pH electrodes optimized for pH measurement in water

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A new generation of pH electrodes feature durable construction, a proven manufacturing process, and pH glass that is well suited for GLP measurements, especially in potable water. Two different test waters were chosen to demonstrate the high performance of BlueLine electrodes (**Schott**, Mainz, Germany) for pH measurement in potable water (*Figure 1*).

The electrodes are 12 mm in diam and 120 mm in length, with a 16-mm-diam head with fixed cable or plug head for compatibility, allowing users to employ a standard electrode holder. Although the plug head is compatible with the classical **Schott** plug system, many changes have been incorporated, including improved shielding properties. The Silamid® silver/silver chloride reference system (**Schott**) is not based on a silver wire, but on structured silver coatings on the surface of an internal glass tube. The platinum junction retains its useful properties, as will be shown later.

An important component of the electrodes is the head with the refill hole for electrolytes and the slide to open and close it. It has an easy-to-operate, KCl-tight shutter of the electrolyte refill hole. Refilling is very convenient and clean using a plastic bottle with a nozzle that fits into the fill hole; the bottle is supplied with refillable BlueLine electrodes.

The plug cable assembly is characterized by a locking nut that can be attached to the electrode without twisting the cable. If a German DIN plug is used in combination with handylab pH meters (**Schott**) then the entire unit is water-tight; thus a safe pH measurement is ensured, even if the operator momentarily drops the unit into water.

In contrast to most pH glass electrodes, the BlueLine 11 pH electrode is cone shaped and is rugged, smooth, and easy to clean. It is well suited for standard pH measurements and for semisolid media such as cottage cheese, paste, and marmalade, and, under certain circumstances, fish, meat, and fruits.

The pH membrane glass is specially designed for fast and stable pH readings in potable water. Many

ment stores mV readings automatically when the condition for a stable reading is fulfilled, for instance, at $dU/dt < 0.05$ mV/sec. In any case, the goal is to attain fast, stable readings in the pH 0.01 range.

The computer-aided test equipment used to obtain the acquired data and to show the plot of Figure 2 can also calculate the characteristic parameters of the three electrodes (*Table 1*).

From Figure 2 and Table 1, it is evident that the BlueLine electrodes deliver a fast and stable output in buffer solutions. The electrode with the ceramic junction (other) shows acceptable values and should be considered a good electrode.

However, when the stirrer is switched on, the electrode with the ceramic junction shows more variance in comparison to the BlueLine electrodes with platinum junctions. The calculated values for the ceramic junction electrodes' slope and zero point differ significantly from the values obtained without stirring. What evidence is there that the type of junction is responsible for this effect? In the above-described experiment, the glass and reference portion of the three combination electrodes are separately connected to six channels of the data acquisition system and measured versus only one external reference electrode. This reference is linked with the solutions via a pressurized salt bridge since it is still common for critical, heavy-duty industrial measurements for high accuracy. By doing this, it is possible to analyze the signals of the glass and reference electrodes separately, as shown in *Figures 3a* and *b*, respectively.

Sometimes the junction of the reference salt bridge becomes unreliable. In such a case, all six channels show a similar drift, which indicates a salt bridge problem. Such a problem disappears when the salt bridge is replaced with a new one. In the above experiment, the reference salt bridge is in good working condition, as can be seen from the different behavior of the test electrodes in the three buffer solutions.

Electrode performance in potable water

The performance of the electrodes in potable water was tested using a method similar to that described above. Potable water usually changes from location to location and from time to time. Therefore, waters of different composition and with different pH values have been used for electrode testing. Typical response curves are shown in *Figure 4* for three BlueLine 11 electrodes showing almost identical responses and three other electrodes showing different responses. The responses of the other electrodes are characterized by a very slow response (other 1), a slow response with a long-term drift (other 2), and a fast response with slow stabilization (other 3). Only the pH glass electrode portion was tested, and all six electrodes were tested in the same experiment and after the same pretreatment in buffer pH 4.01 and 6.87.

