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pH DETERMINATION AND MEASUREMENT

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1. INTRODUCTION

pH is a measure of the hydrogen ion activity not concentration. The modern pH electrodes develop an electromotive force (emf) that is proportional to the H^+ activity. The emf from the glass electrode is compared to the constant emf developed by the liquid junction potential of the reference electrode. The pH measurement is essentially a determination of an emf between the glass and reference electrodes (potentiometric measurement). Inaccurate pH measurements occur when the emf of the glass electrode is not properly calibrated with buffer solutions, or there are fluctuations in the constant potential developed by the reference electrode.

The purpose of this report is to outline the function, calibration, and storage of the glass and reference pH electrodes inorder to reduce problems and errors with pH measurements. Dole (1941) noted that if we wish to compare pH results with those obtained by other workers, we must standardize methodologies, because comparison of numbers based on different standards and conditions are meaningless.

2. DEFINITIONS

2.1 pH

pH is a measure of the hydrogen ion activity (aH^+) of a solution and is defined by the equation $pH = -\log aH^+$.

2.2 CONDUCTIVITY

The electrolytic conductivity of a water body refers to its ability to carry an electric current, which in turn is related to the total concentration of ions (i.e., charged solutes). This relationship depends on the geometry of the electrodes (area and distance apart), the temperature and, to some extent, on the nature of the major ions in solution. A pH electrode is actually a type of conductivity probe which is sensitive to hydrogen ions.

2.3 ACIDITY

Acidity of water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end-point pH used in the determination. Acidity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known. Strong mineral acids, weak acids such as carbonic and acetic, and hydrolyzing salts such as iron or aluminum sulphates may contribute to the measured acidity according to the method of determination (Figure 1).

2.4 ALKALINITY

Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used (pH 4.5 or inflection point; Figure 1). Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is

known (anion/cation balance). For specific discussion on the measurement of alkalinity see McQuaker et al., (1983) and McQuaker (1976).

Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents (Figure 1). The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present.

Very acidic (pH<4.5) or alkaline (pH>10) waters have appreciably higher conductivities than that expected from total ionic concentration, because of the high molar conductivities of H^+ or OH^- ions. In waters of high conductivity (>1000 $\mu S\ cm^{-1}$), including brackish waters, the molar conductivity and H^+ activity are appreciably reduced because of suppression of ionization (ionic inactivation).

When designing a new sampling program on a water system of unknown attributes, determining (or measuring) the anion/cation balance of the conservative elements (sodium, calcium, magnesium, chloride, bicarbonate and sulphate) is recommended. The ion pairs for the water sample can be reconstructed using the procedures by Riehl (1971) (Appendix 1). Because these elements are conservative in nature, a sample taken in winter and summer every 5 years is adequate.

2.5 BUFFERS

A buffer is a weak acid or base which can oppose changes in H^+ concentration by binding or releasing H^+ to resist change in pH. If 10^{-3} moles of a strong acid are added to a litre of water, it dissociates completely changing the H^+ concentration from 10^{-7} to 10^{-3} (pH 7 to 3). If 10^{-2} M of a weak acid is present and half dissociates to A^-* at pH 7, then

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*A = conjugate base of weak acid $HA \geq H^+ + A^-$

the addition of the 10^{-3} moles of strong acid will result in nearly 10^{-3} moles of A^- being converted to HA. A negligible proportion (1 in 50,000) of the 10^{-3} moles of H^+ added will add to the concentration of free H^+. The latter will change from 1.0×10^{-7} to 1.5×10^{-7} M (pH 7.0 to 6.8). This act of resisting pH change is called buffering.

3. BUFFERS

3.1 NORMAL BUFFERS

1) Use commercial buffer reagents outlined in Table 1. Note the pH of the buffer solutions changes with temperature.

2) In situations where the conditions governing the formation of calcium carbonate (marl) are being studied, a standard solution in equilibrium with calcium carbonate is recommended. Using the formula below, the pH of distilled water in equilibrium with $CaCO_3$ (calcite) is 8.34, assuming the partial pressure of $CO_{2(g)}$ is one atmosphere and the temperature is 25 °C.

$$H_2CO_3 \longrightarrow 2H^+ + CO_3^{2-} \qquad \log K^\circ = -16.69$$

At pH 8.34 the above reaction will be in equilibrium with atmospheric CO_2 and calcite.

3.2 LOW IONIC STRENGTH BUFFERS

Low ionic* strength buffers are available for solutions below pH 5; however, low ionic strength buffers for pH 7 have not been developed. The recommended calibration procedure for low ionic strength waters is to use normal pH 7 buffer and a low ionic strength pH 4 buffer. Sandberg (pers. comm.) observed a significant difference in pH between the recommended procedure and the use of normal ionic buffers. The low ionic strength buffers can be purchased from Canlab or prepared using the following procedure:

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* low ionic strength freshwater has a specific conductivity of ≦ 200 µS/cm.

1. Purchase 0.1 N sulphuric acid* and complete 3 serial dilutions to obtain 0.0001 N H_2SO_4 (one serial dilution = 10 mL of acid per 100 mL of distilled water). Use boiled distilled water to eliminate $CO_{2(g)}$ and carbonic acid from solution.

2. Place the pH 4 buffer thus prepared in a sealed container to avoid CO_2 contamination.

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* use assured quality or equivalent acids

4. pH MEASUREMENT

pH may be estimated with coloured indicators (e.g., multi-range pH papers (not recommended for accurate measurements) or Taylor Comparitors etc.), but is measured more accurately with a pH meter, a reference electrode, and a glass electrode. A combination pH electrode consists of a reference and a glass electrode contained in a single unit (Figure 2).

4.1 REFERENCE ELECTRODE

The reference electrode typically has a calomel ($Hg/HgCl_2$) or a silver-silver chloride wire immersed in 3 M or saturated KCl. The reference electrode is in contact with the external solution (sample) by means of a porous ceramic disc, fritted glass, or semipermeable membrane. Diffusion of the reference electrolyte into the sample creats a liquid junction potential, which is relayed to the pH meter by the calomel or silver-silver chlorine lead out. The liquid junction potential is stable and constant in most freshwater environments, however, it can be unstable in very dilute waters ($\leq$ 50 µS/cm).

Most reference electrodes use a 3 M KCl electrolyte saturated with AgCl. Without the saturation of AgCl, the KCl would gradually dissolve the silver chloride layer on the lead-out, causing the response of the electrode to become unstable. Lead-outs used in conjunction with AgCl-free KCl solutions contain sufficient amounts of AgCl within the element to saturate the area around it and eliminate corrosion (e.g., Argenthal electrodes, Ingold Industries Ltd). Check the manufacturers specifications before preparing or purchasing KCl electrolyte.

Silver chloride can precipitate around the liquid junction if the reference electrolyte evaportates, or the molarity of the reference electrolyte increases. Silver sulphide can also precipitate around the liquid junction if the probe is exposed to sulphides. These precipitates contaminate the liquid junction and alter its potential causing zero-point drift and errors in the determination of pH.

A new type of reference electrode has been developed which uses a solid pressure resistant gel material that is saturated with KCl. An aperture exposes the gel to the sample solution, allowing the diffusion of electrolyte, and the formation of a liquid junction potential. One advantage of the gel filled reference electrodes is they do not require a Ag/AgCl lead-out, and AgCl is not required in the electrolyte. Consequently, contamination of the aperture is avoided.

Unlike normal reference electrodes, gel-filled electrodes show definite ageing phenomena because:

1. KCl diffuses continually from the gel into the sample solution. Reduction in electrolyte concentration causes zero-point drift, lower liquid junction potentials, and larger measuring errors.

2. Infiltrated sample solutions cannot be removed easily from the gel.

The storage of gel-filled reference electrode requires special treatment (see Section 5.2).

4.2 GLASS ELECTRODE

In recent years, the glass electrode has tended to replace all other types of pH indicators. The platinum/hydrogen gas electrode is only used for thermodynamic investigations or for the very accurate pH determination.

The glass electrode has the same lead-out (calomel or silver-silver chloride) as the reference electrode. The lead-out extends into a glass reservoir containing a buffered solution with a constant hydrogen ion activity. The glass of the reservoir is made of special glass which is selectively sensitive to H^+ ions. A difference in the hydrogen ion activity between the external solution and the internal buffer solution creates a electronic potential (called the boundary potential) which can be measured with respect to the liquid junction potential of the reference electrode. The boundary potential is proportional to the hydrogen ion activity of the sample solution. A sensitive high-impedance millivolt meter is used to measure the boundary potential.

The potential (E) generated by the glass electrode can be calculated theoretically using Nernst's equation:

$$E = E^\circ + E_N(\log aH^+)$$

where E° = a constant characteristic of the probe, E_N is known as Nernst's potential, and its value is influenced by temperature.

0°C	E_N = 54.2 mV
20°C	E_N = 58.2 mV
25°C	E_N = 59.2 mV
50°C	E_N = 64.1 mV

The measurable electrode-assembly potential E is the result of several components, as shown in Figure 3. E_1 (the boundary potential) is the only potential which is of interest in the pH measurement. All the other individual potentials E_2-E_6, are constant (assuming the probe is working properly), and are included in the standard potential E°. Since these individual potential components are all subject to a certain error, there is a dispersion of E° as a probe ages, and from one probe to another. This is why slope calibration is necessary.

