

INSTRUCTION MANUAL



Using CSIM11 pH and ORP Probes with Campbell Scientific Dataloggers

Revision: 4/10



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Using CSIM11 pH and ORP Probes with Campbell Scientific Dataloggers

1. General

Innovative Sensors, Inc. manufactures the CSIM11 pH and ORP probes. These probes are especially appropriate for field and industrial use because they are built to be rugged and they include a built-in preamplifier. The preamplifier practically eliminates the hypersensitive characteristic of ion-specific probes. The preamplifier is powered by two internal lithium batteries, and thus does not require any current from the datalogger. These batteries are designed to last the lifetime of the sensor.

These probes are intended for non-pressurized systems and were not designed for applications above 30 psi. Please contact a Campbell Scientific water resources applications engineer for recommendations on probes suitable for installations in pressurized pipes.

The CSIM11 Oxidation-Reduction Potential (ORP) probe is identical to the CSIM11 pH probe except the measuring electrode utilizes a large surface area platinum band, making the probe responsive to the electron activity in the fluid. The platinum band helps prevent organic coating, a common source of error in many types of sensors. The practical range of the probe is -700 to +1100 mV, which is also the approximate range of ORP in natural and runoff waters.

Platinum ORP probes should not be used for ozone or peroxide applications, where platinum will act as a catalyst and the expected potential will not form in the case of low concentrations. The use of gold, rather than platinum, is more suitable in these applications.



Threading at either end of probe is 3/4" NPT male

2. Sensor Specifications

Body Material	ABS (Standard version) PPS / Ryton [®] (High Temperature version)
pH Range	0 to 14 pH
Output	±413 mV (±59 mV per unit pH @ 25°C; 0 mV output at 7 pH)
Temperature Range	0°C to 80°C (Standard version) 0°C to +110°C (High Temperature version)
Pressure Range	30 psig (submerged). Mounting to pressurized pipes or tanks requires a non-refillable variation of the sensor. Speak with CSI for details.
Accuracy	±0.1% over full range
Sodium Error	Less than 0.05 pH in 0.1 Molar Na ⁺ ion @ 12.8 pH
Impedance	Less than 1 Mohm @ 25°C
Reference Cell	KCl/AgCl
Zero Potential	7.0 pH ±0.2 pH
Wetted Materials	ABS or PPS (Ryton [®]), Teflon [®] , Viton [®] , Glass
Response Time	95% of reading in 10 seconds
Drift	Less than 2 mV per week
Mounting	Threading at either end of probe is 3/4" NPT male
Power	Internally powered by two 3-volt lithium batteries

3. Installation and Wiring

3.1 Unpacking

Remove the electrode from its package and check that it is undamaged. If damaged, contact your supplier for replacement. Care should be taken when unpacking and handling all electrodes.

3.2 Preparation for Use

All electrodes are shipped with a wetting cap covering the measuring end. This cap contains a solution of pH 4 buffer saturated with potassium chloride (KCl).

Remove the wetting cap before calibration. There may be some dry KCl crystals forming on the outside of the cap. These deposits are expected over time and can be wiped or rinsed off. Save the cap for future long-term storage.

Rinse the electrode with distilled water and it is ready for use.

Do not store the sensor in distilled water, as the gel layer will become depleted. If this happens, the gel layer can often be rehydrated by soaking the sensor in the pH 4 buffer solution overnight.

3.3 Wiring

This sensor can be installed without regard to orientation. Unlike other pH/ORP sensors, the problem with air bubbles adversely affecting the measurement has been eliminated by Innovative Sensors' use of a gelled reference solution and a patented plunger technology.

NOTE

If you use Short Cut to generate your datalogger program and wiring diagrams, follow the directions provided by Short Cut. The information in this manual is background information for Short Cut users.