Frequently asked questions about the platinum junction

1. What accounts for the useful properties of the platinum junction?

The geometry of the electrolyte channels is very uniform. They have a helical and straightforward path, in contrast to a sintered material such as porous ceramic, which appears as a labyrinth. The electrolyte can flow freely through these channels and form a well-defined liquid junction with small and reproducible diffusion potentials.

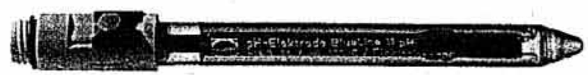

Figure 1 *BlueLine 11 pH electrode with platinum junction, cone-type membrane, and refill hole with slide closed.*

The pH membrane glass is specially designed for fast and stable pH readings in potable water. Many technicians have experienced slow-responding pH electrodes in potable water with a low reproducibility and accuracy, and time wasted with heavily worn electrodes as well as with some new electrodes.

The two main properties of combination pH electrodes that determine its performance are the pH membrane glass and the liquid junction of the reference system. These are discussed below.

Electrode

For calibration, it is common to use buffer solutions with a pH of 4.01, 6.87, and 9.18 according to NIST, DIN,[1] or PTB. For high-precision pH measurement, it is necessary that the electrode output during calibration is fast and stable. Some stir the buffer solution during calibration, and certain electrodes change their output when stirred. A high-precision electrode should be insensitive to stirring. *Figure 2* shows the response of an old and a new BlueLine 11 pH electrode (BL 11) and an electrode with a ceramic junction.

When the mV output of the electrode is stable, the zero point (offset) and span (slope) can be adjusted on the meter. A microprocessor-based instru-

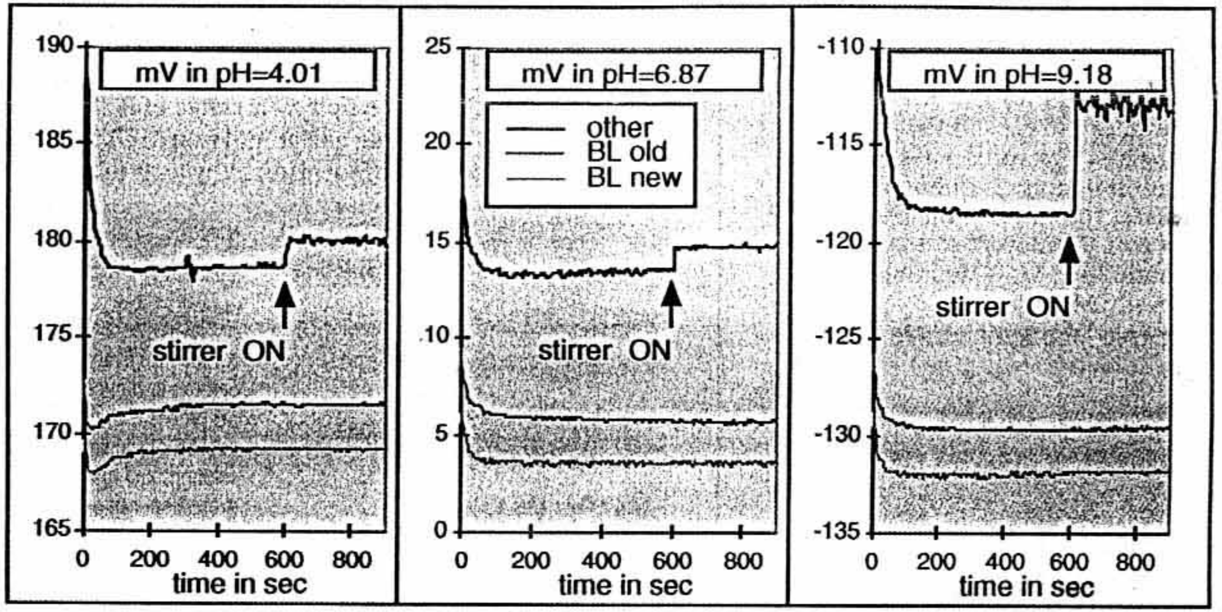

Figure 2 *Response of new versus old BlueLine electrodes and electrodes with ceramic junction (other).*

