Feature Article

Environmentally Conscious Industrial pH Meter HP-48/96 Series

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In the newly developed and environmentally conscious HP-48/96 series industrial pH meter, lead has been eliminated from solder joints on the printed-circuit board in the indication converter section, and lead-free glass materials have been used for the pH electrode body. Resistance of the pH response glass membrane to chemical attack has been increased by improving its composition. At the same time, it became possible to use lead-free glass but this glass is difficult to make using conventional glass processing technology, in terms of heat characteristics. The use of lead-free glass has consequently allowed conformity with the RoHS directive (elimination of hazardous substances) within the EU. This is the first time this conformity has been achieved in this industry. Though the thickness of the pH electrode is approximately 0.1 mm using the traditional type, the durability and physical strength has been improved by forming a glass thickness of up to 1mm maximum. This improves the duration of the pH electrode, especially when used in severe conditions, which results in a reduction of the exchange frequency and therefore less industrial waste.

Introduction

In recent years, studies of technologies for reducing the global environmental burden are being promoted in every industrial field, and the market introduction of these technological achievements is becoming a major issue. In such a situation, the glass electrode pH meter measurement method is dominant in the water monitoring field - widely used as an important measurement indicator for understanding water environments. HORIBA Group has taken the initiative in working toward developing pH meters with lead-free electrodes.

Conventionally, the body materials of pH electrodes consist of glass tubes of approximately 30% lead oxide. Approximately 2.5 million or more pH electrodes are produced annually in the world and of these, HORIBA supplies approximately a hundred thousand. Because used pH electrodes become hazardous industrial waste, which can have a great impact on natural environments, reduction of the environmental burden is a future task. Furthermore, a 'clean analysis' problem arises, because a very small amount of lead dissolves into an acid or alkaline solution.

This time, in response to the background and demands of the market, we have developed as environmentally conscious products, pH electrodes using lead-free glass, and the HP-48/96 series industrial pH meter in which the solders used to mount onto the printed circuit board are lead-free solders.

Usability of Industrial pH Meters

Industrial pH meters are widely used in various fields such as chemistry, food, medicine, metals, and pulp. For instance, they are used for managing raw materials, controlling or monitoring manufacturing processes, overseeing product quality, and controlling wastewater treatment facilities related to agriculture or stock farming. Also, as a result of increasing interest in acid rain and substances leached from soils that can influence global environments, pH meters are often used for grasping the quality variations of natural environmental water such as in lakes, rivers, groundwater, and seawater. Because global environmental conservation and the maintenance of human health are involved, various countries are promoting legal regulations. In Japan, water quality is controlled by the Water Pollution Control Law.

In this way, pH meters are indispensable items for water quality monitoring in various industries and fields all around the world, and the pH electrodes used for the meters are regarded as consumable items in process measurement. Thus, not only the reduction of environmental burden by means of lead-free products, but also the improvement of durability in process measurement was demanded by the market.

Overview of HP-48/96 Series Industrial pH Meter

The newly developed HP-48/96 series industrial pH meter is a panel-mount type. The user-interface is designed to be as foolproof as possible. For example, an icon-style display of the meter's status has been employed. Through miniaturization, the casing has been reduced in size. To comply with the RoHS directive within the EU, the use of lead glass, which had been used in conventional pH electrodes, was restricted. By using lead-free solders and lead-free glass, we aimed to develop a user-friendly and environmentally conscious product (Figure 1).

Figure 1 HP-48/96 Series Industrial pH Meter

Principles of pH Glass Electrodes

The pH glass electrode consists of a special glass membrane with ion conductivity that selectively responds to hydrogen ions in a solution and generates membrane potential according to the activity, and the internal electrode that leads the membrane potential to the pH meter. The most widely used pH electrodes are the complex type pH electrodes in which the pH glass electrodes composed of a glass membrane, a comparative electrode having the same potential against any solution, and an integrated temperature sensor for compensating temperature influence are incorporated.

