	Std. dev.
400	0.056	0.041	0.044	0.015	0.047	0.008
350	0.906	0.886	0.889	0.020	0.894	0.011
300	1.754	1.731	1.733	0.023	1.739	0.013
250	2.577	2.601	2.578	0.024	2.585	0.014
200	3.448	3.422	3.423	0.026	3.431	0.015
100	5.143	5.113	5.113	0.030	5.123	0.017
0	6.837	6.803	6.802	0.035	6.814	0.020
–100	8.532	8.494	8.492	0.040	8.506	0.023
–200	10.227	10.184	10.182	0.045	10.198	0.025
–250	11.074	11.029	11.027	0.047	11.043	0.027
–300	11.921	11.875	11.871	0.050	11.889	0.028
–350	12.768	12.720	12.716	0.052	12.735	0.029

[a] Some experimental points were removed where largest curvature in the electrode response was observed.

stepwise ligand protonation constants, as log *K*, were set to 12.00, 7.00 and 0.50, and the stability of the ML complex, as log K_{ML}, to 19.00. This resulted in 99.60 % of the total metal ion being in the form of ML and 98.38 % of the total ligand being in the form of H_2L (1 % of the ligand is involved in ML). Next, the influence of an error in pH on the computed stability constant was tested. A change in pH from 2.70 to 2.68 resulted in a decrease of the percentage of ML from about 99.60 to 99.56 %. To bring the percentage to its initial value it was necessary to increase log K_{ML} from 19.00 to 19.04. The difference of 0.04 log unit in the log K_{ML} value is equivalent to 0.22 % error, a value that can be regarded as much smaller than expected from typical experimental errors in the study of metal-ligand equilibria, not only by polarography. A similar procedure was followed for pH = 2.72 and the log K_{ML} value had to be decreased by 0.04 log unit to bring the percentage to its original value.

Case 2. We assumed that an error of ±1 % in the computed log K_{ML} value from polarographic experiments can be regarded as rather small and possibly 'tolerable' under the assumed extreme conditions. In our opinion, it is far more desirable and informative to have a metal-ligand model that includes stability constants with 1 % uncertainty, than to have no information at all about the metal-ligand system of interest. For the same conditions as in *Case 1,* we set the log K_{ML} value to either 19.19 or 18.81 and calculated the percentage of ML at pH 2.70 to be 99.739 and 99.377 %, respectively. MBEs for M_T and L_T were then solved at different pH values to find the pH at which the percentage of ML would again be about 99.60 %, as obtained for the error-free determination at pH = 2.70. The pH had to be changed to 2.60 and 2.79 to obtain percentages of ML of 99.586 and 99.587 % for log K_{ML} set to 19.19 and 18.81, respectively. This means that an absolute error in pH of ±0.10 was required to generate an error in computed log K_{ML} of ±1 %; this can be regarded as a very large and rather unexpected uncertainty in pH measurements, even at the extreme conditions discussed in this work.

Case 3. The above simplified but informative examples indicate how rigid polarographic determination of stability constants is where experimental errors in the pH measurements are concerned. However, they do not explain why this technique is so resilient to experimental errors. The same conditions as in *Case 1* above have been assumed again. From solving MBEs at pH 2.68, 2.70 and 2.72 (i.e. a tolerable error of ±0.02 in

voltammetric experiments) one obtains [L] = 2.253×10^{-17}, 2.471×10^{-17} and 2.710×10^{-17} mol L^{-1}, respectively. This constitutes errors in [L] of about –8.8 and 9.7 % at pH = 2.68 and 2.72, respectively, when compared with the expected value of [L] at the error-free pH = 2.70. Similarly, we obtain [M] = 4.419×10^{-8}, 4.030×10^{-8} and 3.676×10^{-8} mol L^{-1}, at pH = 2.68, 2.70 and 2.72, respectively. Here, this translates to errors in [M] of 9.7 and –8.8 % at pH = 2.68 and 2.72, respectively. Even though these errors in [L] and [M] are rather large, they have a small impact on the computed stability constant because the term [M] × [L] (part of an expression used to calculate the stability constant of the ML complex) remains almost constant. It is seen that with an increase in pH, [M] decreases and [L] increases by similar magnitudes and vice versa for a decrease in pH. The changes in [ML] in the pH range considered were 9.956×10^{-6}, 9.960×10^{-6} and 9.963×10^{-6} mol L^{-1} at pH = 2.68, 2.70 and 2.72, respectively, and for any practical purposes can be considered as constant. It is important to add here that when a polarographic experiment is conducted and if a fully dynamic and labile M-L system is present then all metal-containing species are reduced simultaneously. Therefore, the variations in [M] and [ML] do not change significantly the overall reduction current and would not affect the data interpretation and computed stability constants. In addition, the variation in the current intensity is far less significant than the shift in potential of the recorded signal when polarography is employed to study labile metal-ligand systems; this is also why it is not necessary to use standardized metal ion or ligand solutions.

Clearly, polarography must be seriously considered for studies in highly acidic media. It is certainly superior to GEP under these conditions as refined stability constants should have acceptable uncertainty (well below 1 % in absolute error) if one could assure pH measurements with accuracy of about 0.02 pH unit.

