

MINIMIZING USER ERRORS

IN pH MEASUREMENTS

Features, Limitations & Potential Errors
of the Tools of pH Measurements

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Table of Contents

1. pH Electrodes
 - 1.1. pH Range
 - 1.2. Deviations
 - 1.2.1. Alkaline Error
 - 1.2.2. Acidic error
 - 1.2.3. Linearity Error
 - 1.2.4. Temperature Range
 - 1.3. Limitations
 - 1.3.1. Solubility of pH glasses
 - 1.4. Chemical Resistance of pH glasses
 - 1.5. Electrical Resistance of pH glasses
2. Reference Electrodes
 - 2.1. Reference Potential
 - 2.2. Calomel Reference Electrode
 - 2.3. Silver/Silver Chloride Reference Electrode
 - 2.4. Junction Potentials
 - 2.5. Flowing Reference Junctions
 - 2.6. Diffusion Junctions
 - 2.6.1. Renewable Diffusion Junctions
 - 2.7. Solid State Reference Junctions
3. Buffer Solutions
 - 3.1. Stability
 - 3.2. Temperature Coefficient on the Buffer Solutions
 - 3.3. Interaction of Buffers with pH and Reference Electrodes
4. Electronic Devices
 - 4.1. pH Meters
 - 4.2. Pre-amplifier
 - 4.3. Temperature Sensors
5. Practical Considerations
 - 5.1. Mono Electrodes
 - 5.2. Combination Electrodes
 - 5.3. Symmetric Cells
 - 5.4. Interpolation vs. Extrapolation
 - 5.5. Automatic Temperature Compensation
6. Matrix to Select pH Equipment for Preset Accuracy & Reproducibility
 - 6.1. Within +/- 0.5 pH
 - 6.2. Within +/- 0.1 pH
 - 6.3. Within +/- 0.05 pH

1. pH Electrodes

1.1 pH Range

Over one hundred different compositions available from many different manufacturers

None exhibit completely linear pH response in overall pH range specified

Maximum available pH range: -2 to 16 pH in aqueous solutions

Optimum, linear pH range: typically 2 pH units less specified minimum and maximum

1.2 Deviations:

1.2.1 Alkaline error

pH glass composition, alkali ion and ion concentration dependent at a given pH value

Always will reduce the pH value measured from the actual

Error may be as little as 0.05 pH and up to 0.5 pH within specified pH electrode measuring range

Verify alkaline errors before pH measurement if value expected within 2 pH unit of specified upper limit

Determine alkaline error experimentally before performing measurement if information not available

1.2.2 Acidic error

Most pH electrodes exhibit a lower than actual pH value in concentrated acids

Some deviation may start at 0.1 Molar concentration.

Error is different for almost every acid

Error may be as high as 0.5 pH

There is no clear theoretical explanation and no clear relationship to pH glass compositions

Magnitude of error can be determined by using solutions of known concentration

1.2.3 Linearity error

There is some deviation from a linear pH response even in the range where neither alkaline nor acidic error is exhibited

Error may be different for every pH glass composition

The simple compositions show most linearity

Maximum for such an error may be about 0.04 pH but could compound with other potential errors

Depends to a lesser degree on the buffer solutions used

1.2.4 Temperature Range

Most pH electrodes will work within -5 to 105 °C

The general limiting factor is the reference electrode

Short term usage may exceed specified continuous temperature limit by 20 °C

For use in non aqueous solutions and under pressurized conditions limit may go up to 150 °C

1.3 Limitations:

1.3.1 Solubility of pH Glasses

pH glasses in reality are only mixtures of oxides, transparent but otherwise do not exhibit all characteristics of real glasses

Many are soluble in low conductivity solutions especially in distilled, deionized and ultrapure water

Continuous drift, frequent calibration and short service life will result from pH glass dissolution

The dissolving process will accelerate at elevated temperature

There are no data available for selecting the right electrode, trial and error will provide the answer

1.4 Chemical resistance of pH Glasses

Two major groups of chemicals are risk factors, fluorides and carbonates

Hydrofluoric acid and bifluorides form precipitates with most pH glasses. Precipitate is porous and will build up over time