The slope (change in emf potential per pH unit) is a very important parameter of any pH electrode. New electrodes should have a slope exceeding 98% of the theoretical value E_N. Since the slope varies slightly from electrode to electrode, slope calibration is recommended for accurate pH measurements. Some pH meters have a mV setting which can be used to directly calculate the electrode response per unit pH. The Hydrolab multiprobe sensor does not have a mV setting. For these units the glass electrode requires replacing when the slope calibration cannot lower the read out of a pH 4 buffer solution by 0.2 pH units, or raise the read out of a pH 9 buffer above 9.2.

The ablility of certain types of glass separating solutions of different hydrogen ion activities to develop a boundary potential was first demonstrated by Cremer in 1906 (Bates, 1973). Since that time, the formulation of the glass has been steadily improved, so that modern pH electrodes approach the accuracy of a platinum/hydrogen electrode. Studies of glasses by means of X-ray diffraction reveal a network of oxygen atoms (Figure 4), held together in irregular chains by silicon atoms (Bates, 1973). Each silicon atom is presumably associated with four oxygen atoms, and each oxygen atom is shared by two SiO_4 groups, to form a three-dimensional network. The oxygen atoms are relatively large (about 1.4 A in diameter as compared with 0.4 A for silicon), and hence make up the

bulk of the network. The holes in the three dimensional pattern are occupied by cations, held in place by the electrostatic fields of the neighboring oxygen ions. However, as a result of the irregularity of the silicon-oxygen lattice, the cations occupying the holes in the lattice possess many different energy levels. In other words, the work required to remove a cation from the lattice may be different for each individual ion. The ability of a group of negative ions to retain positive ions within the glass, determines the "anionic field strength".

The glass of a glass electrode contains roughly 72 percent by weight SiO_2, 8 percent CaO, and 20 percent Na_2O (Bates, 1973). Systematic investigations led to the production of an effective pH glass, which is still manufactured and sold under the designation Corning 015. It consisted of 72.2% SiO_2, 6.4% CaO and 21.4% Na_2O (molecular percentages). Modern pH glasses usually contain lithium instead of sodium, providing a much wider measuring range for pH.

Over time the sodium content of a glass electrode will become depleted, causing decreased electrode reponse and E_N potential. Once the electrode potential falls below 95% of the theoretical response (Section 3), the electrode should be regenerated (Section 5.5). If the regeneration is unsuccessful, the probe has been depleted of exchangeable sodium, and should be discarded.

4.3 HYGROSCOPICITY

The degree of sorption of water by the glass membrane of an electrode is termed the hygroscopicity of the glass. Water within the glass lattice structure is essential for the exchange of H^+ and sodium to form the boundary potential. The correlation between the water sorption of a glass and the pH response of electrodes made from the glass is a very direct one (Figure 5).

The application of heat to the glass causes the formation of a non-hygroscopic silica-rich layer. The electrical resistance (E_N, Section 4) of glass electrodes increased 230 percent when the electrodes were dried (Bates, 1973). The resistance returned slowly to its original value when the electrodes were immersed in water. Electrodes made from the lithia-silica glasses are influenced less by drying agents than those of Corning 015 glass. The lithia glasses are known to absorb about one-ninth as much water as do the sodium based glass. Hygroscopicity of a glass membrane can also be destroyed by coating the glass electrode with lacquer or oily substances. The maintenance of the hygroscopicity of the glass electrode is essential for fast and accurate pH measurements.

4.4 GEL LAYER

All glass membranes used in pH electrodes react with water to form a hydrated gel layer (Figure 6). The gel layer is of decisive importance for the performance of a glass electrode as it is the layer that interacts with the hydrogen ions in the sample solution.

Upon hydration of a glass electrode, hydrogen ions in solution exchange with the sodium in the glass to set up a gel layer. As the H^+ ions permeate the gel layer and the lattice structure of the glass electrode, the anionic field strength within the electrode is lowered, allowing sodium ions to diffuse from the glass and the gel layer into the sample solution.

The hydrated glass electrode has two gel layers. The inner gel layer interacts with the internal buffer solution which has a constant hydrogen ion activity and hence potential. The outer gel layer interacts with the hydrogen ions in the sample solution; consequently, the difference between the two potentials (boundary potential) is a function of the pH of the solution.

In solutions containing very low hydrogen ions (pH≥9), the hydrogen ions comprising the gel layer can be exchanged with alkali metals from the solution. Some glass membranes respond to charged alkali metals (e.g. Na^+) under high pH conditions. The exchange of alkali metals (alkaline error) with the gel layer under these extreme conditions cause lower pH values (up to 0.3 pH).

The thickness of the gel layer increases with decreasing temperature because the hygroscopicity of the glass increases with decreasing temperature. The result is a change in the anion field strength and probe response. Under fluctuating temperatures, the gel layer has to establish a new equilibrium with the glass before an accurate pH measurement can be made. Instability of the gel layer leads to sluggish electrode response. The effect of temperature on the gel layer demonstrates the need to stabilize the glass electrode by keeping the temperature of the buffer solutions, the sample solution(s), and the glass electrode uniform.

5. FIELD METHODOLOGY

5.1 SAMPLE COLLECTION

To minimize the interaction of atmospheric CO_2 with the sample solution, the sample container should be filled to exclude air. Rinsing the sample container prior to collection will also help to avoid contamination. pH measurements must be performed within a few hours of collection or stored in a cool dark environment to minimize the effects of biological activity on the sample. Planktonic respiration produces CO_2 (and concomitantly carbonic acid) which will lower the pH of the sample. Photosynthesis by phytoplankton is not a concern if the samples are stored in the dark prior to analysis. The post-sampling biological effects on pH are more of a concern in eutrophic lakes because of the higher plankton biomass.

5.2 TEMPERATURE EFFECTS

Temperature is a very important consideration in the determination of pH because it affects the hydrogen ion activity in the buffer and sample solutions, the hygroscopicity of the glass electrode, and the thickness of the gel layer.

Lower solution temperatures reduce the activity of the hydrogen ion, causing higher pH readings. The effect of temperature on a typical buffer is summarized in Table 1. It must be emphasized that pH electrodes measure the hydrogen ion activity, not hydrogen ion concentration, consequently, buffer readings must be adjusted for temperature.

Lower temperatures increase the hygroscopicity of the glass electrode, which in turn increases the thickness of the gel layer. The gel layer may take 15-30 minutes to reach equilibrium when the temperature is changed significantly (20 → 5°C). pH measurements should not be taken until the gel layer has reached equilibrium.

The increased thickness of the gel layer raises the electrical resistance of the glass, which reduces the response time of the electrode to the sample solution. If the electrical resistance of the electrode exceeds the electrical output of the meter, no pH reading can be made by the meter. Glass electrodes, developed for use in cold environments, use low electrical resistance glass to compensate for the effect of low temperatures on the electrical resistance of the glass electrode.

Hydrogen ion activity declines by approximately 0.01 unit for each 1°C increase in temperature. Thus a sample measured in the laboratory (25°C) will be approximately 0.2 units lower than measurements of the same sample in the field at 5°C (e.g., during winter or in the hypolimnion of a lake). During the summer, when the ambient air temperatures exceed the water temperatures, the glass electrode should be allowed to equilibrate to the water temperature for at least 15 minutes or until the read out is stable. The probe and solutions must be shaded from the direct sun to prevent temperature changes of the test solution during measurement.

Winter sampling poses more difficult problems. Ambient air and water temperatures may be sufficiently cold to inactivate the glass electrode. Samples must be taken to a field laboratory to warm the electrodes and solutions to operating temperatures. Winter sampling may require specialized electrodes. Most suppliers offer a low-temperature glass electrode which are suitable for use to -30°C. A special reference electrolyte will be required for measurements below -10°C (the freezing point of 3M KCl).

The Equithal combination electrode from Ingold Electrodes utilizes a different internal buffer solution which allows a very short response time even when there is a large temperature difference between the electrode and the sample solution. These electrodes are more expensive, but may be desirable under certain field conditions.

5.3 PRESSURE EFFECTS

Ionic equilibria of the glass electrode are much less sensitive to pressure changes than to temperature, and the alterations of pH caused by the normal fluctuations in barometric pressure are negligible. Effects from very high pressures are to be expected only when the solutions contain slightly dissociated acids and bases. The hydrogen ion concentration in the weak acid buffer solutions was found to increase by approximately 100 percent when the pressure was raised from 1 to 1000 atm. (Bates, 1973).

Reference electrodes with liquid electrolyte rely on internal pressure to transfer the electrolyte from the electrode to the sample solution. In this type of reference electrode, the electrolyte must be filled to a level 20-30 mm above the surface level of the sample solution to create a positive flow to form a stable liquid junction potential. Electrolytes in gel-filled reference electrodes are pressure resistant, and can be submerged below the air-water interface.

The Hydrolab Surveyor 8000 uses a liquid reference electrode and can be operated to a depth of 150 metres. This liquid reference electrode overcomes pressure problems by using a large electrolytic reservoir with no air chamber so that the electrolyte is non-compressible. Newer models use gel-filled reference electrodes (Pena, pers. comm.). Since there is no flow of the electrolyte in either of these reference electrodes, a large aperture or junction is used to obtain the required potential. The large aperture affords a very stable liquid junction potential; however, the electrolyte required frequent replacement (4-6 months).

5.4 ELECTRODE STORAGE

Storage of glass and reference electrodes for periods of weeks or months requires careful assessment of the probe itself. Wet-stored glass electrodes have the advantage of always being ready to use. However, the constant exposure of the electrode to the storage solution can accelerate the aging process of the glass electrode. The constant hydrogen-sodium

exchange between the glass electrode and the storage solution will eventually breakdown of the gel layer outside the glass membrane. The breakdown of the gel layer leads to pitting in the glass and a reduction in the glass electrode's electrical response. Dry storage reduces the aging of the glass electrodes, but the probes require immersion in pH buffer 7 for a few hours to restore an outer gel layer.