4.3. Strong Acid–Strong Base Titration; Potassium Medium (H,K)NO₃

A similar set of experiments (as described above for a sodium medium) was repeated employing KOH, as pH measurements in potassium medium should exhibit smaller alkaline errors.[17,30–32] When comparing data from 0.01 and 0.5 mol L^{-1} K^+ solutions (see Table 2), larger differences (0.05 pH unit) were observed in a basic region, opposite to that observed for sodium
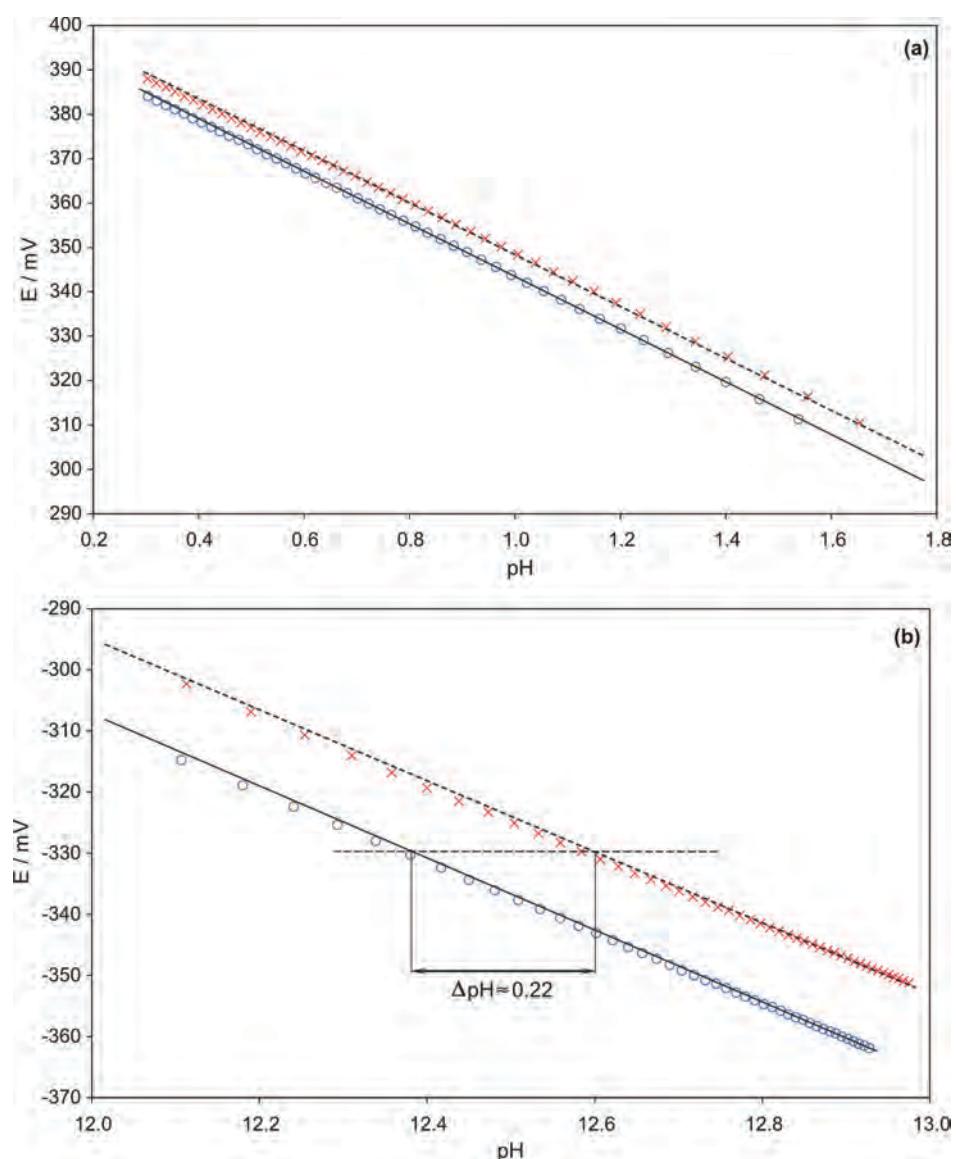
Figure 2 Comparison of calibration data obtained from titrations of 0.5 mol L^{-1} HNO$_3$ by 0.5 mol L^{-1} NaOH ($\times$) and 0.5 mol L^{-1} KOH ($\bigcirc$). Lines indicate fitted regressions obtained for points collected in the entire pH range. Experimental data collected in (**a**) acidic region, (**b**) basic region.

solutions. The response slope of the GE in a potassium medium displayed near theoretical values, but some departure from the theoretical isopotential point was observed and was larger than in the Na$^+$ medium.

For comparison, two calibrations involving 0.5 mol L^{-1} hydroxides of sodium ($\times$) and potassium ($\bigcirc$) are shown in Fig. 2. It can clearly be seen that the response of the same glass membrane was significantly influenced by the presence of different cations, the only difference in the solution composition. The slight decrease in the response slope of the GE in the sodium medium (of about 0.6 mV per pH unit, see Table S1) resulted in a large difference between the two calibration plots, particularly in the basic pH region where, for the same potential value of about –330 mV, the difference in the calculated pH value is about 0.22 pH unit. From this one should draw three important conclusions, namely (i) the GE must be calibrated in the same medium as that used in stability constant determinations, (ii) the use of commercial buffer solutions should be ruled out in the studies of metal-ligand equilibria as rigorous data interpretation is impossible, and (iii) it is imperative to calibrate the GE prior to and after the experiment involving the determination of stability constants to monitor the electrode performance. The change in

the response slope and $E^{o\prime}$ of the calibrations prior to and after the experiment must be carefully evaluated; allowable errors are investigated further in Section 4.4.

4.4. Significance of Errors in GE Response Parameters

It is of interest and importance briefly to analyze the significance of errors in the GE response parameters to estimate their tolerable variations when voltammetric experiments in the study of M-L equilibria are considered. As an example, the response slope and $E^{o\prime}$ of a GE are –58.58 $\pm$ 0.08 mV per pH unit and 408.02 $\pm$ 1.31 mV reported in Table S1 for the calibration of the GE in sodium medium were assumed. Since our main interest is in the low pH range, we first considered errors in the calculated pH caused by uncertainties in these two GE parameters at the potential 350 mV. For $E^{o\prime}$ fixed at 408.02 mV and response slopes of –58.50, –58.58 and –58.64 one obtains 0.992, 0.990 and 0.989 pH, respectively. Taking into account conclusions arrived at in Section 4.2, the observed uncertainty of about $\pm$0.002 pH is of no significance. For pH values of 3, 7 and 12 this uncertainty would increase to $\pm$0.004, $\pm$0.008 and $\pm$0.014 pH, respectively. Let us now assume that uncertainty in the GE response slope has increased more than tenfold, from $\pm$0.08 to $\pm$1.00 mV per

Table 3 Influence of selected calibration data on calculated GE response parameters, slope and $E^{\circ\prime}$. See text for details.

Data subset	A	B	C	D
pH ranges	0.3–2.9 11.6–13.0	0.3–1.5 12.2–13.0	0.6–1.5 12.2–12.8	2.3–2.9 11.6–12.2
Response slope/mV	–58.52 (±0.01)	–58.49 (±0.01)	–58.58 (±0.01)	–58.54 (±0.02)
$E^{\circ\prime}$/mV	406.98 (±0.09)	406.8 (±0.1)	407.38 (±0.08)	406.6 (±0.2)

pH unit; this is a rather large but not unrealistic change in the electrode performance after a long-term experiment. For the same value of $E^{\circ\prime}$ and response slopes of –57.58, –58.58 and –59.58 we obtain pH 1.008, 0.990 and 0.974 (on average 0.991 ± 0.017). Even with 1 mV change in the slope of GE the uncertainty in pH is below ±0.02 and this, as was discussed above, can and possibly should be regarded as tolerable. For pH values of about 3, 7 and 12 this uncertainty would increase to ±0.052, ±0.119 and ±0.206 pH unit, respectively. It follows that if one is interested in voltammetric data only at extremely low pH, say in the pH range between 0.3 and 3, the largest allowable error in the response slope of a glass electrode should be about ±1.00 mV and this can easily be achieved experimentally as demonstrated by the data presented in this work.