To connect the sensor to a CR1000, CR10(X), or other Campbell Scientific dataloggers that permit differential measurements, wire as follows when using the program examples that follow:

<u>Wire</u>	<u>Datalogger Connection</u>	<u>Comments</u>
Red-----	1H -----	positive signal
Green -----	1L -----	negative signal
Brown -----	G-----	solution ground

If using Campbell Scientific's 107 temperature probe to compensate for thermal effects:

<u>Wire</u>	<u>Datalogger Connection</u>	<u>Comments</u>
Black-----	VX1 or EX1 -----	Excitation
Red-----	SE3-----	temperature signal
Purple-----	AG -----	signal ground
Clear -----	G-----	shield

4. Programming

NOTE

You do not need to read this section if using Short Cut.

4.1 Direct Measurement, Not Temperature Compensated

The datalogger is programmed using either CRBasic or Edlog. Dataloggers that use CRBasic include our CR800, CR850, CR1000, CR3000, and CR5000. Dataloggers that use Edlog include our CR510, CR10X, 21X, and CR23X. CRBasic and Edlog are included with LoggerNet and PC400 Datalogger Support Software.

Make the measurement using a differential voltage instruction (VoltDiff instruction in CRBasic or Instruction 2 in Edlog). An example from each language follows. For ORP, the multiplier would be one and the offset would be zero.

CRBasic

```
VoltDiff (pH,1,mV2500,1,True ,0,_60Hz,-0.01695,7)
```

Edlog

```
1: Volt (Diff) (P2)
  1: 1      Reps
  2: 5      2500 mV slow Range      ;Use 4 for 2IX
  3: 1      IN Chan
  4: 1      Loc [ pH ]
  5: -.01695 Mult                  ;Mult = 1 for ORP
  6: 7      Offset                  ;Offset = 0 for ORP
```

4.2 Temperature Compensation of pH Measurement

NOTE ORP measurements are usually NOT temperature compensated, although it makes sense to record the temperature at which the ORP measurement was made. The rest of this section (4.2) pertains to pH probes only.

The CSIM11 pH probe does not automatically correct temperature effects. To compensate for temperature variations, install a submersible temperature probe (such as Campbell Scientific's 107 thermistor) next to the pH probe. Temperature compensation can be calculated after the data has been retrieved from the field datalogger, or immediately using datalogger processing instructions. The first method requires storing the raw pH measurement and the temperature measurement in datalogger final storage. After retrieving data, raw values are processed to obtain compensated values. The second method is to program the datalogger to process the raw data after each measurement sequence. Both the raw data and the temperature corrected pH can be saved at the user's discretion. The following CRBasic and Edlog programs have the datalogger process the raw data after each measurement sequence.

CRBasic

```

'CR1000 Series Datalogger

'declare variables
Public pH, pHMult, TempC

'Define Data Tables
DataTable (pH,1,-1)
    DataInterval (0,1,Min,10)
    Sample (1,pH,FP2)
    Sample (1,TempC,FP2)
EndTable

'Main Program
BeginProg
    Scan (60,Sec,0,0)

        'measure water temperature
        Therm107 (TempC,1,3,Vx1,0,250,1.0,0)

        'calculate the Multiplier for Temperature Correction
        pHMult = -1/ (((TempC + 273) / 298) * 59)

        'measure pH (note this is without the multiplier and offset)
        VoltDiff (pH,1,mV2500,1,True ,0,_60Hz,1.0,0)

        pH=pH*pHMult           'now apply Correction Multiplier to measured pH

        pH=pH + 7              '... and the offset -- initially with a value of 7, adjusting as
                               'necessary during probe calibration

        CallTable pH           'output data once per minute

    NextScan
EndProg

```

Edlog

This program uses Edlog's expression editor; refer to Appendix B for a program not using the expression editor.

```

;Measure Water Temperature

1: Temp (107) (P11)
2: 1          Reps
3: 3          SE Channel
4: 1          Excite all reps w/E1
5: 1          Loc [ TempC  ]
6: 1.0        Mult
7: 0.0        Offset

