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Quantifying the Cross-Sensitivity of Glass pH Electrodes in Alkaline Solutions

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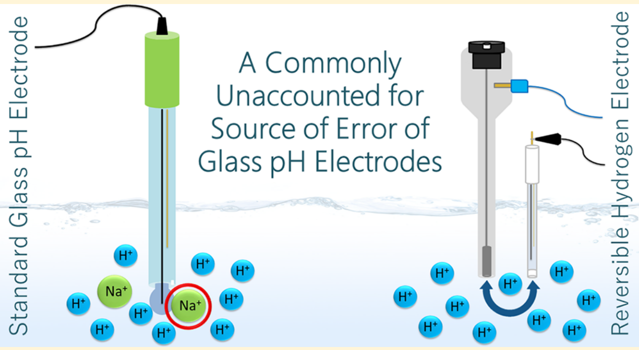
Supporting Information



ABSTRACT: Standard glass pH electrodes are ubiquitous instruments used in research and in classrooms to measure the hydrogen ions present in a solution. While many chemists and educators have communicated ways to support teaching conceptual understanding of solution pH and the function of pH probes and dyes, the community lacks a methodology that enables students to move beyond a qualitative discussion of pH probe cross-sensitivity to other cations such as Li^+ and Na^+. Here, we present an affordable method whereby students learn to quantify such instrumental limitations and cross-sensitivities. The reversible hydrogen electrode (RHE) detects changes in hydrogen ion activity via electrochemical potential and serves as the baseline in this study to standardize the cation sensitivity of several glass membrane pH probes. Increasing additions of a salt, e.g., NaCl, in their corresponding alkali solutions, e.g., 0.10 M NaOH, were used to observe the shift in measured pH between the RHE (nominally only H^+) and glass pH probes (H^+ plus other cations). The generated working curves were found to be specific to each glass pH electrode, the cation identity, and the solution pH. Taken together, this report provides a methodology that equips instructors and research mentors to teach undergraduates about systematic error associated with instrumentation and specifically how to improve the accuracy of pH probe measurements in saline or alkaline environments.

KEYWORDS: *Second-Year Undergraduate, Interdisciplinary/Multidisciplinary, Misconceptions/Discrepant Events, Acids/Bases, Aqueous Solution Chemistry, pH*

INTRODUCTION

Accurate pH measurements are essential across a broad range of disciplines such as ocean buffering, enzyme activity, and food production.[1−3] In 1909, Sørensen reported the seminal quantification of pH as the negative log of the concentration of hydrogen ions in a solution, $-\log[H^+]$.[4] The pedagogy of pH has since been discussed regularly in this *Journal* and other venues,[5,6] and methods for calculating and measuring pH continue to be taught as such in lower division chemistry classrooms today.[7−10] A more inclusive definition of pH mentioned in textbooks, but often quickly left behind, uses the activity of the hydrogen ions, or $-\log \alpha_{H+}$, as the effective concentration of hydrogen ions. This activity is known to decrease at higher concentrations of H^+ due to increased interionic attractions.[11] Thus, a void remains where students take away an incomplete understanding of accurate pH measurements in conditions with varying activity coefficients and typically no knowledge of the effects of the activity of other cations on common measurement methods.

The purpose of this article is to provide lower or upper division chemistry students, teachers, and researchers with an accessible and affordable method for quantifying the sensitivity of glass pH probes to cations other than hydrogen, known as the cross-sensitivity. Cross-sensitivity is a form of systematic error observed when measuring pH with glass electrodes and is the focus of this study. Our desired outcome is to enable students to recognize and quantify systematic error in instrumental measurements. A secondary outcome is for students to be able to quantitatively correct for the inaccuracies that occur with cross-sensitivity in pH probes, particularly in high pH solutions.

While conceptual learning of pH and related topics such as buffering often happens in lecture or classroom style meetings,[12] measurement techniques are usually addressed in teaching laboratory activities. At the secondary and post-secondary levels, common ways to measure pH include utilizing insoluble color indicator dyes, such as litmus paper in which a color change is associated with a pH value,[11] and soluble pH dyes,[13] and measuring a solution electrochemically with a hydrogen-ion-sensitive glass pH electrode.[14] The latter is particularly important from a practical standpoint, as pH probes are ubiquitous across a broad spectrum of research

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disciplines. In the laboratory setting, significant figures are used as a facile way to begin discussions of random error and precision, but students are not usually given the opportunity to learn about the systematic error that occurs as glass pH electrodes are sensitive to cations other than protons. This limits students' understanding of accuracy as it relates to pH measurement.