The correct means of storage is an important factor governing the performance and life of the reference electrode. For electrodes with liquid electrolytes, the electrolyte chamber should always be full and the electrolyte refill aperture closed. This will eliminate contamination of the electrolyte and prevent the calomel or silver/silver chloride lead-outs from drying out. Improper dry storage can cause evaporation and crystalization of the electrolyte and AgCl on the liquid junction, which unless removed will alter the the potential of the liquid junction. Reference electrodes should be immersed in the same reference electrolyte, with the electrolyte refill aperture sealed.

Considering the different storage requirements of glass and reference electrodes, infrequent users of field pH meters should consider purchasing individual electrodes and storing them separately. Since the most suitable storage conditions for glass and reference electrodes are somewhat different, a compromise is needed for storage of combination electrodes. Most manufactures recommend that combination electrodes should be stored immersed in an appropriate reference electrolyte or pH buffer 7 with the refill aperture sealed.

Storage of the Hydrolab units must take into consideration all the electrodes, consequently they are usually stored in water. The glass electrodes are easily replaced while the liquid filled reference electrodes require replacement of the electrolyte every (4-6 months). The Applied Microsystem's Aquamate has individual probe covers which allows the combination gel filled reference electrode to be stored in saturated KCl. Always observe the manufacture's recommendations for probe storage.

Gel-filled reference electrodes are becoming more common, and dry storage can be harmful since the aperture can dry out completely. If the gel becomes dry it may be rehydrated by immersion in a concentrated KCl solution over night. Otherwise there may be an altered liquid junction potential giving rise to unstable readings.

Most manufactures of gel-filled reference electrodes recommend storage in concentrated KCl.

5.5 ELECTRODE REGENERATION

The slope of a glass electrode is a measure of the actual response to hydrogen ion activity (E) versus the theoretical response (E_N calculated using Nernts's equation (Section 4)). The slope is calculated by (E/E_N) x 100. New electrodes should have a slope greater than 98% while old probes should not be used if the slope is lower than 95%. Contamination of the gel layer on the glass electrode or changes in the liquid junction potential are the principal reasons for the reduced slope. The regeneration of the gel layer and the liquid junction potential varies from probe to probe. Check the manufactures specifications and procedures. Some of the more common procedures are outlined below.

Regeneration of the gel layer usually involves immersion of the glass electrode in dilute strong acid (e.g. HCl) for a several minutes. Exposure of the electrode to the dilute acid dissolves some of the aged gel layer. Remove and rinse the electrode, before storing it for 24 hours in a normal storage electrolyte solution. Recalibrate the electrode before using it again.

The most common problem with reference electrodes is zero-point drift, which is a change in the liquid junction potential. The most common causes of zero-point drift are the reference electrolyte becomes contaminated by an ingress of dirt or sample solution, the liquid junction becomes plugged or

contaminated with KCl, AgCl, or AgS precipitates, or the silver chloride has become stripped from the lead-out wire. Regeneration of the reference electrode consists of renewing the reference electrolyte and cleaning the contaminated liquid junction. Check the owners manual for specific instructions of the cleaning procedures for the reference electrode. The stripping of silver chloride from the lead-out resulting in unstable readings, is caused by the use of an incorrect electrolyte. Replacement of the lead-out is a very expensive and complicated procedure, which makes replacement of the electrode more practical.

Regenerated glass and reference electrodes with a slope of less than 95% are beyond further regeneration and should be discarded.

6. STANDARDIZATION OF PROCEDURES

6.1 LITERATURE

pH is a major determining factor in the yield of a chemical process, the rates of growth of organisms, and the solubility of metals. Measurements to determine the effect of pH on these processes from one sample to another have to follow strict guidelines to be comparable with a high degree of reliability. A study by Davison and Gardner (1985) emphasized the need for standardization of procedures in determining pH. In their study, ten participants gathered at one location to compare field and laboratory measurements of the pH of quiescent solutions in natural waters and dilute acids.

Interlaboratory testing at one site showed that standard deviations of measurements on dilute acids and natural waters were generally less than 0.05 pH, and maximum possible bias errors were not usually larger than 0.1 pH. As 95% of all determinations will be within two standard deviations (s.d.) each side of the mean, the maximum error associated with a single measurement of pH will be ±0.2 pH (bias error + 2 s.d.). These results were obtained by laboratories which had been supplied with recommendations regarding equipment and procedures. Focusing of attention on points of detail, and participation in a programme of testing, is sufficient to bring about improvements in accuracy. Therefore, despite any problems caused by the unfamiliar circumstances of the bias tests, the estimate of a total laboratory error of ±0.2 pH is a reasonable assessment of the accuracy which might be achieved routinely when commercial equipment is used.

For field measurements, precision and bias errors were much worse (up to 1 pH unit), apparently because of increased operator error and poor equipment performance (Davison and Gardner, 1985). Electrical equipment marketed specifically for field use can be prone to humidity problems in rain, and the electrodes are selected because of their rugged construction rather than their proven performance. Because pH instability due to CO_2

diffusion enroute to the laboratory, is a recognized problem, high quality field measurements are desirable. In principle, the use in the field of laboratory-grade equipment and well defined analytical procedures should provide the necessary accuracy.

Davison and Gardner (1985) made the following conclusions:

"Considerable bias errors may be due to the preparation of standards, as well as inaccuracies associated with the actual measurement. Undoubtedly, care in the selection and initial testing of electrodes will improve the quality of results. Most important, however, is the unambiguous description of preparation and measurement procedures, and the adoption of routine analytical quality control. The quality of pH data, like those from any other analytical determination, will be greatly improved by strict adherence to a rigorously defined proven routine. Although implementing a programme of quality control will decrease errors, it will not ensure the accuracy of the determination."

The recommended procedures for determination of pH using a glass and reference electrode is outlined in Section 7.

6.2 FIELD AND LABORATORY COMPARISONS

Laboratory and field pH measurements cannot be taken under the same conditions, consequently they are not expected to be the same value. Laboratory measurements from the Environmental Laboratory are assumed to be taken at 1 atmosphere, 22°C, and in equilibrium with atmospheric carbon dioxide. Field pH measurements are taken at ambient temperatures and carbon dioxide concentrations. Altitude and primary productivity can depress carbon dioxide concentrations, while ambient temperatures can be as much as 22°C lower. Decreased ambient temperatures and carbon dioxide concentrations encountered in the field will cause higher pH measurements when compared to the laboratory measurement.

Field pH data determined by a combination glass electrode, pH paper, Hach and Taylor colour comparitors, Surveyor 8000 Hydrolab, and a new relatively inexpensive product, the pH pocket pen were compared to the pH values determined by the Environment Laboratory. The differences between field pH values and Environmental Laboratory pH values are listed in Tables 3 and 4.

Results show the pH pen to have the lowest average and maximum difference. These results may be misleading due to the small sample size and the fact that the pH measurements were taken in the laboratory rather than in the field. The pH pen would certainly be adequate for general, less specific pH measurements (e.g. detection of acid mine drainage). Of the methods commonly used in the field the portable Hydrolab (Surveyor 8000) displayed the lowest average and maximum difference. The new Applied Microsystems Aquamate is expected to have a similar error as it uses the same pH electrode system.

Differences for the combination glass electrode were slightly higher than the differences of the portable Hydrolab. The differences for the Hach and Taylor colour comparitors were 0.2 or 0.1 pH units higher than the average difference of the Hydrolab, and between 0.6 and 0.9 pH units higher than the maixmum difference of the Hydrolab, respectively. The largest deviation between field pH data and lab pH data was found in results determined by the pH paper*. The field pH data measured with the paper showed a 1.2 pH unit average difference from the lab data and maximum differences as large as 2.7 pH units.

A correction factor of 0.01 pH unit was added for every 1°C difference between laboratory temperature (22°C) and the recorded field temperature to allow for temperature induced pH change (Table 4). Comparison of the results show that the addition of the temperature correction factor did not affect the differences between the field pH data and the laboratory pH data.

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*Brand name = ColorpHast sticks

The difference between the field and laboratory pH data were plotted as a function of the laboratory pH (Figures 7 through 11). Figure 7 summarizes the field pH data collected with a Hach kit. The majority of the Hach field pH determinations were less than the laboratory pH, and there was no visual pattern in the variation.

The field pH measurements collected with the ColorpHast pH paper were typically less than the laboratory pH, and there was a distinct increasing bias with increasing pH (Figure 8). These results indicate that the pH paper products are not suitable for field pH measurements.

Field pH measurements collected with the Taylor Comparitor (Figure 9) were usually less than the laboratory pH measurements. There was a general trend for the Taylor Comparitor to overestimate the acid pH measurements, and underestimate the neutral to alkaline field pH measurements. The discrepencies with the Taylor Comparitor were not as drastic as the pH paper, but are sufficiently high as to cause concern regarding the technique.

The combination glass electrode produced field pH measurements that were generally less than the laboratory pH measurements (Figure 10), but no distinct pattern was observed. The Hydrolab (which uses a combination glass electrode) had field pH analyses equally on both sides of the laboratory pH (Figure 11). There was no clear trend in the Hydrolab data.