A variation in $E^{\circ\prime}$ (408.02 ± 1.31 mV), when the response slope value is fixed at –58.58 mV, is analyzed now at the GE potential of 350 mV. For $E^{\circ\prime}$ = 406.71, 408.02 and 409.33 mV we obtain 0.968, 0.990 and 1.013 pH (on average 0.990 ± 0.022), which is still within tolerable errors in voltammetric experiments, as discussed in Section 4.2. It is important to note that uncertainty in calculated pH of ±0.022, due to uncertainty in $E^{\circ\prime}$ of ±1.31 mV, remains the same at all pH values for a given response slope of GE. To achieve an uncertainty of ± 0.050 in the calculated pH (this is equivalent to an absolute error of 0.1 pH unit and at pH 2.70 under conditions discussed in Section 4.2 it would result in a 1 % error in the computed log K_{ML} value from a voltammetric experiment) the value of $E^{\circ\prime}$ would have to change by about ±3 mV.

The above discussion once more documents the rigidity of voltammetric experiment. For any practical reason and to assure high quality results one would recommend allowable variation in response slope and intercept of GE to be below ±0.5 and ±1.3 mV, respectively, when an experiment is to be conducted at extremely low pH values.

4.5. New Calibration Procedure of GE in Highly Acidic Medium

An attempt was made to generate calibration data in as wide a pH range as possible when titration of 0.5 mol L^{-1} HNO$_3$ by 0.5 mol L^{-1} NaOH was performed. Instead of adding aliquots in 0.5 mL steps throughout the experiment, the volume increment of added base was reduced nearer to the equivalence point. The data collected were divided into several subsets (A to D) and each subset was fitted with a straight line; results obtained are shown in Table 3. It is reasonable to say that the slopes do not seem to differ much if variation in the second decimal place is considered as acceptable. Also values of the intercept are within a small fraction of a mV. All of this strongly suggests exceptional linear response and performance of GE in the entire pH range investigated.

On closer inspection of the collected data, however, a significant deviation from linearity is observed in acidic medium that is of particular interest in this work. It became clear that the well-established procedure involving fitting the data with a linear

function results in averaging of errors in the glass electrode response over the entire pH region. We have decided to divide the acidic region, data subset A, into two parts, the one at larger pH values that could be represented by a linear response (a Nernstian-type response) and the other at the lower pH (between 0.3 and 1.5) that was subsequently fitted with a second order polynomial. In this particular case, the equation of the binomial was found to be $y = -1.87 (\pm0.09) x^2 - 53.5 (\pm0.2)x + 404.32 (\pm0.07)$.

The concept of using two functions for fitting experimental calibration data is presented in Fig. 3, where only data from pH 0.3 to 1.0 are shown. The data from subset C, in the pH range between 0.6 and 12.8, were fitted with a straight line that was extrapolated down to pH 0.3. The difference between the predicted GE response in very acidic medium and experimentally observed data (circles in Fig. 3) increases with a decrease in pH, and it depends on the number of experimental points used in generating the linear GE response.

Both functions were used to calculate pH at selected potentials (see Table 4) and the differences between the two calibrations are indicated as ΔpH. Several conclusions were arrived at from the analysis of data presented in Table 4. The data subset B results in pH values at very low and higher pH ranges being uncertain. In this particular example the average error was close to 0.02 log unit, a value considered as tolerable in Section 4.2. It is important to stress here that these data are produced by an electrode with a performance that can be considered as exceptionally good. Unfortunately, the response parameters of an electrode deteriorate significantly with time when used at extreme pH conditions, which results in a significant increase in the departure from linearity; therefore we do not recommend the use of this subset. Removing points (collected at lowest and highest pH), as was done for the data subset C, seems to generate a well-defined GE characteristic response above pH = 0.8; the differences between the linear and binomial functions are well below 0.01 pH unit. All subsets tested here showed large errors at lowest pH values and this led us to the conclusion that one must use a non-linear curve fitting at the lowest pH values. The binomial calibration must be used at the lowest pH values until the straight line calibration intercepts this function, thereafter the linear equation should be used. Thus a novel approach of using both a binomial and a linear calibration to calculate the pH from measured potential values is proposed here.

Results shown in Tables 3 and 4 were obtained from a new GE that produced an exceptional 'linear' response. As pointed out already, as the length of time an electrode is exposed to extreme acidic and particularly basic conditions increases, its quality deteriorates. It means that the difference between the calculated pH values obtained from the linear and binomial functions increases, resulting in extension of the non-linear curve fitting to higher pH values. Because of that the number of points to be fitted by linear and non-linear functions must be established for each calibration by following the procedures described above.
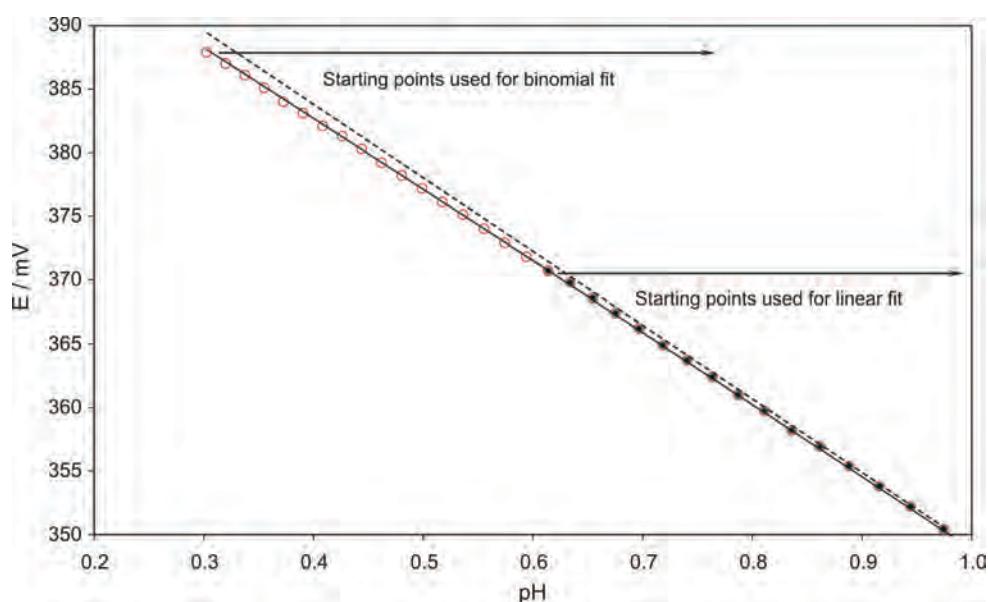
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Figure 3 Deviation between the linear (dashed line, solid circles) and binomial (solid line, all circles) GE calibration functions in the most acidic region. Data were obtained from the titration of 0.5 mol L^{-1} HNO$_3$ by 0.5 mol L^{-1} NaOH.

