All You Need To Know…
The SC24V Sensor Explained

What is Differential pH and How Does it Work?

The SC24V is a *differential* combination pH sensor. The reference side of this sensor offers several advantages over both *conventional* pH reference designs and *alternative* reference electrode designs. While the measuring (glass) portion of these various combination sensor types is fundamentally the same, the design of their reference portion is completely different.

The *conventional* pH reference, figure 1, is comprised of a Silver/Silver Chloride element in a Potassium Chloride (KCl) electrolyte solution. The concentration of the KCl electrolyte determines the output voltage of the reference electrode. The electrolyte is separated from the process by a porous liquid junction which is a traditional source of maintenance problems:

- The process may coat or plug the reference junction, causing the reference voltage to be inaccurate or unstable as there will no longer be electrochemical continuity with the measuring electrode and the process (diffusion potential – junction impedance).
- If the electrolyte depletes (evaporation) or is poisoned by the process ingress, (by diffusion of the process), the reference signal changes and so will the output voltage of the reference cell.

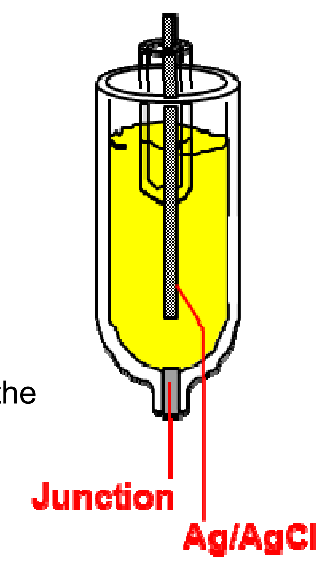


Figure 1: Conventional Reference Design

pH sensors using *conventional* reference electrodes supply a "fixed" reference voltage independent of the process and are considered to be ***absolute*** measurements. An *alternative reference* approach is one where a "glass-in-glass" design, figure 2, is used and may also be considered as an ***absolute*** measurement.

This design uses a standard glass electrode as the measuring electrode which generates a potential proportional to the process pH. The second glass electrode serves as the reference electrode and consists of an internal measurement electrode immersed in a stable buffer solution. The internal electrode makes electrochemical contact with the process via a salt bridge chamber (double junction) and generates a standard reference potential. Both glass electrodes have a common potential developed at the third electrode, the solution ground electrode.

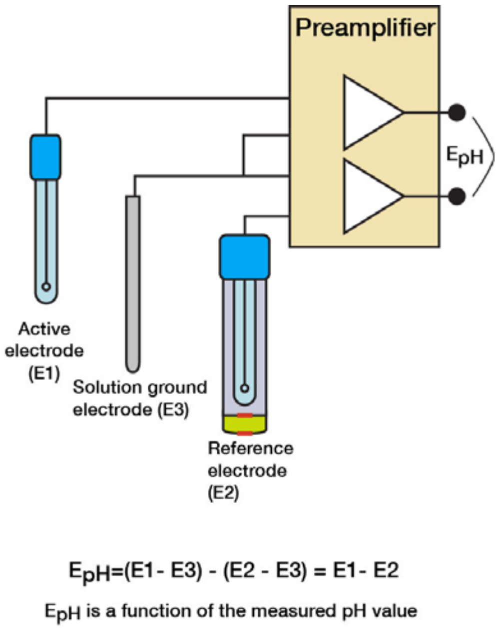


Figure 2: "Glass-in-Glass" Design

This design eliminates the stability problems experienced with *conventional* references due to process poisoning of the reference element. However, since it utilizes a liquid junction interface with the process, this reference design will still suffer from plugging and coating problems.

Differential electrode designs do **NOT** provide an ***absolute*** pH measurement, but a ***differential*** (based on the process Cation concentration) measurement instead.

The reference portion of the SC24V, figure 3, is made entirely of a glass which provides a mV output corresponding to the Cation concentration of the process or solution it is in. Therefore, there is no liquid junction to be coated or clogged and no path for the process to affect the electrolyte or the internal Ag/AgCl element.

The reference voltage is "**process determined**" or **dependent on** the amount of "**salts**" within the sample. Point in fact, it is actually a **measuring electrode** which "**measures**" or responds to the **concentrations of salts**. Therefore, as salt concentrations change, so *will* the reference voltage it generates, therefore it is *process dependent* versus being an *absolute* independent reference.

This is a revolutionary solution for many of the challenges in pH applications that customers struggle with. The sensor reacts on pH changes rather than analyzing the accurate pH value. In that sense it is best to describe the sensor as a pH control sensor rather than a pH measuring sensor.

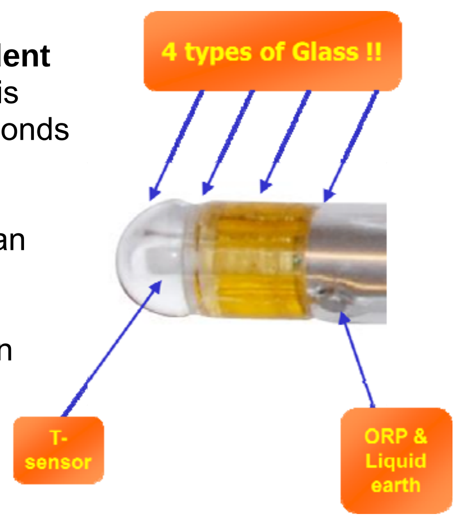


Figure 3: SC24V Design

Benefits and Trade Offs

The SC24V solves all the typical problems that plague a standard reference electrode. Since the Cation Reference has **NO** junction, there is **NO** path from the process to the internal element; so **NO** poisoning can occur. Also since there is **NO** junction, there is **NO** plugging or coating problems to worry about and there is **NO** electrolyte depletion problem, because there is **NO** electrolyte.

This means with the Cation Reference we have a perfect solution to our problems, right? Well, not quite. There are always trade-offs to consider. Just like standard reference electrode designs where some designs work better in certain applications than others, no one solution solves every problem. While the Cation reference does overcome problems we deal with using a standard reference, it does have a few drawbacks that must be considered to gain the best results using this style reference.