Between the membrane potential E of the glass membrane and hydrogen ion activity a_{H+} in a sample solution, equation (1) is formed based on Nernst's equation.

$$E = E_0 + (2.303RT/zF)\log a_{H+} \quad \cdots\cdots (1)$$

In this equation E_0 is the electrode potential against the standard hydrogen electrode, which is determined by the composition, physical properties, and temperature of the membrane. As long as these are fixed, it becomes a constant.

R= Gas constant, T= Absolute temperature, z= Ion valency, and F= Faraday constant.

The $(2.303RT/zF)$ in equation (1) is a constant determined according to temperature, which is called the theoretical response gradient or Nernst's gradient. The theoretical response gradient under 25 ℃ becomes 59.16 mV, since ion valency (z) in equation (1) is 1.

As a matter of convenience, the membrane potential of the pH electrode is designed so that approximately 0 mV is indicated at pH7, the neutral point of water. This point is called the isopotential point and the membrane potential does not change according to temperature variation. Starting from the neutral point, the membrane potential changes according to the Nernst's gradient multiplied by the logarithm of ion activity a_{H+} (the difference between pH7 and the pH of the measurement solution). When the internal solution in the glass membrane is under pH7, the ideal membrane potential E against pHx of the measurement solution under 25 ℃ is expressed simply as in equation (2).

$$E = 59.16 \times (7 - x)\ \mathrm{mV} \quad \cdots\cdots (2)$$

Lead-free Approach

Conventionally, glass tubes as body materials for pH electrodes were joined using a thermal processing method so that a high insulation performance of $10^{12}\ \Omega$ or more was maintained between the pH response glass's thin membrane and the glass tube. To prevent cracks after processing, it is essential to use a glass tube in which the difference in the coefficient of expansion with the pH response glass is 5% or less. For this purpose, glass tubes with high insulation performance suitable for controlling viscosity during processing are required. Every electrode manufacturer has previously used lead glass tubes that had suitably excellent properties in this area. The lead glass tubes were originally glass materials used for vacuum tubes and fluorescent lamps. In Japan these days, however, lead-free fluorescent lamps are becoming dominant. Lead-free technology is also being taken into consideration in the glass industry. For pH electrodes, however, it is difficult to simply substitute lead glass with lead-free glass because it is necessary to develop a new composition for the pH response glass membrane and its processing technology. There has not been any technological progress until now. Recently however, we have been able to develop lead-free pH electrodes giving first priority to alternative technology used for lead-free glass. We selected the candidates from among various lead-free glass materials and prototyped the pH electrode. Because alkali metal elements and lead in the glass in contact with the internal solution of the pH electrode elute and change the pH of the internal solution, such an influence was also taken into account.

From various prototyping results, it was found that lead-free glass containing a large amount of alkaline earth metal oxide as the alternate element to lead oxide was optimum in terms of water resistance and heat characteristics in the glass produced (Table 1). Also, it was found that the lead-free glass with this composition eluted less metal ions to the internal solution and stabilized the pH value even under high temperature conditions (Figure 2). This contributes to the reduction of time-varying drift of the pH electrode.

Table 1 Outline of the Lead-free Glass Composition

Glass composition [% (mass)]		Lead glass	Lead-free glass	Effect of lead elimination
SiO_2		57%	→ 70%	Ratio UP: Improvement of durability
R_2O	Na_2O	4%	15%	Ratio UP:Decline of durability (equal)
	K_2O	9%		
RO	BaO, CaO, SrO, etc.	–	11%	Improvement of durability (BaO: alternate element to lead)
PbO		29%	–	Elimination of lead
Al_2O_3		1%	2%	Ratio UP: Improvement of durability
B_2O_3		–	2%	Improvement of durability

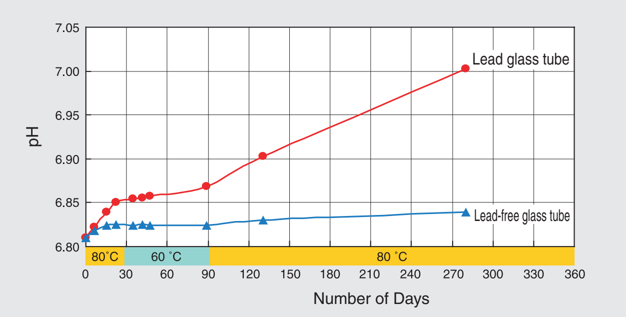


Figure 2 pH Variation of the Internal Solution Encapsulated in the Lead-free Stem Glass under High Temperature Conditions (80℃)

Unlike general glass, pH response glass is a special glass that contains a lot of alkali metal oxide such as lithium oxide. Thermal processing of the glass is very difficult and the skill of an expert is required for forming the glass.