```

```

;Calculate the Multiplier for Temperature Correction
;using Edlog's Expression Writer

pHMult= -1 / (((TempC + 273) / 298) * 59)

;Note: When a datalogger program that contains an expression is compiled,
;the appropriate instructions are automatically incorporated into the .DLD file.
;See Appendix B for a program not using the Expression Editor

;Measure pH

2: Volt (Diff) (P2)
  1: 1      Reps
  2: 5      2500 mV Slow Range
  3: 1      DIFF Channel
  4: 2      Loc [ pH    ]
  5: 1.0    Mult
  6: 0.0    Offset

;Apply the Temperature Correction Multiplier to the Measured pH

pH=pH * pHMult

;The following instruction applies an Offset to the pH. Use an Offset of 7
;initially as shown below. Adjust the Offset if necessary during probe calibration.

3: Z=X+F (P34)
  1: 2      X Loc [ pH    ]
  2: 7      F
  3: 2      Z Loc [ pH    ]

;Example (One Minute) Output Processing Instructions

4: If time is (P92)
  1: 0      Minutes (Seconds --) into a
  2: 1      Interval (same units as above)
  3: 10     Set Output Flag High (Flag 0)

5: Real Time (P77)
  1: 0110   Day,Hour/Minute (midnight = 0000)

6: Sample (P70)
  1: 1      Reps
  2: 2      Loc [ pH    ]

*Table 2 Program
  02: 0.0000 Execution Interval (seconds)

*Table 3 Subroutines

End Program

```

5. Calibration/ORP Check

5.1 pH Sensor Calibration

Calibration should be carried out according to the detailed procedure later in this document (see Appendix A). The following paragraphs are for general information.

The calibration should use two or more pH standards. It is recommended that pH 7 buffer be used to check the zero point and at least an acid or alkaline buffer, that brackets the sample's pH value, be used to set the slope.

An electrode measuring many samples a day should be calibrated at least once a day. The frequency of calibration will depend on the level of accuracy required and the coating/fouling nature of the samples being measured.

Electrodes that are continuously monitoring a sample should be checked at least once a week or whatever period experience dictates.

Grab Sample calibration is a technique where the process electrode has been calibrated and placed on line for some period of time. Its output is then verified by measuring the pH of a sample with another electrode. The grab sample should be measured as soon as possible to avoid errors caused by changes in the sample's temperature or changes in the samples pH due to exposure to the atmosphere.

5.2 ORP Check

Check the ORP sensor when it's initially deployed and after three months of field service. To check the sensor, place it in a known millivolt solution. The sensor manufacturer offers +230 mV and +470 mV solutions. If the sensor reading is within ± 20 mV of the millivolt value of the solution, the sensor is operating properly.

6. Maintenance

Developing an effective maintenance schedule is incumbent on understanding the process effects that are specific to your application. A pH sensor develops a millivolt potential directly proportional to the free hydrogen ion concentration in an aqueous solution. The sensor is composed of a reference electrode and its gelled reference electrolyte, a measurement electrode exposed to the process solution, and a porous junction that maintains electrical contact between the two. Porous Teflon is the newest technology in reference junctions. Innovative Sensors, Inc. offers a patented porous Teflon liquid junction which is chemically inert; and is chemically compatible with virtually all chemicals.

- High Temperature which causes 1) Faster Response / Lower Impedance; 2) Aging acceleration, Lithium Ions Leached from Membrane; 3) Short Span
- Low Temperature which causes Slower Response / Higher Impedance

- Measurement > 10.0 pH causes Alkaline / Sodium Ion Error
- Coatings can cause 1) Slower Response; 2) Zero Offset increase; 3) Dehydration
- Steam Sterilization causes 1) Dehydration; 2) Ag/AgCl Dissolving from Silver Reference Element

6.1 Replacing Reference Electrolyte

Readings that drift indicate the electrolyte should be checked.