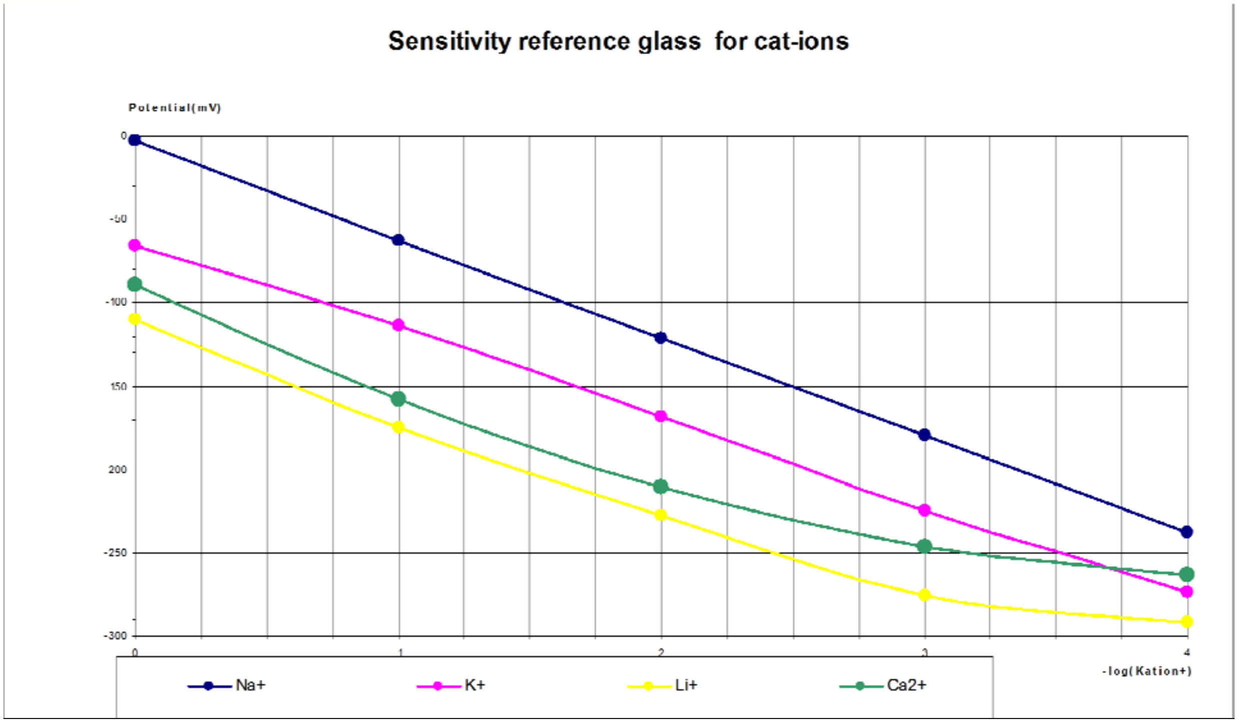
1.) It is NOT a true pH measurement. The sensor is designed for pH Control applications.

2.) It is affected by salt concentration changes in the process.

Cation Reference Explained

The SC24V differential pH sensor reference cell is also a Glass sensor that does not respond to changes in the pH value within the application range of the sensor. This means that the sensor is truly maintenance free. However the drawback of the SC24V is that it is NOT a true pH measurement. The output voltage of the sensor depends only on the salt concentration changes in the process.

In most pH control applications the salt concentration is rather constant, so the mV output of the reference cell is constant and therefore the overall output is only dependent on the pH of the process. The graph below shows the response of the reference glass to changes in different cat-ions concentrations. You can see that it does not matter which salt is present, because the shifts all respond similarly.



However, as a rule of thumb, a change in salt concentration of ± 25% has the effect of less than 0.1pH change of the pH reading.

Proper Application

When determining if the cation differential sensor can be used in a particular application there are two main requirements that must be considered:

1.) Is the process control pH value higher than the process pNa + 2?

2.) How much does the salt concentration of the process vary; or what is the conductivity of the process at 7.00 pH?
   - If the process salt concentration varies ≤ 40%, then the influence on the pH sensor will show a shift will of < 0.15 pH.
   - If the salt concentration change is ≤ 25%, then the influence on the pH sensor will show a shift of only < 0.1 pH.

The concentration shift is a *linear* function while the pH value is a logarithmic function. This relationship is very important to understand because if the pH control needs to be maintained at ±0.1 pH, the salt concentration must not change by more than ± 25%. If it does then a new process calibration must be done to account for the salt change.

Therefore, in order to determine if the cat-ion differential sensor will work in a particular application, *one* of the following must be provided:

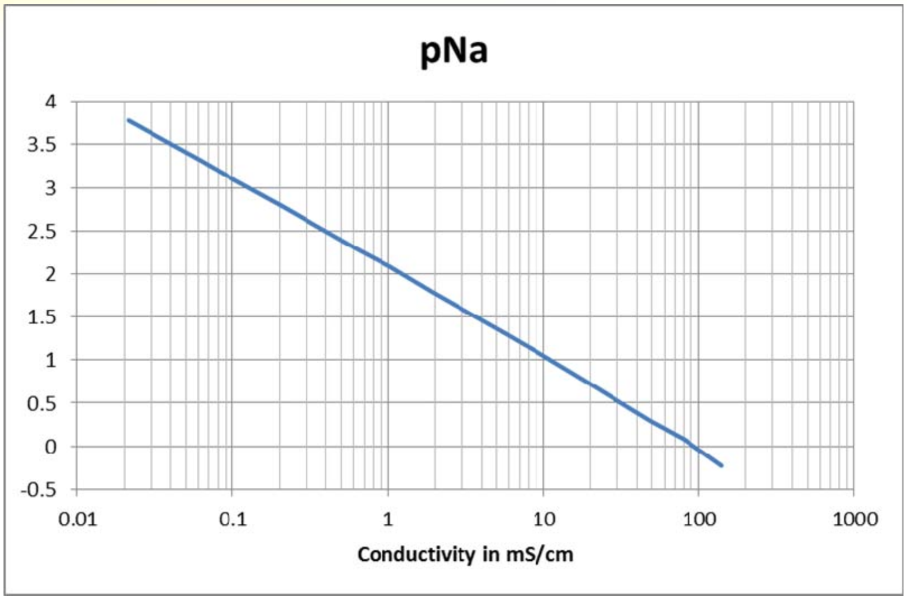
1.) The minimum and maximum salt concentration values throughout the process.