In normal glass tube sealing, a suitable viscosity at the working point*1 is 10^4 P (poise: 0.1 Pa·s) or close to this. In glass processing to form various shapes, the viscosity range of 10^6 to 10^8 P in a temperature range higher than the softening temperature (softening point)*2 is said to be suitable (Figure 3).

*1: Temperature at which viscosity is 10^4 P (slightly higher viscosity than glycerin) suitable for glass sealing.

*2: Temperature at which the glass viscosity is such that it noticeably deforms under its own weight.

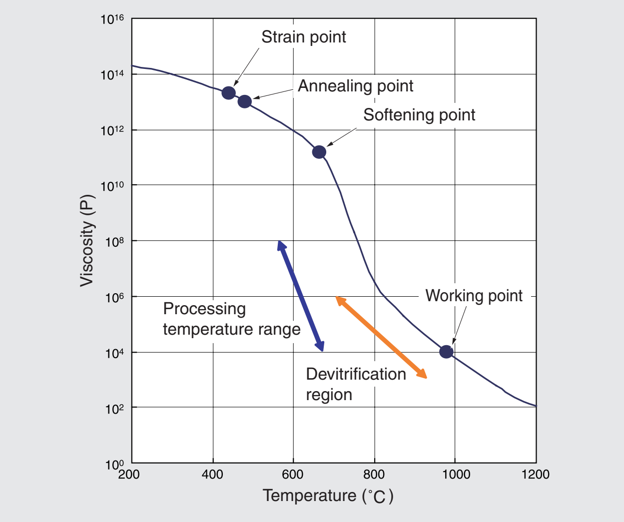


Figure 3 Relationship between Lead-free Glass Viscosity and Temperature

The largest problem due to substitution of lead-free glass is that the working temperature becomes much higher compared to lead glass, which significantly decreases viscosity at the processing temperature. Furthermore, the temperature range at which a viscosity suitable for processing can be obtained is between the working point and softening point. Because this becomes narrower, it becomes more difficult to perform thermal processing below a certain viscosity. Also, because the cooling speed after thermal processing is slow in that the specific heat is larger compared to lead glass, so the duration spent in the devitrification*3 region[1] becomes longer. Devitrification on the glass surface causes a remarkable performance degradation, which has made it necessary to reconsider the composition and dimensions of the pH response glass membrane. On the other hand, it was found that special annealing treatment was not necessary for removing the strain, because temperature decreases slowly from the annealing point*4 to the strain point*5.

*3: This phenomenon occurs when glass is cooled from the liquid phase temperature. Crystals of light element (lithium, etc.) oxide of which diffusion velocity is fast separate out on the glass surface, and as a result, transparency of the glass surface is lost.

*4: The annealing point is reached due to rapid cooling from the processing temperature. At this temperature, the strain produced by the stress is removed in several to several dozen minutes.

*5: The strain point is the lower limit of the annealing point range. At this temperature, by allowing the glass to cool up to the strain point, no permanent strain occurs.