4.6. GE Calibration Procedure using Two Base Solutions of Different Concentrations

In order to reduce alkaline errors and corrosion of the glass membrane in very basic solutions (as discussed further in Section 4.8), the titration procedure involving two standardized base solutions for the GE calibration was implemented. Titration started in the highly acidic medium (0.5 mol L^{-1} H$^+$) initially employing a base solution of the same concentration. From pH of about 1.5, a more dilute base solution (0.1 mol L^{-1} OH$^-$ adjusted to ionic strength 0.5 mol L^{-1}) was used. An example of such a titration is shown in Figs. S3 and S4 of Supplementary Material. Data collected in the basic region were in the pH range 11.7 to 12.2 compared with pH 12.2 to 13.0 if only a 0.5 mol L^{-1} OH$^-$ solution was used. By avoiding prolonged exposure of GE to pH above 12 a significantly longer lifetime of the GE and better reproducibility of its response can be achieved.

4.7. Titration of an Inert Solution

The benefit of using this procedure is that the response slope of the GE is independent of the concentration of the titrant and small errors in the standardized acid or base concentrations do not affect the slope, especially in the low buffer region.[19,25] Two separate titrations of 0.5 mol L^{-1} NaNO$_3$ by 0.5 mol L^{-1} HNO$_3$ or 0.5 mol L^{-1} NaOH also resulted in significant deviations from linearity at the lowest and highest pH values. When the data from both the titrations were combined into a single plot, the extrapolated acidic linear function coincided with the basic region data fairly well and in some cases the acid region calibration is simply extrapolated to the basic region.[19] As the GE calibration must simulate experimental conditions employed in the metal-ligand equilibrium study as closely as possible, one should consider performing the titration for the study of metal complexes in the same way. However, for several reasons it is preferred to study metal-ligand equilibria starting from low pH, i.e. from the smallest degree of complexation, toward higher pH that promotes complex formation reactions. Reverse titration seems to be an option mainly when (i) highly labile metal-ligand systems are investigated where homogeneous

Table 4 Calculated pH at given potentials using indicated functions fitted to the data points obtained for the indicated data subsets. All GE calibration data are from a single titration (0.5 mol L^{-1} HNO$_3$ titrated with 0.5 mol L^{-1} NaOH). ΔpH is the difference between the calculated pH from the linear and binomial functions. See the text for details.

Data subset	B		C		D		
Functions fitted	Linear		Linear		Linear		Binomial
Calibration pH ranges	0.3–1.5 12.2–13.0		0.6–1.5 12.2–12.8		2.3–2.9 11.6–12.2		0.3–1.5
E/mV	pH	ΔpH	pH	ΔpH	pH	ΔpH	pH
400	0.117	0.036	0.126	0.045	0.114	0.033	0.081
390	0.288	0.023	0.297	0.032	0.284	0.019	0.265
380	0.459	0.011	0.467	0.019	0.455	0.007	0.448
370	0.630	0.002	0.638	0.010	0.626	–0.002	0.628
360	0.801	–0.005	0.809	0.003	0.797	–0.009	0.806
350	0.972	–0.010	0.979	–0.003	0.968	–0.014	0.982
340	1.143	–0.013	1.150	–0.006	1.138	–0.019	1.156
330	1.314	–0.014	1.321	–0.007	1.309	–0.019	1.328
320	1.485	–0.013	1.492	–0.006	1.480	–0.018	1.498
310	1.656	–0.010	1.662	–0.004	1.651	–0.015	1.666
300	1.827	–0.005	1.833	0.001	1.822	–0.010	1.832

Table 5 Comparison of slopes calculated separately from data in the basic and acidic regions for 'good' and 'bad' GE. See the text for details.

pH region	Basic Region			Acidic Region		
	12.2–13.0	12.2–12.8	Δslope	0.3–1.5	0.6–1.5	Δslope
GE1 – 'good'						
Slope for 'new' GE/mV	–55.7	–56.9	1.2	–57.5	–57.9	0.4
Slope for well-used GE/mV	–53.6	–56.4	2.8	–57.8	–58.3	0.6
Δslope	2.1	0.5		–0.3	–0.4	
GE2 – 'bad'						
Slope/mV	–51.9	–53.3	1.4	–57.3	–58.0	0.7

kinetics is very fast, (ii) there is no problem associated with limited solubility of a ligand or complexes formed, and (iii) no hydrolysis of metal ions occurs. Hydrolysis is often present when highly acidic metal ions, such as Bi(III), are of interest and it is simply impossible to start titration above pH 1. Thus the titration of a strong acid by a strong base discussed in this work appears to be most suitable and possibly the only analytical procedure available in acquiring data at very low pH.

4.8. Evaluation of Glass Electrode Performance

It is known that corrosion of the glass surface takes place in solutions with pH greater than about 9. It has been suggested that $H_2SiO_3 + NaOH = NaHSiO_3 + H_2O$ is the surface reaction occurring between the hydrous silica and sodium hydroxide.[1] In this study, the slope for the basic region decreased significantly as the GE was progressively used, whereas the acidic region showed no significant changes.

To evaluate the long-term performance of the GE we analyzed several calibration data sets acquired over a period of time that involved titrations of 0.5 mol L^{-1} H^+ solutions by 0.5 mol L^{-1} OH^- titrant; selected results are shown in Table 5. The electrode marked as GE1 performed well and is called a 'good' electrode. GE2 represents a poorly performing electrode that requires reconditioning and is further referred to as a 'bad' electrode. The extended linear correlations for data collected in the very basic pH region for GE1 when it could be characterized as a fairly 'new' (part a) and as a 'well-used' (part b) GE are shown in Fig. 4 Triangles and circles seen in Fig. 4 represent data collected in the pH regions 0.3 to 1.5 and 12.2 to 13.0, respectively. The linear correlations for the acidic and the basic regions do not coincide. Interestingly, the correlation coefficient R^2 for the overall plot (with acidic and basic data fitted together) is 1.0000, a value which does not indicate the discrepancy discussed here. It is apparent from Fig. 3 that the overall linear calibration does not provide adequate information on the glass membrane condition as the overall response slopes for 'new' and 'well-used' electrode GE1 were 58.6 and 58.5 mV per log unit, respectively.

Unfortunately, it is impossible to have constant GE response throughout a multi-hour experiment and there is no other alternative but to generate the calibration plot just prior to and again directly after the study of metal complexes. When comparing the slopes for the 'new' versus the 'well-used' GE1, the only major change in electrode performance is the response slope in the basic region (12.2 to 13.0, solid line), which we have thus used as a test of the GE membrane condition. By discarding data points above pH 12.8 (where a significant curvature is observed, marked with Z in Fig. 4) an improvement in linearity was obtained (dashed line) for both electrodes and the linear correlation moved closer to data in the acidic region. If these two GE responses do not vary significantly then the averaged values of the slopes and intercepts should be used in refinement operations.