2.) The conductivity value of the process at a pH of 7.00. (The conductivity is measured at a pH of 7 to ensure the conductivity value is that of the cat-ions in the process and not the influence of the acid or base in the process.

The following table can be used to assist in determining the process pNa if you know what the process conductivity is at pH 7.00.

mg/kg	mS/cm	pNa
10	0.0214	3.778151
30	0.064	3.30103
50	0.106	3.079181
100	0.21	2.778151
300	0.617	2.30103
500	1.03	2.079181
1000	1.99	1.778151
3000	5.69	1.30103
5000	9.48	1.079181
10000	17.6	0.778151
30000	48.6	0.30103
50000	81	0.079181
100000	140	-0.22185

Example 1: If the process conductivity value at 7.00 pH is 1.03 mS; then the sample would have a concentration of 500 mg/kg and a pNa of 2.08. Since the operating range of the SC24V sensor is defined as pNa + 2, this would mean the sensor would function between a pH range of 4.08-14.00.



Know the concentration at 7.00 pH allows you to calculate the theoretically pNa of the process and the pH shift you would expect to see if the salt concentration changes. Also keep in mind that if there is a mixture of different salts, you cannot tell how much the mix will influence the reference voltage. In this situation the best practice would be to just measure the process.

Example 2: If you have a 0.2 Wt% sodium chloride (NaCl) solution and the process changes to a 0.4 Wt% solution, what would the pH shift be?

- 0.2 Wt% is 0.2 g NaCl/100 g of Water
  - This is 2 g NaCl/ 1000g of Water, so approximately 2G/L
- 0.4 Wt% is 0.4 g NaCl/100 g of Water
  - This is 4 g NaCl/ 1000g of Water, so approximately 4G/L
- Molecular weight of NaCl is 59.5 or 60 if you round up

So using the known equation:

(A-B) * 59 mV = Change in mV Due to Concentration Change

Where:

A = Log (Concentration Before in g/L ÷ Molecular Weight of Process)
B = Log (Concentration After in g/L ÷ Molecular Weight of Process)

You can calculate A and B to be:

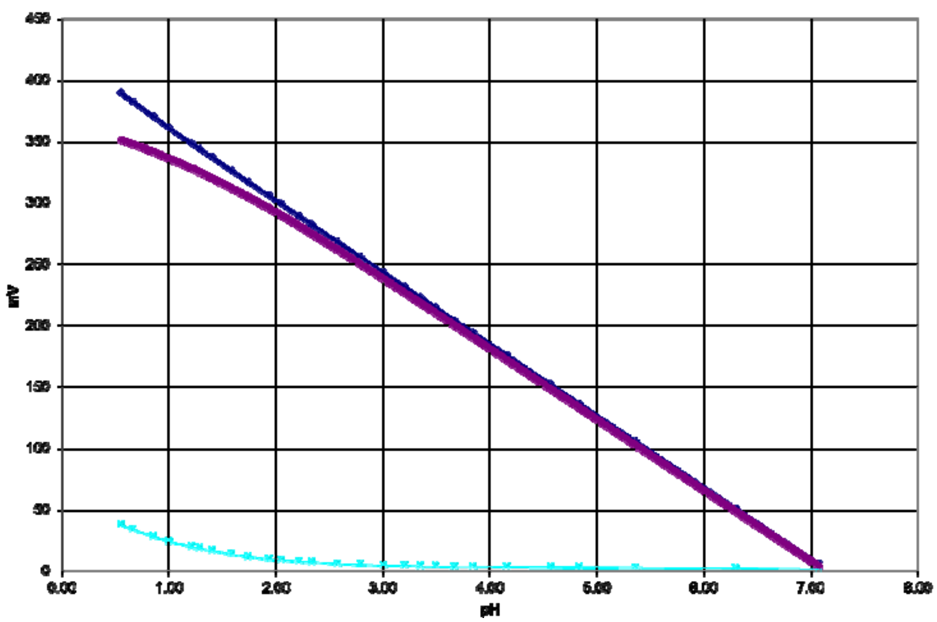
A= Log (2 ÷ 60) = -1.477, so pNa = **1.48**
B= Log (4 ÷ 60) = -1.176, so pNa = **1.18**

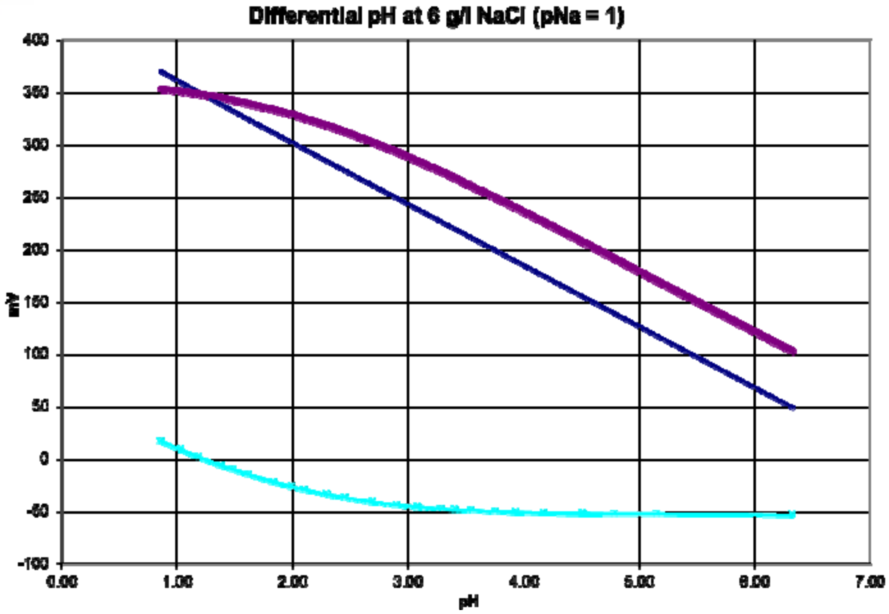
Therefore the expected phase shift can be calculated as:

(1.48-1.18) * 59 = 18 mV ~ is approximately 0.3 pH

It is very important to know the pNa value of the process because the operating range of SC24V *differential* sensor is defined as (pNa + 2) – 14 pH. The reason is the pNa Cation reference cell is affected by changes in pH when the acid concentration is much *higher* than the salt concentration. The following graphs show two different salt concentration samples with different pNa values. In each graph the light blue line represents the half-cell of the cation reference and the dark blue line represents the pH half-cell. The purple line represents the mV output of the SC24 combination sensor as function of the pH. It is the dark blue line minus the light blue line (differential signal). In either graph it can be seen that the output voltage of the cation reference cell is stable below the process (pNa + 2) value.

Differential pH at 60 g/l NaCl (pNa = 0)





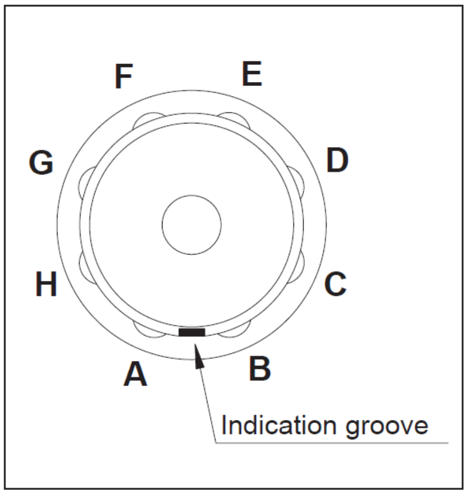
In the first graph the salt concentration is 60 g/l. The pNa value is 0 and you can see that the purple line, representing the differential measuring sensor, becomes nonlinear below 2.00 pH. Therefore, the pH range in this application for SC24V is 2.00-12.00 pH.

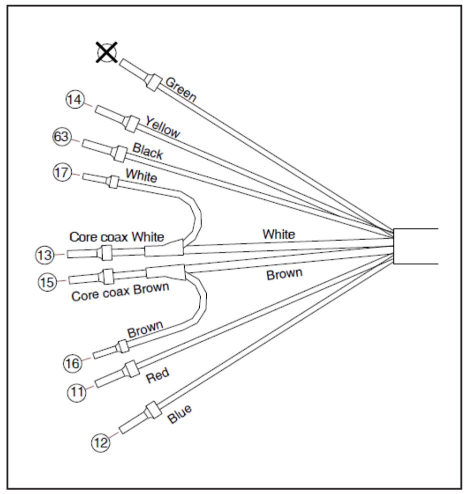
The second graph shows a salt concentration of 6 g/l which means the pNa is 1. In this example the SC24 is only linear over 3.00-14.00 pH.

Proper Wiring

The SC24V has an integral Variopin connector and must be used in conjunction with the WU10 dual coax cable (i.e. WU10-V-D-**). Because of the SC24V differential design, it can only be used with an analyzer capable of accepting *dual high impedance* inputs (i.e. Yokogawa PH202*/FLXA21/PH402G/PH450G where **NO** jumpers should be installed on “input 2”).

Variopin #	WU10 wire color	pH analyzer terminal #	Signal description
A	Brown	15	Core coax pH
B	Brown	16	Shield coax pH
C	White	13	Core coax pNa
D	White	17	Shield coax pNa
E	Red	11	Temperature
F	Blue	12	Temperature
G	Yellow	14	Liquid earth
H	Black	63	WU10 overall shield
	Green		Not used





Initial Installation

Every SC24V includes a Quality Inspection Certificate is in the packing box. Each certificate has, under the Functional Test section, the Zero point pH 7, which is the ASY, value and the calculated slope pH 7- pH 4 value that will be used during start-up. See the following image:

Quality Inspection Certificate

Model SC24V
Combined 12mm 4-in-1
differential pH sensor

1. Sensor description

Model:	SC24V-ALN26-120	Serial number:	N1D900954
Order:	500091699		

2. General characteristics

Measuring range	2 - 14 pH	Temperature element	PT1000
pH response time 90% (pH4-pH7)	< 15 sec	LE element	Platinum
Pressure operating range	0 - 10 Bar	Reference electrolyte	Salt sensitive glas
Temperature operating range	10°C - 120°C	Reference system	Ag/AgCl
Response time temperature 90%	< 90 sec	Wetted parts	Glass, Platinum
Glass membrane	pH / pNa		
Glass impedance nominal	750 / 750 MOhm		

3. Functional test

	Specification	Measured	
Zero point pH7	0 ± 15 mV	-9.9	mV
Slope value pH4	zero point + pH4	158.2	mV
Calculated slope (pH7-pH4)	92 - 100 %	95.7	%
Temperature resistance @ 25 ºC	1092 to 1102 Ohm	1093	Ohm
LE resistance	< 1 Ohm	0.34	Ohm

4. Mechanical inspection

Dimensions	According to DIN 19263:2007-05

5. Certification

This product meets the requirements of the ATEX directive 94/9/EC.

Marking	Ex II 1 G Ex ia IIC T3...T6 Ga
Certifying body	DEKRA 0344
EC-type examination certificate	DEKRA 11 ATEX 0014 X
Manufacturer	YOKOGAWA NL-3825 HD 2
IECEx-type examination certificate	Ex ia IIC T3...T6 Ga IECEx DEK 11.0064X

6. Approval

Date	23-9-2013
Approved by:	

YOKOGAWA
Euroweg 2
3825HD Amersfoort
The Netherlands
QIC 12B6J7-02E-E
4th Edition

Quality Inspection Certificate

Model SC24V
Combined 12mm 4-in-1
differential pH sensor

1. Introduction
This standard applies to model SC24V sensors.

2. Mechanical Inspection
The sensor is checked visually on general appearance and dimensions. Labeling is done according the MS code.

