Soil pH Troubleshooting

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Soil pH is one of the more difficult test to troubleshooting. The first problem is knowing you have a problem and once you know you have a problem it is difficult to isolate the source of problem (e.g. technique or equipment).

Quality Control Program to Identify pH Problems

Most quality program are inadequate to catch a "bad" probe because: 1) over reliance on pH buffer standards; 2) check samples are not "difficult"; 3) lack of cross checking probes; and 4) equilibration time is inconsistent due to manual technique.

Over reliance on pH Buffer Standards

If you walked up to a laboratory technician running pH and asked him how he knew the probe was working properly, he would probably put the probes in the 4.0 and 7.0 buffers to demonstrate the probes have held calibration. The same probe that passes the 4.0 and 7.0 buffer test could fail miserably when analyzing a difficult soil sample. The reason for this problem is that the matrix differences between the buffer solutions and soil are vastly different. Buffered standards are aqueous, highly buffered, and high electrical conductivity (EC >8 mmhos/cm). Soil samples, on the other hand, are slurries, many times poorly buffered (sandy soils), and low electrical conductivity (1:1, EC <0.3 mmhos/cm). The reference buffered solutions are "ideal" versus the soil is by nature a more "difficult" sample. Buffer solutions are such "ideal" solutions that a "half broken" probe will work. As we all known, trying to get a probe to stabilize in distilled water is very difficult because of virtually no buffer capacity and salts. Similarly, soil sample becomes increasing more difficult as the buffer capacity (CEC) and the salts decrease. This problem is further aggravate when laboratories use soil-to-water ratios greater than 1:1. Some laboratories use 1:5 soil:water ratios which further dilutes the soil salts causing more pH stabilization problems. In an ideal world, the salt pH (0.01 M $CaCl_2$ or 1M KCl) would be adopted as the standard pH method which would eliminate most the pH problems encountered today. At Harris Laboratories, I have observed very few probe problems when running the SMP buffer pH test. I credit this to the fact the soil slurry solution is highly buffered salty solution which lends itself to be more of an "ideal" solution. In conclusion, you can not conclude a probe is working properly by just checking them against buffer solutions because of the matrix differences between the buffers solutions and soil slurry. You can only conclude that probes work properly under ideal sample conditions.

Checks are not "Difficult" Samples

Most laboratories select local soils for quality control samples. These samples could be or not be "difficult" sample. More than likely, these soils would be medium texture and average electrical conductivity. Such soils will not really challenge a pH probe to detect a probe problem. An example of an "difficult"sample would be a a sandy soil with EC (1:1) less than 0.10 mmhos/cm. Such a sample will challenge even a good working pH probe. Without difficult QC samples, problematic probes go unnoticed. I would suggest to all laboratories to purchase utility sand from the hardware store and use this as the difficult pH QC sample.

Lack of Cross Checking Probes

The old saying goes "if you have one watch you know what time it is, but with two watches you do not know what time it is". I think this is true for laboratories that might have only one pH probe and meter. It is very difficult to be assured pH data quality when there is not another probe to cross check. I would recommend 1 to 2% of the soil samples to be duplicates or cross check with another prober and meter. If two probes agree the chances of bad data is greatly reduced. At Harris Laboratories, 2.5% of all the samples are randomly analyzed first with one probe and meter then collectively all the samples are analyzed together on a different probe and meter.

Equilibration Time

Soil pH is one of the remaining procedures in the laboratory that is still manual. Because technicians manually read pH, the equilibration time can vary depending on how many samples need to be analyzed. Most pH probe manufacturers consider a fast probe as a probe that can equilibrate/stabilize in 30 seconds. However, I have seen technicians move at the rate of about 8 samples per minute allowing only about 7 seconds for probe equilibration. This is too fast! But, how do you process the needed sample volume without sacrificing equilibration time. The best system that I have seen is to use multiple pH stations. With multiple pH stations, the technician is not having to wait, but is constantly attending a pH station meanwhile another set or probes are equilibrating. Design correctly, it will take more than 30 seconds before the technician makes a complete cycle which gives the needed equilibration time.

Sources of Technique Error

Stirring Technique

I would recommend laboratories to work the probe into the sample gently and then hands off. I have seen more problems associated stirring than the any benefits gained. The fatigue of a long day measuring soil pH results in tunnel carpal wrist injuries, inconsistent probe depth, tendency for hurried pH measurements, and excess abrasion of glass bulb. Also static charge transfer from person to probe has been noted by some laboratories. In fact, I have been told by one laboratory in Ohio that they had to attach a grounding strap to a technician wrist to prevent static charge transfer from this one particular technician to the probe. These problems are prevented and techniques differences between technicians are minimized if continuous stirring is avoided. I would recommend working the gently into the bottom of the cup and then waiting with hands off the probe until equilibration. To manage the technicians boredom during the equilibration wait, I would recommend multiple pH stations as discussed above.