Features of Lead-free pH Electrodes

Figure 4 shows the composition of the newly developed lead-free pH electrode. In order to solve the above-mentioned problems caused by the substitution of lead-free glass, we improved the composition of the response glass membrane. As a result, devitrification at the time of pH response glass membrane formation was eliminated without increasing the electrical resistance of the glass membrane. This was achieved by the following process. First, reducing the Li/Si ratio by increasing the amount of silicon dioxide that is a main component of glass and forms a network structure, and reducing the amount of lithium oxide. Next, barium oxide, an alkaline earth metal whose ion radius is large and water resistance is high, was introduced. Finally, supplementing the increase in resistance of the glass membrane due to the effects above, with an increase in high acid-resistance tantalum (V) oxide[2]. The expansion coefficient of this glass composition could be consistent with that of lead-free glass within 5%. In addition, it was recognized that durability and strength against thermal shock were improved while keeping performance equal to the conventional pH electrode. We gave the highest priority to design in conformity with environmentally conscious products, and eliminated lead from all the components of the entire glass tube body including cables, temperature measurement elements, and packaging materials, and therefore made it possible to comply with the RoHS directive.

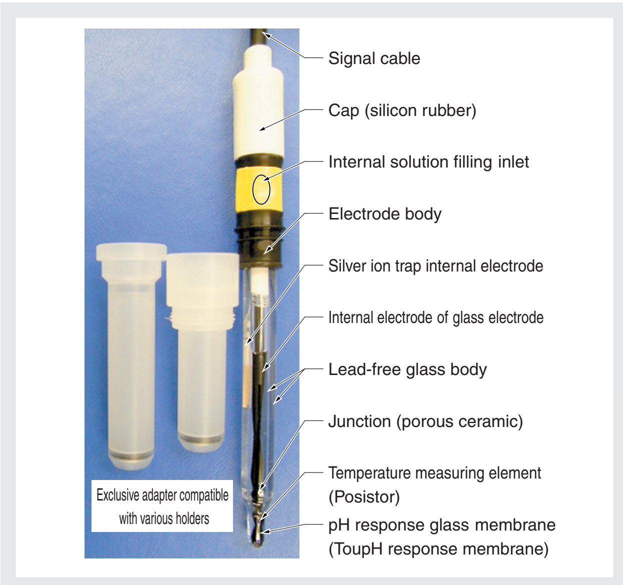


Figure 4 Example of Lead-free pH Electrode Structure

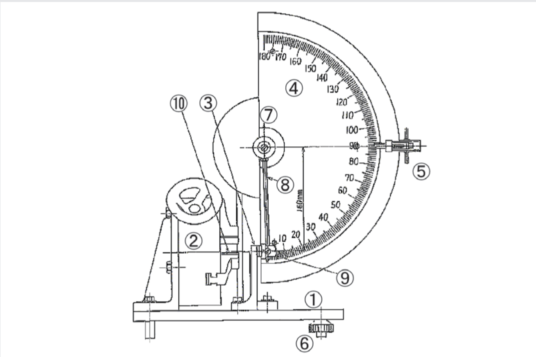
For ToupH types (6106 and 6107), we improved the composition of the pH response glass membrane, that was impossible to measure with unless the thickness of the glass membrane was around 0.1 mm, and made the entire glass membrane wall thicker. In addition, the bottom of the pH response glass membrane that was frequently damaged during handling was specially thickened up to 1 mm, which significantly improved the strength of the glass membrane up to 30 times or more of a conventional glass membrane (comparison by intra-company strength test*6) (Figure 5).

*6: Comparative test of industrial pH electrode strength (JIS Z 8805 pH measurement glass electrode 6.2.9 Impact strength test) JIS standard: The response membrane shall not be damaged under 20℃ or less.

(a) Comparative Test of Industrial pH Electrode Strength (JIS method)

Manufacturer	HORIBA	HORIBA	Company A	Company B
Electrode type	TouphH electrode	Globular electrode	Globular electrode	Globular electrode
Angle				
10°	OK	OK	OK	OK
20°	OK	OK	OK	Failed
30°	OK	Failed	Failed	
40°	OK			
50°	OK			
60°	OK			
70°	OK			
80°	OK			
90°	OK			
100°	OK			
110°	OK			
120°	OK			
130°	OK			
140°	OK			
150°	OK			
160°	OK			
170°	OK			
180°	OK			