3. Functional Testing

3.1 Conditioning
Prior to the test the sensor must be stored in water for a minimum of 24 hours. If the sensor is stored in it's own wet pocket, then the sensor must be thoroughly rinsed prior to the test.

3.2 Equipment for testing
a. High impedance voltmeter for mV measurement (PH450G or equivalent)
b. TeraOhmmeter: high impedance insulation tester with 100 V_{DC} test voltage
c. Multimeter to measure resistance (Yokogawa 7562 or equivalent)
d. pH buffers of 1M ionic strength, e.g. pH 2.00 (K1520BG), pH 4.00 (K1520BH), pH 7.00 (K1520BJ) and pH 9.00 (K1520BK). Temperature dependency of these buffers is given in Table 1. Preferably a temperature adjustable water bath has to be used to keep temperature of buffer and sensor stable.

Table 1: Temperature dependency of pH buffers of 1M ionic strength (All pH values are ± 0.02 pH)

Temp \ pH	2.00	4.00	7.00	9.00
5°C	2.00	3.98	6.93	9.35
10°C	2.00	3.99	6.96	9.22
15°C	2.00	3.99	6.98	9.13
20°C	2.00	4.00	7.00	9.00
25°C	2.02	4.01	7.01	8.89
30°C	2.02	4.01	7.02	8.57
35°C	2.02	4.02	7.03	8.46
40°C	2.04	4.04	7.04	8.35
45°C	2.06	4.06	7.05	8.25
50°C	2.08	4.08	7.07	8.14

3.3 Functional Inspection (with sensor and solutions stabilized in a water bath at 25 ± 0.5°C)
Connect the sensor to a PH450G with terminal numbers matching the numbers on the cable ends:
Temperature sensor (11/12); Reference cell (13); Shield of Reference cell (17); Solution Ground/ Liquid earth (14); pH cell (15); Shield of pH cell (16).
Place the sensor in **a water bath at 25 ± 0.5°C**. Allow 1 - 2 minutes to stabilize.

- Use a multimeter to measure the resistance between wire 14 and the metal surface of the liquid earth electrode. This value should be <1 Ω.
- Place the sensor in pH 7 buffer and read mV value. Allow 1 minute to stabilize. Record the value. This must be 0 mV ± 15 mV. This value is the Asymmetry Potential (Aspot).
- Rinse the sensor in dematerialized water, blot dry with tissue and place in 4 pH buffer. Allow 1 minute to stabilize. Read the mV value and calculate the Slope with the formula: (mV[@4 pH] - mV[@ 7 pH]) / 1.7748
  The value is recorded and must be within 92-100%.

Disconnect the sensor.

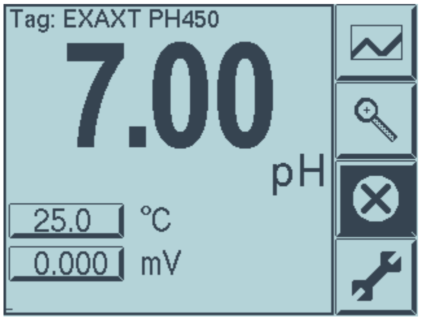
- Use a multimeter to measure the resistance of the temperature sensor between the wires marked 11 and 12. The value must be 1097 ± 5 Ω. When using cable length >10 m, the values are increased by 0.9 Ω/10m.
- Measure the resistance between the Glass cell (wire 15) and liquid earth electrode (wire 14) with the TeraOhmmeter at 100 V_{DC}. The value must be 400-1000 MΩ.
- Measure the resistance between the Reference cell (wire 13) and liquid earth electrode (wire 14) with the TeraOhmmeter at 100 V_{DC}. The value must be 400-1000 MΩ.

YOKOGAWA
Euroweg 2
3825HD Amersfoort
The Netherlands
QIC 12B6J7-02E-E
4th Edition

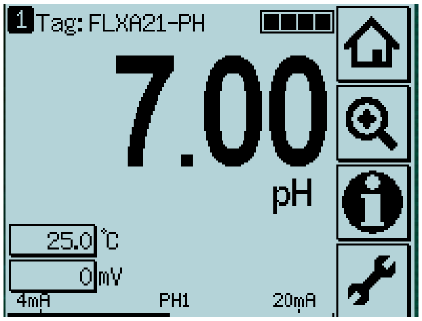
At the initial installation follow the steps below for the FLXA21, PH202*, PH402G or PH450G analyzer programming the corresponding values for the ASY and slope values from the Quality Certificate into the electronics.

FLXA21 and PH450G:

PH450G

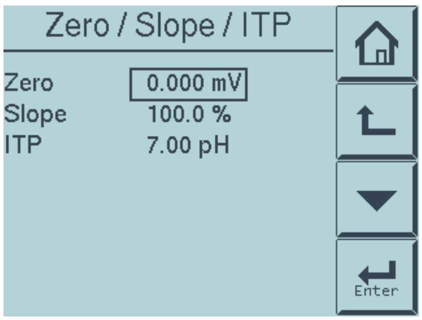


FLXA21

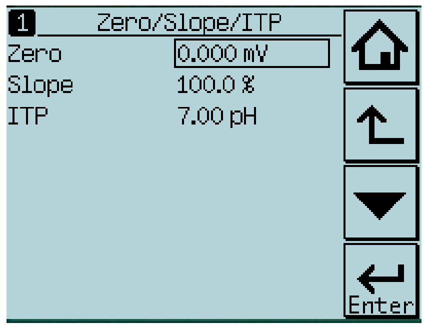


On the Main display, Select the following: Wrench → Commissioning → Measurement Setup → Calibration settings → pH settings → Zero/ Slope/ ITP

PH450G

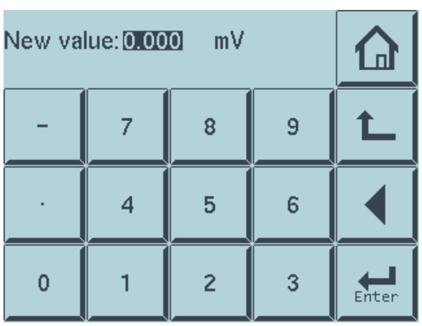


FLXA21

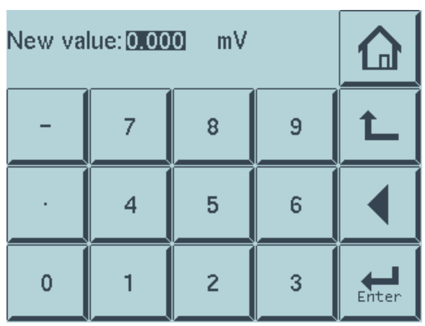


Once you are on the above screen, Select on the data points for the Zero and Slope so that a key board will appear.