Even when students are cognizant of the limitations of pH probes, they may not fully understand the task they often assign to the probe itself: to accurately measure $\{H_3O^+\}$ across 14 orders of magnitude. It is commonly understood that these electrodes do not measure hydrogen ions with high fidelity at high pH, a phenomenon often called alkaline error;[14] however, their cross-sensitivity[15] to other cations, such as Li^+ and Na^+, is seldom discussed quantitatively in the literature and laboratory or instrument instruction manuals. In 1956, Feldman stated, "It is well known that in basic solutions containing high concentrations of the cations of the alkali and alkaline earth series, especially the sodium and lithium ions, the pH response of glass electrodes is imperfect".[16] Like others,[14,17] Feldman acknowledged these limitations of glass electrodes but stopped short of providing a method to quantify and thus mitigate the discrepancies, let alone one that was accessible to teaching laboratories.

Mechanistically, the composition and chemical properties of the glass membrane lead to the erroneous measurements in cation-rich solutions. Standard pH probes comprise a glass bulb that is a mixture of CaO and SiO_2[17] and a silver/silver chloride wire submerged in a chloride-containing reference solution with a stable, known half-cell potential, i.e., a reference electrode. To measure the pH, the silicate in the outer surface of the glass is allowed to react with the hydrogen ions in the sample solution. The silicate sites become protonated and thus more positively charged.[18] This change in potential is referenced to the solid potential of the reference electrode.[19] The circuit with the silver/silver chloride wire then carries this potential to the pH meter where it can be read as a voltage and transmuted to the measured pH. Other cations such as Na^+ behave similarly to hydrogen ions when interacting with the silicate (Figure 1) in the glass bulb.[17] Thus, glass pH probes measure the cations as they would hydrogen ions and effectively include them in the output voltage and pH value. The Nikolsky−Eisenman equation aims to provide a theoretical value for ion selectivity,[20] though this equation has shown to be a poor predictor for membrane electrodes.[21] The present method provides a more practical approach to quantify cross-sensitivity.

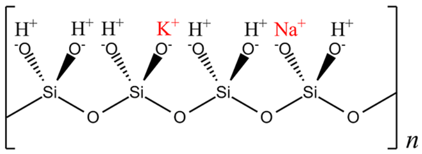


Figure 1. Schematic chemical structure of potassium and sodium ions interacting with silicate as they would at the surface of a glass pH electrode.

Unlike glass membrane pH electrodes, the reversible hydrogen electrode (RHE) determines the pH by measuring hydrogen ions directly in an electrochemical equilibrium with hydrogen gas instead of using a liquid electrolyte/solid half-cell, though in practice one still measures a cell voltage by completing a circuit with a reference half-cell.[11] Traditionally, constructing and using an RHE was rather cumbersome, but a compact and easy-to-use RHE has recently become commercially available. The Hydroflex RHE produced by Gaskatel incorporates a hydrogen gas cartridge and a Pt/Pd electrode and behaves according to the equilibrium in eq 1 when connected in circuit with a reference electrode and a high impedance voltmeter (such as a pH meter operated in "mV mode"):

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E° = 0.00 \text{ V} \tag{1}$$

In brief, the potential between the RHE and an external reference electrode is measured in standardized solutions to create a calibration curve. This is taken to be a more accurate measure of the pH than a glass probe under the conditions described here because the $2H^+/H_2$ reduction potential is largely independent of cation content, effectively measuring changes in $\{H_3O^+\}$ versus a constant pressure of $H_2(g)$. The reference electrode used in this study is typical of aqueous electrochemical measurements: a silver/silver chloride wire submerged in an aqueous potassium chloride solution encased in a glass tube with a porous junction at the bottom, which can be purchased or made in-house. The pH measurement is obtained by detecting changes in the open circuit potential between the two electrodes.[22] When care is taken to remove dissolved oxygen and preclude other redox active molecules (as described below), an RHE provides an excellent and facile direct measurement of pH.

Though the RHE is more selective toward hydrogen ions than glass pH probes, it is worth noting weaknesses that preclude it from replacing glass bulb pH electrodes altogether. The RHE requires the sample to be sparged with argon[23] to eliminate dissolved oxygen, and it utilizes an external reference electrode or purchase of a combined unit with both half cells to conduct measurements.[19] Glass pH electrodes are popular with scientists and students in part because of the portability of the probe and ease of use with its combined, internal reference electrode. Also, the time for a stable measurement with a glass pH probe is typically seconds to minutes, whereas the RHE can at times take upward of an hour to stabilize. These tradeoffs make glass pH probes much more conducive to field work and classroom work, such as titrations, despite the associated cation error.