(b) Glass Strength Tester

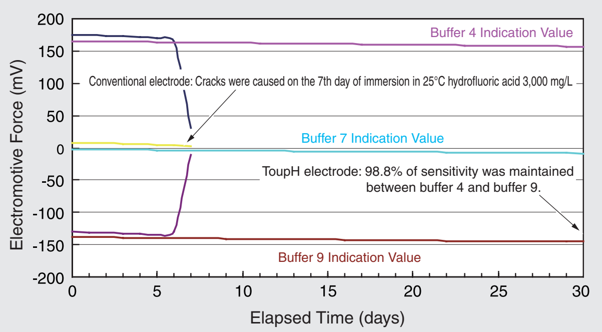


(1) Stand
(2) Chuck for securing electrode stem glass tube
(3) Level bar
(4) Scale plate
(5) Shock spring
(6) Level adjustment screw
(7) Ball bearing
(8) Hammer grip 40 ± 1 g (Brass ϕ6 × 160 mm)
(9) Hammer (with ivory surface) 30 ± 1 g (Brass ϕ15 × 25.5 mm)
(10) Hard rubber for securing electrode support

Figure 5 Strength Test Result and Strength Tester

Also, regarding measurement solutions such as strongly acidic solution and strong alkaline solution that can corrode glass, durability of the pH response glass membrane was improved up to 5 times or more compared to the conventional glass membrane by making the entire glass membrane thicker (according to intra-company durability comparative test) (Figure 6 , 7).

Figure 8 to 11 show the electrode sensitivity and the response after the high-temperature test.



Buffer 4: Phthalate pH standard solution (pH approx. 4)
Buffer 7: Neutral phosphate pH standard solution (pH approx. 7)
Buffer 9: Borate pH standard solution (pH approx. 9)

Figure 6 Potential Behavior in 60℃ Hydrofluoric Acid 3,000 mg/L

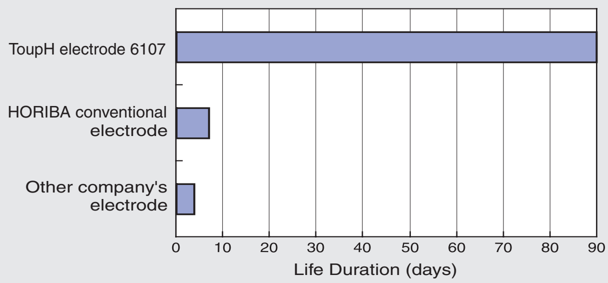


Figure 7 Comparative Example of Life Duration in 25℃ Hydrofluoric Acid 3,000 mg/L

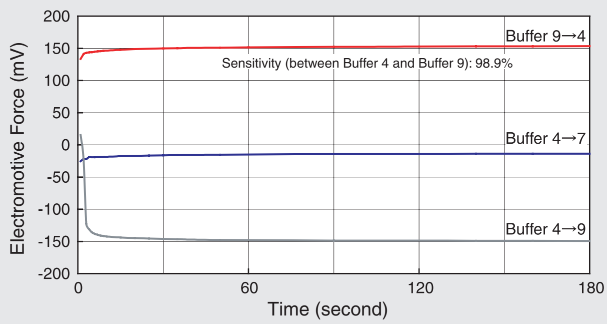


Figure 8 Exchange Response One Month after Immersion in 60℃ Hydrofluoric Acid 3,000 mg/L (pH approx. 2)

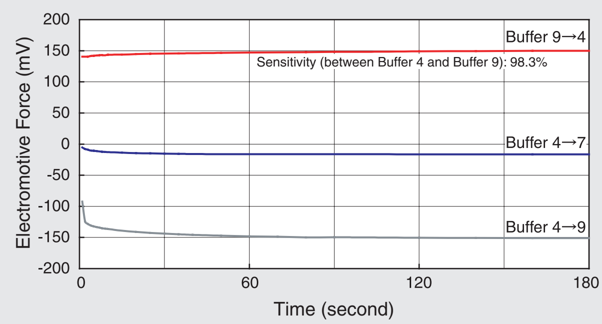


Figure 9 Exchange Response One Month after Immersion in 60℃, 5% Sodium Hydroxide Solution (pH approx. 14.1)

