How well does the LILIAN device measure?

Chlorine and pH value

Status: August 2022

Content

The LILIAN fulfils all requirements of DIN19643. The measuring ranges and accuracies required by DIN are even exceeded. This is described in more detail below:

The aim of Lilian Labs

The decision for or against a new measuring device, regardless of the area of application, is always a question of trust. Based on the measured results, control systems are adjusted, measures are taken or it may be that "only" a documentation on the water quality takes place, which protects the user from legal claims or fulfils legal requirements.

We at Lilian Labs are aware of this. That's why we not only offer you probably the most modern mobile water analyser in the world with a connected digital platform, but also all the processes that go with it:

- In the context of test phases or small projects, we initially clarify all open questions, e.g. about the measurement quality with LILIAN, the benefits for your company or the integration of the LILIAN hardware and software into your facility and processes. In doing so, we take into account your individual requirements on site.

- Support during operation, not only for the measuring device, but also for general questions in connection with the mobile measurements, is possible at any time via us or our partners.

- Training courses on handling or innovations are held regularly at Lilian Labs.

- On request even possible: Development / Production on Demand, e.g. for individual tests, customised software features, etc. .

You decide for yourself whether you want to take advantage of our more extensive offers. The aim of Lilian Labs is not to sell you a measuring device and leave you alone with it. We are your contact for all questions that arise in connection with your mobile measurements. We are only satisfied when you achieve permanently correct measurement results that you can also comprehensively understand.

You should keep this in mind when comparing LILIAN with other products: What added value besides the simple measurements do I get only with LILIAN and is this added value important to me?

This document is designed to help you make that decision. Here you will learn how to assess the measuring accuracy of the LILIAN based on independent data and factors and how to compare it with other measuring systems for water analysis.

So that you can be sure that you have selected the best system at the end of the decision-making process.

In general, how can I objectively evaluate and compare a water analysis system?

The most important point in this question: Do not believe what is written in the marketing brochures! It is possible for manufacturers to have the decisive properties of the measuring system determined by independent institutes and bodies from Germany. Usually the manufacturer then issues a certificate that provides technically verifiable and comprehensible values with which an objective comparison between individual measuring systems is possible.

In the next section we present the Lilian Labs certificate for chlorine and pH. The measurement data and the results on which this document is based were determined and calculated by an independent German institute.

Compare these values with the certificates of other manufacturers to be able to assess the quality of the measurements with other measuring systems. Not every manufacturer can provide these certificates - decide for yourself whether you want to trust the marketing promises alone in this case.

The certificates of Lilian Labs for chlorine and pH value

Method validation data - Free chlorine

Method

Name	SensoStick Pool
Article number	#5012
Measurement	Free chlorine (fCl); sodium hypochlorite solution
Method	Photometry DPD method
Settlement proceedings	DIN EN ISO 7393-2
Measuring range	0.03 - 4.00 mg/l
Photometer	Lilian Pro
Cuvette	10 mm, PMMA

Process characteristics

Absolute standard deviation (N=10)	
Concentration level 0.060 mg/l Cl2 [s_1]	0.0067 mg/l (12.7 %)
Concentration level 0.99 mg/l Cl2	0.013 mg/l (1.3 %)
Confidence interval (95%) at 1 mg/l	± 0.021 mg/l
Detection limit [3 - s_1]	0.020 mg/l
Limit of quantification [10 - s_1]	0.067 mg/l
Coefficient of determination R^2	> 0.99, related to the recovery function in the working range of 0.03 mg/l - 4.00 mg/l Cl_2

The document is valid without signature. Data are recorded to the best of our knowledge and independently confirmed according to the method of good laboratory practice. Nevertheless, no warranty, in particular for damages due to information derived from this document, can be assumed.

Literature on methodology

B. Magnusson and U. Ornemark (eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods - A Laboratory Guide to Method Validation and Related Topics, (2nd ed. 2014). ISBN 978-91-87461-59-0. Available from www.eurachem.org.

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Method validation data - pH value

Method

Name	SensoStick Pool
Article number	#5012
Measurement	pH value (pH)
Method	Photometry, indicator phenol red
Settlement proceedings	DIN EN ISO 10523
Measuring range	6,3 - 8,4
Photometer	Lilian Pro
Cuvette	10 mm, PMMA

Process characteristics

Measuring solution	Mean value (N = 3) pH value	Abs. Standard deviation (N = 3) pH units
pH 6.30 Buffer solution	6,33	0,010
pH 6.50 Buffer solution	6,48	0,029
pH 6.88 Buffer solution	6,84	0,006
pH 7.00 Buffer solution	7,03	0,021
pH 7.50 Buffer solution	7,64	0,012
pH 8.00 Buffer solution	8,13	0,000

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Understanding the certificate

Where can I find the information on total chlorine and combined chlorine?