Unfortunately, no rigorous criterion is available at present and a judgment depends to a large degree on a metal-ligand system studied, the envisaged pH range of the experiment and the duration the GE is to spend in solution (particularly at higher pH values) as well as the experience of an investigator.

Data seen in Table 5 and Fig. 4 lead us to a new testing procedure for the suitability of the glass electrode in the study of metal-ligand equilibria by voltammetry or polarography, not only at extremely low pH values. It is seen in Table 5 that the response slope in the basic region obtained for the GE2 is significantly smaller when compared with that recorded in the acidic region. Even removing points below pH 12.8 did not improve the slope significantly, indicating that permanent damage of the external surface of the glass membrane took place, thus we would not recommend this GE for metal-ligand equilibria studies. The absolute slope in the base region can be used as a simple and sufficient indicator of the overall quality of the glass membrane and suitability of the GE. Our recommended procedure involves an evaluation of the response slopes obtained in pH ranges of 0.3–1.5, 0.6–1.5, 12.2–12.8 and 12.2–13.0 for a single strong acid–strong base titration. A simple guideline for the acceptable range in slopes as well as the difference between the two slopes for the acidic and basic regions is given in Table 6. For electrodes that fail this electrode test, the glass membrane can be regenerated by leaching the membrane with HF, or a new electrode should be acquired.

It is known that to avoid severe corrosion of the glass membrane one must not work at extreme basic pH values for extended times (several hours), thus we strongly recommend the calibration procedure using two base solutions, as described in Section 4.6. The performance test of the GE involving the titration of 0.5 mol L^{-1} H^+ solution by 0.5 mol L^{-1} base solution should *only* be used on suspect electrodes. Since the acid–base titration does not expose the membrane to harsh conditions for an extended period of time, we are of the opinion that the procedure might be considered as a quick and ultimate evaluation of the electrode suitability for the study of metal-ligand equilibria by voltammetry.

There is no universal and rigorous criterion for the evaluation of GE performance. An electrode that might be regarded as excellent for biological measurements might be unacceptable for the purpose of metal-ligand equilibria studies. Modern instruments provide simple and convenient tests for GE performance. For instance, the Metrohm 781 pH meter has a built in GE test program which uses pH buffers of 4, 7 and 9 to determine the streaming potential (i.e. the change in potential between stirred and unstirred solutions), the potential drift, the response time, the slope and the pH at 0 mV, and hence the potential offset at pH 7. According to the manufacturer's criteria,[33] our electrodes which exhibited significant curvature in the basic region were still classified as excellent electrodes. This also includes GE2 that
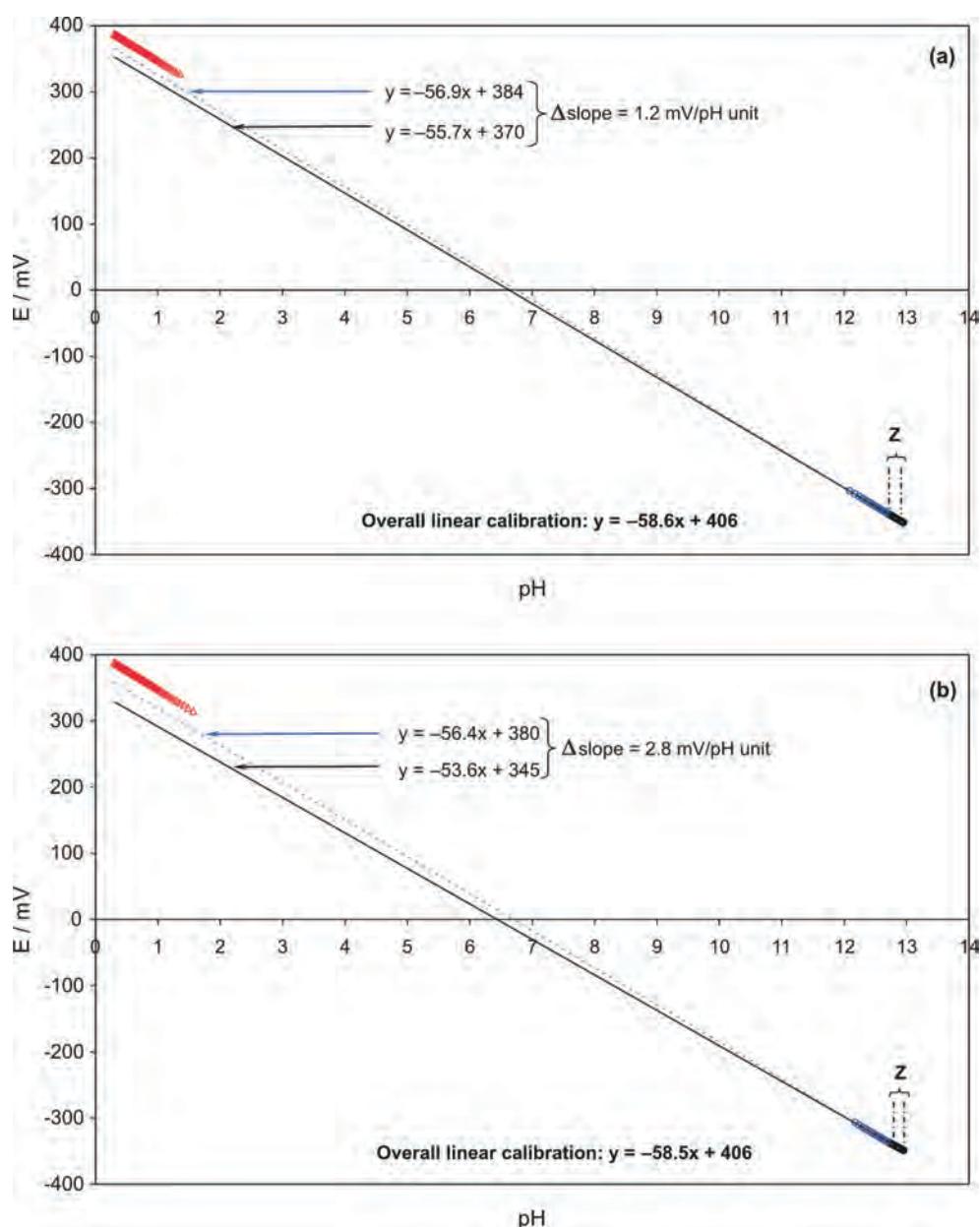
Figure 4 Evaluation of GE suitability for the voltammetric study of metal-ligand equilibria. Parts (**a**) and (**b**) represent results obtained for 'new' and 'well-used' GE, respectively. See the text for details.

we disqualified for the purpose of the metal-ligand equilibria study (see Table 5). Therefore the use of buffers and the built-in test criteria in pH meters do not provide rigorous enough tests for GEs that are to be used in the extreme pH regions. The commercial test might be used as an initial examination of the electrode performance. If failed, the electrode should be replaced by a new one, but when passed, more rigorous testing as proposed here should be followed, incorporating conclusions arrived at in Sections 4.2 and 4.4 as a guide when voltammetric studies are concerned.