PH450G



FLXA21



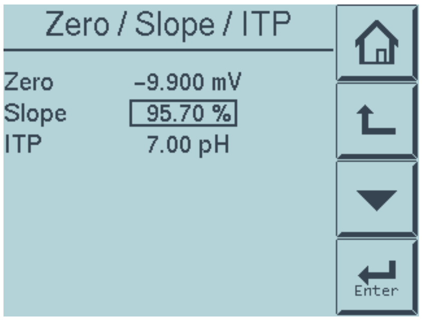
Using the information from section *3. Function test* from the test certificate, program the Zero (Zero point pH7 shown on the certificate) and the Slope values in the analyzer to match what is shown on the certificate.

Glass impedance nominal | 750 / 750 MOhm

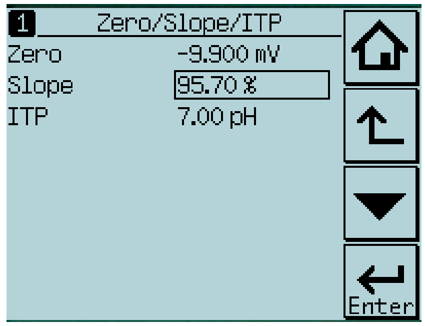
3. Functional test

	Specification	Measured	
Zero point pH7	0 ± 15 mV	-9.9	mV
Slope value pH4	zero point + pH4	158.2	mV
Calculated slope (pH7-pH4)	92 - 100 %	95.7	%
Temperature resistance @ 25 ºC	1092 to 1102 Ohm	1093	Ohm
LE resistance	< 1 Ohm	0.34	Ohm

PH450G



FLXA21

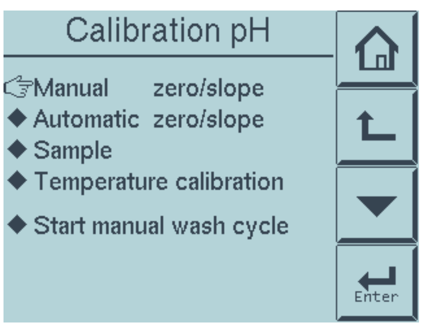


Once this has been done press the Home icon to return to measurement mode. You can use traditional pH7 and pH4 buffers as a ***functional check only***. Place the SC24V sensor in the 7 buffer, allow the sensor to stabilize, and then place it in the pH 4 buffer. If the sensor responds to the pH change then the sensor is operating properly.

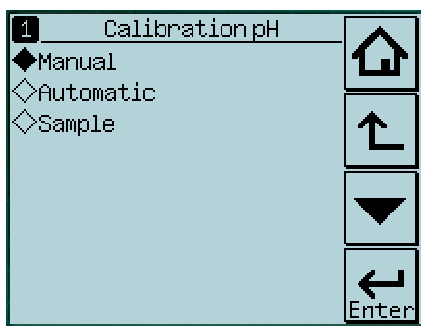
One final step is required before the sensor can be placed online. Take a process grab sample and perform a one point manual sample calibration to correct for the background salts in the process.

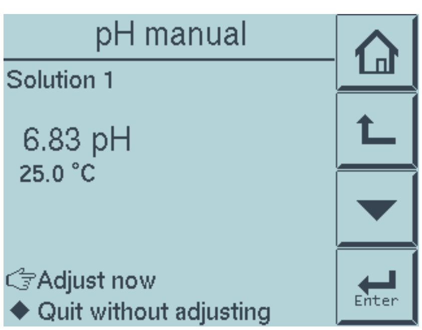
(MANUAL PROCESS CALIRBATION)