In the method we present here, students create a working curve for the hydrogen ion-selective measurements from the RHE that effectively calibrates the glass pH electrodes for various cations at various pH values. Using this curve to correct for the cation error incorporates the accuracy of the RHE via a single day's experiment while maintaining the functionality of the glass pH electrode for a period of general use. In other words, the method presented here allows students to use glass pH probes for rapid measurements as they do now but then to subtract out the contribution of the other cations (e.g., a pNa value) using the curve created with the RHE, promoting higher accuracy measurements in alkaline solutions and providing students with a hands-on, concrete path to a better understanding of systematic error in common instrumentation.

Learning Outcomes

After performing this experiment, students will be able to

- Measure the change in apparent pH over a series of increasing salt concentrations

- Quantify cross-sensitivity using measurements from a glass pH electrode and an RHE
- Use measured cross-sensitivities to calculate a more accurate pH value
- Identify and mitigate systematic error

■ PROCEDURE

Experimental Materials

A high impedance voltmeter such as a pH meter is needed to construct a measurement circuit with sufficiently high impedance. The pH meters described throughout the Procedure section of the paper include the Fisher Scientific, Accumet Research AR 15 pH meter, S/N AR 81211095, from Hampton, NH, and the Oakton pH 700 Benchtop Meter, from Vernon Hills, IL. The reversible hydrogen electrode (RHE) used in this study is the Hydroflex hydrogen reference electrode, from Kassel, Germany. The RHE requires an external Ag/AgCl reference electrode. The one used in this study was obtained from CH Instruments, Inc., from Austin, TX. The two pH probes used indicated in the figures were the Oakton pH probe model WD-35805-06, from Vernon Hills, IL, and the Extech Instruments model 601500, from Waltham, MA.

The chemicals described in this paper were supplied from several sources. The Oakton pH buffer solutions, from Vernon Hills, IL, include model numbers and their respective pH values of 00654-00 (4.01), 00654-04 (7.00), and 00654-08 (10.01). Alfa Aesar, from Ward Hill, MA, supplied the NaOH (97%), NaCl (99%), KCl (99%), NH_4OH (28% NH_3), LiCl (99%), and LiOH (98%). ACS grade NH_4Cl was supplied by VWR Amresco Life Science, and the KOH was supplied by VWR Chemicals, from Radnor, PA.

Measurements with Glass pH Electrodes

Each sample was sparged with ultrahigh purity argon gas for at least 1 min per mL of solution to minimize the concentration of dissolved oxygen. (Note: This is not believed to be strictly necessary for glass pH probe measurements, but it was done to maintain consistency with the RHE protocol described below.) The pH probe under study was connected to a pH meter set to measure cell voltage in millivolts. The electrode was then placed in the solution with the glass bulb fully submerged without touching the glass walls or the bottom of the container.[24] The meter exhibited a change in potential and then visually indicated that the reading was "stable", i.e., that the drift had slowed an acceptable amount. The potential measurement displayed at that time was accepted and recorded. The electrode was removed from the sample, rinsed thoroughly, and placed in a beaker of deionized water until the next sample was measured. Overnight or between experiments, the glass electrodes remained submerged in pH electrode storage solutions.

Measurements with the RHE

Each sample was sparged with argon as described above while it was capped with a lid fitted with drilled holes to insert electrodes but minimize the ingress of ambient air. The RHE and reference electrode were positioned upright with the tips of the electrodes fully submerged in the solution. A BNC connecter with alligator clips attached to the pH meter was used to complete the circuit between the RHE and reference electrode. The potential of the RHE-reference cell moved substantially over the course of several minutes as the RHE moved toward equilibrium. A measurement was accepted when the rate of drift from the RHE slowed to less than 1 mV within 45 s. We note that consistency with these measurements was critical for quantifiable results and calibrations and that the input impedance of common voltmeters is not sufficient for the measurement circuit. The electrodes were then removed from the solution and rinsed thoroughly with deionized water before being placed in their storage solutions (1 M KCl for the reference electrode and deionized water for the RHE). These electrodes were stored thusly between uses and overnight.