An attacked electrode will develop a slow response, the magnitude of change depending upon thickness of precipitate

Precipitate will adsorb on its large surface sample or buffer causing calibration errors and requiring repeated calibration. Error may be in the tenth of pH units

Precipitate may be removed with concentrated Hydrochloric acid. Electrode will have drastically shortened lifetime

There are some glass compositions not building precipitate which, after initial exposure do not need recalibration and have reasonable service life

Carbonates and bicarbonates will slowly react with oxides on the surface of the pH glass. These slightly soluble carbonates will be dissolved causing drift if exclusively used in such solutions (NIST traceable pH 10 buffer)

Limited time exposure to bifluoride and/or bicarbonate solutions may be utilized to rejuvenate contaminated surface of pH electrodes

1.5 Electrical resistance of pH Glasses

Electrical resistance of pH electrodes has no limit in developing electrode potential

Electrical resistance will influence speed of response and accuracy related to instrumentation (refer to sections following)

Electrical resistance sharply changes with temperature, will double with approx. every 7.5 °C decrease of temperature, and will be cut in half with increase of temperature

Special glasses are available for extremely low, and extremely high temperatures

Low temperature pH glasses may not function well and may have a limited lifetime above room temperature

High temperature glasses exhibit very high resistance at room temperature, which rapidly changes by aging. This will further increase the resistance at room temperature, making calibration difficult and creating potential error in conjunction with instrumentation

Electrical resistance changes with the aging of the electrode and closely resembles an exponential curve

pH electrodes with wall thickness above 0.015 " change resistance at a lower rate than electrode with much thinner walls of 0.005"

2. Reference Electrodes

2.1 Reference Potential

Reference electrodes typically are electrodes of the second kind, their potential depends on the anion concentration of their filling solution.

Ideal reference electrodes would produce a reference potential independent of temperature, pressure, composition of sample and have no junction potential.

The ideal reference electrode does not exist, the design and its selection is always a compromise to achieve maximum accuracy and reproducibility in a particular application.

2.2 Calomel Reference Electrode

Once the most widely used reference electrode.

Exhibits low temperature coefficient.

Saturated Potassium Chloride generates low junction potential.

Nowadays mercury is not welcomed in many laboratories.

Not convenient to build into combination pH electrodes.

Continuous operational temperature limit is about 60 °C.

In flowing junctions, does not create a precipitate.

With proper maintenance, produces stable and reproducible reference potential for many years

2.3 Silver/Silver Chloride Reference Electrode

Reference potential dependent of fabrication of half cell.

Exhibits high temperature coefficients.

The higher the chloride concentration, the higher the temperature coefficient.

The higher the chloride ion concentration, the lower the junction potential.

Silver Chloride has high solubility in Potassium Chloride in a complex form resulting in potentially high hysteresis at high chloride ion concentrations.

The high complex concentration may result in precipitation of Silver Chloride in flowing single junction reference electrodes if the Chloride ion concentration of sample is much lower than that of the filling solution. Silver Chloride will react with many biological solution. The prevention is to use double junction reference electrodes.

May be easily accommodated in combination pH electrodes of any size.

Potentially sensitive to. u.v. light.

2.4 Junction Potentials

The junction potential is the source of the most hidden error in pH measurements. It develops in the reference junction separating the internal filling solution of the reference electrode from the buffer or sample solutions. The cause of the development is the different diffusion rate of cations and anions on both sides of the reference junction.

It is difficult to detect, difficult to measure, depends on the kind of reference electrode used, the type of junction employed and the composition and concentration of the buffer or sample solutions.

The resulting error may be as high as 0.5 pH.

The system least likely to develop junction potential is when low concentration buffers and sample solutions are measured and a saturated Potassium Chloride filling solution is used.

Higher than or much lower than theoretical slope should be a warning sign for junction potentials.

2.5 Flowing Reference Junctions

The most advantages type in generating the lowest junction potential. High velocity, low flow rate is the key of the elimination of junction potential.

Typical junction materials are a bundle of quartz fibers, collimated holes, single crystals of asbestos fiber.