Refill Procedure:

1. Clean the probe tip as discussed in the maintenance procedures below.
2. Remove the reference reservoir plug. Place it where it will stay clean.
3. Rinse the reservoir with deionized water repeatedly to remove the old solution. Drain out all remaining water.
4. Completely fill the reservoir with the new reference solution. It does not take very much. Make sure you keep the bottle tip clean, and replace the bottle cap immediately after using the bottle.

NOTE

The bottle of refill solution contains undissolved salts; this is to ensure the solution remains saturated.

5. Replace the red plug applying new pipe tape. Make sure the plug is screwed back in as far as it was originally.

Because the new reference solution is viscous, you may need to wait a few minutes while the reference solution settles. If necessary, take the probe in hand and GENTLY swing it in a downward arc to speed the flow of solution and remove air pockets. Add more solution as needed to completely fill the reservoir.

6.2 Electrode Cleaning

pH and ORP sensors require more maintenance than many other types of sensors. The ORP platinum band can foul with algae and other biological sources. Cleaning will be required approximately every 1 to 2 weeks. Fouling can be minimized by locating the probe in a very dark place.

Slow response and large offsets may indicate the measurement electrode has become coated. The nature of the coating will dictate the type of cleaning technique that should be used.

Soft coatings, like foodstuffs or bacterial films are best removed using a squirt bottle or the water jet from a faucet. If this is not successful, then wiping with a soft wet cloth is the best choice.

Hard coatings, like calcium or lime scale are best removed with a solvent appropriate for the particular coating. A 5 percent solution of HCl would be a good choice for the calcium scale. If unsure of the proper solvent to remove a hard mineral coating, alternate between 5 percent HCl and 4 percent NaOH for 10 minutes each. After treating the electrode with these strong acids or bases, rinse the electrode with water and soak it in pH 4 buffer for at least 1/2 hour.

Greasy and oily coatings are best removed with a detergent solution or a solvent that will not attack the electrode's body. Methanol and isopropyl alcohol are good choices for solvents. Acetone, MEK, THF, or trichloroethane will irreparably harm the electrode. A soft toothbrush can be used with the detergent to remove stubborn coatings.

The pores of the reference junction may become clogged and surface cleaning may not restore proper function. The electrode should then be heated to 60°C in 3 molar KCl and allowed to cool in the same solution. Rinse it with distilled water and soak in pH 4 buffer for 1/2 hour before testing. The electrolyte should be removed and replaced with fresh electrolyte before treating as above.

Electrodes age with time and eventually become desensitized. Extended periods of service at temperatures greater than 80°C or exposure to de-ionized water accelerate this phenomenon. As a last resort, dip the electrode in a 10 percent ammonium bifluoride solution for 10-20 seconds, then rinse it with tap water and soak it in 5-6 molar HCl for 30 seconds. Rinse it with tap water and soak it in pH 4 buffer for 1/2 hour before testing.

The platinum sensing tip of an ORP electrode should be cleaned just like a pH electrode. The surface can also be cleaned with an abrasive as a last resort. Gently scour the platinum with a 600 grit wet emery cloth or preferably 1-3 micron alumina polishing powder.

6.3 Electrode Troubleshooting Guide

I. SYMPTOM: Probe pegs at 14 pH or drifts off scale high.

POSSIBLE REASON: Open circuit in either glass electrode or reference electrode.

CHECK:

1. Visually inspect cable and connector looking for a crushed or broken cable jacket or a brittle cable jacket due to exposure to solar radiation. Discard electrode if damage is present.
2. Move wires at datalogger to test for intermittent connection. Tighten connectors if necessary.
3. Visually inspect bulb for a coating. If coated, use an appropriate solvent or a high-quality detergent with a Q-tip to wipe bulb clean. Rinse well with distilled water; soak in 4.0 buffer for at least 10 minutes, retest. If electrode now responds, but erratically, soak in 10 percent HCl solution for five (5) minutes, rinse well with distilled water; soak in 4.0 buffer for at least 10 minutes, retest.