The known chlorine values free chlorine and total chlorine are determined using the same method (DPD. Photometry), combined chlorine is calculated from the measured values obtained. The certificate of Lilian Labs GmbH validates the methodology and is therefore applied to all chlorine values.

What methodology was used?

The method describes the way the measurement process is carried out. In our case, the measurement is carried out photometrically in combination with a detection method (DPD method for free chlorine, colour change indicator phenol red for the pH value).

Free chlorine (fCl): Sum of the mass concentration of elemental dissolved chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite (OCl^-) given in mg/l.

Total chlorine (tCl): The sum of all oxidising (chlorine) compounds, including chloramines in mg/l.

pH value: The pH value (abbreviation for potential of hydrogen, Latin pondus hydrogenii or potentia hydrogenii) is a measure of the acidic or basic character of an aqueous solution. It is the opposite number of the decadic logarithm (logarithm of ten) of the hydrogen ion activity and a quantity of the dimension number. The higher the concentration of hydrogen ions in the solution, the lower the pH value.

Which settlement procedures were used?

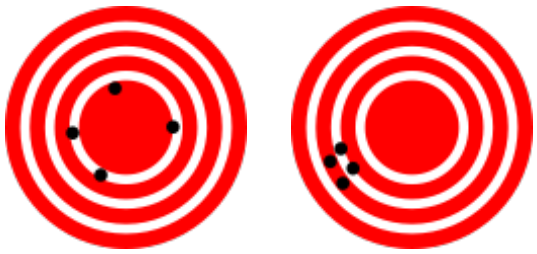
Settlement procedures are standardised methods according to which the comparison or reference values of the standard solutions are determined. For chlorine this is DIN EN ISO 7393-2, for the pH value DIN EN ISO 10523.

A standard solution is a solution with defined and traceable properties that has been prepared according to a standard manufacturing specification under laboratory conditions and checked according to the comparison procedure.

What does accuracy actually mean?

Accuracy refers to the extent to which individual values approximate a reference value. According to this definition, a result is accurate if it is both correct and precise: accuracy = precision and correctness.

Precision characterises the spread of the measured values obtained. Accuracy means the correctness of a statement. The simplest way to explain this is with a picture:



In the left figure, the hits show high accuracy but low precision: the readings fluctuate widely around the correct value. In the figure on the right, the accuracy is low but the precision is high: The measured values hardly fluctuate but around the wrong value (image source: Wikipedia).

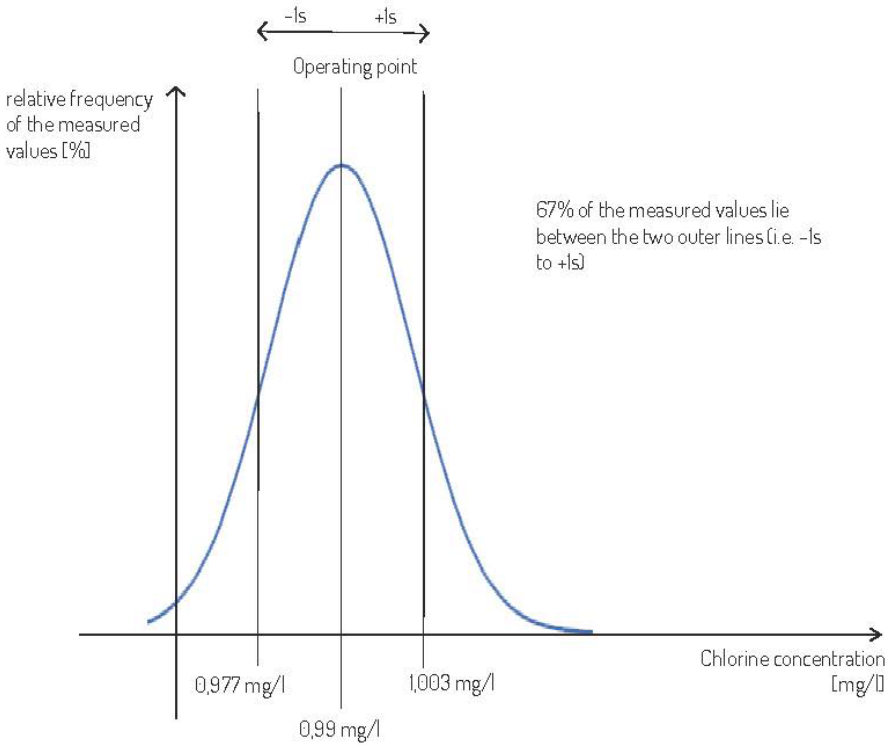
A practical example: The distinction between the terms is also important when distinguishing between calibration and adjustment. In calibration, the measuring device is set to accuracy. In practice, however, it may be that certain factors "shift" the accuracy. When I shoot at a target in archery, for example, I have to take the wind into account and aim slightly offset. This is then the adjustment, which also includes "zeroing" during a measurement: one sets an offset of the accuracy in such a way that the desired accuracy is achieved.