The working principal of the junction is to keep ions from the outside to diffuse into the junction.

2.6 Diffusion Junctions

The most widely used type of junction. This type includes junction materials of wide diversity from porous ceramics and plastics to porous wood. They may be combined with viscosity reducing agents in the filling solution like CIVIC, agar-agar, natural and synthetic gums, water soluble polymers etc.

There will always be a junction potential developed on the surface of the junction, which will enter the interior of the filling solution creating multiple layers of junction potentials.

Reduction in time of exposure to buffer or sample solution will help to reduce the junction potential.

Junction potentials may reach an equilibrium if the reference electrode is exposed to a solution of constant composition and concentration for prolonged time. Change of either composition or concentration will require significant time to establish new equilibrium after a long term exposure.

2.6.1 Renewable diffusion junctions

This type is a more advantageous type of diffusion junction. All utilize a design where the internal filling solution is in direct contact with the buffer or sample solutions. When solution is changed, the portion of the filling solution in contact with the solution will be discarded and a new portion of the filling solution will be in contact with the solution.

This design does not eliminate the junction potential, but makes it very reproducible.

Such junctions typically utilize tapered ground glass junctions or single large size capillaries. The renewal of the contacting filling solution either happens by gravity when separating the two sides the ground glass junction or by temporarily pressurizing the chamber of the reference electrode filling solution.

These type of reference junctions need significant maintenance to keep the junction area contamination free. They also need frequent refilling of the filling solution.

2.7 Solid state reference junctions

Most of them are considered diffusion junctions. The solid state part is typically a crosslinked solid plastic with high concentration of solid Potassium Chloride and a potential reservoir for solid crystalline salts.

The diffusion process creating the junction potential is made almost impossible. The dissolution of the solid salt will slowly exhaust the conducting ions in the solid matrix and stop the function of the reference electrode. They are mainly used in difficult process control applications.

3. Buffer Solutions

There are many different types of buffer solutions covering the whole pH range and designed for diversified applications. The primary function of these solutions is to provide a known pH value for calibration purposes and preserve this value for a long period of time.

3.1 Stability

The chemical composition of the buffers is selected of highly stable compounds. There are many different exposures in using them, which tend to reduce the stability of the buffer solution.

Contamination of acidic or alkaline media will slowly change the pH value. The amount of acid or alkali to change the pH value of a buffer by 0.1 pH is referred to as buffer capacity.

Repeated use of the buffer will exhaust this capacity and cause an error in calibration.

Dilution of the buffer with deionized or distilled water will also change the pH value of the solution. The lesser the change by the addition of the same amount of water represents a higher resistance to dilution.

The addition of solid salt will result in a so-called salt effect shifting the equilibrium of the components and changing the pH value of the buffer solution.

3.2 Temperature coefficient of the buffer solutions

The buffer solutions will change their pH value with temperature. This is a result of the shifting of the chemical equilibrium of the components, mainly of dissociation. Knowing the temperature dependency of any given buffer will greatly enhance the accuracy of the calibration when utilizing the proper pH value at any given temperature.

The temperature limits of the buffer solutions where sufficient stability is still achieved, are different. These limits should be taken into account when selecting a temperature for calibration.

3.3 Interaction of buffers with pH and reference electrodes

Some buffer solutions, like carbonate/bicarbonate buffers may effect the function of the pH electrode and exposure should be limit in time.

In order to develop the least amount of junction potentials the buffer solutions are typically dilute solutions. The concentrations selected may represent a balance between stability, temperature coefficient and junction potential.

Some buffer solutions, like tris buffers may develop high junction potential and may require special, controlled diffusion reference junctions.

4. Electronic Devices

4.1 pH Meters

pH Meters are a special type of millivolt meters with some added features. They are capable of converting the electrode potential into pH units. They are also equipped with temperature sensor to measure and compensate the temperature effect of the pH measurement. The other special feature is the capability to measure the electrode potential of high resistance pH electrodes with least amount of distortion to this value.

There are many different kinds of pH meters on the market and in the workplace from analog to digital and to microprocessor controlled with memory and interactive capabilities.