5. Conclusion

A novel approach of using a combined linear and non-linear calibration of GE was developed. The binomial calibration was used only at the lowest pH values until the straight line calibration intercepted this function. The pH ranges used for linear and non-linear fitting vary and a simple protocol is proposed to decide on which data should be discarded and how to establish the pH ranges for fitting operations. The proposed calibration

procedure of GE allows measurements between 0 and 2 pH with uncertainty better than ±0.01 pH unit. From the analysis of the significance of experimental errors on accuracy in computed stability constants from voltammetric data, it follows that uncertainties of about ±0.5 mV per pH unit in the response slope and ±1.3 mV in $E^{\circ'}$ might result in an absolute error in pH of about 0.02 that should not generate errors larger than 0.3 % in optimized log K values determined at extremely low pH values.

One must avoid prolonged exposure of the GE to very basic solutions even when a commercial GE is labelled for the use in the entire pH range, pH 0 to 14. We strongly recommend the use of two standardized base solutions for the GE calibration to study metal-ligand equilibria at very low pH. The calibration must start in a highly acidic medium (e.g. 0.5 mol L^{-1} H$^+$) employing a titrant of the same concentration up to pH of about 1.5, followed by the use of a more dilute base solution, e.g. 0.1 or 0.05 mol L^{-1}.

A test of the GE suitability for the study of metal complexes by voltammetry is proposed. A set of simple and arbitrary criteria

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Table 6 Simplified criteria of the GE performance and suitability for metal-ligand equilibria studies by voltammetry. Data obtained from the titration of 0.5 mol L^{-1} acid by 0.5 mol L^{-1} base.

pH range	Acceptable slope range or difference/mV per log unit
basic region	
(1) 12.2–12.8	56–60
(2) 12.2–13.0	55–60
Δslope: (2) – (1)	<3
acidic region	
(3) 0.3–1.5	57–60
(4) 0.6–1.5	57–60
Δslope: (4) – (3)	<1.0
(acidic – basic) region	
Δslope: (4) – (1)	<1.5

was arrived at from GE calibration operations involving the titration of 0.5 mol L^{-1} acid with 0.5 mol L^{-1} base solution. This test, however, should be implemented with caution and only for suspect electrodes that show response parameters outside the values regarded by us as still tolerable when uncertainties in computed log *K* values are expected to be below 0.5 %. The commercial test (built into pH meters) must be used only as a preliminary examination; passing the test is a necessary but not sufficient condition for the envisaged use of the GE in this work. For instance, GEs that were classified as excellent by commercial test, were found unsuitable for studying metal-ligand equilibria.

Procedures proposed in this work should significantly minimize experimental errors in pH readings and make them suitable for use in voltammetric studies of metal complexes, giving uncertainties well below 1 % in computed log *K* values. The ionic strength and ionic composition vary unavoidably when the GE calibration and study of metal-ligand equilibria are performed in a highly acidic medium. This means that stability constants should be reported at an averaged value of ionic strength.

Acknowledgements

References

1 R.G. Bates, *Determination of pH. Theory and Practice,* 2nd edn., John Wiley and Sons, Inc., New York, NY, USA, 1973.

2 W.A.E. McBryde, *Analyst,* 1969, **94**, 337–346.

3 H.M. Irving, M.G. Miles and L.D. Pettit, *Anal. Chim. Acta,* 1967, **38**, 475–488.

4 G.H. Nancollas and M.B. Tomson, *Pure Appl. Chem.,* 1982, **54**, 2675–2692.

5 A. Braibanti, G. Ostacoli, P. Paoletti, L.D. Pettit and S. Sammartano, *Pure Appl. Chem.,* 1987, **59**, 1721–1728.

6 www.acadsoft.co.uk/soleq/soleq.htm. Accessed 26 September 2009.

7 D.I. Hitchcock and A.E. Taylor, *J. Am. Chem. Soc.,* 1937, **59**, 1812–1818.

8 J.I. Partanen, P.M. Juusola and P.O. Minkkinen, *J. Solution Chem.,* 1999, **28**, 413–433.

9 E.A. Guggenheim, *J. Phys. Chem.,* 1930, **34**, 1758–1766.

10 C.W. Davies, *Ion Association,* Butterworths, London, UK, 1962.

11 K.S. Pitzer, *Activity Coefficients in Electrolyte Solutions,* 2nd edn., CRC Press, Boca Raton, FL, USA, 1991.

12 J.L. Barriada, I. Brandariz, R Kataky, A.K. Covington and M.E. Sastre de Vicente, *J. Chem. Eng. Data,* 2001, **46**, 1292–1296.

13 D.K. Nordstrom, C.N. Alpers, C.J. Ptacek and D.W. Blowes, *Environ. Sci. Technol.,* 2000, **34**, 254–258.

14 I. Brandariz, T. Vilariño, P. Alonso, R. Herrero, S. Fiol and M.E. Sastre de Vicente, *Talanta,* 1998, **46**, 1469–1477.

15 G.R. Hedwig and H.K.J. Powell, *Anal. Chem.,* 1971, **43**, 1206–1212.

16 P.M. May, D.R. Williams, P.W. Linder and R.G. Torrington, *Talanta,* 1982, **29**, 249–256.

17 H.K.J. Powell and M.C. Taylor, *Talanta,* 1983, **30**, 885–886.

18 P.M. May, *Talanta,* 1983, **30**, 889–900.

19 I. Brandariz, J.L. Barriada, T. Vilariño and M.E. Sastre de Vicente, *Monatsh. Chem.,* 2004, **135**, 1475–1488.

20 J.-F. Chen, Y.-X. Xia and G.R. Choppin, *Anal. Chem.,* 1996, **68**, 3973–3978.

21 A.E. Martell, R.M. Smith and R.J. Motekaitis, *NIST Standard Reference Database 46,* Version 8.0, Critically Selected Stability Constants of Metal Complexes, NIST, Gaithersburg, MD, USA, 2004.

22 I. Cukrowski, *Anal. Chim. Acta,* 1996, **336**, 23–36.

23 I. Cukrowski, *Electroanalysis,* 1999, **11**, 606–613.

24 I. Cukrowski and M. Adsetts, *J. Electroanal. Chem.,* 1997, **429**, 129–137.

25 S. Fiol, F. Arce, X.L. Armesto, F. Penedo and M. Sastre de Vicente, *Fresenius' J. Anal. Chem.,* 1992, **343**, 469–472.