Standard deviations and confidence interval

The first information in the certificate under "Method characteristics" is the absolute standard deviation. In descriptive statistics, a standard deviation is a measure of the dispersion of a finite number of real values around their mean value, or more simply: it describes the precision of the measuring instrument. The specification can be absolute (Absolute Standard Deviation) or relative (Relative Standard Deviation).

With a simple standard deviation, approx. 67% of all measured values lie within the mentioned interval. The LILIAN certificate specifically states: At a free chlorine concentration of 0.060 mg/l, the absolute simple standard deviation is 0.0067 mg/l. This means: If the mean measured concentration of free chlorine is 0.060 mg/l, the LILIAN will show a value between 0.0533 mg/l and 0.0667 mg/l in 67% of all cases.

With a concentration of free chlorine of 0.99 mg/l, the standard deviation is 0.013 mg/l, i.e. 67% of the measurements are between 0.977 mg/l and 1.003 mg/l. This is illustrated again in the following figure:



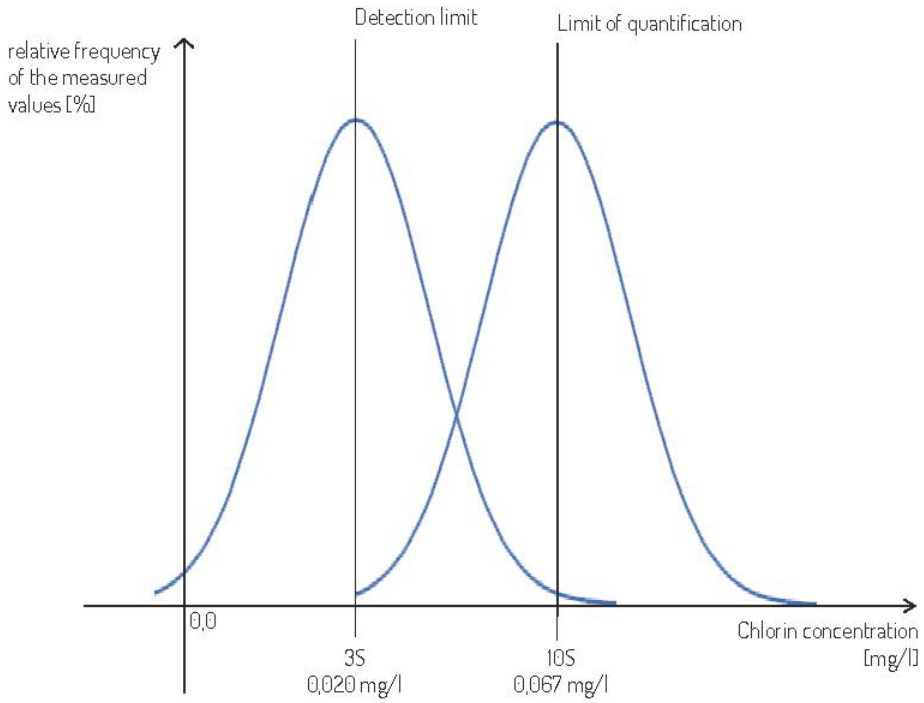
Here a problem becomes apparent: If a measuring device achieves this precision in only 2 out of 3 cases, the statement for a practical application is rather low. Therefore, the confidence range was still given at 1.00 mg/l free chlorine (+- 0.021 mg/l): In 95 out of 100 measurements, the measured values ranged from 0.979 mg/l to 1.021 mg/l. The operating point for this is 1.00 mg/l free chlorine, as this is a typical working value for swimming pool applications.