A common pH meter characteristic is expressed as an input resistance, the capability to handle the high impedance of the pH electrodes. This capability needs some maintenance and may be reduced by aging and elevated temperature.

The maintenance is mainly needed to keep the exposed connector contamination free. Significant reduction of the insulation of the connector will result in an error.

The operating temperature limit also has to be honored. Temperatures higher than the limit may deteriorate the electronic components handling the high impedance pH electrode, lower temperature may inactivate the same component. The electrical resistance of the pH electrode in relationship to the input resistance may have a great influence on the potential error generated by the pH meter itself.

In order to perform a measurement with 0.1 % error of the actual electrode potential, the input resistance has to be 1000 times higher than the resistance of the electrode. 1 % error will result when this ratio is only 100, and 10% error, when the ratio is a mere 10.

This characteristic will also result in a change of the displayed pH value and reduce the difference between the real pH value of a sample and pH 7 with the appropriate percentage. This error is more pronounced if only a single point calibration is performed.

Older type pH meters typically are outfitted with a pH range of 0-14 units. Newly developed meters were designed with the recognition that the range extends below 0 and above 14 pH. There is a risk that some pH meters display 0 pH value, when the pH is below 0 and 14 when it is above. This design feature may result in substantial error especially when not recognized.

The temperature measuring range of many pH meters is limited by the linearity of the temperature sensor or by the electronic circuitry handling it. Be sure to know what this limit is before using the pH electrode at an elevated temperature. This limit will also limit the temperature compensation of the pH measurement.

The accuracy of the temperature compensation is also greatly influenced by the design and the distance of the measured asymmetry potential from the actual isopotential point, where the correction is zero. The typical isopotential point in most pH meters is at pH 7. The instrument expects 0 mV reading in a pH 7 buffer. Any deviation will result in an erroneous temperature compensation of a pH value.

There is though an accepted limit to permit variations from manufacture, which generally is about ± 20 mV. Beyond this value the error becomes significant and many pH meters may reject a calibration. There are some other factors which may create a hidden error in temperature compensation and will be noted in a later chapter.

Many microprocessor controlled pH meters have features, generally called Auto Read. There is a part of the program which monitors the change of electrode potential and at a preset or a selected rate to lock up the reading. This feature may create some potential error. If the electrode response is slow, for whatever reason, or there is also a constant drift, the pH meter may lock up prematurely. This will prevent the pH meter from coming reasonably close to the reading it is approaching (limit).

Repeated engagement of the auto read system will greatly reduce this error.

An other convenient feature is the so called Auto Calibration. The most advanced auto calibration systems have the temperature corrected pH buffer values in their memory. Always use a temperature sensor with this feature. The lack of using the proper calibration value will result in significant error if the calibration was performed at anything other than room temperature.

There is also an upper limit in temperature when the calibration is performed at an elevated temperature. The buffers used may not have the corrected buffer pH value available at that temperature. In this case, a lower temperature need to be selected for the calibration.

Another factor in auto calibration needs to be taken into account. The temperature corrected buffer value of only 3 to 5 different buffers are typically available. Check the values of these buffers when selecting the calibration points. The temperature corrected buffer values often must be manually entered as a custom buffer value if the meter does not contain the value of the buffer at the calibration temperature or does not have the desired buffer programmed into memory.

The buffer pH values selected for calibration are stored in the memory until erased or a new calibration is performed. When entering into a different range in pH value of a new sample, check that the calibration is bracketing the expected pH reading. This technique will greatly enhance the linearity of the measurement and redistribute occasional junction potentials generated on the reference junction by buffer solutions.

Many new pH meters also have diagnostic features. These pH meters may check the initial resistance of the pH electrode, the resistance of the reference electrode, the asymmetry potential, etc. These values may permit the monitoring of the aging of the electrode, the contamination of the reference junction or the reduced ability of the system to perform reasonable temperature compensation.

