

## PROCESS CONTROL

Guarantee the best continuously pH measurement for your liquid process !

### 1. Introduction:

Most pH sensors are installed directly into the process. For some samples and processes this is the best way to do.

However under certain conditions this will lead to unreliable and inaccurate results because of the harsh environment.

High solid concentration, high ionic strengths, solids and certain chemical reactions during the process will deteriorate the pH electrode performance.

In such situations it is better to take the pH electrode out of the process and to do a measurement in a controlled condition.



figure 1: **EZ-AutoCal<sup>®</sup><sub>pH</sub>** online analyzer

The **EZ-AutoCal<sup>®</sup><sub>pH</sub>** is a batch pH analyzer with high short-term and long-term accuracy.

For removal of potential precipitations that could fool the electrode the analyzer is equipped with a programmable cleaning and rinse.

The automatic calibration function assures the best accuracy.

At the same time this results in a long electrode life, low maintenance and highly validated analysis.

The **EZ-AutoCal<sup>®</sup><sub>pH</sub>** is using Best Available Technology ( BAT ). [ Low Detection Limits with Laboratory Accuracy | Unique Design → High Up-time | High mean time between Failure ( preventive maintenance intervals of 30d ) | Fully remotely control possible | Automatic Cleaning, Calibration and Validation | Data logging ].

The use of dis-continuously on-line pH analyzers is preferred over continuously operating units. Continuously operating on-line analyzers have the following disadvantages:

- They appear to run continuously but they have a delay time.
- They have drift problems
- They have contamination problems

The dis-continuously on-line **EZ-AutoCal<sup>®</sup><sub>pH</sub>** is designed to operate continuously, meaning that once the analysis is performed and the result is produced, the analyzer will immediately start the next measuring cycle on a new sample. The pre-treatment of the sample, flushing and cleaning steps are included in the analysis time. After each analysis cycle the analyzer is cleaned and restored in its original condition.

On top of that the **EZ-AutoCal<sup>®</sup><sub>pH</sub>** on-line analyzer system for the determination of pH includes automatic calibration / validation and cleaning.

### 2. pH Definition:

pH is the negative of the base-10 log of the activity of the hydrogen ion.

$$pH = -\log_{10}(a_{H^+}) = \log_{10}\left(\frac{1}{a_{H^+}}\right)$$

Solutions with a pH less than 7 are acidic and solutions with pH greater than 7 are basic or alkaline.

	[H <sup>+</sup> ]	pH	Common examples
Acids	1 x 10 <sup>0</sup>	0	Hydrochloric acid
	1 x 10 <sup>-1</sup>	1	Stomach acid
	1 x 10 <sup>-2</sup>	2	Lemon juice
	1 x 10 <sup>-3</sup>	3	Vinegar
	1 x 10 <sup>-4</sup>	4	Soda (carbonic acid)
	1 x 10 <sup>-5</sup>	5	Rainwater
Neutral	1 x 10 <sup>-6</sup>	6	Milk
Bases	1 x 10 <sup>-7</sup>	7	Pure water
	1 x 10 <sup>-8</sup>	8	Egg whites
	1 x 10 <sup>-9</sup>	9	Baking soda
	1 x 10 <sup>-10</sup>	10	Antacid
	1 x 10 <sup>-11</sup>	11	Ammonia
	1 x 10 <sup>-12</sup>	12	Quicklime (calcium hydroxide)
	1 x 10 <sup>-13</sup>	13	Drain cleaner
	1 x 10 <sup>-14</sup>	14	Lye (sodium hydroxide)

figure 2: pH examples acid / bases

3. Measuring principle:  
 In the analyzer a potentiometric pH glass electrode is installed. Ideally the electrode potential, E, follows the Nernst equation:

$$E = E^0 + \frac{RT}{F} \ln(a_{H^+})$$

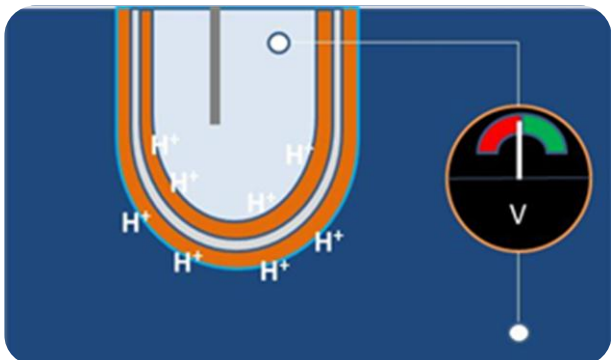


figure 3: pH potentiometric measuring principle

4. Online EZ-AutoCal<sup>®</sup><sub>pH</sub> analyzer system:

4.1. Preconditioning:

Prior to analysis, the preconditioning system will make the sample available to the process analyzer. Depending on the process conditions (temperature, pressure, chemical composition and number of sample streams) a dedicated preconditioning can be provided.

4.2. Analysis procedure:

- Flushing of sample in the tubing
- Sampling
- Draining
- Sampling
- Stabilization of pH
- Output 4-20 mA, Modbus, ...
- Draining
- Rinse (Tap water)
- Waiting for next measurement

4.3. Automatic Temperature Compensation (ATC):

The pH of any solution is a function of its temperature and the temperature determines the slope of the electrode. One pH unit corresponds to 59.18 mV at 25°C (the standard voltage and temperature to which all calibrations are referenced). The slope decreases to 54.20 mV / pH at 0°C and increases to 74.04 mV / pH at 100 °C.

Due to the temperature dependency of the pH values, the **EZ-AutoCal<sup>®</sup><sub>pH</sub>** analyzer is equipped with Automatic Temperature Compensation ( ATC ) to receive a correct pH based on the temperature of the solution.

Typical pH electrode response as function of temperature:

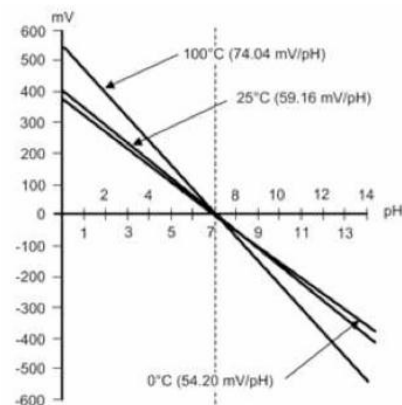


figure 4: pH = f( mV ) at different temperatures

The **EZ-AutoCal<sup>®</sup><sub>pH</sub>** will contain both a pH electrode and a temperature measurement.



figure 5: analysis vessel with stirrer, pH probe and temp. sensor

Although pH measurements has an automatic temperature compensation, the values of the calibration buffer changes by the temperature which cannot be compensated by the electrode. Therefore during automatic calibration, the temperature of the buffer will be measured prior to calibration to use the correct values.

**6. EZ-AutoCal®<sub>pH</sub> Design:**

The **EZ-AutoCal®<sub>pH</sub>** is designed having two completely separated compartments that are easily accessible:

- compartment for the chemical analysis (wet part)
- compartment for the electronics and the built-in industrial PC

The **EZ-AutoCal®<sub>pH</sub>** has an ergonomic, corrosion resistant analyzer IP55 housing, designed for operation in industrial environments. Purging with instrument air is possible in case of risk of accumulation of corrosive gases or extreme humidity.

The batch-wise operating principle guarantee you following advantages:

- allows you to program the analysis sequence according to your needs
- rinsing and cleaning after each analysis cycle
- limited loading of the electrodes

The **EZ-AutoCal®<sub>pH</sub>** has an outstanding reliability and accuracy thanks to the use of first class and robust wet-part components such as precision micro- and low-speed peristaltic pumps and measuring vessel configuration.

Purging with instrument air is possible in case of risk of accumulation of corrosive gases or extreme humidity. The hardened glass door assures instant visual inspection of the wet-chemical part.

