How can I fix my pH function?

There's pretty much only two causes of pH calibration error: The pH electrode or the instrument (well, duh! But hopefully not both at once!).

Checking and cleaning the electrode

The following steps provide ways to check electrode function (steps 1-5), and to attempt to recondition a dirty electrode.

1. Be sure the pH electrode has been stored at least 24 hours in a proper electrode storage solution (Vinmetrica's product is 3M potassium chloride in 10 mM potassium hydrogen phthalate; other similar products may be used). The entire bottom 1 inch of the electrode needs to have been submerged for at least 24 hours. If this has NOT happened, wait until it has!

NOTE: when calibrating or measuring with a pH electrode, always be sure the solution is gently stirred or swirled constantly! Stagnant solutions can give pH values that are erroneously high.

2. If the instrument has firmware version 3.2.d, or 3.0.6 through 3.1.2, perform a pH cal reset in Test Mode. See Appendix A, Section 13 in the manual for how to do this. Exit Test Mode and try to calibrate again if possible.

3. Check the voltage of the pH electrode. On the newer versions of our instrument's firmware (version X.1.1, X.1.2, or X.2.d, where X = 2 for an SC-200 and X=3 for an SC-300) you can check the raw voltage coming out of the pH probe (see your manual about "potential Mode). A good electrode should have +5 to -15 millivolts (mV) at pH 7 and at least an additional 160 mV on top of this pH 7 value at pH 4.01 (e.g., 165 to 145, resp.).

Note: do not check the voltage of a pH electrode with a voltmeter! You will get meaningless results, because even very good voltmeters do not have the necessary high input impedance to accurately measure a pH electrode's voltage.

a. Put the instrument into Potential Mode (push the Mode button once when in pH mode); now the pH LED blinks.
b. Rinse the pH electrode and place it in the pH 7.00 reference solution. Stir or swirl the solution gently and continuously so that the electrode is not sitting stagnant in the liquid.
c. Write down the mV reading on the LCD screen once it stabilizes. On instruments with FW version 3.1.1 and 3.1.2, a negative mV value is indicated by the red STOP LED illuminating.
d. Repeat steps a. and b. using the pH 4.01 reference solution.

On Table 1 below are shown acceptable values for the pH 4 responses for pH 7.0 values, assuming an acceptable slope is 59.2 +/- 102/95% at 25°C. If your electrode is falling outside of these ranges, and/or if its response time is very slow (see (4.) below), you should try to clean and/or recondition it (see 6. below), or if these steps do not restore proper function, it probably needs to be replaced.

Table 1. Acceptable mV responses in potential mode for pH electrodes. Red is marginal.

Measured pH 7 value, mV	Ideal pH 4.01 mV value	Lower OK pH 4.01 mV value (95% slope)	Upper OK pH 4.01 mV value (102% slope)
-20	158	148.	161.
-15	163	153.	166.
-10	168	158.	171.
-5	173	163.	176.
0	178	168.	181.
5	183	173.	186.
10	188	178.	191.

4. Check the response time of your electrode. In a well-stirred solution, the pH electrode should reach to within 0.05 pH of its final value in 15 seconds and should hit its final value in 30 seconds. If it is much slower than this, you probably need to replace it; but you can try the cleaning recommendations on the Vinmetrica web site (see 6. below).

5. Cream of Tartar test: measure the pH of a saturated solution of cream of tartar which has a pH of 3.55 at 25 °C.

a) Get pure cream of tartar powder (grocery store stuff is fine, provided it's pure and not too old), or reagent grade potassium hydrogen tartrate, also known as potassium acid tartrate or potassium bitartrate. Call it KHT for short.
b) Place about 1/4 teaspoon of KHT in 20 mL of distilled water. Mix well for about 30 seconds. You want to be sure the solution is *saturated*, i.e., everything that can dissolve, has dissolved. There should be some undissolved solid left.
c) Decant or filter the solution off the solids.
d) This solution has a standard pH of 3.55 at 25 degrees C (78 °F). The calibrated pH electrode should measure within 0.05 pH of this value at temperatures from 20 to 30 °C. Discard the solution after 24 hours.

If the above tests confirm a problem, you can try some of the cleaning tricks in step 6-12 below. If the pH electrode seems to be OK, try "Checking and adjusting the instrument" at the end of this document.