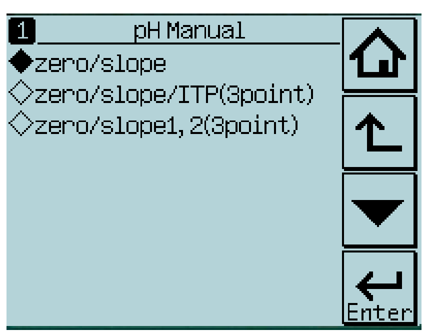
PH450G

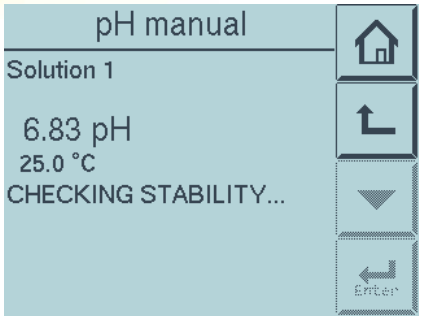


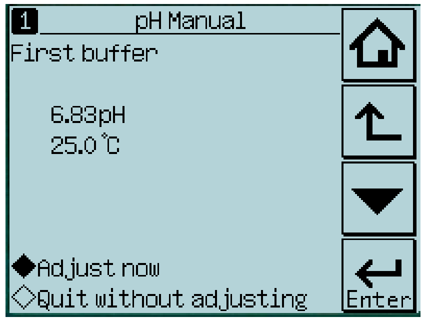
FLXA21

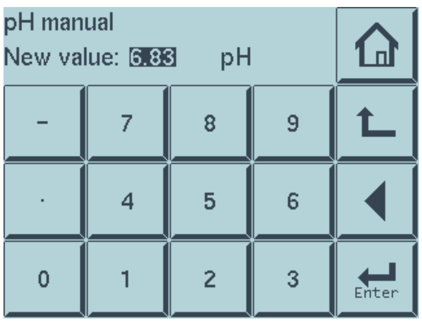


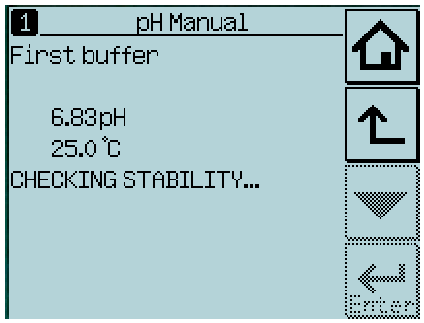


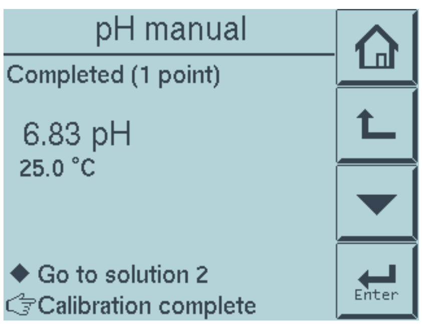


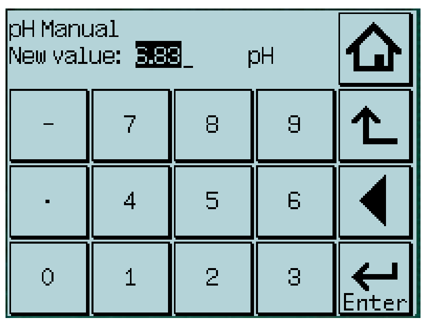

pH manual
Solution 1
6.83 pH
25.0 °C
CHECKING STABILITY...
Enter

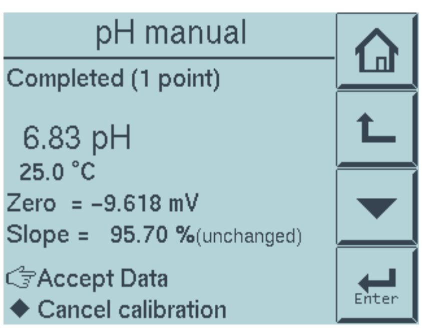

1
pH Manual
First buffer
6.83pH
25.0℃
◆Adjust now
◇Quit without adjusting
Enter

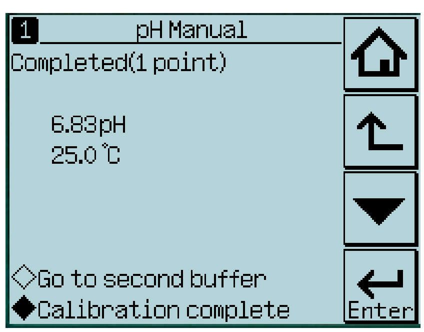

pH manual
New value: 6.83 pH
– 7 8 9
. 4 5 6
0 1 2 3
Enter

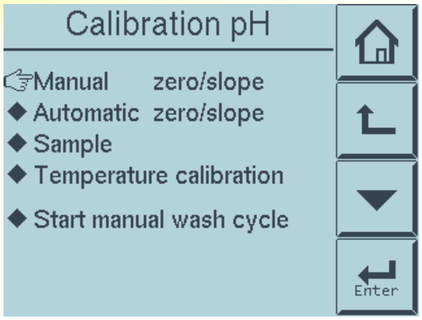

1
pH Manual
First buffer
6.83pH
25.0℃
CHECKING STABILITY...
Enter

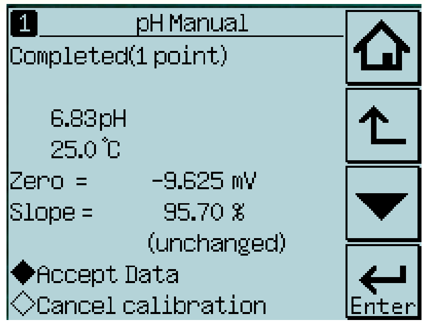

pH manual
Completed (1 point)
6.83 pH
25.0 °C
◆ Go to solution 2
Calibration complete
Enter

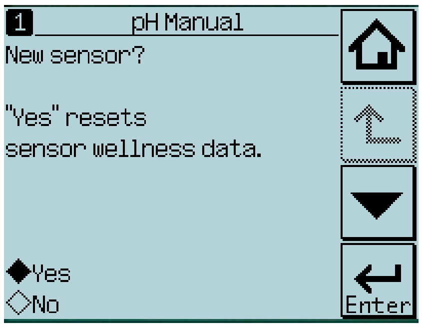

pH Manual
New value: 6.83_ pH
- 7 8 9
. 4 5 6
0 1 2 3
Enter


pH manual
Completed (1 point)
6.83 pH
25.0 °C
Zero = −9.618 mV
Slope = 95.70 %(unchanged)
Accept Data
◆ Cancel calibration
Enter

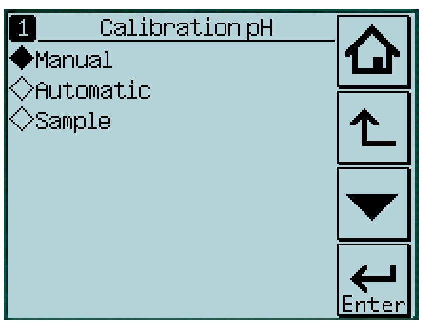

1
pH Manual
Completed(1 point)
6.83pH
25.0℃
◇Go to second buffer
◆Calibration complete
Enter