4. Visually inspect reference junction (large white surface at front of sensor). If coated, clean by rinsing well; retest. If electrode still reads high, place sensor in 3.5 molar KCl, or water if KCl is not available, and heat to approximately 60°C for 15 minutes; retest.

II. SYMPTOM: Slow response and/or noisy, erratic readings.

POSSIBLE REASON: Slow response is caused by a very high impedance in either glass or reference electrode.

CHECK:

1. Visually inspect pH bulb and reference junction for coating or clogging. If coated, clean as listed above (I. 5)
2. Allowing a pH electrode to dry out raises the impedance dramatically. Soaking the electrode in 0.1 normal HCl for 1/2 hour and rinsing with distilled water should speed response (always keep electrodes wet).
3. Chemical degradation of pH glass can occur rapidly in a high temperature or high pH environment. This also increases impedance yielding sluggish response.
4. Low temperature environments also increase impedance, with impedance doubling every 8°C temperature drop from 25°C.

Test wiring for intermittent connections by moving wires at the connector on the datalogger wiring panel. Tighten as necessary. This is a common source of erratic signals.

III. SYMPTOM: No response to pH change.

POSSIBLE REASON: A cracked glass bulb.

CHECK:

If electrode reads between 5.8 and 6.2 pH in all solutions, visually inspect glass bulb for cracks. Discard probe if it is cracked.

POSSIBLE REASON: Short circuit.

CHECK:

If electrode reads 7.0 pH or 0.0 mV when connected to the datalogger, visually inspect cable for damage. If there is no visible damage, test electrode in 4.0 buffer.

Appendix A. Detailed Calibration Procedure and Tips from Innovative Sensor, Inc.

A.1 Calibration

CAUTION

Good laboratory practices should be used and protective gloves and safety glasses should be worn while handling any solvents or chemicals. If you are unsure of the proper technique for handling a chemical or of its hazardous properties, it is best to discard the electrode eliminating the risk of danger.

MATERIALS

Buffers

- a) 4.01 pH (potassium biphthalate)
- b) 7.00 pH (potassium phosphate)
- c) 10.00 pH (sodium borate and carbonate)

Thermometer

Beakers

Datalogger programmed to read the pH probe

PROCEDURE

1. Fill beakers with appropriate buffers and continuously measure the temperature of the buffer in use. If possible, temperature should be at equilibrium (probe and buffers) before continuing with calibration.
2. Calculate the Nernst temperature compensation for the probe's current temperature and adjust the multiplier in the differential voltage instruction (VoltDiff in CRBasic or Instruction 2 in Edlog) to the appropriate value. The slope change is usually taken to be -0.2 pH/mV/deg C . Examples of adjusted multipliers would be the multiplicative inverse of the following slopes: -58 mV/pH at 20°C , -59 mV/pH at 25°C , and -60 mV/pH at 30°C .
3. Zero the pH probe (pH 7 corresponds to 0.0 mV at 25°C) by placing the electrode in a 7.0 buffer with the probe connected to the datalogger. Place the datalogger in real time monitor mode. Electrode should read 7.0 (or whatever the solution pH should be at the present temperature) $\pm 0.2 \text{ pH}$.
4. Using the offset in the differential voltage instruction (VoltDiff or Instruction 2), adjust the datalogger to read 7.0 pH, or whatever the solution pH should be at the present temperature.
5. Remove the probe from the pH buffer, rinse the electrode with distilled water, and place in 4.01 buffer.

6. Place datalogger in real time monitoring mode. The electrode should read 4.01 ± 0.2 , depending on temperature.
7. Remove and rinse the electrode, then place it in the 10.00 buffer.
8. In the datalogger real time monitor mode, the electrode should read 10.00 pH, ± 0.2 , depending on temperature.
9. If the readings in Steps 6 and 8 show a slope error (error proportional to the difference between the buffer pH and 7), then the probe has a slight slope error, which should be easy to correct by adjusting the multiplier in VoltDiff or Instruction 2.