Some of these diagnostic features require the increase of complexity of electrodes, some type of electronic features may interface with the basic measurement circuitry creating some hidden errors. If any doubt, compare the pH value on a not so sophisticated pH meter. In particular, if the instrument displays absolute or relative millivolts (mV), a given calibration or measurement can be checked manually.

4.2 Pre-amplifier

The high electrical resistance of pH electrodes require the use of special, coaxial shielded cable to reduce noise by electrostatic and magnetic fields. Even the use of such coaxial cables will limit the maximum length of the cable that may be used.

The motion of a long cable also may change the capacitance of the cable and create a temporary change in the reading of the pH meter.

These disadvantages can be greatly eliminated by using so called preamplifiers. These devices convert the high impedance analog signal either into a low impedance analog or digital signal. The devices are either built into the electrode or are located in the vicinity of the electrode. The converted (conditioned) signal may be transmitted distances which is many multiples that of the unconditioned signal sent via a coaxial cable.

Many such preamplifiers may also contain memories, which will store information about that particular electrode. This eliminates the risk of using data collected from an other electrode, when a new electrode is attached to the pH meter. The increased complexity may also increase the price and potential failure of the electrode.

4.3 Temperature Sensors

Temperature sensors are becoming a standard accessory of pH meters. There are a large number of different type of devices used to perform the task, like resistors, thermistors, diodes, transistors and microchips. Some pH meters utilize the known temperature coefficient of the resistance of the pH electrode to measure and perform temperature compensation. These temperature sensors in most instances are not interchangeable with each other. When using temperature compensation, always check the temperature display for correct temperature before calibration.

Some of these devices may have limited linear ranges. Check this range before performing a pH measurement with automatic temperature compensation.

With the exception of some uncurve thermistors, which are interchangeable, most temperature sensors need calibration to eliminate variations in the values at a specified temperature. Perform the calibration before use to enhance the accuracy of the pH measurement.

5. Practical Considerations

5.1 Mono Electrodes

The use of a separate pH and reference electrode, so called mono electrodes has some advantages. It provides the option to change only one electrode if there is a change in electrode requirements to best fit the application. This arrangement will provide the option to change the reference electrode for enhanced performance or select a pH electrode to reduce a chemical attack. The mono design also permits the use of many different type of flowing junctions, which are difficult if not impossible to implement into a combination electrode.

In the case of breakage, only one electrode need to be changed, reducing replacement cost. This would be though counteracted by the higher initial acquisition cost of a pair of electrodes.

Based on the design of the mono electrodes they are less prone to noise because of more complete shielding, exhibit faster response because of the more advantageous mechanical configuration and are less prone to carryover, reducing a potential source of hidden error.

5.2 Combination Electrodes

Combination electrodes are more convenient to handle, can be manufactured almost in any size and typically require small size samples. Most of these combination electrodes are also available in maintenance free, permanently filled versions. These electrodes in most cases exhibit a higher junction potential and slower response than a pair of mono electrodes.

The mechanical arrangement of the combination electrodes limits the use of some type of more advantageous junctions, makes the complete shielding of the electrodes more challenging and the overall design more fragile than a pair of mono electrodes.

The introduction of the plastic bodied electrodes, which further limits the durability of the components and needed the addition of protection of the bulb or junction, also can entrap the solution in these so called protector tips, resulting in a carryover, which may add a significant error. This carryover phenomenon poses a greater risk when changing the electrode from a solution of high concentration to a much lower one. In such cases it may cause errors up to one pH unit or more. This type of carryover may be so repeatable that the

detection of it is almost impossible. The potential risk of carryover is also significantly enhanced by the difficulty of rinsing and blotting dry such combination electrodes after each measurement or calibration.

5.3 Symmetric Cells

Many of the earlier electrode designs, especially combination electrode designs did not employ the same half cells in the reference electrode and the pH electrode in regard of chloride ion concentration. This non symmetric arrangement resulted in different temperature coefficients for the two half cell, creating a significant difference in the generated electrode potential from the theoretical value at elevated temperature. This difference can be significant at temperatures close to the limit of the electrode and at low and high pH values.