Based on the results presented, the field pH measurements were usually below the laboratory pH results. The field and laboratory measurements should be routinely compared to provide a check for both procedures. Idealy, the field pH measurements should be slightly higher than the laboratory measurement. Field procedures producing measurements less than, or 0.5 units higher than the equivalent laboratory measurement should be documented and investigated.

7. PROCEDURE FOR pH MEASUREMENT

The following procedure is adapted from those suggested by Bates (1973, pp. 422) and the Department of Biology at Simon Fraser University. It is designed to ensure a high degree of accuracy with the unusual conditions in the field. However, the optimum procedure may vary in detail with the application and the required accuracy (see Bates, 1973). For example, locating acid mine drainage at a mine site requires a pH probe capable of differentiating pH 4 from pH 7. Accuracy to 0.1 pH units is not required for this application. In contrast, very accurate field pH measurements are required to calculate calcite saturation indicies in marl lake.

7.1 PREPARATION

Allow the instrument to warm up thoroughly. If the electrodes have been stored dry, soak in 0.1 M HCl for 2 hours, rinse thoroughly and soak in pH 4 buffer, replacing with fresh buffer periodically, until drift stops.

For reference electrodes with liquid electrolyte, check that the reference electrode is filled and the filling hole is uncovered.

Buffers, sample solutions, wash water, and electrodes should be brought to within 2°C of each other. The electrode temperature can be adjusted by immersing for 10 minutes in a large volume of water having the desired temperature.

All the pH measurements should be taken under quiescent conditions to eliminate error caused by residual streaming potential (McQuaker *et al.* 1983).

Standardization

1. Set the temperature compensation dial to temperature of standard and test solutions.

2. Choose 2 standard buffers whose pH's differ by about 2-3 pH units and which bracket the estimated pH of the sample solution. Use the buffer nearest pH 7 for calibration ("calibration buffer") and the other for adjusting slope ("slope buffer").

3. Rinse electrodes and remove adhering drops with adsorbant tissue without touching the glass membrane.

4. Immerse reference and glass electrodes in the calibration buffer. The entire glass membrane of the glass electrode should be immersed. Do not allow it to touch the beaker.

5. Set function switch to "pH". Set mode switch to normal range (not expanded scale). Some meters have only one operating range.

6. Observe the pH. If present, use the mirror behind the indicating needle to prevent parallax error (align the needle and its reflection by moving your head).

7. Allow drift to decrease to less than 0.005 of a pH unit per minute. This may require several minutes if the electrodes have just been soaking in distilled water.

8. Adjust the calibration knob until the meter indicates the correct pH of the buffer solution at the temperature of the solution (usually room temperature).

9. Set function switch to "stand-by", remove electrodes and replace solution with fresh standard buffer. Do not rinse or blot electrodes.

10. Re-insert electrodes, set switch to "operate" and allow drift to stop (about a minute).

11. Repeat steps 9-10 until the reading is within 0.02 pH units of the correct pH for 2 successive portions of buffer. If several portions are needed the electrodes may not have been initially at the same temperature as the standard.

12. Set meter to "stand-by", remove electrodes, rinse briefly, remove adhering drops and place in the second "slope buffer" solution. Note the pH after drift is negligible (<0.005 unit/min). This should take about a minute.

13. Compare this pH with the correct pH at the temperature of the measurement. Normally the difference should be <0.02 unit. If much greater than this the electrode or meter may be malfunctioning. Small errors in slope can be corrected by adjusting (1) the slope control if present, or (2) the temperature compensator control.

14. Repeat steps 12 and 13 with additional portions of the second standard until successive readings agree within 0.02 unit.

For occasional pH measurements the pH assembly should be restandardized each time. If a series of test measurements are to be done, check the standardization between the first several measurements. If agreement is within 0.02 pH unit, then standardization can be checked less frequently. This will depend greatly on the nature of the test solution. Solutions of some biological materials leave a deposit on the electrode which makes it necessary to wipe the electrode frequently (as in step 3) and restandardize.

7.2 DETERMINING pH - NORMAL PROCEDURE

15. If a weakly buffered solution, such as low ionic strength fresh water, is to be tested see special procedure below (Section 7.3).

16. Set function switch to "stand-by", rinse electrodes well but briefly with distilled water, then remove adhering drops with a tissue without touching the glass membrane.

17. Fill a cup with a portion of the test solution and obtain a preliminary reading of the pH. Repeat without rinsing electrodes until pH is reproducible to ±0.02 unit and drifts less than 0.005 unit per minute.

18. If you are planning more measurements, see the discussion after step 15 and restart either at step 3 or step 15.

7.3 DETERMINING pH: LOW IONIC STRENGTH SAMPLES (<200 µS/cm)

i) Glass and reference electrodes should be designed for low ionic strength conditions. Innovative Electrodes of California have developed a gel-filled reference electrode for use on the Hydrolab and Applied Microsystems multiprobe units which are adequate to 50 µS/cm. Special liquid filled reference electrodes are available from Innovative Electrodes for low ionic solutions ≤ 50 µS/cm. Ingold Electrodes Ltd.[1] is one electrode company specializing in low ionic strength combination electrodes for laboratory use.

ii) Low ionic strength buffers should be used, which can be made up using the procedures in Section 2.

Follow procedure of steps 15-16 except:

a) rinse electrodes additionally with a portion of the test solution.

b) repeat until drifts are less than 0.05 unit/min and successive portions agree within 0.1 unit.

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[1] 261 Ballardvale Street, Wilmington, MA 01998, 617-658-7615

8. CONCLUSIONS

A combination pH electrode works by exchanging sodium or lithium ions with hydrogen ions in solution through an intermediate gel layer associated with the glass electrode. A boundary potential is generated in the glass electrode which is proportional to the hydrogen ion concentration of the sample solution. The boundary potential of the glass electrode when compared to the liquid junction potential of the reference electrode will provide an accurate estimate of the hydrogen ion activity in solution.

The care and storage of glass and reference electrodes is critical to maintain the life and accuracy of the electrodes. Typically the glass and reference electrodes should be stored in the reference electrolyte or, in the case of gel-filled reference electrodes, in concentrated KCl. Glass electrodes should be stored dry for long periods, while reference electrodes should always be stored in the reference electrolyte.

Glass and reference electrodes should be reconditioned when the electrode response to 1 pH unit decreases below 95% of the theoretical response. If the reconditioned response is below 95% the probe should be discarded.

Low temperatures increase the thickness of the gel layer which slows the sodium to hydrogen exchange. As a result, the electrical resistance of the glass electrode increases and response of the electrode to the hydrogen ion activity is slowed. Sample solutions in winter should be warmed to the temperature of the buffers and electrode in a field lab to obtain an accurate reading. The pH taken in the field lab can be corrected to ambient temperature by adding 0.01 pH unit per °C increase.

The liquid junction potential of the reference electrode is influenced by low ionic strength solutions. Low ionic strength pH buffer 4 should be used to eliminate potential liquid junction error when the specific conductance of the sample solution in below 200 µS/cm. Special reference electrodes should be used when the specific conductance of the sample solution is below 50 µS/cm.

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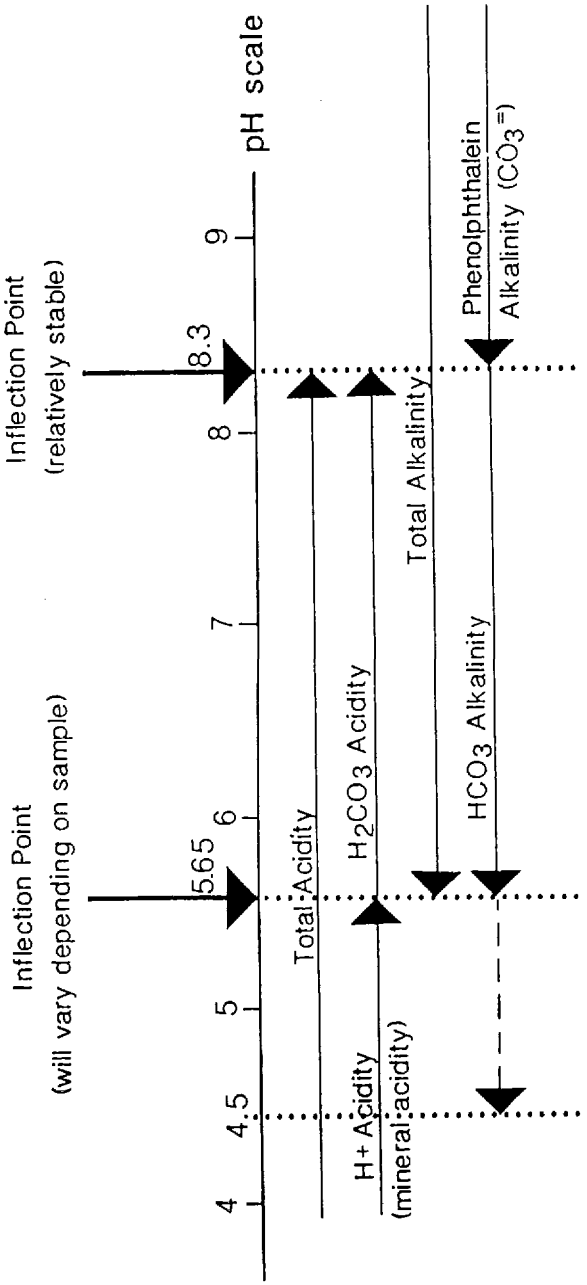