26 R. Naumann, C. Alexander–Weber, R. Eberhardt, J. Giera and P. Spitzer, *Anal. Bioanal. Chem.,* 2002, **374**, 778–786.

27 F.G.K. Baucke, *Anal. Chem.,* 1994, **66**, 4519–4524.

28 I. Cukrowski, T. Mkwizu and P. Magampa, *Helv. Chim. Acta,* 2006, **89**, 2934–2952.

29 P. Gameiro, S. Reis, J.L.F.C. Lima and B. de Castro, *Anal. Chim. Acta,* 2000, **405**, 167–172.

30 I. Feldman, *Anal. Chem.,* 1956, **28**, 1859–1866.

31 M. Filomena, G.F.C. Camoes and A.K. Covington, *Anal. Chem.,* 1974, **46**, 1547–1551.

32 F.G.K. Baucke, *Fresenius' J. Anal. Chem.,* 1994, **349**, 582–596.

33 780 pH Meter – 781 pH/Ion Meter User Manual (Cat. No. 8.781.1003), Metrohm Ltd., Herisau, Switzerland, 2002.

Supplementary material to:

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For electrodes that failed the performance test, the glass membranes were regenerated by leaching the membrane with HF; this improved the performance of the electrode which once again displayed less curvature in the basic region. The procedure used was to treat the glass membrane with 40 % HF solution for about 5 s and then rinse it in a 1:1 HCl:H$_2$O solution for about 10 s. The electrode was then immersed in deionized water at 50 °C for 5 h before the filling solution was removed and replenished with fresh 3 mol L^{-1} KCl. The electrode was then left to stand in the 3 mol L^{-1} KCl storage solution for at least 24 h before use.

Table S1 Response slope and $E^{\circ\prime}$ obtained from linear GE calibration data involving the titration of HNO$_3$ with either NaOH or KOH, at 25 °C.

	Calibration solutions										
	HNO$_3$ + NaOH				Average	Std. dev.	HNO$_3$ + KOH			Average	Std. dev.
Acid and base molarity	0.005	0.01	0.5	0.5 [a]	–	–	0.01	0.5	0.5 [a]	–	–
Total pH range	2.3–11.0	2.0–11.3	0.3–13.0	0.6–12.8	–	–	2.0–11.3	0.3–13.0	0.6–12.8	–	–
Response slope/ (mV/pH unit)	−58.65 (±0.006)	−58.64 (±0.01)	−58.47 (±0.01)	−58.55 (±0.007)	−58.58	0.08	−59.01 (±0.02)	−59.15 (±0.005)	−59.18 (±0.005)	−59.11	0.09
$E^{\circ\prime}$/mV	408.72 (±0.05)	409.50 (±0.09)	406.70 (±0.01)	407.17 (±0.06)	408.02	1.31	403.50 (±0.1)	402.43 (±0.05)	402.59 (±0.04)	402.84	0.58

[a] Some data points (where largest curvature was observed) were removed – for details, see the text.
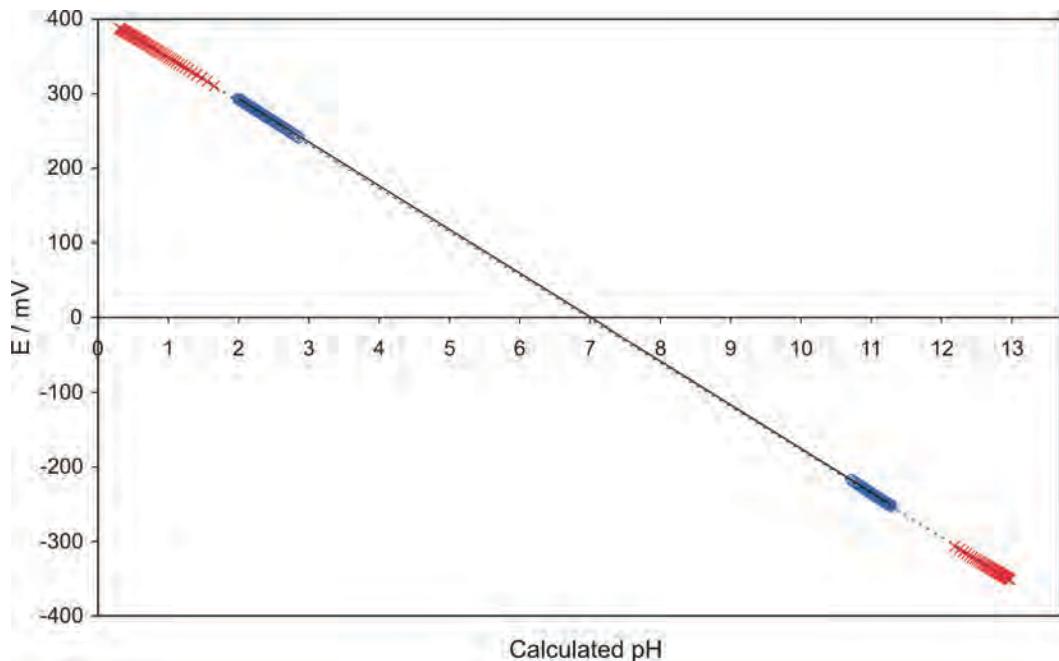