A user-friendly 5 ¾" color touch screen industrial computer guarantees stable operation and a superior human interface.



**7. EZ-AutoCal®<sub>pH</sub> Advantages:**

- can be purged with instrument air
- low-volume analysis vessel design
  - ⇒ results in a low consumption of chemicals and a relatively long autonomy
- automatic Cleaning
  - ⇒ The user can program the sequence and interval of the Analysis and Cleaning cycles
- automatic Validation
  - ⇒ The user can program the sequence and interval of the Analysis and Validation cycles. A Validation can be performed with a validation solution with known concentration in order to check the analysis program and the analyzer
- manual grab sample
  - ⇒ The user can program an unknown manual sample analysis
- gas-tight vent & drain collector

- adjustable stirrer speed

- robust Masterflex® Pumps

- Precision Micro Pumps 50 µl/pulse EPDM or Kalrez™ for performing of the titration or for addition of required reagent solutions

- Precision Stepping Motor Controlled Dispensers for sample dilution (range dependent!) or performing the titration

➤ UNIQUE HUMAN INTERFACE:

Industrial touch-screen PC with flash disc controls the **EZ-AutoCal®<sub>pH</sub>** and memorizes trends, alarms, results and data log files.

① REMARK: The control of the on-line **EZ-AutoCal®<sub>pH</sub>** touch screen can remotely be taken over by another PC over a Local Area Network (LAN) using commonly available VNC Ethernet software.

**8. EZ-AutoCal®<sub>pH</sub> Specifications:**

Methodology: Potentiometric pH measurement

Range: 0 – 14

Precision:  
< 0.1 full scale range for standard test solutions

Accuracy:  
< 0.2 full scale range for standard test solutions

Cycle time: 1 cycle/5 minutes

Stream selection: 1 stream (8 streams optionally)

**9. Field Results - stability test:**

Buffer 4		
Date and time	Value	T (°C)
Wed Jul 8 06:28:38 2015	4,02	26,4
Wed Jul 8 00:20:13 2015	4,018	26,5
Tue Jul 7 18:09:06 2015	4,016	26,7
Tue Jul 7 12:25:43 2015	4,009	26,6
Tue Jul 7 06:21:04 2015	4,005	26,4
Tue Jul 7 00:16:24 2015	3,998	26,5
Mon Jul 6 18:11:45 2015	4,017	26,8
Buffer 7		
Date and time	Value	T (°C)
Wed Jul 8 06:26:33 2015	6,979	26,5
Wed Jul 8 00:18:09 2015	6,981	26,6
Tue Jul 7 18:07:01 2015	6,981	26,8
Tue Jul 7 12:23:38 2015	6,993	26,7
Tue Jul 7 06:18:59 2015	7,004	26,6
Tue Jul 7 00:14:20 2015	7,024	26,7
Mon Jul 6 18:09:40 2015	7,026	26,7

**10. Hydraulic Schedule:**

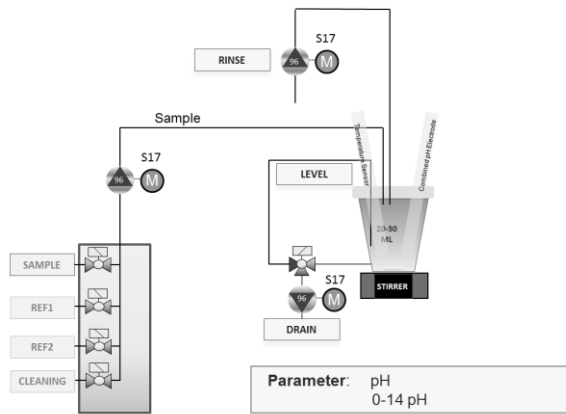


figure 6: wet part lay out

**11. Field Picture:**



figure 7: field example

**12. References and Acknowledgements:**

Special thanks to the AppliTek application and on-line analyzer manufacturing team.



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