FIGURE 1: pH Scale with Acidity and Alkalinity Terminology

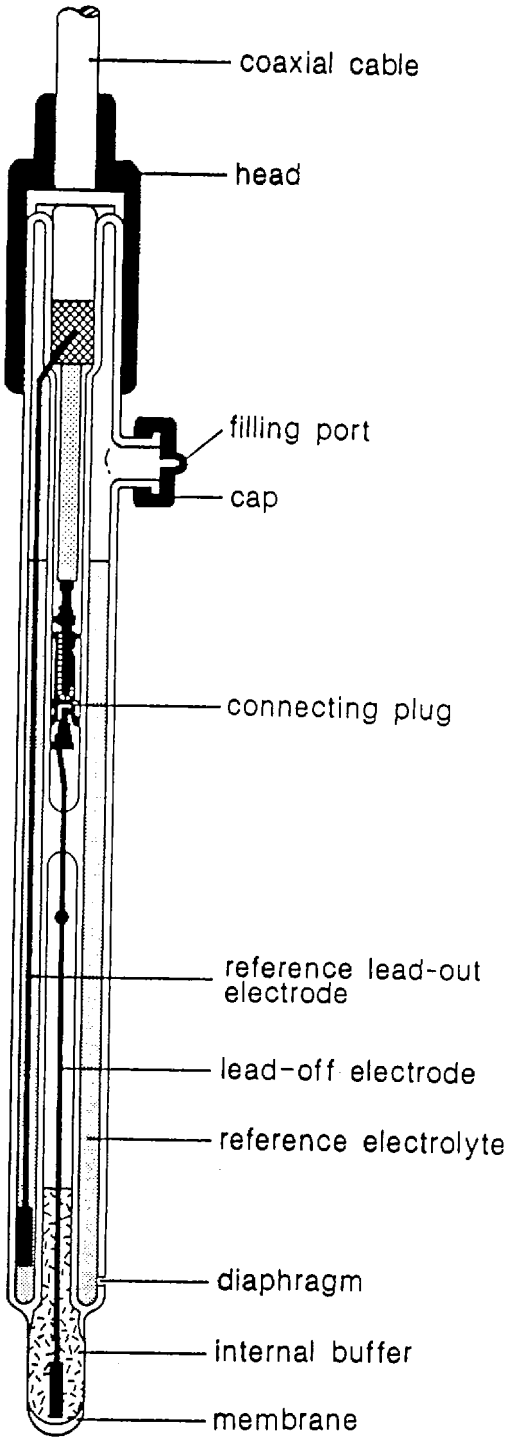
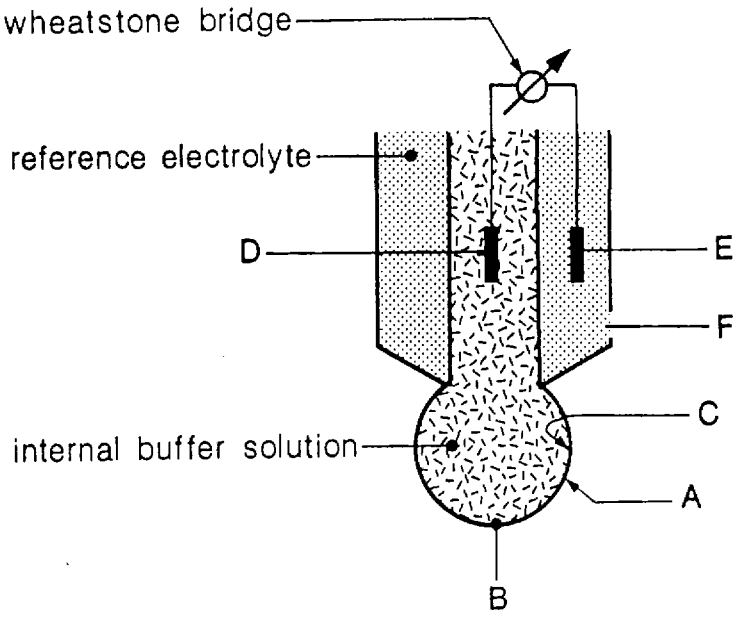


FIGURE 2: Structure of a Typical Combination pH Electrode



A = Potential on outer surface of membrane, dependent on the pH value of the sample solution.

B = Asymmetry (bias) potential, being the potential of the glass membrane with identical solutions and lead-out systems on each side of it. B is determined by the thickness of the glass membrane and by its manufacturing process.

C = Potential on inner surface of glass membrane, depending on the pH value of the internal buffer solution.

D = Potential of the internal Ag/AgCl lead-out electrode, dependent on the a_{Cl^-} value of the internal buffer solution.

E = Reference electrode potential, dependent on the a_{Cl^-} value of the reference electrolyte.

F = Diaphragm or diffusion potential.

FIGURE 3: Electrical Potentials Associated with a pH Combination Electrode

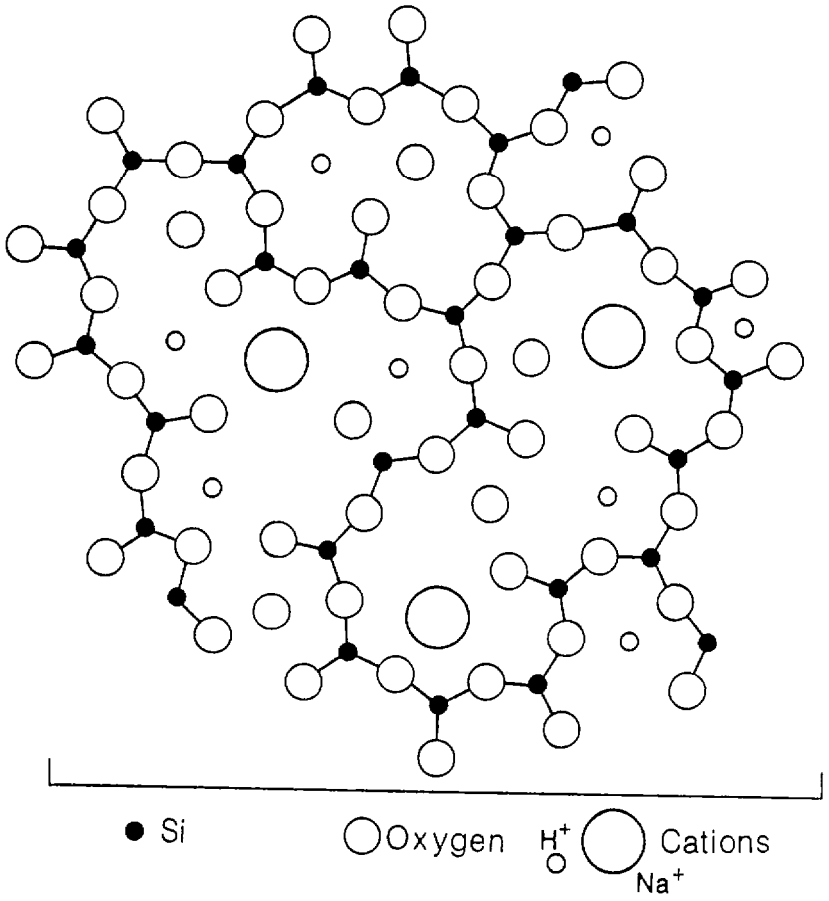


FIGURE 4: Lattice Structure of the Glass Electrode

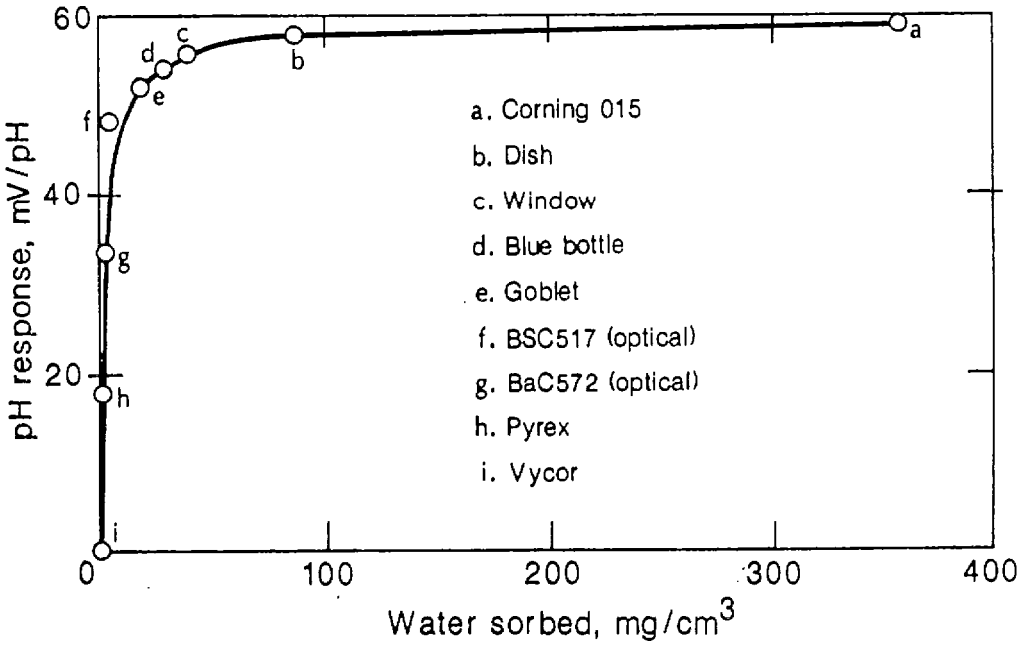


FIGURE 5: Hygroscopicity and pH Response of Nine pH Sensitive Glasses.