Figure S1 GE calibration data (glass electrode potential *versus* calculated pH) collected from two titrations using the same glass electrode and standardized solutions, that of 0.5 or 0.01 mol L^{-1} HNO$_3$ by 0.5 mol L^{-1} (×, dashed line) and 0.01 mol L^{-1} (○, solid line trace) NaOH, respectively.
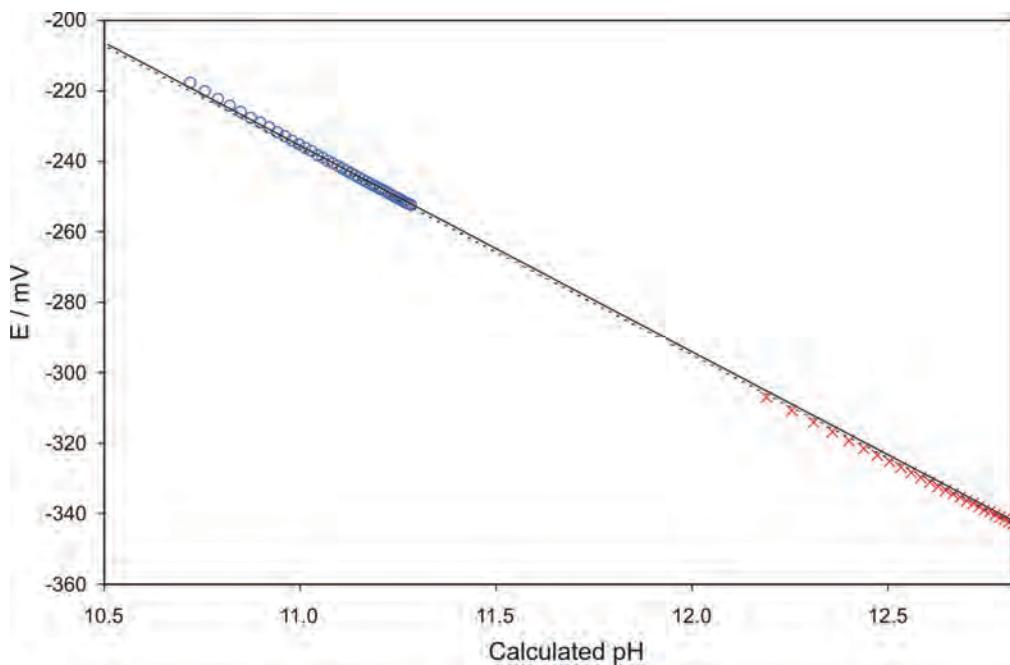
Figure S2 Basic region of titrations seen in Fig. S1. Calibration plot obtained from titration involving 0.01 mol L^{-1} HNO$_3$ and NaOH standardized solutions (circles, solid line trace) was extrapolated to the entire pH range.
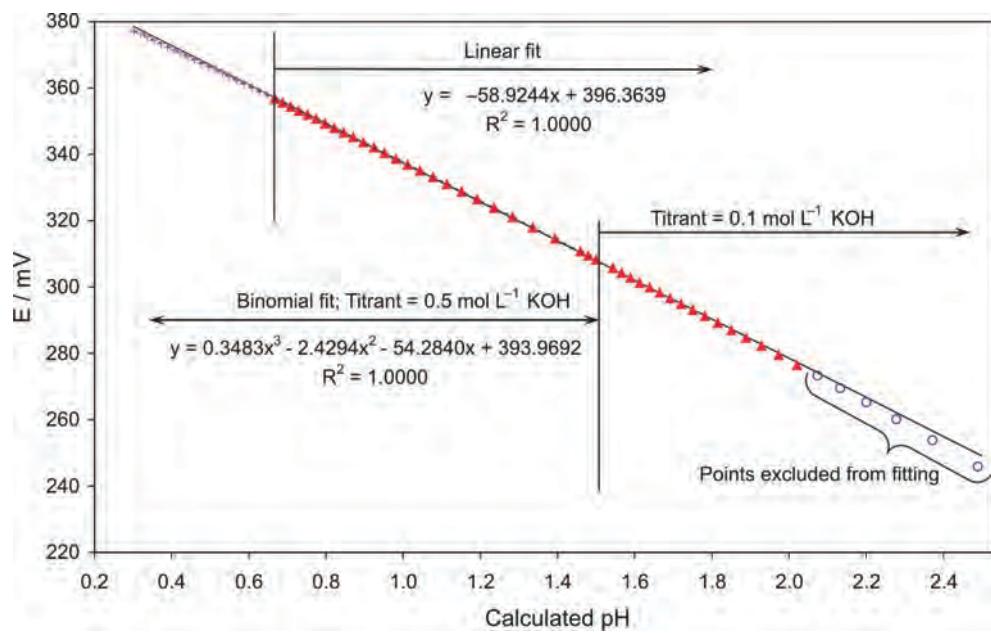

Figure S3 Treatment of data collected from titrations by 0.5 and 0.1 mol L^{-1} KOH, used in calibration of a glass electrode involving linear and binomial functions – acidic region. Triangles – acidic data points used for fitting a linear function (solid line trace obtained with inclusion of basic data points). All points in pH range between 0.3 and 1.5 (crosses and triangles) were used for fitting binomial function. Points that were excluded from calibration of glass electrode are shown as circles.
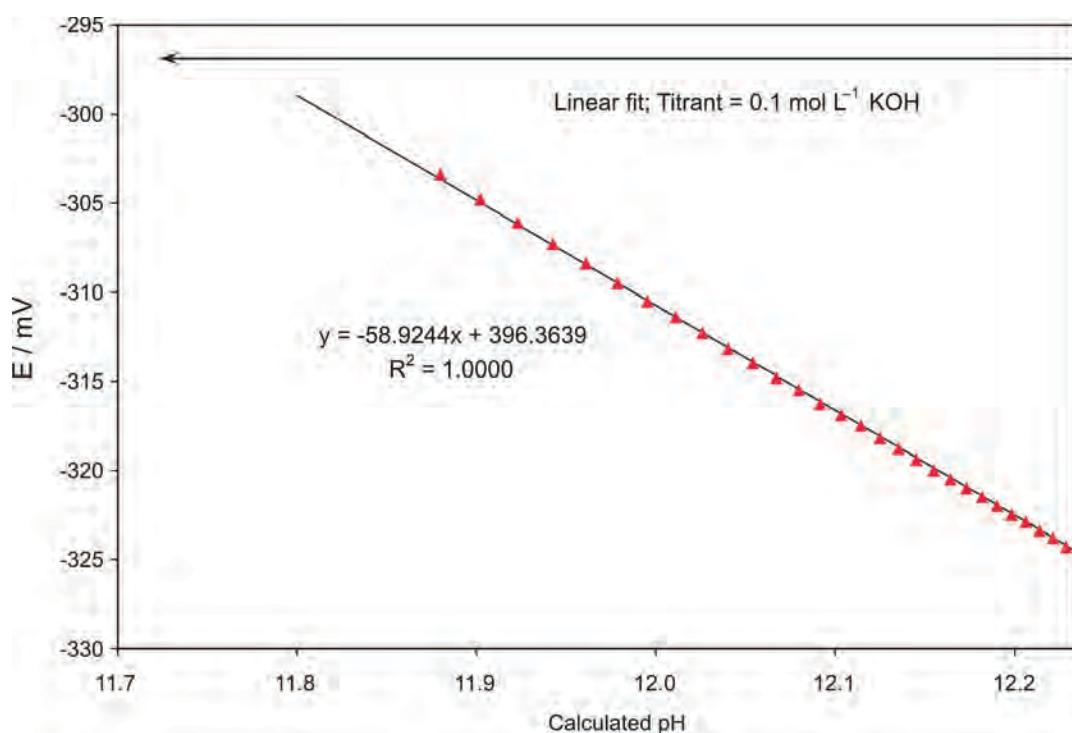
Figure S4 Treatment of data collected from titrations by 0.5 and 0.1 mol L^{-1} KOH, used in calibration of a glass electrode involving linear and binomial functions – basic region. Triangles – basic data points used for fitting a linear function (solid line trace obtained with inclusion of acidic data points).