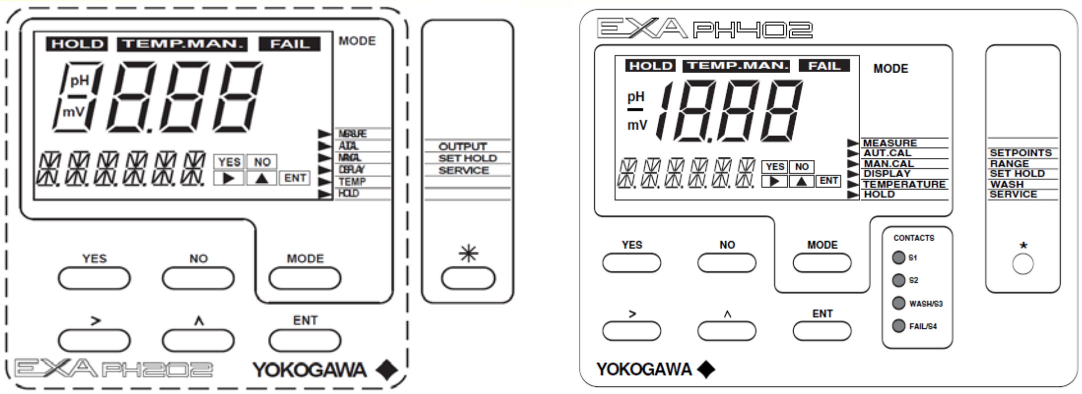
Indicate **YES** *for initial setup only, otherwise indicate* ***NO***



Once the Calibration is complete and the analyzer returns to the *Calibration pH* screen, press the Home icon to return to measurement mode and the sensor is now ready to be installed into the process

PH202* and PH402G:

Remove the front cover of the PH202* or the PH402G. Press the * key and press NO until ***SERV** is displayed. Press YES to enter the Service menu.



Enter Service Code **23** by pressing ^ and > until the display shows **23**, press ENT. ***ITP*** will appear, press ENT. ***Slope*** will appear, using the information from section *3. Function test* from the test certificate program the Slope value in the analyzer to match what is shown on the certificate by using the ^ and >. Once the value is changed press ENT. ***ASP.1D*** will appear press NO. ***ASP*** will appear press YES to change the value. Again using the information from section *3. Function test* from the test certificate program the ASP value (Zero popint pH7 shown on the certificate) in the analyzer to match what is shown on the certificate by using the ^ and >. Once the value is changed press ENT.

Glass impedance nominal	750 / 750 MOhm		
3. Functional test			
	Specification	Measured	
Zero point pH7	0 ± 15 mV	-9.9	mV
Slope value pH4	zero point + pH4	158.2	mV
Calculated slope (pH7-pH4)	92 - 100 %	95.7	%
Temperature resistance @ 25 ºC	1092 to 1102 Ohm	1093	Ohm
LE resistance	< 1 Ohm	0.34	Ohm

It should return you to the screen that shows ***SERV***. Press YES to enter the Service menu. Enter Service Code **03** by pressing ^ and >, press ENT. ***Z1.CHK*** will appear, using the ^ and > keys set the anlayzer to 1.1.1 and press ENT. ***Z.L.xΩ*** will appear, press YES. Using the ^ and > keys set the low impedance reading to **1 MOhm**, press ENT once complete. ***Z.H.xΩ** will appear, press YES. Using the ^ and > keys set the low impednance reading to 1 MOhm. Press ENT once complete. Using the ^ and > keys set the low impednance reading to **1 GOhm**, press ENT once complete.

It should return you to the screen that shows *** *SERV***. Press YES to enter the Service menu. Enter Service Code **04** by pressing ^ and >, press ENT. ***Z2.CHK** will appear, using the ^ and > keys set the anlayzer to 1.1.1 and press ENT. ***Z.L.xΩ** will appear, press YES. Using the ^ and > keys set the low impednance reading to **1 MOhm**, press ENT once complete. ***Z.H.xΩ** will appear, press YES. Using the ^ and > keys set the low impednance reading to 1 MOhm. Press ENT once complete. Using the ^ and > keys set the low impednance reading to **1 GOhm**, press ENT once complete.

NOTE:** *In some applications the impedance measurement might cause instability, especially at low sample temperatures. If so then code 03 and code 04 must be set to **1.1.0.** In some applications the Asymmetry Potential may be too high for standard setting if the zero offset of the reference cell is more than 120 mV. This can be resolved by setting Service **code 05** to **0.1.

It should return you to the screen that shows *** *SERV***. From you here can press the MODE to return to the home screen.

You can use traditional pH7 and pH4 buffers as a ***functional check only***. Place the SC24V sensor in the 7 buffer, allow the sensor to stabilize, and then place it in the pH 4 buffer. If the sensor responds to the pH change then the sensor is operating properly.

One final step is required before the sensor can be placed online. Take a process grab sample and perform a one point manual sample calibration to correct for the background salts in the process.

(MANUAL PROCESS CALIRBATION)

Press the MODE key and press NO once until ***MAN>CAL** is displayed. Press YES. ***NEW.SENS** will appear, press YES (*for initial setup only, otherwise indicate **NO***).

PH.CAL will appear, press YES. ***START*** will appear, press YES. Using the ^ and > set the pH value of the sample to the predetermined known value and press ENT. ***CAL.END*** will appear, press YES. The analyzer will return to normal measuring mode and the sensor is now ready to be installed intot he process.

Proper Calibration

Differential sensors having both a standard pH glass and a cation reference like the SC24V, need to be calibrated to correct both the **ZERO** and **SLOPE**. However, conventional pH buffers (N.I.S.T 4.00, 6.86 and 9.18) can NOT be used because they have low strength and different values from one another (0.005- 0.01 m). Therefore, when used for calibration a slope of > 105% will be received. In order to properly perform a 2-point calibration use buffers specifically designed for cation-based references which have the same sodium level for each pH value. Yokogawa offers such solutions. By using these solutions the differential sensor will react like a traditional pH sensor. These buffer solutions have an ionic strength of 1 mol/l NaCl so they will have a theoretical zero point of 0 mV at pH 7. The Isopotential point (ITP) of the sensor in these solutions is at 7 pH.

However because the process salt concentration will be different than the buffer concentrations a one point manual grab process sample calibration always has to be performed before the sensor is placed back online in the process. Follow the steps shown above for the appropriate analyzer's ***Manual Process Calibration***. Then the ZERO point will be updated accordingly.

NOTE: *For optimal performance the Isopotential point (ITP) should be updated as well. This ITP is set in the software and is typically (7+pNa).*