Calibration Curves

The RHE and glass pH probes were calibrated daily using standard buffer solutions with pH values of 4.01, 7.00, and 10.01. Measurements were conducted as above in each of the three solutions.[25] To create the curve, the potential obtained was plotted against its known pH value. As expected, linear equations for each electrode were obtained with R^2-values of 0.9999 or better with the exception of the RHE. The x-value denoted in the equation was the pH, and the y-value was the measured potential in millivolts. A pH value of each sample was calculated using these curves by substituting the potential obtained from the pH meter for the y-value in the equation and solving for x (Table 1).

Table 1. Calibration Curve Equations and the R^2-Values for Each of the Four Electrodes and RHE

Electrode	Calibration Curve Equation[a]	R^2
Extech 1	$y = -58x + 3.8 \times 10^2$	0.99997
Extech 2	$y = -58x + 4.1 \times 10^2$	0.99996
Oakton 1	$y = -57x + 4.0 \times 10^2$	0.99998
Oakton 2	$y = -57x + 3.9 \times 10^2$	0.99994
RHE	$y = -57x - 2.2 \times 10^2$	0.994

[a] In the equations, y is the potential measured in mV and x is pH.

Solutions

The cations analyzed by the present method were H^+ (or H_3O^+), Na^+, K^+, Li^+, and NH_4^+. These cations were selected for their relevance at common ionic strengths[26] and were measured under basic conditions where systematic cation error is more prevalent. A solution series composed of 0.10 M base with the corresponding cation (e.g., NaOH) was used with increasing additions of salt (e.g., NaCl) from 0.00 to 1.00 M for each of the subsequent working curves.

Working Curves

The working curves were created by first using the calibration curve equations to calculate the measured pH value from the measured potential for each of the electrodes (Figure 2). The pH values from the RHE remained relatively constant as the salinity increased. In contrast, the pH values from the glass pH electrodes have a downward slope as the salinity increases, indicating the cross-sensitivity. As the RHE gives a pH measurement for hydrogen as its only nominal cation, the discrepancies between the RHE and the pH probes were taken to be dominated by the additional cations. Thus, subtracting the pH probe reading from that of the RHE yielded a quantitative "pCation" at that pH value and for that pH probe. This quantity for cross-sensitivity plotted in Figures 5–7 can be defined as

$$\text{cross-sensitivity} = \text{pH}_{\text{apparent}} - \text{pH}_{\text{determined}} \tag{2}$$

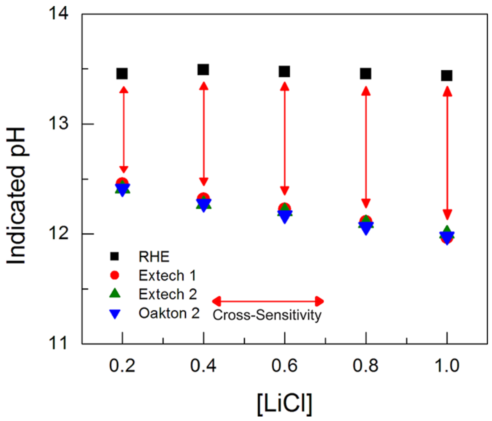
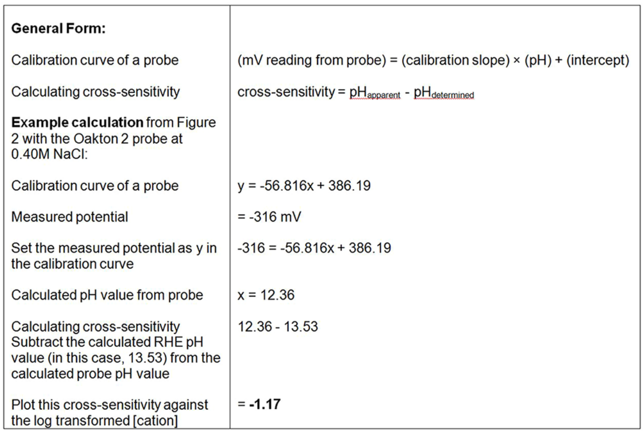


Figure 2. pH value plotted against the concentration of LiCl. For data with NaCl, please see Figure S1 of the Supporting Information.

See Figures 4 and 5 for a sample calculation of cross-sensitivity and a graphical concept map of the overall process.