A.2 Tips and Techniques

Stirring the buffers and samples improves the stability and speed of response of the measurement.

Rinse the electrode with distilled water between samples and lightly blot the water on a paper towel before immersing it in the next sample. Never wipe the pH bulb since dust may scratch the delicate gel layer impairing response.

Rinsing the electrode with a small amount of the sample before immersing it will eliminate any contamination of the sample.

The simplest form of temperature compensation compensates for the change in the electrode's slope due to temperature, in accordance with the Nernst factor. It does not compensate for changes in the actual pH of the sample that occurs with a change in temperature. The pH of a sample at 25°C is most likely different than the pH of that same sample at 75°C.

The temperature of the electrode, the sample, and the calibration buffers should be the same. Allow the electrode to come to temperature equilibrium with the sample before recording the measurement value. Measurements made more than 20°C from the calibration temperature should include a one-point calibration at that temperature for maximum accuracy.

Low ionic strength samples, highly viscous samples, and salt brines slow the speed of response of the electrode. While the electrode will be stable to a change in pH buffers after 10-15 seconds, it may take up to five minutes for the electrode to stabilize in a difficult sample.

Appendix B. Datalogger Program Not Using Edlog's Expression Editor

;Measure Water Temperature

1: Temp (107) (P11)

1:	1	Reps
2:	1	SE Channel
3:	1	Excite all reps w/E1
4:	1	Loc [TempC]
5:	1.0	Mult
6:	0.0	Offset

;Calculate the Multiplier for Temperature Correction

;Note: See Section 4.2 for a program using Edlog's Expression Editor

2: Z=F (P30)

1:	298	F
2:	0	Exponent of 10
3:	4	Z Loc [K_25C]

3: Z=X+F (P34)

1:	1	X Loc [TempC]
2:	273	F
3:	3	Z Loc [pHMult]

4: Z=X/Y (P38)

1:	3	X Loc [pHMult]
2:	4	Y Loc [K_25C]
3:	3	Z Loc [pHMult]

5: Z=X*F (P37)

1:	3	X Loc [pHMult]
2:	59	F
3:	3	Z Loc [pHMult]

6: Z=1/X (P42)

1:	3	X Loc [pHMult]
2:	3	Z Loc [pHMult]

7: Z=X*F (P37)

1:	3	X Loc [pHMult]
2:	-1.0	F
3:	3	Z Loc [pHMult]

```

;Measure Ph

8: Volt (Diff) (P2)
  1: 1      Reps
  2: 5      2500 mV Slow Range
  3: 1      DIFF Channel
  4: 2      Loc [ pH    ]
  5: 1.0    Mult
  6: 0.0    Offset

;Apply the Temperature Correction Multiplier to the Measured pH

9: Z=X*Y (P36)
  1: 2      X Loc [ pH    ]
  2: 3      Y Loc [ pHMult ]
  3: 2      Z Loc [ pH    ]

;The following instruction applies an Offset to the pH. Use an Offset of 7
;initially as shown below. Adjust the Offset if necessary during probe calibration.

10: Z=X+F (P34)
  1: 2      X Loc [ pH    ]
  2: 7      F
  3: 2      Z Loc [ pH    ]

;Example (One Minute) Output Processing Instructions

11: If time is (P92)
  1: 0      Minutes (Seconds --) into a
  2: 1      Interval (same units as above)
  3: 10     Set Output Flag High (Flag 0)

12: Real Time (P77)
  1: 0110   Day,Hour/Minute (midnight = 0000)

13: Sample (P70)
  1: 1      Reps
  2: 2      Loc [ pH    ]

*Table 2 Program
  02: 0.0000 Execution Interval (seconds)

*Table 3 Subroutines

End Program

```


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