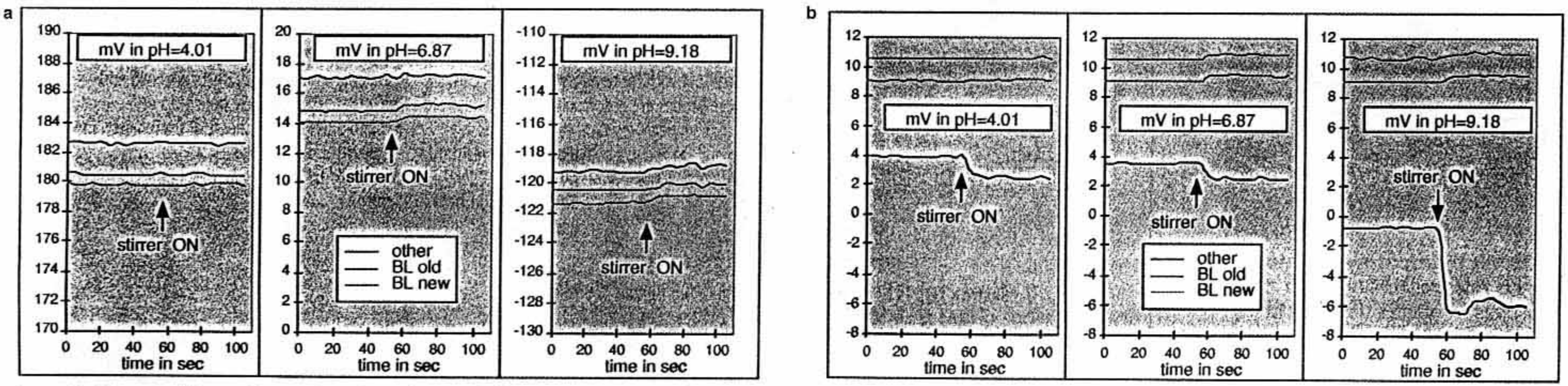

Figure 3 *a) Stirring effect on the pH glass electrode signal of the new and old BlueLine electrodes and ceramic junction electrode (other). b) Stirring effect on the reference electrode signal of the new and old BlueLine electrodes with platinum junction and electrode with ceramic junction.*