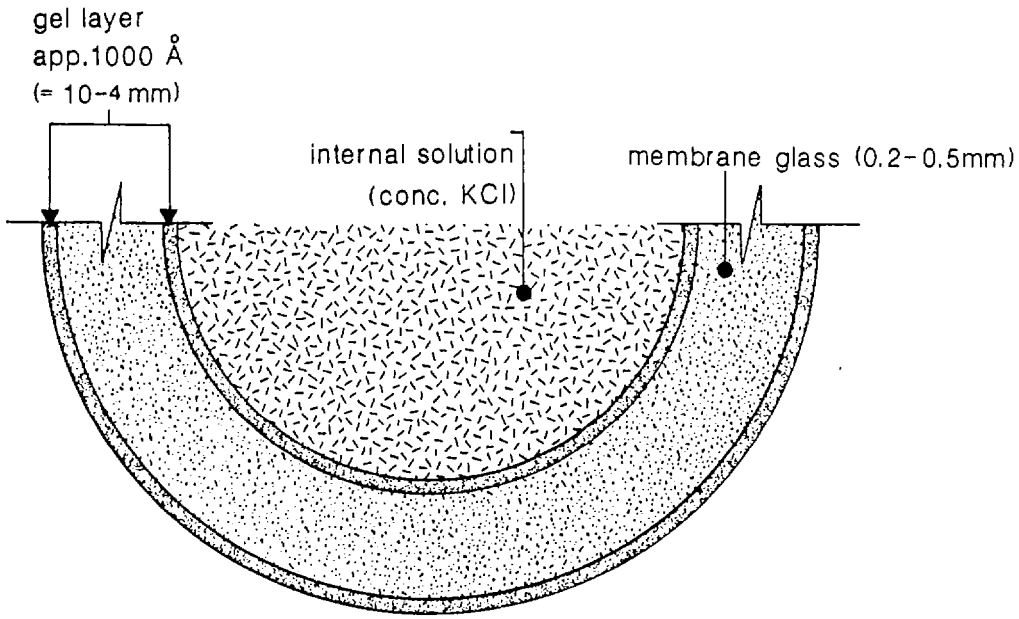


FIGURE 6: Schematic Illustrations of the Structure of a Glass Membrane

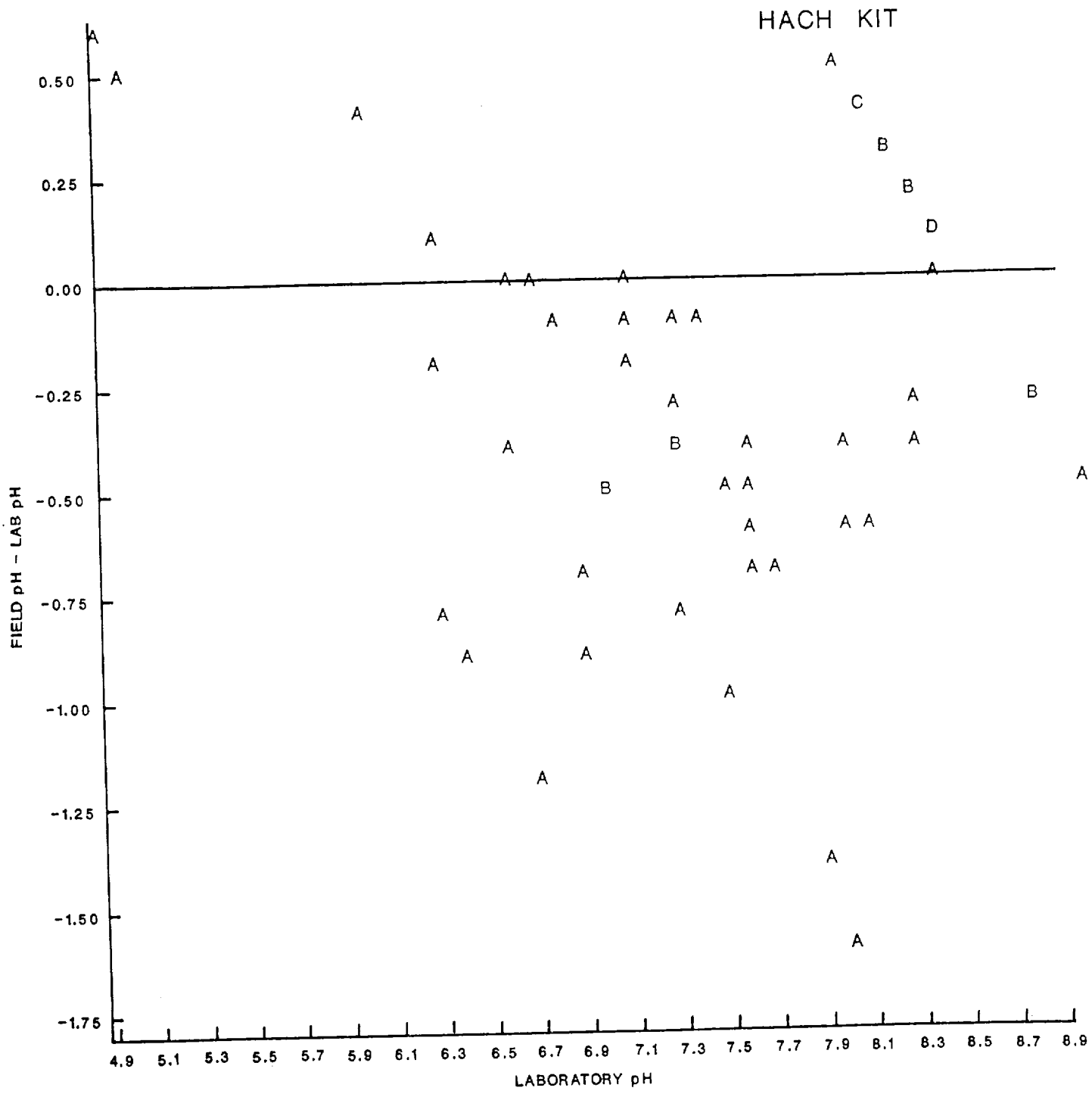


Figure 7: Difference between Hach field pH and laboratory pH as a function of laboratory pH

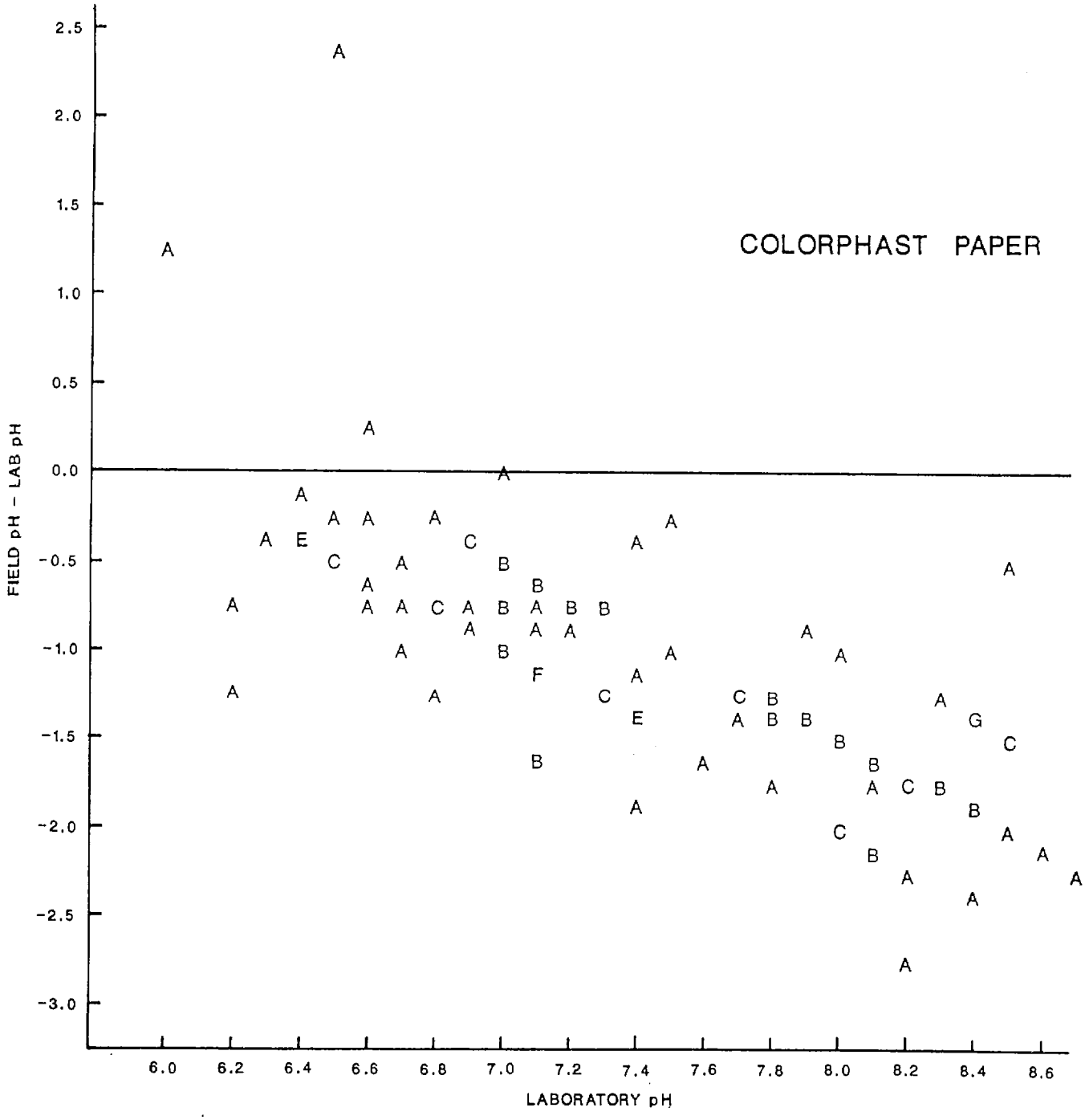


Figure 8: Difference between Colorphast Paper field pH and laboratory pH as a function of laboratory pH