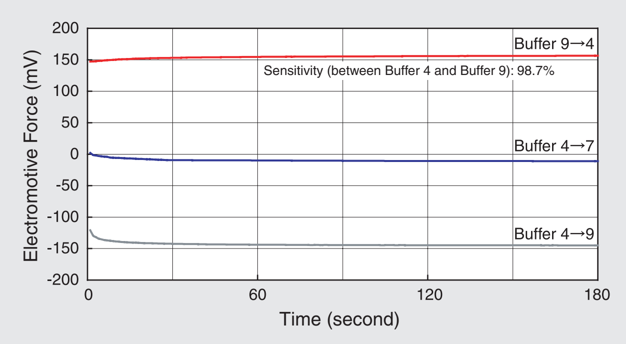


Figure 10 Exchange Response One Month after Immersion in 60℃, 10% Hydrochloric Acid Solution (pH approx. -0.4)

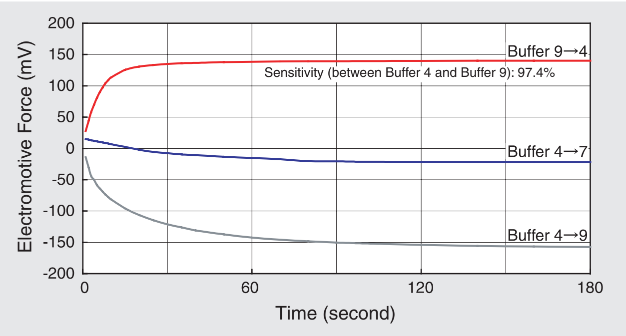


Figure 11 Exchange Response One Month after Immersion in 100℃ Potassium Chloride 3.33 mol/L (pH approx. 5.8)

The glass membrane, which has a superior response in low conductivity water, was used in the general-purpose electrode for general drainage (6105 pHast membrane). Because the response in running water was remarkably improved, this electrode is suitable for measuring environmental water (Figure 12).

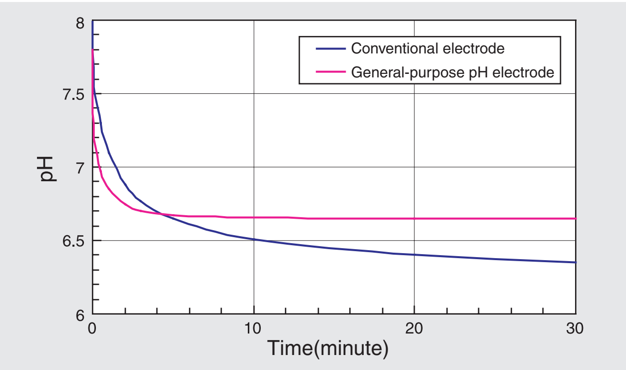


Figure 12 Exchange Response for Running Water after Three Months Use

Conclusion

Elution of lead from the electrode during measurement was avoided by eliminating lead from the pH electrode. As a result, there is no more need to worry about environmental impact. Because the old pH electrode and signal converter now no longer required became industrial waste containing hazardous components, there was an adverse impact on natural environments. However, a reduction of the environmental burden has at last been achieved with the newly developed HP-48/96 series meter.

In recent years, technological progress in pH meters using the glass electrode method is reaching a period of maturity and no large technological innovation is expected. In such a situation, we have been able not only to improve the conventional pH electrode technology but also instantaneously introduce to the market RoHS directive compliant products that do not contain hazardous substances. It is thought that we have taken the first step in reducing the environmental burden and towards 'clean analysis' in water environments.

The core technology for eliminating lead obtained from the HP-48/96 series industrial pH meter has been already applied to the ORP electrode for measuring redox potential in a solution. Hereafter, we would like to expand the technology to other water quality monitoring products and introduce further environmentally conscious products.

Reference

[1] Akira Naruse, Glass engineering, 6.3 Devitrification P. 57-63, Kyouritsu Shuppan (1979).

[2] Yasukazu Iwamoto and Shinji Takeichi, Glass electrode, Publication number P-2002-195974 (2002).

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