General Form:	
Calibration curve of a probe	(mV reading from probe) = (calibration slope) × (pH) + (intercept)
Calculating cross-sensitivity	cross-sensitivity = $pH_{apparent}$ - $pH_{determined}$
Example calculation from Figure 2 with the Oakton 2 probe at 0.40M NaCl:	
Calibration curve of a probe	y = -56.816x + 386.19
Measured potential	= -316 mV
Set the measured potential as y in the calibration curve	-316 = -56.816x + 386.19
Calculated pH value from probe	x = 12.36
Calculating cross-sensitivity Subtract the calculated RHE pH value (in this case, 13.53) from the calculated probe pH value	12.36 - 13.53
Plot this cross-sensitivity against the log transformed [cation]	= **-1.17**

Figure 3. Sample calculation of the cross-sensitivity.

■ HAZARDS AND SAFETY

When handling concentrated bases and salts described in this experiment, such as NaOH and LiCl, eye protection and gloves should be used at all times. The experiment space should be well-ventilated when using argon gas. There are no major instrumental safety concerns.

■ RESULTS AND DISCUSSION

The cross-sensitivity for each pH electrode was plotted against the log transformed concentration of the salt to create a working curve (Figure 5, with concentrations in molar plotted on a log scale). Table 2 indicates the slope of the working curve as the change in apparent pH and acts as a practical sensitivity coefficient. For reference, the approximate sodium ion concentration in typical seawater is shaded in red.[27] At this concentration, glass electrodes measurements can be half a pH unit or more from the actual pH value. Critically, each glass pH electrode, even those of the same brand, exhibited a unique cross-sensitivity in their slopes and *y* intercepts (Table 2). This indicates that working curves are not universal and a separate curve is needed for each electrode.

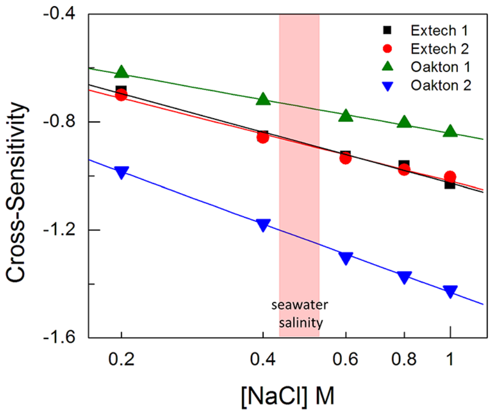


Figure 5. Calculated cross-sensitivity to NaCl in 0.10 M NaOH for four glass pH electrodes and a typical salinity range for seawater included for reference to an example environmental application.[27] Note that the *x*-axis is plotted in molar but spaced as a logarithmic relationship. Please see Supporting Information Figures S2–S4 for data with KCl, LiCl, and NH_4Cl.

Table 2. Change in Apparent pH/log [cation] and R^2-Values of the Lines in Figures 3–5

	Cross-Sensitivity with Each Electrode	
Electrode	Cross-Sensitivity/log[NaCl]	R^2
Extech 1	−0.47	0.990
Extech 2	−0.44	0.999
Oakton 1	−0.31	0.994
Oakton 2	−0.64	0.998
	Cross-Sensitivity with Each Cation	
Cation	Cross-Sensitivity/log[Cation]	R^2
NH_4^+	−0.19	0.995
K^+	−0.27	0.994
Na^+	−0.64	0.998
Li^+	−0.59	0.996
	Cross-Sensitivity at Each pH for Na^+	
pH	Cross-Sensitivity/log[NaCl]	R^2
~11	−0.33	0.992
~12	−0.42	0.991
~13.5	−0.44	0.999

These four cations yielded slopes that generally correlated with the relative size of the cation (Figure 6), though we note

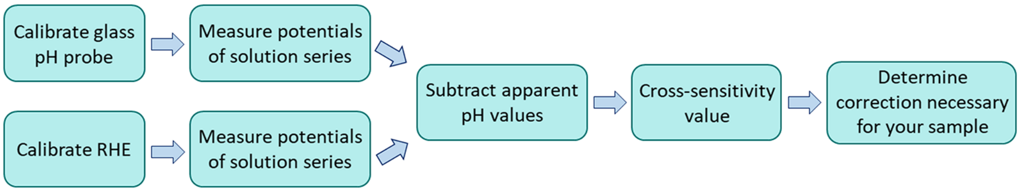


Figure 4. Graphical concept and action map.