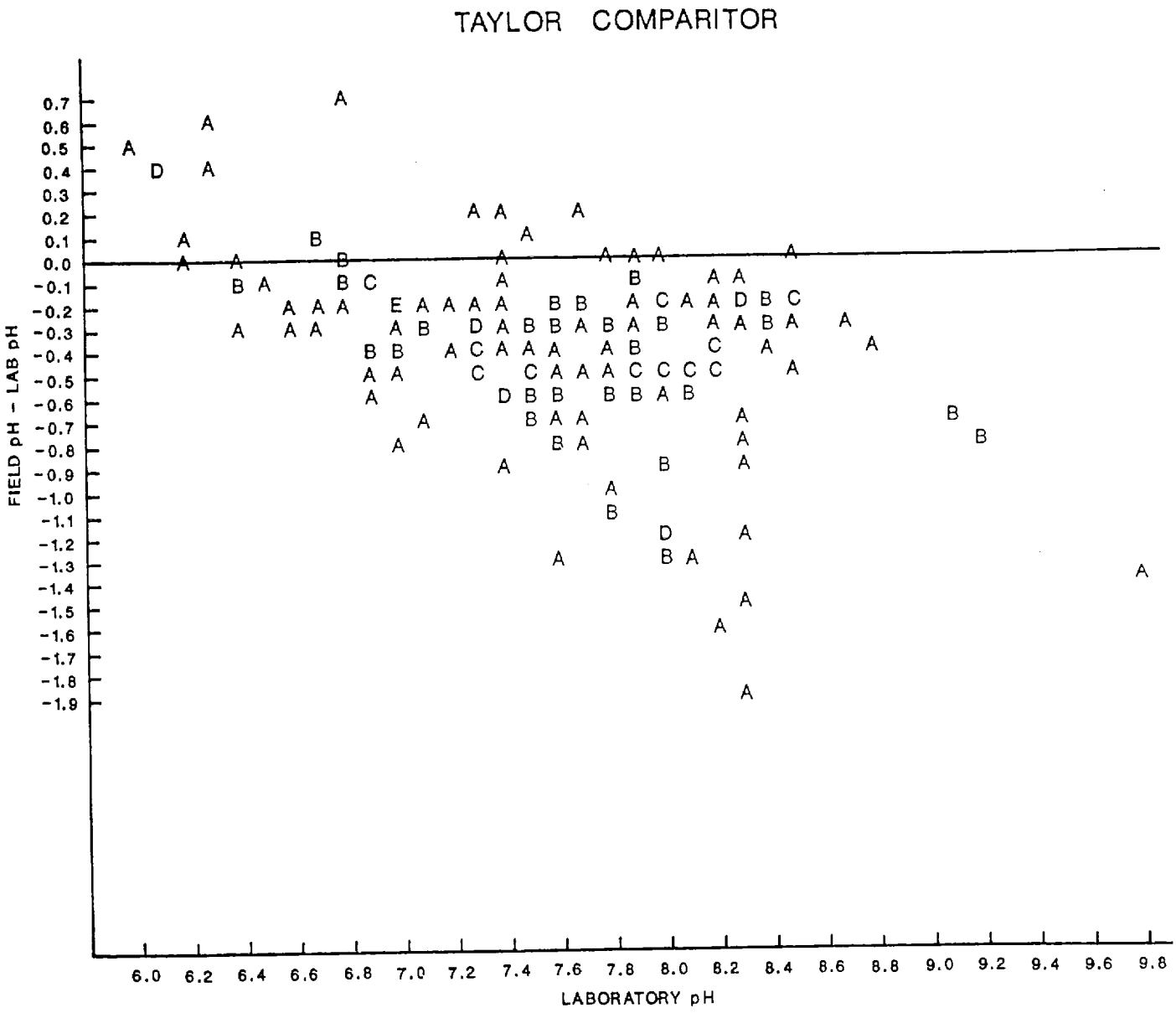


Figure 9: Difference between Taylor Comparitor field pH and laboratory pH as a function of laboratory pH

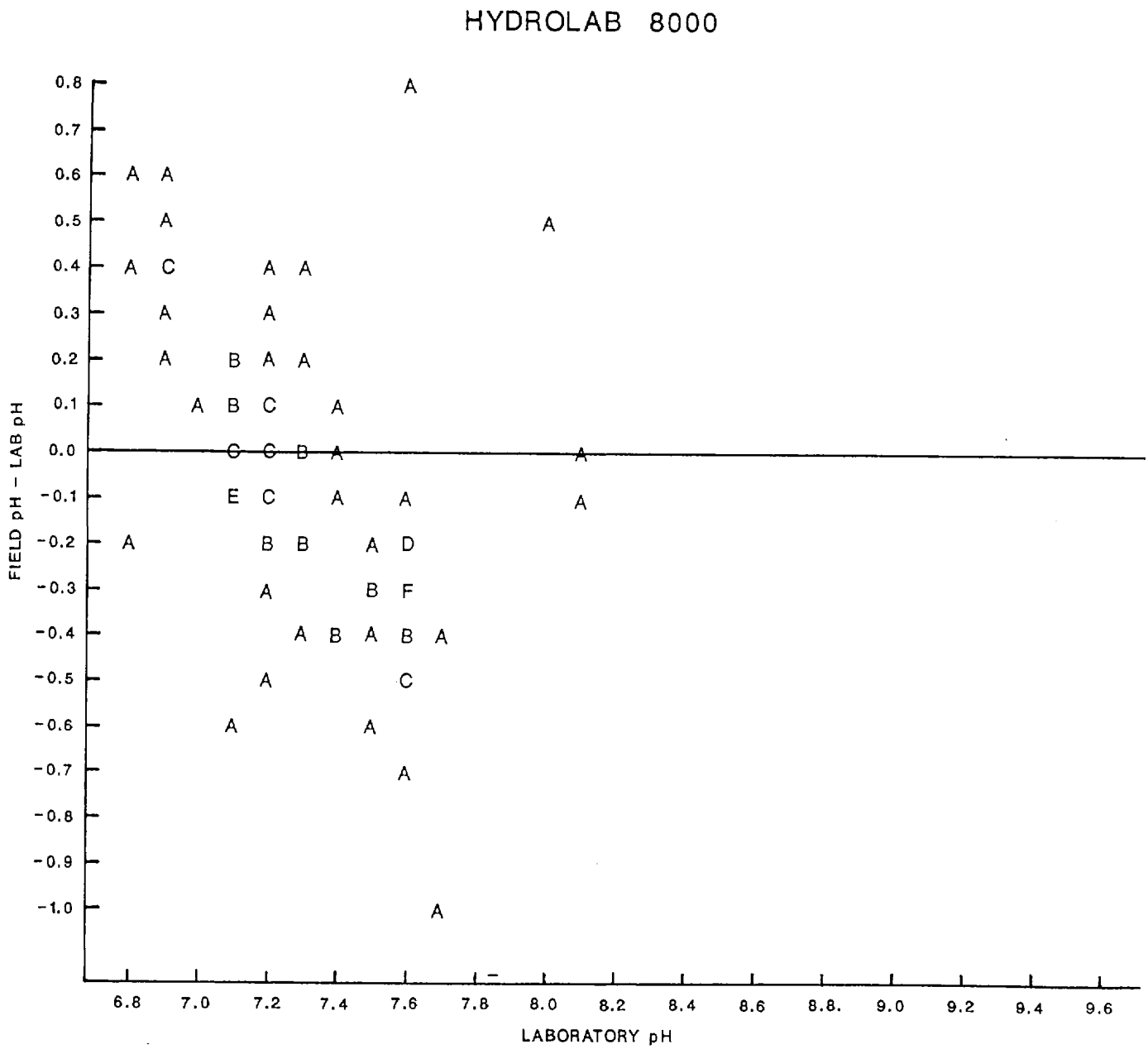


Figure 10: Difference between Hydrolab field pH and laboratory pH as a function of laboratory pH