The two different half cells will also change the potential at a different rate, creating a deviation of the pH value when going full cycle from low temperature to high and back. The difference in the pH value of the same sample is called hysteresis. This hysteresis will change its magnitude by the frequency of the temperature cycle and the temperature difference.

The hysteresis could also be the result of different thermal conductivity of the parts employed to fabricate the pH and reference electrode creating a delay in thermal equilibrium of the two electrodes.

5.4 Interpolation vs. Extrapolation

Accurate and reproducible pH measurements require a two point calibration. The measurement performed within the limits of the two point calibration will result in higher accuracy than any measurements performed outside of the calibration. Any factor influencing the accuracy and reproducibility within the calibration limits can be detected by the computed slope. The instrumentation will measure the difference in the electrode potential from the calibration point and will perform an interpolation computing the measured pH value. If there is any junction potential developed, non linearity exhibited, even if not detected, the error will be distributed to the full difference of the calibration values.

When performing a measurement outside of the calibration limits neither the junction potential nor any non linearity can be detected and may result in a hidden error.

The convenience of auto calibration and its limit in preprogrammed buffer solution enhances the chance of such extrapolation processes. If accuracy and reliability of the pH measurement is to be obtained always select two buffer solution below and above the expected pH value of the sample. If it accidentally falls outside of the limits, recalibrate utilizing buffer solutions filling this requirement.

5.5 Automatic Temperature Compensation

The use of automatic temperature compensation poses a fair number of potential errors. The non symmetric cells, deviation of the isopotential point from pH 7, increased asymmetry potential all will contribute to an invisible error.

The lack of proper information of the buffer pH values at elevated temperature, calibration with buffers of unknown temperature coefficient or high temperature calibration outside the limits of the buffer solutions may accumulate this error.

One other risk of creating an error may be the result of an overall non Nernstian temperature coefficient. This coefficient will be a result of the coefficient of the two half cell, the coefficient of the internal filling buffer solution in regard of pH value and the coefficient of the potential junction potential.

In order to enhance the accuracy of the automatic temperature compensation there is new generation of pH equipment coming on the market. These new pH meters let the user select the practical isopotential point and input the actual temperature coefficient of the electrodes employed.

6. Matrix to Select pH Equipment for Preset Accuracy and Reproducibility

6.1 Within +/- 0.5 pH

1. **pH Electrode:** Mono or Combination, special attention should be paid to rinsing and blotting electrodes to eliminate carryover; apply specified data to compensate for acidic and alkaline errors
2. **Reference Electrode:** Silver/Silver Chloride gel filled, diffusion junction
3. **pH Meter:** Any with 0.01 pH resolution, manual or automatic temperature compensation
4. **Buffer Solutions:** Any calibrate at room temperature
5. **Temperature Compensator:** Compatible with pH Meter with +/- 2 °C accuracy

6.2 Within +/- 0.1 pH

1. **pH Electrode:** Mono or Combination, low carryover design, symmetric half cells, determine and correct for acidic and alkaline errors
2. **Reference Electrode:** Silver/Silver Chloride , gel filled, double junction with diffusion junction
3. **pH Meter:** Microprocessor Controlled with automatic temperature compensation, buffer recognition including temperature effect
4. **Buffer Solutions:** Any NIST Traceable Buffer, calibrate at room temperature
5. **Temperature Compensator:** Compatible with pH Meter with +/- 1 °C accuracy

6.3 Within +/- 0.05 pH

1. **pH Electrode:** Glass Mono or Combination, with symmetric half cells, determine and correct for acidic and alkaline error, also for asymmetry potential
2. **Reference Electrode:** Silver/Silver Chloride with symmetric half cell, liquid fill, diffusion or flowing junction, determine and correct for junction potential if measurement within 2 pH units of range of pH electrode
3. **pH Meter:** Microprocessor Controlled with 0.001 pH resolution, automatic temperature compensation, buffer recognition with correction of temperature effect
4. **Buffer Solutions:** Any NIST Traceable Buffer, calibrate as close to sample temperature as possible
5. **Temperature Compensator:** Compatible with pH Meter with +/- 0.5 °C accuracy, calibrate temperature sensor, calibrate before using for pH calibration or measurement