6. Cleaning and reconditioning pH electrodes: from our FAQ under Vinmetrica support: pH issues.
Note: before you try the procedures that follow in steps 7-12, try the simple step of soaking the electrode in pH 4.01 reference solution for about 1 hour, then try to calibrate.

Even in normal use and storage, performance of pH electrodes may show deterioration over time, which typically shows up as noisy, erratic or sluggish electrode readings, and/or difficulty calibrating. Assuming the meter itself is working (see "Meter test" below), then there are two main causes for this:
A. Clogging of the reference junction (most likely).
B. Fouling of the glass membrane (happens occasionally, or after prolonged service).

The following procedures will often provide renewed stability and pH sensitivity. If the electrode cannot be restored by one of these methods, it needs to be replaced.

Unblocking the reference junction: The reference electrode junction is usually the problem when the electrode can't calibrate in its expected ranges. This junction is a fine-pored frit that allows electrical contact of a reference electrode with the solution being tested. It can become clogged over time.

7. Soak electrode in hot (NOT boiling!) water, about 60 °C, for 10 mins. Allow to cool to room temperature then rinse and place in pH 4 reference solution for 5 minutes. Try to recalibrate. If this does not work, try the next step.
8. Place electrode in electrode storage solution (from Vinmetrica, or 3M KCl with optionally added 0.01M potassium acid phthalate, KHP) at 60 °C and allow electrode and solution to cool to room temperature, then rinse and place in pH 4 reference solution for 5 minutes. Try to recalibrate. If this does not work, try the next step.
9. Soak in 0.1M HCl (note: this can be made by diluting 1 mL of the SO2 Acid Solution with 20 mL DI water) or HNO3 for 1 hour. Rinse with DI water, then place in 0.1 N NaOH or a little of the TA Titrant for 10 minutes. Then rinse and place in pH 4 reference solution for 5 minutes. Try to recalibrate. If this does not work, try the next step.
10. Soak in 1:10 dilution of bleach in a 0.1 – 0.05 % solution of liquid detergent in hot water with vigorous stirring for 15 mins. Rinse with DI water, then place in pH 4 reference solution for 5 minutes. Try to recalibrate. If this does not work, try step 11.

Cleaning the pH electrode's glass membrane: The glass bulb is a thin membrane of a special kind of glass that actually does the job of responding to the pH of the solution. It can sometimes become dirty and poorly responsive.

11. Immerse electrode tip in 0.1M HCl (see above for how to make) for about 15 secs., rinse with distilled water, then immerse in 0.1M NaOH (you can use a little of your TA Titrant for this) for another 15 sec. Cycle the electrode through these solutions several times (rinsing with DI water in between), then rinse and check for performance in pH buffer 4.00 and 7.00.
12. Some other tricks: protein deposits can be removed by soaking in 1 % pepsin in 0.1M HCl for 15 mins. Inorganic deposits may be removed by soaking in 0.1M tetrasodium

EDTA solution for 15 mins. Grease and oil deposits may be removed by rinsing electrode in mild detergent in methanol solution.

Checking and adjusting the instrument

If the electrode appears to be normal per table 1, there may be an instrument issue known as "pH bias error" that's preventing calibration. You can try adjusting this bias with the "set pH DAC" section (#14) in Test Mode (firmware versions 3.2.d or 3.1.2 only). This changes the pH Bias in an attempt to bring the pH response into reference range. See Appendix A, Section 14 in the manual for more information.

1. Enter Test Mode: turn on the instrument holding down the POWER button until the firmware version is displayed, then immediately release the button).

2. Scroll through the sections of Test Mode by briefly pressing the POWER button. Pressing it 13 times from the first section should bring you to section 14.

3. Section 14 will show a message "SEt PH dAC", then will cycle between two numbers, a voltage number like 2.23, followed by an integer whose default value is 16. This integer is the "pH DAC Index".

4. Pressing "Enter" will raise the pH DAC Index value which will lower the apparent pH value. Pressing the "Mode" button does the opposite. So if, as is most common, your calibration values are too high (like 4.6 in pH 4 reference solution), you'll want to press ENTER. You'll see the pH DAC Index increase to 17.

5. To exit Test Mode, hold down the POWER button again until the instrument shuts off.

6. Now try your normal calibration.

If adjusting the pH DAC Index up or down two steps (i.e. from 16 to 18 or to 14) does not bring the calibration values into line, there is a likely an "impedance problem". Contact Tech Support.

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