Limit of quantification and detection

The so-called limits of determination and detection are also specified in the certificate. The detection limit refers to the extreme (low) value of a measurement procedure up to which the measurand can just be reliably detected. Detection is when the measured value is at least three standard deviations above zero. In simple terms, this means: In 99 out of 100 cases, the measuring device detects that the value is not "0".

The limit of quantification is the smallest concentration of an analyte that can be determined quantitatively with a specified precision. A measured value is considered quantitative if the precision is 3.33x better than the detection limit. As a rule, the entire possible measurement interval is completely above the detection limit.

The following diagram is intended to illustrate this described relationship once again:



Drawn in blue are the possible measurement results of the meter with their relative frequency at different chlorine concentrations. This is called a measured value distribution. It is gaussian, i.e. the middle measured value is most likely to be measured and the probability of measuring corresponding values decreases towards higher and lower measured values up to 0% probability.

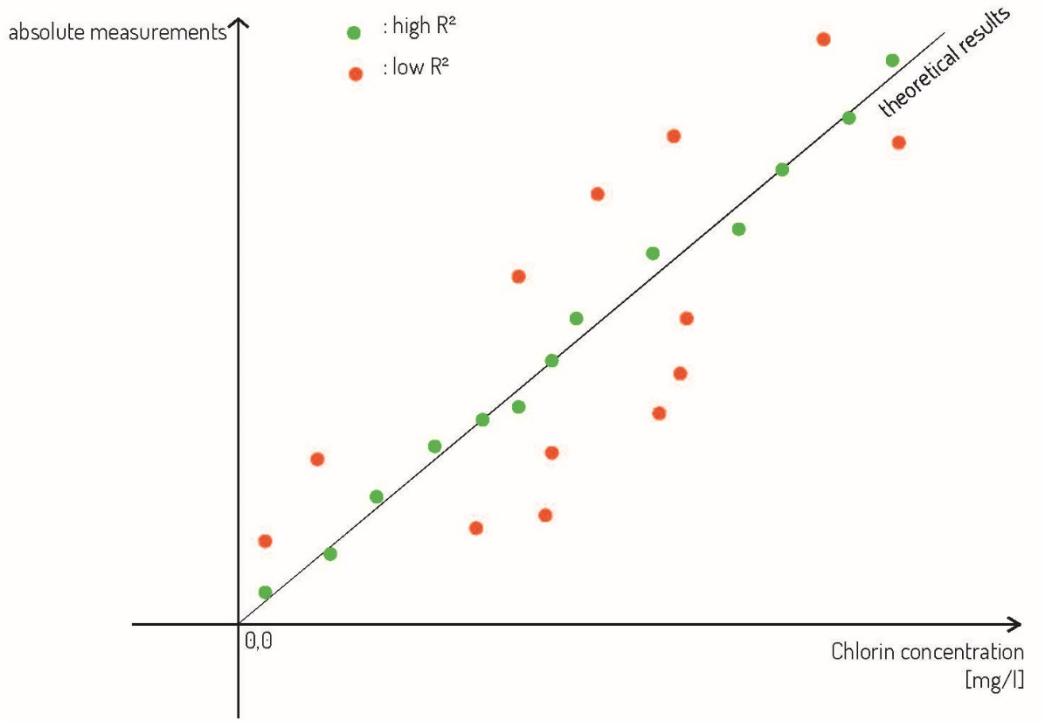
With the detection limit (3S = 3-fold standard deviation), the distribution of measured values is such that measured values greater than 0 are detected in 99 % of cases. Hence the name "detection limit", specified in the LILIAN certificate at 0.020 mg/l chlorine concentration. This is still in the range indicated by LILIAN as "Under Range (UR)", or "<0.03 mg/l", i.e. not yet measurable. A measured value is only displayed from 0.030 mg/l to provide more safety here.

At the limit of determination (10S = 10-fold standard deviation), it can be seen that the distribution of measured values is completely above the detection limit. In the LILIAN certificate, the limit of determination is given at a chlorine concentration of 0.067 mg/l.

The coefficient of determination R^2

The last figure in the LILIAN certificate is the coefficient of determination R^2. In statistics, the coefficient of determination is a key figure for assessing the goodness of fit of a regression - for example, to evaluate how well measured values fit a model.

In the diagram, the absolute measured values are plotted against the chlorine concentration (only illustrative, not quantitative).



The different colours of the measured values (red and green) represent two measurement series. The theoretical target values are drawn as a line. The following applies: The closer the measured values are to the line, the higher the accuracy (not only the precision) of the measuring device.