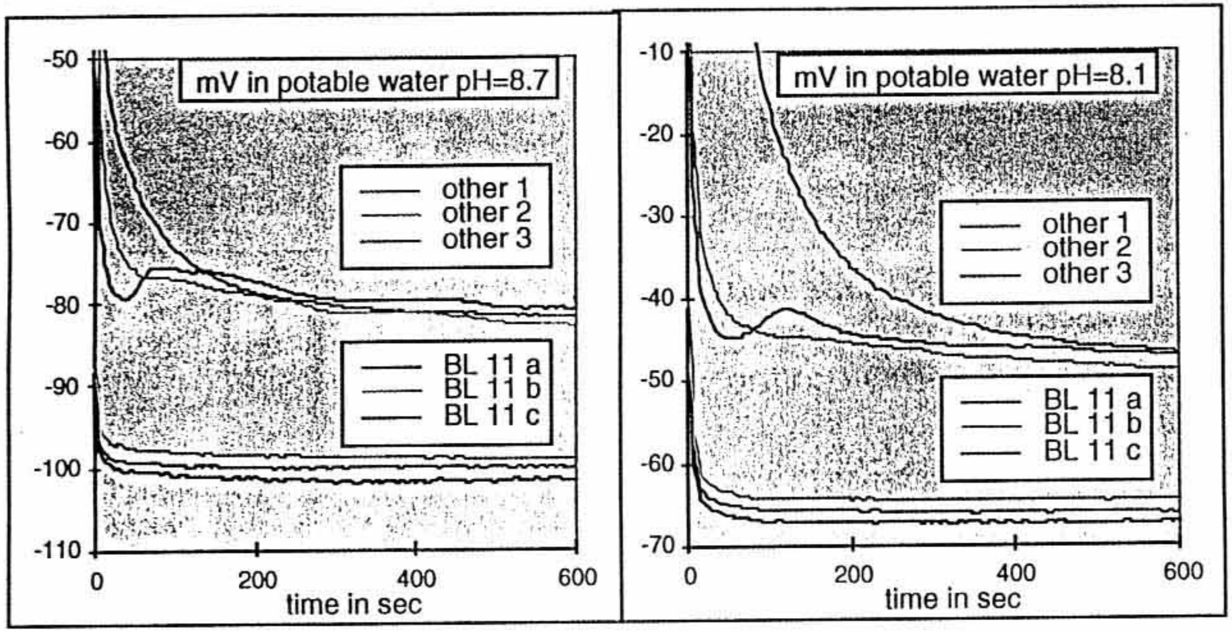

Figure 4 *Response of BlueLine electrodes (BL 11 [a–c]) in comparison to other electrodes (other 1–3) in potable waters with pH 8.7 and 8.1.*

Table 1

Electrode parameters from test in Figure 2

	Unit	Without stirring Other	BL (old)	BL (new)	With stirring Other	BL (old)	BL (new)
Slope (4.01–9.18)	mV/pH	57.46	58.26	58.29	56.59	58.24	58.27
Zero point (4.01–9.18)	pH	7.11	6.97	6.93	7.13	6.97	6.93
Response time (pH = 0.01)	sec	64	58	47			

2. What is the electrolyte flow rate of a platinum junction?

The flow rate is much higher than that of a ceramic junction. This is one reason for its good properties. If the wetting cap is pushed over the electrode and small air bubbles are pressed through the junction, *it is not a failure; it indicates a properly working* platinum junction. To avoid clogging of the platinum junction, it must be cleaned only chemically, not mechanically. The chemical durability of platinum is excellent and allows treatment in almost every mineral acid. Hydrofluoric acid (HF) should not be used.

3. Is the platinum junction sensitive to redox potentials (ORP)?

A free-flowing, properly working platinum junction is not sensitive to redox potentials, except in a few rare situations in which errors occur. It is not the redox potential directly that causes false potentials, but rather the current forced through the electrolyte path of a semiclogged junction. This situation can be illustrated by the schematic in *Figure 5*. The platinum junction establishes the electrolytic connection of the KCl electrolyte and the measuring solution. The platinum metal is parallel to the electrolytic path. If the electrolyte flows through the junction, then only the outer portion of the platinum wire is exposed to different redox potentials. These different redox potentials are short-circuited at the outside of the measuring circuit and do not affect the electrode signal.

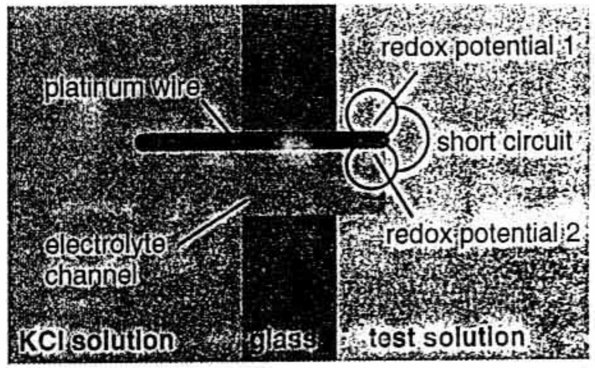

Figure 5 *Redox potentials at the platinum wires do not affect the pH measurement.*

Summary

BlueLine electrodes demonstrate high performance in buffer solutions and potable water. They are well suited for high-accuracy pH measurements for this application. The fast response time and stable readings are a result of the pH glass type and improved platinum junction. The performance of the platinum junction in low-ionic-strength pH measurement has been reported.[2] The platinum junction is not sensitive to redox potentials, as long as the electrode can flow freely through the electrolyte channels.

References

1. DIN 19266. pH measurement, standard buffers. 1979.08.
2. Kopelove A, Franklin S, McGaha Miller G. Low ionic strength pH measurement. Am Lab June 1989; 21(6):40.

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