COMBINATION GLASS ELECTRODE

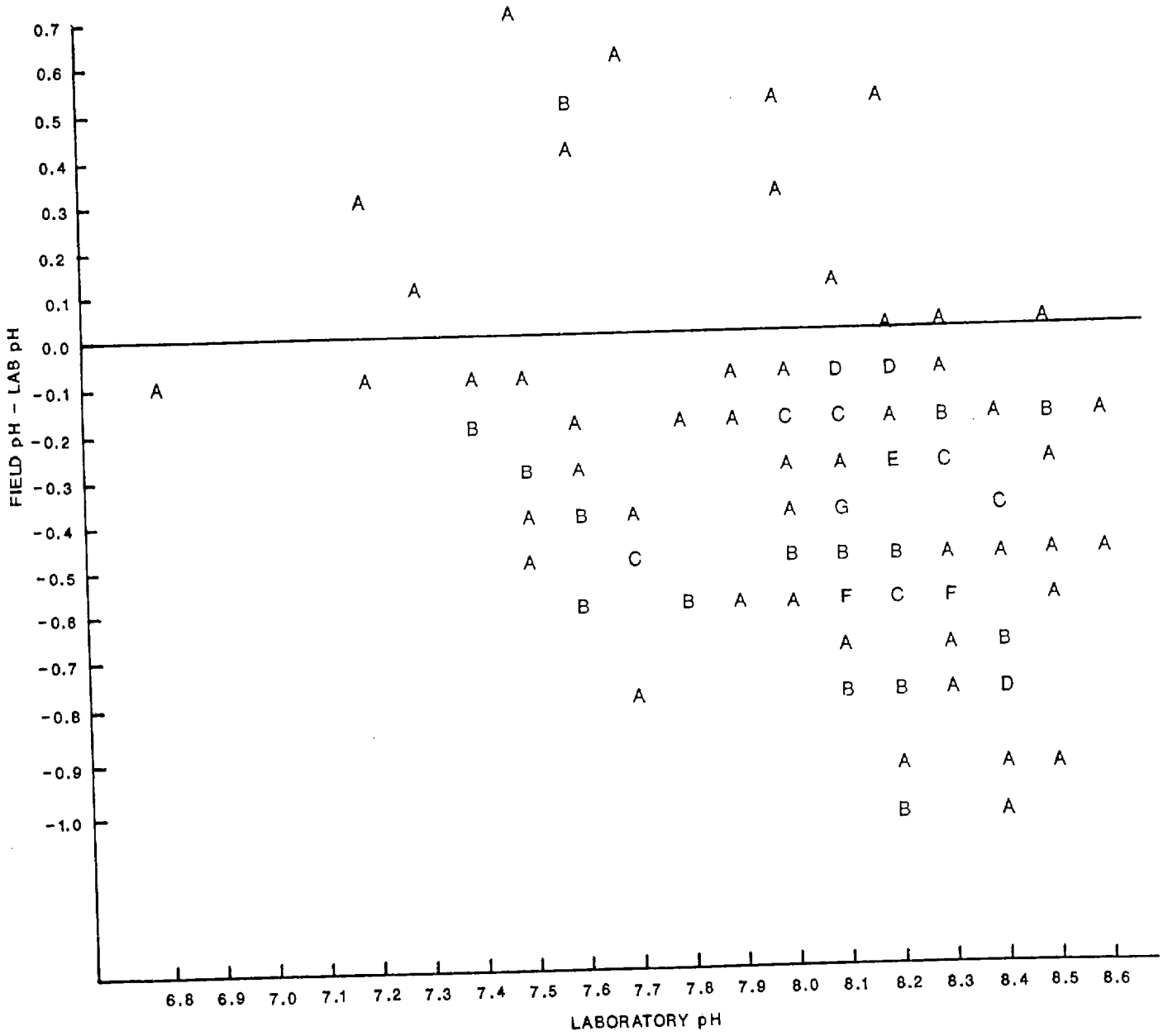


Figure 11: Difference between Combination Glass Electrode field pH and laboratory pH as a function of laboratory pH

TABLE 1

THE pH OF THREE COMMONLY USED BUFFERS AT DIFFERENT TEMPERATURES

Temperature °C	Phthalate	Phosphate	Borate
0	4.01	6.98	9.46
5	4.00	6.95	9.39
10	4.00	6.92	9.33
15	4.00	6.90	9.27
20	4.00	6.88	9.22
25	4.01	6.86	9.18
30	4.01	6.85	9.14

TABLE 2

CHARACTERISTICS OF SOME COMMERCIAL ELECTRODE GLASSES AT 25°C

Designation of Glass or Electrode	Composition of Glass	Glass Resistance (megohms)
Beckman E2	Li_2, O, BaO, SiO_2	375
Beckman General Purpose	Li_2O, BaO, SiO_2	150
Beckman Amber	Li_2O, BaO, SiO_2	550
Cambridge Standard	Na_2O, CaO, SiO_2	87
Cambridge Alki	Li_2O, BaO, SiO_2	560
Corning 015	Na_2O, CaO, SiO_2	90
Doran Alkacid	Li_2O, BaO, SiO_2	200
Electronic Instruments GHS	Li_2O, Cs_2O, SiO_2	200
Ingold U	--	250
Ingold T	--	140
Ingold UN	Li_2O, SiO_2	30
Jena H	--	105
Jena U	--	30
Jena HT	--	800
Jena HA	--	290
L & N Blue Dot	Na_2O, CaO, SiO_2	50
L & N Black Dot	Li_2O, La_2O_3, SiO_2	70
L & N White Dot	Li_2O, La_2O_3, SiO_2	250
Lengyel 115	Li_2O, BaO, UO_3, SiO_2	15
Metrohm H	Li_2O, BaO, SiO_2	1400
Metrohm X	Li_2O, CaO, SiO_2	100
Metrohm U	Li_2O, BaO, SiO_2	500

TABLE 3

DIRECT COMPARISON OF FIELD AND LABORATORY pH DATA

Method	No. of Records	Average Difference*	Standard Deviation	Median	90th Percentile	Maximum Difference
Combination Glass Electrode	415	0.4	0.24	0.4	0.8	1.0
HACH Comparitor	55	0.4	0.34	0.4	0.8	1.6
ColorpHast Sticks	118	1.2	0.58	1.2	1.9	2.7
Taylor Comparitor	189	0.5	0.34	0.4	0.9	1.9
Hydrolab	83	0.3	0.20	0.2	0.5	1.0
Hach Pocket Pen	40	0.135	0.14	0.1	0.3	0.5

*absolute difference between laboratory pH and field pH.

TABLE 4

COMPARISON OF FIELD AND LABORATORY pH DATA AFTER CORRECTING FOR TEMPERATURE DIFFERENCES

Method	No. of Records	Average Difference*	Standard Deviation	Median	90th Percentile	Maximum Difference*
Hach Comparitor	52	0.4	0.34	0.4	0.8	1.7
ColorpHast Sticks	116	1.1	0.59	1.1	1.9	2.8
Taylor Comparitor	179	0.5	0.33	0.4	0.9	2.0

*absolute difference between laboratory pH and temperature corrected field pH.

APPENDIX 1

Anion/Cation Balance in Fresh Water
(from Riehl, 1971)

The accuracy of an analysis may be estimated by comparing the sum of the milliequivalents per litre (me/L) of the positive radicals (cations) with the sum of the milliequivalents per litre of the negative radicals (anions). In a perfect analysis they would be exactly the same. The percentage of error may be figured readily by the Stabler formula:

$$e = \frac{rp-rn}{rp+rn} \times 100$$

e = percentage of error
rp = sum of me/L of positive radicals
rn = sum of me/L of negataive radicals

The milliequivalts per litre are determined as follows:

$$\text{me/L} = \text{mg/L of element or compound (found by analysis)} \times \frac{\text{Valence}}{\text{Atomic Weight}}$$

Conversely, if results are expressed as milliequivalents per litre, milligrams per litre are determined as follows:

$$\text{mg/L} = \text{me/L} \times \frac{\text{Atomic Weight}}{\text{Valence}}$$

The following table shows the coefficients for converting milligrams per litre (mg/L) into milliequivalents per litre (me/L):

Positive Radicals

mg/L Calcium	(Ca)	x 0.0499 = me/L
mg/L Magnesium	(Mg)	x 0.0823 = me/L
mg/L Sodium	(Na)	x 0.0435 = me/L
mg/L Potassium	(K)	x 0.0256 = me/L
mg/L Manganese	(Mn)	x 0.0364 = me/L
mg/L Hydrogen	(H)	x 0.9921 = me/L

Negative Radicals

mg/L Carbonate	(CO_3)	x 0.0333 = me/L
mg/L Bicarbonate	(HCO_3)+	x 0.0164 = me/L
mg/L Sulphate	(SO_4)	x 0.0208 = me/L
mg/L Chloride	(Cl)	x 0.0282 = me/L
mg/L Fluoride	(F)	x 0.0526 = me/L
mg/L Nitrate	(NO_3)	x 0.0161 = me/L

The following table shows the coefficients for converting me/L into mg/L.

Positive Radicals

me/L Calcium	(Ca)	x 20.04 = mg/L
me/L Magnesium	(Mg)	x 12.16 = mg/L
me/L Sodium	(Na)	x 23.00 = mg/L
me/L Potassium	(K)	x 39.10 = mg/L
me/L Manganese	(Mn)	x 27.46 = mg/L
me/L Hydrogen	(H)	x 1.01 = mg/L

Negative Radicals

me/L Carbonate	(CO_3)	x 30.00 = mg/L
me/L Bicarbonate	(HCO_3)	x 61.01 = mg/L
me/L Sulphate	(SO_4)	x 48.03 = mg/L
me/L Chloride	(Cl)	x 35.46 = mg/L
me/L Fluoride	(F)	x 19.00 = mg/L
me/L Nitrate	(NO_3)	x 62.01 = mg/L

Reporting results in terms of positive and negative radicals does not always satisfy the layman for it gives him a hazy impression of the composition of the water; therefore the results may be reported according to a graphic scheme or a possible hypothetical combination.

+Bicarbonate alkalinity expressed as 1.22 X (T-2 Phenothaline Alkalinity)

Graphic Scheme

Graph the milliequivalents/L using the following conventions. The length corresponding to the calculated milliequivalent is graphed in two columns, the cations in the first column and the anions in the second. The anions and cations should be arranged according to a recognized system of pairing. Use the order of positive and negative radicals outlined previously.

The graph provides a visual assessment of the ionic pairs, and anion/-cation balance which is a fundamental requirement in any freshwater study.