The green measured values are very close to the theoretical target values and one would calculate a correspondingly high R^2. The red measured values are further away from the theoretical target values, therefore these measured values would result in a low R^2.

The R^2 is given as a number between 0 and 1, whereby a value of 1 would mean that all measured values correspond exactly to the theoretical results. The LILIAN certificate specifies an R^2 of more than 0.99. Accordingly, the measurement results regarding the chlorine values you achieve with the LILIAN are accurate. The recovery function, in the working range of 0.03 - 4.00 mg/l Cl_2, is thus mapped with a correspondingly high correlation over the entire range, i.e.: An exact measured value is obtained over the entire measuring range.

Process characteristics in the LILIAN certificate for pH value

With the explanations regarding the chlorine certificate, it is now easy to understand the certificate regarding the pH value. For measuring solutions with specified pH values, the

mean measured value from three measurements was determined. One can read in the second column how close these mean values are to the target values.

The third column additionally shows the value for the simple standard deviation, also for a sample size of 3. For a pH value of 7.03, for example, this results: In 67% of all cases the LILIAN device measures a pH value between 7.01 and 7.05.

What is specifically required in DIN19643 with regard to hygiene measurement and how does the LILIAN certificate prove this?

In the current version of DIN19643 (Status August 2022), the specifications for hygiene measurements are regulated in "Chapter 11.4.2 Measurement value recording". In the following, quotations are given in italics, followed by our comments in normal font.

The time delay due to sample water transport must not exceed 0.5 min and the inertia of the measuring system should not exceed 1 min.

Here, the problem of chlorine escaping from the water sample is countered when measuring chlorine. According to DIN19643, the time from taking the sample to the measurement result should not exceed 90 seconds. This is the case with the LILIAN.

The measuring range for free chlorine shall be at least up to 1.5 times the upper value for the free chlorine content according to 5.3, Table 2, footnote i. The error limits shall be less than 0.05 mg/l free chlorine.

The LILIAN meter has a measuring range of 0.03 mg/l - 4.00 mg/l for chlorine and thus fulfils the requirement regarding the "upper value for the free chlorine content" according to DIN19643. The error limit of ± 0.021 mg/l is clearly below the required 0.05 mg/l (according to the LILIAN certificate for free chlorine, confidence range at 1.00 mg/l)!

For amperometric/potentiostatic transducers, the influence of pH and temperature on the measurement signal must be taken into account. An adjustment of the transmitter must be carried out if there are deviations between the indicator and the results of the daily photometric control measurements according to the DPD method.

It is described here that the measured values obtained by manual measurement are decisive for the operation of the system. The control of the permanently measured, electrical measured values is prescribed and requires a regular adjustment of the system. Measurements with electrodes are always subject to a time drift due to oxide layer formation on the electrode during operation, so that this specification is necessary.

The pH value measurement must be carried out continuously with an electrometric pH electrode. The daily function check of this permanently installed pH electrode must also be carried out by an electrometric pH measurement (hand-held meter). Deviations between the continuous display device and the control device must not be greater than ± 0.2 pH units with simultaneous compliance with the values according to 5.3, Table 2.

According to the old DIN19643, only electrodes may be used for manual pH measurements. In practice, the pH value is often determined photometrically, as this method is more error-tolerant and the measured values obtained usually agree well with those of the electrochemical

measurement. For this reason, DIN 19643 is to be improved accordingly in the next amendment. This will most likely be implemented in 2022.

Draft text from the preprint of DIN 19643-1:2022 Chapter 11.4.2 (extract):

The pH value must be measured continuously with an electrometric pH electrode. The daily function check of this permanently installed pH electrode should be carried out by an electrometric pH measurement (hand-held meter). The measurement can also be made by means of a photometer using phenol red as an indicator, if the buffer capacity or the salt content of the water does not limit this method. Furthermore, the limited measuring range of pH 6.4 to pH 8.2 must be taken into account. Deviations between the continuous display unit and the control unit must not be greater than ±0.2 pH units and must be tolerated if the deviation is always the same or stored by means of an offset setting on the control unit.

According to the LILIAN certificate, the LILIAN device has a deviation significantly below the required ± 0.2 depending on the pH value. You can therefore use the LILIAN for pH value measurements without hesitation.

Conclusion and contact

As you could see from the document, you can use the LILIAN water analysis system in the pool area without hesitation. If you have any questions or would like more information about the LILIAN, please do not hesitate to contact us.

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