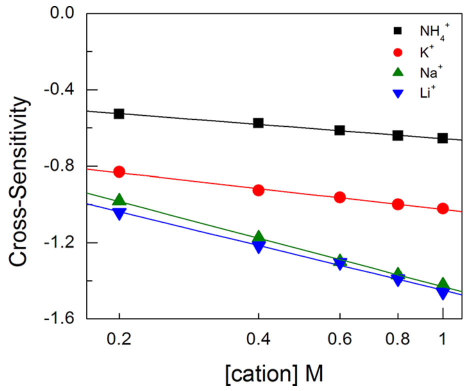


Figure 6. Cross-sensitivity of the different cations in 0.10 M alkali solutions for a single pH probe. Note that the *x*-axis is plotted in molar but spaced as a logarithmic relationship.

that Na^+ and Li^+ gave comparable responses for this probe. Glass electrodes are generally less sensitive to larger ions of a given charge, such as NH_4^+ and K^+, as their size reduces ion-pairing-type interactions with the silicate sites in the glass.[28] Conversely, the smaller cations in this study (Na^+ and Li^+) have greater effects on the apparent pH/log[cation], as their sizes are closer to that of the hydrogen ion. We note again that a new working curve must be made specific to the cation or cations in question for each electrode in each study.

The cross-sensitivity to sodium was tested at three different pH values (Figure 7). As expected, the slopes increased with higher pH values, though the intercepts did not yield a simple trend. It has been reported that the error is greater[17] with increasingly basic media, and the cross-sensitivity rate would be higher at these values as well. We found it impractical to use the RHE at pH values approaching neutral at low salt concentrations because there were not enough ions in these solutions to provide facile ionic conductivity between the RHE and reference electrode. This is a limitation of the present method when evaluating cross-sensitivity for measurements to be made in neutral and/or low conductivity solutions.

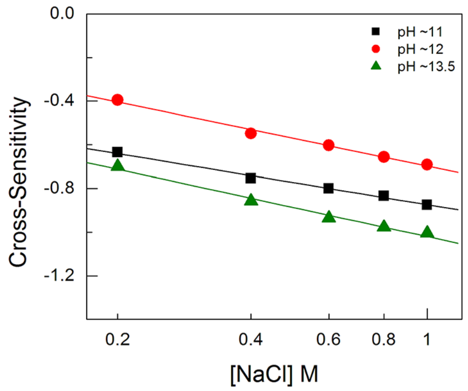


Figure 7. Cross-sensitivity of a glass pH electrode to NaCl at pH values of ~11, ~12, and ~13.5. Note that the *x*-axis is plotted in molar but spaced as a logarithmic relationship.

■ CONCLUSION

Training the next generation of scientists must include training them in methods for understanding and quantifying systematic errors in instrumentation. In particular, accurate pH measurements are critical for monitoring the health of our oceans and other waterways and for biochemical experimentation. Using pH probes found in every chemistry classroom and an accessible RHE, the method presented here enables student outcomes that address the importance of identifying and quantifying such errors, useful in nearly any disciplinary offshoot of chemistry.

Until the present report, students and scientists that were aware of the error that occurs at the surface of glass pH electrodes still lacked a facile and affordable means for quantifying it. A working curve generated with a compact RHE can be used to mitigate error in cation-rich or alkaline solutions. The working curves in this study indicate linear, quantifiable changes in pH electrode response occur as the concentration of salt and cations in the solution increases. The data presented here support that the response is unique to each electrode and for each of the cations present in a solution. Higher pH values appeared to have greater cross-sensitivity differences; though this is intuitive, this effect appears to be less well-defined and systematic at pH ~ 11 or higher. For the best results, it is recommended to the user that this method is performed immediately before the cross-sensitivity analysis, just as a typical pH probe calibration is best performed immediately before use.

These results have implications for educating students who will go on to many fields, but it is of particular import for those who may study highly saline environments such as those of extremophilic bacteria in alkaline lakes with sodium concentrations exceeding 1.7 M.[29] This method is also useful for battery research; several new battery chemistries operate in alkaline or mildly alkaline conditions,[30] where high concentrations of Na^+ or Li^+ can aid in conductivity or charge storage reactions.[31] Generally, this method enables quantification of the cross-sensitivity of pH electrodes to diminish the inaccuracies of data reported from glass electrode pH probes and, more broadly, to provide an accessible method for the community at large to do so in their own work.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.8b00812.

> Experimental materials, sample calibration curve for RHE, and sample cross-sensitivity data (PDF, DOCX)

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Notes

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