Probe Cleaning Technique

Probes equilibrate faster under warmer conditions. The probe membrane resistance doubles for every 14 F degrees drop in probe temperature. I noted this problem when it seemed that we had more pH problems in the winter versus the summer. Harris Laboratories uses running tap water to rinse the probe. In the winter, cold tap water can get rather cold in comparison to summer water temperatures. I finally figured out that the cold water rinse was shocking the probes which causing sluggish and erratic performance and plugged junctions because of KCl salt out. We have since adopted a tepid (lukewarm) water rinse. This results in fast responsive probes and good junction flow. I would recommend to laboratories to use tepid water to rinse probes.

Sources of Equipment Error

Reference Electrode

Reference electrodes are usually the problem 75% of the time. Poor junction flow rates results in an incomplete electrical circuit with the sample. Since maintaining good flow rates is such a critical part of the pH measurement, the biggest changes in pH probe design has been the junction type. Junction flow rates for quartz and asbestos junctions are very low, ceramic and frit junctions are low, annular junctions are medium flow, and sleeve junctions are very high. Reference junctions with high flow rates would be recommended for soil samples. Perhaps this why the Ross Sure-Flow pH probe with the sleeve type junction is so popular with many soil testing laboratories.

Symptoms of a bad reference electrode are pH changes when stirring is stopped, erratic pH readings stop when stirring is stopped, and pH changes when hand movement towards and away from probe. Diagnosing the reference electrode requires connecting the pH meter to two reference electrodes. This procedure is called the Bucking Test. One reference probe is connected to the pH sensing jacks of the meter and the reference electrode is connected to the reference meter jacks. The millivolt differences between the reference electrode in question and a well functioning reference electrode should be less than 5 millivolts. Male and female adapter connectors need be purchased (Fisher Scientific) to make these connections.

A bad reference electrode often means that the junction is plugged. The reference electrode can be unplugged by the flowing methods listed in the order of least aggressive to most aggressive.

1. Junction soak - soak junction in 10% solution of KCl that is tepid for 30 minutes.
2. Ammonia soak - soak in conc. ammonia hydroxide. Removes Ag precipitates by forming $AgNH_3^+$.
3. Urea soak - Two hour soak in 8M urea to remove stubborn protein.
4. Vacuum - Attach hose to tip of probe and apply vacuum to remove debris.
5. Boiling Junction - Place only Ag/AgCl electrodes in boiling water for 30 seconds
6. Sanding Junction - Use as last resort

These steps are unnecessary for reference electrodes with sleeve junction or replaceable junction. For these junction types, junction contact can re renewed with depressing junction sleeve or replacing junction.

pH Sensing Electrode

Symptoms of a bad pH sensing electrode is a narrow span which is the inability to calibrate with 4.0 and 7.0 buffered standards. The span error should be less than $\pm$ 0.04 when calibrating on 4.0 and 7.0 standards. The pH probe response time to go from 4.0 to 10.0 should be less than 10 seconds. The pH measurement repeatability should be $\pm$ 0.02 pH for 10 replications of the same sample with a rinse between each replication.

The glass bulb can be rejuvenated by:

1. Acid-Base-Acid Soak - 0.1N acid and base concentrations for 5 minutes in each solution.
2. Last resort, soak in Bray or Mehlich III for 10 to 30 seconds then 5 minutes in 5 M HCl.

If these treatments do not rejuvenate a probe, throw it away! Probes are like batteries they deteriorate with time. Probes older than one year should be thrown away.

pH Meter

Seldom are pH problems associated with the meter unless meter is more than 10 to 15 years old. Many of the newer meters come with a self diagnosis built into the meter. Older meter models can be tested by shortening the inputs to separate the meter from electrode behavior and then observe the reading as the controls are changed

Electrode Storage

The glass electrode should be stored in an acid solution such as the 4.0 buffer solution. In principle, the glass membrane is an cation exchange membrane. By storing the glass membrane in acid solution, the membrane becomes recharged with H^+ which allows the probe to be more responsive. Therefore, never store the probe in distilled water or 10.0 buffer. This would result in membrane hydrogen ion depletion and sluggish probe response.

The reference electrode should be stored in a slightly salty solution such as the 4.0 buffer solution (~8 mmhos/cm). High salt storage solution should be avoided to prevent KCl precipitation or reverse osmotic flow of storage solution into reference probe. Storage solution of distilled water is the other extreme. Distilled water causes excessive KCl leakage from the reference probe. It is also important to prevent storage solution back flow into filling solution by maintaining storage solution height below filling solution height.

Conclusion

Never assume probes are working properly by relying on 4.0 and 7.0 buffer solutions. Utilize a "difficult" QC soil sample that is sandy and has very low salt (EC 1:1, less than 0.10 mmhos/cm). Minimize soil pH measurement technique by eliminating stirring. Reference electrode are the biggest source of soil pH problems.